

Masked deposition of decorative coatings on large area glass and plastic sheets

B. Straumal^{a, c, *}, N. Vershinin^{b, d}, K. Filonov^d, R. Dimitriou^c, W. Gust^a

^a*Institut für Metallkunde, Universität Stuttgart, Seestr. 92, 70174 Stuttgart, Germany*

^b*I.V.T. Ltd. (Institute for Vacuum Technology), P.O. Box 47, 109180 Moscow, Russia*

^c*Institute of Solid State Physics, Chernogolovka, Moscow District 142432, Russia*

^d*SONG Ltd., P.O. Box 98, Chernogolovka, Moscow District 142432, Russia*

Abstract

An industrial installation for vacuum arc deposition is presented. Its potential in the field of decorative coatings for large area glass and plastic sheets is demonstrated, particularly its ability to deposit the patterned coatings with the aid of a textile polymeric mask. Titanium nitride, titanium dioxide and bilayer TiN/TiO₂ coatings on silica glass have been characterized in terms of composition and corrosion resistance. The corrosion resistance of TiN coatings is higher than the corrosion resistance of TiO₂. The corrosion resistance of vacuum arc deposited TiN coatings on glass prove to be higher than that of TiN coatings produced by DC reactive sputtering and plasma assisted chemical vapour deposition. Mask-deposited TiN coatings do not show any signs of accelerated corrosion along the border between coated and uncoated glass. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium nitride; Titanium dioxide; Glass; Corrosion; Auger electron spectroscopy

1. Introduction

Due to their attractive properties, TiN coatings have been extensively used in various fields of application. This nitride of a transition metal has a high melting point, a high hardness value, advantageous optical properties and metallic conductivity. Coating of cutting tools for increasing wear resistance is probably the best known application [1,2]. More specific examples of TiN utilization include diffusion barriers for semiconductors [3] or filtering by ultra fine particles [4]. TiN coating on glass is also popular for the production of decorative panels in architecture or solar glass in automotive industry. The reflected colours are silver, blue and gold whereas transmitted ones are brown and grey [5]. Titanium dioxide is widely used in optics because it is a low cost transparent material, having a high refractive index and good stability. TiO₂ possess also a high dielectric constant and excellent transmittance in the visible and near-infrared frequencies. Therefore, TiO₂ coatings have found extensive use in a great variety of applications, including antireflection coatings, sensors and photocatalysts [6,7]. TiN and TiO₂ films can be prepared by various deposition techniques

such as reactive DC and rf diode or magnetron sputtering, ion beam techniques, chemical vapour deposition (CVD) techniques, evaporation under vacuum [8–18] and by wet chemical deposition methods (TiO₂, [19]). With all these deposition techniques TiN and TiO₂ films can be produced with largely varying structures and properties [19,20].

Vacuum arc deposition is a process in which material to be deposited is vaporized under the impact of an electric arc formed between an anode and the target which acts as the cathode. The discharge does not require the introduction of a gas like in sputtering. Advantages are a low contamination, a high degree of ionization of the evaporated species and a high deposition rate. The ionized species travel towards the substrate at much greater energies than in conventional evaporation, thus increasing the quality of the resulting deposited layer. Together with charged species, the arc impact generates also microdroplets which prevent the utilization of vacuum arc deposition for the production of optical coatings. However, the high coverage capacity and the low substrate temperature during deposition open a wide range of possibilities in the field of decorative coatings. Low thermally resistant materials like plastics, wood or paper can be coated with metals, nitrides or oxides. Light polymeric masks can also be used for the production of patterned decorative glass. Generally, the vacuum arc deposition is a low cost process, easy to manipulate and

* Corresponding author. Tel.: + 49-711-121-1276; fax: +49-711-121-1280.

