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NOVOSIBIRSK NATIONAL RESEARCH STATE UNIVERSITY
SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES
INSTITUTE OF SOLID STATE CHEMISTRY AND MECHANOCHEMISTRY SB RAS
TOHOKU UNIVERSITY, JAPAN

PROCEEDINGS

OF THE 2016 RUSSIA-JAPAN CONFERENCE

ADVANCED MATERIALS: SYNTHESIS, PROCESSING AND PROPERTIES OF NANOSTRUCTURES

October, 30th - November, 3rd, 2016

Novosibirsk
2016

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МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РОССИЙСКОЙ ФЕДЕРАЦИИ
НОВОСИБИРСКИЙ НАЦИОНАЛЬНЫЙ ИССЛЕДОВАТЕЛЬСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ
СИБИРСКОЕ ОТДЕЛЕНИЕ РОССИЙСКОЙ АКАДЕМИИ НАУК
ИНСТИТУТ ХИМИИ ТВЕРДОГО ТЕЛА И МЕХАНОХИМИИ СО РАН
УНИВЕРСИТЕТ ТОХОКУ, ЯПОНИЯ

МАТЕРИАЛЫ РОССИЙСКО-ЯПОНСКОЙ КОНФЕРЕНЦИИ

ПЕРЕДОВЫЕ МАТЕРИАЛЫ – 2016: СИНТЕЗ, ОБРАБОТКА И СВОЙСТВА НАНОСТРУКТУР

30 октября – 3 ноября, 2016

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Dear Professor Goto, guests and colleagues, the participants of the conference!

Welcome to NSU!

I wish you a fruitful work at the conference “2016 Advanced materials: synthesis, processing and properties of nanostructures”. Our University has tight and reliable relationships with Tohoku University, and we hope that this conference on materials science will establish closer interactions between leading universities of Russia and Japan.

About NSU

Novosibirsk State University was established by the Decree of the Council of Ministers of the USSR dated January 9, 1958, six months after the decision to found the Siberian Branch of the USSR Academy of Sciences. On September 29, 1959 Academician S.L. Sobolev gave the first lecture to students of the new University.

The University was growing up together with Novosibirsk Scientific Center focusing on training highly qualified specialists for science and education. Since the establishment the total number of NSU graduates has exceeded 50 000. More than 6 000 of them have defended their Ph.D. theses, over 1600 have been awarded Doctor’s degree. 48 graduates of NSU became full members of the Russian Academy of Sciences.

Among the University graduates there are many laureates of prestigious world awards and prizes such as Fields Medal, EPS Europhysics Prize, etc. There are also more than 100 laureates of the Lenin and State Prizes, the Prizes of the Council of Ministers of the USSR and the Russian Federation, Presidential Awards in Science and Education, the Prize of the Russian Federation Government as well as prizes of eminent scientists. Among graduates of NSU there are top businessmen and entrepreneurs as well as managers of large enterprises and academic research organizations.

The feature of NSU is the system of competitive selection and training of talented young people. NSU is the only University in Siberia with the developed multilevel system of continuing education. The system of selection and training of highly qualified specialists consists of Olympiads, correspondence schools on various subjects, winter and summer schools for students and applicants as well as undergraduate, graduate and postgraduate training at NSU.

Let me once again congratulate you on the beginning of the conference and wish you success!

Rector
Mikhail P. Fedoruk, Doctor of Physics and Mathematics, Professor
More information about NSU: http://www.nsu.ru/?lang=en

About the Physics Department of NSU

Physicists are highly appreciated in modern society for the universal character of their knowledge and their ability to solve problems of different origin. An important feature of the chair training system is the large volume of students’ research work. Starting with the third academic year students conduct scientific research in research institutes of The Siberian Branch of The Russian Academy of Sciences. Thus, by the moment of bachelor thesis defense plenty of students have some research works already published. The Department graduates work in leading research centers from Australia to Canada and from the USA to Japan. http://www.nsu.ru/?lang=en

Head of Department of Physics
Alexandr E. Bondar, Doctor of Physics and Mathematics, the corresponding member of The Russian Academy Sciences, Professor

Уважаемые профессор Гото, гости и коллеги, участники конференции!

Приветствую вас в стенах Новосибирского государственного университета и желаю плодотворной работы на конференции «Передовые материалы: синтез, обработка и свойства наноструктур - 2016». Наш университет имеет прочные и надежные связи с Университетом Тохоку, и мы надеемся, что очередная конференция в области материаловедения будет способствовать укреплению научных связей, добрососедских отношений, укреплению дружбы между лидирующими университетами России и Японии.

Несколько слов о нашем университете

Новосибирский государственный университет был создан Постановлением Совета Министров СССР от 9 января 1958 года через полгода после решения о создании Сибирского отделения Академии наук СССР. 29 сентября 1959 года академик С.Л. Соболев прочитал первую лекцию студентам нового университета.

Университет строился и развивался вместе с Новосибирским научным центром, ориентируясь на подготовку высококвалифицированных кадров для науки и образования. Со дня основания из стен НГУ вышло более 55 тысяч специалистов. Свыше 6,5 тысяч из них защитили кандидатские диссертации, более 1600 стали докторами наук. В Российскую академию наук избрано 55 выпускников НГУ. Среди окончивших НГУ – лауреаты престижных международных наград и премий (Филдсовская медаль и премия, Премия Европейского физического общества), более 100 лауреатов Ленинской и Государственной премий, премий Совета Министров СССР и РСФСР, Президентских премий в области науки и образования, премий Правительства РФ, премий выдающихся ученых. Среди выпускников - ведущие бизнесмены, предприниматели, руководители крупных производств и научных академических организаций.

Спецификой НГУ является система конкурсного отбора и подготовки талантливой молодежи. НГУ – единственный вуз Сибири, в котором развита многоуровневая модель непрерывного образования. Олимпиады, заочные школы по различным предметам, Зимние и Летние школы для абитуриентов и студентов, обучение в НГУ бакалавров, специалистов, магистрантов, аспирантов, докторантов - все это звенья единой системы отбора и подготовки высококвалифицированных специалистов.

Позвольте еще раз поздравить вас с началом работы конференции и пожелать вам успеха!

Ректор
Михаил Петрович Федорук, Д.ф.-м.н., профессор
Подробнее: http://www.nsu.ru/?lang=en

Несколько слов о Физическом факультете НГУ

Начиная с третьего курса студенты занимаются научной работой в исследовательских институтах Сибирского отделения Российской академии наук. Поэтому, к моменту защиты бакалаврского диплома, некоторые студенты уже имеют опубликованные исследовательские работы. Выпускники факультета работают в ведущих научно-исследовательских центрах от Австралии до Канады и от США до Японии.

Декан
Александр Евгеньевич Бондарь, Д.ф.-м.н., член-корр. РАН, профессор
Подробнее: http://www.nsu.ru/?lang=en

Program of
The Russia-Japan conference
“Advanced Materials:
Synthesis, Processing and Properties of Nanostructures – 2016”

October 30 – November 3, 2016
Novosibirsk, Russia

Day 1, October 30

Arrival of Japanese guests

Day 2, October 31

The Little Hall of The House of Scientists

13:30 – 14:30	Registration & Coffee-break

Opening ceremony
The Little Hall of The House of Scientists

Chairs: A. S. Zolkin, T. Goto

Welcoming speech

14:30 – 14:50	M. P. Fedoruk, the rector of NSU
	A.Ye. Bondar, the head of Faculty of Physics of NSU
	T. Goto, the head of laboratory of multi-functional materials science, Tohoku university
	A. S. Zolkin, the head of the laboratory of experimental physics, Faculty of Physics of NSU

Session 1
The Little Hall of The House of Scientists
Chairs: S. Novopashin, R. Belosludov

14:50 – 15:10 Invited	***T. Goto*** *Laser Chemical Vapor Deposition of Functional Films*

15:10 – 15:30 Invited	***S. Novopashin*** *Arc-discharge synthesis of nanomaterials*
15:30 – 15:50 Invited	***V. Ulianitsky*** *Detonation spraying. Technology, equipment and applications*
15:50 – 15:55	D.-S. Kang, Yu. Koizumi, K. Yamanaka, A. Chiba Characteristics of Ni based superalloy fabricated by electron beam melting
15:55 – 16:00	A. Yunoshev, S. Rafeichik, A. Plastinin, V. Sil'vestrov Applications of emulsion explosives for explosive welding of thin foils
16:00 – 16:05	I. Batraev, D. Dudina, D. Rybin CCDS facilities as dynamic chemical reactors
16:05 – 16:10	Y. Hou, Y. Li, A. Chiba Copper Influence on Corrosion Resistance to HF Acid Solution of Cu-modified Ni-Co-Cr-Mo Alloys
16:10 – 16:15	A. Larichkin, K. Zaharchenko, B. Gorev, V. Kapustin Influence of creep-age forming on fatigue life of the components from B95 aluminum alloy
16:15 – 16:20	D. Rybin, D. Dudina, I. Batraev, V. Ulianitsky Phase formation in metal-carbon systems during detonation spraying and post-spray annealing
16:20 – 16:35	**Coffee-break**
16:35 – 17:35	Poster session 1

Day 3, November 1

Session 2

Room 4117 (New Building of NSU)

Chairs: V. Volodin, K. Fujiwara

09:30 – 09:50 Invited	***H. Katsui, T. Goto*** *Melt solidification of high-temperature eutectic non-oxide ceramics*
09:50 – 10:10 Invited	***B. Bokhonov*** *In Situ electron microscopic investigations of Metal-Silicon interactions*
10:10 – 10:30 Invited	***T. Wada, H. Kato*** *Preparation of nanoporous base metals by dealloying in metallic melt and their application for energy related materials*
10:30 – 10:50 Invited	***M. Chen*** *3D nanoporous materials: new horizons of functional materials*
10:50 – 10:55	V. Kuznetsov, A. Romanenko, A. Berdinsky, B. Kholkhoev, V. Makotchenko, V. Fedorov Temperature dependences of electrical resistances of SWCNTs in PET matrixes films

10:55 – 11:00	S. Stolyarova, V. Koroteev, M. Kanygin, L. Bulusheva, A. Okotrub Synthesis of MS_2/C (M=Mo, Ti) composites at high temperature and pressure
11:00 – 11:05	M. Kozlova, P. Poltarak, V. Fedorov Composites based on low-dimensional transition metal chalcogenides with noble metal nanoparticles
11:05 – 11:10	A. Ivanov, E. Svezhentseva, S. Gyrylova, O. Kurskaya, M. Gulyaeva, Y. Vorotnikov, A. Alekseev, Y. Mironov, M. Shestopalov, A. Shestopalov. Materials based on X-ray contrast octahedral metal cluster complexes and oxo-polymers
11:10 – 11:15	M. Vlasov, N. Nikolaev, I. Merkulova Terahertz spectroscopy of nonlinear media
11:15 – 11:30	**Coffee-break**
11:30 – 11:35	G. Yakovleva, A. Romanenko, A. Berdinsky, A. Ledneva, V. Fedorov Optimization of thermoelectric properties of materials based on transition metals chalcogenides
11:35 – 11:40	Yu. Mateyshina, L. Brezhneva, N. Uvarov Synthesis and electrochemical properties of nanoporous carbon electrode materials for supercapacitors
11:40 – 11:45	Y. Taki, M. Kitiwan, H. Katsui, T. Goto Effect of carbon and silicon doping on electrical property of SiC
11:45 – 11:50	A. Ukhina, D. Dudina, B. Bokhonov, D. Samoshkin, S. Stankus, H. Katsui, H. Kato Morphological features of W- and Ni-containing coatings on diamond crystals and properties of copper-coated diamond composites obtained by spark plasma sintering
11:50 – 11:55	A. Myz, O. Kichai, G. Karagedov, R. Shutilov Design of electroconductive MWCNT-Al_2O_3 composite ceramics
11:55 – 12:00	M. Popov, S. Bychkov, A. Nemudry New approaches for enhancement of oxygen fluxes of hollow fiber membranes
12:00 – 12:05	D. Maslennikov, A. Matvienko, A. Sidelnikov, S. Chizhik A study of the effect of structural transformations in the course of $Ce_2(C_2O_4)_3 \cdot 10H_2O$ thermal decomposition on the morphology of CeO_2 obtained
12:05 – 12:10	P. Tyapkin, S. Petrov, A. Chernyshev, Y. Larichev, N. Uvarov Physical and chemical properties of iron oxides inserted into SBA-15 mesoporous silica
12:10 – 12:15	J. Chen, A. Ito, T. Goto Effect of deposition temperatures on preparation of Sr-Zr-O films using laser CVD
12:15 – 12:20	V. Lozanov, N. Baklanova, V. Shayapov, A. Berezin Crystal growth and photoluminescence properties of reactive CVD-derived monoclinic hafnium dioxide
12:20 – 12:25	N. Sankova, V. Semeykina, D. Selishchev, E. Parkhomchuk, E. Kozlova Synthesis of titania materials for photocatalytic applications using template - assisted method

12:25 – 12:30	V. Semeykina, A. Polukhin, A. Lysikov, E. Parkhomchuk Novel structured catalysts with regular macroporosity for heavy oil hydroprocessing
12:30 – 12:35	X. Liang, P. Sharma, Y. Zhang, A. Makino, H. Kato Magnetic properties of nanocrystalline $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ cores processed with two-step annealing method
12:35 – 12:40	E. Dobretsov, Yu. Mateyshina, N. Uvarov Effect of lithium oxide excess and alumina on electric properties of $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ solid electrolyte
12:40 – 12:45	A. Brester, D. Dudina Phase formation and microstructure evolution during Spark Plasma Sintering and hot pressing of Fe+Al powder mixtures
12:45 – 12:50	A. Skrypnik, A. Matvienko The study of nickel product morphology developed during the gaseous reduction of nickel oxide
12:50 – 12:55	W.-Y. Park, S.-G. Yu, T. Wada, H. Kato Graphitization and Activation of Open-Cell Type Porous Carbon Prepared by Dealloying in Metallic Melt
13:00 – 14:30	**Lunch**
14:30 – 14:35	S. Chepkasov, A. Zolkin, E. Gladkikh Some features of pulsed cathodic arc deposition of diamond-like carbon films
14:35 – 14:40	I. Krasnikova, I. Mishakov, A. Vedyagin Synthesis of nanostructured carbon-carbon and carbon-mineral nanocomposites
14:40 – 14:45	A. Semerikova, A. Zolkin Characteristic features of Raman spectra of hydrogenated DLC (a-C:H) films containing fullerene-like structure
14:45 – 14:50	M. Khomyakov, V. Demin, T. Smirnova, V. Borisov, G. Grachev, A. Smirnov Mechanical properties of silicone carbonitride thin films obtained by laser-plasma synthesis
14:50 – 14:55	V. Kuznetsov, D. Krasnikov, S. Moseenkov, V. Suslyaev, E. Korovin, A. Romanenko, I. Kranauskaite, J. Macutkevic, J. Banys Polymer composites with carbon nanotubes of different properties
14:55 – 15:00	M. Konishcheva, D. Potemkin, P. Snytnikov, V. Sobyanin Selective CO methanation in the presence of CO_2 over Co/CeO_2 catalysts
15:00 – 15:05	I. Merenkov Synthesis and properties of materials in B-Si-C-N system
15:05 – 15:10	A. Safonov, V. Sulyaeva, K. Kubrak, S. Starinskiy, N. Timoshenko Deposition features of fluoropolymer coatings by Hot Wire CVD method using nichrome activator
15:10 – 15:15	M. Kanygin, O. Sedelnikova, E. Korovin, V. Suslyaev, L. Bulusheva, I. Dorofeev, A. Okotrub Electromagnetic properties of polymers based composite materials with various carbon inclusions

15:15 – 15:20	T. Ito, Y. Yokota, S. Kurosawa, K. Kamada, A.Yamaji, Y. Ohashi, A. Yoshikawa Crystal growth and evaluations of Ce:CsLiYCl6 single crystal growth by halide-micro-pulling-down
15:20 – 15:25	M. Simonov, Yu. Demidova, I. Simakova, D. Murzin Controlled synthesis of PVP-capped Ni and Co metal nanoparticles
15:25 – 15:30	A. Shutilov, R. Shutilov, G. Zenkovets The use of the nanocrystalline catalysts V_2O_5, $WO_3/(Ce(Y)\text{-}TiO_2)$ with enhanced thermal stability for NO reduction by NH_3 to N_2
15:30 – 15:35	A. Shutilov, G. Zenkovets Effect of alumina additives on the nanostructure and thermal stability of TiO_2 with anatase structure
15:35 – 15:40	P. Gribov, A. Matvienko, S. Chizhik, A. Sidelnikov, B. Zakharov The study of structural and morphological changes during thermal decomposition of $Y_2(C_2O_4)_3{\cdot}10H_2O$
15:40 – 15:45	V. Ponomareva, E. Shutova, I. Bagryantseva CsH_2PO_4 – proton electrolytes, modified by divalent cations
15:45 – 15:50	Yu. Shorstkaya, Yu. Bauman, I. Mishakov, P. Plyusnin, Yu. Shubin Preparation and research of catalytic properties of bimetallic alloys Ni_xPd_{1-x}
15:50 – 15:55	O. Gurova, L. Omel’yanchuk, A. Okotrub Investigation of hyperthermic properties of nanohorn’s aqueous suspensions for biological applications
15:55 – 16:10	**Coffee-break**
16:20 – 17:20	Poster session 2

Day 4, November 2

Session 3

Room 3122 (New Building of NSU)

Chairs: A. Zolkin, T. Goto

12:45 – 13:05 Invited	***R. Belosludov*** *Role of Computational Materials Science in Realization of Advanced Energy Materials and Nanostructure*
13:05 – 13:25 Invited	***K. Fujiwara*** *Morphological transformation of crystal/melt interface of silicon*
13:25 – 13:45 Invited	***A. Zolkin*** *Synthesis of DLC films. Ion-beam technologies*
13:45 – 14:05 Invited	***V. Volodin*** *Optical properties of nanocrystals formed with the use of laser pulse annealing*
14:05 – 15:35	**Lunch**

15:35 – 15:40	N. Korobeishchikov, M. Roenko, V. Kalyada, G. Tatancev Diagnostics of intensive gas cluster-ion beams for materials processing
15:40 – 15:45	T. Nihei, Y. Yokota, M. Arakawa, Y. Ohashi, S. Kurosawa Growth of platinum fiber using the micro-pulling-down method and the local struccture
15:45 – 15:50	N. Korobeishchikov, V. Kalyada, I. Nikolaev, M. Roenko Ultra-smooth surface polishing by argon cluster ion beam
15:50 – 15:55	V. Khudozhitkov, A. Zarvin The possibility of the launch of plasmochemical reactions and generate clusters with electronic activation of the gas flow
15:55 – 16:00	K. Prasertsuk, S. Tanaka, T. Tanikawa, K. Shojiki, A. Miura, R. Nonoda, F. Hemmi, S. Kuboya, R. Katayama, T. Suemitsu and T. Tanikawa Fabrication of inverted gallium nitride-hemt structure with flat interface grown by metalorganic vapor phase epitaxy
16:00 – 16:05	D. Markovskaya, E. Kozlova, V. Parmon The application of catalysts based on $Cd_{0.3}Zn_{0.7}S$ doped by copper and nickel species for photocatalytic hydrogen production from Na_2S+Na_2SO_3 aqueous solutions
16:05 – 16:10	Yu. Demidova, I. Simakova, J. Gläsel, B. J. Etzold, T. Schubert, D. Murzin. Carbon based Ru colloidal catalysts: synthesis approaches and catalytic behavior
16:10 – 16:15	L. Basalaeva, Yu. Nastaushev, F. Dultsev Fabrication and characterization of silicon nanopillars
16:15 – 16:20	A. Lyamkina, S. Moshchenko Non-radiative energy transfer in quantum dot ensemble mediated by localized surface plasmons
16:20 – 16:35	**Coffee-break**
16:45 – 17:45	Poster session 3

Day 5, November 3

Session 4

Room 4310 (New Building of NSU)

Chairs: B. Bokhonov, V. Ulianitsky

09:50 – 10:10 Invited	***K. Shefer*** *Investigation of nanocatalysts using the PDF method*
10:10 – 10:30 Invited	***V. Prinz*** *Metamaterials, topological photonic crystals and original hybrid micro-nanomaterials*
10:30 – 10:50 Invited	***D. Dudina, B. Bokhonov, A. Ukhina, A. Brester, M. Esikov, A. Anisimov, V. Mali*** *Microstructural non-uniformities in Spark Plasma Sintered compacts observed at different length scales*
10:50 – 10:55	E. Baranov, A. Zamchiy, S. Khmel Plasma-enabled low temperature growth of high-density, aligned arrays of

	silicon oxide nanowires bunches via VLS mechanism
10:55 – 11:00	K. Sashkina, A. Polukhin, V. Labko, A. Ayupov, A. Lysikov, E. Parkhomchuk Design of hierarchical zeolite catalysts
11:00 – 11:05	M. Serebryakova, S. Novopashin Thermophysical properties of nanofluids based on hollow Al_2O_3 nanoparticles and water
11:05 – 11:10	A. Zaikovskii, S. Novopashin Effect of the arc-discharge parameters on the morphology and the electrical conductivity of the synthesized carbon materials
11:10 – 11:25	**Coffee-break**
11:25 – 11:30	A. Kurenkova, E. Kozlova, P. Kolinko The effect of hydrothermal treatment on activities of $Cd_{0.3}Zn_{0.7}S$ and Au/ $Cd_{0.3}Zn_{0.7}S$ under visible light
11:30 – 11:35	N. Filippov, S. Romanov Silicon microchannel membrane and microfluidic devices on its basis
11:35 – 11:40	S. Sakhapov, S. Novopashin Synthesis and nanoparticles dynamic in spherical glow discharge
11:40 – 11:45	L. Lapteva, Yu. Fedoseeva, A. Okotrub, and L. Bulusheva Investigation of interactions of carbon nanomaterials with lithium by X-ray spectroscopy
11:45 – 11:50	N. Kolobov, D. Selishchev, A. Gubanov, D. Kozlov, E. Kozlova UV-LED Photocatalytic Oxidation of Carbon Monoxide over the Pd-loaded Catalysts Synthesized by the Decomposition of $Pd(acac)_2$
11:50 – 11:55	A. Shevyrin, A. Pogosov Electromechanical coupling in nanoelectromechanical systems with a two-dimensional electron gas
11:55 – 12:00	N. Mironnikov, V. Korolkov, D. Derevyanko, V. Shelkovnikov, Hybrid photopolymer material “Hybrimer-TATC”: peculiarities of laser processing and properties of thin films
12:00 – 12:05	V. Sadykov, Yu. Fedorova, A. Lukashevich, Z. Vostrikov, N. Eremeev, A. Krasnov, A. Skryabin Novel nanocomposte materials for oxygen separation membranes
12:15 – 12:20	I. Kostogrud, D.Smovzh Transferring of CVD-graphene from the copper substrate to the polymer substrate
12:30 – 13:30	Poster session 4
13:30 – 15:00	**Lunch**

Closing Ceremony

Room 3107 (New Building of NSU)

15:00	Farewell speech Awarding

2016 Russia-Japan Conference "Advanced Materials: Synthesis, Processing and Properties of Nanostructures"

Abstracts

October 31

Session 1

The Little Hall of The House of Scientists

Chairs: S. Novopashin, R. Belosludov

Invited Lectures

- ***T. Goto*** *Laser Chemical Vapor Deposition of Functional Films*
- ***S. Novopashin*** *Arc-discharge synthesis of nanomaterials*
- ***V. Ulianitsky*** *Detonation spraying. Technology, equipment and applications*

Oral reports

D.-S. Kang, Yu. Koizumi, K. Yamanaka, A. Chiba
Characteristics of Ni based superalloy fabricated by electron beam melting
A. Yunoshev, S. Rafeichik, A. Plastinin, V. Sil'vestrov
Applications of emulsion explosives for explosive welding of thin foils
I. Batraev, D. Dudina, D. Rybin
CCDS facilities as dynamic chemical reactors
Y. Hou, Y. Li, A. Chiba
Copper Influence on Corrosion Resistance to HF Acid Solution of Cu-modified Ni-Co-Cr-Mo Alloys
A. Larichkin, K. Zaharchenko, B. Gorev, V. Kapustin
Influence of creep-age forming on fatigue life of the components from B95 aluminum alloy
D. Rybin, D. Dudina, I. Batraev, V. Ulianitsky
Phase formation in metal-carbon systems during detonation spraying and post-spray annealing

LASER CHEMICAL VAPOR DEPOSITION OF FUNCTIONAL FILMS

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CVD (Chemical Vapor Deposition) has been widely used for preparing thin films. Thick films and bulky plates mainly non-oxides (nitrides and carbides) such as SiC wafer have also been prepared by CVD. Although oxides have useful applications for dielectrics, optics, superconductors and catalytic materials, CVD oxide thick films has hardly been obtained, because precursors mainly metal-organic (MO) compounds are generally too reactive with oxidant gas and easily decompose at high temperature resulting in premature reactions in a gas phase. This would result in decreasing deposition efficiency and deposition rate, and thus the deposition rate of CVD oxide films has commonly been less than several μm/h. Auxiliary energy such as laser, termed as laser CVD, can effectively enhance the deposition rate and lower the deposition temperature. Laser CVD has been categorized into two types, i.e., photolytic laser CVD and pyrolytic laser CVD. Photolytic laser CVD usually employs a high-energy laser, such as excimer laser. Photochemical reactions occur in a gas phase yielding deposition of film without heating substrate. However, films cannot be prepared at high-speed in a form of thick film. On the other hand, pyrolytic laser CVD commonly employs an infra-red laser, typically CO_2 laser. By introducing source gases into the locally heated area by the laser, the deposition reaction may occur at a significantly high speed. The deposition area of the pyrolytic laser CVD can be a laser beam size, usually less than a few millimeters. Since source gases can easily access such a small deposition area, the deposition rate can be significantly enhanced by laser energy. The deposition rate (in length of deposit) can be at most 10^7 times as high as those of conventional thermal CVD. However, it has been thought that high-speed, wide-area and thick coating is impossible by pyrolytic laser CVD due to the small laser beam size.

We have developed a new kind of laser CVD enabling high-speed and wide-area coating by using high-power lasers. The deposition rates in volume of our laser CVD are several orders higher than those of common pyrolytic laser CVD. We have prepared various oxides and non-oxide films at significantly high deposition rates at most 27.5 mm/h for SiO_2 film1).

Laser CVD can prepare various functional films. Calcium phosphate, calcium titanate and calcium silicate films as bio-active and bio-degradable films were prepared on Ti implant. Highly c-axis oriented hydroxyapatite film prepared by the laser CVD exhibited the highest regeneration rate of hydroxyapatite in a simulated body fluid. A non-lead ferroelectric $BaTi_2O_5$ film, discovered by us, with highly (010) orientation was prepared2). The laser CVD was applied to prepare superconducting c-axis oriented $YBa_2Cu_3O_{7-\delta}$ (YBCO)3) and CeO_2 buffer layer4) epitaxial films on Hastelloy tape. It is commonly difficult to prepare Na and Li containing compound films by CVD due to high vapor pressure of Na and Li. Na-β/β" aluminas because of high vapor pressure of Li and Na at high temperature. In the present work, crystalline Na β/β"-alumina films have been prepared using $Al(acac)_3$ (acac: acetylacetonate) and Na(dpm) (dpm: dipivaloymethanate) as precursors. Na β/β"-alumina films were prepared by laser CVD, The deposition rate of Na β/β"-alumina films reached 44 $\mu m\ h^{-1}$ at $T_{dep} = 1316$ K5), Various Li conducting compound films were prepared by laser CVD6). α-$LiAl_5O_8$, γ-$LiAlO_2$ and β-Li_5AlO_4 films were prepared around 1000 K at 70 to 100 $\mu m\ h^{-1}$.

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ARC-DISCHARGE SYNTHESIS OF NANOMATERIALS

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The report is devoted to the review of opportunities of synthesis of nanomaterials with use of the arc-discharge. The report is based on the experimental studies conducted at the Institute of Thermophysics of the Siberian Branch of the Russian Academy of Science.

Features of synthesis of the following nanomaterials are presented:

1. Carbon nanomaterials (fullerenes, nanotubes, decanter, nanocrystal carbon);
2. Encapsulated nanoparticles of metals;
3. Synthesis of intermetallic nanoparticles;
4. Synthesis of nanoparticles of oxides;
5. Synthesis of carbide nanoparticles;
6. Synthesis of ferromagnetic nanoparticles.

In the report the fields of possible practical use of plasma-arc technology are considered:

1. Ecology (conversion of associated petroleum gas, catalytic burned up exhaust gases of cars);
2. Power (material for catalytic cathodes of fuel elements);
3. Technologies of synthesis of magnetic liquids;
4. Metalworking (synthesis of heavy-duty nanopowders of carbide of tungsten);
5. Synthesis of new materials (nanoceramics).
6. Synthesis of bactericidal materials on the basis of silver.

DETONATION SPRAYING.
TECHNOLOGY, EQUIPMENT AND APPLICATIONS.

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Gaseous detonation is well-known as the phenomenon of highest concentration of gas-fuel combustion energy. As occurs in a gun barrel, it produces a detonation products flow with a temperature up to 4500K and velocity about 1200 m/sec. This advantage has been used for powder material spraying in the middle of the XX century already [1]. Usually so-called Chapman-Jouguet (or self-sustained) detonation is realized in a barrel.

The new generation installation (CCDS*2000*) for detonation spraying was developed [2] at Lavrentyev Institute of Hydrodynamics SB RAS as a result of extensive research of the detonation process and its peculiarities in the barrel of a detonation gun in the presence of particles in detonation products. The principal features of CCDS*2000* installation are as follows:

i) high-precision gas distribution system, with a damping chamber between the mixer and the barrel, ensures safety of operation for all explosive mixtures;

ii) pulsed and localized powder feeding into the barrel guarantee high uniformity of the particle spray and the ability to work with several feeders simultaneously;

iii) removable barrels and nozzles permit changing size of the coating spot from 1 to 10 cm^2;

iiii) the process is controlled by a PC which ensures stability of the detonation regime and coordinates the operation of the manipulator and the detonation gun.

New generation D-gun is portable, high frequency operation (up to 10 Hz) and can work with any gaseous fuel mixed with an oxidizer in any proportion; it permits one to inject simultaneously two fuels. It is an ideal device both for technology development and for industrial use.

Spraying conditions has been studied for different powders: metals (aluminum, copper, iron, nickel, cobalt, molybdenum etc), alloys (steel, cast iron, nickel-chrome, brass, duralumin, self-fluxing etc), ceramics: (alumina, chromia, zirconia, titania), cermets (carbides of tungsten, chromium, titanium with binder). To establish optimum spraying modes all necessary techniques of analyses has been used: *SEM*, X-rays, adhesion and cohesion measurement, micro-hardness, residual stress, chemical analysis, abrasive and erosive resistance, electro insulation. Some our result on coatings properties can be found in [3].

Detonation spraying can have a lot of industrial application. Detonation coatings can be deposited on the substrates made of metals, ceramics, plastics, even wood and can coat surfaces of arbitrary shapes with the incidence angle up to 60°. For the majority of materials, the coating thickness can exceed some millimeters. Due to the pulsed nature of detonation spraying processes an overheating of the treated component can be practically excluded, so any changing of component shape or extraneous structural changes in its material will be prevented; it is possible to coat substrates with thickness less than 1 mm. Detonation spraying is very effective for restoration of worn-out components.

In our experience [3], detonation coatings are applied in: aerospace industries, machine-building and ship-building, equipment for oil mining and chemical processes, machines for wood processing and paper production, equipment for metal mills and food industries, components of electrical and electronic devices.

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CHARACTERISTICS OF NI BASED SUPERALLOY FABRICATED BY ELECTRON BEAM MELTING

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Improvement of high temperature performances in Ni based superalloy is substantially associated with its microstructure stability at high temperature. Microstructure stabilities can be controlled by various method such as alloying element addition, heat treatment and fabrication technique evolution. Electron beam melting (EBM) is one of additive manufacturing technologies which are also known as “3D printing”. One of powerful advantages is that EBM can control the solidification morphology during building (or stacking) because the building process is progressed in layer by layer. In other words, the grain growth can be progressed in direction of heat flow during building. Therefore, this method allows us to make the desirable solidification morphology. However, the relationship between solidification morphology and mechanical properties of conventional Ni based superalloy fabricated by EBM have not been well established. This study aims to reveal the characteristic of a conventional Ni-based superalloy, fabricated by EBM.

Testing rod specimens were prepared by two methods for comparison. One is conventional Investment casting using Vacuum induction melting furnace. The other is Arcam A2 EBM system (Arcam, Sweden) with gas atomized powder. Chemical compositions of alloys were analyzed by Inductively coupled plasma (ICP). Heat treatment was conducted as follows: solution heat treatment at 1473K for 2 hours, primary aging at 1323 K for 4 hours, furnace cooling up to 923 K and kept for 10 min, stabilization at 1327 K for 4 hours and furnace cooling to 923 K, hold at 923 K for 10 min and secondary aging at 1118 K for 16 hours and then air cooling. Solidification morphologies and microstructures of Ni based superalloys were observed with optical microscope, field emission scanning electron microscopy, electron backscatter diffraction and transmission electron microscopy. Hardness was measured at room temperature by Vickers hardness test. Tensile test was conducted at temperature ranging from room temperature to 1253 K with a strain rate of $1.5 \cdot 10^{-4} s^{-1}$.

Figure 1 shows the solidification morphologies of Ni based superalloys fabricated by Investment casting (IC) and EBM process, respectively. Equi-axed grain morphologies could be shown in IC alloy, while columnar grain growth along building direction with <100> orientation could be observed. These differences of solidification morphologies might be due to different solidification behavior and heat flow direction.

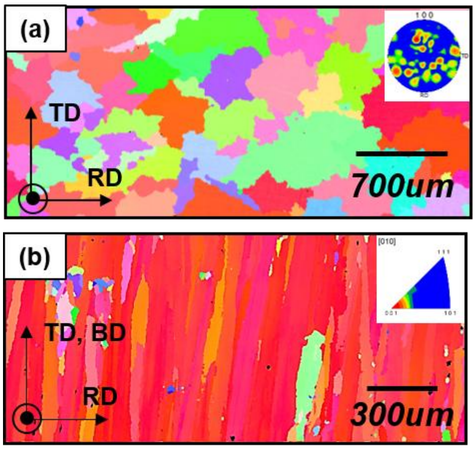

Figure 1. Solidification morphologies of Ni based superalloy ;
(a) Investment casting specimen and (b) EBM specimen.

APPLICATIONS OF EMULSION EXPLOSIVES FOR EXPLOSIVE WELDING OF THIN FOILS

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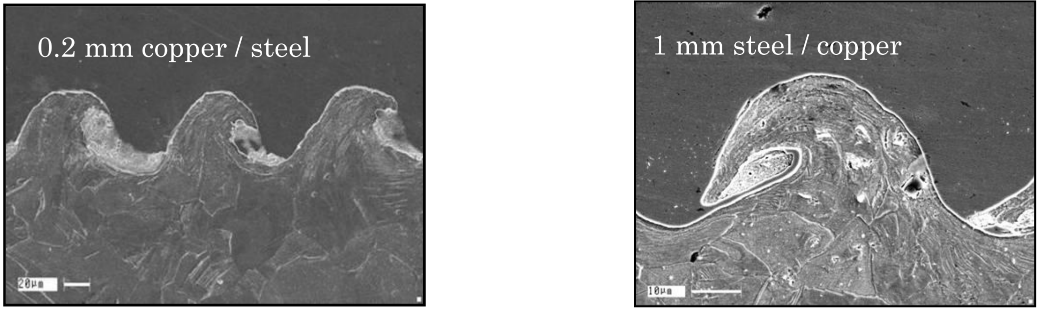
Low-velocity emulsion explosives (EMX) are used in present work for explosive welding of thin foils. Low values of the density of explosive and its detonation pressure are obtained by addition of high amount of porous sensitizer glass microballoons MS-V or ultralight polymeric microballoons Expancel.

EMX layer of 3 mm thickness is used for explosive cladding of steel by 0.2 mm copper foil in parallel welding scheme. It contains 8 weight % of MS-V and has density of ρ_0 = 1 g/cm^3 with detonation velocity of D = 3 km/s. In other case 12 mm EMX layer containing 35 % MS-V is used to weld 1 mm steel plate with copper plate. The parameters are ρ_0 = 0.63 g/cm^3 and D = 2.5 km/s.

Estimated turning angle and contact point velocity are in the area of parameters of strength joint [1]. Microphotographs of polished welds obtained with scanning electron microscope LEO-420 are on fig. 1.



20 μ

10 μ

Fig. 1. Microphotographs of polished welds for copper / steel pair.

For explosive welding of lead foil it needs significantly more soft parameters, so welding scheme with the angle and buffering copper plate is chosen. EMX layer of 10 mm, angle of slope $\alpha = 6^0$ and initial gap of 5 mm are used. Thicknesses of the lead foil and buffering plate are 0.05 mm and 0.2 mm respectively. The parameters of low-density EMX are ρ_0 = 0.2 g/cm^3 and D = 2 km/s obtained by using ultralight polymeric microballoons.

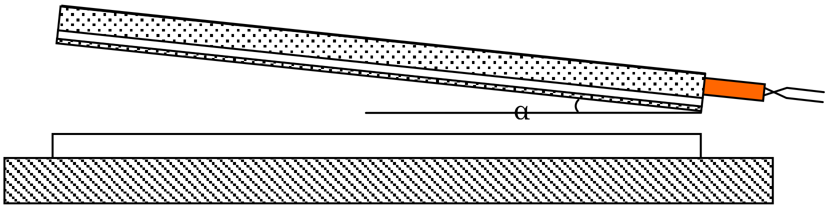


Fig. 2. Experiment of explosive welding of lead foil with steel plate.

It is shown that EMX with low detonation velocity and low density down to 0.2 g/cm^3 can be used for explosive welding of thin foils including lead foil of 0.05 mm thickness.

This work was supported by RFBR (project № 15-03-00883).

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НЕКОТОРЫЕ ПРИМЕРЫ ПРИМЕНЕНИЯ НИЗКОСКОРОСТНЫХ ЭМУЛЬСИОННЫХ ВВ ДЛЯ СВАРКИ ВЗРЫВОМ ТОНКИХ ФОЛЬГ

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Приведены результаты экспериментов по применению эмульсионных взрывчатых веществ для сварки взрывом тонких фольг. Низкие значения плотности ВВ и давления детонации достигались путем добавления значительной доли пористого сенсибилизатора, в качестве которого применялись полые стеклянные микробаллоны МС-В и ультралегкие полимерные микробаллоны Expancel.

Для плакирования стали медной фольгой толщиной 200 мкм использовался 3 мм слой ЭмВВ с 8 % МС-В плотностью $\rho_0 = 1$ г/см^3 и со скоростью детонации $D = 3$ км/с. Для сварки взрывом пластинки из нержавеющей стали толщиной 1 мм с медным основанием использовался 12 мм слой ЭмВВ с 35 % МС-В $\rho_0 = 0{,}63$ г/см^3 и $D = 2{,}5$ км/с. По оценкам, значения угла поворота и скорости точки контакта попадают в область свариваемости пары медь/сталь [1]. Микрофотографии разрезов сварных швов, полученные на электронном сканирующем микроскопе LEO–420, приведены на рис. 1.

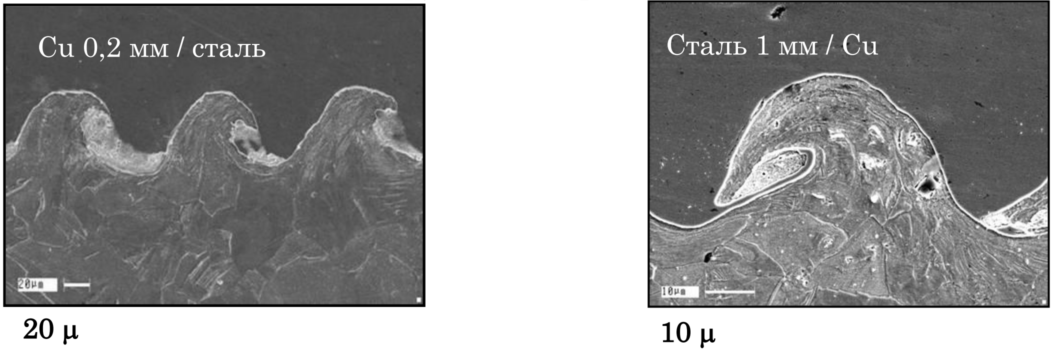

Рис. 1. Фотографии шлифов сварных швов в паре медь/сталь.

Для сварки взрывом свинца, в отличие от меди, не удается использовать параллельную схему расположения пластин – требуются заметно более «мягкие» параметры – поэтому была выбрана схема сварки под углом. С учетом толщины свинцовой фольги 0,05 мм, применялась буферная пластина из меди толщиной 0,2 мм, и ЭмВВ с очень низкой плотностью 0,2 г/см^3, полученное при добавлении большого количества полимерных микробаллонов Expancel. Скорость детонации равнялась 2 км/с, угол наклона пластины $\alpha = 6^0$, начальный зазор между пластинами – 5 мм.

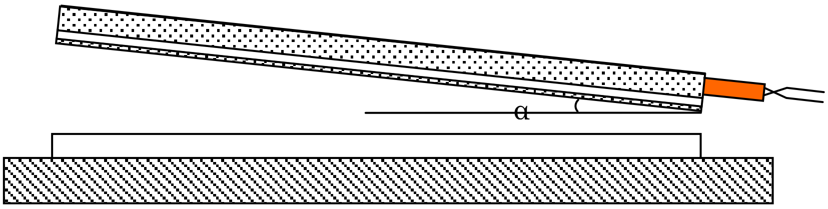

Рис. 2. Эксперимент по сварке взрывом свинцовой фольги со сталью.

Показано, что эмульсионные ВВ с низкой скоростью детонации и низкой плотностью до 0,2 г/см^3 могут успешно использоваться для сварки взрывом тонких фольг, в том числе из свинца.

Работа выполнена при финансовой поддержке РФФИ (проект № 15-03-00883).

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CCDS FACILITIES AS DYNAMIC CHEMICAL REACTORS

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Detonation spraying is a promising method for deposition of functional coatings from powders of various metals, alloys, ceramics and composites. Computer-controlled detonation spraying (CCDS2000) facilities developed in LIH SB RAS as a result of comprehensive studies of detonation in gas fuels [1] allows for flexibility in varying the parameters of the process and tailoring the phase composition and microstructure of coatings.

Recently, our group has investigated the chemical aspects of the behavior of a number of materials in the process of detonation spraying using CCDS2000 [2]. The goal of the present work was to study the mechanisms of the formation and control tools of the microstructure and coatings properties. The possibility of obtaining different phases in composite coatings by varying the deposition parameters, such as explosive charge (the amount of an explosive mixture used in one shot), oxygen/carbon molar ratio, nature of the carrier gas and stand-off distance, was examined. The phases of the coatings can be formed in situ as a result of interaction of the chemically reactive powders with the detonation products and the carrier gas. Deposition of titanium [3], Ti-Al intermetallics [4] and Ti-TiC composites [5] using CCDS2000 showed the possibilities of controlling the phase composition and crystallite size of the phases of the coatings. It was demonstrated that the phase composition of the coatings can differ significantly from that of the feedstock powders.

This research is partially supported by the Russian Foundation for Basic Research, project 14-03-00164 a.

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COPPER IFLUENCE ON CORROSION RESISTANCE TO HF ACID SOLUTION OF Cu-MODIFIED Ni-Co-Cr-Mo ALLOYS

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Developing materials with both high strength and high resistance to hydrofluoric acid (HF) is of great importance for industrial applications such as the fabrication of chlorofluorocarbon compounds, components in injection moulding of polyfluoroalkoxy resin (PFA), and high-pressure containers used in the chemical industry. Various studies have indicated that Ni-Cr-Mo alloys can offer excellent corrosion resistance to HF solutions because a Mo-oxide-dominant passive film can form on the sample surface; the film is both compact and inert to any further attack by HF. Therefore, Ni-16Cr-15Mo (NiCrMo, wt.%) alloy is widely used in HF conditions despite their lower strength compared to Co-Cr-Mo alloys.

Our research has indicated for the first time that substituting Co for Ni by up to 30 wt.% can greatly increase the strength of the alloy without sacrificing its corrosion resistance to HF solutions. This is made possible by greatly reducing the stacking fault energy (SFE) of the alloy by alternating its plastic deformation mechanism because the cross slip is significantly inhibited in low-SFE materials, leading to higher work hardening of materials and therefore higher hardness or stress.

This study examined the effect of partially substituting cobalt for nickel in Ni-16Cr-15Mo alloy on corrosion resistance to 5mol/L HF acid solution at 100 °C. Microstructural characterisations revealed that cobalt substitution did not have a detrimental effect on corrosion resistance, but rather, it seems to enhance the formation of a compact and thin Mo-rich passive film by selective dissolution of elements. Heat-annealing drastically lowered the corrosion resistance due to Mo-rich precipitate of alloy, which lowered the concentration of Mo in bulk matrix, in particular close to precipitate sections, leading to inhibition of formation of homogenous and compact Mo-rich passive film.

A small addition of Cu yielded a further improvement in the corrosion resistance of Ni-30Co-16Cr-15Mo-6Fe alloy, even after cold forging. The passivation of Ni-30Co-16Cr-15Mo-6Fe alloy by a Mo-oxide-dominated passive film completely changed to passivation by a Cu-dominated one in Ni-30Co-16Cr-15Mo-6Fe-2Cu alloy during immersion in HF solution because the segregation behaviour of Cu was much stronger compared to that of Mo.

INFLUENCE OF CREEP-AGE FORMING ON FATIGUE LIFE OF THE COMPONENTS FROM B95 ALLUMINIUM ALLOY

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Due to the improvement of the forms of aircraft, methods of complex surfaces forming using rectangular solid plates and elevated temperatures have become popular. Compared with the production of prefabricated elements, such molding techniques allow saving resources, reducing weight, getting rid of assembly and fitting work on the stage of manufacturing. How different will the fatigue life of pre-deformed at different temperatures and deformation rates products be? The answer to this question is relevant to aerospace industry. A pilot study of the issue is conducted.

The technological process of forming panels of a given geometry made of the B95 alloy (Al- Zn -Mg- Cu) has been simulated including: plastic strain in the range 10^{-5} - 10^{-2} s^{-1} at normal (20°C) temperature, artificial ageing temperature (165 °C) and annealing temperature (420°C), followed by heat treatment at the T2 mode in accordance with the production instruction PI 1.2.699-2007. It has been experimentally found how the process parameters (temperature and strain rate) influence the fatigue limit. It has been shown that resistance to fatigue of the B95 alloy does not decrease after pre-strain at annealing temperature.

Pre-strain of the samples made of the B95 alloy at annealing temperature (420°C) and strain rate of 10^{-2} s^{-1} , followed by heat treatment in the T2 mode does not reduce the resistance to fatigue (twice) as compared with the samples deformed at 20°C.

It is shown that the fatigue limit of B95 after pre-strain at the ageing temperature (165°C) with subsequent heat treatment become higher with the pre-strain rate decreased.

In these series there is a trend to reduce the number of cycles before destruction which correlates with the results of the forming method proposed in [1].

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Key words: processing technique, forming, strain rate, experiment, durability, aluminum alloy, creep, fatigue

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PHASE FORMATION IN METAL-CARBON SYSTEMS DURING DETONATION SPRAYING AND POST-SPRAY ANNEALING

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Thermal spraying processes are based on heating and acceleration of powder particles by high-temperature gas flows. In detonation spraying, the phase composition of the coatings is very sensitive to the O_2/C_2H_2 ratio and the nature of the carrier gas. Thanks to a flexible process of forming an explosive mixture, the CCDS*2000* detonation spraying equipment allows initiating the detonation process in a wide range of O_2/C_2H_2 ratios. During deposition of detonation coatings, depending on the concentration of the fuel in the explosive mixtures, the formation of oxides (in the case of low fuel contents) and carbides (in the case of high fuel contents) is possible.

In the coatings obtained by deposition of a titanium powder using oxygen-rich mixtures at O_2/C_2H_2=2.5, titanium nitrides, oxides and oxynitrides were observed. During deposition of titanium in strongly reducing conditions (O_2/C_2H_2=0.7), titanium carbides and titanium carbonitrides formed. The formation of nitrides, oxynitrides and carbonitrides in the coatings is influenced by the nature of the carrier gas (nitrogen or air). The behavior of titanium during the deposition process and the phase composition of the coatings obtained in various deposition conditions are described in detail in ref. [1].

