ELSEVIER

Thin Solid Films 383 (2001) 224–226

thin solid films

www.elsevier.com/locate/tsf

Vacuum arc deposition of protective layers on glass and polymer substrates

B.B. Straumal[a,b,*], N.F. Vershinin[b], A. Cantarero-Saez[c], M. Friesel[d], P. Zieba[e], W. Gust[a]

[a] *Institut für Metallkunde, Seestr. 92, D-70174 Stuttgart, Germany*
[b] *I. V. T. Ltd. (Institute for Vacuum Technology), P.O. Box 47, RU-109180 Moscow, Russia*
[c] *Institut de Ciència de Materials, Universitat de València, P.O. Box 2085, E -46071 Valencia, Spain*
[d] *SIMS Laboratory, Chalmers University of Technology, S-41296 Gothenburg, Sweden*
[e] *Institute of Metallurgy and Materials Science, Reymonta St. 25, PL-30059 Cracow, Poland*

Abstract

Vacuum arc deposition allows one to deposit various coatings on insulating and temperature-sensitive substrates (like polymers). An advantage of the vacuum arc deposition technique is the low substrate temperature during the deposition process. A vacuum arc deposition apparatus for the coating of large-area substrates has been developed. Ti, TiN, TiO_2 and diamond-like single and multilayer coatings have been deposited on plastic and glass substrates. The vacuum arc technology permits formation of multilayer colour filters of high uniformity on substrates with dimensions up to 2000×1400 mm^2. The microstructure, chemical composition and optical properties of the deposited coatings have been characterised with the aid of secondary-ion mass spectrometry, optical and Raman spectroscopy, and scanning electron microscopy.

Keywords: Diamond-like coating; Large-area substrate; Ti; TiN; TiO_2; Vacuum arc deposition

1. Introduction

Vacuum arc deposition allows the deposition of various coatings on insulating and temperature-sensitive substrates (like polymers). An advantage of the vacuum arc deposition is the low substrate temperature during the deposition process. Recently, the apparatus 'Nikolay' for the coating of large-area substrates has been developed [1]. This installation includes a large aperture, Hall current accelerator and six high-power sources able to work in the vacuum arc and magnetron regimes. Decorative and functional coatings can be deposited on substrates with dimensions up to 1400×2000 mm^2. The deposition of large-area carbon diamond-like films is especially important due to the unique combination of physical and chemical properties that cannot be realised in other materials [2]. Among these are hardness, wear resistance, chemical inertness, high electrical resistivity, optical transparency, and high thermal conductivity. These properties make them suitable candidates for various applications like wear-resistant coatings, field emission displays [3], electronic devices [4], solar cells, and heat sinks [5].

2. Experimental

The Ti, TiN, TiO_2 and diamond-like coatings were deposited on silicate glass and polymethylmethacrylate substrates with the aid of the installation 'Nikolay' which comprises the vacuum arc unit and Hall current accelerator [1]. The microstructure of these coatings was studied by scanning electron microscopy (SEM)

* Corresponding author: Tel: +49-711-1211276; fax: +49-711-1211280.
E-mail address: straumal@mf.mpi-stuttgart.mpg.de (B.B. Straumal).

0040-6090/01/$ - see front matter
PII: S0040-6090(00)01799-5

using the JEOL JSM-6300F apparatus with an electron-beam microanalysis facility. The reflectivity, R, measurements of the coatings have been carried out with standard lock-in techniques. The distribution of C, O and H in the diamond-like coatings was determined using the secondary-ion mass spectrometry (SIMS). A Cameca IMS, 6F secondary ion-mass spectrometer has been used for in-depth analyses of the films and substrates. Cs^+ ions accelerated with energy of 11.1 keV were used as primary ions. The distributions of C, O and H were studied by profiling the isotopes $^{12}C^-$, $^{16}O^-$ and $^{1}H^-$, respectively. The Bruker FT Fourier Raman Spectrometer was used for the characterisation of the coatings. The microhardness of the diamond-like coatings was measured at loads from 0.1 to 0.85 N with the aid of a PMT instrument.