E-mail addresses: straumal@mf.mpi-stuttgart.mpg.de (B. Straumal); straumal@issp.ac.ru (B. Straumal)

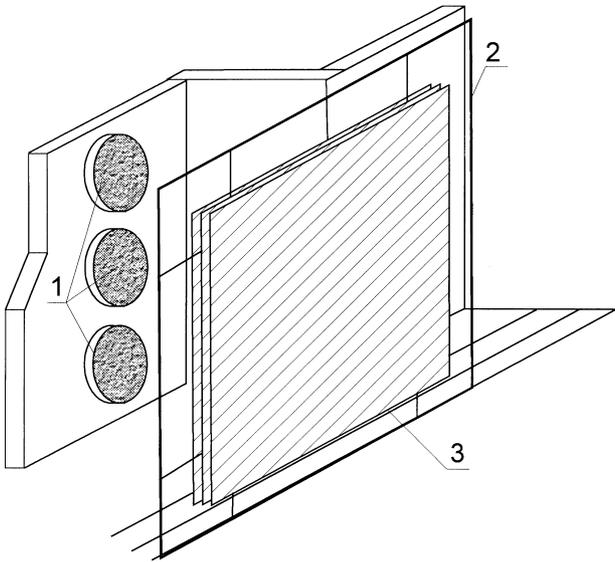


Fig. 1. Scheme of the industrial configuration for glass decorative coating: (1) Metallic cathodes, (2) mobile frame, (3) glass sheets mounted back to back.

applicable to obtain coatings on large-areas. The apparatus 'Nikolay' was used for the vacuum arc masked deposition of decorative coatings on large area glass and plastic sheets. Examples of nylon mask-coated silica glass with titanium nitride, titanium dioxide and bilayer TiN/TiO₂ coating are

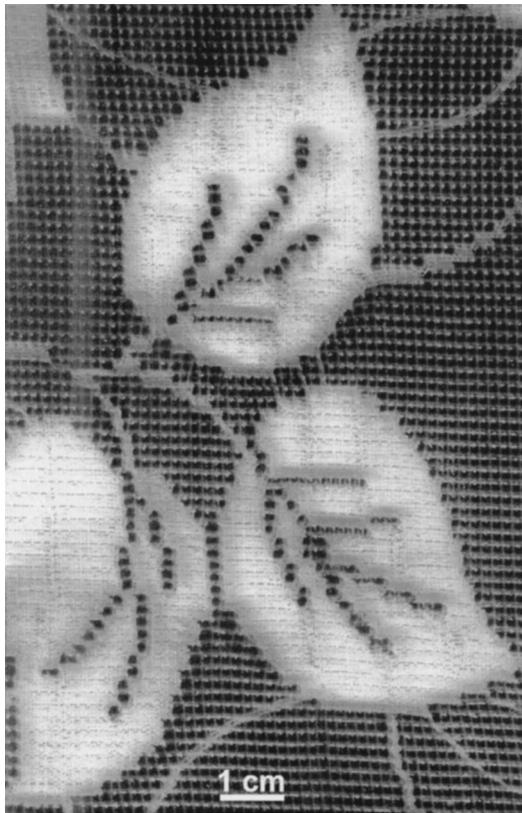


Fig. 2. Detail of a decorative pattern obtained by masking during TiN arc deposition on silica glass.

presented. The composition and corrosion resistance of the coatings are discussed.

2. Experimental

2.1. Deposition of TiN and TiO₂

The industrial scale set-up 'Nikolay' (Fig. 1) used for the sample production has the following characteristics: size 6000 × 3000 × 3000 mm, mass 15 500 kg, maximum power consumed 75 kW, ultimate vacuum 5×10^{-4} Pa, maximum size of treated glass 2100 × 1300 × 8 mm, maximum size of roll material 400 × 1400 mm, output capacity for glass 30 glass sheets 2100 × 1300 × 5 mm in a cycle, up to 1000 m²/month, output capacity for the roll materials up to 1 m²/min. A standard procedure for glass decorative coating includes three steps. The glass sheet before being loaded into the machine is precleaned using hot distilled water. After precleaning, the glass sheets are mounted on metallic frames and placed in the machine vacuum chamber. Each frame contains two glass sheets, mounted back to back. The frame is inserted into a slot (15 slots are available) and allowed to move independently inside the machine, in order to receive different treatment operations. The displacement velocity of the frame is monitored and can be controlled. Each frame receives in turn a cleaning treatment followed immediately by a coating in order to prevent recontamination. The complete treatment involves one return of the frame for cleaning and another return for coating. Cleaning is performed using a large aperture Hall current accelerator, providing high energetic ions which impact and sputter the substrate surface. The description of the Hall current accelerator and its performances is given elsewhere [21]. A Hall current accelerator is placed on each side of the machine in order to clean the two sheets of the frame in one shot. The sputter dose received by the glass sheet depends mostly on the frame velocity and the distance to the cleaning source. Due to the asymmetry of the frame position relative to the two sources, the thickness of the sputtered layer differs for the two sheets mounted back to back on a given frame.