The formation of metastable phases in the coatings obtained by detonation spraying using a nickel powder and mixtures of nickel and amorphous carbon was investigated [2]. It was found that solid solutions based on metastable hcp-Ni and fcc-Ni formed in the detonation coatings at O_2/C_2H_2 =0.7 and explosive charges 50-70%. Metastable phases were not detected in the coatings obtained from the nickel powder at O_2/C_2H_2 equal to 1.1 and at higher oxygen contents. In the coatings obtained at O_2/C_2H_2=2.0, partial oxidation of nickel was observed (formation of nickel oxide).

Studies were conducted to determine the phase composition of the metal-carbon detonation coatings after annealing in a Spark Plasma Sintering (SPS) facility, which offers a convenient way to rapidly heat the samples in a reducing atmosphere. Investigations show that annealing leads to transformation of metastable phases in the coatings. During annealing of the coatings obtained from the Ni-C_{am} powders, metastable phases — solid solutions based on cubic and hexagonal nickel — decomposed, the cubic nickel becoming the main component of the metallic part of the coating.

Detonation coatings obtained from the Fe-C_{am} powders contained iron carbide Fe_3C of hexagonal modification. During annealing of the coatings in the SPS, Fe_3C transformed into its orthorhombic modification.

These studies have shown that wide possibilities exist to flexibly control the phase compositions of metal-carbon detonation coatings.

This work is partially supported by the Russian Foundation for Basic Research, project 15-33-20061 mol_a_ved.

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2016 Russia-Japan Conference "Advanced Materials: Synthesis, Processing and Properties of Nanostructures"

Abstracts

November 1

Session 2

Room 4117 (New Building of NSU)

Chairs: V. Volodin, K. Fujiwara

Invited Lectures

- ***H. Katsui, T. Goto*** *Melt solidification of high-temperature eutectic non-oxide ceramics*
- ***B. Bokhonov*** *In Situ electron microscopic investigations of Metal-Silicon interactions*
- ***T. Wada, H. Kato*** *Preparation of nanoporous base metals by dealloying in metallic melt and their application for energy related materials*
- ***M. Chen*** *3D nanoporous materials: a new horizons of functional materials*

Oral reports

V. Kuznetsov, A. Romanenko, A. Berdinsky, B. Kholkhoev, V. Makotchenko, V. Fedorov Temperature dependences of electrical resistances of SWCNTs in PET matrixes films

S. Stolyarova, V. Koroteev, M. Kanygin, L. Bulusheva, A. Okotrub Synthesis of MS_2/C (M=Mo, Ti) composites at high temperature and pressure **M. Kozlova, P. Poltarak, V. Fedorov** Composites based on low-dimensional transition metal chalcogenides with noble metal nanoparticles

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A. Ukhina, D. Dudina, B. Bokhonov, D. Samoshkin, S. Stankus, H. Katsui, H. Kato Morphological features of W- and Ni-containing coatings on diamond crystals and properties of copper-coated diamond composites obtained by spark plasma sintering

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MELT SOLIDIFICATION OF HIGH-TEMPERATURE EUTECTIC NON-OXIDE CERAMICS

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Silicon carbide and transition metal based carbides possess a high refractoriness (melting points > 2500 K), high hardness and corrosion resistance at high temperatures; however, their low sinterability and toughness limit the application under severe stress. While the solid state sintering is commonly used to manufacture compacts of these high-temperature non-oxides, a melt-solidification technique is another route to fabricate fully dense compacts. The high volatility and sublimation of these non-oxides are problematic to employ melt-solidification techniques for fabricating monolithic materials. This study demonstrates synthesis of $SiC–VB_2$ and $TiC–TiN–TiB_2$ composites via eutectic melt solidification by arc-melting, forming self-assembled fine and dense microstructures in submicron sizes with coherent crystal orientation relationships.

SiC, VB_2, TiC, TiN and TiB_2 powders were used as the starting materials. The powders were mixed and milled with ZrO_2 balls with a small amount of ethanol for 4 h in a polyethylene bottle. The mixed powder slurry was dried at 333 K for 12 h, and pressed into disks. The disks were arc-melted twice under an N_2 atmosphere at 80 kPa. Crystal phases were identified by X-ray diffraction (Cu-Kα, θ–2θ, ULTIMA IV, Rigaku, Japan). Microstructures were observed by scanning electron microscopy (SEM, model S-3100H, Hitachi) and transmission electron microscopy (TEM, model EM-002B, TOPCON, and JEM-ARM200F, JEOL).

Figure 1 depicts a SEM image of a $SiC–VB_2$ eutectic composite ($42SiC–58VB_2$). Elongated VB_2 grans with a bright contrast were separated by SiC layers with a dark contrast in several hundred nanometers, forming anisotropic labyrinth eutectic microstructure. This labyrinth eutectic comprised single crystal grans of SiC and VB_2 with the orientation relationship of SiC(111) // VB_2(1-210) and SiC(110) // VB_2(0001). The arc-melted $44TiC–20TiN–36TiB_2$ formed the quasi-binary eutectic TiB_2-TiC_xN_{1-x} composite. Fig. 2 presents the SEM image of the $44TiC–20TiN–36TiB_2$ composite. Hexagonal single-crystalline TiC_xN_{1-x} rods (a bright contrast) were grown in a single-crystalline TiB_2 matrix (a dark contrast) with a crystal orientation relationship of TiB_2 (11-20) // TiC_xN_{1-x} (-202) and TiB_2 [0001] // TiC_xN_{1-x} [111]. A long-range ordered structure of Ti–B–C–N was formed at the TiB_2/TiC_xN_{1-x} interface by the intermixing of the coherent interplanar spacings of seven TiB_2 (0001) and nine TiC_xN_{1-x} (111) planes.

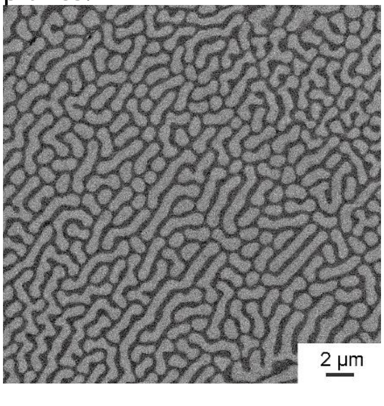

Fig. 1 SEM image of $SiC–VB_2$ eutectic composite.

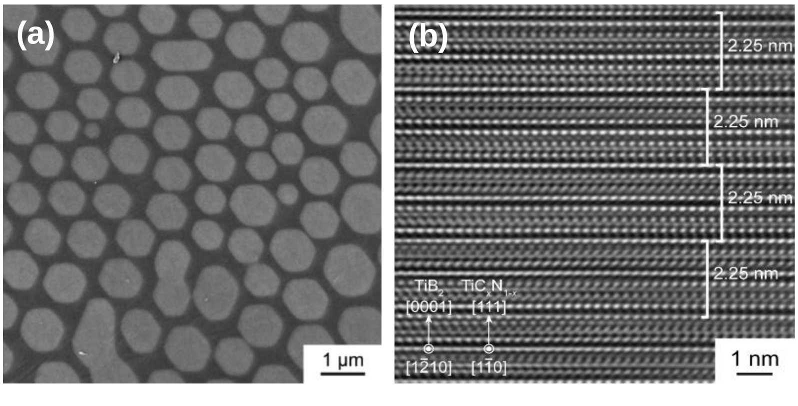

Fig. 2 Microstructure of $44TiC–20TiN–36TiB_2$ composite. (a) SEM image, (b) STEM image at the TiB_2/TiC_xN_{1-x} interface.

IN SITU ELECTRON MICROSCOPIC INVESTIGATIONS OF METAL-SILICON INTERACTIONS

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The in situ electron microscopic investigations of the formation of eutectic alloys in the systems: crystalline Si/ Metal particle, amorphous Si/Metal particle (Metal = Au. Ag, Cu) showed that the formation of eutectics is preceded by metal diffusion into amorphous silicon with the formation of metastable amorphous metal silicide. Supersaturation and decomposition of the metastable amorphous metal silicide leads to the evolution of polycrystal silicon. Morphological characteristics of the liquid eutectic formation in the systems crystalline (100)Si/ particle Au and crystalline (100)Si/ particle Al are similar to the well known morphological characteristics of the formation of etch pits in crystals. For the systems crystalline (100)Si/ particle Au, an oriented formation of the liquid eutectic alloy is observed. The growth of the eutectic melt during the annealing of the system crystalline (100)Si/Al particle takes place isotropically. The crystallization of liquid eutectic alloy leads to topotaxial evolution of gold silicide islands at the interface: crystal eutectics - single crystal silicon.

In situ investigations of the formation of alloys in the systems: crystalline Si/Nickel particle, amorphous Si/Nickel particle showed that the sequence of phase formation during interaction of nickel particles with single crystalline (100) silicon and amorphous silicon corresponds to the following sequence of stages during the annealing of thin-film systems:

a) Within a temperature range up to 500°C, the first and prevailing phase formed is Ni_2Si,

b) Annealing at temperatures above 600°C is accompanied by the formation and epitaxial growth of the $NiSi_2$ phase. The growth of the nickel disilicide crystalline phase is accompanied by the formation of dislocations both in the nickel disilicide phase and in the silicon phase.

The interaction of the amorphous silicon film with nickel particles at temperatures above 600^oC leads to the crystallization of several silicide phases: $NiSi_2$, NiSi, Ni_3Si_2.

PREPARATION OF NANOPOROUS BASE METALS BY DEALLOYING IN METALLIC MELT AND THEIR APPLICATION FOR ENERGY RELATED MATERIALS

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Nanoporous metals have attracted much attention due to the excellent functional properties which come from extremely large surface area and unique bicontinuous structure. Normally, such nanoporous metals were prepared by a selective corrosion of base component(s) from the multicomponent alloy precursor in an acid or alkaline aqueous solution, termed dealloying. One can utilize dealloying to prepare nanoporous noble metal but can’t to obtain nanoporous base metal because it is immediately oxidized by the aqueous solution. To overcome this problem, we have recently developed an innovative dealloying method using metallic melt. In our novel method, an alloy precursor is immersed in a metallic melt and one component is selectively dissolved, while the other component remains and forms three dimensional nanoporous metals spontaneously. Not like the dealloying in aqueous solution, which is essentially the oxidization of metals, the dealloying in metallic melt is the mixing of elements by metal-metal reaction. Thus, independent of oxidation potential of element, formation of nanoporous metal is possible by dealloying in metallic melt. We have successfully prepared various nanoporous base metals such as Ti, Zr, Nb, V, Cr, Fe, Si, and C.

These nanoporous base metals exhibit excellent performance as the energy related materials such as battery. For example, nanoporous Si is potentially useful for Li-ion battery (LIB). Si is considered as the promising active material of LIB negative electrode, because it has a theoretical Li capacity of ~4200 mAh/g, about 10 times that of carbon-based electrodes. However, Si electrodes suffer from volume changes of more than 400% with Li insertion and extraction. The large volume change caused by Li insertion pulverizes the conductive network between the active material and the current collector, rapidly degrading the cyclic performance. Nanoporous Si is expected to improve cyclic performance because the many open channels in such structures act as ideal volume expansion buffers.

In this presentation, we will introduce the basic of the novel dealloying method in metallic melt and the application of dealloyed nanoporous base metals as LIB electrode. We will report that the dealloyed nanoporous Si with the controlled porous structure exhibits superior LIB performances such as high capacity, improved cycle life time and high rate characteristics[1,2].

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3D NANOPOROUS MATERIALS: NEW HORIZONS OF FUNCTIONAL MATERIALS

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Historically de-alloying is well known in corrosion science and refers to the selective dissolution of one or more components out of an alloy. It was received significant attention in the context of corrosion but has recently been receiving renewed attention because nanoporous metals can be fabricated by this traditional method. De-alloyed nanoporous metals represent a new class of functional materials with the unique structural properties of large surface area, mechanical rigidity, electrical conductivity and high corrosion resistance. Coupled with their rich surface chemistry for further functionalization, nanoporous metals have great potential for applications in catalysis, sensing, surface enhanced spectroscopy, energy storage and conversion, and so on. With advanced electron microscopy, three-dimensional structure and surface atomic configuration of nanoporous metals have been realized, which yield quantitative characterization of the key structure parameters involved in the intricate 3D nanoporous structure. Catalytic and electrocatalytic investigations demonstrate that nanoporous metals are catalytically active for many important energy- and environment-related reactions and organic transformations. Nanoporous metals are also proved to be excellent plasmonic substrates for ultra-sensitive chemical detection and biomolecular diagnostics. By utilizing the high electric conductivity and large internal surface, nanoporous metals have also been successfully employed as robust electrodes of supercapactiors and batteries for energy storage.

TEMPERATURE DEPENDENCES OF ELECTRICAL RESISTANCES OF SWCNTs IN PET MATRIXES FILMS

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In the last few decades nanostructured carbon materials have been attracting much attention of many researchers. Single-walled carbon nanotubes (SWCNTs) are major representatives of that class of new functional materials. Electron transport properties of free-standing SWCNTs and ones placed in different types of polymeric matrixes have been studied up to date. Authors describe temperature dependences of electrical resistances of such films in different ways. One of possible conduction mechanisms is variable range hopping conduction (VRHC). Alternative one is fluctuation induced tunnelling conduction (FITC). The latter describes electron transport in disordered systems in which conduction electrons are delocalized and free to move in conduction particles separated by insulating gaps over distances much bigger than atomic dimension [1]. It is in contrast to disordered systems with localized charge carriers with VRHC taking place [2]. Networks of disordered SWCNTs in polyethylene terephthalate (PET) matrixes are promised for applications and simple enough to be formed, and in this work temperature dependences of electrical resistances of such systems are studied.

SWCNTs were synthesized by catalytic disproportionation of carbon monoxide (CO) on Fe particles formed by vapour decomposition of ferrocene ($(C_5H_5)_2Fe$). Four samples were deposited in one synthesis on different silicon substrates with individual deposition times: 5, 10, 60 and 120 min. The resulted SWCNTs were transferred by pressing onto PET substrates 0.1 mm in thickness at a temperature of 170°C for 15 min at a pressure of 98 kPa. In that way the nanotubes were placed into PET matrixes. Temperature dependences of resistances of resulted films were measured from room temperature down to 77.4 K. The experimental data were fitted by both FITC model and VRHC one.

If FITC takes place resistance behaves as $\exp[T_t/(T_s+T)]$, and as $\exp[T_0/T^{1/4}]$ if VRHC does, where: T_t – is regarded as a measure of energy necessary for electron transition over energy barriers (between conduction particles); T_s – is the temperature above which thermal induced tunnelling conduction becomes considerable; T_0 – temperature independent coefficient. Coefficient of determination R^2 is somewhat similar for both models applied to the experimental data. And as the dependences obtained are described by both models equally well within the temperature range and effective activation energies can be evaluated as product of Boltzmann constant k_B and T_t applying only FITC model to the experimental data is shown in Fig. 1.

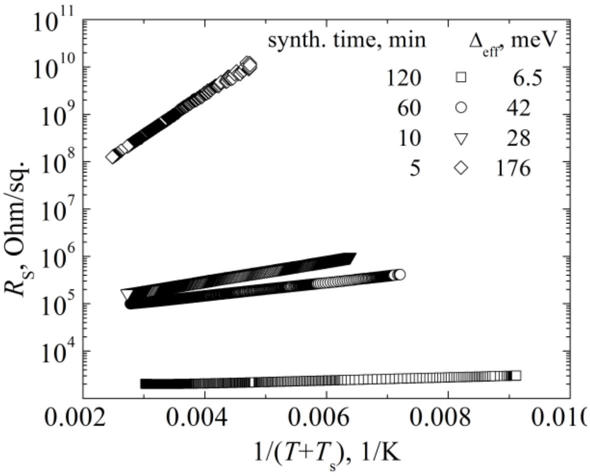

Fig. 1. Temperature dependences of sheet resistances of networks of disordered SWCNTs in PET matrixes for differnet synthesis times.

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ТЕМПЕРАТУРНЫЕ ЗАВИСИМОСТИ ЭЛЕКТРОСОПРОТИВЛЕНИЯ ПЛЕНОК ОУНТ В ПЭТФ МАТРИЦАХ

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Последние несколько десятилетий наноструктурированные углеродные материалы привлекают внимание большого количества исследователей. Одними из ярких представителей данного класса новых функциональных материалов являются одностенные углеродные нанотрубки (ОУНТ). До настоящего времени были изучены электронные транспортные свойства как отдельных ОУНТ, так и ОУНТ, помещенных в различные полимерные матрицы. Температурные зависимости электросопротивления таких пленок авторы описывают в рамках различных моделей механизмов проводимости. Одним из возможных механизмов является прыжковая проводимость с переменной длинной прыжка (*англ.* VRHC). Ещё один механизм – туннельная проводимость, обусловленная тепловыми флуктуациями (*англ.* FITC). Модель FITC описывает электронный транспорт в разориентированных системах, в которых электроны проводимости делокализованы в проводящих частицах, разделенных барьерами, на расстояниях много больших межатомных [1], в отличие от систем с локализованными носителями заряда, как в модели VRHC [2]. Массивы разупорядоченных ОУНТ в матрицах на основе полиэтилентерефталата (ПЭТФ) просты в получении и перспективны для практических применений. В работе изучаются температурные зависимости электрического сопротивления таких систем.

ОУНТ были синтезированы путем каталитического диспропорционирования оксида углерода (CO) на частицах Fe, полученных разложением паров ферроцена ($(C_5H_5)_2Fe$). ОУНТ осаждались на кремниевые подложки в одном синтезе в течение промежутков времени: 5, 10, 60 и 120 мин. Полученные ОУНТ помещались в матрицы ПЭТФ (подложки толщиной 0,1 мм) путем впрессовывания под давлением 98 кПа при 170°C в течение 15 мин. Температурные зависимости сопротивления были измерены от комнатной температуры до 77,4 К. Экспериментальные данные были аппроксимированы обеими моделями – FITC и VRHC.

В случае модели FITC сопротивление ведет себя как $\exp[T_t/(T_s+T)]$, в случае VRHC $\exp[T_0/T^{1/4}]$, где: T_t – мера энергии, необходимой для преодоления электроном барьера между проводящими частями; T_s – температура, выше которой туннелирование, обусловленное тепловыми флуктуациями, становится существенным; T_0 – температурно независимый коэффициент. Обе модели описывают полученные зависимости одинаково хорошо и дают схожий коэффициент детерминации R^2, и, поскольку эффективные энергии активации могут быть оценены как произведения постоянной Больцмана k_B и T_t, на рис. 1 показаны аппроксимации только моделью FITC.

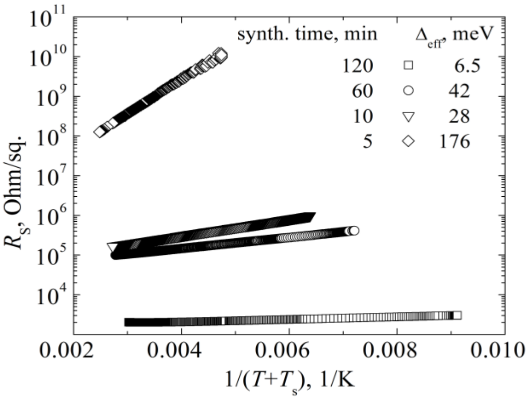

Рис. 1. Температурные зависимости поверхностнгого сопротивления массивов разориентированных ОУНТ в ПЭТФ матрицах для разных времен синтеза.

Работа выполнена при поддержке РФФИ (Грант № 15-53-45041).

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SYNTHESIS OF MS_2/C (M=Mo, Ti) COMPOSITES AT HIGH TEMPERATHURE AND PRESSURE

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Modern research has aim to create composite materials that allow combining the different properties of the initial components. Metal disulfide (MoS_2 and TiS_2), and graphite are two-dimensional layered materials with covalent bonds between atoms in the layer and van der Waals interactions between the layers. These compounds have a high resistance to temperature and pressure. The hybrid structures of MS_2 layers and graphite have properties different from the properties of the individual components. In particular, the hybrids based on metal sulfides may exhibit unusual electronic properties due to the contact of the semiconductor with carbon having a metallic conductivity. According to the literature in the theory MoS_2 and TiS_2 may have a high specific capacity [1]. However, there is a problem of chemical degradation of metal disulfides during the lithium intercalation [1,2], which can be solved by introducing of supporting carbon component. It is expected, that multilayered graphene will increase the mechanical stability of the resulting composite in the intercalation process and perhaps will result in a higher capacity of the composite in comparison with those of individual components. MS_2 interaction with the surface of the carbon can provide a high stability during lithium ions intercalation into the interlayer space of MS_2 using the MS_2/C as anode material in lithium-ion batteries. Enhanced temperature and pressure in the synthesis process should provide a strong bonding between components of the composite, and thus increase the working performance of the electrode.

In this work we used ammonium thiomolybdate, trisulfide of titanium, detonation nanodiamonds (ND) and perforated graphite (PG) as starting materials for the synthesis of composite materials. Perforated graphite was synthesized by partial reduction of graphite oxide in a large amount of sulfuric acid at 280°C for an hour. Titanium trisulfide (TiS_3) was synthesized by the ampoule method [3]. Stoichiometric mixture of titanium powders and sulfur was placed in a quartz ampule, the ampule was evacuated and heated at ~ 450˚C during several weeks. Thiomolybdate was decomposed in admixture with nanodiamonds or perforated graphite in an acidic medium. The PG and TiS3 was mixed using a small amount of alcohol. The mixture (MoS_3/PG, MoS_3/ND or TiS_3/ PG) was heated under vacuum at 500 atm. During thermobaric synthesis metal trisulfides are decomposed by the reaction: $MS_3 \rightarrow MS_2 + S \uparrow$. The synthesis product was investigated by X-ray diffraction techniques, Raman spectroscopy, SEM and XPS.

The work was conducted with the financial support from the Russian Science Foundation (Grant 16-13-00016).

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COMPOSITES BASED ON LOW-DIMENSIONAL TRANSITION METAL CHALCOGENIDES WITH NOBLE METAL NANOPARTICLES

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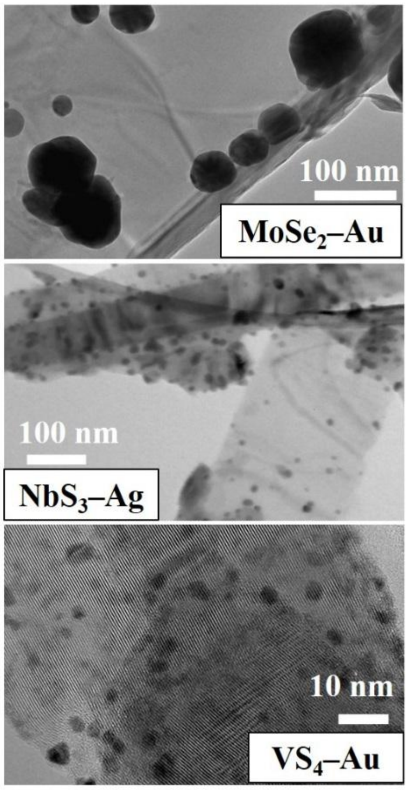
In the last few years, wide attention is being payed to preparation of nanosized low-dimensional inorganic materials, *e.g.* graphene-based materials, hexagonal boron nitride nanosheets and 1D and 2D nanomaterials based on transition metal chalcogenides. In particular, wide family of low-dimensional transition metal chalcogenides, namely dichalcogenides (MoS_2, $MoSe_2$, WS_2, etc.) [1], trichalcogenides (NbS_3, TaS_3) [2] and tetrachalcogenides (VS_4) [3], are attracting wide attention due to their improved electronic, optical, catalytic properties, *etc*. The most applicable and cost-effective method to produce nanosized 1D or 2D metal chalcogenides is liquid phase exfoliation of bulk samples [4]. Decorating the surface of such nanomaterials with noble metal nanoparticles is an effective way to functionalize the material and to bring new and enhanced properties for many areas such as energy storage, catalysis and surface enhanced Raman spectroscopy devices. Composites based on transition metal chalcogenides can be prepared by so-called *in situ* process where the nanoparticle deposition occurs in the presence of the dispersed matrix.

The work aims at preparing nanomaterials based on transition metal dichalcogenides, trichalcogenides and vanadium tetrasulfide and designing composites with noble metal nanoparticles (Ag, Au, Pt, Pd) by using the *in situ* approach. The composites obtained were investigated by modern methods, namely X-ray diffraction, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Average sizes of noble metal nanoparticles were shown to be from 2 to 30 nm depending on the system investigated.



This work was supported by Russian Foundation for Basic Research (Project 15-53-45041).

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КОМПОЗИТЫ НА ОСНОВЕ НИЗКОРАЗМЕРНЫХ ХАЛЬКОГЕНИДОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ С НАНОЧАСТИЦАМИ БЛАГОРОДНЫХ МЕТАЛЛОВ

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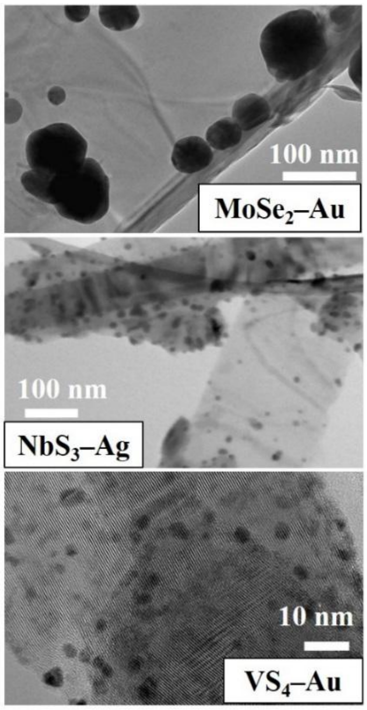
В последние несколько лет обширное внимание уделяется получению наноструктурированных низкоразмерных неорганических материалов, таких как материалы на основе графена, нанолистов гексагонального нитрида бора и 1D и 2D халькогенидов переходных металлов. В частности, низкоразмерные халькогениды переходных металлов, а именно дихалькогениды (MoS_2, $MoSe_2$, WS_2 и т.д.) [1], трихалькогениды (NbS_3, TaS_3) [2] и тетрахалькогениды (VS_4) [3], привлекают значительное внимание благодаря их улучшенным электронным, оптическим, каталитическим и др. свойствам. Наиболее подходящим и экономичным методом получения наноразмерных 1D и 2D халькогенидов металлов является метод жидкофазного расщепления массивных образцов [4]. Декорирование поверхности таких наноматериалов с помощью наночастиц благородных металлов представляет собой эффективный способ функционализации материала и привнесения новых и усиленных свойств во многие области, например, хранение энергии, катализ, и поверхностно-усиленная спектроскопия комбинационного рассеяния. Композиты такого типа можно получить с помощью так называемого *in situ* процесса, при котором осаждение наночастиц происходит в присутствии дисперсии матрицы.

Целью данной работы было получить композиты на основе ди-, три- и тетрахалькогенидов переходных металлов и наночастиц благородных металлов (Ag, Au, Pt, Pd) используя *in situ* подход. Полученные композиты изучали набором современных методов, а именно РФА, ВРПЭМ и РФЭС. Было показано, что средние размеры наночастиц составили от 2 до 30 нм в зависимости от исследуемой системы.



Работа была поддержана Российским Фондом Фундаментальных Исследований (проект 15-53-45041)

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MATERIALS BASED ON X-RAY CONTRAST OCTAHEDRAL METAL CLUSTER COMPLEXES AND OXO-POLYMERS

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Chemistry of octahedral metal cluster complexes with general formula $[\{M_6Q_8\}L_6]$ (M – rhenium or molybdenum, Q – inner chalcogenide or halogen ligands, L – terminal organic or inorganic ligands) is rapidly developing due to their superb physicochemical properties such as luminescence or radiocontrast. Combination of these properties may be used in medical applications as agents for computed tomography, photodynamic therapy or in biology as agents for bioimaging. However, most of the known water-soluble rhenium cluster complexes show high toxicity [1], while the majority of molybdenum cluster complexes do not even stable in aqueous solutions at physiological pH [2]. Thus to improve the water stability and decrease toxicity of the clusters, they can be either coated by high hydrophilic biocompatible molecules or immobilized in water soluble/dispersible biocompatible nontoxic matrix. This work was aimed at study the interaction of clusters complexes with organic oxo-polymers such as polyethylene oxide or dextran and investigation of materials obtained.

First we start to study the reactions of clusters with oxo-polymers under different conditions. For example, saturation of oxo-polymers by molybdenum cluster complexes were carried out in acetone solutions while by rhenium cluster were carried out in water. Such reactions can lead to the two types of interaction between cluster complexes and organic-matrix, namely hydrogen bonds with formation of supramolecular adducts or covalent interactions with formation of conjugates. Formation of adducts is most preferably for rhenium complexes due to their immobile ligands (CN, $P(CH_2CH_2COO)_3$). However for rhenium complexes with labile SO_3- and OH-ligands it is possibly to form both conjugates and adducts. Molybdenum complexes have labile terminal ligands (NO_3) and in this case formation of conjugate in preferably. All obtained materials were characterized by a number of physicochemical methods.

Also we studied the cytotoxicity and intracellular localization *in vitro* of conjugates/adducts of octahedral metal cluster complexes $[\{M_6Q_8\}L_6]^n$ (M = Re, Q = S, Se; L = SO_3, OH, $P(CH_2CH_2COO)_3$, CN; M = Mo, Q = Cl, Br, I, L = NO_3) with polyethylene oxide Mv = 4000 (peg4) and 40000 (peg40) Da, dextran Mv = 70000 (dex70) Da and their oxidized forms (peg4.ox, peg40.ox, dex70.4% and dex70.30%). Generally, it was found that a decrease of the toxicity took place.

This work was supported by the Russian Science Foundation (Grant 15-15-10006).

[1] T.N. Pozmogova, A.A. Krasilnikova, A.A. Ivanov, etc., *Bull. Exp. Biol. Med.*, 161, № 1, 64 (2016).
[2] K. Kirakci, P. Kubat, M. Kucerakova, etc., *Inorg. Chim,. Acta*, 441, 42 (2016).

МАТЕРИАЛЫ НА ОСНОВЕ РЕНТГЕНОКОНТРАСТНЫХ ОКТАЭДРИЧЕСКИХ МЕТАЛЛОКЛАСТЕРНЫХ КОМПЛЕКСАХ И ОКСОПОЛИМЕРАХ

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Химия октаэдрических металлокластерных комплексов с общей формулой $[\{M_6Q_8\}L_6]$ (M – рений или молибден, Q – внутренние халькогенидные или галогенидные лиганды, L – терминальные органические или неорганические лиганды) быстро развивается благодаря их физико-химическим свойствам, таким как люминесценция и рентгеноконтрастность. Комбинация этих свойств может найти применение в медицине в качестве агентов для компьютерной томографии, фотодинамической терапии и в биологии в качестве агентов для биовизуализации. Однако, большинство из известных водорастворимых кластерных комплексов рения имеют высокую токсичность [1], в то время как большинство кластерных комплексов молибдена не стабильны в водных растворах при физиологическом pH [2]. Таким образом, для улучшения стабильности в воде и уменьшения токсичности кластерных комплексов их можно либо покрыть высокогидрофильными биосовместимыми молекулами или иммобилизировать в водорастворимую/дисперсную биосовместимую нетоксичную матрицу. Целью этой работы было изучить взаимодействие между кластерными комплексами и органическими оксополимерами, такими как полиэтиленгликоль или декстран, и исследовать полученные материалы.

Для начала были изучены реакции кластерных комплексов с оксополимерами при различных условиях. Например, пропитку оксополимеров кластерными комплексами молибдена проводили в растворе ацетона, в то время как для рениевых кластерных комплексов реакцию проводили в воде. Такие реакции могут приводить к двум типам взаимодействий между кластерными комплексами и органичекой матрицей, а именно к водородным связям с формированием супрамолекулярных аддуктов или к ковалентным связям с образованием конъюгатов. Формирование аддуктов наиболее предпочтительно для рениевых кластерных комплексов связи с нелабильностью лигандов (CN, $P(CH_2CH_2COO)_3$). Однако для рениевых кластерных комплексов с лабильными SO_3- и OH-лигандами возможно формирование как конъюгатов, так и аддуктов. Кластерные комплексы молибдена, которые имеют лабильные терминальные лиганды (NO_3), формируют предпочтительно конъюгаты. Все полученные материалы были охарактеризованы рядом физико-химических методов.

Также мы изучили цитотоксичность и внутреклеточную локализацию *in vitro* конъюгатов/аддуктов октаэдрических металлокластерных комплексов $[\{M_6Q_8\}L_6]^n$ (M = Re, Q = S, Se; L = SO_3, OH, $P(CH_2CH_2COO)_3$, CN; M = Mo, Q = Cl, Br, I, L = NO_3) с полиэтиленгликолем (M = 4000 (peg4) и 40000 (peg40) Да), декстраном (M = 70000 (dex70)) и их окисленными формами (peg4.ox, peg40.ox, dex70.4% и dex70.30%). В целом было установлено, что токсичность уменьшается.

Работа была поддержана Российским научным фондом (Грант 15-15-10006)

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[2] K. Kirakci, P. Kubat, M. Kucerakova, etc., *Inorg. Chim,. Acta*, 441, 42 (2016).

TERAHERTZ SPECTROSCOPY OF NONLINEAR MEDIA

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Terahertz (THz) radiation is an electromagnetic radiation with frequencies from 0,1 to 10 THz. This range is promising for different branches of science, including biology, medicine, materials science and diagnostics of semiconductor materials and structures. Nowadays the problem of finding new materials to control the broadband THz radiation is topical. In particular there is an active investigation of THz properties of nonlinear optical materials previously used in the optical range. In this paper ferroelectric lead germanate ($Pb_5Ge_3O_{11}$), which is experiencing a strong change in optical properties upon reaching the phase transition temperature of 177 □C, is studied as a material.

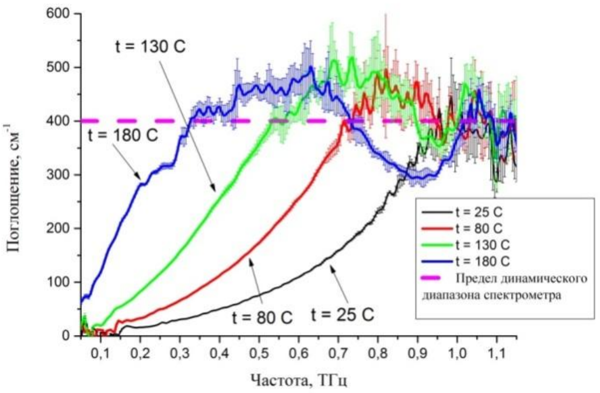

Fig.1. The dependence of the absorption coefficient of the frequency of the crystal lead germanate. The vector polarization of THz radiation is parallel to the optical

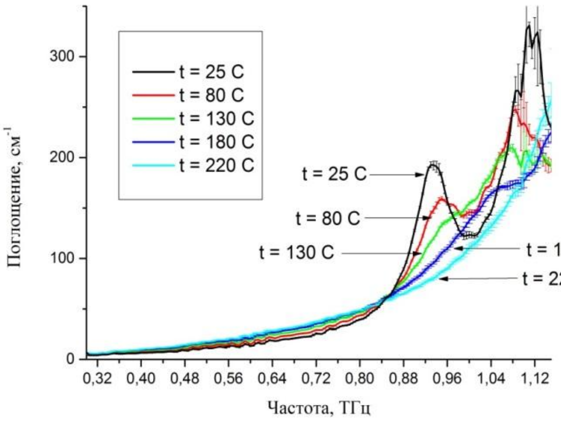

Fig. 2. The dependence of the absorption coefficient of the frequency of the crystal lead germanate. The vector polarization of THz radiation is perpendicular to the optical axis of the crystal.

In this paper the optical properties of lead germanate crystals at temperatures from ambient to 300 ° C in the frequency range from 0.1 to 1.2 THz with a spectral resolution of 20 GHz were first determined. It is shown that at a temperature near the phase transition ratio of bandwidth to different axes is more than 10^4, from which we can conclude about the prospects of the use of lead germanate crystals as THz polarizers and filters [1][2].

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ТЕРАГЕРЦОВАЯ СПЕКТРОСКОПИЯ НЕЛИНЕЙНЫХ СРЕД

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Терагерцовым (ТГц) излучением называется электромагнитное излучение с частотой от 0,1 до 10 ТГц, данный диапазон перспективен для различных отраслей науки, в том числе биологии, медицины, материаловедения, диагностики полупроводниковых материалов и структур. В настоящее время является актуальной задача поиска новых материалов для управления широкополосным ТГц излучением. В частности, идет активное исследование ТГц свойств нелинейно-оптических материалов применяемых ранее в оптическом диапазоне. В данной работе в качестве такого материала исследован сегнетоэлектрик германат свинца ($Pb_5Ge_3O_{11}$), который испытывает сильное изменение оптических свойств при достижении температуры фазового перехода 177 градусов Цельсия.

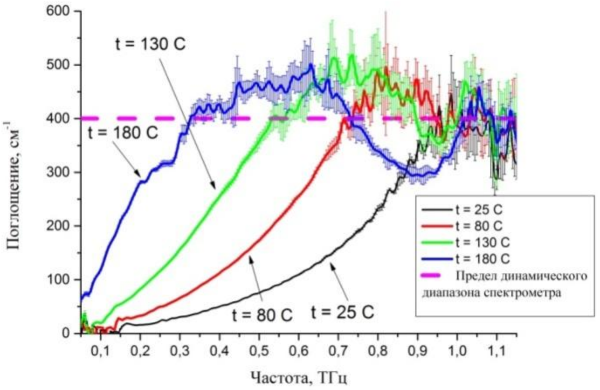

Рис.1. Зависимость коэффициента поглощения от частоты кристалла германата свинца. Вектор поляризации ТГц излучения параллелен оптической оси кристалла.

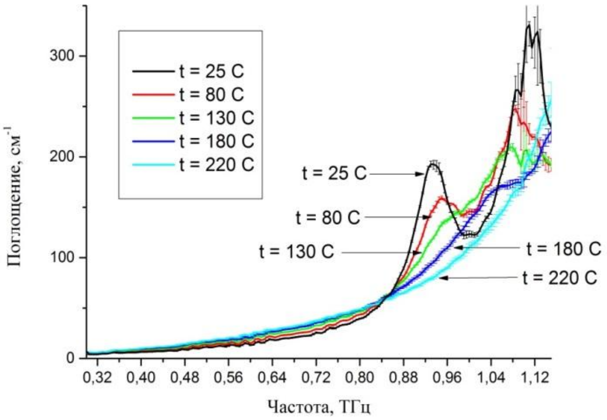

Рис. 2. Зависимость коэффициента поглощения от частоты кристалла германата свинца. Вектор поляризации ТГц излучения ортогонален оптической оси кристалла.

В работе впервые исследованы оптические свойства кристаллов германата свинца при температурах от комнатной до 300 °C в диапазоне частот от 0,1 до 1,2 ТГц со спектральным разрешением 20 ГГц. Показано, что при температуре вблизи точки фазового перехода отношение пропускания образцов по разным осям составляет более 10^4, из чего можно сделать вывод о перспективности использования кристаллов германата свинца в качестве терагерцовых поляризаторов и фильтров [1][2].

[1] В. Д. Анцыгин, М. Ю. Власов, А. А. Мамрашев, Н. А. Николаев, О. И. Потатуркин. Терагерцовые свойства германата свинца в области фазового перехода // Международная конференция по фотонике и информационной оптике. НИЯУ МИФИ. - Москва, 2016. – С. 31–32.

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OPTIMIZATION OF THERMOELECTRIC PROPERTIES OF MATERIALS BASED ON TRANSITION METAL CHALCOGENIDES

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The interest in the field of thermoelectricity is due to need for more efficient thermoelectric materials for power generation and electronic refrigeration. The main problem is to obtain the high-performance thermoelectric materials [1]. The efficiency of thermoelectric materials is characterized by dimensionless figure of merit ZT. According to this parameter, the high-performance thermoelectric materials have to possess high electrical conductivity, high Seebeck coefficient and low thermal conductivity.

The perspective thermoelectric materials at high temperature range are the transition metal chalcogenides, in particular WSe_2. The electrical conductivity of WSe_2 is too low to provide the high ZT. It is the aim of this work to increase electrical conductivity by means of replacement W on Nb. This approach allows us to optimize the thermoelectric properties by Nb concentration.

The main results of this work are presented on the Fig. The addition of Nb atoms has lead to increase in electrical conductivity and decrease in Seebeck coefficient. The addition of 0.5% Nb has changed the behavior of temperature dependence of Seebeck coefficient. The inverse relationship between Seebeck coefficient and temperature has been observed in the temperature range 77 - 230 K. Such behavior is typical for semiconductors. The linear temperature dependence of Seebek coefficient has been observed in the range of 230 - 300 K. Such behavior is typical for metals. Other samples have had metallic behavior of temperature dependences of Seebeck coefficient. In this way, the best value of PF has had $W_{0.98}Nb_{0.02}Se_2$ sample. This value has been equal to $2.7 \cdot 10^{-4}$ $W/m \cdot K^2$ at room temperature.

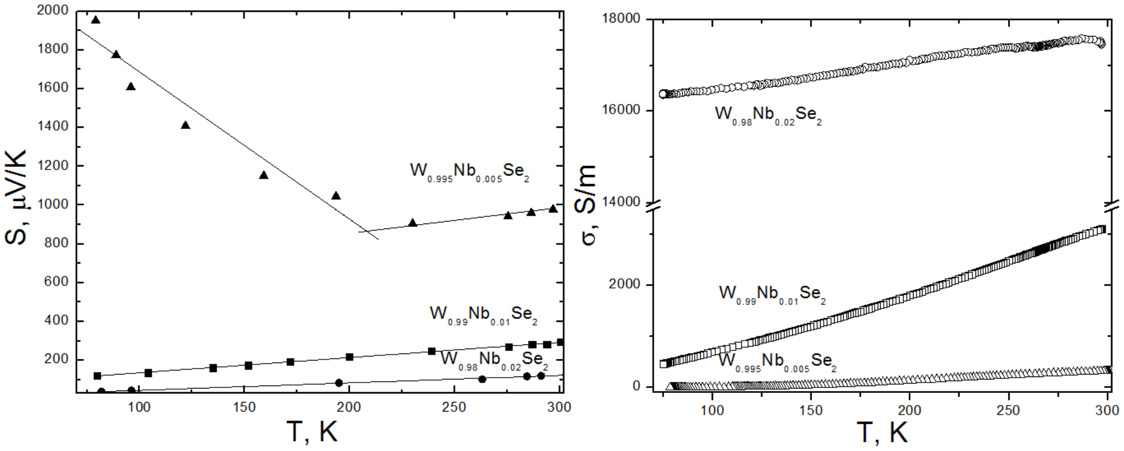

Fig. The temperature dependences of electrical conductivity and Seebeck coefficient of $W_{1-x}Nb_xSe_2$ samples.

This work was supported by the Russian Science Foundation (Grant 14-13-00674).

[1] Jong-Young Kim, Soon Mok Cho, etc., Korean Chem. Soc,vol.3, pp.3225-3227 (2010)

ОПТИМИЗАЦИЯ ТЕРМОЭЛЕКТРИЧЕСКИХ СВОЙСТВ МАТЕРИАЛОВ НА ОСНОВЕ ХАЛЬКОГЕНИДОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ

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Интерес к такой области исследований, как термоэлектричество, обусловлен необходимостью более высокоэффективных термоэлектрических материалов для генерации электроэнергии и систем охлаждения [1]. Эффективность термоэлектрических материалов характеризуется безразмерным параметром добротности ZT. Согласно этому параметру, высокоэффективный термоэлектрический материал должен обладать высокой электропроводность, высоким коэффициентом Зеебека и низкой теплопроводностью.

Перспективными термоэлектрическими материалами в области высоких температур являются халькогениды переходных металлов, а именно WSe_2. Электропроводность WSe_2 мала. Поэтому цель данной работы состояла в увеличении электропроводности путем замещения атомов W на Nb. Такой подход поможет оптимизировать термоэлектрические свойства путем изменения концентрации Nb.

Основные результаты данной работы представлены на Рис. Добавление атомов Nb привело к увеличению электропроводности и уменьшение коэффициента Зеебека. Добавление 0.5% Nb изменило поведение температурной зависимости коэффициента Зеебека. Обратно пропорциональная температурная зависимость коэффициента Зеебека наблюдалась в температурном диапазоне 77 - 230 K. Такая зависимость характерна для полупроводников. Линейная температурная зависимость коэффициента Зеебека наблюдалась в температурном диапазоне 230 – 300 K. Такое поведение характерно для металлов. Остальные образцы $W_{1-x}Nb_xSe_2$ продемонстрировали металлическую температурную зависимость коэффициента Зеебека. Таким образом, наилучшее значение PF=$2.7\cdot10^{-4}$ W/m·K^2 имеет образец $W_{0.98}Nb_{0.02}Se_2$ при комнатной температуре.

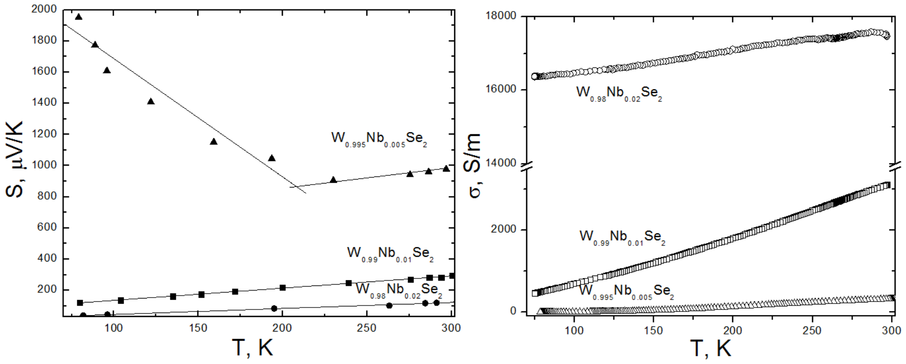

Рис. Температурная зависимость электропроводности и коэффициента Зеебека $W_{1-x}Nb_xSe_2$.

Работа была выполнена при поддержке Российского научного фонда (Грант №14-13-00674).

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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF NANOPOROUS CARBON ELECTRODE MATERIALS FOR SUPERCAPACITORS

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Electrochemical double-layer capacitors have tremendous potential as high-energy and high-power sources for using in the low weight hybrid systems. Commercial applications for such devices include uninterruptible power applications, telecommunications, and public transportation. Electrochemical double layer capacitors, commonly called “supercapacitors”, are intermediate systems that bridge the power/energy gap between traditional dielectric capacitors (high power) and batteries (high energy). Carbon-based supercapacitors have been largely investigated because of their low-cost, high cycle life and high capacitance.

Phenol-formaldehyde based resins have shown to be excellent precursors for the soft-template synthesis of ordered mesoporous phenolic resins and carbons [1]. New microporous and mesoporous carbon electrode materials have been synthesized by carbonization and activation derived from phenol-formaldehyde or resorcin-formaldehyde resins, in which potassium hydroxide acts as both the catalyst of polymerization and the chemical activation reagent [2]. The obtained carbons were characterized by a specific surface area of 1000-2000 m^2/g. Electrochemical properties of new microporous and mesoporous carbon electrode materials were investigated in cells with electrolytes of various type (1M H_2SO_4, 1 M Li_2SO_4, 6 M KOH, 1M $LiClO_4$ in acetonitrile, 1M $LiClO_4$ in EC:DMC=1:2). The materials were modified by treatment in acids (H_2SO_4, HNO_3) and mixture of K_2CO_3 and Na_2CO_3 followed by heat treatment. In this work, electrochemical properties of new microporous and mesoporous carbon electrode materials were studied. The aim of the work was to investigate the relationship between the specific capacitance, specific surface area, surface modification and the type of the electrolyte in which capacitance was measured. The porous carbon materials under study show high performance as potential electrode materials for supercapacitors possessing the optimized capacitance of 330 F/g in organic electrolyte with high capacitive retention.

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EFFECT OF CARBON AND SILICON DOPING ON ELECTRICAL PROPERTY OF SiC

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Introduction Silicon carbide (SiC) has been widely used as a ceramic heater. The resistivity control at high temperature is very important for an electrical system design. A various kind of elements and compounds were successfully used as sintering additives to enhance the densification of SiC. However, the effect of some doping on the electrical property of SiC was not well understood. Therefore, the purpose of this study is to clarify the effect of carbon and silicon doping on the electrical properties of SiC at high temperature.

Experimental SiC, C, and Si powders were used as starting materials. The C and Si amount of 1–5 mol% were doped into SiC by mixing in ethanol using ball mill. The powder mixture was sintered using SPS in a vacuum with a 5 min holding time and under 50 MPa. For undoped SiC, the sintering temperature was varied from 1750 to 2100°C, while the powder mixtures were sintered at 2100°C. The density of sintered sample was calculated from mass and volume. Phase composition was identified by XRD. The microstructure was observed by SEM. The Seebeck coefficient was analyzed by ZEM. The electrical conductivity was measured via four probe method from room temperature to 850°C.