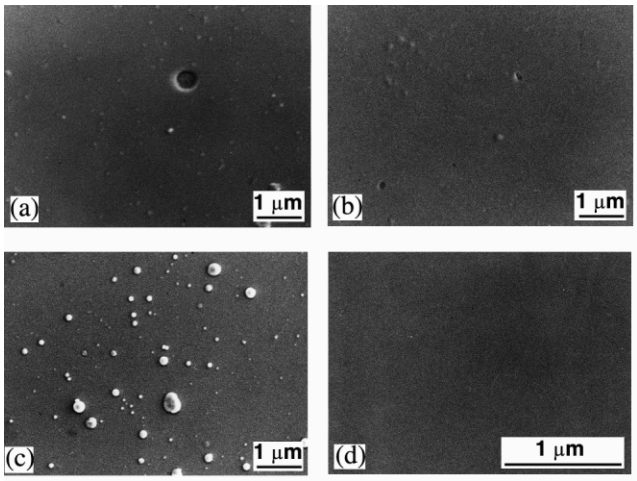

Fig. 1. SEM micrographs of the (a) Ti, (b) TiN, (c) TiO_2 and (d) diamond-like coatings deposited on large-area (1300×1600 mm^2) silicate glass substrates.

3. Results and discussion

The coatings were deposited on large-area silicate glass substrates in the 'Nikolay' plant. The dimensions of the polished glass substrates were 1300×1600 mm^2. The maximal possible dimension of substrates is 1400×2100 mm^2. The coatings have high thickness uniformity (below 5%). It permits to use TiN and TiO_2 for the deposition of interferencially coloured coatings. The uniformity of the thickness ensures that a difference in the colour of the coatings (pink, green, blue) on the whole substrate cannot be resolved by the naked eye [6]. SEM micrographs of the deposited coatings are shown in Fig. 1(a–d). The microstructure of the Ti, TiN and TiO_2 coatings contains microdroplets, and defects remained after the delamination of the microdroplets. The diamond-like coating is free from these defects. The defects mentioned are rather small and therefore, they are not visible by the naked eye and are not harmful for the application of coated large area glass, polymer or metallic sheets in the architecture or automotive industry. Though a few microdefects are present in the coatings, the coating itself is very uniform, and has a dense nanograined structure. The corrosion resistance of the coatings on steel and glass are proved to be high [1,6,7]. TiN and TiO_2 do not loose the adhesion to the substrate even after 12 months corrosion tests in a highly corrosive atmosphere.

The diamond-like coating is almost uniformly transparent in the visible part of the spectrum (R is approximately 25–40% in the wavelength range between 400 and 800 nm). The microhardness increases from 8.4 GPa (load $P = 0.5$ N) to 9.7 GPa ($P = 0.2$ N). The microhardness of glass substrate is 6.5 GPa. The SIMS depth profiles for $^{12}C^-$, $^{16}O^-$ and $^{1}H^-$ in the diamond-like coating are shown in Fig. 2a. A gold layer was evaporated on the surface of the coating due to the very low conductivity of the diamond-like coating (left part of the spectrum). The count rate I for the $^{1}H^-$ secondary ions is approximately 0.001 I for $^{12}C^-$, and I ($^{16}O^-$) is approximately 0.01 I ($^{12}C^-$). This feature indicates the low concentration of H and O. I for C, O and H is constant in the whole film. The Raman scattering spectrum of the diamond-like coating is