Nevertheless, the high power provides a sufficient cleaning of both surfaces in any circumstances. The coating in the industrial set-up is performed using four circular targets of 200 mm diameter. Two targets are placed on each side of the installation. When depositing titanium, the source voltage is 20 V for a 300 A current. A reactive gas (oxygen) is introduced at 0.05 Pa if oxide coating is to be formed. TiN coating is obtained by introducing nitrogen at a pressure of about 0.05 Pa. The arc generation is continuous and random. As microdroplets are ejected at small angles [22] with respect to the target surface, this configuration provides shielding and enables to increase the charged particles component of the beam. As for cleaning, the thickness of the deposited layer is controlled by varying the translation speed of the

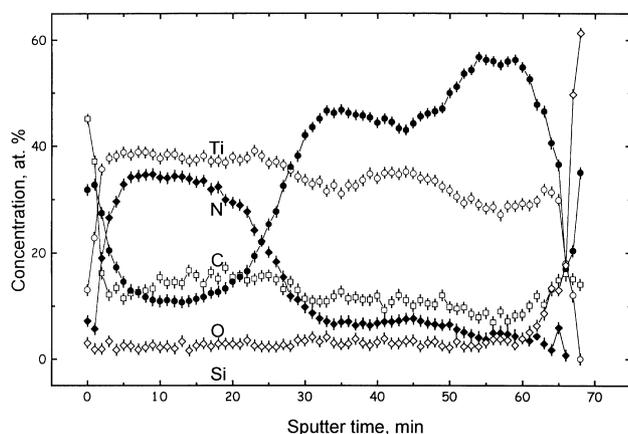


Fig. 3. AES depth profile for TiN/TiO₂ bilayer coating on silica glass. The experimental points are connected with the guidelines for the eye. The bars correspond to the statistical error of the spectrometer counting.

frame. Glass, metal and plastic sheets have been successfully coated with TiN, TiO₂ and bilayer of TiN/TiO₂. When decorative patterns have to be produced, light nylon patterned sheets are used to provide masking. Fig. 2 shows an example of pattern on TiN decorative glass masked with a textile nylon material. Various colours can be produced depending on the gas and deposition parameters used. In this study TiN, TiO₂ and TiN/TiO₂ coated silica glass samples were cut from large glass sheets and analysed regarding composition and corrosion resistance.

2.2. Auger electron spectroscopy

The composition depth profile of TiN/TiO₂ coated silica glass was made by Auger electron spectroscopy (AES). The specimens were mounted in the loadings of the spectrometer carousel holder and sequentially rotated into the analysis position. The analysis was carried out with the excitation beam normal to the specimens. The spectra were taken during argon ion sputtering which produced a relatively clean surface of the sample under study without baking the system. The etching rate was considerably faster than the adsorption rate of the active residual gases. The Auger spectra were measured on a PHI-551 spectrometer with a double-pass cylindrical mirror analyzer. The base pressure was less than 2×10^{-8} Pa. The spectra were excited by an electron beam with an energy of 3 keV and a current of 8 μ A through the sample. The peak-to-peak modulation was 3 V. The sputtering was accomplished using a 5 keV Ar⁺ ion beam. An ion gun was mounted to give a beam incidence angle of 70°, and in order to minimize possible crater effects, it was rastered. The pressure of argon during sputtering was equal to 3×10^{-3} Pa. The sputter rates were determined to be 25 nm/min relative to SiO₂. Auger studies of the Ti–N system are complicated by the fact that the main Auger KL_{2,3}L_{2,3} transition for nitrogen (379 eV) overlaps the titanium L₃M_{2,3}M_{2,3} transition (383 eV) to produce a single peak at 385 eV [23]. Auger spectra of titanium nitride coat-