Results and Discussion The relative density of undoped SiC was increased from 67 to 74% with the increasing of sintering temperature. The conduction of undoped SiC was identified to be *n*-type as investigated by Seebeck coefficient. The C- and Si-doped SiC was also densified by adding dopants; however, the density was slightly increased between 73 and 79% with the increasing of the additive amount. In all sintered samples, the crystal structure was mainly identified as 6H-SiC. Fig. 1 shows the electrical conductivity from room temperature to 850°C. The electrical conductivities of undoped samples are shown in Fig. 1 (a), and the higher sintering temperature resulted in the lower electrical conductivity. Figure 1 (b) and (c) show electrical conductivities of Si- and C-doped samples, respectively. The electrical conductivity was improved by adding dopant. The effect of the additive amount was more remarkable in C-doped SiC compared to that of Si-doped SiC. The highest electrical conductivity was achieved from 3 and 5 mol% C-doped SiC, while there was almost no temperature dependence of the electrical conductivity observed in these samples. It is suggested that the degenerated semiconductor property became pronounced by adding excess C.

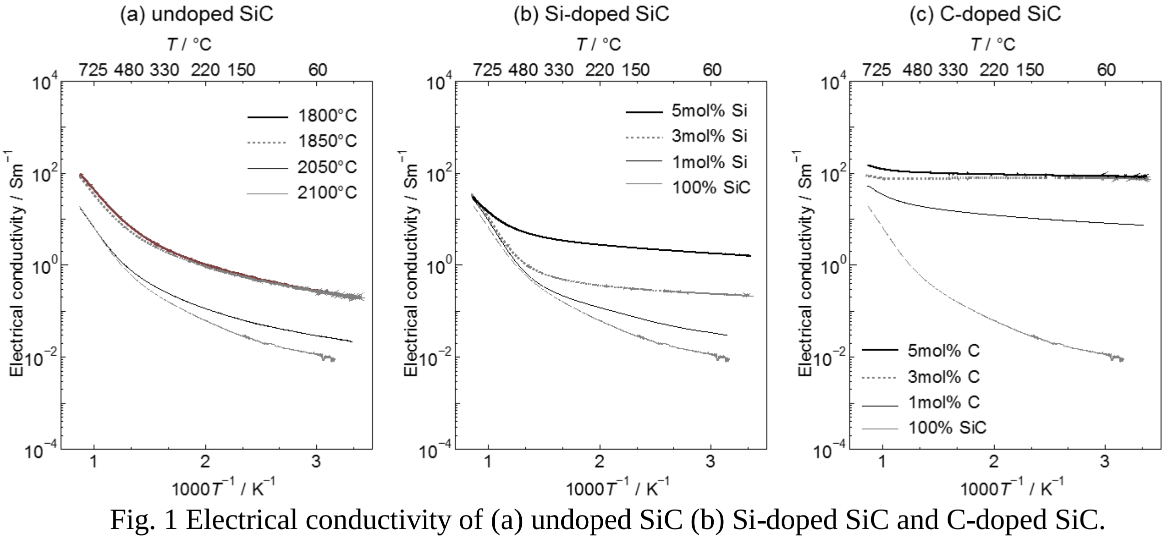

Fig. 1 Electrical conductivity of (a) undoped SiC (b) Si-doped SiC and C-doped SiC.

MORPHOLOGICAL FEATURES OF W- AND Ni-CONTAINING COATINGS ON DIAMOND CRYSTALS AND PROPERTIES OF COPPER-COATED DIAMOND COMPOSITES OBTAINED BY SPARK PLASMA SINTERING

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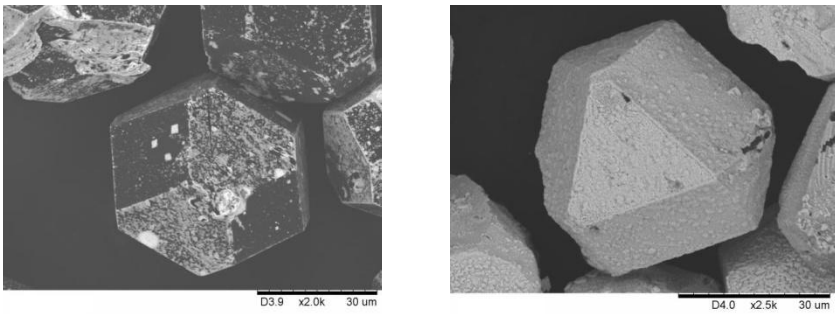
Diamond has a number of unique properties such as high hardness, wear resistance and thermal conductivity, but it is difficult to obtain compacts from diamond crystals without any binder. Diamond-copper composites have attracted a lot of attention in recent years as promising heat sink materials. The difficulty of obtaining such composites originates from a low affinity of copper to carbon. As a result, the thermal conductivity of copper-diamond composites can be lower than that of pure copper. To solve this problem, metallic coatings on the surface of diamond crystals are often used to increase the wettability of the particles by the copper matrix.

In the present study, tungsten-containing and nickel-containing coatings on diamond crystals were obtained by chemical vapor deposition (CVD) using tungsten carbonyl and nickelocene as precursors. Ni-containing coatings were obtained using rotary CVD. The main characteristic of this method is the possibility of obtaining uniform coatings on powder particles. By changing the conditions of the coatings formation (deposition time, deposition temperature) it was possible to tailor the structure of the coatings and control the diamond/metal interaction during the CVD process (Fig. 1). For obtaining copper-diamond composites, Spark Plasma Sintering (SPS) of the mixtures of the coated diamond crystals with a copper powder was used. In this presentation, the influence of the presence of coatings on the diamond particles, SPS conditions and size of the initial diamond particles on the microstructure, relative density and thermal conductivity of the consolidated copper-diamond composites will be reported.



a b

Fig.1 Morphology of W-containing layers on the diamond surface after 30 min (a) and 60 min (b) of the CVD treatment.

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DESING OF ELECTROCONDUCTIVE MWCNT-AL$_2$O$_3$ COMPOSITE CERAMICS

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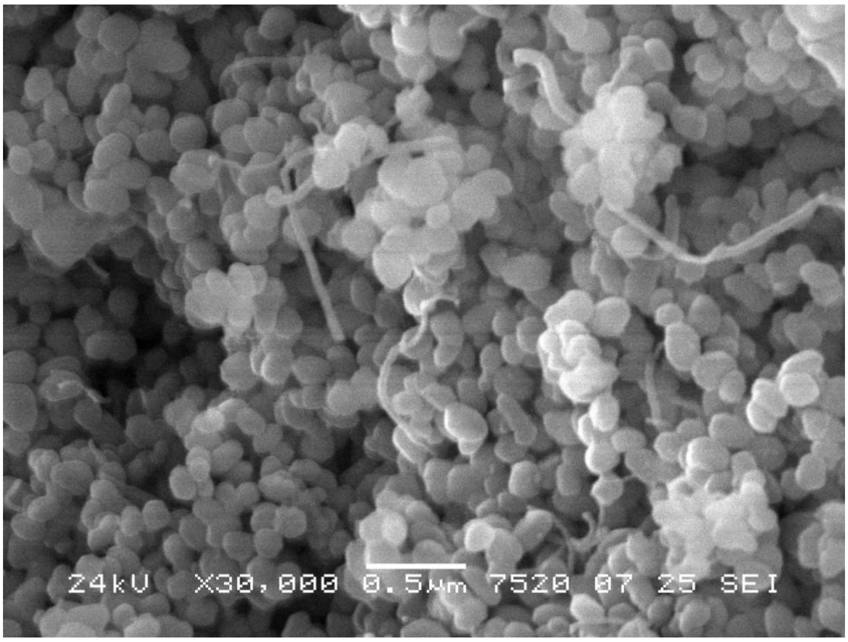
Electroconductive ceramic composites have many special applications for electronics, wireless communications and nuclear physics. In the latter case, additional requirements appear such as narrow range of conductivity, vacuum-tightness and unbirth of longlife isotopes. Multiwall carbon nanotubes (MWCNT)-Al$_2$O$_3$ composite ceramics can satisfy the conditions, if dense material is received.

In this work, attempts to receive such material are made. Dependencies of start particle size (0.1-1μ), methods of synthesis (sol-gel and mechanochemical) and consolidation (cold and hot isostatic techniques) are obtained and analyzed. Vacuum-tight (10^{-7} torr/l/s), dense (98%TD) composite material was sintered at 1520^{o}C 200 MPa in hot isostatic press, having electroconductivity level 10^{-3} Sm/cm.



Alumina powder, doped multiwall carbon nanotubes

NEW APPROACHES FOR ENHANCEMENT OF OXYGEN FLUXES ON HOLLOW FIBER MEMBRANES

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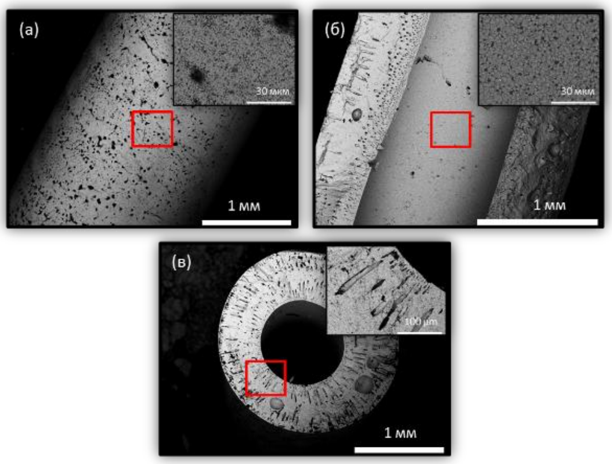
Materials based on oxides with mixed ion-electron conductivity (MIEC) attract attention due to the possibility of their application in chemical, gas and energy industries. During the recent years, innovative technologies of oxygen separation from air are developing intensively. These technologies are based on selective oxygen permeability of MIEC oxides. At present, the material having the composition $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) possesses the highest oxygen permeability [1]. A disadvantage of this compound is the occurrence of the undesirable phase transition from cubic to hexagonal perovskite at temperatures below 900°C [2]. In order to improve the functional properties of BSCF the method of isomorphous substitution of A and/or B cations is widely used. We demonstrated previously that the isomorphous substitution of Co in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ by highly charged cations M(V)=Nb, Ta with stable oxidation state allows one to enhance the chemical stability of membrane materials with the conservation of the high oxygen permeability [3]. In the present work we synthesized the hollow fiber membranes (Figure below) having the composition $Ba_{0.5}Sr_{0.5}Co_{0.78}W_{0.02}Fe_{0.2}O_{3-\delta}$ (BSCFW2) and studied the functional properties. It is shown that the introduction of highly charged cation W^{6+} in the B–site, up to 2% inclusive, improves the functional properties of membrane materials: suppresses the phase transition from cubic to hexagonal perovskite at temperatures below 900°C, enhances the chemical stability of membranes in the atmosphere of carbon dioxide, and increases the long-term stability of oxygen fluxes.



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A STUDY OF THE EFFECT OF STRUCTURAL TRANSFORMATIONS IN THE COURSE OF $Ce_2(C_2O_4)_3{\cdot}10H_2O$ THERMAL DECOMPOSITION ON THE MORPHOLOGY OF CeO_2 OBTAINED.

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The structural transformation mechanism of a chemical reaction determines the reaction product morphology and also strongly influences the reaction kinetics. If the reaction consists of two or more stages, there is opportunity to influence the final product morphology by controlling the phase composition of the intermediate products. Thermal decomposition of precursors is a widely used method for the synthesis of metal oxides. In the work we subjected cerium oxalate decahydrate to a thermal decomposition to obtain nanocrystalline ceria. The reaction occurred in two stages: dehydration and a subsequent oxidative thermolysis. It was shown that dehydration conditions strongly influence the final product's morphology. In the case of dehydration under vacuum or in air the final product can be obtained in pseudomorph-form, i.e. the initial crystal shape and sizes are retained (Fig.1). Otherwise, dehydration under quasi-equilibrium conditions (very slow water removal rate) leads to fragmentation of the initial crystals, with each piece's size being in the range of 1-10 μm (Fig. 2). It is uncommon that a decreasing reaction rate leads to such drastic changes in morphology, namely a fragmentation into small pieces. It was shown that the changes of dehydration conditions lead to the formation of different polymorphs of dehydration product. We suggested two variants of structural transformations during dehydration, which occur under different conditions. These transformations cause different deformations to the initial structure, which lead to the differences in fragmentation scale and a change to the crystals size and shape. In addition, the oxidation rate of the product obtained under quasi-equilibrium conditions is ca. 10 times higher than for another dehydrated product (Fig.3). As a result of the dehydrated products' oxidation, nanocrystalline ceria was obtained with the particles' size 5-6 nm, which was determined by TEM and from the broadening of XRD pattern peaks. The specific surface area was measured by nitrogen adsorption and its value was $140 m^2/g$.

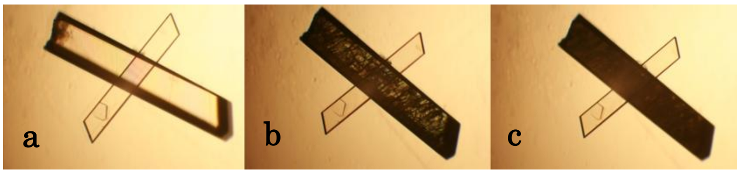

Figure 1. The whole process of $Ce_2(C_2O_4)_3{\cdot}10H_2O$ thermal decomposition in air: a) initial crystals, b) dehydrated product, c) CeO_2. (Images from an optical microscope, magnification 100x)

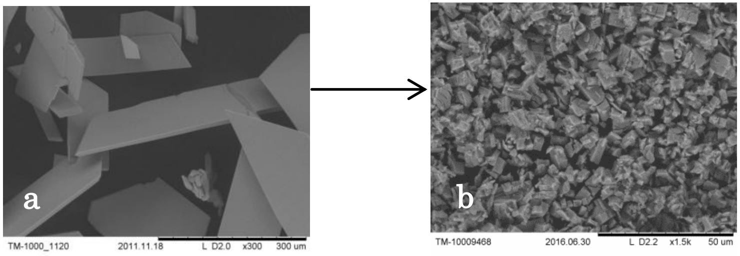

Figure 2. The crystals morphology change during dehydration under quasi-equilibrium conditions: a) initial precursor crystals, b) dehydrated product. (Images from a scanning electron microscope)

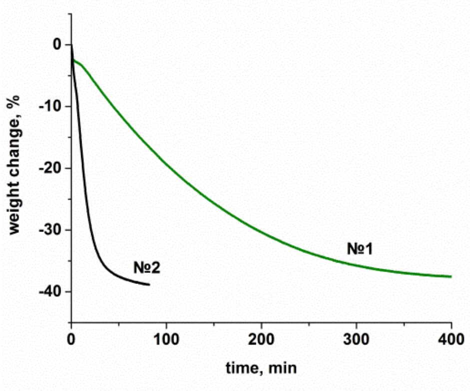

Figure 3. Comparison of the oxidation rates for different dehydration products: №1 – the product dehydrated in air, №2– the product dehydrated under quasi-equilibrium conditions.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ СТРУКТУРНЫХ ПРЕВРАЩЕНИЙ В ХОДЕ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ $Ce_2(C_2O_4)_3 \cdot 10H_2O$ НА МОРФОЛОГИЮ ПОЛУЧАЕМОГО CeO_2.

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Механизм структурного превращения при химической реакции определяет морфологию продукта реакции, а также сильно влияет на кинетику реакции. Если реакция состоит из двух или более стадий, то есть возможность влиять на морфологию конечного продукта, контролируя фазовый состав промежуточных продуктов. Термическое разложение прекурсоров – это широко используемый метод синтеза оксидов металлов. В данной работе мы провели термическое разложение декагидрата оксалата церия с целью получить нанокристаллический диоксид церия. Эта реакция протекает в две стадии: дегидратация и последующий окислительный термолиз. Было показано, что условия дегидратации сильно влияют на морфологию конечного продукта. При дегидратации в вакууме или на воздухе конечный продукт может быть получен в виде псевдоморфозы, то есть с сохранением формы и размеров исходных кристаллов. (Рис.1). Дегидратация в квазиравновесных условиях (очень медленный отвод воды от образца) приводит к разрушению исходных кристаллов на куски размером 1-10 μm (Рис. 2). Удивительно, что уменьшение скорости реакции приводит к таким сильным изменениям в морфологии. Было показано, что изменения условий дегидратации приводит к образованию различных полиморфных модификаций продукта дегидратации. Мы предложили два варианта структурных превращений в ходе дегидратации, которые реализуются при различных условиях. Эти превращения вызывают различные деформации исходной структуры, которые приводят к различиям в масштабах разрушения и изменении размеров и формы кристаллов. Кроме того было обнаружено, что скорость окисления продукта, полученного при дегидратации в квазиравновесных условиях примерно в 10 раз выше, чем продукта дегидратации в вакууме. (Рис.3). В результате окисления продуктов дегидратации был получен нанокристаллический оксид церия с размером частиц 5-6 нм, что было определено методом ПЭМВР и из уширения дифракционных максимумов. Площадь удельной поверхности, измеренная по адсорбции азота составила 140 $м^2/г$.

Рисунки представлены в английской версии тезисов

Данная работа поддержана грантом РНФ № 14-23-00037

PHYSICAL AND CHEMICAL PROPERTIES OF IRON OXIDES INSERTED INTO SBA-15 MESOPOROUS SILICA

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The present work is dedicated to the research of nanocomposites based on particles of different iron oxides developed inside mesoporous SBA-15 silica with the typical hexagonal quasiordered (stretched cavities several nanometers across) porous system. The impact of precursor thermolysis conditions (temperature, environment) on properties and phase composition of the samples was studied. To achieve this purpose the following methods were applied: X-ray diffraction, Mossbauer spectroscopy, microscopy (transmission and scanning), IR spectroscopy, differential scanning calorimetry with thermogravimetric analysis and mass spectroscopy (for evolved gaseous products identification).

Iron (III) oxalate was chosen as the primary precursor. Thermolysis of the compound (no matter it occurs in oxidizing or inert media) is known to pass through the temporary iron(II) oxalate formation, which is a widely used precursor for nanosized iron oxide particles obtaining. This fact allows us to apply the divalent salt thermolysis results to the analysis of trivalent salt transformations. Thermal decomposition of the both compounds is accompanied by significant changes in crystal lattice volume, contributing to the accumulation of mechanical stresses and leading to formation of a product with particle size down to a few nanometers.

Ferric oxalate, as opposed to ferrous salt, is water-soluble, and this fact makes it possible to obtain nanocomposites based on mesoporous materials simply by impregnating a matrix with an iron(III) oxalate aqueous solution, followed by a thermal treatment. The usage of porous materials as the matrices for iron oxide nanoparticles stabilization enables us to control their size and shape as well as to protect them from being affected by the external environment. Since the thermolysis of the precursor occurs inside the pores acting as nanoreactors, the substance conversions observed differ from the case of free iron(III) oxalate or have other temperature limits. It does not also exclude the possibility of interactions between the matrix and filling compound.

It should be noted that the investigated objects can potentially find applications in medicine (magnetic cell separation, cancer magnetotherapy, targeted drug delivery, as a MRI contrasting agent), catalysis (catalyst retention inside the reaction chamber and its separation from the reaction mixture), or industry (as a coating ingredient).

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ФИЗИЧЕСКИЕ И ХИМИЧЕСКИЕ СВОЙСТВА ОКСИДОВ ЖЕЛЕЗА, ПОМЕЩЕННЫХ В МЕЗОПОРИСТЫЙ СИЛИКАГЕЛЬ МАРКИ SBA-15

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Данная работа посвящена исследованию нанокомпозитов на основе частиц различных оксидов железа, сформированных внутри пор мезопористого силикагеля марки SBA-15 с характерной гексагональной квазиупорядоченной системой пор (вытянутые каналы диаметром несколько нанометров). Изучено влияние условий термолиза прекурсора (температура, среда) на характеристики образцов и их фазовый состав, для чего были применены следующие методы: рентгенофазовый анализ, мессбауэровская спектроскопия, микроскопия (просвечивающая и сканирующая), ИК-спектроскопия, дифференциально-сканирующая калориметрия в связке с термогравиметрическим анализом и масс-спектроскопией (для анализа состава выделяющихся газообразных продуктов).

В качестве основного прекурсора используется оксалат железа(III). Это соединение известно тем, что его термолиз (как в окислительной, так и инертной средах) проходит через формирование промежуточного продукта – оксалата железа(II), который является широко используемым прекурсором для получения наноразмерных частиц оксидов железа. Данный факт позволяет использовать результаты исследований термолиза двухвалентной соли как опорную точку при анализе превращений трехвалентной. Термическое разложение обоих солей сопровождается значительным изменением объема кристаллической решетки, что способствует накоплению механических напряжений и, как следствие, формированию частиц продукта с малым (единицы-десятки нанометров) размером.

Оксалат железа(III) в отличие от оксалата железа(II) растворим в воде, что дает возможность получать нанокомпозиты на основе мезопористых материалов простым способом, конкретно, импрегнированием выбранной матрицы водным раствором соли с последующей температурной обработкой. Использование пористых материалов как матриц, стабилизирующих наночастицы оксидов железа, позволяет управлять их размером и формой, а также защитить их от воздействия внешней среды. Поскольку термолиз прекурсора происходит внутри пор матрицы, выступающих в роли своеобразных нанореакторов, наблюдаемые превращения вещества могут отличаться от случая свободного оксалата железа(III), либо иметь иные температурные пределы. Не следует исключать также возможность взаимодействия матрицы и наполнителя.

Стоит отметить, что исследуемые объекты потенциально способны найти применение в медицине (магнитная сепарация клеток, магнитотермическая терапия рака, адресная доставка лекарств, контраст для МРТ), катализе (удержание катализатора в реакционном объеме и отделение его от реакционной смеси) или промышленности.

Работа поддержана Российским Научным Фондом (грант 14-23-00037).

EFFECT OF DEPOSITION TEMPERATURE ON PREPARATION OF Sr–Zr–O FILMS USING LASER CVD

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Compounds in Sr–Zr–O system have been attracting much attention since their various applications. $SrZrO_3$ is a promising candidate for the usage of electric devices because of its high dielectric constant. It is also known as a wide-gap photocatalytic material (band gap: 5.6 eV). ZrO_2 has been widely studied as a structural material with excellent mechanical properties and an efficient photocatalyst. $SrZrO_3/ZrO_2$ nanocomposite is expected to be widely used since their enhanced photocatalytic property and chemical stability. We prepared Sr–Zr–O films on polycrystalline AlN substrate by laser chemical vapor deposition (CVD). Effects of Zr mole fraction in vapor (R_{Zr}) and deposition temperature (T_{dep}) on the phase composition, orientation and microstructure of the films were investigated.

Sr–Zr–O films were prepared on AlN substrates. An Nd:YAG laser (wavelength: 1064 nm, output: 10–150 W) was employed. The substrate was heated on a heating stage at a pre-heating temperature of 773 K. The $C_{20}H_{28}O_8Zr$ and $Sr(dpm)_2$ were used as precursors. The vaporization temperatures were held at 453–473 K and 573 K, respectively. The deposition temperature changed from 793 to 1003 K by increasing the laser power from 43 to 125 W. Ar and O_2 were used as the carrier and reaction gases, respectively. The gas flow rates of Ar were 50 sccm for each precursor. The gas flow rate of O_2 was 100 sccm. The total pressure in the CVD chamber was held at 800 Pa. The deposition was conducted for 600 s.

Figure 1 shows the XRD patterns of $SrZrO_3$ films prepared at different T_{dep} and R_{Zr} = 50 mol%. A $SrZrO_3$ film with significant (110) orientation was obtained at T_{dep} = 883 K (Fig. 1(a)). With increasing T_{dep}, the orientations of $SrZrO_3$ films changed from (110) to (111). a $SrZrO_3$ film with significant (111) orientation was obtained at T_{dep} = 943 K (Fig. 1(b)).

Figure 2 shows the surface and cross-sectional SEM images of (a, b) (110)-oriented $SrZrO_3$ film prepared at T_{dep} = 883 K and R_{Zr} = 50 mol%, and (c, d) (111)-oriented $SrZrO_3$ film prepared at T_{dep} = 943 K and R_{Zr} = 50 mol%. The (110)-oriented $SrZrO_3$ film shows columnar structured grains with elongated roof-like caps and a columnar cross section (Fig. 2 (a, b). The (111)-oriented $SrZrO_3$ film shows a surface with pyramidal grains and a cross-section with columnar grains (Fig. 2(c, d)).

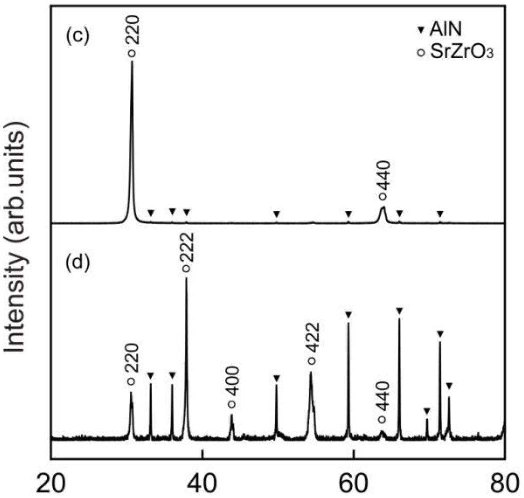

Fig. 1 XRD patterns of $SrZrO_3$ films prepared at different T_{dep} of (a) 883 K and (b) 943 K.

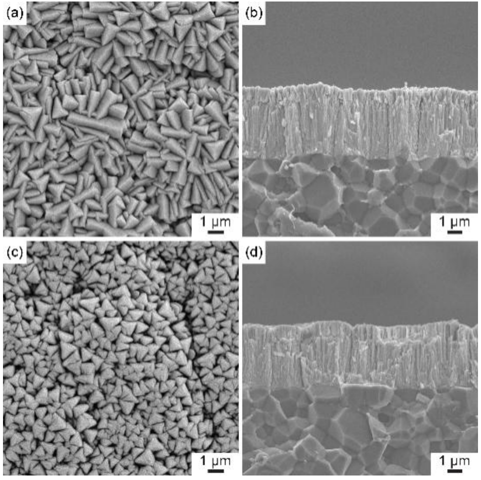

Fig. 2 SEM images of (a, b) (110)-oriented $SrZrO_3$ film prepared at 883 K and (c, d) (111)-oriented $SrZrO_3$ films prepared at 943 K.

CRYSTAL GROWTH AND PHOTOLUMINESCENCE PROPERTIES OF REACTIVE CVD-DERIVED MONOCLINIC HAFNIUM DIOXIDE

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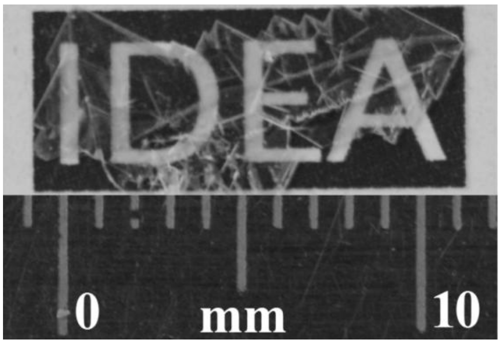
Hafnium dioxide is widely demanded by the semiconductor industry for the transparent resistive memory device production. Also, the perspective of its applying has geared up for biosensing applications and white light-emitting diodes. Despite numerous needs in monoclinic HfO_2 single crystals, the fabrication of single crystals remains a real challenge since several years. As one of the most convenient approach to grow the crystals of refractory compound such as hafnium dioxide, the reactive chemical vapor deposition (RCVD) or chemical transport through the gas phase can be proposed [1]. The aim of this work is the investigation of the monoclinic HfO_2 crystal growth possibility by the RCVD.

The thermodynamic modelling is a convenient way to understand in details the chemical equilibria that occur in the multicomponent transport systems. It was performed within the 1100 – 1600 K temperature range (with 100 K interval) and the 1 – 1000 Torr total pressure range (with the interval of one order of magnitude) for the Hf – C – Si – O – F system. Based on the modelling results, it was shown that HfO_2 formation occurs through the decomposition of $HfOF_2$. The formation of $HfOF_2$ is resulted in the reaction between coming from the “Hf-containing” zone HfF_4 and SiO_2. The most favourable conditions for the crystal growth are high temperatures and pressures.

It was demonstrated that the crystal growth of the monoclinic HfO_2 through the gas phase is possible. The results of modelling are in good agreement with experimental results and help to explain the formation of different solid products in the course of chemical transport through the gas phase. The obtained crystals are plate-like (up to 2 cm), transparent for visible light and high purity (not less than 99.99%). The photograph of the crystal is shown on the left figure [1]. Vicinal hills, numerous growth steps, kinematic waves and twins were observed on the plate surface by scanning electron microscopy. The plates are oriented in the [001] direction.



The investigation of the crystal photoluminescence was shown that the most intensive emission bands are 2.69 eV (at excitation energy 4.43 eV) and 1.96 eV (at excitation energy 5.17 eV). The cause of the blue emission is oxygen vacancies in the crystal structure and the origin of red emission is excited $O(^1D)$ atoms. The generation of $O(^1D)$ excited atoms is resulted in UV ionization of oxygen interstitial ions or adsorbed oxygen on the crystal surface.

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SYNTHESIS OF TITANIA MATERIALS FOR PHOTOCATALYTIC APPLICATIONS USING TEMPLATE - ASSISTED METHOD

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Titania-based materials are regarded as one of the most promising for the photocatalytic applications and a range of commercial products have already being produced [1]. However in order to promote such materials on the market and to make competitive products from them it is important to enhance photocatalytic activity in the visible range of the solar spectrum.

To achieve this goal we used two approaches, namely N-doping of TiO_2 and the synthesis of 3 dimensionally ordered macroporous (3DOM) materials. We also tried to combine these two methods.

Inverse opal configuration even with the certain degree of disorder can be favorable for the photocatalytic applications via enhancement of photocatalytic efficiency due to the optical effects [2]. Apart from this, the general advantage of bimodal pore size distribution in heterogeneous catalyst remains valid and is suitable for photocatalysis.

3DOM materials based on TiO_2 were prepared using template-assisted and sol-gel methods. Hierarchical porosity was molded by infiltration of titatium dioxide precursor into the voids of polymethylmetacrylate (PMMA) and polystyrene (PS) spheres of different diameters. The special attention was paid to experimental conditions of titanium tetraisopropoxide hydrolysis and template removing by calcination.

Crystalline phases of the materials were identified using XRD method, surface morphology was observed by SEM. Surface area and porosity were determined using BET method. Optical properties were measured by diffuse reflectance spectroscopy.

Non - metal doping attracts attention due to high photocatalytic activity of the doped material under visible light, simplicity of preparation and low-cost of such catalysts [3].

N-doped titanium dioxide was synthesized by sol-gel method in the presence of tetrapropylammonium hydroxide as the nitrogen source.

N-doped titanium dioxide catalysts were characterized using XRD, BET and XPS methods.

The photocatalytic activity of prepared samples was tested in the oxidation reaction of acetone in the gas phase on the continuous flow unit under visible light irradiation with the wavelength of the source of ca. 450 nm. The experimental methodology and installation diagram of the unit was previously described in details [4].

The results of photocatalytic activity measurements have shown tenfold increase compared to commercial catalyst KRONOS vlp 7000 in the oxidation of acetone when N-doped catalyst was used. However no significant improvement was observed in the photocatalytic activity when analogous trials were conducted with undoped 3DOM titania.

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NOVEL STRUCTURED CATALYSTS WITH REGULAR MACROPOROSITY FOR HEAVY OIL HYDROPROCESSING

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Depletion of conventional oil resources requires appealing to alternative motor fuel sources, the most popular of which are being heavy oil. Catalytic processing of heavy feed seems to be challenging in terms of high viscosity, density and significant content of impurities (Ni, V, S, N-containing compounds, asphaltenes). To increase the efficiency of hydrocraking, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and hydrodeasphatenization (HDA), catalysts with developed macropore system are needed, as they are capable of lowering diffusion limitations for high molecular weight constituents [1,2].

This study is focused on multistage hydroprocessing of heavy oil from Tatarstan with high viscosity and S content over the macroporous catalysts based on alumina and prepared by a template technique using polymeric microbeads 250-300 nm in diameter. The method allows one to obtain highly porous alumina (0.6-1.2 cm^3/g) with a bimodal narrow pore size distribution – maximums at 10 nm, assigned to intrinsic material mesopores, and 200-250 nm, ascribed to spherical macropores (Fig.1). Adjusting template parameters and synthesis conditions gives us an opportunity to precisely control size and fraction of macropores, as well as mechanical strength of the pellets, which is an important characteristic in the real industrial process.

On the first stage of the process, the feed was hydrotreated on the “guard-type” catalyst comprised of pellets of macro-mesoporous or conventional mesoporous Al_2O_3 (process parameters 420°C, 7 MPa, H_2/feed volume ratio = 1000, contact time 4 s). After 800 h on stream, mesoporous Al_2O_3 was found to deactivate to a great extent, whereas macro-mesoporous catalyst showed 5-fold HDS (total conversion 25%), 2.6 times higher asphaltene conversion (58%) and 5-10 times more effective metal removal.

On the second stage of the process, the oil products obtained were supplied to the hydrotreating catalyst: macro-mesoporous or conventional mesoporous Al_2O_3 with NiMoS active component. The templated catalyst demonstrated higher HDS (61% vs. 55%) and decreased the product viscosity almost twice as much in comparison with conventional mesoporous analogue. Macro-mesoporous NiMoS/Al_2O_3 was also shown to be more effective in heavy oil hydroprocessing when compared to the commercial catalyst COSMO-80.

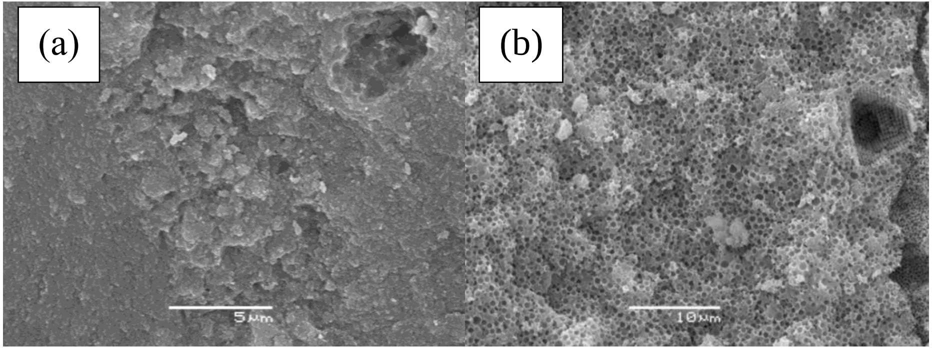

Fig. 1. SEM images of (a) conventional and (b) templated Al_2O_3.

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НОВЫЕ СТРУКТУРИРОВАННЫЕ КАТАЛИЗАТОРЫ С РЕГУЛЯРНОЙ МАКРОПОРИСТОСТЬЮ ДЛЯ ПЕРЕРАБОТКИ ТЯЖЕЛОЙ НЕФТИ

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Истощение запасов традиционной нефти требует обращения к альтернативным источникам моторных топлив, наиболее популярным из которых остается тяжелая нефть. Каталитическая переработка тяжелых фракций нефти представляет собой сложную задачу ввиду высокой вязкости, плотности и большого содержания примесей (Ni, V, S, N-содержащие соединения, асфальтены) в исходном сырье. Для повышения эффективности реакций гидрокрекинга (ГК), гидрообессеривания (ГОС), гидродеазотирования (ГДА) и гидродеметаллизации (ГДМ) необходимо использовать катализаторы с развитой системой макропор, облегчающей диффузию высокомолекулярных реагентов к каталитическим центрам [1,2].

В данной работе исследовалась многостадийная гидропереработка высокосернистой тяжелой Татарской нефти на катализаторах с регулярной макропористой структурой, полученных *темплатным методом* с использованием монодисперсных полимерных микросфер диаметра 250-300 нм. Указанная методика позволяет получать материалы с высоким объемом пор (0,6-1,2 см^3/г) и узким бимодальным распределением пор по размерам – с максимумом при 10 нм, соответствующим собственным мезопорам Al_2O_3, и 200-250 нм, отвечающим сферическим макропорам (Рис.1). Изменение параметров темплата и условий его введения дает возможность строго контролировать размер и количество макропор, а также механическую прочность носителя.

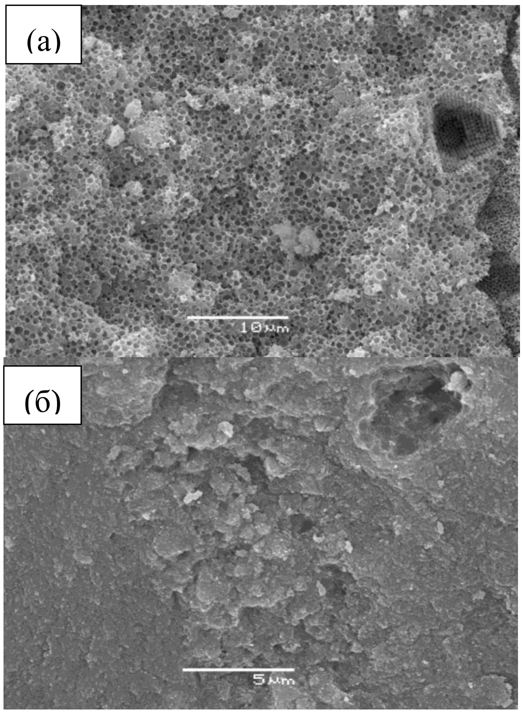

Рис. 1. Снимки СЭМ (а) темплатного и (б) традиционного Al_2O_3.

На I стадии процесса сырье подвергалось переработке на защитном слое катализатора, представляющего собой гранулы макро-мезопористого или традиционного оксида алюминия (420°С, 70 атм, H_2/сырье= 1000, время контакта 4 с). После 800 часов гидропереработки мезопористый Al_2O_3 подвергался значительной дезактивации, в то время как макро-мезопористый защитный катализатор показывал в 5 раз большее удаление S-содержащих соединений (25%), в 2,6 раза большую конверсию асфальтенов (58%) и в 5-10 раз более высокую активность в удалении металлов.

На II стадии процесса полученные нефтепродукты направлялись на катализатор гидроочистки, представляющий собой макро-мезопористый или традиционный Al_2O_3 с нанесенным активным компонентом NiMoS. Образец, полученный темплатным методом, проявлял большую активность в ГОС (61% против 55%) и уменьшал вязкость нефтепродуктов почти в 2 раза по сравнению с мезопористым аналогом. Макро-мезопористый NiMoS/Al_2O_3 также показывал большую эффективность в гидроочистке тяжелой нефти в сравнении с коммерческим катализатором COSMO-80.

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MAGNETIC PROPERTIES OF NANOCRYSTALLINE $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ CORES PROCESSED WITH TWO-STEP ANNEALING METHOD

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1. Introduction

Nanocrystalline structure with good soft magnetic properties in FeSiBPCu alloys is usually obtained by thermal annealing of as-quenched amorphous alloys. But in terms of a core of weight a few grams, we noticed a huge amount of extra heat because of precipitating a large volume fraction of α-Fe and inefficient dissipation of this extra heat would rise the annealing temperature and damage the soft magnetic properties and nanocrystalline structure. Thus in order to control the influence of exothermic heat, we have developed the two-step annealing method, which could basically divide the nanocrystallization process into nucleation in the first step annealing and grain growth in the second step annealing. And high density of nuclei in the first step annealing is very important for the final structure and properties. To achieve it, high heating and cooling rate and the optimum annealing temperature are required. Comparing with the first step annealing, the second step annealing is not so critical. This important requirement of the first step annealing is easy to meet for small samples by a conventional furnace in laboratory. But it is difficult to treat a large quantity of long and continued ribbon to make a core. Thus we designed and improved new continued heating equipment to anneal amorphous ribbon of length several meters with fast heating and cooling rate in the first step annealing.

2. Experiment

In my experiment, master ingots were made by arc melting process and the single roller melt-spinning method was used to make amorphous ribbons. In the heat treatment, the first step annealing is achieved by the roll to roll annealing equipment. For this equipment, as-quenched ribbon can be pulled through the furnace by the driving roller. And the second step annealing is achieved by infrared lamp heating equipment. And after heat treatment, samples were characterized by DSC, XRD, TEM, and so on.

3. Result

This research reports on nanocrystalline structure and magnetic properties in the ribbons of length more than a few meters and the toroidal shaped cores made by these ribbons. Results showed formation of a large number of nuclei after first step annealing, which could develop into nanocrystalline grains during the second step annealing. Low coercivity and core loss were obtained for both the ribbons and toroidal cores. However, the cores (coercivity is 15~20A/m; and core loss measured at 1.5T and 50Hz is 0.68~0.86W/kg) exhibit relatively a higher core loss compared to single sheet ribbons (coercivity is 5 A/m; and core loss measured at 1.5T and 50Hz is 0.38W/kg), due to non-zero magnetostriction of $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ alloy, and structural fluctuations in different parts of the ribbon. In spite of this, the two-step annealing method can achieve the ideal soft magnetic and structural properties for the $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ cores.

EFFECT OF LITHIUM OXIDE EXCESS AND ALUMINA ON ELECTRIC PROPERTIES OF $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ SOLID ELECTROLYTE

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Lithium oxide excess and powder bed method are conventionally used for synthesis of lithium-conducting solid electrolytes with cubic garnet structure. In this work $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ garnet was sintered at 1200°C on alumina and zirconia supports with controlled amount of lithium oxide excess. It was found that the powder bed method did not prevent garnet pellets from alumina contamination. Alumina penetration into samples was observed in situ. The quantity of alumina penetrated into samples correlated with the amount of lithium oxide excess added and varied from 0.4 to 0.9 wt. %, as indicated by ICP AES. In contrast to alumina, zirconia did not affect chemical composition of the pellets. Taking this into account a modified powder bed method that permits to eliminate any alumina contamination was developed. However, non-contaminated samples showed lower density after sintering when compared to contaminated ones. Lithium oxide excess in the samples is likely to react with the alumina with formation of eutectic that melts at 1200°C. The liquid eutectic phase acts as a sintering aid and promotes densification up to relative densities of 92%. Electrical properties of the pellets were measured by EIS technique. Bulk conductivity of the dense pellets was 5×10^{-4} S/cm at 25°C with the activation energy of 0.3 eV and depends on density. Bulk lithium ion conductivity was in agreement with literature data [1]. Due to grain boundary resistance dc-conductivity of pellets was lower than 10^{-8} S/cm at 25°C with the activation energy of 0.8 eV. Possible reasons of high grain boundary resistance are discussed.

This work was partially supported by the Russian Science Foundation [RSF 14-23-00037].

[1] V. Thangadurai, S. Narayanan, D. Pinzaru, Chem. Soc. Rev., 2014, 43, 4714.

ВЛИЯНИЕ ИЗБЫТКА ОКСИДА ЛИТИЯ И ОКСИДА АЛЮМИНИЯ НА ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА ТВЕРДОГО ЭЛЕКТРОЛИТА $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$

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Для синтеза литий проводящих твердых электролитов с кубической структурой граната традиционно используется избыток оксида лития и метод засыпки. В данной работе гранат $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ с контролируемым количеством избытка оксида лития спекали при 1200°C на подложках из корунда и из оксида циркония. Обнаружено, что метод засыпки не предотвращает загрязнение таблеток граната алюминием. Проникновение алюминия в образцы наблюдалось in situ. Количество проникшего в образцы алюминия, как показал ICP AES, коррелировало с добавленным избытком оксида лития и изменялось от 0,4 до 0,9 вес. %. В отличие от алюминия, цирконий не повлиял на химический состав таблеток. На основе этого был разработан модифицированный метод засыпки, позволяющий предотвратить загрязнение алюминием. Тем не менее, незагрязненные образцы имели меньшую плотность после спекания нежели загрязненные. Вероятно, избыток оксида лития реагирует с оксидом алюминия с образованием эвтектики, плавящейся при 1200°C. Жидкая эвтектическая фаза действует как спекающая добавка и улучшает спекаемость до значений относительной плотности в 92%. Электрические свойства таблеток измерялись методом EIS. Объемная проводимость плотных таблеток составила 5×10^{-4} См/см при 25°C с энергией активации 0,3 эВ и зависит от плотности. Объемная проводимость по ионам лития согласуется с данными литературы [1]. Из-за межзеренного сопротивления проводимость таблеток при постоянном токе была ниже чем 10^{-8} См/см при 25°C с энергией активации 0,8 эВ. Обсуждаются возможные причины высокого межзеренного сопротивления.

Эта работа была частично поддержана Российским Научным Фондом [РНФ 14-23-00037].

[1] V. Thangadurai, S. Narayanan, D. Pinzaru, Chem. Soc. Rev., 2014, 43, 4714.

PHASE FORMATION AND MICROSTRUCTURE EVOLUTION DURING SPARK PLASMA SINTERING AND HOT PRESSING OF FE + AL POWDER MIXTURES

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Materials based on FeAl intermetallic compound possess unique physical, chemical and mechanical properties. They are characterized by a low specific weight and resistance to high-temperature corrosion in sulfur-containing atmospheres. They are less expensive compared with heat-resistant steels. Porous materials based on FeAl are promising for making gas filters. Dense and porous materials based on FeAl intermetallic can be produced by reactive sintering [1].

The aim of this work was to study the evolution of the phase composition and morphological characteristics of the formation of porous compacts from a mixture of Fe + Al powders during Spark Plasma Sintering (SPS) [2-3] and hot pressing.

Compaction of the porous materials was carried out in a graphite die without applying pressure or at a low pressure. For convenient investigation of the morphological changes, powder particles of spherical morphology were chosen. It was found that the conversion degree in the Fe-Al system depends on the method of compaction, green density, sintering temperature pressure and particle size of aluminum.

Sintering of the Fe-40at% Al mixtures at 700-900°C from loose packing allows obtaining porous FeAl-based materials with an open porosity of about 40%. The beginning of the chemical interaction in the system is accompanied by the formation of hollow particles of aluminum. The architecture of the FeAl porous product repeats the architecture of the iron particle network. On the basis of the X-ray diffraction analysis, scanning electron microscopy and porosity measurements, we will compare the behavior of the Fe-40at%Al powders during SPS and hot pressing and discuss the structural features of the porous materials synthesized by reactive processes.

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THE STUDY OF NICKEL PRODUCT MORPHOLOGY DEVELOPED DURING THE GASEOUS REDUCTION OF NICKEL OXIDE.

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Nowadays porous metals are widely used for adsorption, catalysis, substances separation and as electrode materials. Porous structure, pore volume and pore size distribution are of great importance and determine the material application field. It is well known that during the reduction process of NiO by H_2 or CO porous metal is formed. This reaction is widely used in industry for nickel metal obtaining and there are a great number of works that are devoted to investigation of the reaction. However, the main focus of researches is given to the study of reaction kinetics but factors determining the morphology of porous metal are insufficiently studied. The main goal of this work was to study temperature and H_2 partial pressure influences on the porous Ni morphology. In our work we carried out the bulk NiO samples reduction in pure hydrogen atmosphere and in a mixture of hydrogen and argon. The morphology was studied on scrapped partially transformed samples by scanning electron microscopy (SEM). It was shown that during the nickel oxide reduction process at 300°C in pure hydrogen atmosphere thin plates of nickel metal assembled into bundles and separated by cracks were formed (Figure 1a). The reaction temperature increase up to 500°C leads to a significant change in the metal morphology, namely formation of the porous cellular structure with mesh size ca. 0.1-0.2 μm (Figure 1b). Decreasing the partial pressure of H_2 also leads to morphology changes from plate-like to cellular one (Figure 1c). We analyzed processes occurring in the course of the reaction and suggested the metal porous structure formation mechanism. The gas/solid reduction process occurs on the pore surface. The competition between the surface chemical reaction rate with the formation of metal atoms and their diffusion rate to the metal walls of the cells determines the size and the architecture of the metal Ni mesh. Both increasing the surface diffusion of metal atoms and decreasing the surface reaction rate lead to a change from plate-like to cellular morphology and the growth of cell size. The relation between the cell walls size and the pore volume is defined by volume changes during the reaction and architecture of metal mesh.

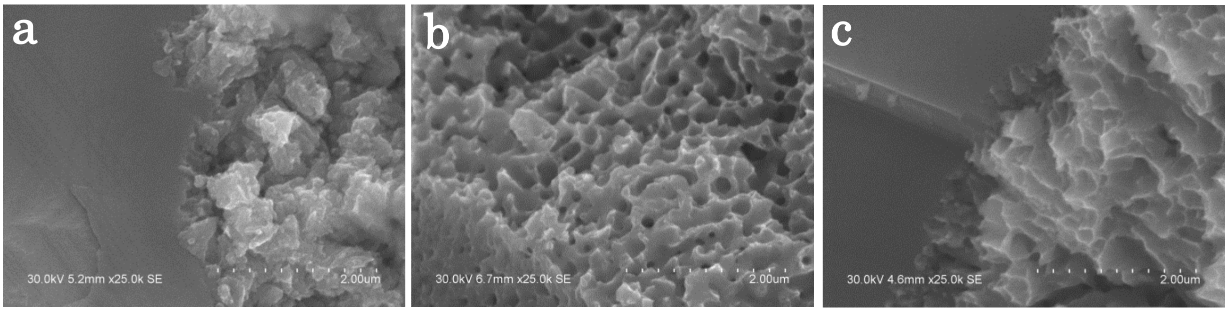

Figure 1. The morphology of porous metal Ni obtained from the NiO by gaseous reduction under different conditions
. а) 300°C, pure H_2; б) 500°C, pure H_2; в) 300°C, 1% H_2 +99%Ar.