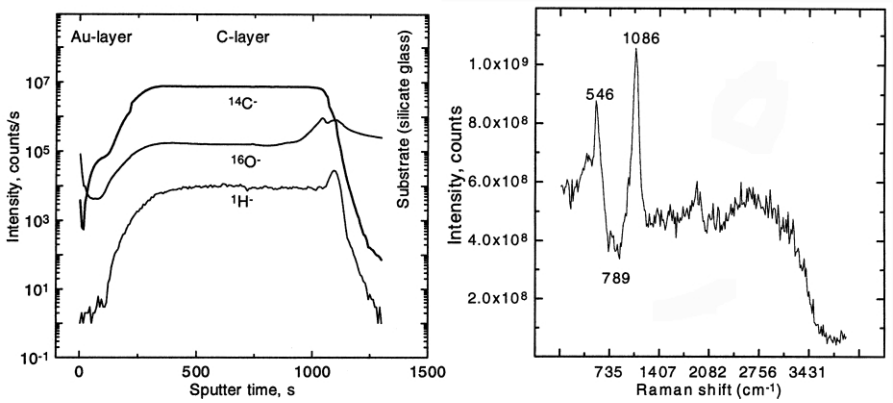

Fig. 2. SIMS depth profile (a) and Raman spectrum (b) for the diamond-like coating deposited on the silicate glass substrate.

shown in Fig. 2b. Two high peaks at 546 and 1086 cm^{-1}, and a weaker one at 789 cm^{-1} are present. Neither the characteristic sharp diamond peak at 1332 cm^{-1} nor the broad feature at 1550 cm^{-1} corresponding to the graphitic G band [8], are present in the spectrum. The peaks obtained can be assigned to nanophase diamond [9]. Particularly, the peaks at 1086 and 789 cm^{-1} correspond to the C–C modes in diamandoids like adamantane $C_{10}H_{14}$ and diamantane $C_{14}H_{20}$ [9–11]. On the other hand, the high energy lines (2600–3000 cm^{-1}) corresponding to the C–H modes are not present in the spectra. This fact is supported by the low H content in the coating (Fig. 2a). In conclusion, the vacuum arc technology permits one to deposit hard coatings (TiN, TiO_2) on the temperature-sensitive substrates like polymers. The deposition of Ti, TiN and TiO_2 coatings on polymethylmetacrylate shows that the adhesion of the coatings is very good immediately after the deposition. However, after approximately two weeks the coatings start to delaminate spontaneously from the organic glass substrate. The adhesion problem can arise due to the very high difference in the properties of such coatings and the substrate. The application of the diamond-like coatings as sublayers can help to solve this adhesion problem, and this deposition process will be characterised in detail in the near future.

Acknowledgements

The financial support of the programme of the Royal Swedish Academy of Sciences for the co-operation with the former Soviet Union, the programme for the co-operation between Russian and Polish Academy of Sciences, the INTAS Programme, the German Federal Ministry for Education, Science, Research and Technology and the University of Valencia is acknowledged.

References

[1] B. Straumal, N. Vershinin, K. Filonov, R. Dimitriou, W. Gust, Thin Solid Films 351 (1999) 204.
[2] S.B. Ogale, A.P. Malshe, S.M. Kanetkar, Solid State Commun. 84 (1992) 371.
[3] N. Kumar, H. Schmidt, C. Xie, Solid State Technol. 38 (1995) 71.
[4] P. Stumm, D.A. Drabold, P.A. Fedders, J. Appl. Phys. 81 (1997) 1289.
[5] E. Marotta, N. Bakhru, A. Grill, V. Patel, B. Meyerson, Thin Solid Films 206 (1991) 188.
[6] N. Vershinin, K. Filonov, B. Straumal, W. Gust, R. Dimitriou, A. Kovalev, J. Camacho, Surf. Coat. Techn. 125 (2000) 223.
[7] N. Vershinin, K. Filonov, B. Straumal, W. Gust, I. Wiener, E. Rabkin, A. Kazakevich, Surf. Coat. Techn. 125 (2000) 229.
[8] D.S. Knight, W.B. White, J. Mater. Res. 4 (1989) 385.
[9] P.W. May, S.H. Ashworth, C.D.O. Pickard, M.N.R. Ashfold, T. Peakman, J.W. Steeds, Phys. Chem. Comm. 1 (1998) 4.
[10] L. Bistricic, G. Baranovic, K. Mlinaric-Majerski, Spectrochim. Acta A51 (1995) 1643.
[11] T.E. Jenkins, J. Lewis, Spectrochim. Acta A36 (1980) 259.