ing hence include two peaks, the one corresponding to the Ti L₃M_{2,3}M_{4,5} transition (418 eV) and the TiN peak resulting from overlapping (385 eV). For quantitative analysis, one must be able to resolve the nitrogen peak by removing the titanium contribution to the 385 eV peak. This was performed using the method described in [24] where the approach [23] was improved.

2.3. Electrochemical tests

The corrosion behaviour of both TiN and TiO₂ coatings on silica glass was characterized. The standard accelerated tests on atmospheric corrosion were carried out according to the Russian standards RST 9.012, 9.017 and 9.020 (temperature 22–25°C, humidity 96–98%, no water condensation, under influence of gaseous chlorides, ammoniac and SO₂). The accelerated test in 3.5% NaCl solution at 22–25°C under both full and partial immersion was also carried out. Both uniform and mask-deposited TiN coatings were studied because on the border between coated and uncoated glass the TiN/glass interface is exposed to the corrosion medium. The polarization behaviour was measured potentiodynamically with the aid of a potentiostatic apparatus PI-50-1/PR8. All potential values are given versus the Ag/AgCl electrode ($E_{\text{Ag/AgCl}} = 0$ corresponds to -200 mV in the hydrogen electrode scale). The scanning rate was 1 mV/s. The polarization was changed from -0.8 V to $+1.5$ V. Before potentiodynamic measurements, the corrosion potential E_c was monitored for 1.5 h. The measurement was carried out in an electrolyte of 3.5% NaCl solution with pH = 7 and pH = 3. The correction of the pH of NaCl solution was carried out by addition of 0.01 mol of HCl. The pH value of a solution was controlled by a pH-meter 'pH-121'. The solution was prepared from reagent-grade chemicals and distilled water. The area exposed to solution was 1 cm². The test temperature was 22–25°C.

3. Results and discussion

3.1. Mask-deposited TiN coating on silica glass

In Fig. 2 the fragment of the TiN mask-coated glass sheet is shown. A nylon textile material is used as mask. The dark gray colour corresponds to the TiN coated areas, the masked areas are white. It can be easily seen that a gradual transition between coated and uncoated areas exist because the mask was kept at a certain distance from the glass substrate. The textile mask does not show any sign of thermal deterioration even after tens of deposition runs. The mask has to be exchanged only after heavy contamination with deposited TiN and/or TiO₂.

3.2. Coating composition

The depth concentration profile obtained from the Auger spectra is shown in Fig. 3 for the TiN/TiO₂ bilayer coating

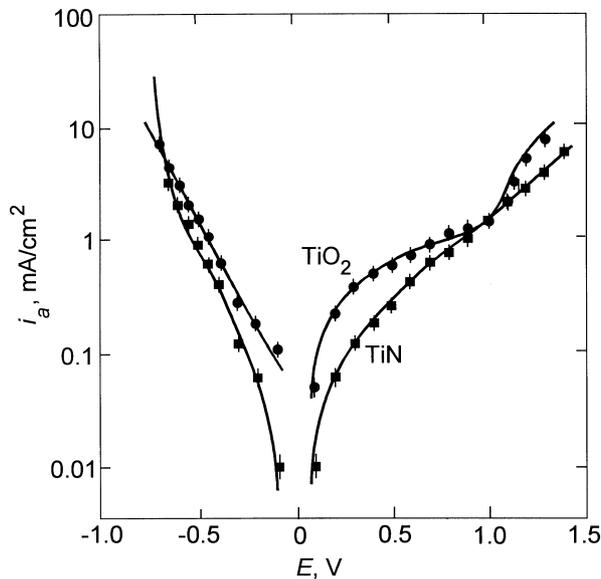


Fig. 4. Dependence of the anodic current i_a on the polarization voltage E for TiO_2 and TiN coatings on silica glass in NaCl solution at $\text{pH} = 7$. The experimental points are connected with the guidelines for the eye. The error bars correspond to the standard deviation of the measurements.