ИЗУЧЕНИЕ МОРФОЛОГИИ ПОРИСТОГО МЕТАЛЛИЧЕСКОГО НИКЕЛЯ, ПОЛУЧЕННОГО ПРИ ВОССТАНОВЛЕНИИ ОКСИДА НИКЕЛЯ.

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В настоящее время пористые металлы широко используются для адсорбции, катализа, разделения веществ и в качестве электродных материалов. Пористая структура, объём пор и распределение пор по размерам имеют огромное значение и определяют область применения материала. Хорошо известно, что при восстановлении оксида никеля водородом или CO образуется пористый металл. Эта реакция широко используется в промышленности для получения металлического никеля и её изучению посвящено огромное количество работ. Однако основное внимание исследователей посвящено изучению кинетики реакции, а факторы, определяющие морфологию пористого металла, недостаточно изучены. Целью данной работы являлось изучение влияния температуры и концентрации водорода на морфологию пористого никеля. В работе проводилось восстановление массивных образцов оксида никеля в атмосфере чистого водорода и смеси водорода с аргоном. Морфология изучалась на сломах частично превращенных образцов методом сканирующей электронной микроскопии. Было показано, что при восстановлении оксида никеля при 300^{o}C в атмосфере чистого водорода образуются тонкие пластинки металлического никеля, собранные в пачки и разделенные трещинами (рис.1а). Увеличение температуры реакции до 500^{o}C приводит к значительному изменению морфологии металла и образованию пористой, ячеистой структуры с размерами ячеек около 0.1-0.2 мкм (рис.1б). Уменьшение концентрации водорода при 300 С также приводит к превращению пластинчатой морфологии в ячеистую (рис.1с). В работе проведен анализ процессов, происходящих при реакции, и предложен механизм образования пористой структуры металла. Реакция восстановления идет на границе раздела газ/оксид – на поверхности пор. Конкуренция между скоростями поверхностной, химической реакции с образованием атомов металла и их диффузии к стенкам металлических ячеек определяет размер и архитектуру металлической сетки. Как ускорение поверхностной диффузии атомов металла, так и уменьшение скорости поверхностной реакции приводят к переходу от пластинчатой морфологии к ячеистой и росту размера ячеек. Соотношение между размерами стенок ячеек и пор задается изменением объема при реакции и архитектурой металлической сетки.

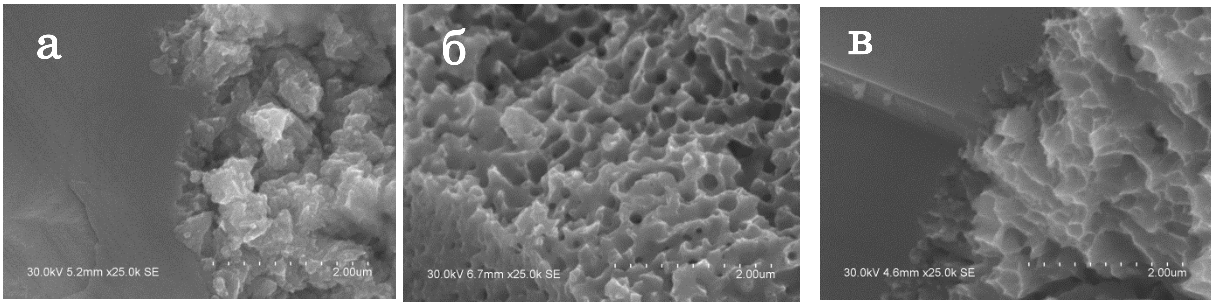

Рис.1. Морфология металлического никеля, полученного при восстановлении оксида никеля в различных условиях. а) 300^{o}C, чистый водород; б) 500^{o}C, чистый водород; в) 300 ^{o}C, 1% H_2 +99%Ar.

GRAPHITIZATION AND ACTIVATION OF OPEN-CELL TYPE POROUS CARBON PREPARED BY DEALLOYING IN METALLIC MELT

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Carbon materials have been intensively studied because of theirs special properties as industrial materials for electrode due to its high specific surface area, high electric conductivity and low density [1]. Many researchers have tried to obtain high specific surface area concurrently with crystallinity to improve properties of carbon materials, but impressive results have not been reported. Recently, an innovative synthesize method of the open-cell type porous(OP) using dealloying in a metallic melt was reported, and fabricated various OP materials, such as Nb, Si, Fe, Cr, etc. have been expected to apply to catalyst, capacitor and electrode due to their remarkable specific area [2-3]. In this research, OP-carbon was fabricated using dealloying in Ag metallic melt, and graphitization and activation processes were followed to optimize specific surface area and crystallinity.

Powder precursor of $Mn_{85}C_{15}$ (at.%) was immersed in Ag melt at 1100 °C for 10 min. And then OP-carbon was obtained after chemical etching. X-ray diffraction and Raman spectrum were measured to identify crystallinity of OP-carbon. Specific surface area was measured by N2 adsorption using a physisorption analyzer and calculated by the Brunauer-Emmett-Teller (BET) method. Graphitization was carried out from 1700 °C to 2500 °C for 2 hours and 1 hour at 2800 °C. Activation was carried out from 800 °C to 950 °C for 2 hours.

The morphology of synthesized OP-carbon is shown in Figure 1. BET and Raman intensity ratio of D-band and G-band of the as dealloyed OP-carbon was 121.9 m^2/g and 0.538, respectively. After the activation process, BET was increased from 121.9 to 368.7 m^2/g. it is considered due to a creation of new pore. After graphitization, crystallinity was increased. It was caused by reduction of defects and straighten of bent graphenes.

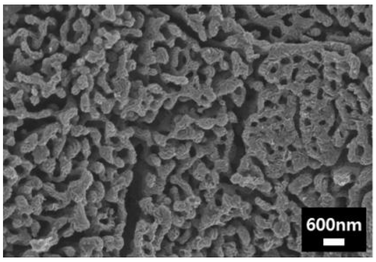

Fig. 1 SEM image of OP-carbon

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SOME FEATURES OF PULSED CATHODIC ARC DEPOSITION OF DIAMOND-LIKE CARBON FILMS

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The pulsed cathodic arc deposition technique allows prepare the DLC films with a significant amount of sp^3-bonded carbon atoms (80-90 %). The main advantages of this method are sufficiently high growth rate of layers, a low temperature of deposition, high mechanical properties and ability of their regulation during deposition process [1].

Some features of the pulsed cathodic arc sputtering technique for formation of diamond-like carbon films under different deposition conditions were presented. Diamond-like carbon films were deposited on the silicon substrates (111) by the pulsed cathodic arc sputtering technique. Deposition was carried out under pulsed voltage of 350 V, pulse frequency of 5 and 10 Hz and pulse number, changing in the range of 1000-5000. Before the deposition the substrates were cleaned for 20 minutes by argon ions from End-Hall ion source with energy of 350 eV and anode current of 3 A.

The structure and bonding nature of deposited films were characterized by Raman spectroscopy. Raman spectra were fitted by Gaussians to get the intensity ratio of the D and G bands, G band position and G band width. Hardness and Young’s modulus were measured by dynamic mechanical analysis technique. This method is often called continuous stiffness measurement and it is nanoindentation experiment wherein harmonic oscillations supplement the indenter’s translational penetration into the specimen [2]. This method allows determine hardness and Young’s modulus almost in all points of indentation, i.e. receive nearly continuous mechanical characteristics depending on the depth. Hardness of the DLC films was varied from 20 GPa to 41 GPa at pulse frequency of 5 Hz and from 30 GPa to 44 GPa at pulse frequency of 10 Hz. Young’s modulus values were in the range of 180-260 GPa.

By using ellipsometry the thickness and the refraction index were determined. Ellipsometric measurements were taken by laser ellipsometer at multiangle mode with the angles range of 45-70°. Ellipsometric data were obtained by fitting method. The film thickness was varied in the range of 35-240 nm. The refraction index was changed from 2.38 to 2,71 and from 2.31 to 2.95 at 5 Hz and 10 Hz respectively.

The results showed that pulse frequency and pulse number influence the hardness, Young’s modulus, the thickness, the refraction index and the structure of deposited films. The hardest DLC film (45 GPa) was deposited at 10 Hz and pulse number of 3000 while at 5 Hz and pulse number of 3000 the film hardness was 40 GPa. Thus, one can say that there are an optimum pulse frequency and pulse number wherein the hardness of film is maximum. After fitting of Raman spectra it is was found that the standart fitting model with two Gaussians is not suitable fo every sample.

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НЕКОТОРЫЕ ОСОБЕННОСТИ ИМПУЛЬСНОГО КАТОДНО-ДУГОВОГО ОСАЖДЕНИЯ АЛМАЗОПОДОБНЫХ ПЛЕНОК УГЛЕРОДА

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Технология импульсного катодно дугового напыления позволяет получать АПУ пленки со значительным количеством sp^3-связаных атомов углерода (80-90%). Основными преимуществами этого метода являются достаточно высокие скорости роста слоев, низкая температура осаждения, высокие механические свойства и способность их регулирования в процессе осаждения [1].

Представлены некоторые особенности технологии импульсного катодно дугового напыления для формирования алмазоподобных пленок углерода при различных условиях осаждения. Алмазоподобные пленки углерода наносились на кремниевые подложки (111) методом распыления импульсной катодной дугой. Осаждение проводили при импульсном напряжении 350 В, частоте импульсов 5 и 10 Гц и количестве импульсов, меняющемся в диапазоне 1000-5000. Перед осаждением подложки очищались в течение 20 минут ионами аргона из источника ионов типа End-Hall с энергией 350 эВ и анодным током 3 А.

Структура и характер связи осажденных пленок исследовались спектроскопией комбинационного рассеяния света. Спектры КРС были подогнаны Гауссианами, чтобы получить отношение интенсивностей D и G полос, положение G полосы и ее ширину. Твердость и модуль Юнга были измерены с помощью методики динамического механического анализа. Этот метод, часто называемый методом непрерывного измерения жесткости, представляет собой испытание индентированием, в процессе которого на поступательное внедрение индентора накладываются гармонические колебания с помощью данного метода можно определить твердость и модуль Юнга почти в каждой точке углубления индентора, т.е. получить практически непрерывные зависимости механических характеристик от глубины. Твердость АПУ пленок варьировалась в пределах от 20 ГПа до 41 ГПа при частоте импульсов 5 Гц и от 30 ГПа до 44 ГПа при частоте импульсов 10 Гц. Значения модуля Юнга были в диапазоне 180-260 ГПа.

С помощью эллипсометрии определены толщина и показатель преломления. Эллипсометрические измерения проводились с помощью лазерного эллипсометра в многоугловом режиме с углами падения в диапазоне 45-70°. Эллипсометрические данные были получены методом подгонки. Толщина пленки изменялась в диапазоне 35-240 нм. Показатель преломления изменялся от 2,38 до 2,71 и от 2,31 до 2,95 при 5 Гц и 10 Гц соответственно.

Результаты показали, что частота импульса и количество импульсов влияют на твердость, модуль Юнга, толщину, показатель преломления и структуру осажденных пленок. Самая твердая пленка (45 ГПа) наносилась при 10 Гц и количестве импульсов 3000, в то время как при 5 Гц и количестве импульсов 3000 твердость пленки составляла 40 ГПа. Таким образом, можно сказать, что существует оптимальная частота импульсов и количество импульсов, где твердость пленки является максимальной. После подгонки спектров комбинационного рассеяния было установлено, что стандартная модель подгонки с двумя Гауссианами не подходит для каждого образца.

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SYNTHESIS OF NANOSTRUCTURED CARBON-CARBON AND CARBON-MINERAL COMPOSITES

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Materials with improved crack resistance and strength are of a great importance in the terms of severe climate conditions and corrosive environment. Such materials could be produced via hybrid reinforcement, i.e. addition of fibers with different nature or length into composition of polymer. Such approach provides delaying the propagation of cracks at different scales. Nevertheless, low adhesion level between fiber and polymer matrix seems to be a challenge as it leads to fiber detachment followed by composite damage. For this reason, we suggest using nanostructured carbon-carbon and carbon-mineral composites as reinforcement additives with high surface area. Such composites represent microfibers covered with CNF layer (hybrid nanocomposites).

Carbon-carbon and carbon-mineral composites were synthesized using CCVD technique. Firstly, catalytic particles of nickel and Ni-Cu alloy were deposited via impregnation technique with the following drying and reduction in hydrogen flow. Then growth of CNF layer on microfiber surface was carried out by chemical vapor deposition of various hydrocarbons.

It was shown that surface area of hybrid nanocomposite could be 40 times higher than that of initial material. It is worth mention that the developed method allows obtaining CNF and hybrid nanocomposites with different morphology.

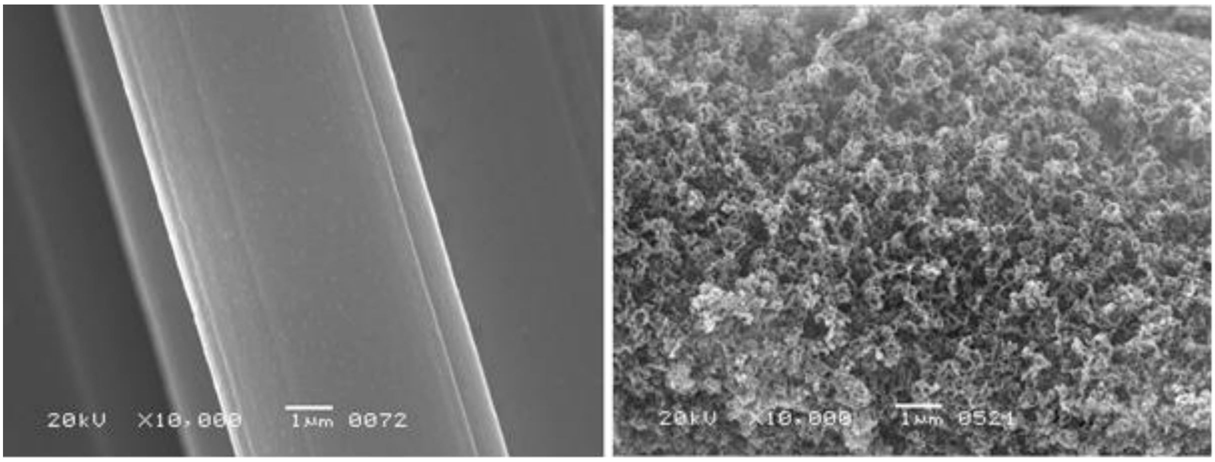

Fig.1. Microfiber surface before (left) and after (right) treatment
(2,5 wt.% Ni-Cu/carbon fiber, C_2-C_4, 700°C)

Carbon-carbon and carbon-mineral composites was proved to be effective reinforcement additive to polymer matrix.

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CHARACTERISTICS OF THE RAMAN SPECTRA OF DIAMONDLIKE CARBON FILMS.

INFLUENCE OF METHODS OF SYNTHESIS

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Diamond-like carbon (DLC) films, either hydrogenated, can be an antireflective and protective coating for elements of IR-optics [1]. There are different structural factors which influence, for example, on a high hardness of the film. Among them there is the content of sp3-hybridizated atoms. Authors [2, 3] report about the increased hardness of films which is connected with the maintenance of ordered sp2 bounded atoms in the form of fullerene-like, onion-like structures in the amorphous carbon matrix. At the same time authors tell about a connection between features of the Raman spectra and results of electronic microscopy.

In this work we consider the Raman spectra of the diamond-like films (a-C and a-C:H) received by ion-beam and arc-discharge methods for the purpose of search of connection between features Raman spectra and results of a high resolution transmittance electron spectroscopy (HRTEM).

1-Films were synthesized by end-hall ion source (ion energy was about 50-300 eV). The methane (CH_4) was used as a precursor. The substrate was monocrystalline Si. 2-Films were obtained by the use of a linear anode layer source (ion energy was about 1000 eV). The C_3H_8 was used as a precursor. The substrate was monocrystalline Si. 3-Films were synthesized by the pulse arc spraying of graphite (energy was about 30-100 eV) on silicon substrate.

The Raman spectra are obtained on a Jobin Yvon T64000 spectrometer with excitation wavelength – 514,5 nm. For determination of thickness and refractive coefficient of films the laser ellipsometer LEF – 752 (Russia) with the wavelength of 632 nanometers were used. Hardness was defined by the nanoindentation method on scanning nanoindenters Nanoskan-3D and Nanoskan-4D (Russia). The structure of the specimens was studied by a plan-view transmittance electron microscopy (TEM) on JEOL JEM-4000EX and JEM-2200FS microscopes. FTIR spectra are obtained FT-801 spectrometer (Russia) in range from 2,5 to 16,7 μm.

In summary, the films received by the pulse arc method contain elements of the ordered structures. Blurring of rings in the electron diffraction pattern is explained by presence of preferential amorphous phase. In the films, received by LIS and end-hall source, the amorphous phase is most expressed. Significant blurring of rings can be connected with the excess thickness of films (120-170th). In this case the amorphous phase "hammers" the signal from structural educations.

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ХАРАКТЕРНЫЕ ОСОБЕННОСТИ РАМАНОВСКИХ СПЕКТРОВ АЛМАЗОПОДОБНЫХ ПЛЕНОК УГЛЕРОДА. ВЛИЯНИЕ МЕТОДОВ СИНТЕЗА

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Алмазоподобные углеродные (a-C и a-C:H) пленки, могут выступать одновременно просветляющим и защитным покрытием для элементов ИК оптики [1]. Существует различные структурные факторы, влияющие, например, на высокую твердость покрытия. Среди них содержание sp3-гибридизованных атомов. Авторы [2,3] сообщают о повышенной твёрдости пленок, которую связывают с содержанием упорядоченных sp^2 связанных атомов в виде фулереноподобных, луковичноподобных структур в аморфной углеродной матрице. При этом авторы указывают на связь между особенностями рамановских спектров и результатами электронной микроскопии.

В данной работе исследованы спектры комбинационного рассеяния света алмазоподобных плёнок (a-C и a-C:H), полученных ионно-лучевым и дуговым методами, с целью поиска связи между особенностями спектров КРС и результатами просвечивающей электронной микроскопией (TEM) высокого разрешения.

1- Плёнки синтезированы из ионных пучков низких энергий (50-300 эВ) с помощью источника типа END-Hole. В область ионизации подавался газ CH_4 и ускоренные ионы осаждались на подложку из монокристалла Si. 2- Плёнки, полученные из ионных пучков высоких энергий (1000эВ), синтезировались с помощью источника ионов с азимутальным дрейфом электронов. В область ионизации подавался C_3H_8 и ионы осаждались на Si. 3- Плёнки, синтезированные импульсным дуговым способом при распылении графита (энергия, примерно, 10-300 эВ) и осаждались на монокристалл кремния.

Рамановские спектры получены на спектрометре Jobin Yvon T64000 с длиной волны возбуждения – 514,5 нм. Для определения толщины и показателя преломления покрытий использовался лазерный эллипсометр LEF – 752 (Россия) с длиной волны 632 нм. Твердость определялась методом индентирования на сканирующих нанотвердомерах «НаноСкан-3D» и «НаноСкан-4D» (Россия). Исследование структуры образцов проводилось на просвечивающих электронных микроскопах JEOL JEM-4000EX и JEM-2200FS. Для пробоподготовки использовалась установка прецизионной механической полировки LEICA-EM TXP, на которой образец утонялся со стороны подложки до толщины 10 – 20 мкм с последующим вытравлением оставшегося материала ионами аргона с энергией 3 – 5 кВ на установке ионного травления GATAN PIPS до появления отверстия. ИК спектры пропускания и поглощения измерены на ИК фурье-спектрометре ФТ-801 (Россия) в диапазоне от 2,5 до 16,7 мкм.

Установлено, что, пленки, полученные импульсным дуговым методом, содержат элементы упорядоченных структур. Размытость колец на электронограмме (TEM) объясняется присутствием преимущественно аморфной фазы. В плёнках, полученных из ионных пучков низких и высоких энергий, наиболее выражена аморфная фаза. Сильная размытость колец может быть связана с избыточной толщиной плёнок (120-170нм). В этом случае на фоне дифракции от преимущественно аморфной фазы сигнал от структурированных образований практически незаметен.

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MECHANICAL PROPERTIES OF SILICONE CARBONITRIDE THIN FILMS OBTAINED BY LASER-PLASMA SYNTHESIS

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Laser-plasma synthesis method of functional nanocomposite silicon carbonitride (SiCN) coatings from hexamethyldisilazane vapor $Si_2NH(CH_3)_6$ based on the application of the optical pulsating plasma discharge in combination with high-speed (100-300 m/s) gas flow for the laser plasma-chemical deposition in reactor at atmospheric pressure. Process parameters allow to deposit the coatings at a speed of about 1 mkm/min on the surface of structural materials (steel, titanium). Thicknesses of the coatings produced, usually ranges from 100 to 1000 nm [1]. To measure the mechanical properties of such objects at the present time is used method of instrumental indentation (nanoindentation) and the method of application and analysis of scratches (sclerometry) [2].

This paper presents results of a study of mechanical properties of SiCN coatings deposited on the surface of stainless steel. Measurements were performed with scanning nano-hardness tester “NanoScan-3D” [2]. The device was equipped with a diamond tip in the form of three-edged pyramid of Berkovich, which was used in all the studies. The mode of scanning probe microscope was used to get surface image of the coatings, roughness parameters were calculated. Using nanoindentation method (ISO 14577) were defined hardness, Young's modulus and elastic recovery of the coatings. Measurements were made with loadings in the range from 1 to 100 mN, it was done at least 10 indentations for each indent load. Thus, the hardness dependence of coating-substrate system on the indenter penetration depth was formed. Analyzing this dependence as described in [3] was defined the hardness of the coating without the influence of the substrate. Sclerometry method with variable load was applied to evaluate the adhesive strength and coating thickness measurement.

For measurement of wear resistance the tip moved at a constant normal force pressing on a circular path in contact with the surface. As a result, the dependence of the tip penetration into the sample's surface on time was formed [4]. Linear wear rate - the ratio of the amount of wear to the way of friction at which it occurred was chosen as a wear resistance characteristic. Was used a formula $J = Ltv/h$, where L - length of scratch (μm), t - stroke frequency (1/sec), v - wear time (sec), h - depth of residual scratches (μm) [5]. Thus, wear resistance of the coatings and critical load at which the destruction of the coating occurs were determined.

It was established that coating hardness was 18-20 GPa, a Young's modulus was 150-200 GPa, and wear resistance of the coatings was superior wear resistance of the substrate is more than 6 times.

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МЕХАНИЧЕСКИЕ СВОЙСТВА ТОНКИХ ПЛЕНОК КАРБОНИТРИДА КРЕМНИЯ, ПОЛУЧЕННЫХ ЛАЗЕРНО_ПЛАЗМЕННЫМ МЕТОДОМ

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Лазерно-плазменный метод синтеза функциональных нанокомпозитных покрытий карбонитрида кремния (SiCN) из паров гексаметилдисилазана $Si_2NH(CH_3)_6$ основан на применении плазмы оптического пульсирующего разряда в сочетании со скоростным (100-300 м/с) потоком газа для лазерного плазмохимического осаждения в реакторе атмосферного давления. Параметры процесса, позволяют осаждать покрытия со скоростью ~ 1 мкм/мин на поверхность конструкционных материалов (сталь, титан). Толщины получаемых покрытий, как правило, составляют от 100 до 1000 нм. [1] Для измерения механических свойств подобных объектов в настоящее время применяются методы вдавливания индентора в материал (наноиндентирования) и метод нанесения и анализа царапин (склерометрия) [2].

В работе приводятся результаты исследования механических свойств SiCN покрытий, нанесенных на поверхность нержавеющей стали. Измерения проводились на сканирующем нанотвердомере НаноСкан-3D [2]. Прибор был оборудован алмазным наконечником в форме трёхгранной пирамиды типа Берковича, который использовался во всех проведенных исследованиях. В режиме сканирующего зондового микроскопа были получены изображения поверхности покрытий, вычислены параметры шероховатости. Методом наноиндентирования (ГОСТ Р 8.748-2011) определены твердость, модуль Юнга и упругое восстановление покрытий. Измерения проводились с нагрузками в диапазоне от 1 до 100 мН, причем для каждой нагрузки делалось не менее 10 индентов. Таким образом, формировалась зависимость твердости системы покрытие-подложка от глубины внедрения индентора. Анализируя данную зависимость по методике [3] определялась твердость покрытия без влияния подложки. Метод склерометрии с переменной нагрузкой применялся для оценки адгезионной прочности и измерения толщины покрытий. Для измерения износостойкости наконечник перемещался при постоянной нормальной силе прижима по круговой траектории в контакте с поверхностью. В результате получали зависимость заглубления наконечника в поверхность образца от времени [4]. В качестве характеристики износостойкости выбиралась линейная интенсивность изнашивания – отношение величины износа к пути трения, на котором он происходил. Использовалась формула $J=Ltv/h$, где L – длина царапины (мкм), t – частота хода, v – время износа, h – глубина остаточной царапины (мкм) [5]. Таким образом была определена износостойкость покрытий и критическая нагрузка при которой происходит разрушение покрытия. Установлено что твердость покрытий достигает 18-20 ГПа, модуль Юнга 150-200 ГПа, а износостойкость покрытий превосходит износостойкость подложки более чем в 6 раз.

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POLYMER COMPOSITES WITH CARBON NANOTUBES OF DIFFERENT PROPERTIES

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Carbon nanotubes (CNT) have been attracted the top attention of scientific community during the last 25 years. This is due to the unique set of the properties of carbon nanotubes such as mechanical, electrical, structural, as well as high thermal conductivity. Such an outstanding feature makes carbon nanotubes a promising material for a wide range of applications: from constructions to aerospace, from medicine to energy storage, from electronics to catalysis *etc.*

However, despite the great efforts devoted to the investigation of carbon nanotube synthesis, processing, and applications, the implementation of CNTs into the human life is still limited. For instance, polymer composites of carbon nanotubes are considered to change the properties of matrix dramatically allowing possible wide applications as construction material. Nevertheless, the issues of the CNT distribution in matrix as well as achievement of the tailored level of adhesion have not been solved. Moreover, CNTs are happened to be a class of materials of different characteristics. In spite of greater characteristics provided by single-walled carbon nanotubes with respect to multi-walled once, the difference in price between these two classes of CNT is as big as 3 orders of magnitude. This limits application of polymer composites based on single-walled CNTs only to the aerospace industry. Thus, only the systematic investigation with carbon nanotubes with tailored properties (*i.e.* diameter, length, the amount and defectiveness of graphene walls, morphology, and the chemical composition of the surface *etc.*) allows one to tune such fundamental characteristics of composite materials as the quality for the distribution of reinforcement, as well as its adhesion with matrix.

The aim of the present work is to examine the properties the systematic set of polymer composites with multi-walled carbon nanotubes (MWCNTs) of different characteristics (length, diameter, and the chemical composition of the surface) obtained via different techniques. We have found that the fine dispersion of MWCNT agglomerates, which cannot be achieved via ultrasound treatment, reduces the percolation threshold of polymethylmethacrylate composites more than three times. We have also observed chemical functionalization of MWCNT surface to have a great impact on the adhesion with different matrices. We have shown that different ranges of characterizes are needed for different applications of carbon nanotubes. For example, MWCNTs of low diameter provide polymer composites of higher electrical conductivity and lower percolation threshold when compared to thicker nanotubes. However, while studying the thermal conductivity of the composites, the situation is vice versa. This phenomenon can be attributed to a relative amount and defectiveness of carbon nanotubes of different diameter.

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СОЗДАНИЕ ПОЛИМЕРНЫХ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ УГЛЕРОДНЫХ НАНОТРУБОК С КОНТРОЛИРУЕМЫМИ СВОЙСТВАМИ

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За последние 25 лет одним из наиболее активно изучаемых материалов стали углеродные нанотрубки (УНТ). Подобный интерес обусловлен их уникальным набором структурных, механических и теплофизических характеристик, который открывает широкий круг потенциальных применений углеродных нанотрубок, охватывающим различные сферы человеческой жизнедеятельности: строительная и аэрокосмическая промышленности, медицина и конструкционные материалы и т.д.

Тем не менее, несмотря на высокую перспективность и значительный объем выполненных исследований полимерные композиты на основе углеродных нанотрубок до сих пор не находят широкого применения, что связано, в первую очередь, со сложностью равномерного распределения армирующего компонента в матрице и достижения необходимого уровня адгезии между ними. Более того, углеродные нанотрубки представляют собой широкий класс материалов, которые могут значительным образом отличаться по характеристикам и цене. Так, несмотря на то, что многослойные нанотрубки обеспечивают несколько худшие характеристики материалов, чем однослойные, практически тысячекратная разница в их цене практически исключает широкое применение композитов однослойных нанотрубок, кроме аэрокосмической промышленности. Возможность же контроля структуры углеродных нанотрубок, их морфологии и состава поверхности открывает возможности для тонкого контроля таких фундаментальных характеристик композиционных материалов, как гомогенность распределения армирующего компонента и работа адгезии на границе раздела фаз с матрицей.

В настоящей работе приведен систематический анализ влияния таких параметров, как длина, диаметр, химический состав поверхности многослойных углеродных нанотрубок (МУНТ) и способ их введения в полимерную матрицу на свойства получаемых материалов. Показано, что разрушение вторичных агломератов МУНТ, которое не может быть достигнуто обработкой ультразвуком, позволяет снизить порог перколяции композитов более чем в 3 раза. Вариация химического состава поверхности нанотрубок, в свою очередь, позволяет управлять их адгезией с заданным полимером. Показано, что для различных приложений композитов оптимально использовать нанотрубки со специально заданным для случая набором характеристик. Так, уменьшение диаметра нанотрубок приводит к увеличению проводимости композитов при постоянной доле армирующего компонента, уменьшая при этом коэффициент теплопроводности.

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SELECTIVE CO METHANATION IN THE PRESENCE OF CO_2 OVER Ni/CeO_2 CATALYSTS

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Nowadays fuel cells with polymeric proton exchange membrane (PEM FC) are considered as alternative and clean energy sources. Fuel for PEM FC is hydrogen. The H_2-rich gas (reformate) obtained from catalytic conversion of hydrocarbon fuels with subsequent CO water gas shift reaction usually contains 0.5–2.0 vol.% CO, which poisons the PEM FC anode catalyst and must be removed to a level below 10 ppm. Selective CO methanation is one of the promising methods for CO removal from hydrogen–rich gas mixtures. However, the reformate typically contains about 20 vol.% CO_2 and 10 vol.% H_2O. In this case undesirable CO_2 methanation and reverse water–gas shift (RWGS) reactions may occur, causing considerable consumption of hydrogen and increasing CO outlet concentration. Therefore, there is a need for highly active and selective CO methanation catalyst that prevent both undesirable CO_2 methanation and RWGS reactions. Recently, we have shown that Ni/CeO_2-based systems are efficient catalysts for selective CO methanation [1-3].

In this work we show the results on the comparative study of the CO selective methanation in the realistic H_2-rich gas mixture containing 1 vol.% CO, 10 vol.% H_2O and 20 vol.% CO_2 over free and halogen (F, Cl, Br) promotion Ni/CeO_2 catalysts. Catalytic performance of the Ni/CeO_2, $Ni(F)/CeO_2$, $Ni(Cl)/CeO_2$ and $Ni(Br)/CeO_2$ catalysts were studied in the reaction. BET, XRD, HRTEM, EDX, XPS and CO chemisorption techniques were used for catalysts characterization. The Ni/CeO_2 catalyst was prepared by incipient wetness impregnation of ceria support by nickel(II) nitrate. Halogen-promoted $Ni(F)/CeO_2$, $Ni(Cl)/CeO_2$ and $Ni(Br)/CeO_2$ catalysts were prepared by treatment of Ni/CeO_2 by the aqueous solutions of $NH_4F{\cdot}HF$, NH_4Cl and NH_4Br respectively. It was shown that halogen ions strongly influence on the catalytic properties in the CO preferential methanation: fluorine does not change catalytic activity; chlorine inhibits CO_2 methanation activity providing high selectivity towards CO methanation; while bromine totally inhibits both CO and CO_2 methanation activity. This phenomenon was associated with the formation of halogen-containing surface species and bulk phases in the halogen-promoted Ni/CeO_2 catalysts. Only $Ni(Cl)/CeO_2$ catalyst showed sufficient performance in selective CO methanation, in contrast to $Ni(F)/CeO_2$ and $Ni(Br)/CeO_2$. $Ni(Cl)/CeO_2$ catalyst showed much higher CO cleanup efficiency and provided CO removal from reformate gas to the level of $\leq$ 10 ppm. In particular, $[CO]out \leq 10$ ppm and S_{CO} ~90÷50% were reached at at 285÷335 °C for $Ni(Cl)/CeO_2$.

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СЕЛЕКТИВНОЕ МЕТАНИРОВАНИЕ СО В ПРИСУТСТВИИ CO_2 НА Ni/CeO_2 КАТАЛИЗАТОРАХ

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В настоящее время энергоустановки на основе топливных элементов с полимерной протонобменной мембраной (ПОМТЭ) рассматриваются как альтернативные и экологически чистые источники электроэнергии. Топливом для ПОМТЭ является водород, который может быть получен посредством каталитической паровой конверсии углеводородов в синтез-газ и его последующего кондиционирования в водородсодержащий газ с незначительным (~10 ppm) содержанием монооксида углерода. Одним из возможных методов столь тонкой очистки водородсодержащего газа от монооксида углерода является очистка при помощи каталитической реакции селективного метанирования СО в присутствии диоксида углерода. Было показано, что Ni/CeO_2 катализаторы являются активными в реакции селективного метанирования СО [1,2]. Однако, вопросы влияния состава и структуры Ni/CeO_2 катализаторов на активность и селективность остаются открытыми.

В данной работе представлены результаты сопоставительного исследования закономерностей протекания реакций селективного метанирования СО в присутствии CO_2 в водородсодержащих смесях на хорошо охарактеризованных физико-химическими методами (РФА, ПЭМ, РФЭС, хемосорбция СО) Ni/CeO_2 катализаторах. Рассмотрены вопросы влияния добавок галогенов и способа приготовления на каталитические свойства.

Катализатор Ni/CeO_2 готовили пропиткой по влагоемкости порошка CeO_2 водными растворами нитрата никеля (II) с последующей сушкой и восстановлением в токе H_2. Для исследования влияния добавок галогенов на селективность катализатора были приготовлены $Ni(F)/CeO_2$, $Ni(Cl)/CeO_2$ и $Ni(Br)/CeO_2$ образцы обработкой Ni/CeO_2 катализатора водным раствором $NH_4F{\cdot}HF$, NH_4Cl и NH_4Br, соответственно. Катализатор Ni(F)/CeO2 обладает низкой селективностью, $Ni(Br)/CeO_2$ не активен в реакции селективного метанирования СО. Катализатор $Ni(Cl)/CeO_2$ способен снижать концентрацию СО до уровня ниже 10 ppm в широком температурном диапазоне при высокой селективности. На поверхности $Ni(Cl)/CeO_2$ катализатора образуется фаза CeOCl, которая ингибирует метанирование CO_2 [2,3].

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SYNTHESIS AND PROPERTIES OF MATERIALS IN B-Si-C-N SYSTEM

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B-C-N system phases based films are promising hard coatings. Unfortunately, they cannot be widely used in industry because of the crystallization started at high temperature. It leads to degradation of the film functional properties (for example, adhesion and Young's modulus). One of the problem solution ways is using four-component Si-B-C-N system based materials that possess the same mechanical characteristics and keep the amorphous state up to 1400°C.

This work is devoted to the synthesis and characterization of new organoboron-silicon compounds, which are potential precursors in film deposition by CVD technique. The most available CVD-precursor was chosen based on the equilibrium vapor pressure study depending on temperature. The $SiB_xC_yN_z$ films were produced by low pressure chemical vapor deposition (LPCVD) and their composition and structure depending on growth conditions were investigated.

A new organoboron-silicon compounds such as $MeB[N(SiMe_3)_2]_2$ **(1)**, $HC{\equiv}CB[N(SiMe_3)_2]_2$ **(2)** and $Me_3SiC{\equiv}CB[N(SiMe_3)_2]_2$ **(3)** were produced by reaction between $FB[N(SiMe_3)_2]_2$ and MeLi, $NaC{\equiv}CH$, $Me_3SiC{\equiv}CLi$, respectively. The compound composition and structure were verified by NMR, FTIR, Raman spectroscopies. The equilibrium vapor pressure dependencies on temperature were measured by static tensimetry method with glass-membrane zero manometer using. The enthalpy and entropy of vaporization were calculated from tensimetry data. The collected tensimetry data comparison showed that compound **(3)** is the most volatile from room temperature to 140°C. Further mixture of this compound and additional das was used for the $SiB_xC_yN_z$ film deposition by LPCVD technique. The partial vapor pressures of additional gas was in the range of 0-2.2·10-2 Torr. The EDS and XPS researches showed that carbon, boron, silicon and nitrogen are main film components. Si-C, Si-N, $Si-CH_3$, B-N and B-C bonds were detected in films by FTIR spectroscopy. According to Raman data it was found that there is amorphous carbon inclusions in the films deposited at high temperature. The film surface was investigated by SEM and AFM. The refraction index increases from 2.4 to 2.7 under rising deposition temperature. The film transparency increases and achieves a more than 80% value in case of ammonia as additional gas. The $SiB_xC_yN_z$ coating hardness and Young's modulus values were studied by nanoindentation.

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СИНТЕЗ И СВОЙСТВА МАТЕРИАЛОВ В СИСТЕМЕ B-Si-C-N

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Пленки на основе фаз системы B-C-N являются перспективными упрочняющими покрытиями. К сожалению, они не могут широко использоваться в промышленности из-за кристаллизации, протекающей при высоких температурах. Это может привести к деградации функциональных свойств пленок (например, адгезии и модуля Юнга). Одним из решений данной проблемы является использование материалов на основе фаз четырехкомпонентной системы Si-B-C-N, которые обладают сопоставимыми механическими характеристиками и сохраняют аморфное состояние вплоть до 1400°C.

Данная работа посвящена получению и характеризации новых кремний- борорганических соединений, которые являются потенциальными предшественниками для осаждения пленок в процессах CVD. Наиболее подходящий предшественник был выбран на основе исследования температурных зависимостей давления насыщенных паров соединений. Пленки $SiB_xC_yN_z$ были получены методом LPCVD. Были исследованы зависимости изменения состава и структуры пленок в зависимости от условий осаждения.

Новые боркремнийорганические соединения - $MeB[N(SiMe_3)_2]_2$ **(1)**, $HC{\equiv}CB[N(SiMe_3)_2]_2$ **(2)** и $Me_3SiC{\equiv}CB[N(SiMe_3)_2]_2$ **(3)** были синтезированы из $FB[N(SiMe_3)_2]_2$, MeLi, $NaC{\equiv}CH$ и $Me_3SiC{\equiv}CLi$. Состав и строение соединений были подтверждены с помощью ЯМР-, ИК- и КРС- спектроскопий. Температурные зависимости давления насыщенных паров соединений были определены методом тензиметрии с использованием мембранного нуль-манометра. Из данных тензиметрии были рассчитаны энтальпии и энтропии испарения. Сравнение полученных данных показало, что наибольшей летучестью в интервале от комнатной температуры до 140°C обладает соединение **(3)**. Впоследствии данное соединение было использовано для получения пленок $SiB_xC_yN_z$. Осаждение пленок проводилось методом LPCVD в проточном кварцевом реакторе на подложки Si(100) и кварцевого стекла при температурах 850-1000°C как из соединения **(3)**, так и из его смеси с аммиаком в различных соотношениях. Исследование элементного состава пленок с помощью энергодисперсионной спектроскопии показало, что основными компонентами пленок являются углерод (до 75%), а также кремний, бор и азот (каждого до 15%). В ИК-спектрах пленок в зависимости от условий эксперимента были обнаружены полосы колебаний, соответствующие связям B-N, B-C, Si-C, Si-N и $Si-CH_3$. Наличие включений аморфного углерода было обнаружено спектроскопией КРС. Поверхность пленок, изученная с использованием сканирующего электронного микроскопа, однородная с видимыми неровностями в виде шарообразных объектов размерами до 100 нм. Показатель преломления с ростом температуры синтеза пленок увеличивается от 2.4 до 2.7. Прозрачность пленок увеличивается с увеличением содержания аммиака в исходной газовой смеси и достигает значении >80%.

Исследование выполнено при финансовой поддержке РФФИ в рамках научного проекта № 16-33-00404 мол_а.

DEPOSITION FEATURES OF FLUOROPOLYMER COATINGS BY HOT WIRE CVD METHOD USING NICHROME ACTIVATOR

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The use of new technologies for surface modification is a common trend in the development of many branches of science and technology. One of the most important directions is the surface modification of fluorocarbon polymer thin films with high hydrophobic and dielectric properties. Such coatings can protect the surface from corrosive liquids, to increase the heat transfer coefficient, to give the surface a high dielectric and antifriction properties, etc. it is Obvious that the above properties depend mainly on the structure of the resulting film. Thus, there is a need to develop methods of structure of the deposited film. There are two main approaches to obtain films of polymers from solutions and gas phase. The use of liquid-phase methods for obtaining the fluoropolymer is hampered by its poor solubility in various solvents. Existing methods of deposition of fluoropolymer films from the gas phase, such as plasma polymerization precursors [1], magnetron sputtering [2], laser deposition [3], activating a gas precursor on the catalytic surface, followed by deposition of a fluoropolymer on a substrate [4,5] needs to be improved and studying the ongoing processes.

The presented work focuses on the development of the method of deposition of fluoropolymer films from a gas phase activated catalyst hot wire (HWCVD). The method allows managing the structure of the resulting film by changing process parameters of her deposition. These settings include: temperature of the filament of an activator, substrate temperature, gas pressure, precursor during the deposition process, the distance to the substrate.

The surface morphology and coating thickness were determined by the methods of scanning electron microscopy (SEM) using the JEOL JSM-6700F microscope. The contact angle of the coating with water was measured by DSA-100 KRUSS device with high-precision system of liquid supply.

The research is shown a significant influence of parameters of deposition process (temperature of the activator, pressure) on the structure of the deposited fluoropolymer film. As materials of the substrate for deposition was used stainless steel, copper, glass, silicon.

The research of the obtained samples showed that the obtained films depending on their structure show hydrophilic, hydrophobic, and superhydrophobic properties.

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Использование новых технологий для модификации поверхности - это общая тенденция развития многих отраслей науки и техники. Одним из важнейших направлений является модификация поверхности тонкими фторполимерными пленками, обладающими высокими гидрофобными и диэлектрическими свойствами. Такие покрытия способны защищать поверхность от агрессивных жидкостей, увеличить коэффициент теплоотдачи, придать поверхности высокие диэлектрические и антифрикционные свойства и т.д. Очевидно, что вышеперечисленные свойства зависят в основном от структуры получаемой пленки. Таким образом, существует потребность в разработке методов управления структурой осаждаемой пленки. Существует два основных подхода к получению пленок полимеров: из растворов и газовой фазы. Использование жидкофазных методов для получения фторполимера затруднено его плохой растворимостью в различных растворителях. Существующие методы нанесения фторполимерных пленок из газовой фазы, такие как: плазменная полимеризация перфтормономеров [1], магнетронное [2], лазерное распыление мишени, активация газа – предшественника на каталитической поверхности с последующим осаждением фторполимера на подложке [3,4] нуждается в совершенствовании и изучении происходящих при этом процессов.

Предлагаемая работа направлена на развитие метода осаждения фторполимерных пленок из газовой фазы, активированной горячим проволочным катализатором (HWCVD). Метод позволяет управлять структурой получаемой плёнки изменением параметров процесса её осаждения. К таким параметрам относятся: температура нити активатора, температура подложки, давление газа предшественника во время процесса осаждения, расстояние до подложки.

Проведённые исследования показали существенное влияние параметров процесса осаждения (температура активатора, давление) на структуру осаждающейся фторполимерной пленки. В качестве материалов подложки для осаждения были использованы нержавеющая сталь, медь, стекло, кремний.

Изучение гидрофобных свойств полученных образцов показало, что полученные пленки в зависимости от их структуры показывают, как гидрофильные, так гидрофобные и супергидрофобные свойства.

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ELECTROMAGNETIC PROPERTIES OF POLYMERS BASED COMPOSITE MATERIALS WITH VARIOUS CARBON INCLUSIONS

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Composite materials based on dielectric polymers matrixes with various conductive inclusions are promising materials for different electromagnetic applications. Carbon nanomaterials have attracted interest as fillers due to the extremely high shielding efficiency at different frequency ranges [1-3]. Electromagnetic characteristics of composite depend on many factors, such as geometry, length, defectiveness, concentration and orientation of filler in the matrix. Variation of any of these parameters could drastically change property of composite materials.

Here we demonstrate some effects of interaction of electromagnetic radiation with composites with various carbon fillers. Different carbon materials like nanotubes, onion-like carbon and reduced graphene oxide were used as fillers for composite preparation. The electromagnetic response from obtained samples was investigated in the THz, GHz, visible and low-frequency regions. The efficiency of stretching and forge-rolling techniques for anisotropic composite production was demonstrated. Different anisotropic transmission at THz, visible and low frequency region depend on the method of composite production was found. Influence of fabrication on the structure and properties of obtained carbon filler/polymer composite was discussed.

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CRYSTAL GROWTH AND EVALUATIONS OF Ce:Cs_2LiYCl_6 SINGLE CRYSTAL GROWTH BY HALIDE-MICRO-PULLING-DOWN

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Ce:Cs_2LiYCl_6(CLYC) neutron scintillator has high light yield (70,000 photons/neutron) under thermal neutron irradiation and it is expected to be applied to a next-generation neutron detector[1]. While the decay curve has a fast component (~35 ns), it also contains the slow decay component (~2 μs) which deteriorates its scintillation properties. Thus, it is necessary to perform further material researches of the Ce:CLYC single crystal. On the other hands, we developed the halide-micro-pulling-down (H-μ-PD) method to grow hygroscopic single crystals such as like CLYC at high growth rate compared to the Bridgman method with a quartz ample. The Bridgman method was the general method to grow the halide single crystal. And, there was no reports for crystal growth of the Ce:CLYC single crystal by H-□-PD method. Therefore, in this study, we developed growth technique of the CLYC single crystal by the H-μ-PD method and evaluated the scintillation properties to compered with the Ce:CLYC grown by the Bridgman method.

Undoped and Ce doped CLYC single crystals were grown by the H-μ-PD method with the nominal compositions of $Cs_2Li(Y_{1-x}Ce_x)Cl_6$, (x = 0.000, 0.005 and 0.010). The grown crystals were prepared using (a)raw powder and (b)pre-melted raw material as a starting material, respectively, as shown in Fig. 1. The Grown undoped CLYC crystal using raw powder as starting material looked cloudy, and secondary phases were observed by powder XRD pattern as shown in Fig. 2(a). On the other hands, there are no secondary phases were observed were observed as shown in Fig. 2(b). For the scintillation properties of the Ce doped CLYC crystals were measured. Emission peak originating from the 5d-4f transition of Ce^{3+} ion was observed at around 370 nm for Ce:CLYC as shown in Fig. 3. The light yield and the fast component of decay time of the Ce0.5%:CLYC were estimated as 18,500 photons/MeV and 40.7 ns, and these values were almost consistent with the Ce0.5%:CLYC grown by Bridgman method[2,3]. The details of crystal growth and other scintillation properties is going to be reported.

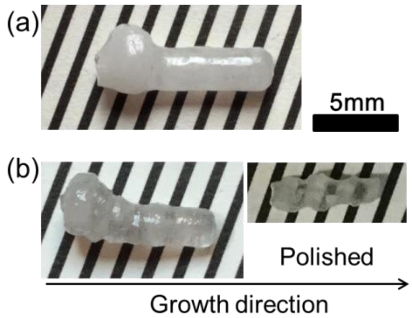

Fig. 1 The grown crysals using (a)raw powder and (b)pre-melted raw material as a strating material.