on silica glass. The peaks characteristic for titanium, oxygen, nitrogen, carbon and silicon were analyzed. After about 3 min of sputtering, the surface contamination of carbon and oxygen disappear from the spectra. After that, the oxygen content remains unchanged in the TiN layer and the carbon concentration is nearly constant in the whole coating (slightly below 10 at.%). Quantitative analysis reveals that the Ti to N ratio in the TiN layer is about 1.1. After about 25 min of sputtering, the transition from the TiN

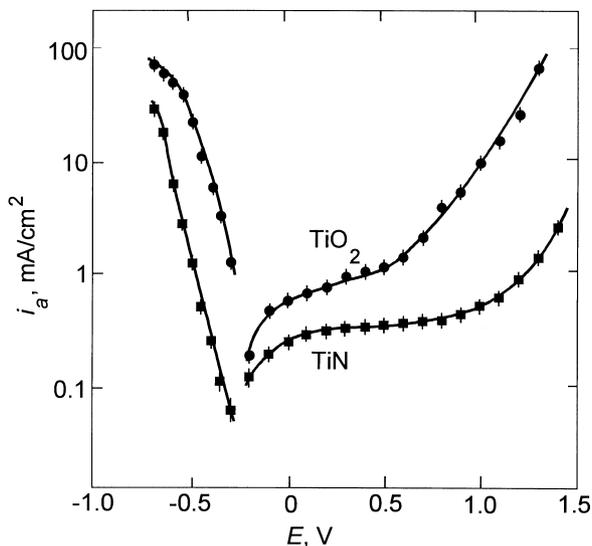


Fig. 5. Dependence of the anodic current i_a on the polarization voltage E for TiO_2 and TiN coatings on silica glass in NaCl solution at $\text{pH} = 3$. The experimental points are connected with the guidelines for the eye. The error bars correspond to the standard deviation of the measurements.

to TiO_2 layer can be clearly seen. The titanium content is roughly uniform along the depth of the coating. The increasing concentration of silicon marks the transition from the coating to substrate. At the coating/substrate interface, nitrogen is virtually absent and the oxygen content climbs up to 60 at.% as the titanium content slightly falls down to 30 at.%. The stability of the composition of the TiN layer which does not change significantly with depth is comparable with that of TiN coatings obtained with the CVD technique [25]. Regarding composition, our TiN samples are similar to those ones obtained by the use of plasma-assisted chemical vapor deposition (PACVD) deposited at 430°C substrate temperature, 60 W rf power presented in [26]. With such films the stoichiometric composition was obtained for substrate temperatures above 500°C [26]. In our case the substrate temperature is well below 100°C which allows one to use polymer masks for the deposition of patterned TiN and TiO_2 coatings. It was shown [17] that even a rather high residual carbon content does not affect drastically the properties of TiO_2 . In our case, the high corrosion resistance of the vacuum arc deposited coatings (see Section 3.3) also reveals that the carbon contamination is not critical.

3.3. Electrochemical properties

After 3 months of tests in atmospheric corrosion with conditions which correspond to the most aggressive part of the industrial atmosphere, no changes of mass and appearance in the characterized samples was monitored. It demonstrates the high resistance against atmospheric corrosion of the characterized TiN and TiO_2 coatings on silica glass. The corrosion tests carried out in a NaCl solution during 3 months also showed no changes in the mass and appearance of the samples both by full immersion and by partial immersion in the zone of contact between solution and air. This high corrosion resistance is comparable with the properties of vacuum arc deposited TiN coatings on steel and brass substrates [27]. The mask-deposited TiN coatings do not show any signs of accelerated corrosion along the border between coated and uncoated glass.

The data of electrochemical tests are displayed in Fig. 4 ($\text{pH} = 7$) and 5 ($\text{pH} = 3$). For both TiN and TiO_2 no active peaks are present and the coatings are in the self-passivated state. For $\text{pH} = 7$ $E_c(\text{TiN}) = 0.12$ V and $E_c(\text{TiO}_2) = 0.25$ V. Therefore, in a neutral NaCl solution the corrosion potential of TiN is lower than that of TiO_2 . Nevertheless, it can be seen in Fig. 3 that both cathodic and anodic processes are less pronounced on the surface of TiN in comparison with TiO_2 . Furthermore, the anodic current i_a for TiN is very small up to +0.5 V, and by the anodic polarization of TiO_2 the i_a value is rather high already at +0.1 V. This means that though the E_c value of TiO_2 is high enough, its surface can be activated and the local corrosion process of TiO_2 can start.

In acidic solution the difference between TiN and TiO_2

coatings is more pronounced (Fig. 5). For $\text{pH} = 3$ $E_c(\text{TiN}) = 0.47 \text{ V}$ and $E_c(\text{TiO}_2) = 0.17 \text{ V}$. Therefore, in acidic NaCl solutions the corrosion potential of TiN is higher than that of TiO_2 . The rate of the corrosion process for TiN coating remains practically unchanged compared to $\text{pH} = 7$ (Fig. 4), but i_a of TiO_2 is about one order of magnitude higher than at $\text{pH} = 7$. It is also important to mention that at voltages of anodic polarization of TiO_2 oscillations of i_a take place. These oscillations mean that the local repeated corrosion attack of the coating surface layer proceeds and that the surface is repeatedly activated.

Numerous papers report data on the electrochemical properties of TiN deposited on metallic substrates like tool steel [26–32]. The corrosion process of TiN/steel is rather complicated and includes, together with corrosion of TiN, the corrosion of the steel substrate. It can be controlled by the penetration of the corrosion agents both along the interface between the coating and substrate and through defects in the coating. In order to discuss correctly our results, we should use the data on electrochemical properties of TiN deposited on glass by reactive DC sputtering [32] and on Al_2O_3 by PACVD [28]. Both glass and Al_2O_3 substrates are inert from the corrosion point of view. Therefore, these data characterize the intrinsic properties of TiN rather than a combination of corrosion processes of both substrate and coating. The values of corrosion current density, i_c (established as the current density on the cathodic polarization curve corresponding to the E_c) reported in [28,32] are of the same order of magnitude as in our work. The corrosion potential E_c of TiN in a neutral NaCl solution in our work is about 0.15 mV more positive than E_c reported in [31] for the same electrochemical conditions. In [28] the data are given for $\text{pH} = 1$ ($E_c = -0.23 \text{ V}$, recalculated for the Ag/AgCl electrode) and $\text{pH} = 12$ ($E_c = -0.33 \text{ V}$) which is much lower than both values obtained in this work. The pronounced anodic peak is present in all potentiodynamic curves presented in [32]. In this work no active peak is present and the coatings are in the self-passivated state. Therefore, the corrosion resistance of TiN deposited by the vacuum arc process is definitely higher than that of TiN coatings deposited on silica glass substrates by reactive DC sputtering [32] and on Al_2O_3 substrates by PACVD [28].

4. Conclusions

The vacuum arc deposition process proved to be an industrially viable technique to provide a wide range of decorative coatings on large area substrates. The low substrate temperature and the coverage efficiency of vacuum arc deposition make it possible to coat plastics or use them as mask to create patterns. Due to the attractive properties, titanium has been deposited alone or in presence of a reactive gas (nitrogen, oxygen) to produce various coloured coatings. TiN, TiO_2 and TiN/ TiO_2 layers deposited

on silica glass have been investigated. TiN and TiO_2 layers exhibited a high corrosion resistance.

Acknowledgements

The financial support of the German Federal Ministry for Education, Science, Research and Technology (under contract BMBF 03N9004), NATO Linkage Grants programme (under contract HTECH.LG.970342), INTAS programme, Copernicus network PL978089, CRV PECHINEY and Alexander von Humboldt Foundation is heartily acknowledged. We thank Dr. Ju. Shulga and Dr. A. Kazakevich for fruitful discussions.