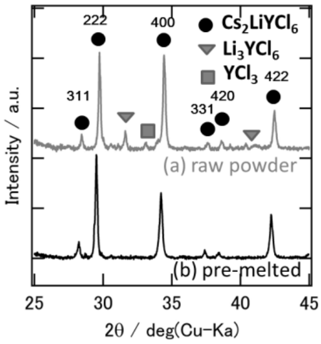

Fig. 2 Powder XRD pattern of the crystals grown by using (a)raw powder and (b)pre-melted raw material, respectively.

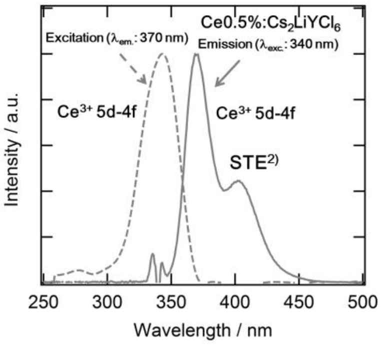

Fig. 3 Emission and excitation spectra of the Ce0.5%:CLYC crystal.

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CONTROLLED SYNTHESIS OF PVP-CAPPED Ni AND Co METAL NANOPARTICLES

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Catalysts on the basis of VIII group metals have a high potential in catalytic aqueous phase reforming (APR) of biomass resources resulting in a mixture of hydrogen and alkanes. However, high amounts of expensive noble metals (Pt, PtRe) [1] are required for APR, which is a promising route for sustainable fuel production. In this work a series of colloidal Ni and Co metal NPs solutions was prepared by microemulsion and polyol methods using $NiCl_2{\cdot}6H_2O$ and $CoCl_2{\cdot}6H_2O$ as metal precursors to compare possibility of approaches to provide controllable particle size for APR.

Polyol synthesis of Ni and Co NPs by hydrazine reduction of metal precursors in ethylene glycol at high pH was studied. In order to find out the operating parameters of the polyol synthesis determining a controllable formation of Ni and Co NPs the role of the reduction temperature under an inert gas atmosphere was studied. The reduction temperature was varied from 23 to 170°C for Ni NPs and from 7 to 23ºC for Co NPs. TEM micrographs and histograms of Ni and Co particles size distribution prepared at different reduction temperatures showed that the average diameter of Ni NPs size increased from 2.6 to 3.2 nm when the reduction temperature increased from 23 to 140ºC. With respect to Co NPs the temperature increase from 7 to 23ºC resulted in the increase in Co NPs size from 1.8 to 2.6 nm, whereas further change from 23 to 100ºC affected less significantly the metal particles size. These results indicate that the size of basic metal NPs increases with the synthesis temperature increase. To investigate the role of gas atmosphere on the formation of Ni NPs the gas-dependent evolution of the NPs size was carried out in air or in Ar at 140^{o}C. As a result, the size of NPs formed at 140ºC in air was 5.4 nm compared to 3.2 nm for that formed in Ar. When the temperature was increased to 180 C, the Ni NPs size increased to 9.8 nm. Thus, Ni NPs synthesized under an inert atmosphere were characterized with a smaller particle size as well as a narrower particles size distribution [2].

To synthesize Ni and Co NPs by the microemulsion method two microemulsion solutions were mixed and heated up to 80^{o}C: microemulsion I - the cationic surfactant cetyltrimethyl bromide (CTAB), n-octane, n-butanol, nickel or cobalt chloride (wt.% -20/15/12/53) and microemulsion II - hydrazine hydrate (64% wt.) mixed with sodium hydroxide (20% wt.), CTAB, n-butanol, n-octane (wt.% -20/15/12/53) [3]. The formation process for Ni and Co synthesized in CTAB and hydrazine was monitored by UV-vis spectroscopy. The original $NiCl_2$ solution (before heating) exhibited peaks at 400, 650, and 725 nm in UV-vis spectrum. As the heating time was increased, these peaks totally disappeared after 2 min indicating that $NiCl_2$ has been completely converted and that Ni colloids were formed with NPs size 2.6÷3.3 nm. UV-vis spectra indicated formation of metallic Ni nanoclusters at the beginning of the reduction with subsequent formation of stable complex compounds in the absence of reducing agents. Utilization of CTAB afforded formation of Co bearing NPs with the mean NPs size 2.6÷5.4 nm while stabilization with sodium dodecylsulphosuccinate (AOT) resulted in formation of cobalt hydroxide instead of metallic Co NPs. UV-vis spectra indicated generation of metallic Co nanoclusters for all samples except those heated below 80^{o}C probably resulting in formation of Co complexes. $Co(NO_3)_2$ was used to synthesize Co NPs according to [3] $CoCl_2$ used as a Co NPs precursor provided a narrower particle size distribution.

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КОНТРОЛИРУЕМЫЙ СИНТЕЗ МЕТАЛЛИЧЕСКИХ НАНОЧАСТИЦ NI И CO

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Коллоидные методы являются перспективными методами для направленного синтеза нанесенных металлических катализаторов с заданным размером частиц. Данная работа направлена на исследование физико-химических закономерностей синтеза Ni и Co наночастиц различными коллоидными методами для получения эффективных катализаторов водяного риформинга сахарных спиртов с целью получения H_2 и компонентов топлив.

Серия коллоидных растворов была приготовлена микроэмульсионным и полиольным методами с использованием $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ в качестве предшественника активного компонента. Для синтеза наночастиц Ni и Co микроэмульсионным методом две микроэмульсии смешивали и нагревали при 80°C: м/э I - раствор предшественника, поверхностно-активного вещества СТАБ, н-бутанола и н-октана (вес.% -20/15/12/53) и м/э II - раствор гидразина гидрата с NaOH (0.5 M), СТАБ, н-бутанола и н-октана (вес.% -20/15/12/53) [1]. Для синтеза полиольным методом раствор предшественника в этиленгликоле с боргидридом натрия (восстановитель) нагревали при температуре кипения этиленгликоля [2]. Для установления закономерностей формирования и разработки направленного метода синтеза Ni и Co наночастиц было изучено влияние температуры восстановления, соотношения металл/стабилизатор и масштабирования. Процесс формирования наночастиц Ni и Co и их стабильность исследовали различными физико-химическими методами, включая ЭСДО, РФЭС и ПЭМ. Полученные коллоидные растворы с размером частиц Ni 2,6÷3,3 и Co 2,6÷5,4 нм, были использованы для синтеза нанесенных катализаторов на мезопористом углеродном носителе. Было изучено влияние предварительной обработки носителя на закономерности нанесения наночастиц Ni и Co и стабильность катализатора в условиях, близких к условиям реакции. В результате предложена методика синтеза нанесенных Ni и Co катализаторов коллоидным методом с сохранением исходного размера наночастиц.

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THE USE OF THE NANOCRYSTALLINE CATALYSTS V_2O_5,WO_3/(Ce(Y)-TiO_2) WITH ENHANCED THERMAL STABILITY FOR NO REDUCTION BY NH_3 TO N_2

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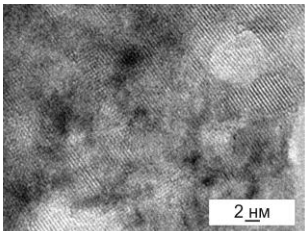
Diesel vehicles have attracted a large market share for its benefits as high power and good fuel economy. However, the emission of nitrogen oxides (NO_x) by diesel vehicles is harmful to the environment and human health. In order to eliminate NO_x in many cases the harmful gas is cleaning by selective catalytic reduction (SCR) with ammonia to nitrogen using a V_2O_5/TiO_2 and V_2O_5,WO_3/TiO_2 catalysts. These catalysts are characterized by high activity in the temperature range 220-350 °C where nitrogen oxide conversion reaches 90-97%, and the main reaction product is nitrogen. TiO_2 (anatase) is the most widely used as the support of the V_2O_5,WO_3/TiO_2 catalyst due to its better electron transfer and superior resistance to poisoning. Compared to the other supports, TiO_2 can remarkably improve the dispersion state of the VO_x species on the surface of catalysts. The main disadvantage of these catalysts is their low thermal stability. The activity dramatically and irrevocably degrades at temperatures above 350 °C. This is due to a change in the status of the active component (conversion of the high dispersed forms of vanadium to a coarse phase of V_2O_5), which is also accompanied by a phase transition of anatase to rutile.

The aim of this work is to study the effect of ceria and yttria additives on microstructure and thermal stability of TiO_2 support for the development of a new generation of active and thermostable supported vanadium catalyst for SCR NO with ammonia.

Synthesis of the support Me-TiO_2 where Me = Ce, Y was performed by incipient wetness impregnation of titanium dioxide (anatase) xerogel with an aqueous solution of cerium nitrate or yttrium nitrate salts followed by drying and heat treatment in air at 500-800 °C [1-2]. Obtained supports have higher specific surface area and more developed porous structure after calcination, compared to pure TiO_2. It indicates on their more higher thermal stability compared to pure TiO_2 due to the formation of the nanocrystalline structure Ce-TiO_2(fig.1a) and Y-TiO_2 oxides. (fig.1b)



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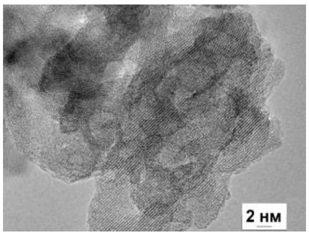

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Designed materials were used for the preparation of supported V_2O_5,WO_3/Ce(Y)-TiO_2 catalysts which were tested in the NO SCR reaction with ammonia in the presence of oxygen and water vapor. Catalysts have demonstrated a high thermal stability up to the reaction temperature of 500 °C providing almost complete cleaning from nitrogen oxide.

This work was supported by the RFBR grant № 16-33-00798 mol_a.

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ПЕРСПЕКТИВЫ ИСПОЛЬЗОВАНИЯ НОВОГО НАНОКРИСТАЛЛИЧЕСКОГО V_2O_5, WO_3/Ce(Y)-TiO_2 КАТАЛИЗАТОРА ВОССТАНОВЛЕНИЯ NO АММИАКОМ

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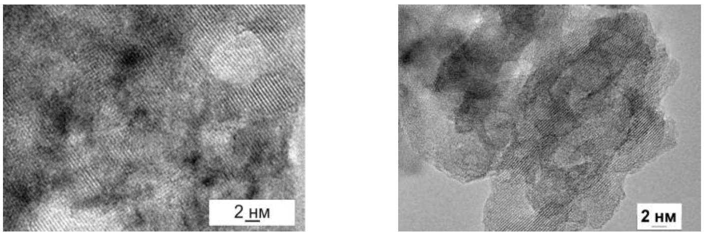
При существующем развитии технологии самым топливно-эффективным из двигателей является дизельный двигатель, однако он характеризуется высоким уровнем эмиссии NO, по сравнению с бензиновыми двигателями. В условиях избытка кислорода, характерных для выхлопных газов дизельного двигателя, оксид азота может быть переведен в азот с использованием восстановителей, например NH_3 из мочевины, на нанесенных V_2O_5/TiO_2 и V_2O_5,WO_3/Ce(Y)-TiO_2 катализаторах. Основным недостатком данных катализаторов является их низкая термостабильность: активность резко и безвозвратно ухудшается при температуре выше 350 °С. Это обусловлено изменением состояния активного компонента (превращением поверхностных высокодисперсных форм ванадия в грубодисперсную фазу V_2O_5), что также сопровождается и фазовым переходом анатаза в рутил.

Целью данной работы является изучение влияние добавки CeO_2 или Y_2O_3 на микроструктуру и термостабильность носителя TiO_2 используемого для разработки нового поколения активных и термостабильных нанесенных ванадиевых катализаторов реакции селективного каталитического восстановления (СКВ) NO аммиаком.

Синтез носителей Ce-TiO_2 и Y-TiO_2 проводили методом пропитки по влагоемкости ксерогеля диоксида титана анатазной модификации водными растворами азотнокислых солей церия или иттрия с последующей сушкой и термообработкой на воздухе в интервале температур 500-800 °С.

Полученные в работе носители Ce-TiO_2 и Y-TiO_2 характеризуются более высокой удельной поверхностью и более развитой пористой структурой в широком интервале температур прокаливания, по сравнению с чистым TiO_2. Это свидетельствует об их более высокой термостабильности по сравнению с чистым TiO_2 в следствие формирования нанокристаллической структуры оксидов Ce-TiO_2 (рис.1а) and Y-TiO_2 (рис.1б).



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Разработанные носители были использованы для получения нанесенных V_2O_5, WO_3/Ce(Y)-TiO_2 катализаторов, которые были исследованы в реакции СКВ NO аммиаком в присутствии кислорода и паров воды. Полученные катализаторы характеризуются более высокой термостабильностью и в реакционной среде вплоть до температуры 500 °С обеспечивают практически полную очистку газовой смеси от оксида азота.

Работа выполнена при финансовой поддержке РФФИ (грант №16-33-00798 мол_а.)

EFFECT OF ALUMINA ADDITIVES ON THE NANOSTRUCTURE AND THERMAL STABILITY OF TiO_2 WITH ANATASE STRUCTURE

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Titanium dioxide (anatase) is widely used as an adsorbent and support for the metal and oxide catalysts. It is also employed in materials converting solar energy into electricity and in chemical sensors. However, anatase is metastable and when the temperature is raised to 700 °C it irreversibly convert to rutile form. It leads to a significant reduction of the surface area and changes the pore structure. In this regard, the increase of the thermal stability of TiO_2 (anatase) is an actual task.

The aim of this work is to study the effect of aluminum oxide additives on the formation of nanostructure of titanium dioxide (anatase modification) during the heat treatment in a wide range of temperatures.

Titanium dioxide samples with Al_2O_3 (1-10 wt. %) were synthesized by incipient-wetness impregnation. Anatase obtained by the industrial sulfuric acid technology [1] was impregnated with an aluminium nitrate solution and was dried in air and then in dry box at 110 °C for 12 h. and then was heated in air at 300-1000 °C for 4 h.

The physicochemical properties of the obtained samples were studied by XRD, HREM, and low-temperature (77 K) nitrogen sorption methods.

X-ray diffraction data show that aluminum oxide causes a significant increase in the anatase to rutile phase transition temperature in titania doped with aluminia samples. The calcination of the doped samples containing 1-10 wt.% Al_2O_3 does not yield rutile until 950 °C, while the rutile phase in undoped titanium is detectable at 750 °C. The unit cell parameters (***a*** and ***c***) are not changes by doping.

According to HRTEM data introduction of additives of alumina into the titanium dioxide after the heat treatment at 500 °C leads to the formation of nanocrystalline structure while undoped titanium dioxide has a well-ordered crystal structure. The nanocristalline structure of doped TiO_2 consists of intergrown fine anatase crystallites 5-7 nm in size separated by interblock (intercrystalline) boundaries, in which the aluminum ions are stabilized. This stabilization is due to the fact that in the area of boundaries anatase structure strongly disordered. Formation of TiO_2 with nanocrystalline structure stabilize the anatase phase at much higher temperatures (900-950 °C) compared with the pure TiO_2.

Increasing the thermal stability of the anatase phase leads to the keeping of a higher specific surface area and a developed porous structure under the heating at the high temperature.

It was shown earlier that the doping of titania with additives of ceria, yttria and silica leads also to the formation of nanocrystalline structure of titania with increasing thermal stability [2-4].

This work was supported by the Russian Science Foundation (grant № 14-23-00037).

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[4] A.A. Shutilov, G.A. Zenkovets, V.Yu. Gavrilov, S.V. Tsybulya, *Kinet .Catal.*, 52, 113, (2011)

ВЛИЯНИЕ ДОБАВОК ОКСИДА АЛЮМИНИЯ НА НАНОСТРУКТУРУ И ТЕРМОСТАБИЛЬНОСТЬ ДИОКСИДА ТИТАНА АНАТАЗНОЙ МОДИФИКАЦИИ

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Диоксид титана анатазной модификации широко используется в качестве носителя металлических и оксидных катализаторов. Он также используется при прозводстве материала для солнечных батарей и химичесих сенсоров. Однако, анатаз является метастабильным и при повышении температуры до 700 °C необратимо переходит в рутил, что ведет к значительному снижению поверхности и изменению пористой структуры. В связи с этим, увеличение термостабильности TiO_2 (анатаза) является актуальной задачей.

Целью данной работы является изучение влияния добавок оксида алюминия на формирование наноструктуры диоксида титана анатазной модификации при термообработке в широком интервале температур.

Исходный TiO_2 (анатаз) был получен по промышленной сернокислотной технологии. Образцы диоксида титана, модифицированные добавками оксида алюминия (1-10 вес. %), синтезировали пропиткой ксерогеля TiO_2, водным раствором азотнокислого алюминия с последующей сушкой при 110 °C в течение 12 часов и термообработкой на воздухе при 300-1000 °C в течение 4 часов.

Физико-химические свойства исследовали методами РФА, ПЭМВР, низкотемпературной адсорбции азота.

Данные рентгенофазового анализа показывают, что введение добавки оксида алюминия в приводит к значительному увеличению температуры фазового перехода анатаза в рутил в образцах, модифицированных Al_2O_3. В образцах, содержащих 1-10 вес.% Al_2O_3 фаза рутила не регистрируется вплоть до 950 °C, в то время как для не модифицированного TiO_2 фаза рутила регистрируется при 750 °C. Следует отметить, что параметры кристаллической решетки анатаза (***a*** and ***c***) не меняются при введении модифицирующей добавки.

Согласно данным ПЭМВР, введение добавок оксида алюминия в диоксид титана при термообработке при 500 °C приводит к формированию нанокристалической структуры, состоящей из некогерентно сросшихся высокодисперсных кристаллитов анатаза размером 5-7 нм с образованием между ними межблочных (межкристаллитных) границ, в области которых стабилизируются ионы алюминия. Такая стабилизация обусловлена тем, что в области границ структура анатаза сильно разупорядочена.

Увеличение термостабильности фазы анатаза приводит к сохранению более высокой удельной поверхности и более развитой пористой структуре при прокаливании при высоких температурах. Это позволяет использовать полученные материалы при высоких температурах обработки.

Ранее в литературе было показано, что модифицирование TiO_2 анатаза добавками CeO_2, Y_2O_3 и SiO_2 также приводит к формированию нанокристаллической структуры TiO_2 и увеличению термостабильности.

Работа выполнена при финансовой поддержке РНФ (грант № 14-23-00037).

THE STUDY OF STRUCTURAL AND MORPHOLOGICAL CHANGES DURING THERMAL DECOMPOSITION OF $Y_2(C_2O_4)_3 \cdot 10H_2O$

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During solid state chemical reaction formation of the reaction product with new crystal lattice usually occurs. Mechanism of the structural transformation defines the product morphology and significantly influences the reaction kinetics. If the reaction includes several stages there is possibility to affect product morphology by controlling phase composition of intermediates.

The aim of this work was to study stages sequence of yttrium oxalate decahydrate thermal decomposition and to investigate the effect of reaction conditions on morphology and structure of the reaction product at each stage. The following methods were used: optical microscopy, SEM, thermogravimetry, X-ray diffraction analysis.

It was found that thermal decomposition includes two main stages: dehydration and oxalate thermolysis, with the dehydration being occurred through the formation of intermediate 6-, 4- and 2-hydrates. Effect of different dehydration conditions during hexahydrate formation on its structure and morphology was studied. X-ray analysis showed that depending on dehydration conditions mixture of triclinic and monoclinic hexahydrates with different ratio can be obtained. Triclinic hexahydrate is predominantly formed under low water pressure (heating in air) and monoclinic hexahydrate is predominantly formed under high water pressure (closed container).

Besides it was found that during dehydration in both cases structural transformations proceeds by deformation (martensitic) mechanism. The main feature of this mechanism is crystal shape change, which was observed in the experiment (Fig.1). According to phenomenological theory of martensitic phase transformations mechanisms of the structural transformation were proposed. Orientation relationships were also found.

Furthermore the following stages of thermal decomposition were determined and products at each stage were identified. Conditions for obtaining yttrium oxide with the smallest particles size were found.

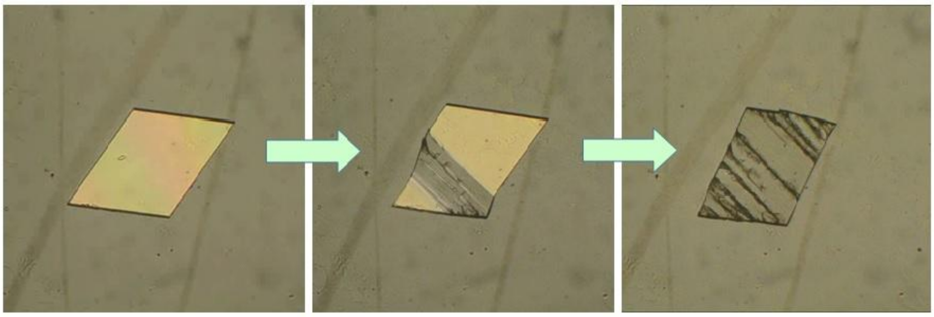

Fig.1. The change of shape of initial crystal of decahydrate yttrium oxalate during dehydration on air

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ИССЛЕДОВАНИЕ СТРУКТУРНЫХ И МОРФОЛОГИЧЕСКИХ ИЗМЕНЕНИЙ В ПРОЦЕССЕ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ $Y_2(C_2O_4)_3 \cdot 10H_2O$

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В процессе твердофазной химической реакции обычно происходит образование твердого продукта с новой кристаллической структурой. Механизм структурного превращения определяет морфологию продукта реакции и оказывает существенное влияние на кинетику реакции. Если реакция включает несколько стадий, то появляется возможность влиять на морфологию конечного продукта реакции, контролируя фазовый состав промежуточных продуктов.

Целью настоящей работы было детальное изучение стадийности термического разложения декагидрата оксалата иттрия и исследование влияния условий реакции на морфологию и структуру продукта реакции на каждой стадии. В работе были использованы следующие методы исследования: оптическая и сканирующая электронная микроскопия, термогравиметрия, рентгенофазовый и рентгеноструктурный анализы.

Было определено, что термическое разложение состоит из двух стадий: дегидратация и термолиз оксалата, причем дегидратация проходит с образованием промежуточных 6-, 4- и 2-гидрата. Было изучено влияние различных условий дегидратации до гексагидрата на его структуру и морфологию. Рентгенофазовый анализ показал, что в зависимости от условий дегидратации получается смесь продуктов различного состава. При низких давлениях паров воды (нагревание на воздухе) преимущественно образуется гексагидрат с триклинной структурой, при высоких (закрытый контейнер, 85˚C, 100 ч) - с моноклинной.

Также было обнаружено, что структурные превращения при дегидратации в обоих случаях имеют сдвиговый (мартенситный) характер, признаком чего является изменение формы исходного кристалла, наблюдаемое в эксперименте (рисунок 1). В рамках феноменологической теории мартенситных фазовых превращений были предложены механизмы структурной стадии. Были также определены ориентационные соответствия между фазами.

Далее были определены последующие стадии термического разложения и продукты, получающиеся на каждой из них. Также были найдены условия получения оксида иттрия, обладающего наибольшей дисперсностью.

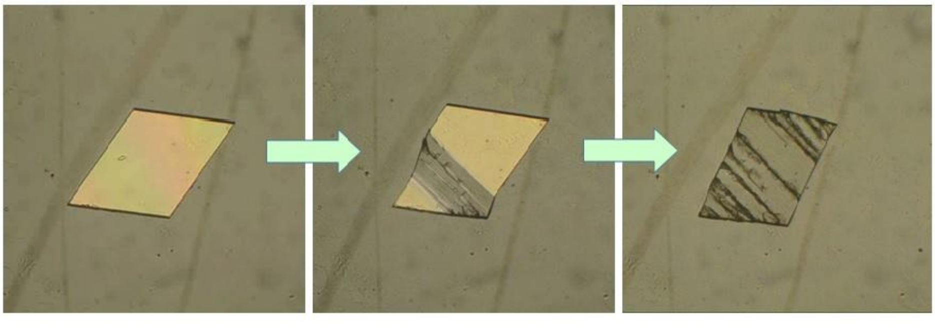

Рисунок 1. Изменение формы кристалла $Y_2(C_2O_4)_3 \cdot 10H_2O$ в процессе дегидратации на воздухе.

Работа выполнена при поддержке гранта РФФИ 16-33-60093.

CsH_2PO_4 - PROTON ELECTROLYTES, MODIFIED BY DIVALENT CATIONS

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Cesium dihydrophosphate is a promising proton membrane for intermediate fuel cells at superionoic phase. The sharp decrease of conductivity during the phase transition to the low temperature phase significantly limits its application. The creation of highly conductive and thermally stable systems based on CsH_2PO_4 at intermediate temperatures ~150-230°C and low relative humidity is very important for practice.

The heterogeneous and homogeneous substitution CsH_2PO_4 usually improves the transport properties of low-conducting phase due to formation of disordered phases on the interphase, the changes of hydrogen bond network, the formation of solid solutions and superionic disordered phases. Thus, substituting for the alkaline metals in $Cs_{1-x}M_xH_2PO_4$, M = Rb, K, Na, results in the formation of solid solutions isostructural to CsH_2PO_4.

Modification of CsH_2PO_4 by double-charged cations results in vacancies in Cs-sublattice, determining changes in hydrogen bond energy and the degree of structure disordering. This work is devoted to investigation of transport, structural and thermal properties of CsH_2PO_4 modified by Ba^{2+}cations.

The partial substitution has been shown to form the $Cs_{1-2x}Ba_xH_2PO_4$ solid solutions at x = 0-0.1, isostructural CsH_2PO_4 ($P2_1/m$) with a slight decrease of the unit cell parameters. The unit cell parameters of $Cs_{1-2x}Ba_xH_2PO_4$ ($P2_1/m$) were determined depending on x. With x increasing the BaH_2PO_4 reflexes were appeared and two phases coexist, forming a composite system. Superionic phase transition disappears with x increase. Proton conductivity increases more than three orders of magnitude even at x = 0.03 and reaches values ~ 10^{-3} S/cm at T = 150°C. The conductivity in superionic phase doesn't change. The stability of high conductivity values has been verified at high temperatures for long term storage. A mechanism of conductivity improvement includes the formation of Cs vacancies during heterovalent replacement which lead to phosphate tetrahedra reorientation and structural disordering of the salt up to its amorphization with x increase. While the residual water molecules in composites could also take place in the proton transport. Synthesized high conductive systems should be perspective for electrochemical devices.

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МОДИФИЦИРОВАНИЕ ПРОТОНПРОВОДЯЩЕГО ЭЛЕКТРОЛИТА CsH_2PO_4 ДВУХВАЛЕНТНЫМИ КАТИОНАМИ

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CsH_2PO_4 является перспективным материалом протонпроводящих мембран среднетемпературных топливных элементов (150-230°C). Однако резкое снижение проводимости при фазовом переходе из суперионного состояния в низкотемпературную фазу существенно ограничивает его применение. В настоящее время значительный интерес представляет создание протонных электролитов на основе CsH_2PO_4, обладающих высокой электропроводностью и термической стабильностью в диапазоне средних температурах при низкой относительной влажности. Применение методов гетерогенного и гомогенного замещения способно улучшить транспортные характеристики низкотемпературной фазы CsH_2PO_4 вследствие образования разупорядоченного состояния на интерфейсе, изменения сетки водородных связей, образования твердых растворов и суперионных неупорядоченных фаз. Так, например, гомогенное замещение Cs^+ щелочными металлами приводит к образованию твердых растворов $Cs_{1-x}M_xH_2PO_4$, (M=Rb, K, Na), изоструктурных CsH_2PO_4.

Модифицирование CsH_2PO_4 двухзарядными катионами вызывает появление вакансий в катионной подрешетке и, как следствие, высокую степень разупорядочения структуры и изменения в энергии водородных связей. Данная работа посвящена исследованию транспортных, структурных и термических характеристик CsH_2PO_4, модифицированного катионами Ba^{2+}.

Было показано, что при частичном замещении в $Cs_{1-2x}Ba_xH_2PO_4$ при x=0-0.1 происходит образование твердых растворов, изоструктурных CsH_2PO_4 ($P2_1/m$) с уменьшенным параметром элементарной ячейки. При увеличении x на рентгенограммах появляются рефлексы BaH_2PO_4, что свидетельствует о сосуществовании двух фаз и образовании своего рода композиционной системы. В твердых растворах $Cs_{1-2x}Ba_xH_2PO_4$ в сравнении с CsH_2PO_4 с ростом x суперионный фазовый переход исчезает, протонная проводимость низкотемпературной фазы возрастает более чем на три порядка величины даже при x = 0.03, достигая значений ~ 10^{-3} См/см при T=150°C, значения проводимости в суперионной фазе сохраняются. Стабильность высоких значений проводимости была проверена при длительной изотермической выдержке. Увеличение протонной проводимости при гетеровалентном замещении обусловлено образованием цезиевых вакансий, последующей реориентацией тетраэдров и структурным разупорядочением соли, вплоть до аморфизации. В то же время, остаточные молекулы воды также могут принимать участие в механизме переноса протона. Исследованные высокопроводящие системы $Cs_{1-2x}Ba_xH_2PO_4$ перспективны для дальнейших исследований в качестве мембран электрохимических устройств.

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PREPARATION AND RESEARCH OF CATALYTIC PROPERTIES OF BIMETALLIC ALLOYS Ni_xPd_{1-x}

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A recent very high need for chlorinated hydrocarbons, especially in polymer production, determines a steady increase of their amount of products. The commercial production of these compounds is accompanied by accumulation of high amounts of chlorine-containing organic wastes. The recycling of Cl-containing organic wastes, including variety of chlorinated hydrocarbons, is known to be rather difficult and important ecological problem. One of the actively used recycling methods is catalytic decomposition of chlorinated hydrocarbons with Ni, Co, Fe metals. It results in formation of carbon nanomaterial – an extended surface nanofibers (CNF) [1]. Depending on reaction's conditions the decomposition of chlorinated hydrocarbons can proceed in several directions [2]. At T<500 °C the process proceeds as hydrogenolysis of C-Cl bound, which results in formation of hydrocarbons without chlorine in their composition. If the temperature is higher than 500 °C, catalytic decomposition of Cl-containing hydrocarbons occurs and results in formation of carbon nanomaterial, hydrogen and hydrogen chloride (1).

$$C_xH_yCl_z \rightarrow C\,(CNF) + H_2 + HCl \qquad (1)$$

For this research 1,2-dichloroethane was selected as a model chlorinated hydrocarbon to be processed via catalytic decomposition over Ni_xPd_{1-x} alloy. These catalysts are formed spontaneously in the reaction medium on the initial stage of the process. This process is lately considered as a method of a purposeful synthesis of carbon nanofibers [3,4]. Particularly, CNF-metal composites may be used in supercapacitors production [5]. CNF also may be used in creation of next generation displays [6].

In present work we consider in detail the synthesis of homogenious Ni_xPd_{1-x} alloys by the reduction in the hydrogen atmosphere at 800°C of precursor synthesized by coprecipitation of Ni- and Pd-salts. A number of alloys with Pd containing of 1-10 at.% were synthesized. The powder X-ray diffraction analysis (XRD) of Ni_xPd_{1-x} alloys confirms the formation of a single-phase Ni-Pd for all samples. A catalytic activity of synthesized alloys in the 1,2-dichloroethane decomposition results in formation of CNF was studied. An effect of H_2 concentration in the reaction mixture $C_2H_4Cl_2/H_2/Ar$ on kinetics of CNF growth over Ni_xPd_{1-x} alloys ($C_2H_4Cl_2/H_2/Ar$ = 7.5/37.5/55.0, vol.%) is shown. The comparison of catalytic activities of the samples, which were synthesized by the reduction of precursors at 400 ºC, 600 ºC and 800 ºC is also shown. The optimal temperature of 1,2-dichloroethane decomposition (600 ºC) was determined. Transmission electron microscopy (TEM) data indicate that carbon material is generated as segmental nanofibers and is characterized by high degree of morphological homogeneity.

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ПОЛУЧЕНИЕ И ИССЛЕДОВАНИЕ КАТАЛИТИЧЕСКИХ СВОЙСТВ БИМЕТАЛЛИЧЕСКИХ СПЛАВОВ NI_XPD_{1-X}

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В последнее время востребованность хлорорганических соединений очень высока, особенно при производстве полимеров, что определяет неуклонный рост объемов их производства. Промышленное производство этих веществ сопровождается накоплением больших объемов хлорорганических отходов. Утилизация этих отходов представляет непростую проблему в силу высокой химической стойкости большинства хлорорганических соединений. Одним из используемых при этом методов основан на каталитическом разложении хлоруглеводородов на металлах подгруппы железа (Ni, Co, Fe) с образованием углеродного наноматериала – нановолокон с развитой поверхностью (УНВ) [1]. В зависимости от условий проведения реакции разложение хлоруглеводородов может протекать по нескольким направлениям [2]. При температуре ниже 500°С процесс идет через гидрогенолиз связи C-Cl с получением углеводородов, не содержащих хлора. При более высокой температуре – через каталитическое разложение хлоруглеводородов с образованием углеродного материала, водорода и хлороводорода (1).

$$C_xH_yCl_z \rightarrow C\ (УНВ) + H_2 + HCl \qquad (1)$$

В настоящей работе рассматривается процесс разложения 1,2-дихлорэтана на самоорганизующихся Ni_xPd_{1-x} катализаторах. Данные катализаторы формируются самопроизвольно в реакционной среде, на начальных стадиях процесса. В основе формирования самоорганизующихся катализаторов лежит явления углеродной эрозии или дезинтеграции металлов подгруппы железа и их сплавов в ходе реакции [3,4]. Этот процесс в последнее время рассматривается как способ целенаправленного синтеза углеродных структур на массивных изделиях [5,6]. В частности, металл-УНМ композиты могут применяться при производстве суперконденсаторов [7].

В данной работе подробно рассмотрен синтез гомогенных сплавов Ni_xPd_{1-x} восстановлением в водородной атмосфере многокомпонентных соединений-предшественников – смешанных гидроксокомплексов. Синтезирована серия образцов с варьированием содержания Pd в пределах 1-10 ат.%. Методом рентгенофазового анализа подтверждено формирование однофазных сплавов во всех полученных образцах. Изучена каталитическая активность полученных образцов в реакции разложения 1,2-дихлорэтана (ДХЭ) с получением УНВ. Показаны кинетические кривые для процесса образования углеродных волокон на сплавах разного состава при разложении реакционной смеси ДХЭ/H_2/Ar (ДХЭ/H_2/Ar = 7.5/37.5/55.0, об.%). Также приведено сравнение каталитической активности образцов катализаторов, полученных восстановлением прекурсоров при температурах 400 ºС, 600 ºС и 800 ºС. Установлено, что оптимальной температурой проведения разложения 1,2-дихлорэтана является 600°С. Углеродный материал образуется в виде сегментированных нановолокон и характеризуется высокой степенью морфологической однородности, о чем свидетельствуют приведенные в работе снимки просвечивающей электронной микроскопии.

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INVESTIGATION OF HYPERTHERMIC PROPERTIES OF NANOHORN'S AQUEOUS SUSPENSIONS FOR BIOLOGICAL APPLICATIONS

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In last years inorganic nanomaterials have growing application in industry, and need to study their biological activities due to security issues. On the other hand, it is expected that controlled interaction between nanoparticles and cells or organisms can be used to create new methods of medical treatment of disease [1].Carbon nanohorns (CNH) penetrating in biological tissue can effectively absorb and convert infrared (IR) radiation in heat which necessary for the local heating of tissue and organs. Thus, CNH can be used to prevent the growth of tumors using a method of hyperthermia.

The aims of this work are investigation of the properties of aqueous suspensions of carbon nanohorns and testing of penetration nanohorns in *Drosophila melanogaster* tissues.

In this study, we used carbon nanohorns powders synthesized by evaporation of a graphite target by arc discharge [2] and electron of beam emitted from an electron accelerator [3]. Two methods oxidation were used for functionalization nanohorns surface. The first method is oxidation in solution of nitric acid (3M) at 70˚C temperature for 1 hour [4]. The second method is oxidation of a mixture of sulfuric and nitric acids (H_2SO_4: HNO_3 = 1: 3) as described in [5]. Nanohorns structure was characterized by scanning electron microscopy, infrared, optical and Raman spectroscopy. Thermal properties of structural and morphological features of the aqueous suspensions of the original and modified CNH were investigated.

Implementation of CNH in tissue of Drosophila melanogaster larva carried out through the culture medium. In experiment larvae have genotype hs-Gal4; UAS-GFP.nls. Then larvae irradiated IR - laser. The heated nanohorns caused "heat shock" reaction (response of cells to stress). After 4 hour, we observed GFP-reporter luminescence. The GFP synthesized in response to "heat shock" reaction.

According to the results, it showed that, after oxidation, aqueous suspensions nanohorns absorb in the IR region stronger than the initial sample. Oxidation of samples also leads to an improvement of the thermal properties nanohorns. It is showed that the nanomaterials are capable of penetrating into the tissues of Drosophila larvae, it is seen by the fluorescent GFP signal in the imaginal discs.

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ИССЛЕДОВАНИЕ ГИПЕРТЕРМИЧЕСКИХ СВОЙСТВ ВОДНЫХ СУСПЕНЗИЙ НАНОХОРНОВ ДЛЯ БИОЛОГИЧЕСКИХ ПРИМЕНЕНИЙ

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В последние годы наноматериалы получают все большее применение в индустрии, и необходимость исследования их биологического действия обусловлена вопросами безопасности. С другой стороны, ожидается, что контролируемое воздействие наночастиц на клетки или организмы в целом может быть использовано для создания новых медицинских методов лечения заболеваний [1]. Углеродные нанохорны (УНХ), проникая в биологическую ткань, способны эффективно поглощать и преобразовывать инфракрасное (ИК) излучение в тепло, необходимое для локального разогрева тканей и органов, поэтому УН можно применять для предотвращения роста опухоли при использовании метода гипертермии.

Цели данной работы – исследование свойств исходных и модифицированных порошков УНХ в водных суспензиях и тестирование проникновения нанохорнов в ткани дрозофилы.

В данной работе использовались порошки УНХ, синтезированные методом электродугового синтеза [2] и методом испарения графитовой мишени электронным пучком ускорителя [3]. Для модификации поверхности нанохорнов было использовано два метода окисления. Первый из них – окисление в растворе азотной кислоты (3M) при температуре 70˚C в течение 1 ч [4], второй метод - окисление смесью кислот (H2SO4:HNO3 в соотношении 1:3) по методике, описанной в работе [5]. Структура нанохорнов была охарактеризована методами сканирующей электронной микроскопии, инфракрасной, оптической спектроскопии и спектроскопии комбинационного рассеяния света. Были исследованы термические свойства структурных и морфологических особенностей водных суспензий исходных и модифицированных нанохорнов.

Внедрение УН в ткани личинок дрозофилы особей генотипа hs-Gal4; UAS-GFP.nls осуществлялось через питательную среду. Затем личинок облучали ИК - лазером. Нагретые таким образом нанохорны вызывали реакцию «теплового шока» (ответная реакция клетки на стресс). Через 4 часа наблюдалось свечение GFP-репортера - белка, синтезированного в ответ на «тепловой шок».

По результатам показано, что после окисления, водные суспензии нанохорнов поглощают в ИК – области сильнее, чем исходный образец. Окисление образцов также приводит к улучшению термических свойств нанохорнов. Показано, что наноматериалы способны проникать в ткани личинок дрозофилы - это видно по флуоресцентному сигналу GFP в имагинальных дисках.

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2016 Russia-Japan Conference
"Advanced Materials: Synthesis, Processing and Properties of Nanostructures"

Abstracts
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Chairs: A. Zolkin, T. Goto

Invited Lectures

- ***R. Belosludov*** *Role of Computational Materials Science in Realization of Advanced Energy Materials and Nanostructure*
- ***K. Fujiwara*** *Morphological transformation of crystal/melt interface of silicon*
- ***A. Zolkin*** *Synthesis of DLC films. Ion-beam technologies*
- ***V. Volodin*** *Optical properties of nanocrystals formed with the use of laser pulse annealing*

Oral reports

N. Korobeishchikov, M. Roenko, V. Kalyada, G. Tatancev Diagnostics of intensive gas cluster-ion beams for materials processing

T. Nihei, Y. Yokota, M. Arakawa, Y. Ohashi, S. Kurosawa Growth of platinum fiber using the micro-pulling-down method and the local structure

N. Korobeishchikov, V. Kalyada, I. Nikolaev Ultra-smooth surface polishing by argon cluster ion beam

V. Khudozhitkov, A. Zarvin The possibility of the launch of plasmochemical reactions and generate clusters with electronic activation of the gas flow

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Yu. Demidova, I. Simakova, J. Gläsel, B. J. Etzold, T. Schubert, D. Murzin Carbon based Ru colloidal catalysts: synthesis approaches and catalytic behavior

L. Basalaeva, Yu. Nastaushev, F. Dultsev Fabrication and characterization of silicon nanopillars

A. Lyamkina, S. Moshchenko Non-radiative energy transfer in quantum dot ensemble mediated by localized surface plasmons

ROLE OF COMPUTATIONAL MATERIALS SCIENCE IN REALIZATION OF ADVANCED ENERGY MATERIALS AND NANOSTRUCTURES

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In order to design materials with novel composition and desirable characteristics it is important to have a good understanding of the atomic-scale chemical and physical properties of materials. Using powerful computer system installed in Institute for Materials Research, Tohoku University and highly accurate methods we try to accurately estimate the important properties of various complex materials in order to accelerate the realization of novel materials, hand-in-hand with experiment and propose these materials for energy storage applications. Here, the recent achievements of our group have been reviewed.

The fundamental strategy to realize specific or highly selective guest adsorption is based on the design and synthesis of nanoporous compounds that can recognize the differences between the guest molecules. This requires precise control of the structure and detailed understanding of the structure-property relationships. The metal–organic framework (MOF) material as new functional adsorbents with novel topologies and exceptional host-guest properties has been selected due to scientific interest in their application for storage and separation. In collaboration with experimentalists, it has been shown that the concept of using designable regular MOF material could be applicable to a highly stable, selective adsorption system [1]. A new soft nanoporous crystalline material that selectively adsorbs CO with adaptable pores has been studied using first-principles calculations in collaboration with experimentalists. The high selectivity has been achieved by the synergetic effect of the local interaction between CO and accessible metal sites and a global transformation of the framework [2].

Recently, we have presented a design for functional 3D porphyrin-based nanostructures, which would bridge the gap between the well-known fullerenes and nanotubes and a new class of the functional nanomaterials. It was shown that the electronic structures and optical properties of studied structures could be easily tuned via their size, topology, and the presence of bridging sp^3 carbon atoms. The optical properties of the new materials can rival those of known quantum dots. The ability to store large quantities of methane (106–216 cm^3 (STP)/cm^3) was observed in all cases with several compounds being close to or exceeding the DOE target of 180 cm^3 (STP)/cm^3 [3].

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MORPHOLOGICAL TRANSFORMATION OF CRYSTAL/MELT INTERFACE OF SILICON

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In the photovoltaic market, solar cells made of polycrystalline Si (commonly expressed as multicrystalline Si, mc-Si) are the main products both at present and potentially in the future. The mc-Si ingot obtained by casting based on a unidirectional solidification technique contains various types of defects such as grain boundary, twin boundary, dislocation, and metallic impurity, which prevent the realization of high-efficiency solar cells. The morphology of the crystal/melt interface during crystal growth processes affects the macro- and micro-structures, and thus controlling the interface morphology is crucial to obtaining high-quality crystals.

We fundamentally investigated the mechanism of the morphological transformation of crystal/melt interface of Si by in situ observations. The effects of the interface morphology on the impurity accumulation and the twin boundary formation were also investigated.

Figure 1 shows a typical image of the crystal/melt interface of Si at (a) low growth velocities and (b) high growth velocities. It was found that the morphology of the interface was transformed from planar to zigzag facets with the increase in the growth velocity [1]. We observed that a wavy perturbation was introduced into a planar interface, and that the perturbation grew to zigzag facets at a high growth velocity. The theoretical calculation showed that the negative temperature gradient was locally formed at the interface in the Si melt owing to the latent heat when the growth velocity was higher than its critical value, which leads to the amplification of the perturbation and zigzag facet formation. We also found that the impurities accumulated at valleys of zigzag facets [2].

We will also introduce the study on the impurity accumulation and twin boundary formation at grain boundary grooves at the crystal/melt interface [3].

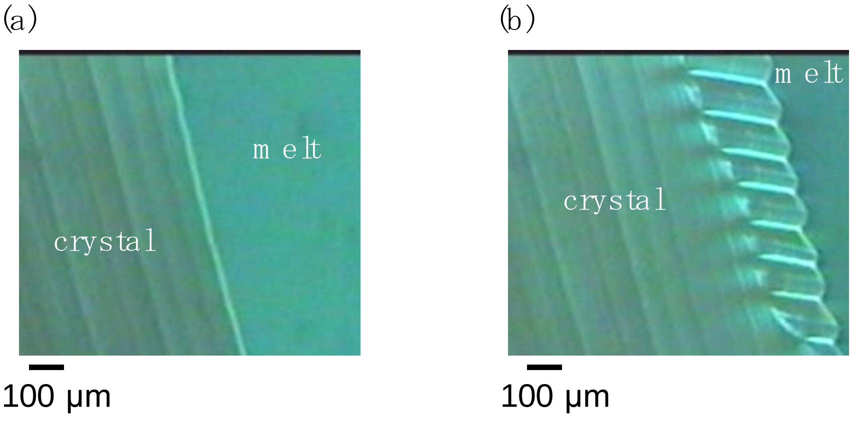

Fig. 1 (a) Planar crystal/melt interface at low growth velocities, and (b) zigzag faceted crystal/melt interface at high growth velocities.

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SYNTHESIS OF DLC FILMS. ION-BEAM TECHNOLOGIES

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For the first time diamondlike (DLC) films were synthesized in 1971 by S. Ayzenberg (USA) [1], then V. M. Golyanov and V. P. Demidov (USSR) [2] and V. E. Strelnitsky with colleagues (USSR) [3]. It is established that films possess the combination of the chemical, physical and mechanical properties close to diamond. Since then they are used in different areas: from optical systems to medicine. Methods of their synthesis are diverse: from methods of high-temperature thermal evaporation to modern pulse magnetron systems. Each method has the advantages and restrictions. It is difficult to find the way which would satisfy all. Combines one – not simply to receive coverings with the set properties and high degree of reproducibility. Accurate recipes are absent or are unavailable. Results in many respects are defined by art of researchers and technologists.

The ion-beam method is interesting by the possibility of smooth management of parameters of the besieged flow: energy, current density, charging structure, the direction to the surface of sedimentation, the chemical composition of the flow. As a result it is possible to receive quality coverings where the main: adhesion, hardness, optical characteristics, good tribological properties, chemical passivity and others. However, many problems constantly require attention. These are mechanical stresses which destroy (blow up) coverings, the roughness to which impose high requirements at the level of the nanosizes, uniformity of structure or constancy of properties on the surface today. Among sensitive scopes – optical systems, including laser and coverings of medical assignment.

In the report examples of use of ion-beam technologies, generally on the basis of sources of ions of low energy (50-300ev) the END-Hole type with use of gases of hydrocarbons and sources of ions with azimuthal drift of electrons or the source the anode layer with energy to 5000ev are given. It is established that in each case diamond-like coverings (DLC) can be synthesized with close characteristics: good coupling with the substrate (adhesion), sufficient hardness (18 GPa and above), good optical transparency and in some cases – the high enlightenment on substrates: silicon, germanium (for example). High chemical passivity is noted. This fact gives the grounds for more detailed research of process of synthesis and search of models.

Results of the analysis by means of methods are given: KR-spectroscopy, nanoindenting, atomic-force microscopy, spectroscopy (190nm-16mkm), the electron transmission (TEM) and scanning microscopy, and the ellipsometry. The Raman Spectrums are received on the Jobin Yvon T64000 device (France) with excitation wavelength – 514,5 nm. For determination of thickness and index of refraction of coverings – the laser LEF ellipsometer – 752 (Russia) with the wavelength of 632 nm. Hardness was defined by the nanoindenting method on Nanoskan-3D and Nanoskan-4D devices (Russia). Thickness of coverings was measured by the scribing method. The research was conducted by TEM on JEOL JEM-4000EX and JEM-2200FS devices (Japan). The substrate was sprayed near $350*10^{-6}$m by setting the machining Leica EM TXP (Germany). Then samples of films on silicon were sputtered by ions beam of Ar with energy 5 кэВ on the PIPS Gatan Model device of 691 (USA). IR spectrums of the transmission and absorption are measured on IK the Fourier spectrometer FT-801 (Russia) in range from 2,5 to 16,7 microns.

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СИНТЕЗ АЛМАЗОПОДОБНЫХ ПЛЕНОК УГЛЕРОДА. ИОННО-ЛУЧЕВЫЕ ТЕХНОЛОГИИ

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Впервые алмазоподобные (DLC) плёнки были синтезированы в 1971 году С. Айзенбергом (США) [1], затем В.М.Голяновым и В.П. Демидовым (СССР) [2] и В.Е. Стрельницким с коллегами (СССР) [3]. Установлено, что плёнки обладают сочетанием химических, физических и механических свойств, близких к алмазу. С тех пор они используются в различных областях: от оптических систем до медицины. Методы их синтеза многообразны: от методов высокотемпературного термического испарения до современных импульсных магнетронных систем. Каждый метод имеет свои достоинства и ограничения. Трудно найти способ, который бы удовлетворял всех. Объединяет одно – не просто получить покрытия с заданными свойствами и высокой степенью воспроизводимости. Чёткие рецепты отсутствуют или недоступны. Результаты во многом определяются искусством исследователей и технологов.

Ионно-лучевой метод интересен возможностью плавного управления параметрами осаждаемого потока: энергией, плотностью тока, зарядовым составом, направлением к поверхности осаждения, химическим составом потока. В результате удаётся получать покрытия высокого качества, где основные: адгезия, твёрдость, оптические характеристики, хорошие трибологические свойства, химическая пассивность и другие. Однако, многие проблемы постоянно требуют внимания. Это механические напряжения, которые разрушают (взрывают) покрытия, шероховатость, к которой сегодня предъявляют высокие требования на уровне наноразмеров, однородность структуры или постоянство свойств по поверхности. Среди чувствительных областей применения – оптические системы, включая лазерные и покрытия медицинского назначения.

В докладе приведены примеры использования ионно-лучевых технологий, в основном, на основе источников ионов низких энергий (50-300эВ) типа END-Hole с использованием газов углеводородов и источников ионов с азимутальным дрейфом электронов или источником анодным слоем с энергией до 5000эВ. Установлено, что в каждом случае алмазоподобные покрытия могут быть получены с близкими характеристиками: хорошая сцепление с подложкой (адгезия), достаточная твёрдость (18Гпа и выше), хорошая оптическая прозрачность и в отдельных случаях – высокое просветление на подложках: кремний, германий (например). Отмечается высокая химическая пассивность. Этот факт даёт основания для более детального исследования процесса синтеза и поиска моделей.

Приведены результаты анализа с помощью методов: КР-спектроскопии, наноиндентирования, атомно-силовой микроскопии, спектроскопии (190нм-16мкм), электронной просвечивающей (TEM) и сканирующей микроскопии, и эллипсометрии. Рамановские спектры получены на приборе Jobin Yvon T64000 (Франция) с длиной волны возбуждения – 514,5 нм. Для определения толщины и показателя преломления покрытий – лазерный эллипсометр LEF – 752 (Россия) с длиной волны 632 нм. Твердость определялась методом наноиндентирования на приборах «НаноСкан-3D» и «НаноСкан-4D» (Россия). Толщина покрытий измерялась методом скрайбирования. TEM исследование проводилось на приборах JEOL JEM-4000EX и JEM-2200FS (Япония). С помощью установки для механической обработки Leica EM TXP (Германия) удалялось порядка 350 мкм толщины подложки. Затем образцы пленок на кремнии утонялись распылением ионным пучком Ar с энергией 5 кэВ на приборе PIPS Gatan Model 691 (США). ИК спектры пропускания и поглощения измерены на ИК фурье-спектрометре ФТ-801 (Россия) в диапазоне от 2,5 до 16,7 мкм.

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OPTICAL PROPERTIES OF NANOCRYSTALS FORMED WITH THE USE OF LASER PULSE ANNEALING

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Nowadays, application of nano- and femtosecond laser pulse annealing for manufacturing of nanostructures has become very popular. In some cases only laser pulse crystallization can be use, because it can be local, allow to avoid undesirable inter-diffusion of elements consisting nano-heterostructures (for example, this effect take place in the case of long-time thermal annealings). The nano-heterostructures like semiconductor nanocrystals in dielectric films can be perspective in optoelectronics and nano-electronics of future. The recent year's progress in the field of giant-microelectronics ("reverse Moor's law") demands the development of technology for manufacturing of semiconductor films with good electro-physical parameters on large-scale low-price substrates.

Nanosecond and femtosecond laser annealings were applied for crystallization thin amorphous silicon films and amorphous silicon nanoclusters in silicon-rich nitride and oxide films. Regimes of crystallization of amorphous Si nanoclusters in the initial films were found. Effect of laser assisted formation of a-Si nanoclusters in the non-stoichiometric dielectric films with relatively low concentration of additional Si atoms was also observed. This approach is applicable for the creation of dielectric films with semiconductor nanoclusters on non-refractory substrates [1].

Facilities of Raman spectroscopy and IR Fourier spectroscopy for study of silicon and germanium based nanostructures were demonstrated. NSU has Raman spectrometer (T64000 Horiba Jobin Yvon) with a micro-Raman setup and FTIR-spectrometer (FT-801). Raman spectroscopy data allow getting information about phase composition of semiconductor nanoclusters, about sizes of semiconductor nanocrystals and about states of impurities (for example from analysis of Si-H vibrations in hydrogenated silicon [2] and Si-B vibrations in doped silicon).

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ОПТИЧЕСКИЕ СВОЙСТВА НАНОКРИСТАЛЛОВ СФОРМИРОВАННЫХ С ИСПОЛЬЗОВАНИЕМ ИМПУЛЬСНЫХ ЛАЗЕРНЫХ ОТЖИГОВ

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В настоящее время, применение нано- и фемтосекундных импульсных лазерных отжигов для изготовления наноструктур весьма актуально. В некоторых случаях можно использовать только импульсную лазерную кристаллизацию, потому что её воздействие локально, позволяет избегать нежелательной взаимной диффузии элементов, из которых состоят нано-гетероструктуры (этот нежелательный эффект имеет место в случае печных отжигов). Такие нано-гетероструктуры как полупроводниковые нанокристаллы в диэлектрических плёнках перспективны в оптоэлектронике и наноэлектронике будущего, и в области широкоформатной микроэлектроники (прогресс в которой показывает так называемый «обратный закон Мура»), это требует разработки технологии для изготовления полупроводниковых плёнок с хорошими электрофизическими параметрами на широкоформатных недорогих подложках.

Нано- и фемтосекундные лазерные отжиги применялись для кристаллизации тонких плёнок аморфного кремния и аморфных нанокластеров кремния в плёнках нестехиометрических нитридов и оксидов кремния. Были отработаны режимы кристаллизации аморфных нанокластеров кремния в исходных плёнках. Было также обнаружено, что лазерные отжиги приводили к формированию аморфных нанокластеров кремния в нестехиометрических диэлектрических плёнках с относительно низкой концентрацией атомов избыточного кремния. Этот подход применим для создания диэлектрических плёнок с полупроводниковыми нанокластерами на нетугоплавких подложках [1].

Продемонстрированы возможности спектроскопии комбинационного рассеяния света и ИК-Фурье-спектроскопии для изучения наноструктур на основе кремния и германия. В АТИЦ НГУ имеются спектрометр комбинационного рассеяния света (T64000 Horiba Jobin Yvon) с микро-Рамановской приставкой и ИК-Фурье-спектрометр (ФТ-801). Данные спектроскопии комбинационного рассеяния позволяют получить информацию о фазовом составе полупроводниковых нанокластеров, о размерах полупроводниковых нанокристаллов и о состояниях примесей (например, из анализа колебаний Si-H [2] и Si-B связей в кремнии).

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DIAGNOSTICS OF INTENSIVE GAS CLUSTER-ION BEAMS FOR MATERIALS PROCESSING

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In the last decade it has been shown that the accelerated gas-phase ion cluster beams are unique tool for different technological applications of materials processing. In particular, in practice by cluster ion the polishing of surfaces of various materials down to subnanometer roughness, the cluster-ion-assisted deposition of defect-free thin films, and the ultrashallow implantation are successfully approved [1, 2]. The source of the high intensity flow of neutral clusters is a supersonic jet of condensing gas. The neutral cluster beam is extracted from supersonic jet by using a conical diaphragm (skimmer). Physical limitations of gas condensation in supersonic flow require compliance with the optimal conditions for the formation of a neutral cluster beam with a maximum intensity [3]. The limiting kinetic energy of cluster in the supersonic flow is a few dozens of electron volts typically, which is insufficient for processing materials. To increase energy neutral cluster beam is ionized, and then the cluster ions are accelerated to the desired energy (typically 20-30 keV). The cluster beam contains a large number of neutral monomers and clusters with very broad size distribution. For the processing of materials it is necessary to separate out the ion-monomers from the accelerated cluster ion beam, which is carried out using a magnetic separator [4].

Obviously, the quality of the surface treatment material depends on the spatial homogeneity of the ion-cluster beam. In this paper, a description of the equipment for the formation of intense gas jet ion cluster beam is presented. With the use of original diagnostic procedures research of mass composition and spatial characteristics of accelerated ion cluster beam Ar and N_2 are carried out. The measurements were performed at different average cluster size ($N = 10^1 \div 10^3$ molecules/cluster), at operating the ion energy E_i = 20-25 keV. The mass spectra of the accelerated ion cluster beam at different pressures in the gas source P_0 = 0.5 - 6 bar are registered. Cross-sections of the ion current of the ion-cluster beam for magnetic separator and without a separator are studied.

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ДИАГНОСТИКА ИНТЕНСИВНЫХ ГАЗОВЫХ ИОННО-КЛАСТЕРНЫХ ПУЧКОВ ДЛЯ ОБРАБОТКИ МАТЕРИАЛОВ

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В последнее десятилетие было показано, что ускоренные газофазные ионно-кластерные пучки являются уникальным инструментом для разных технологических приложений обработки материалов. В частности, на практике успешно апробированы ионно-кластерная полировка поверхностей различных материалов до субнанометровой шероховатости, кластер-ион-ассистированное осаждение тонких бездефектных пленок, приповерхностная имплантация на ультрамалую глубину [1, 2]. Источником интенсивного потока нейтральных кластеров является сверхзвуковая струя конденсирующегося газа, из которой с помощью конусной диафрагмы (скиммера) выделяют нейтральный кластерный пучок. Физические ограничения процесса конденсации газа в сверхзвуковом потоке требуют соблюдения оптимальных условий для формирования нейтрального кластерного пучка с максимальной интенсивностью [3]. Предельная кинетическая энергия кластеров в сверхзвуковом потоке, как правило, составляет несколько десятков электрон-вольт, что недостаточно для обработки материалов. Для увеличения энергии нейтральный кластерный пучок ионизуется, затем кластерные ионы ускоряются до нужной энергии (как правило, до 20-30 кэВ). В кластерном пучке содержится большое количество нейтральных мономеров и кластеры с очень широким распределением по размерам. Для обработки материалов необходимо отсепарировать ускоренный ионно-кластерный пучок от ионов-мономеров, что осуществляют с помощью магнитного сепаратора [4].

Очевидно, качество обработки поверхности материалов зависит от пространственной однородности ионно-кластерного пучка. В данной работе представлено описание оборудования для формирования интенсивных газоструйных ионно-кластерных пучков. С использованием оригинальных диагностических методик выполнены исследования массового состава и пространственных характеристик ускоренных ионно-кластерных пучков Ar и N_2. Измерения выполнялись при различных средних размерах кластеров ($N = 10^1 \div 10^3$ молекул/кластер), при рабочей энергии ионов E_i = 20-25 кэВ. Зарегистрированы массовые спектры в ускоренном ионно-кластерном пучке при разных давлениях в газовом источнике P_0 = 0.5 – 6 бар. Изучены поперечные сечения ионного тока ионно-кластерного пучка за магнитным сепаратором и без сепаратора.

Работа выполнена при финансовой поддержке Министерства образования и науки Российской федерации (грант № 2292).

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GROWTH OF PLATINUM FIBER USING THE MICRO-PULLING-DOWN METHOD AND THE LOCAL STRUCTURE

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Industrial noble metals as represented by the Platinum (Pt) and Iridium (Ir) have been applied in various fields due to the high oxidation resistance and the high melting point. There are used in various configuration such as a fiber shape. However, it is difficult to make the fibers directly, and forming process to the fiber increases the manufacturing cost. We have developed various functional single crystals by the micro-pulling-down (μ-PD) method [1], which can grow single crystal from the melt using a crucible with a hole at the bottom and the μ-PD method can grow the shape-controlled single crystal with designed crucible [2]. In this study, we developed the growth technique the shape-controlled Pt fiber by the μ-PD method and investigated the local structure and the crystal orientation.

Pure Pt ingots (4N) were prepared as stating material. Pt fibers were grown from its melt by the μ-PD method with a ZrO_2 ceramic crucible and a commercial Pt wire as a seed under N_2 atmosphere. Because the temperature gradient was optimized previously, the Pf fiber was kept stable crystal growing as shown in Fig.1(a) during the crystal growth at 10 mm/min growth rate. The diameter of the grown Pt fiber was controlled by the capillary of the hole at the bottom of the crucible. The Pt fiber of 0.95 mm ± 0.03 mm in diameter and more than 5 m in length could be obtained as shown Fig.1(b). In addition, the Pt fiber could also be grown at 1 ~ 110 mm/min growth rates. Few grain boundaries could be observed in the Pf fibers at the growth rate 10, 50 and 110 mm/min with cross-section polishing. Pole figures and X-ray rocking curve (XRC) of Pt fiber on the surface perpendicular to the growth direction were measured at the growth rate 10 mm/min. In the pole figure measurements, some spots were showed with high intensity for the reflect from the (100) and (200) plane and the result indicated the Pt fiber was composed of a single-crystal-like structure. In the XRC measurement for the reflection from the (111) plane (Fig.2), a single peak was observed and the Full Width at Half Maximum (FWHM) was approximately 4,000 arcsec. The XRC result suggests that the grown Pt fiber had the high orientation of the grains.

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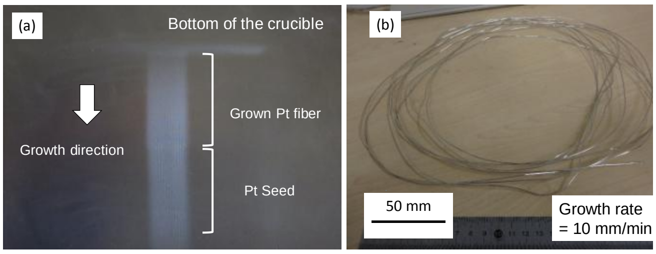

Fig.1 (a) As-grown Pt fiber around the bottom of the crucible during the crystal growth. (b) Pt fiber grown at 10 mm/min growth rate.

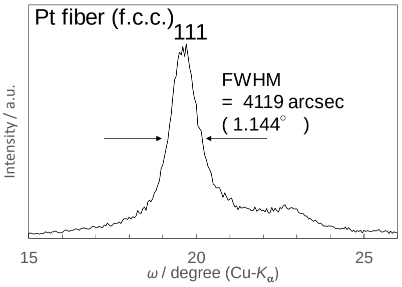

Fig.2 XRC on the surface perpendicular to the growth direction of the Pt fiber grown at 10 mm/min.

ULTRA-SMOOTH SURFACE POLISHING BY ARGON CLUSTER ION BEAM

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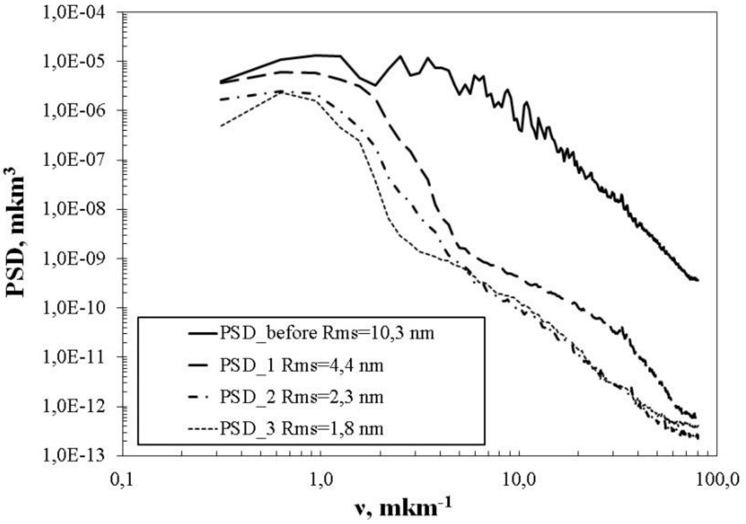
At present, the development of techniques is increasingly moving to nanosize level that significantly increases the demands on the topography of the surface of the functional materials, including its roughness. It is expected that modern technology should provide "atomically-smooth" surface without physical-chemical pollution or destruction of the structure of the processed material. The processing of cluster ion beams formed from supersonic gas jets is a promising method of materials polishing. The use of non-reactive element (e.g. argon) eliminates a contamination of the treated surface. The collective interaction of a large number of cluster particles with approximately the same number of the near-surface target particles leads to the lateral sputtering effect. Because of this effect an ultra-smooth surface with a subnanometer surface roughness can be obtained practically for any material [1, 2].

In this work, the study of effect of the cluster ion beam on the surface topography of different materials (polished stainless steel and optical glass) is performed. Surface roughness parameters before and after irradiation are measured by atomic force microscopy. The dependencies of the basic roughness parameters (mean-square deviation of height Rms, power spectral density function (PSD)) on the radiation dose have been studied. The figure shows the PSD functions and Rms values for mirror-stainless steel before and after processing. It can be seen that at the maximum dose of $3*10^{17}$ cluster ion/cm^2 the lateral roughness decreased by more than three orders of magnitude in the range of the high and medium frequencies. At the same time the low-frequency roughness with a characteristic size more than 1 micrometer reduced at 10 times only. Further decreasing of the roughness is limited micro granular anisotropic structure of the processed material.



This work was supported by grant of the Ministry of Education and Science of the Russian Federation (No 2292).

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СВЕРХГЛАДКАЯ ПОЛИРОВКА ПОВЕРХНОСТИ ИОННО-КЛАСТЕРНЫМ ПУЧКОМ АРГОНА

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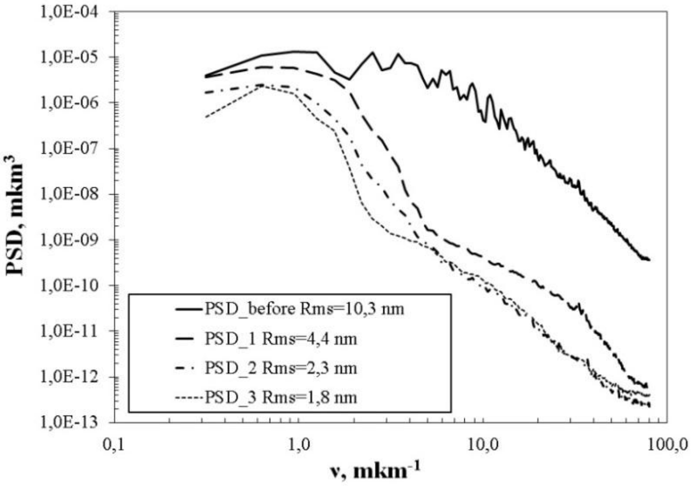
В настоящее время развитие техники все больше переходит на наноразмерный уровень, что заметно повышает требования к топографии поверхности функциональных материалов, в т.ч. ее шероховатости. Ожидается, что современные технологии должны обеспечивать «атомарно гладкую» поверхность без физико-химического загрязнения или нарушения структуры обрабатываемого материала. Перспективным способом полировки материалов является обработка ионно-кластерными пучками, сформированными из сверхзвуковых газовых струй. Использование нереактивного вещества (например, ионов аргона) позволяет полностью исключить загрязнение обрабатываемой поверхности. Благодаря коллективному взаимодействию большого количества частиц кластера с примерно таким же количеством приповерхностных частиц мишени, происходит боковое распыление материала, что позволяет получать сверхгладкие поверхности с субнанометровой шероховатостью поверхности практически любых материалов [1, 2].

В данной работе проведено исследование влияние ионно-кластерного пучка на топографию поверхности различных материалов: полированной нержавеющей стали и оптического стекла. Параметры шероховатости поверхности до и после облучения измерялись методом атомно-силовой микроскопии. Исследованы зависимости основных параметров шероховатости (среднеквадратичное отклонение высоты R_{ms}, функция спектральной плотности мощности (PSD)) от дозы облучения. На рисунке приведены PSD функции и значения R_{ms} для зеркальной нержавеющей стали до и после обработки. Видно, что при максимальной дозе $3*10^{17}$ класт. ион/см^2 латеральная шероховатость в области высоких и средних частот падает более чем на 3 порядка. В тоже время низкочастотная шероховатость с характерным размером более 1 мкм уменьшается только в 10 раз. Дальнейшее понижение шероховатости ограничивается микрогранулированной анизотропной структурой обрабатываемого материала.



Работа выполнена при финансовой поддержке Министерства образования и науки Российской федерации (грант № 2292).

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THE POSSIBILITY OF THE LAUNCH OF PLASMOCHEMICAL REACTIONS AND GENERATE CLUSTERS WITH ELECTRONIC ACTIVATION OF THE GAS FLOW

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The literature describes a number of ways to launch the plasmochemical reactions in the gas flow by using different kinds of discharge, electron and ion beams. We (or here) considered the option of using an electron beam as the method of activation of plasmochemical reactions in the generation of clusters in supersonic flow, expanding into a vacuum.

This paper presents an attempt to use clusters as nanoreactors, which will perform the process of direct synthesis of a useful product. Light hydrocarbons and their mixture with the noble gases were used as a model system. The interest in the conversion of light hydrocarbons into heavy and liquid hydrocarbons arises due to the technological needs of the oil production. Unfortunately, there is no plasma-chemical method of synthesis of heavy hydrocarbons suitable for industrial use, which could be exploited directly at the gas production. One of the attempts of conversion light hydrocarbons by electron-beam activation of the flow in a condensation made in [1]. In this paper we used a hydrocarbon mixture similar in composition to the associated petroleum gas. As a result we observed an increase in relative proportion of C_2H_n and C_3H_n. The initiation of the chemical reactions in the flow can be the possible cause of such increase. We have attempted to combine electron-beam activation of supersonic hydrocarbon stream with the formation of clusters in order to initiate the electron-stimulated condensation and electronic cross-linking molecules in the cluster. For this purpose, the ethylene was selected, which, as shown by preliminary experiments, is condensed in a supersonic flow.

During the experiments we have investigated the possibility of ethylene conversion in the supersonic jet activated by electrons. In the recorded longitudinal and transverse profiles of the jets, as well as mass spectra of ethylene oligomers the growth of $(C_2H_4)_2$ (1), $(C_2H_4)_3$ (2), $(C_2H_4)_4$ (3) and $(C_2H_4)_5$ (4) components after electron impact on the supersonic jet were detected (fig. 1). The possible reason of the synthesis of heavy hydrocarbons is the result of the conversion of van der Waals bonds in the chemical bonds in cluster complexes. It is also possible that the electron beam initiation of the condensation process contributes to the observed effect of increasing the proportion of the oligomer components in the mass spectrum. The study and the realization of this effect is expected in the future.

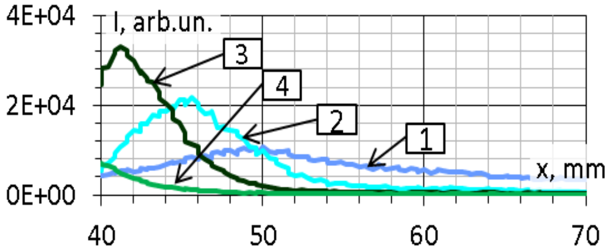

Figure 1 – Longitudinal profile of the $(C_2H_4)_2$ (1), $(C_2H_4)_3$ (2), $(C_2H_4)_4$ (3) and $(C_2H_4)_5$ (4) components of the ethylene after ionization by the electron beam. The

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О ВОЗМОЖНОСТИ ЗАПУСКА ПЛАЗМОХИМИЧЕСКИХ РЕАКЦИЙ И ГЕНЕРАЦИИ КЛАСТЕРОВ ПРИ ЭЛЕКТРОННОЙ АКТИВАЦИИ ГАЗОВЫХ ПОТОКОВ

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В литературе описано множество способов запуска плазмохимических реакций в газовых потоках при использовании различных видов разряда, электронного и ионного пучков. Здесь рассмотрен вариант использования электронного пучка в качестве метода активации плазмохимических реакций при генерации кластеров в сверхзвуковом потоке, расширяющемся в вакуум.

В данной работе представлена попытка использования кластеров в качестве нанореакторов, в которых будет осуществляться процесс направленного синтеза полезного продукта. Задача рассматривается на примере легких углеводородов и их смесей с благородными газами. Интерес к конверсии легких углеводородов в тяжелые и, прежде всего, жидкие углеводороды обусловлен технологическими потребностями нефтедобычи. К сожалению, до сих пор не удается разработать пригодный для технологического использования плазмохимический метод синтеза тяжелых углеводородов, который обеспечил бы необходимые превращения непосредственно в местах газодобычи, особенно проблемные в условиях Российского Севера. Одна из попыток конверсии легких углеводородов электронно-пучковой активацией потока в условиях конденсации предпринята в работе [1]. В данной работе использовалась углеводородная смесь, схожая по составу с попутным нефтяным газом. В результате наблюдалось увеличение относительной доли комплексов C_2H_n и C_3H_n, возможной причиной чего является инициация в потоке химических реакций синтеза в кластерах. Нами предпринята попытка совмещения электронно-пучковой активации сверхзвукового потока углеводорода с формированием кластеров с целью инициации электрон-стимулированной конденсации, а также электронной сшивки молекул в кластере. Для этой цели был выбран этилен, который, как показали предварительные опыты, конденсируется в сверхзвуковом потоке.

В ходе проведенных экспериментов была исследована возможность конверсии в активированной электронами сверхзвуковой струе этилена. В зарегистрированных продольных и поперечных профилях струй, а также масс-спектрах олигомеров этилена обнаружен рост димерной, тримерной, тетрамерной и пентамерной компоненты после воздействия электронов на сверхзвуковую струю (рис. 1). Высказано предположение, что возможной причиной является синтез тяжелых углеводородов вследствие преобразования Ван-дер-Ваальсовых в химические связи в кластерных комплексах. Возможно также, что вклад в наблюдаемый эффект увеличения доли олигомерной компоненты в масс-спектре связан с инициацией электронным пучком процесса конденсации. Изучение и детализация данного эффекта предполагается в дальнейшем.

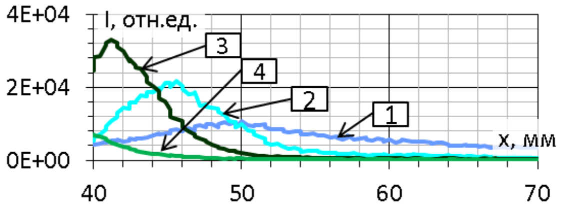

Рисунок 1 – Продольный профиль димеров (1), тримеров (2), тетрамеров (3) и пентамеров (4) этилена после ионизации электронным пучком. Давление торможения P_0 = 0.4 МПа.

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FABRICATION OF INVERTED GALLIUM NITRIDE-HEMT STRUCTURE WITH FLAT INTERFACE GROWN BY METALORGANIC VAPOR PHASE EPITAXY

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Nitride-based semiconductors have been considered to be promising a candidate material for the application of high-power and high-frequency electronic devices. Recently, the N-polar GaN/$Al_xGa_{1-x}N$/GaN heterostructure has been attracted much attention because of its built-in back-barrier for the strong electron confinement [1-2]. It also has an advantage that the ohmic contacts of both a source and a drain to GaN instead of $Al_xGa_{1-x}N$ are low resistive [3]. In this paper, the growth of an N-polar GaN/$Al_xGa_{1-x}N$/GaN heterostructure with flat interface by MOVPE on the sapphire substrate with a small off-cut angle has been performed.

The N-polar GaN/$Al_xGa_{1-x}N$/GaN with a smooth surface was successfully grown by MOVPE on sapphire substrates with an off-cut angle of 0.8º. From x-ray diffraction analyses, the GaN/$Al_xGa_{1-x}N$ heterostructure with x_{AlN}=0.4 was coherently grown on an N-polar GaN layer. The smooth surface of an N-polar GaN/$Al_xGa_{1-x}N$/GaN heterostructure with less step bunching has been observed by AFM measurements. The surface roughness was about 0.9 nm of root-mean-square in the area of 5 x 5 μm^2. The electrical properties of both 2DEG formed at the GaN/$Al_xGa_{1-x}N$ interface and an individual N-polar GaN epitaxial layer were evaluated by Hall-effect measurements in the temperature range of 17 to 300 K. Their temperature dependence of Hall mobility are shown in Fig. 1. Their mobility is influenced at high temperature by the polar optical phonon scattering because GaN is a highly polar material, and polar interactions due to the polar optical phonon dominate the scattering process at high temperature [4]. The mobility of a GaN epitaxial layer decreases with temperature as expected because ionized impurities dominate at low temperatures [5]. For 2DEG in an N-polar GaN/$Al_xGa_{1-x}N$/GaN heterostructure, the electron mobility reached to 1250 cm^2/Vs at room temperature. It also monotonically increased with decreasing temperature and saturated at the maximum value of 3050 cm^2/Vs at 17 K. The realization of the smooth interface between GaN and AlGaN on small off-cut substrates, and the confirmation of a 2DEG in this paper show that N-polar GaN HEMTs are very promising.

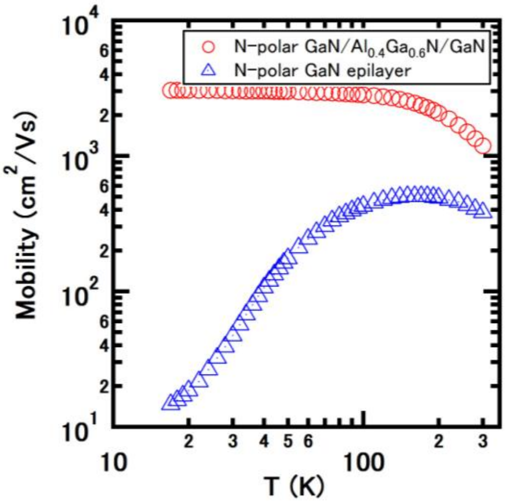

Fig. 1. Mobility as a function of temperature for a 2-μm-thick N-polar GaN epitaxial layer and an N-polar GaN/$Al_{0.4}Ga_{0.6}N$/GaN HEMT.

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THE APPLICATION OF CATALYSTS BASED ON $Cd_{0.3}Zn_{0.7}S$ DOPED BY COPPER AND NICKEL SPECIES FOR PHOTOCATALYTIC HYDROGEN PRODUCTION FROM Na_2S+Na_2SO_3 AQUEOUS SOLUTIONS

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Semiconductor materials such as CdS and ZnS have a wide range of different applications, e.g. as pigments, luminophors, photoresistors, and scintillators. The solid solutions $Cd_{1-x}Zn_xS$ (especially, $Cd_{0.3}Zn_{0.7}S$) may also be used as effective photocatalysts for hydrogen evolution under visible light irradiation [1]. Deposition of transition metal species allows enhancing the photocatalytic activity and the stability of sulfide photocatalysts [2, 3].

In the present work the $Cd_{0.3}Zn_{0.7}S$ support was modified by $Cu(OH)_2$ (CuO-x), $Ni(OH)_2$ (NiOH-x), Cu (Cu-x), and Ni (Ni-x). FT-IR results demonstrated the presence of metal hydroxides in the CuO-x and the NiOH-x samples. HAADF-STEM and TEM images revealed that metal sulphides were formed during the preparation of the CuO-x and NiOH-x catalysts. The metallic state of copper and nickel was confirmed by the XPS technique for the Cu-x and the Ni-x photocatalysts, respectively.

The photocatalytic properties of all prepared samples were studied in the reaction of hydrogen production from Na_2S + Na_2SO_3 aqueous solutions under irradiation by visible light. As for the CuO-x, the NiOH-x, and the Ni-x photocatalysts, the reaction rate increased with the growing of the x value, reached the peak and declined. Hydrogen production on the Cu-x samples was independent of the copper content; moreover, these photocatalysts were less active than the support. After that, we studied the evolution of the most active photocatalysts during several irradiation cycles. For the CuO-0.1 sample, the XPS spectra showed the increase in the copper content during hydrogen production due to the transformation of copper hydroxide to copper sulfide. The Cu-0.3 photocatalyst was also studied by the XPS method. The changing of the Auger parameter α for fresh CuO-0.3 and CuO-0.3 after 8 irradiation cycles was associated with the oxidation of metallic copper to copper sulfide. Besides, the rate of hydrogen production equaled for the CuO-0.1 and the Cu-0.3 samples during the last three cycles, which was in good accordance with Borescov's rule [4].Concerning nickel-modified photocatalysts, the high activity of NiOH-0.06 was connected with the transformations between divalent nickel species and trivalent ones which was obtained by the XRD and TEM methods. Photoinduced holes were involved in these transformations that allow enhancing charge separationand catalytic activity. The XPS spectra of the Ni-0.1 sample before and after irradiation indicated that metallic nickel migrated from the catalyst surface according to the reaction: $Ni^0 + 4OH^- + 2h^+ = [Ni(OH)_4]^{2-}$.

Summarizing this work, it should be noted that $Cd_{0.3}Zn_{0.7}S$ doping by different transition metal species increases both the photocatalytic activity and the photostability. Totally, 50 ml, 63 ml, 58 ml, 44 ml of hydrogen was evolved on NiOH-0.06, CuO-0.1, Ni-0.1, Cu-0.3 photocatalysts after irradiation during 12 h.

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ПРИМЕНЕНИЕ КАТАЛИЗАТОРОВ НА ОСНОВЕ $Cd_{0.3}Zn_{0.7}S$, ДОПИРОВАННЫХ СОЕДИНЕНИЯМИ МЕДИ И НИКЕЛЯ, ДЛЯ ФОТОКАТАЛИТИЧЕСКОГО ВЫДЕЛЕНИЯ ВОДОРОДА ИЗ ВОДНЫХ РАСТВОРОВ $Na_2S+Na_2SO_3$

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Полупроводниковые сульфидные материалы (CdS и ZnS) имеют широкий спектр практического применения: от пигментов и люминофоров до фоторезисторов. Особого внимания заслуживают фотокаталитические свойства твёрдых растворов сульфидов кадмия и цинка $Cd_{1-x}Zn_xS$ (особенно, $Cd_{0.3}Zn_{0.7}S$), с помощью этих катализаторов можно проводить процессы фотокаталитического выделения водорода [1]. Нанесение соединений переходных металлов позволяет увеличить эффективность целевого процесса [2, 3]. В данной работе на сульфидную матрицу $Cd_{0.3}Zn_{0.7}S$ наносили следующие соединения: $Cu(OH)_2$ (CuO-x), $Ni(OH)_2$ (NiOH-x), Cu (Cu-x) и Ni (Ni-x). Фазовый состав полученных катализаторов был подтверждён комплексом физико-химических методов (РФА, РФЭС, ПЭМ).

Фотокаталитическую активность синтезированных образцов изучали в реакции выделения водорода из водных растворов Na_2S + Na_2SO_3 под действием видимого излучения. Для всех серий фотокатализаторов, кроме Cu-x, зависимость скорости выделения водорода от содержания нанесённого компонента проходит через максимум. Фотокатализаторы, модифицированные металлической медью, являются менее активными в изучаемом процессе, причём содержание меди на поверхности фотокатализатора не оказывает влияния на скорость фотокаталитического процесса. Для наиболее активных образцов из каждой серии с помощью физико-химических методов изучали изменение фазового состава в процессе фотокаталитического выделения водорода. Так, методом РФЭС было показано увеличение содержания Cu_xS на поверхности катализатора CuO-0.1, что связано с сульфидированием $Cu(OH)_2$ и фотоиндуцированными процессами диспергирования исходных частиц Cu_xS. В случае образца Cu-0.3 происходит постепенный переход металлической меди в окисленное состояние Cu_xS, в пользу чего свидетельствует одинаковое значение Оже-параметра для фотокатализаторов CuO-0.1 и Cu-0.3 после 8 последовательных циклов освещения. Каталитическая активность образца NiOH-0.06 связана с фотоиндуцированными превращениями соединений двухвалентного никеля. Катализатор Ni-0.1 также подвержен фотоиндуцированным превращениям, в результате которых никель мигрирует с поверхности катализатора в форме растворимого комплексного соединения: $Ni^0 + 4OH^- + 2h^+ = [Ni(OH)_4]^{2-}$. Несмотря на этот факт, нанесение соединений переходных металлов на поверхность $Cd_{0.3}Zn_{0.7}S$ благотворно сказывается на эффективности фотокаталитического выделения водорода.

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CARBON BASED RU COLLOIDAL CATALYSTS: SYNTHESIS APPROACHES AND CATALYTIC BEHAVIOR

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Nowadays nanosized metal nanoparticles (NPs) attract a lot of attention due to their unique chemical and physical properties. Among different applications of metal NPs a special attention is focused on catalysis. In particular, a colloidal method based on immobilization of colloidal metal NPs over different types of supports is an effective approach for the synthesis of supported metal catalysts with well-defined particles. The purpose of the current work is to explore regularities of Ru NPs formation via polyol reduction and to optimizecatalystsynthesis by the colloidal method focusing on the effect on the nanoparticle size, resistance to leaching and oxidation state of the active component, matching subsequent catalytic application in aqueous phase transformationof bioderived sugar and sugar alcohols.

In order to develop an approach to the synthesis of Ru NPs with a controllable particle size the regularities of PVP-stabilized Ru NPs formation from $RuCl_3$ through the polyol method were studied. The effect of the PVP/Ru, Ru concentration, reduction temperature and the reducing mode on the mean diameter and size distribution of Ru-NPs was investigated[1]. The particle size prepared by the polyol technique does not depend strongly on the Ru/PVP ratio and reduction temperature varied in the range 1/1-1/50 and 170-198°C, respectively, while an increase in the metal concentration in the solution favored NPs growth. Faster reduction by $NaBH_4$ at an ambient temperature was found to result in formation of smaller NPs of ca 1.8 nm compared to that reduced by EG (2.5 nm). According to UV-Vis and XPS data Ru NPs were found to be in the metallic state independent on the PVP/Ru ratio, the reducing agent and the heating mode. Highly concentrated Ru colloids with a controllable NPs size were immobilized over different carbon supports.To remove PVP from the catalysts surface both solvothermaland thermal treatment under different conditions were applied. There was a pronounced effect of preliminarily support modification, additional colloidal Ru NPs washing with acetone prior to its support immobilization and PVP removal procedures on catalytic properties and behavior in galactose hydrogenation. TEM, XPS, XRF, water adsorption and desorption experiments and N_2physisorption were applied to characterize the carbon supports and synthesized catalysts.

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FABRICATION AND CHARACTERIZATION OF SILICON NANOPILLARS

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Silicon nanopillars (Si NPs) are promising as future building blocks in solar cells, nanosensors and optical interconnects [1-3]. Si NPs can improve the efficiency lower costs of photovoltaic solar cells. Si NPs represent a qualitatively new control by light.

In this paper, the formation of SiNPs arrays by means electron-beam lithography and dry etching was described. As substrate, we used single-crystal n-type Si (100) wafer. Electron lithography was performed using Pioneer setup.Si NPs with diameters ranging from 50 nm to 350 nm with heights from 80 nm to 800 nm were fabricated. Figure 1 shows SEM images of Si NPs.

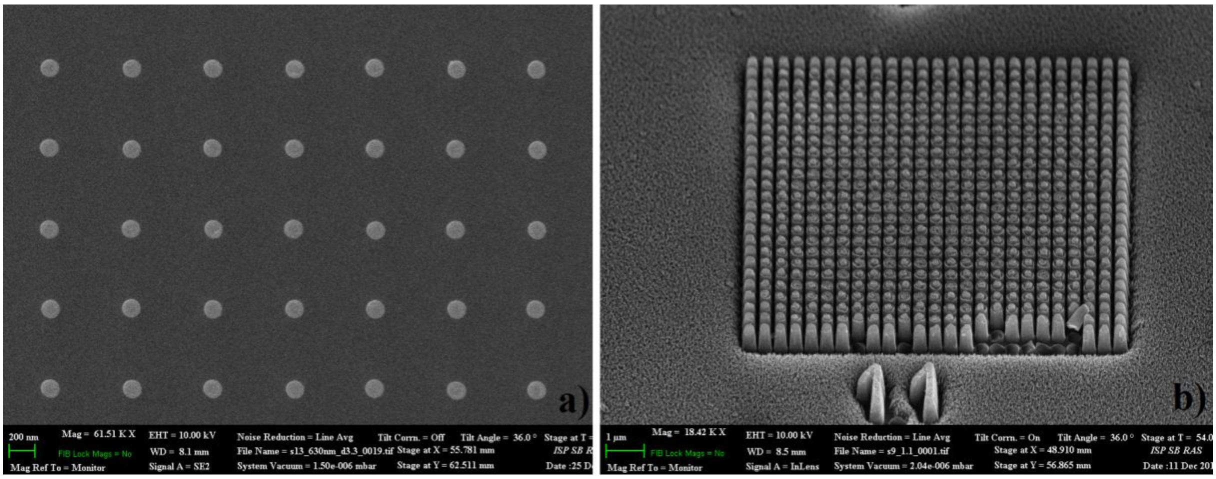

Fig. 1. a) SEM image of Si NP array, pitch 630 nm (view from above), the scale bar is 200 nm, b) SEM image of Si NP array, pitch 400 nm (tilt angle = 54◦, the scale bar is 1µm).

The pillar diameter was changed by varying the radiation dose. For deep etching of silicon (to a depth of 600 nm and larger), we used anisotropic plasma etching using a mixture of SF_6/C_4F_8 in a two-stage cyclic mode (the Bosch process). Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM) were used to characterize the Si NPs. It was found that passivation of the surface using titanium oxinitride improves the electrical properties of the nanopillars. We also performed passivation by the method of boiling in concentrated nitric acid, as a result of which silicon oxide was formed. Oxidation in nitric acid was required for samples formed by the Bosch method in order to remove the polymer which remained on the walls of the Si NPs; in this case, insignificant heating of the NP walls was observed and roughness of the edge increased. The technology of the formation of silicon cone and tapered Si NP was also developed.

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NON-RADIATIVE ENERGY TRANSFER IN QUANTUM DOT ENSEMBLE MEDIATED BY LOCALIZED SURFACE PLASMONS

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Semiconductor quantum dots (QDs) are one of the major candidates for practical implementation of single photon source in solid-state optical devices of new generation. A promising approach to control QDs optical properties is using plasmonic particles to enhance luminescence of QDs by Purcell effect and to direct their emission. In our work [1] plasmon-exciton interaction was experimentally investigated in hybrid systems with InAs/AlGaAs QDs, located under indium nanoclusters and a mechanism of this interaction via plasmon-mediated energy transfer between QDs was proposed.

To study the interaction dependence on the distance hybrid structures with 5 layers off QDs were fabricated. The interdistance between layers was set to be 10 nm, After the formation of the last QD layer a buffer layer of 10 nm of Al0.3Ga0.7As was grown. Then As valve was closed and In amount of nominally 1.7 InAs monolayers was deposited to the surface. In the absence of As indium formed metal nanoclusters. In the photoluminescence (PL) spectra of this structure besides a wide QD peak centered at 1080 nm there was a weak feature at 1200 nm, that according to [1] is due to energy transfer between QDs .

It is well known that plasmon-exciton interaction strongly depends on the distance. To study this effect we denote the partial PL signal from a single QD layer under metal clusters as I', and PL signal of other QDs as I. According to AFM analysis, metal clusters occupy just 5% of the sample area. The PL signal from QDs taking part in the plasmon-exciton interaction decreases with the layer number, but all five layers of uninteracting QDs have equal contribution to the main QD peak. Then the ratio of these signals a can be described as

$$a = 0.05*(I'_1 + I'_2 + I'_3 + I'_4 + I'_5)/(0.95*\_5*\_I)$$

The contribution of I'_i decreases with increasing i, so the effective plasmon-exciton interaction in the structure drops. If all parts of the sum but I'_1 are neglected, the ratio in five-layered structure drops by a factor of 5 when compared to a single-layer one. When the PL spectrum of the layered structure is decomposed to Gaussians, the area of the long-wavelength peak is around 6% of the main QD peak, while for the single-layer structure it is 30%. Therefore, our PL analysis revealed that in the hybrid structures there is a strong dependence of plasmon-exciton interaction on the distance between QDs and metal clusters. It was demonstrated that only QDs from the layer that is closest to clusters can interact with the plasmon mode. The results obtained may be used for design of more complex hybrid multilayered structures.

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БЕЗЫЗЛУЧАТЕЛЬНЫЙ ПЕРЕНОС ЭНЕРГИИ В АНСАМБЛЕ КВАНТОВЫХ ТОЧЕК ЗА СЧЁТ ЛОКАЛИЗОВАННЫХ ПОВЕРХНОСТНЫХ ПЛАЗМОНОВ

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Полупроводниковые квантовые точки (КТ) являются основными кандидатами для реализации однофотонного квантового излучателя в твёрдотельных оптических приборах нового поколения. Перспективным подходом для управления их оптическими свойствами является использование плазмонных частиц, способных усиливать люминесценцию КТ за счёт эффекта Парселла и направлять их излучение. В нашей работе [1] было экспериментально изучено экситон-плазмонное взаимодействие в системе с InAs/AlGaAs КТ, расположенными под нанокластерами индия, и предложен механизм взаимодействия посредством переноса энергии в подансамбле КТ под кластером.

Для изучения взаимодействия от расстояния были изготовлены гибридные структуры со столбцами КТ InAs/Al0.3Ga0.7As из пяти слоёв КТ, расстояние между которыми было выбрано равным 10 нм. После роста последнего слоя КТ и буферного слоя Al0.3Ga0.7As на поверхность в отсутствии потока мышьяка было нанесено количество индия, номинально соответствующее 1.7 монослоя InAs, и сформированы металлические кластеры. В спектре фотолюминесценции (ФЛ) структуры с пятью слоями КТ и кластерами индия на поверхности кроме широкого пика КТ на 1080 нм присутствует слабая особенность на 1200 нм, согласно [1] связанная с переносом энергии между КТ. Известно, что экситон-плазмонное взаимодействие сильно зависит от расстояния. Для выяснения этого эффекта обозначим удельный сигнал одного слоя КТ, которые находятся под кластерами, как I', а сигнал от слоя остальных КТ как I. Согласно АСМ измерениям металлические кластеры занимают 5% площади образца. При этом сигнал от КТ, участвующих в экситон-плазмонном взаимодействии, уменьшается с номером слоя, а все пять слоёв невзаимодействующих КТ дают одинаковый вклад в основной пик КТ. Тогда отношение этих сигналов a можно записать как

$$a = 0.05*(I'_1 + I'_2 + I'_3 + I'_4 + I'_5)/(0.95*\_5*\_I),$$

Вклад I'_i уменьшается с ростом i, что приводит к падению общей эффективности экситон-плазмонного взаимодействия в структуре. В пренебрежении всеми членами суммы, кроме I'_1, величина в пятислойной структуре уменьшается в 5 раз по сравнению со случаем одиночного слоя. При разложении спектра ФЛ многослойной структуры на гауссианы площадь длинноволнового пика составляет около 6% от площади основного пика, а для одиночного слоя эта величина составила 30%. Таким образом, анализ данных ФЛ позволяет утверждать, что в такой системе имеется сильная зависимость взаимодействия от расстояния, и только экситоны из квантовой точки, расположенной в ближнем к кластеру слое, могут взаимодействовать с плазмоном. Полученные данные могут быть использованы для дизайна многослойных гибридных структур.