References

- [1] A. Matthews, Surf. Eng. 1 (1985) 93.
- [2] T. Arai, H. Fujita, K. Oguri, Thin Solid Films 165 (1988) 139.
- [3] J.P. Noel, J. Vac. Sci. Technol. A 2 (1984) 284.
- [4] R.A. Andrievski, J. Mater. Sci. Technol. 14 (1998) 97.
- [5] R. Gordon, J. Non-Cryst. Solids 218 (1997) 81.
- [6] J. Augustinski, Aspects of Photo-electrochemical and Surface Behaviour of Titanium (IV) Oxide, Springer, Berlin, 1988.
- [7] M. Fleischner, H. Meixner, Sensors and Actuators B 4 (1991) 437.
- [8] W.D. Sproul, Thin Solid Films 207 (1983) 141.
- [9] J.M. Molarius, J. Vac. Sci. Technol. A 3 (1985) 2459.
- [10] D.J. Cheng, Thin Solid Films 146 (1987) 45.
- [11] C.Y. Ting, J. Vac. Sci. Technol. 21 (1982) 14.
- [12] H.K. Pulker, G. Paesold, E. Ritter, Appl. Opt. 15 (1976) 2986.
- [13] L.-J. Meng, M.P. dos Santos, Thin Solid Films 226 (1993) 22.
- [14] A. Wicaksana, A. Kobayashi, J. Vac. Sci. Technol. A 10 (1992) 1479.
- [15] G.J. Exarhos, J. Vac. Sci. Technol. A 4 (1986) 2962.
- [16] S. Miyake, K. Honda, T. Kohno, Y. Setsuhara, M. Satou, A. Chayahara, J. Vac. Sci. Technol. A 10 (1992) 3253.
- [17] P. Babelon, A.S. Dequiedt, H. Mostéfa-Sba, S. Bourgeois, P. Sibillot, M. Sacilotti, Thin Solid Films 322 (1998) 63.
- [18] P. Löbl, M. Huppertz, D. Mergel, Thin Solid Films 251 (1994) 72.
- [19] J.M. Bennett, E. Pelletier, G. Albrand, J.P. Borgogno, B. Lazarides, C.K. Carniglia, R.A. Schmell, T.H. Allen, T. Tuttle-Hart, K.H. Guenther, A. Saxer, Appl. Opt. 28 (1989) 3303.
- [20] J.E. Sundgren, Thin Solid Films 128 (1985) 21.
- [21] N. Vershinin, B. Straumal, W. Gust, K. Filonov, R. Dimitriou, M. Benmalek, Thin Solid Films 351 (1990) 190.
- [22] J.E. Daadler, J. Phys. D 9 (1976) 2379.
- [23] P.T. Dawson, K.K. Tzatzov, Surf. Sci. 149 (1985) 105.
- [24] Ju.M. Shulga, A.N. Khodan, Phys. Chem. Mech. Surf. 5 (1989) 116 (in Russian).
- [25] D.W. Kim, Y.J. Park, J.G. Lee, J.S. Chun, Thin Solid Films 165 (1988) 149.
- [26] B. In, S.P. Kim, Y.I. Kim, W.W. Kim, I.H. Kuk, S.S. Chun, W.J. Lee, J. Nucl. Mater. 211 (1994) 223.
- [27] A.K. Vershina, I.A. Bel'chin, A.A. Pitel'ko, S.D. Izotova, Fiz. Chim. Obr. Mater. No. 5 (1990) 93 (in Russian).
- [28] E. Lunarska, J. Michalsky, J. Mater. Sci. 30 (1995) 4125.
- [29] W. Brandl, C. Gendig, Thin Solid Films 290–291 (1996) 343.
- [30] C.B. In, S.P. Kim, J.S. Chun, J. Mater. Sci. 29 (1994) 1818.
- [31] E. Lunarska, S. Al Ghanem, Phys. Stat. Sol. (a) 145 (1994) 587.
- [32] Y. Massiani, A. Medjahed, P. Gravier, L. Argème, L. Fedrizzi, Thin Solid Films 191 (1990) 305.