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2016 Russia-Japan Conference

"Advanced Materials: Synthesis, Processing and Properties of Nanostructures"

Abstracts

November 3

Session 4

Room 4310 (New Building of NSU)

Chairs: B. Bokhonov, V. Ulianitsky

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- ***K. Shefer*** *Investigation of nanocatalysts using the PDF method*
- ***V. Prinz*** *Metamaterials, topological photonic crystals and original hybrid micro-nanomaterials*
- ***D. Dudina, B. Bokhonov, A. Ukhina, A. Brester, M. Esikov, A. Anisimov, V. Mali*** *Microstructural non-uniformities in Spark Plasma Sintered compacts observed at different length scales*

Oral reports

E. Baranov, A. Zamchiy, S. Khmel Plasma-enabled low temperature growth of high-density, aligned arrays of silicon oxide nanowires bunches via VLS mechanism

K. Sashkina, **A. Polukhin, V. Labko, A. Ayupov, A. Lysikov, E. Parkhomchuk** Design of hierarchical zeolite catalysts

M. Serebryakova, S. Novopashin Thermophysical properties of nanofluids based on hollow Al_2O_3 nanoparticles and water

A. Zaikovskii, S. Novopashin Effect of the arc-discharge parameters on the morphology and the electrical conductivity of the synthesized carbon materials

A. Kurenkova, E. Kozlova, P. Kolinko The effect of hydrothermal treatment on activities of $Cd_{0.3}Zn_{0.7}S$ and Au/ $Cd_{0.3}Zn_{0.7}S$ under visible light

N. Filippov, S. Romanov Silicon microchannel membrane and microfluidic devices on its basis

S. Sakhapov, S. Novopashin Synthesis and nanoparticles dynamic in spherical glow discharge

L. Lapteva, Yu. Fedoseeva, A. Okotrub, and L. Bulusheva Investigation of interactions of carbon nanomaterials with lithium by X-ray spectroscopy

N. Kolobov, D. Selishchev, A. Gubanov, D. Kozlov, E. Kozlova UV-LED Photocatalytic Oxidation of Carbon Monoxide over the Pd-loaded Catalysts Synthesized by the Decomposition of $Pd(acac)_2$

A. Shevyrin, A. Pogosov Electromechanical coupling in nanoelectromechanical systems with a two-dimensional electron gas

N. Mironnikov, V. Korolkov, D. Derevyanko, V. Shelkovnikov Hybrid photopolymer material "Hybrimer-TATC": peculiarities of laser processing and properties of thin films

V. Sadykov, Yu. Fedorova, A. Lukashevich, Z. Vostrikov, N. Eremeev, A. Krasnov, A. Skryabin Novel nanocomposte materials for oxygen separation membranes

I. Kostogrud, D.Smovzh Transferring of CVD-graphene from the copper substrate to the polymer substrate

INVESTIGATION OF NANOCATALYSTS USING THE PDF METHOD

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The structure diagnistic of nanomaterials, including nanocatalysts, is a necessary step of their investigation, because their structure specificities determine the properties of these materials. An important moment is the identification of the phase composition and structure features of phases, which constitute studied nanomaterials. The application of usual X-ray diffraction methods, based on the analysis of the position and intensities of diffraction peaks, and giving of information of the averaged atomic and real structure, for this investigation, in the case of nanosystems can be difficult. In this case the use of special methods that take into account the specific features of X-ray scattering from small objects is required.

A diffraction pattern of the polycrystals with coherent scattering region sizes below 1-3 nm is similar to some extent to a diffraction pattern of an amorphous material, because it is characterized by a strong broadening of the diffraction peaks. Therefore, it is reasonable to employ a method used for the analysis of X-ray amorphous materials to the analysis of the structure of nanoobjects. The structure of such materials is studied by an X-ray diffraction method of the radial distribution of atoms or the radial electronic density distribution, also known as the analysis of atomic pair distribution function (PDF-analysis). The PDF method is based on the integral analysis of the X-ray scattering intensity curve and reveals the short range order of atoms regardless of the degree of studied material dispersity and disorder. The method provides information on the interatomic distances and coordination numbers of atoms in the structure. The method can be used to detect and evaluate the size of phases less than 3 nm, which are not detected by the usual powder X-ray diffraction analysis of interplanary distances, as well as to detect defects in the atomic structure of nanoobjects too.

An investigation of the alumina and aluminum hydroxide structure is given as the method application in this work. These substances are of great importance for catalysis and they are used mainly in nanoscale view. The improvement of methods of dispersed materials structure investigation and the appearance of novel methods of their synthesis give a new impetus to the study of their structure and properties. The local structure of aluminium hydroxides and alumina, obtained by different methods and having various characteristics, was considered using the PDF method.

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ИССЛЕДОВАНИЕ НАНОКАТАЛИЗАТОРОВ МЕТОДОМ PDF

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Структурная диагностика наноматериалов, в том числе нанокатализаторов, является необходимым шагом при их исследовании, поскольку особенности структуры определяют свойства этих материалов. Важным моментом является установление фазового состава и структурных особенностей фаз, составляющих исследуемые наноматериалы. Применение для этого обычных рентгенографических методов, основанных на определении положения и ширины дифракционных пиков, и дающих информацию об усредненной атомной и реальной структуре материалов, в случае наносистем может быть затруднено. Поэтому в этом случае требуется использование специальных методик, учитывающих особенности рассеяния рентгеновских лучей на объектах малого размера.

Дифракционная картина от поликристаллов с размерами области когерентного рассеяния менее 1-3 нм похожа на дифракционную картину от аморфного материала, поскольку она характеризуется сильным уширением дифракционных пиков. В связи с этим к изучению структуры нанообъектов целесообразно приложить метод, который используется для изучения рентгеноаморфных материалов. Таким методом является метод радиального распределения электронной плотности, который также известен как PDF-метод (Atomic Pair Distribution Function). Метод PDF основан на интегральном анализе кривой интенсивности рассеяния рентгеновских лучей в широком интервале углов и позволяет получить информацию о ближнем порядке независимо от степени дисперсности и разупорядоченности исследуемого материала. Метод дает информацию о межатомных расстояниях и координационных числах атомов в структуре. Он может быть использован для обнаружения и оценки размеров нанообразований менее 3 нм, которые не выявляются при обычном фазовом анализе по межплоскостным расстояниям, а также для установления дефектов атомной структуры в нанообъектах.

В качестве приложения метода в данной работе приведено исследование структуры алюмооксидных систем, поскольку эти вещества имеют огромное значение для катализа, и используются преимущественно в наноразмерном виде. Совершенствование методов изучения структуры дисперсных веществ и появление новых методов синтеза дают новый толчок к изучению их структуры и свойств. С помощью метода PDF рассмотрена локальная структура гидроксидов и оксидов алюминия, полученных разными способами и имеющих различные характеристики.

METAMATERIALS, TOPOLOGICAL PHOTONIC CRYSTAL AND ORIGINAL HYBRID MICRO-NANOMATERIALS

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Passage from micrometer to nanometer sizes has allowed formation of new materials and devices with substantially improved properties. Nanotechnology is subject to the same general requirements which are imposed on microtechnology. These are the possibility of mass fabrication of products, and high precision and reproducibility of nanostructures and nanomaterials. Here we discuss 4 nanotechnologies (additive manufacturing, nanoimprint-lithography, our original rolling-up technology, and graphene growth technology) as well as novel materials formed by means of them in Rzhanov Institute of Semiconductor Physics SB RAS.

Additive manufacturing (3D printing) can be described as the fabrication of structures and devices by depositing a material (as a rule, in layer-upon-layer manner) according to a 3D CAD model. Additive manufacturing provides the opportunity for unprecedented breakthroughs in new materials, structures and devices for a wide range of applications. 3D printing ideally suits the purpose of formation of intricately shaped objects. This technique allows deposition of various materials in 3D space with high precision according to a CAD model. It is important that, in many cases, we have obtained a means enabling the fabrication of new materials and devices that cannot be produced by any other technology. Special emphasis is laid on two-photon polymerization processes, where a minimum line width of 9 nm has already been achieved, and on electrohydrodynamic jet printing, which techniques have enabled the formation of device elements sized smaller than 20 nm.

High technology can be made chip on condition of mass parallel production of nanostructures and nanomaterials on large areas. A most appropriate large-area technology is imprint (stamp) nanolithography.. In the world, imprint lithography and continuous die forming technology on flexible polymer films with resolution from several ten micrometers to tens and several nanometers are under development. Imprint lithography was used to demonstrate scalability of fabricated metamaterial elements.

With use of our technology we have created seven new electromagnetic metamaterials with 3D resonators, including chiral isotropic and anisotropic resonators, high-frequency magnetic resonators, tubular resonators with helical conductivity, and resonators with polymer-embedded elements. Materials with such properties were never found in nature. Electromagnetic metamaterials are artificial materials composed of resonant elements whose interaction with electromagnetic radiation provides for extraordinary electromagnetic properties of such materials not found in their natural counterparts. Electromagnetic metamaterials offer much promise in many important applications, ranging from lenses with subwavelength focusing to cloaking.

Original methods and technologies for fabrication of 3D semiconductor, graphene and polymer nanostructures are discussed.

One of the most promising materials is the photopolymers containing vanadium dioxide (VO2) nanoparticles and thin film coatings for laser-induced forward transfer and graphene.

VO2 is a strongly correlated oxide that undergoes a sharp metal-insulator transition in the vicinity of room temperature. Graphene is a new modern material pertaining to the field of nanotechnology. For applications of this material, one has to be capable of growing single-crystal graphene sheets on large substrate areas (more than 1 cm^2) and forming conducting graphene films with high charge-carrier mobility values on insulating substrates. Also, the possibility of functionalization of graphene sheets during their exposure to chemical agents, the possibility of creation of heterostructures involving graphene sheets, and the formation of metamaterials and devices on the basis of such heterostructures are required.

The realization of metamaterials, topological insulators for photons could have a major impact on optical devices, making them more robust and more energy efficient.

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MICROSTRUCTURAL NON-UNIFORMITIES IN SPARK PLASMA SINTERED COMPACTS OBSERVED AT DIFFERENT LENGTH SCALES

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Spark Plasma Sintering (SPS) is normally conducted in graphite dies using graphite punches and graphite foil, which protects the punches and the die wall from the chemical action of the sintered materials and establishes better conditions of electric contact between the punch and the die wall and the punches and the sample. Foils made of other materials can be used when contact with carbon is undesirable. Caused by electric current-related effects and features of the tooling design, microstructural non-uniformities can appear in the Spark Plasma Sintered compacts at the particle size and compact size scales. In this presentation, different aspects of their formation will be considered.

At the particle size scale, the microstructural differences arise from melting of the sintered material or chemical reactions occurring locally – at the inter-particle contacts or involving several powder particles. To illustrate this, pressureless SPS of an iron powder in contact with Cu foil (used instead of graphite foil) will be described. The rim areas of the porous Fe compact showed a microstructure different from that of the rest of the volume. Regions that experienced melting and solidification had a size of several particle diameters [1]. Local melting was caused by a temperature rise due to a high contact resistance of the compact-foil contact spots in the rim areas.

At the sample size scale, the differences in the microstructure can be caused by radial temperature gradients, interaction of the sintered material with the material of the foil and asymmetry of the die-punch assembly. In this work, we focused on (1) situations when the material of the foil participated in the phase formation and (2) SPS conducted without the upper punch. When Ni-diamond mixtures were Spark Plasma Sintered in contact with tantalum foil, tantalum carbide TaC was detected on the flat end of the compact due to chemical interaction of diamond with tantalum [2]. Carbon of graphite foil was shown to diffuse into the sample forming carbide phases with the elements of sintered metallic alloys [3]. It was found that SPS of the Fe-40at.%Al mixtures conducted without the upper punch produces porous compacts with gradients in the phase composition and microstructure [1]. In the upper part of the compact, which was not in contact with the punch, only partial transformation of Fe and Al into FeAl took place, fully consuming Al and leaving unreacted Fe, while complete transformation into FeAl was observed in the layers adjacent to the flat end of the lower punch (SPS at 650°C). Along with FeAl as a major phase, the fully reacted material contained $AlFe_3C$ as a minor phase due to the presence of carbon in the surface layers of the particles of carbonyl iron. The presence of the $AlFe_3C$ phase in the compacts, in which free Al was still present (SPS at 500°C with both punches), indicates that its formation depends on the reaction initiation between the surfaces of Fe and Al particles. As Al was fully transformed in the upper part of the compact, the absence of $AlFe_3C$ cannot be explained by a lower temperature. Rather, it shows that the reaction was ignited in fewer initiation sites in the upper part of the compact due to current redistribution in the assembly without the upper punch.

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PLASMA-ENABLED LOW TEMPERATURE GROWTH OF HIGH-DENSITY, ALIGNED ARRAYS OF SILICON OXIDE NANOWIRES BUNCHES VIA VLS MECHANISM

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Low-dimensional structures have attracted scientific and technological interest in recent years because of their unique physical and chemical properties. Among them, the silicon oxide nanowires having high intense and stable blue light emission at the room temperature [1], a low refractive and absorption indices [2], biocompatibility [3] can be applied as building blocks in optoelectronic devices.

Usually, silicon oxide (SiO_x, $x \leq 2$) nanowires are synthesized by the vapor-liquid-solid (VLS) mechanism on catalyst particles using the thermal evaporation method at temperatures around 1100°C [4]. Plasma enhanced chemical vapor deposition method can significantly lower the synthesis, but in any case the synthesis temperature should be higher than Si-catalyst eutectic point according to the VLS mechanism [5]. Considering this limitation, tin (Sn) and indium (In) are one of the most suitable catalysts for low-temperature growth. The Si-Sn and Si-In system eutectic point is 232°C and 157°C respectively.

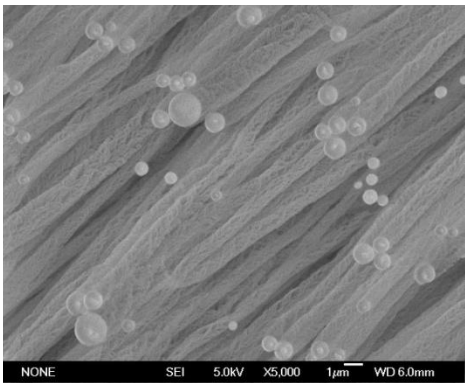

Fig.1. SEM image of array of SiO_x nanowires synthesized at 335°C.

In this study, gas-jet electron beam plasma chemical vapor deposition along with Sn and In catalysts was used to synthesize the SiO_x nanowires in particular, arrays of oriented bunches (“microropes”) of it (Fig.1) at reduced substrate temperatures (260-335°C for Sn and 200-335°C for In, respectively) from monosilane–argon-hydrogen mixture on monocrystalline silicon wafers.

The morphology of the structures was investigated by microscopy using a JEOL JSM-6700F instrument. Fourier transform infrared spectra were measured with a Scimitar FTS 2000 FTIR spectrometer in the range of 4000–400 cm^{-1} with a resolution of 1 cm^{-1} to investigate the bond structure of the synthesized material. The photoluminescence at room temperature of the nanostructures was investigated using a 10 mW He–Cd laser at 325 nm as the exciting source.

In the case of the Sn catalyst utilization, substrate temperature decreasing to 270 and 245°C leads to transformation of “microropes” to cocoon-like structures. And at 200°C, formation of arrays almost consisting from such structures occur. In the case of the In catalyst utilization, substrate temperature decreasing to 150°C leads to the cocoon-like structures formation, and decreasing the temperature to 100°C leads to overgrowing of catalyst particles by silicon suboxide film.

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DESIGN OF HIERARCHICAL ZEOLITE CATALYSTS

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Zeolites represent a unique class of crystalline aluminosilicates with ordered micropores of molecular dimensions (<2 nm) having a high specific surface area (350–450 m^2/g). The key problem of zeolite catalysts is intracrystalline diffusion constraints resulting in low utilization of zeolite active surface especially in adsorption and catalytic processes involving large molecules. The effective approach for enhancing zeolite surface utilization is to produce hierarchically porous zeolites, having besides micropores an additional system of meso- and macropores. To increase accessibility of the active zeolite surface, two main approaches are applied: top-down – chemical treatment of conventional zeolite crystals for mesopore formation and bottom-up – the synthesis of meso/macroporous zeolites with desired texture ab initio.

The present study describes the synthesis of hierarchically porous zeolites by bottom-up approach using the following routes: zeolite crystallization in pores of polystyrene matrix and the patterning of nanocrystals [1].

Synthesis methods of zeolite ZSM-5, beta and Fe-silicalite-1 with different morphology and crystal size in the range from 30 to 5000 nm have been developed. Uniform zeolite nanocrystals were used as initial blocks for building hierarchical zeolites, the texture of material depending on the size and packing of nanocrystals. Monodisperse polystyrene microspheres (150–1100 nm) were produced as templates. Meso/macroporous Fe-silicalite materials were synthesized in PS matrix followed by the template removal via calcination. The synthesized samples were characterized by laser diffraction analysis, dynamic light scattering, X-ray diffraction, scanning and transmission electron microscopy, argon and nitrogen adsorption measurements, inductively coupled plasma optical emission spectrometry, UV visible diffuse reflectance spectroscopy and temperature-programmed desorption of ammonia. All zeolite samples exhibited high crystallinity, high BET surface area (480–650 m^2/g), external surface area (180-350 m^2/g) and total pore volume (0.50–0.75 cm^3/g). Catalytic performance of hierarchically porous Fe-silicalite materials was studied in total liquid-phase oxidation organic molecules, including phenol, antibiotic – clarithromycin lactobionate and metal ion complexing agent – ethylenediaminetetraacetate (EDTA) by H_2O_2 at low temperatures (298-323 K) compared with the reference Fe-silicalite microcrystals. Hierarchical Fe-silicalites were shown to be more efficient catalysts vs Fe-silicalite microcrystals due to increasing catalytic sites accessibility. A new method of radiocobalt removal from EDTA chelates by catalytic oxidation of EDTA by H_2O_2 *via* heterogeneous Fenton-type zeolite catalysts have been suggested and patented [2].

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ДИЗАЙН ИЕРАРХИЧЕСКИ ПОРИСТЫХ ЦЕОЛИТНЫХ КАТАЛИЗАТОРОВ

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Цеолиты – уникальный класс кристаллических алюмосиликатов, имеющих большую площадь поверхности (350–450 м^2/г) вследствие упорядоченных микропор молекулярного размера (< 2 нм). Ключевая проблема цеолитных катализаторов − диффузионные ограничения, которые приводят к низкой степени использования поверхности цеолита, особенно в процессах с участием крупных молекул. Для решения проблемы эффективного использования цеолитных катализаторов, бурно развиваются различные методы приготовления иерархических цеолитов, содержащих помимо микропор дополнительную систему транспортных мезо/макропор. Существует два принципиально разных подхода к синтезу иерархических цеолитов: сверху-вниз – создание иерархической пористости путем частичной деструкции либо перестройки решетки кристаллов цеолита и снизу-вверх – формирование дополнительных пор непосредственно во время кристаллизации.

Наше исследование посвящено синтезу иерархически пористых цеолитов с помощью подхода снизу-вверх с применением методов: кристаллизации цеолита в порах полистирольной матрицы и структурирования нанокристаллов [1]. В рамках исследования были разработаны методы синтеза цеолитов ZSM-5, β и Fe-силикалита-1 с различной морфологией и размером кристаллов в диапазоне от 30 до 5000 нм и иерархически пористых образцов Fe-силикалита и цеолита β. Материалы были охарактеризованы методами лазерной дифракции, динамического рассеяния света, рентгенофазового анализа, сканирующей и просвечивающей электронной микроскопии, низкотемпературной адсорбции аргона и азота, атомно-эмиссионной спектрометрии с индуктивно связанной плазмой, электронной спектроскопии диффузного отражения и термопрограммируемой десорбции аммиака. Каталитические свойства иерархически пористых материалов на основе Fe-силикалита были изучены в процессе глубокого жидкофазного окисления органических молекул пероксидом водорода: фенола, антибиотика – клацида и комплексона – ЭДТА. Предложен и запатентован метод обезвреживания жидких радиоактивных отходов атомных электростанций путем выделения радионуклидов из прочных комплексов с органическими кислотами с помощью каталитического окисления комплексонов пероксидом водорода в мягких условиях [2].

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THERMOPHYSICAL PROPERTIES OF NANOFLUIDS BASED ON HOLLOW AL_2O_3 NANOPARTICLES AND WATER

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Practical application of nanofluids is connected with a possibility to create the high-performance liquid heat carrier. However, when nanoparticles are introduced into the liquid, together with a change in thermal conductivity some other thermal-physical properties change. The most important characteristic is viscosity because a gain obtained due to an increase in thermal conductivity can be lost through a rise of energy spent for liquid pumping. Therefore, it is reasonable to measure thermal conductivity and viscosity of nanofluids, simultaneously.

In the current study, we used water and hollow and spherical nanoparticles of γ-Al_2O_3 (ITP SB RAS, Russia) with a typical size of 10 nm. To synthesize nanofluids, we used ultrasonic dispersion for an hour. Thermal conductivity was measured by the nonstationary hot wire method [1]. Viscosity was measured by the rotation viscometer Fungilab Expert L.

The dependence calculated by the Maxwell's theory for low volume content of nanoparticles and the measurement results for thermal conductivity are shown in Fig. 1 (a). Experimental data are significantly lower than the theoretical dependence, and thermal conductivity differs significantly from data of other authors. Comparison of experimental data with the theory showed that the presence of cavity has a little effect on thermal conductivity of nanofluids while the interfacial thermal resistance has a significant influence on thermal conductivity of nanofluids. The dependence calculated by the Batchelor's theory and the measurement results for viscosity are shown in Fig. 1 (b). Experimental data are significantly higher than the theoretical dependence. These values indicate that the studied nanofluids have no prospects for use as an effective heat carrier in comparison with the basic liquid.

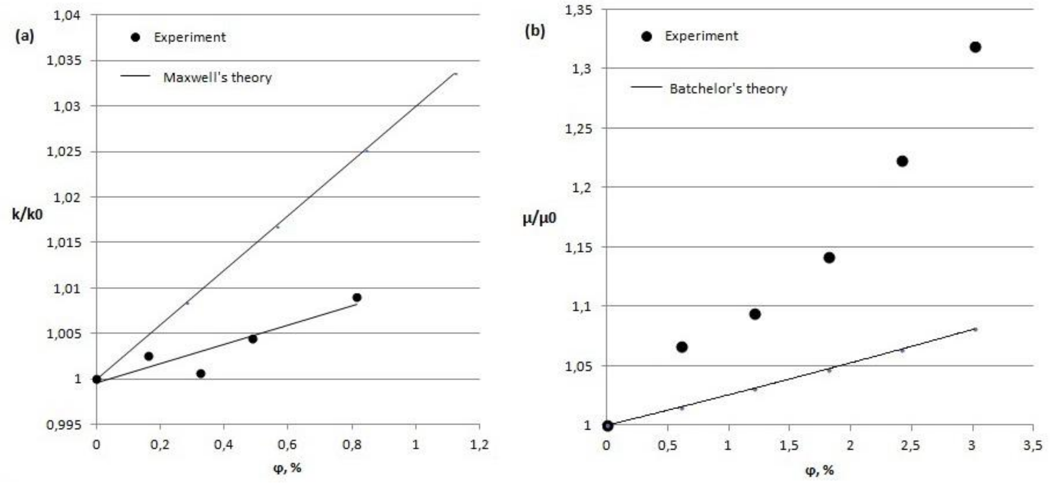

Figure 1. (a) Relative thermal conductivity versus nanoparticle volume fraction. (**b)** Relative viscosity versus nanoparticle volume fraction.

This work was supported by Russian Scientific Foundation, Project №14-19-01379.

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EFFECT OF THE ARC-DISCHARGE PARAMETERS ON THE MORPHOLOGY AND THE ELECTRICAL CONDUCTIVITY OF THE SYNTHESIZED CARBON MATERIALS

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Method of arc-discharge synthesis allows producing metal / oxide / carbide nanoparticles with dimensions of a few nanometers. Problems of coagulation and size growth of the nanoparticles are solved by usage of a composite metal-carbon electrode that provides synthesis of a carbon matrix encapsulating the nanoparticles. However, this carbon matrix should have sufficient electroconductive properties to use the synthesized nanoparticles in such areas as: electrocatalysis, including in fuel cells; creation of electrochromic devices, and others. In this study, the effects of the external parameters of the arc discharge synthesis are disclosed which influence on the electrical conductivity of the synthesized carbon material.

In result of arc-discharge synthesis the produced carbon materials are condensate which consists of the globules of a size of 10 - 40 nm. The more detailed study of the structure of the carbon soot globules showed both amorphous carbon and clearly visible graphite-like structure in the stacked, curved, twisted and closed forms of graphene layers. The presence of the graphite structure confirmed by X-ray diffraction phase analysis (XRD) and Raman spectroscopy (MRS).

The arc-discharge synthesis at pressure of the inert buffer gas of several Torr leads to the formation of globules with average size of about 10 nm. Using higher buffer gas pressures increases an average size of globules which increases monotonously up to 40 nm with increasing pressure.

Mechanical pressing of the synthesized carbon material leads to increasing of conductivity according to percolation theory. Value of conductivity asymptotically approaches to a specific value, which is determined for each test material. The pressure and current dependences of conductivity value calculated for density of 2 g/cm^3 seems complicated and nonmonotonic.

The sizes of La of the graphite nanofragments were estimated by the results of the MRS and get into the interval 0.5 - 2 nm. On this size interval of La conductivity of the synthesized material doesn’t depend on a graphite structure size due to large value of the contact resistance, which appears because of the presence of large amount of amorphous carbon. Contact resistance is determined by amount of amorphous carbon in material. Its influence is minor when result of the arc-discharge synthesis at pressure of 25 Torr and current of 140 A is graphene structures ranging in size from 20 to 180 nm, with average of 65 nm, which is comparable and larger than sizes of soot globules. In this case, the electrical conductivity is determined by the concentrations of graphene structures and soot globules and described by percolation theory.

This work was supported by grant RFBR 16-38-00322

ЭФФЕКТЫ ПАРАМЕТРОВ ДУГОВОГО РАЗРЯДА НА МОРФОЛОГИЮ И ЭЛЕКТРОПРОВОДНОСТЬ СИНТЕЗИРУЕМОГО УГЛЕРОДНОГО МАТЕРИАЛА.

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Электродуговой метод синтеза позволяет получать металлические/оксидные/карбидные наночастицы с размерами всего в несколько нанометров. Проблему коагуляции и роста размеров наночастиц решает использование композитных металл-углеродных электродов, что обеспечивает синтез углеродной матрицы, обволакивающей наночастицы. Тем не менее, данная углеродная матрица должна обладать хорошими электропроводящими свойствами для применения синтезированных наночастиц в таких областях как: электрокатализ, в том числе в топливных элементах; создание электрохромных устройств и др. В данной работе раскрываются эффекты внешних параметров электродугового синтеза, влияющие на электропроводность синтезирующегося углеродного материала.

Углеродный материал, получающийся в результате электродугового метода синтеза, представляет собой сажу из разупорядоченного углеродного конденсата со случайными σ-/π-связями. Углеродный конденсат состоит из глобул с размерами от 10 до 40 нм. При более детальном рассмотрении строения сажевой глобулы, наряду с аморфным углеродом, отчетливо видны участки с графитоподобной структурой в виде искривленных, замкнутых, скрученных и упакованных в стопки графеновых слоев. Присутствие графитовой структуры подтверждается результатами рентгено-дифракционного фазового анализа (РФА) и спектроскопии комбинационного рассеяния (СКР).

Экспериментально было установлено, что синтез при давлении инертного буферного газа в несколько Торр приводит к образованию сажевых глобул со средним размером около 10 нм. Использование больших давлений буферного газа приводит к увеличению размера сажевых глобул, который монотонно увеличивается до 40 нм с увеличением давления. С другой стороны, использование различных значений силы тока разряда существенно не влияет на средний размер глобул.

При механическом уплотнении синтезированного углеродного материала, электропроводность увеличивается согласно перколяционной теории, асимптотически приближаясь к конкретному значению, которое определяется для каждого исследуемого материала. При сжатии плотность достигала значений от 0,4 до 1,7 г/см^3 для разных синтезированных материалов. Значения электропроводности при расчёте для плотности 2 г/см^3 показали сложные зависимости от давления буферного газа и силы тока разряда.

По результатам СКР были оценены размеры нанофрагментов графита. Было установлено, что в материалах с большими размерами таких нанофрагментов электропроводность принимает большие значения.

Заключено, что электропроводность зависит от квантовых эффектов, связанных со структурой графитоподобных нанофрагментов, но основное влияние оказывает явление контактного сопротивления, связанное с морфологией и структурой синтезированных углеродных сажевых глобул, на которые влияют внутренние параметры горения дугового разряда и течения газа в камере реактора.

THE EFFECT OF HYDROTHERMAL TREATMENT ON ACTIVITIES OF $Cd_{0.3}Zn_{0.7}S$ AND $Au/Cd_{0.3}Zn_{0.7}S$ UNDER VISIBLE LIGHT

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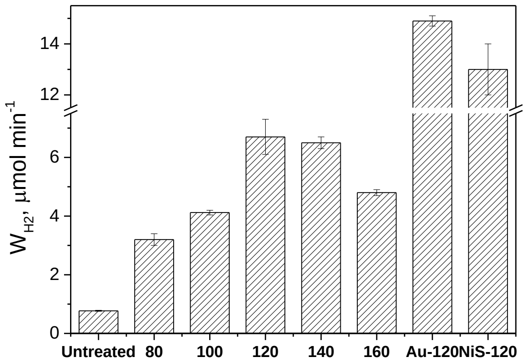
Hydrogen seems to be an attractive alternative to traditional energy sources, but it exists in nature in the form of compounds with other elements. Water is an ideal hydrogen source. One of the most effective ways of water splitting is photocatalysis on semiconductors, but catalytic activity in this process is quite low due to the recombination of photogenerated charge carriers on the semiconductor surface. The addition of sacrificial agents in the system reduces the rate of charge recombination and increases the rate of hydrogen evolution. CdS is considered to be one of the most well-known semiconductor photocatalyst. The photocatalytic properties of CdS could be modified by mixing with wide band gap chalcogenide semiconductors such as ZnS [1].

In this study a series of $Cd_{0.3}Zn_{0.7}S$ photocatalysts were prepared by the coprecipitation method with subsequent hydrothermal treatment at different temperatures in the range 80-160 °C in air atmosphere. To measure of the activities of synthesized samples, a water suspension with a catalyst and 0.1M Na_2S/0.1M Na_2SO_3 solution was illuminated with a 450-nm LED. The best result equals to 6,7 µmol min^{-1} has been obtained using particles of CdS, treated at 120 °C. Further, NiS and Au were deposited on the surface of this $Cd_{0.3}Zn_{0.7}S$ sample. The activities of composite samples equal to 13,0 µmol min^{-1} and 14,9 µmol min^{-1} for $NiS/Cd_{0.3}Zn_{0.7}S$ and $Au/Cd_{0.3}Zn_{0.7}S$, respectively. The results of the kinetic measurements are presented in fig. 1.



An improvement of H_2 evolution in the case of the treated samples likely caused by a change to a hexagonal lattice. It has been recognized early on, that the hexagonal structure is far more active than the cubic one [2]. With the addition of NiS and Au, photogenerated electrons in $Cd_{0.3}Zn_{0.7}S$ are migrated to the cocatalyst. Owing to the longer lifetime of photogenerated electrons, photocatalytic H_2 evolution rate is improved.

This work was supported by base budget project V.44.2.11 and additionally was supported by RFBR via project # 15-33-20458 mol_a_ved, RF President Grant МК-3141.2015.3.

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ВЛИЯНИЕ ГИДРОТЕРМАЛЬНОЙ ОБРАБОТКИ НА АКТИВНОСТЬ КАТАЛИЗАТОРОВ НА ОСНОВЕ $Cd_{0.3}Zn_{0.7}S$ В РЕАКЦИИ ВЫДЕЛЕНИЯ ВОДОРОДА ПОД ДЕЙСТВИЕМ ВИДИМОГО ИЗЛУЧЕНИЯ

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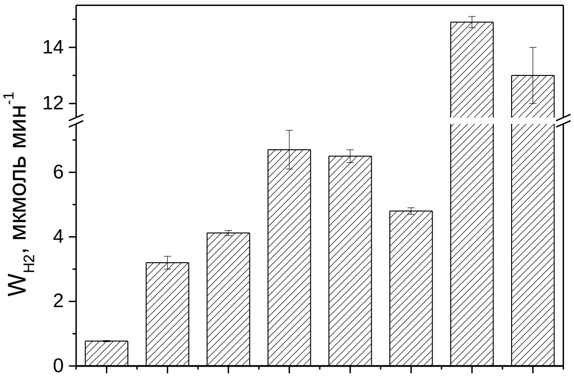
Водород привлекает внимание ученых как альтернативный источник энергии. Одним из способов получения H_2 является фотокаталитическое разложение водных растворов на полупроводниковых материалах. Наиболее распространенным катализатором является CdS. Фотокаталитические свойства CdS могут быть улучшены добавлением ZnS [1].

В данной работе была получена серия образцов $Cd_{0.3}Zn_{0.7}S$ методом соосаждения растворов солей кадмия и цинка с последующей гидротермальной обработкой в автоклаве в диапазоне температур 80-160 °C. Наилучшая скорость выделения водорода, равная 6,7 μмоль мин$^{-1}$, была достигнута на катализаторе, обработанном при 120 °C. Далее на поверхность данного образца были нанесены частицы NiS и Au. Активность композитных катализаторов составила 13,0 μмоль мин$^{-1}$ и 14,9 μмоль мин$^{-1}$ для $NiS/Cd_{0.3}Zn_{0.7}S$ и $Au/Cd_{0.3}Zn_{0.7}S$, соответственно. Результаты кинетических экспериментов представлены на рисунке.



Активности полученных фотокатализаторов в реакции выделения H_2. Условия: 50 мг кат. в 100 мл раствора $Na_2S(0.1M)/Na_2SO_3(0.1M)$, $\lambda = 450$ нм.

Увеличение скорости выделения водорода после гидротермальной обработки образцов вызвано изменением решетки от кубической к гексагональной, что подтверждается результатами анализа РФА. Ранее было показано, что гексагональная структура является более активной [2]. При нанесении частиц NiS и Au на поверхности возникают гетеропереходы, при которых фотогенерированные электроны мигрируют с поверхности твердого раствора $Cd_{0.3}Zn_{0.7}S$ на поверхность сокатализатора. Данное явление способствует улучшению разделения носителей заряда и, следовательно, увеличивает скорость выделения водорода.

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SILICON MICROCHANNEL MEMBRANE AND MICROFLUIDIC DEVICES ON ITS BASIS

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Porous silicon is widely used in various fields of fundamental and applied science. Its application extends from supercapacitors and sensors [1, 2] to energetic and insulating materials [3, 4]. Porous silicon features are vast surface area, controlled pore size and ease of surface modification. Porous silicon materials are applied in different microfluidic devices as transporting [2, 5], separating and sensing elements [2].

Porous silicon membranes with array of arranged channels have been fabricated by developed and patented technology [6, 7]. This work describes silicon membrane fabrication technique and microfluidic devices based on porous silicon: electroosmotic pump, volumetric flow rate meter and pulse wave sensor. All the devices consist of same parts: porous silicon membrane with electrodes on both sides – this sandwich structure was inserted into a PTFE frame with through channel filled with working liquid (Fig.1).

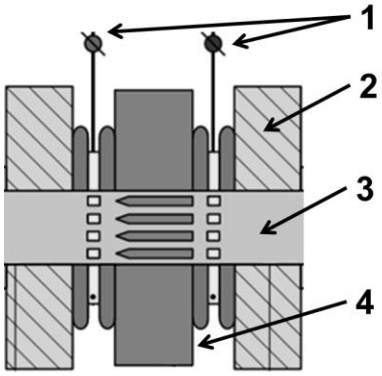

Fig. 1. Microfluidic device scheme: 1 – electrodes, 2 – PTFE frame, 3 – channel with working liquid, 4 – silicon membrane.

Electroosmotic pump operating principle is based on a same name electrokinetic phenomenon - electroosmosis. Electric field arises along the membrane microchannels when none zero voltage is applied to the electrodes. If working liquid is electrolyte – it is started to flow through the membrane due to electrostatic forces. Flow rate meter works on an opposite principle. When electrolyte flows through the membrane microchannels – potential difference is arisen on opposite sides of the membrane which is measured by the electrodes. Voltage measured by the electrodes depends on a flow rate through the membrane.

Pulse wave sensor is based on a same working principle as volumetric flow meter. Pressure difference creates liquid flow through the membrane channels which creates voltage on the electrodes of the sensor. This device has been used to monitor brachial artery pulse wave of a human.

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SYNTHESIS AND NANOPARTICLES DYNAMIC IN SPHERICAL GLOW DISCHARGE

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Synthesis of nanoparticles in low-temperature plasma plays an important role in fundamental research and in plasma technology [1]. Dust particles may be found in astrophysical experiments, in the ionosphere, and in fusion plasma. The possibility of formation of nanometer or micron size particles in laboratory plasma was described in [2-4].

In 2015, a new phenomenon was discovered [5]: in spherical strata, the clouds of dust particles are formed; they occasionally explode, split into two clouds and scatter in opposite directions. It turned out that the compact cloud entrained to the reactor wall decelerates many times slower than it could be expected from the evaluation on Epstein force of nanoparticles on a neutral background gas.

Spherical striations appear around a point anode (placed at the center of a grounded vacuum chamber, whose walls serve as cathode) at low pressures (10-50 Pa) of high-molecular gases (acetone, ethanol, methane, acetylene, etc.) and present a set of concentric luminous regions [6]. In discharge plasma in the high-molecular gas the complex plasma-chemical processes of dissociation, ionization and recombination result in the appearance of radicals, ions and small clusters. Their coagulation and recharge lead to the formation of negatively charged clusters and dust particles of nano or micro size. A special feature of the spherical gas discharge is absence of transverse and the presence of only radial flows of particles and energy, which allows concentrating high-density plasma in the central part of the discharge and enables considering discharge to be a one-dimensional problem. Complex plasma-chemical processes in a spherical glow discharge in high-molecular gases result in formation a variety of molecules, active radicals and ions. It was discovered that the differential conductivity in the formed gas can be non-monotonic, which probably leads to the formation of spherical stratification [7].

It has been shown that dust particles are produced in the glow discharge in ethanol and under nitrogen. In the case of a stratified discharge particles are concentrated at the boundary strata. In the unstratified discharge in nitrogen dust particles collected in the cloud that increasing the current moving away from the anode so that the current density in it will continue. Estimates have shown that the particle size of the dust cloud of nitrogen in a glow discharge is on the order of several microns on the assumption that the thermophoretic force on the particles is small.

Transmission electron microscopy showed that in the stratified discharge multilayered particles having an iron core coated with two carbon cloths are generated. The shell adjacent to the iron core is graphite. The outer shell is an amorphous carbon material.

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СИНТЕЗ И ДИНАМИКА НАНОЧАСТИЦ В СФЕРИЧЕСКОМ ТЛЕЮЩЕМ РАЗРЯДЕ

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Синтез наночастиц в низкотемпературной плазме играет важную роль в фундаментальных исследованиях и в плазменных технологиях [1]. Пылевые частицы обнаруживаются в астрофизических экспериментах, в ионосфере, и в термоядерной плазме. Возможность образования нанометровых или микронных частиц в лабораторной плазме была описана в работах [2-4].

В 2015 году было обнаружено новое явление [5]: в сферических стратах образуются облака пылевых частиц, которые периодически взрываются, делятся на два облака и разлетаются в противоположных направлениях. Оказалось, что компактное облако, улетающее на стенки реактора, тормозится во много раз медленнее, чем можно было бы ожидать согласно оценке по эпштейновскому торможению наночастиц на нейтральном фоновом газе.

Сферические страты возникают вокруг точечного анода, помещенного в центр заземленной вакуумной камеры, стенки которой являются катодом, при низких давлениях высокомолекулярных газов (ацетон, этанол, метан, ацетилен, и т.д.) и представляющие собой набор концентрических светящихся областей [6]. В плазме в высокомолекулярных газах в результате сложных плазмохимических процессов диссоциации, ионизации, рекомбинации возникают радикалы, ионы, малые кластеры, коагуляция которых и их перезарядка приводят к образованию отрицательно заряженных кластеров или пылевых частиц нано или микронных размеров [7].

Показано, что пылевые частицы образуются в тлеющем разряде как в этиловом спирте, так и в азоте. В случае стратифицированного разряда частицы концентрируются на границе страт. В нестратифицированном разряде в азоте пылевые частицы собираются в облако, которое по мере увеличения тока отдаляется от анода так, что плотность тока в нем сохранятся. Оценки показали, что размер частиц в пылевом облаке в тлеющем разряде азота составляет порядка нескольких микрон в предположении, что термофоретическая сила на частицы мала.

Просвечивающая электронная микроскопия показала, что в стратифицированном разряде формируются многослойные частицы с железным ядром, покрытой двумя углеродными оболочками. Оболочка, прилегающая к железному ядру, является кристаллической с расстояниями между кристаллиесими слоями, близкими к графиту. Внешняя оболочка представляет собой аморфный углеродный материал.

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INVESTIGATION OF INTERACTIONS OF CARBON NANOMATERIALS WITH LITHIUM BY X-RAY SPECTROSCOPY

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Investigation of interactions of lithium with materials based on carbon structures possessing an increased specific surface and conductivity is currently a promising task as there is the active search for new carbon electrode materials could improve the electrochemical characteristics of lithium-ion batteries [1]. It is necessary study of the electronic structure of lithium intercalation compounds in order to predict the electrochemical properties of new carbon anode and cathode materials for lithium-ion batteries. Lithium reacts actively with nitrogen and oxygen in the air, which makes lithium intercalation compounds difficult them to obtain and study. This work is devoted the x-ray spectrum in situ investigation of electron interaction lithium atoms with carbon-base materials with different graphitization degree that is a highly oriented pyrolytic graphite (HOPG) crystal, synthetic graphite and mesoporous carbon.

Lithiation of carbon-base materials was carried out with the help of thermal spraying on surfaces of said materials in spectrometer chamber with high vacuum. After that lithiated carbon-base materials were investigated in situ by x-ray photoelectron spectroscopy (XPS), near edge x-ray absorption fine structure spectroscopy (NEXAFS), x-ray emission spectroscopy (XES) to estimate the chemical composition and to probe the electronic structure of the samples.

XPS and NEXAFS spectra of lithiated HOPG and mesoporous carbon were obtained at the Russian-German beam line of the BESSY II synchrotron. C 1s- and Li 1s- spectra were received at different excitation energies, from which it follows that concentration of lithium changes with the sample depth. Changes in carbon *K*-edge NEXAFS spectra of lithiated mesoporous carbon testify to presumably localization of lithium atoms near the defects where there are dangling carbon bonds. XES carbon K_α - spectra of lithiated synthetic graphite and mesoporous carbon were recorded with a laboratory X-ray spectrometer. It is demonstrated that the carbon K_α - spectra of lithiated synthetic graphite and spectra of lithiated mesoporous carbon differ in the intensity of the short-wavelength lines.

Interpretation of experimental emission spectra of lithiated carbon-base materials was carried out the DFT (density functional theory) quantum-chemical calculation on cluster models that was performed using B3LYP method. The atomic orbitals were described in the polarized 6-31G basis set.

As a result of the performed researches it has been determined, that interactions of lithium vapor with carbon-base materials lead to the formation of the surface layer with a high concentration of lithium and to modification in the electronic structure of the surface of the carbon layer.

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ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ ЛИТИЯ С НАНОРАЗМЕРНЫМИ УГЛЕРОДНЫМИ МАТЕРИАЛАМИ МЕТОДАМИ РЕНТГЕНОВСКОЙ СПЕКТРОСКОПИИ

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Изучение взаимодействия лития с материалами на основе углеродных структур, обладающими высокой удельной поверхностью и электропроводностью, является актуальной задачей, так как в настоящее время ведется активный поиск новых электродных углеродных материалов, которые могут улучшить электрохимические характеристики литий-ионных аккумуляторов, [1], [2]. Чтобы прогнозировать электрохимические свойства новых углеродных анодных и катодных материалов для литий-ионных аккумуляторов, необходимо изучение электронного строения литий-интеркалированных соединений таких материалов. Однако, литий-интеркалированные углеродные материалы неустойчивы на воздухе, что осложняет их получение и исследование, так как литий активно реагирует с кислородом и азотом. Данная работа посвящена рентгеноспектральному исследованию электронного взаимодействия атомов лития с углеродными материалами различной степени графитизации (кристалл высокоориентированного графита, спектральный графит, мезопористый углерод).

Литирование углеродных материалов осуществлялось с помощью высоковакуумного термического напыления лития на поверхность углеродных материалов, затем применялись методы рентгеновской и рентгеноэлектронной спектроскопии in situ для исследования электронной структуры и элементного состава полученных образцов.

Рентгеноэлектронные и NEXAFS спектры литированных углеродных материалов были сняты на Российско-Германском канале Берлинского центра синхротронного излучения (BESSYII). C1s и Li1s – спектры были сняты при разных энергиях возбуждения, из которых следует, что концентрация лития изменяется с глубиной образца. Изменения в CK-спектрах поглощения для мезопористого углерода предположительно свидетельствуют о локализации атомов лития на дефектах, где присутствуют оборванные углеродные связи. Рентгеновские эмиссионные CKα -спектры были сняты на лабораторном спектрометре «Стеарат», по данным которых наблюдалось увеличение интенсивности в области π – системы после напыления лития на спектральный графит и уменьшение в случае мезопористого углерода.

Интерпретация экспериментальных эмиссионных спектров осуществлялась с помощью квантово-химических расчетов в рамках кластерной модели методами теории функционала плотности (функционал B3LYP) с помощью программного обеспечения Jaguar [3]. В результате проведенных исследований было установлено, что взаимодействие паров лития с углеродными материалами приводит к формированию поверхностного слоя с высокой концентрацией лития и к изменению электронного строения поверхности углеродного слоя.

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UV-LED PHOTOCATALYTIC OXIDATION OF CARBON MONOXIDE OVER THE Pd-LOADED CATALYSTS SYNTHESIZED BY THE DECOMPOSITION OF Pd(acac)$_2$

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Carbon monoxide is a major concern for environmental protection. CO can be considered as either a primary pollutant from different emissions or a secondary pollutant resulting from the partial (photo)oxidation of VOCs [1]. CO is poorly photooxidized on the pure TiO_2 photocatalyst. One of the reasons for that is a weak adsorption of CO and oxygen on TiO_2 surface at ambient conditions [2]. The deposition of metallic nanoparticles (e.g., Pd) on TiO_2 surface can enhance adsorption capacity of the catalysts and provide reactive sites for CO oxidation [3].

An important role for producing highly active catalyst is the method of metal deposition. Thus, the aim of this study was to prepare Pd/TiO_2 photocatalysts by the decomposition of Pd(acac)$_2$ and investigate in CO oxidation at ambient conditions both without and with UV irradiation. The decomposition of metal-organic precursors (e.g., Pd(acac)$_2$) is a good method to deposit metal nanoparticles with a very small size and narrow size distribution on the surface of various supports. The effect of several parameters including UV or thermal treatment, the calcination temperature, the metal content and the type of support on the (photo)catalytic activity was studied.

The 0.05-4 wt.% Pd/TiO_2 catalysts were synthesized by the impregnation of TiO_2 with a certain amount of Pd(acac)$_2$ dissolved in acetone with subsequent the photo- or thermodecomposition of adsorbed Pd(acac)$_2$. In the former case, the sample was UV irradiated for 12 hours. In the latter, the sample was calcined at 210, 250 or 310 °C for 3 hours. Catalytic activity of the synthesized samples was investigated in the reaction of CO oxidation in a static reactor at ambient conditions.

The photocatalytic rate of CO oxidation under UV irradiation was up to 3.5 times greater than the rate of catalytic oxidation without UV irradiation. The activity of the samples prepared by the photodecomposition way was much higher than the activity of the calcined samples both without and with UV irradiation. XPS analysis showed that the photodecomposition way led to a higher amount of palladium in metallic form resulted in a higher activity. An increase in the cacination temperature from 210 to 310 °C led to a decrease in the activity.

One of the most important results is that the photocatalytic rate of CO oxidation increased as the Pd content increased from 0.05 to 4 wt.%. TEM analysis showed that at a high metal content (e.g., 4 wt.%) the amount of particles was increased but their size and distribution was the same as at a low content.

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ФОТОКАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ МОНООКСИДА УГЛЕРОДА С ИСПОЛЬЗОВАНИЕМ УФ-СВЕТОДИОДОВ НА Pd-СОДЕРЖАЩИХ КАТАЛИЗАТОРАХ, СИНТЕЗИРОВАННЫХ РАЗЛОЖЕНИЕМ $Pd(acac)_2$

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Монооксид углерода является серьезной проблемой для окружающей среды. CO можно рассматривать как основное загрязняющее вещество в составе различных выбросов, либо как побочный продукт в результате частичного (фото)окисления летучих органических соединений [1]. К сожалению CO практически не подвергается фотокаталитическому окислению на чистом диоксиде титана. Одной из причин низкой активности является слабая адсорбция CO и O_2 на поверхности TiO_2 в условиях окружающей среды [2]. В свою очередь, нанесение наночастиц благородных металлов (например Pd) на поверхность TiO_2 может существенно увеличить сорбционную емкость катализатора и обеспечить активные центры для окисления CO[3].

Важную роль в получении высокоактивного катализатора играет метод нанесения металла. Цель данного исследования состояла в синтезе фотокатализаторов Pd/TiO_2 путем разложения $Pd(acac)_2$ и их исследования в реакции окисления CO без и под воздействием УФ-излучения. Разложение металлоорганических предшественников (например, $Pd(acac)_2$) является перспективным методом для нанесения наночастиц металлов на поверхность различных носителей. В данной работе исследовалось влияние нескольких параметров, включая УФ и термическую обработку, температуру прокаливания, содержание металла и типа носителя на (фото)каталитическую активность.

Катализаторы Pd/TiO_2 с содержанием Pd 0,05-4 масс.% были синтезированы разложением $Pd(acac)_2$ на поверхности TiO_2 путем воздействия высоких температур или УФ-излучения. Активность катализаторов была исследована методом ИК-Фурье спектроскопии in situ в статическом реакторе.

Фотокаталитическая скорость окисления CO под действием УФ-излучения до 3,5 раз выше, чем скорость окисления без УФ-излучения. Активность образцов синтезированных фоторазложением значительно выше, чем активность прокаленных образцов. РФЭС анализ показал, что метод фоторазложения приводит к более высокому количеству палладия в металлической форме, что объясняет более высокую активность. Повышение температуры прокаливания от 210 до 310 °C приводит к снижению активности.

Фотокаталитическая скорость окисления CO растет вместе с увеличением содержания палладия от 0,05 до 4 масс.%. Анализ с помощью ПЭМ показал, что при высоком содержании металла (например 4 масс.%) происходит рост количества наночастиц, при сохранении их малого размера таким же, как и при низком содержании Pd.

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ELECTOMECHANICAL COUPLING IN NANOELECTROMECHANICAL SYSTEMS WITH A TWO-DIMENSIONAL ELECTRON GAS

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The use of sacrificial layers and the technology of selective etching give an opportunity to create the nanostructures with a two-dimensional electron gas (2DEG) freely suspended over a substrate. These nanostructures are mechanically moveable, and their vibrations are known [1,2] to affect electron transport. It is often supposed that the electromechanical coupling in the systems based on GaAs/AlGaAs heterostructures has piezoelectric nature; however, there is a lack of experimental evidence for this hypothesis. In the present work [3] we present such experimental evidence based on anisotropy of the piezoelectric effect and, moreover, quantitatively describe the features of this coupling.

The studied nanoelectromechanical system represents two identical cantilevers oriented in $[110]$ and $[\bar{1}10]$ crystallographic directions. The cantilevers' vibrations are driven perpendicularly to the surface by means of the electrostatic actuation method using side gates [2]. Near the bases of the cantilevers, i.e., in the points of maximum mechanical stress, there are conductive channels. The conductance change due to the vibrations is measured using the heterodyne down-mixing method. It is found that identical vibrations of the cantilevers lead to opposite (180° phase-shifted) changes in the channels conductance. A quantitative physical model is developed, which describes the physical mechanism of the conductance change and agrees with the experiment. The model is based on the assumption that the 2DEG screens the piezoelectric bound charge to maintain constant electrochemical potential. It is shown that the change in the conductivity of the 2DEG is caused mainly by the rapid change in mechanical stress near the boundary of suspended and non-suspended areas, rather than by the stress itself. Thus, the discussed electromechanical coupling can be considered as an edge effect.

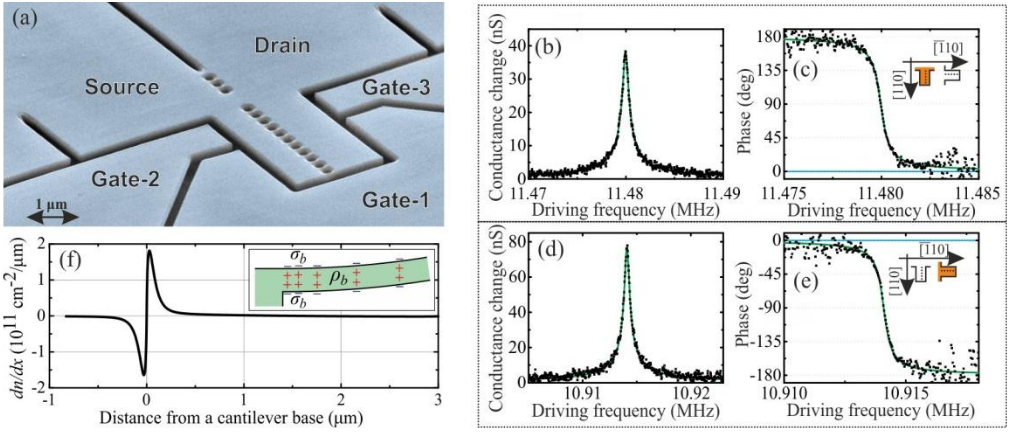

Fig. 1. (a) Nanomechanical resonator with a two-dimensional electron gas. Amplitude (b,d) and phase (c,e) of the conductance response to the resonant vibrations of the perpendicularly oriented cantilevers (f) The calculated change in electron density per unit displacement of the cantilever's free end predicted by the developed model.

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СВЯЗЬ МЕЖДУ ЭЛЕКТРОННЫМ ТРАНСПОРТОМ И МЕХАНИЧЕСКИМИ КОЛЕБАНИЯМИ В НАНОЭЛЕКТРОМЕХАНИЧЕСКИХ СИСТЕМАХ С ДВУМЕРНЫМ ЭЛЕКТРОННЫМ ГАЗОМ

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Использование жертвенных слоев и технологии селективного травления позволяет создавать наноструктуры с двумерным электронным газом, свободно подвешенные над полупроводниковой подложкой. Такие структуры механически подвижны, и их колебания, как известно [1,2], влияют на электронный транспорт. Часто предполагается, что электромеханическая связь в системах на основе гетероструктур GaAs/AlGaAs имеет пьезоэлектрическую природу, однако, экспериментальные доказательства этой гипотезы отсутствуют. В настоящей работе [3] приводится такое экспериментальное доказательство, основанное на анизотропии пьезоэффекта, а также количественное описание особенностей этой связи.

Изученная наноэлектромеханическая система представляет собой два одинаковых кантилевера, ориентированных в направлениях $[110]$ и $[\bar{1}10]$. Резонансные колебания кантилеверов возбуждались в направлении, перпендикулярном к подложке, по емкостной схеме с использованием боковых затворов [2]. Вблизи оснований кантилеверов, т.е. в местах максимальных механических напряжений, располагались каналы проводимости. Изменение кондактанса вследствие колебаний измерялось методом гетеродинного смешивания. Было обнаружено, что идентичные колебания кантилеверов приводят к противоположным (сдвинутым по фазе на 180°) изменениям кондактанса каналов. Построена количественная физическая модель, описывающая физический механизм изменения кондактанса и согласующаяся с экспериментом. Модель основывается на предположении о том, что двумерный электронный газ экранирует пьезоэлектрический связанный заряд и сохраняет постоянный электрохимический потенциал. Показано, что изменение проводимости двумерного электронного газа обусловлено главным образом резким изменением величины механических напряжений вблизи границы подвешенной и неподвешенных областей, а не собственно механическим напряжением. Таким образом, обсуждаемая электромеханическая связь может рассматриваться как краевой эффект.

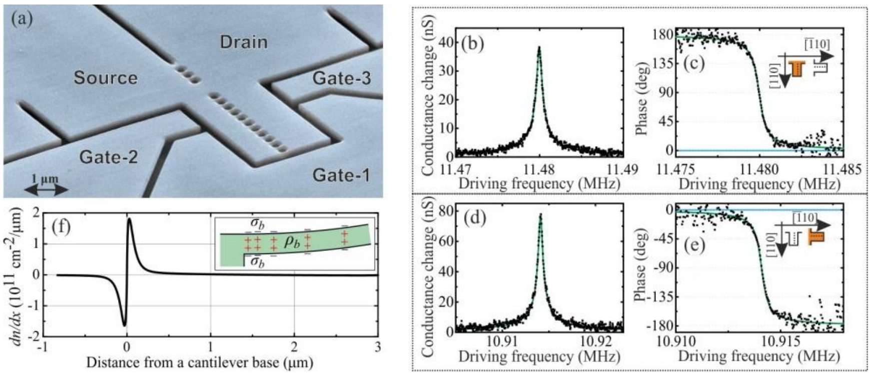

Рис. 1. (a) Наномеханический резонатор с двумерным электронным газом. Амплитуда (b,d) и фаза (c,e) отклика кондактанса на резонансные колебания перпендикулярно ориентированных кантилеверов. (f) Изменение концентрации двумерного электронного газа в расчете на единичное смещение свободного конца кантилевера, предсказываемое построенной физической моделью.

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HYBRID PHOTOPOLYMER MATERIAL “HYBRIMER-TATC”: PECULIARITIES OF LASER PROCESSING AND PROPERTIES OF THIN FILMS

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The applications of hybrid organic-nonorganic photopolymers are being actively researched for fabrication of microstructured components of purposes. The optical microstructures fabricated on the photopolymers have much better chemical inertness and thermomechanical stability than the structures formed in standard positive photoresists based on novolac resins. Hybrid photopolymers (HP) have potential for manufacturing phase multi-level micro-optical elements without transfer of surface profile from photoresist to optical substrate, which is usually made by expensive reactive ion etching. However, HP such as OrmoComp® [1] (one of the UV-photocurable Ormocer® polymers manufactured by Micro Resist Technology GmbH) are mainly used for replication of micro-optical elements. It is also known the OrmoComp® due to high-contrast characteristic curve can be used for direct laser writing of deep binary microstructures intended for micro-electromechanical systems. Our task was to investigate a possibility of direct laser writing of multilevel diffractive structures on hybrid photopolymers. Besides OrmoComp® we investigated and Hybrimer-TATC synthesized in NIOCH SB RAS (Russia). It is based on thiolsiloxane and acrylate oligomers. The optical and thermos-optical properties were studied in work [2].

Laser writing was done by circular laser writing system CL WS-300IAE developed in I&E SB RAS.

Possibility of direct laser writing of multi-level diffractive structures has been investigated for two hybrid photopolymer. It was offered to use additional steps of pre-exposure and post-exposure to obtain more linear characterisitc curves. Stuided hybrid photopolymers can be used for fabrication of diffractive structure with 1-3 micron profile depth. Hybrimer-TATC allows one to fabricate deeper multi-level structures but with larger backward slope. It makes the material more suitable for microoptical elements like refractive microlens arrays.

[1]Micro resist technology GmbH
URL: ww.microresist.de/de/produktwelt/hybridpolymere/uv-imprint-uv-abformung/ormocomp®
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ГИБРИДНЫЙ ФОТОПОЛИМЕРНЫЙ МАТЕРИАЛ «ГИБРИМЕР-ТАТС»: ОСОБЕННОСТИ ЛАЗЕРНОЙ ОБРАБОТКИ И СВОЙСТВА ТОНКИХ ПЛЕНОК

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Фотополимерные органические-неорганические композиции активно исследуются для задач построения различных микрооптических элементов. Фотоотверждённые структуры из таких фотоматериалов значительно превосходят по механическим качествам стандартные фоторезисты типа AZ15XX и S18XX. Среди самых известных и коммерчески доступных являются Ormocer и SU-8. Материал Ormocer (сокращение от organically modified ceramics), разработанный Фраунгоферовским институтом исследования силикатов (ISC), является гибридным УФ-фотоотверждаемым полимером Из нескольких вариантов композиции Ormocer наиболее подходящим для задач лазерной записи является фотополимер OrmoComp®, который позволяет наносить методом центрифугирования слои толщиной менее 10 мкм, а также обладает повышенной механической твердостью и низким температурным расширением.

Также существуют отечественные разработки гибридных органически-неорганических фотополимеров. В НИОХ СО РАН на основе тетракрилатных (ТА) и тиол-силоксановых (ТС) олигомеров была синтезирована гибридная фотополимерная композиция «Гибример-ТАТС» [2]. В качестве инициатора фотополимеризации в композицию добавляется гексафторфосфат 2,4-диэтил-9-оксо-10-(4-гептилоксифенил)-9Н-тио-ксантения в качестве 5%-ой по весу добавке к раствору тетраакрилатных олигомеров в хлороформе. Добавление инициатора фотополимеризации приводит к увеличению поглощения в области 370-430 нм [3]. В работе [4] показано, что олигомеры в композиции можно смешивать в различных соотношениях, что приводит к модификации термооптических, механических и прочностных характеристик фотоотвержденного материала в широких пределах.

В этой работе изучены оптические методы формирования многоуровневого микрорельефа в тонких пленках фотополимеризованного гибридного материала «Гибример-ТАТС», и коммерчески выпускаемого аналога OrmoComp® из серии гибридных фотополимеров Ormocer®.

В работе были определены параметры технологических процессов изготовления многоуровневых микроструктур методом прямой лазерной записи на длине волны 405 нм в пленках «Гибример-ТАТС» и OrmoComp®. Показано, что использование дополнительных этапов равномерной экспозиции пленок существенно увеличивает квазилинейный диапазон зависимости рельефа от мощности пучка.

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NOVEL NANOCOMPOSITE MATERIALS FOR OXYGEN SEPARATION MEMBRANES

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Developing catalytic membranes reactors for producing syngas from biofuels by selective oxidation by oxygen separated from air is important problem of hydrogen energy field. The key parts of this problem are design of materials for such membranes functional layers and optimization of techniques of their deposition. General requirements for these materials are chemical and thermomechanical stability under high gradient of the oxygen chemical potential, high oxygen mobility and surface reactivity, high selectivity in the partial oxidation of fuels into syngas and relative cheapness. Nanocomposite materials based upon praseodymium nickelate-cobaltite $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ – $Ce_{0.9}Y_{0.1}O_{2-\delta}$ (PNC – YDC) are promising here due to high oxygen mobility provided by the fast oxygen diffusion channel (D_O up to ~ 10^{-7} cm^2/s at 700 °C), which appeared due to cation redistribution between PNC and YDC nanodomains and developed interface [1,2].

Individual oxides $PrNi_{0.5}Co_{0.5}O_{3-\delta}$ and $Ce_{0.9}Y_{0.1}O_{2-\delta}$ were synthesized by modified Pechini route with PNC – YDC nanocomposite being obtained via ultrasonic dispersion of these powders in isopropanol in weight ratio 1:1. A few PNC – YDC functional layers (mesoporous, microporous and dense), dense $MnFe_2O_4$ – $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ buffer layer and porous $Pt/Sm_{0.15}Pr_{0.15}Ce_{0.35}Zr_{0.3}O_{2-\delta}$ catalytic layer were consecutively deposed on Ni/Al foam substrate. Each layer was sintered at 1100 °C (900 °C for catalytic layer). The membranes obtained were tested in CH_4 selective oxidation into syngas/oxidry reforming.

According to results of testing, the temperature distribution on the membrane surface is sufficiently uniform. The selectivity of methane oxidation into syngas rises with the inlet methane concentration due to decreasing the coverage of the catalytic particles surface by reactive oxygen species. The oxygen permeability of membrane (the oxygen flux is up to 10 ml O_2/cm^2min at 950 °C under air/methane gradient) meets criteria of the practical application [3]. Syngas yield and methane conversion increase with temperature and contact time. The outlet H_2 and CO concentrations ratio varies depending on contact time and the inlet carbon dioxide concentration. H_2/CO concentration ratio is < 1 for contact times < 0.14 s at 950°C (feed 46 % CO_2 + 48 % natural gas + N_2), CH_4 conversion is up to 60 %. Stable performance of the membrane was demonstrated for at least 200 h time-on-stream.

Hence, the materials applied in this work are promising as the functional components of membranes for the oxygen separation from air and methane oxidation into syngas by this oxygen.

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НОВЫЕ НАНОКОМПОЗИТНЫЕ МАТЕРИАЛЫ ДЛЯ КИСЛОРОДПРОВОДЯЩИХ МЕМБРАН

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Разработка каталитических реакторов на основе кислородпроводящих мембран для получения синтез-газа из биотоплив в процессе селективного окисления кислородом, выделяемым из воздуха, является важной задачей современной энергетики. Ключевыми частями данной задачи являются дизайн материалов для функциональных слоёв таких мембран и оптимизация методики их нанесения. Основными требованиями к материалам являются химическая и термомеханическая стабильность при больших градиентах химического потенциала кислорода, высокая подвижность и реакционная способность кислорода, высокий выход синтез-газа и относительная дешевизна. Нанокомпозитные материалы на основе никелата-кобальтита празеодима $PrNi_{0,5}Co_{0,5}O_{3-\delta}$ – $Ce_{0,9}Y_{0,1}O_{2-\delta}$ (PNC – YDC) являются перспективными в данной области благодаря высокой подвижности кислорода (D_O до 10^{-7} см^2/с при 700 °C) [1,2], обеспечиваемой перераспределением катионов между нанодоменами PNC – YDC и развитой межфазной границей. Индивидуальные оксиды $PrNi_{0,5}Co_{0,5}O_{3-\delta}$ и $Ce_{0,9}Y_{0,1}O_{2-\delta}$ были получены модифицированным методом Пекини, а нанокомпозит PNC – YDC – методом ультразвукового диспергирования исходных порошков в изопропаноле в массовом отношении 1:1. На Ni/Al пенометаллическую подложку были последовательно нанесены несколько функциональных слоёв PNC – YDC (мезо-, микропористый и плотный), плотный буферный слой $MnFe_2O_4$ – $Ce_{0,9}Gd_{0,1}O_{2-\delta}$ и пористый слой катализатора $Pt/Sm_{0,15}Pr_{0,15}Ce_{0,35}Zr_{0,3}O_{2-\delta}$. Каждый слой был спечен при 1100 °C (900 °C для каталитического слоя). Полученные мембраны были испытаны на специально оборудованной установке в реакциях селективного окисления и смешанной конверсии природного газа.

Согласно результатам испытания, распределение температуры по поверхности мембраны достаточно однородно. Селективность окисления метана в синтез-газ возрастает с увеличением концентрации метана в подаваемой смеси, что связано с уменьшением степени покрытия кислородом поверхности частиц катализатора. Кислородная проницаемость мембраны (поток кислорода достигает 10 мл O_2/см^{2}мин при 950 °C) достаточно высока для практического применения [3]. Выход синтез-газа и конверсия метана возрастают с увеличением температуры и времени контакта. Отношение концентраций H_2 и CO в продуктах варьируется в зависимости от времени контакта и концентрации CO_2 в подаваемой смеси. Отношение концентраций H_2/CO < 1 при времени контакта $< 0,14$ с при 950 °C (смесь 46 % CO_2 + 48 % природного газа + N_2). Была показана стабильная работа мембраны в течение как минимум 200 ч.

Таким образом, используемые в работе материалы являются перспективными для дизайна мембран селективного выделения кислорода из воздуха и окисления им метана в синтез-газ.

Работа выполнена при финансовой поддержке проекта BIOGO FP7, Российской Академии Наук и Федерального Агентства Научных Организаций (проект № V.45.3.8).

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TRANSFERRING OF CVD-GRAPHENE FROM THE COPPER SUBSTRATE TO THE POLYMER SUBSTRATE

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Graphene is a single layer of graphite. Due to such properties as: high thermal - and electro conductivity, chemical stability, mechanical strength, transparency, graphene has become a promising material for numerous applications: optoelectronics and nanoelectronics, composites, gas sensors, transparent electrodes, and others.

One way to obtain graphene is a chemical vapor deposition (CVD) on copper. Investigation of electrical and optical properties of graphene on copper is impossible, because copper is conductor and not transparent to the optical radiation in the visible range. Therefore it is necessary to transfer the graphene on a non-conductive transparent substrate. Various methods of transfer on polymer and silicon substrates are used for this purpose [1].

The aim of this work is investigation of the various transfer methods CVD-graphene to the polymer, and the measurement of electrical resistance and transparency of the samples.

In this paper we used a few layer graphene (3-5 layers), prepared by the CVD method on copper [2]. Transfer of graphene to the polymer implemented in two ways. In the first case, the PET polymer with EVA adhesive composition under heat and pressure was applied to the copper coated with graphene, then mechanically cleaved (G/PET-mech). Graphene is transferred to the polymer because the adhesion with polymer is greater than with copper. Also, copper was removed by dissolving in a 40% solution of nitric acid (G/PET-chem). In the second case PMMA polymer dissolved in acetone and applied to copper coated with graphene by spin coating. When the polymer has hardened, copper dissolved in 40% solution of nitric acid (G/PMMA-chem). In mechanical separation of the PMMA and copper substrate, graphene transfer did not occur or occurred in part (G/PMMA-mech). In the sample there is no conductivity.

For G/PET-mech resistance was 21 ohms / sq. For G/PET-chem resistance was 2.6 ohms / sq. Increased resistance can be explained by mechanical deformation of graphene transfer. For G/PMMA-chem resistance was 1.2 ohms / sq. When hot pressing form the mechanical stresses that can damage the graphene film and hence increase its resistance.

Transmittance in the visible range of the spectrum for the PMMA film without graphene is 90% and the PET - 85%. Transparency of G/PMMA-chem was 65%. Transparency of G/PET-mech was 55%. Transparency of G/PET-chem was 70%. Transmittances have an error in the vicinity of 10%, related to the heterogeneity of the thickness of the polymer films. A significant reduction in the transmittance in the G/PET-mech case is associated with deformation of graphene. In the G/PMMA-chem case, the formation of air bubbles observed in the resulting film, it affects on transparency. Degassing of PMMA solution would lead to increasing the transparency of the G/PMMA-chem composite.

The paper compares the transfer methods CVD-graphene with hot pressing on a PET polymer and by applying the dissolved PMMA. The most promising is a method of transfer by applying the dissolved PMMA with followed chemical etching of copper. Graphene is less damaged; the electrical resistance of the sample is lower.

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With 125 research and engineering facilities worldwide, we place strong emphasis on developing innovative technology that adds value for our customers. In 2015, we invested $1.1 billion in R&E.

The search for oil and gas has three objectives: to identify and evaluate hydrocarbon-bearing reservoirs; to bring hydrocarbons to the surface safely and cost-effectively, without harming the environment; and to maximize the yield from each discovery. These objectives can be advanced only by ongoing research into all aspects of the exploration, drilling, and production processes.

Since it first established a research laboratory in 1948 in Ridgefield, Connecticut, USA, Schlumberger has maintained an unwavering, long-term commitment to research. Schlumberger research has grown geographically and in its range of disciplines into a global network of research centers, expressly to tap into the astonishing breadth and diversity of technology innovation in the 21st century.

In 2007, the Ridgefield lab, renamed Schlumberger-Doll Research in 1965, moved to a new facility in Cambridge, Massachusetts, USA, one of six Schlumberger research labs worldwide. Schlumberger Gould Research opened in 1982 near the campus of Cambridge University in the UK; Schlumberger Moscow Research and Schlumberger Stavanger Research opened in their eponymous cities in the mid-1990s. The company’s two newest research labs are the Schlumberger Dhahran Carbonate Research Center, opened in 2006 near the campus of King Fahd University of Petroleum and Minerals in Saudi Arabia, and Schlumberger Brazil Research and Geoengineering Center, which opened in 2010 on the campus of the Federal University of Rio de Janeiro.

Our research is often conducted in partnership with universities and customers around the world. This ensures close contact with leading-edge research in all relevant disciplines, improves understanding of clients' challenges, and facilitates the validation of research ideas in field experiments at an early stage in the product development cycle.

The first Schlumberger research laboratory, founded in 1948 in Ridgefield, onnecticut, focused on a scientific research program assembled by Henri Doll. The objective of the program was to invent new subsurface measurements that would expand the growing Schlumberger wireline business. In 1965, the laboratory was renamed Schlumberger-Doll Research Center (SDR) after Henri Doll, then-retiring chairman, who was by that time the foremost technical contributor at Schlumberger. SDR has since focused on scientific research to invent and develop the Schlumberger products and services of the future.

In 2006, SDR moved to Cambridge, Massachusetts, a major hub of science and technological innovation in the US, placing the center in close proximity to institutions working at the forefront of numerous disciplines. Currently, SDR comprises five major scientific groups reflecting its historical strength in subsurface measurements as well as new directions that are enabled by a presence in Cambridge, Massachusetts.

Sensor physics: Sensor physics looks at the experimental and theoretical aspects of developing the hardware of subsurface measurements, conveyed by a variety of methods from wireline to wire drilling and coiled tubing, through permanent installations.

Mathematics and modeling: The mathematics and modeling department works on the issues surrounding the processing and inversion of data produced by subsurface measurements conveyed by all possible means.

Reservoir geosciences: Reservoir geosciences scientists investigate how processed and inverted data from oil and gas measurements can be translated into relevant petrophysical decisions for Schlumberger's customers.

Mechanics and materials science: Scientists in mechanics and materials science conduct leading-edge research into how mechanical engineering and in materials science can effectively impact for oil and gas applications.

CO_2 mitigation and sequestration: The CO2 mitigation department investigates all aspects of science and understanding of injecting CO2 into the subsurface, ranging from wellsite evaluation and selection, monitoring, geomechanics, and thermodynamics, for CO2 sequestration and enhanced recovery.

Компания «Шлюмберже» (Schlumberger) является ведущим мировым поставщиком технологий для комплексной оценки пласта, строительства скважин, управления добычей и переработки углеводородов.

Компания работает более чем в 85 странах мира и насчитывает около 113 000 сотрудников свыше 140 национальностей. «Шлюмберже» предоставляет самый широкий в отрасли спектр продуктов и услуг — от проведения геологоразведочных работ до управления добычей, а также комплексные решения, охватывающие весь производственный цикл — от пласта до трубопровода, для оптимизации добычи углеводородов и эффективной эксплуатации месторождения.

Штаб-квартиры компании «Шлюмберже Лимитед» (Schlumberger Limited) расположены в Париже, Хьюстоне, Лондоне и Гааге. В 2015 году выручка компании составила 35,47 млрд долл. США. Для получения более подробной информации посетите сайт www.slb.com.

Новосибирский технологический центр (НТЦ) был открыт в 2004 году. В общей структуре «Шлюмберже» он является основным центром разработки технологий в области гидравлического разрыва пласта (ГРП) и экологических аспектов тестирования скважин.

Центр базируется на территории новосибирского Академгородка, известного во всем мире своим научным потенциалом. НТЦ активно взаимодействует с партнерами из Сибирского отделения РАН, проводя совместные научные исследования и опытные разработки. Специалисты НТЦ известны в других подразделеняхй компании «Шлюмберже» за счет высокого уровня знаний, технической экспертизы и активной жизненной позицией. Сотрудников, которые заложили основы карьерного роста в НТЦ, можно встретить во многих подразделениях компании по всему миру.

Новосибирский технологический центр «Шлюмберже», Новосибирск, 630060, ул. Зеленая горка, 1/10, Телефон: +7 (3833) 63 05 44

The *Nauchnoe Oborudovanie* group of companies was founded in 1999

It is one of the biggest suppliers of scientific and industrial equipment in Siberia and in the Far East with core activities covering provision of research institutes and industrial enterprises with high-tech equipment.

We analyze the customer's problem and select appropriate equipment to deal with a specific challenge. We supply instruments, provide technological and methodological support as well as warranty and post-warranty service. From delivering a single product to fulfilling complete enterprise supply programs, *Nauchnoe Oborudovanie* always meets its commitments and has gained the reputation of so reliable partner that some customers entrust us with complete equipping of their laboratories including both instruments and consumables.

Highly skilled technical specialists with their own research experience who constantly improve their professional level make our team. We regularly get acquainted with the new equipment and approaches in instrument engineering, and attend international exhibitions and training seminars organized by the manufacturers. We can offer the most advanced solutions for any customers' task. The existing working relationship with many laboratories of SB RAS allows inviting field experts to satisfy the customer's unique needs. Moreover, we conduct workshops providing our customers with an opportunity to try the latest equipment.

We have established partnership relations with many the world's leading manufacturers of scientific and technological equipment, both in Russia and abroad. Besides, we have our own engineering department; if necessary, we can develop and produce an instrument to solve the customer's problem.

The institutes of the Siberian Branch of the Russian Academy of Sciences focused on the fundamental research, many industrial enterprises, engineering companies, higher education institutions of the Siberian and Far Eastern regions are among our customers.

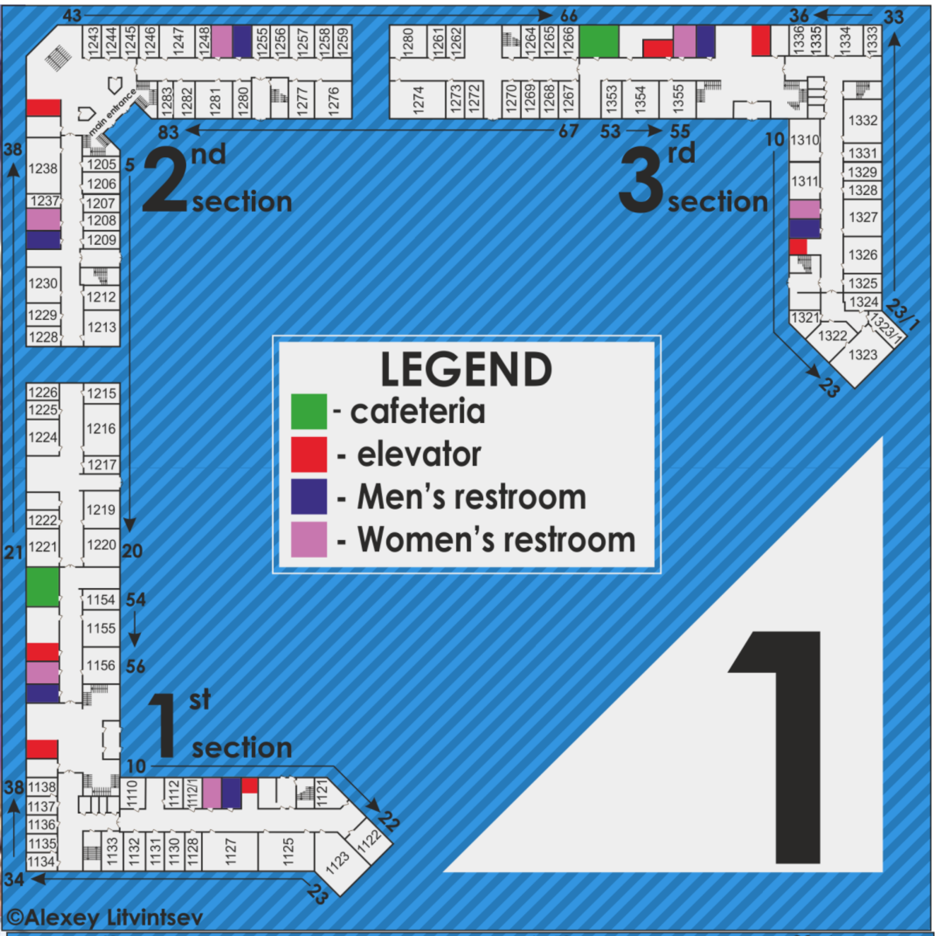
In addition to supply and production of equipment, we are engaged in the promotion of the scientific developments with commercial potential of institutes of the Russian Academy of Sciences in the foreign markets, and organize joint projects of the SB RAS institutes with different organizations to develop specific technological and knowledge-based solutions

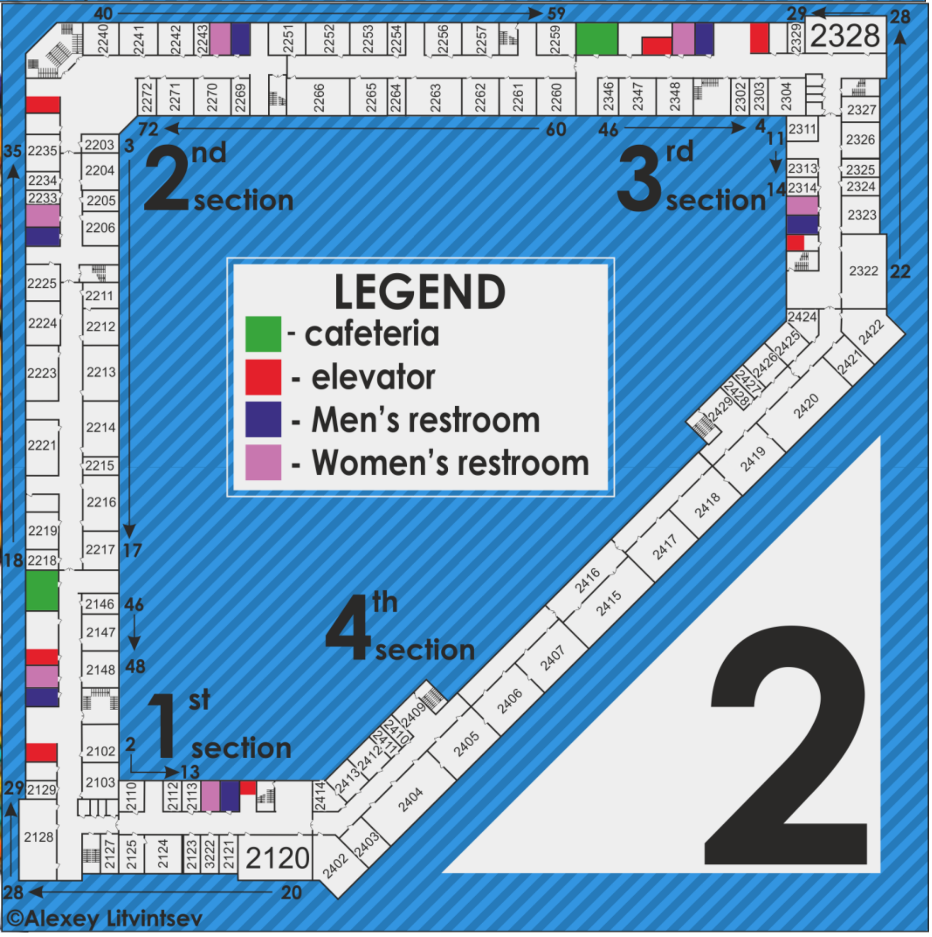
.

We see our goal to create and maintain long-standing mutually beneficial relationships with each customer.

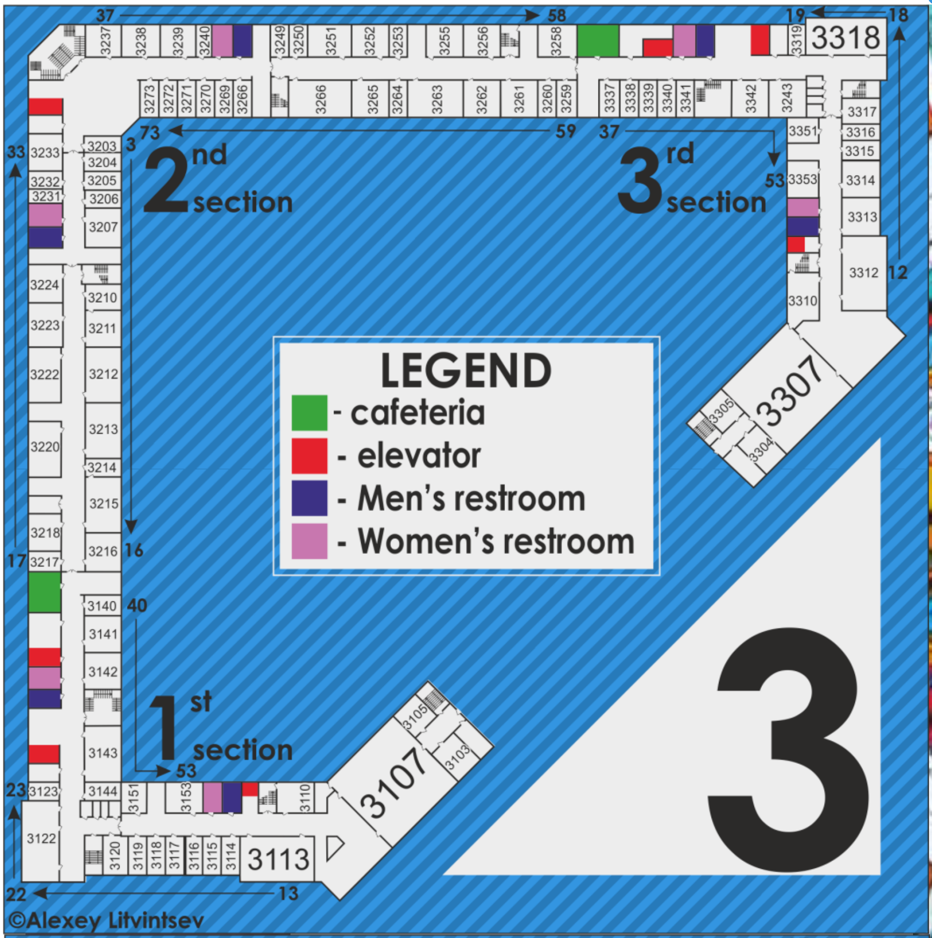
http://spegroup.ru/

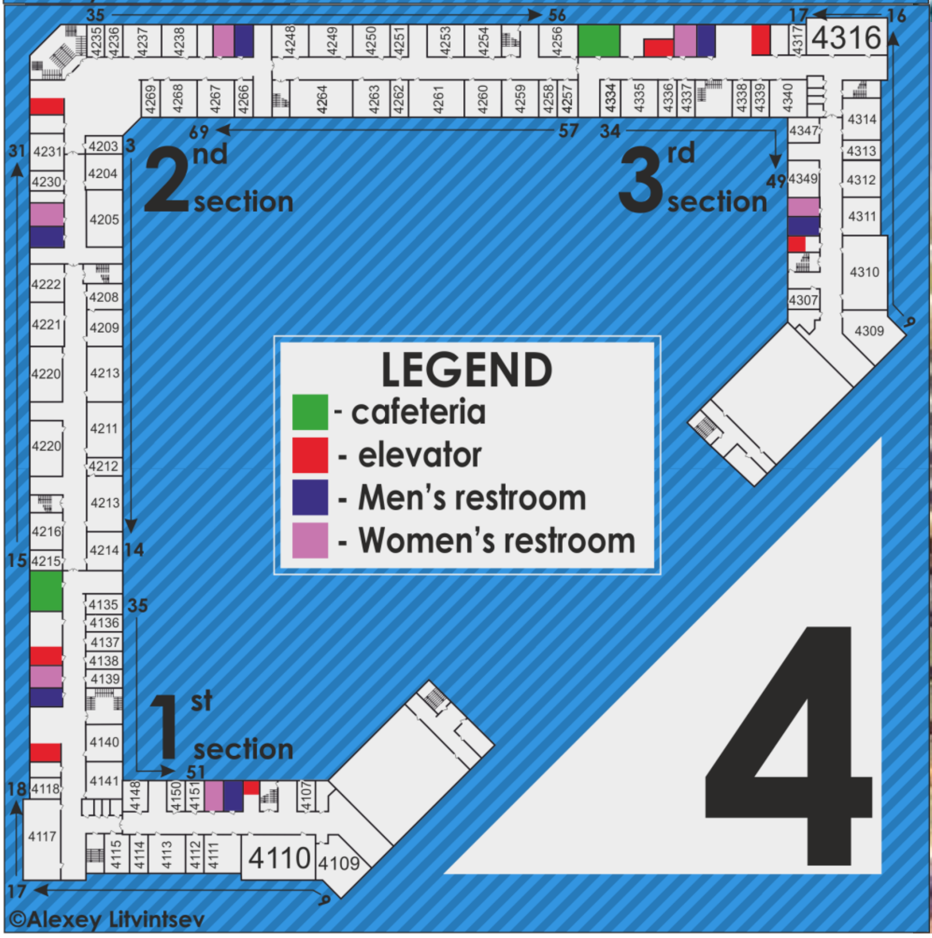
Plan of NSU new building



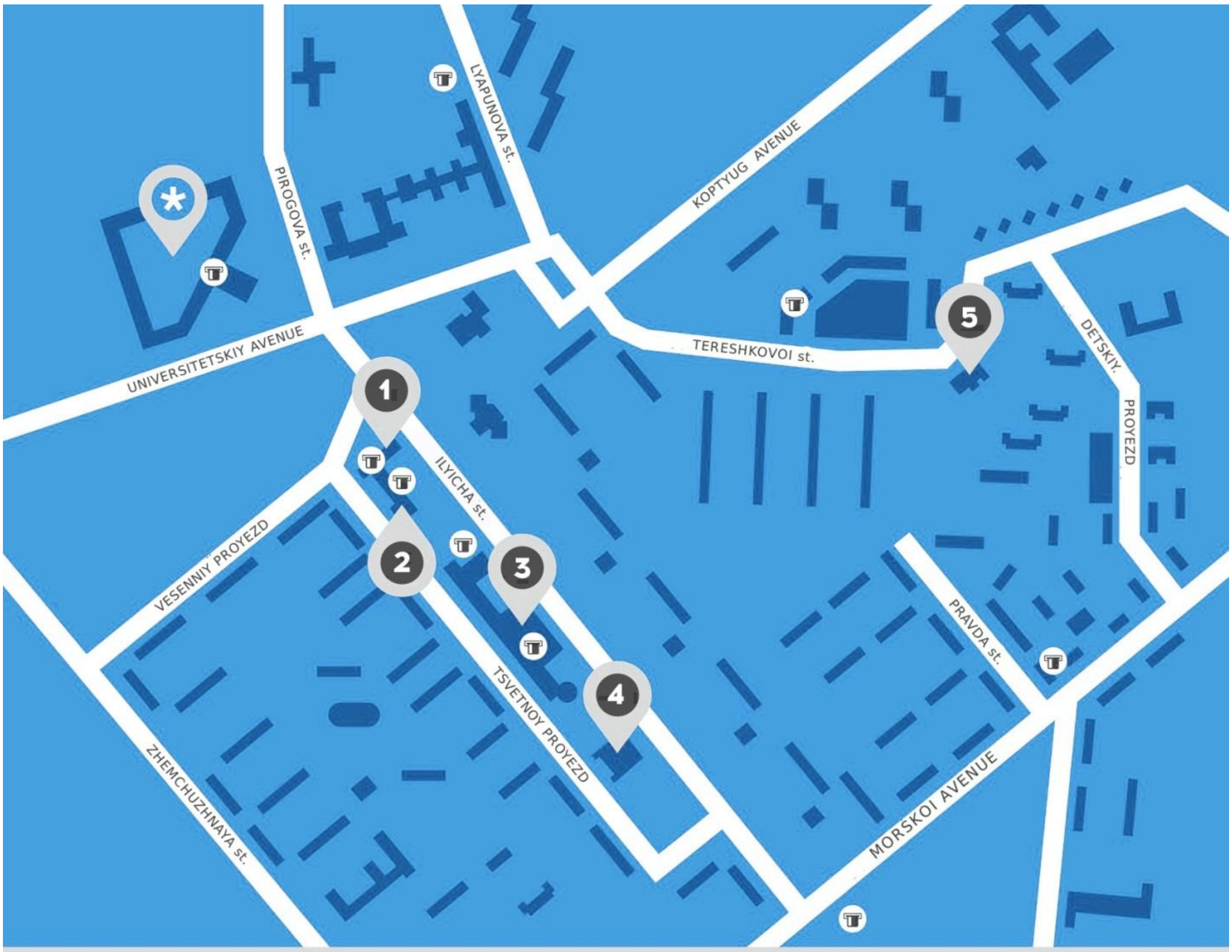


Plan of NSU new building





Akademgorodok



MAP OF RESTAURANTS & PLACES TO EAT NEARBY

✪ NSU

1 Pirogova Street

① 10 Ilyicha Street

✪—○ 300 м

Veranda

Teahouse

+7 905-934-08-09

💵 💳

SPOT & CHOO'S BURGERS

Burger shop

💵 💳

② 8 Ilyicha Street

✪—○ 380 м

SPARKS HOME KITCHEN

Bar, Cafe

+7 (383) 286-20-50

💵 💳

③ 6 Ilyicha Street

✪—○ 450 м

Vostok-Zapad

Cafe, 1-2 floor

+7 (383) 330-84-40

💵 💳

Vilka-Lojka

Canteen

+7 (383) 330-82-90

💵 💳

Pechki-Lavochki

Pub

+7 (383) 330-82-90

💵 💳

④ 4 Ilyicha Street

✪—○ 720 м

TRAVELER'S COFFEE

Coffee house

+7 (383) 233-22-70

💵 💳

⑤ 12a Tereshkovoy Street

✪—○ 900 м

АРТ П.А.Б.

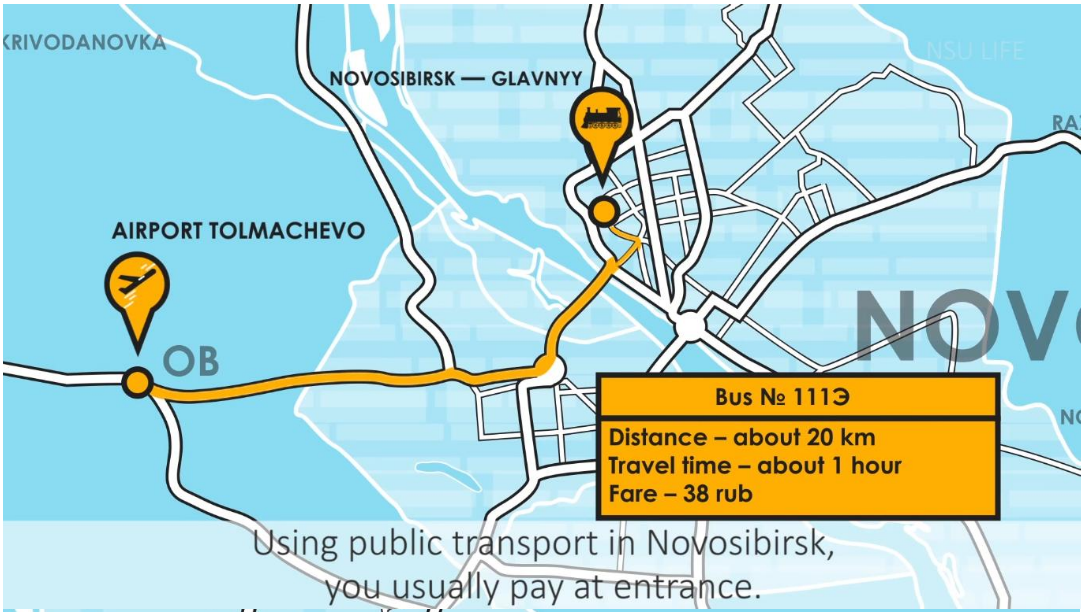
Bar, restaurant

+7-913-773-86-11

💵 💳

🏧 **CASH MACHINE**	💵 **CASH PAYMENT**
✪—○ **DISTANCE FROM NSU**	💳 **PAYMENT BY CARD**

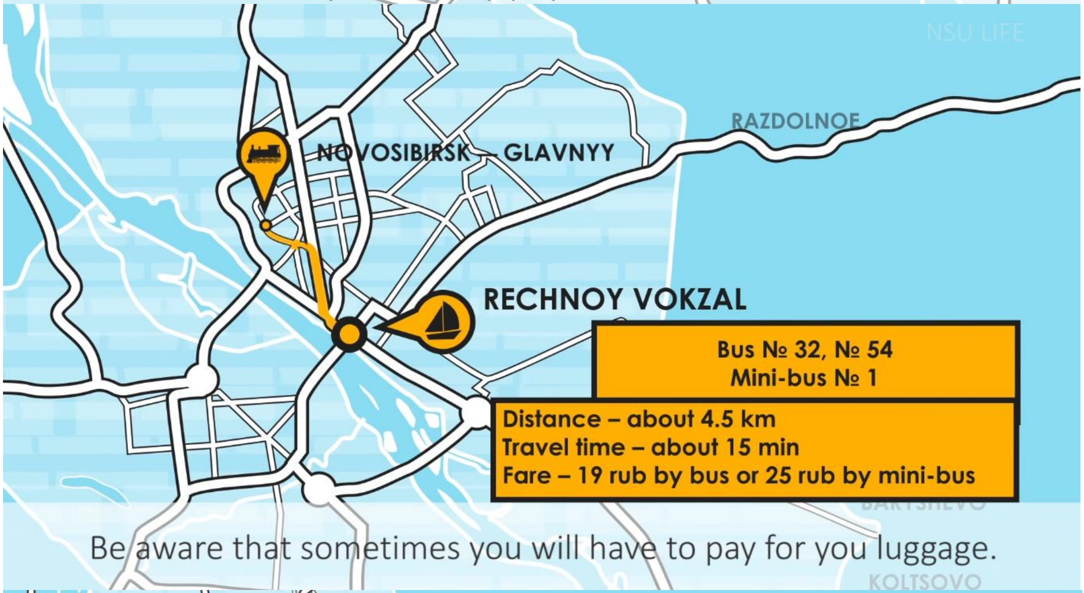
Novosibirsk



Bus № 111Э

Distance – about 20 km
Travel time – about 1 hour
Fare – 38 rub

Using public transport in Novosibirsk, you usually pay at entrance.



Bus № 32, № 54
Mini-bus № 1

Distance – about 4.5 km
Travel time – about 15 min
Fare – 19 rub by bus or 25 rub by mini-bus

Be aware that sometimes you will have to pay for you luggage.

Mini-bus № 35

Distance – about 27 km
Travel time – about 45 min
Fare - 43 rub.

Bus № 8

Distance – about 27 km
Travel time – about 1h 20 min
Fare — 19 rub

Useful contacts

The secretaries of the Organizing Committee:

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Scientific Publication

PROCEEDINGS
OF THE 2016 RUSSIA-JAPAN CONFERENCE

ADVANCED MATERIALS: SYNTHESIS, PROCESSING AND PROPERTIES OF NANOSTRUCTURES

October, 30st - November, 3rd, 2016

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For notes

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