FORMING OF PROTECTIVE NANOSTRUCTURE COATINGS ON METALS AND GLASSES AND THEIR PROPERTIES INVESTIGATION

Alla Deshkovskaya[1)], Leonid Lynkov[1)], Andrey Nagibarov[2)],
Vasiliy Glybin[3)], Edgar Richter[4)], M. Pham[4)]
[1)]*BSUIR, Minsk, Belarus*
[2)]*«Para la Oro», Minsk, Belarus*
[3)]*BTU, Minsk, Belarus*
[4)]*R&D center, Rossendorf, Germany*

Transparent heat-resistant coatings of 10-30 nm thickness described by $(ZrO_2)_x \cdot (Y_2O_3)_y$ composition are formed on the surface of metals and glasses by thermolysis technique.

Produced coatings possess high adhesive strength, high corrosive and abrasive resistance. Nanocrystalline formations are revealed on samples surface, with quantity of these formations depending on basic solution concentration, formed layers number and thermal treatment mode.

Ion-beam modification of obtained coatings under mixing mode enables said properties enhancing owing to zirconium oxiboride formation at substrate-coating interface as a result of ion-beam synthesis.

Introduction

During their utilization all materials undergo different conditions (climatic, mechanical, thermal etc.) thus forming of quality protective coatings is always of great importance.The goal of our work is to develop thin protective coatings possessing high thermal, corrosion resistance and durability to be formed on the surface of metals and glasses.

We chose zirconium-containing compounds as initial material for coating as they possess a unique combination of valuable properties with regard to the goal of our work such as: high chemical resistance in a wide range of temperature, high strength, hardness, thermal resistance and durability.

We used the techniques of thermolysis and ion-beam surface modification to form the protective coatings on the surface of glasses and metals.

2. Experiment, results and discussion

2.1 Forming of protective coatings on the surface of metals and glasses

The subject of investigation was the substrates made from glasses of various compositions and steel in the shape of parallel-sided plates of 10x10 mm^2 in dimensions and of 1-2 mm in thickness. Before being coated the substrates were subjected to ultrasonic cleaning and water rinse.

The coating solution contained a mixture of compounds obtained from the synthesis of organic zirconium derivative with the addition of the concentrated solution of $Y_3 (NO_3)_3$. [1,2].

The coating process was performed in three stages [2,3]:

1. The film-forming solution of the reaction mixture was applied on the substrate surface.

2. Thermal treatment: 1) drying at the temperature of 100-200^{0}C; 2) annealing at the temperature of 500-700^{0}C.

3. Ion-beam modification.

The reaction mixture solution was applied on the metal substrate surface using the brush and the glass substrates were dipped into the solution and spun.

Processing in this way allows retaining high optical characteristics of the glasses. During thermal treatment the solvent and organic products were completely removed thus forming a transparent plane uniform film of zirconium dioxide (≈10 nm in thickness) with a high adhesion to the substrate.

In order to strengthen the durability and the adhesion of the formed coating we performed the third stage – the ion-beam modification in the mixing mode (ion mixing). The samples were bombarded with boron ions (with the fluence $F=10^{15}$- 10^{18} ions/cm^2, with the current density lower than 2 $\mu A/cm^2$). We chose the bombarding ions energy depending on the formed coating thickness to obtain the implantation of the recoil atoms (Zr and O) into the substrate and to ensure an intensive atom mixing within the contact layer (coating-substrate) [3].

Multiple repetition of the described stages resulted in a step-by-step growth of the multilayered oxide-containing coating on the substrate.

2.2 Abrasive durability

We performed two procedures to study the durability of the samples. The glass substrates underwent gasoabrasive wearing. The samples were subjected to the exposure of abrasive material particles having a specific mass with the velocity of 100 m/s in a gas environment [2]. The gasoabrasive wearing degree was assessed through comparing the optical parameters, such as directional transmission of radiation with the wavelength of λ=0.633 μm, of the coated samples to the non-coated ones.

The results of gasoabrasive wearing of calcium-aluminate glass coated with the standard SiO_2 (industrially used to protect the glass of this kind) in comparison to the glass coated with the zirconium dioxide are shown as an example in Fig. 1. It is evident from the figure that the transmission of the standardly coated glass decreases sharply if the mass of the abrasive particles increases from 0.05 to 0.22 g (curve 3), as a result of abrasive wear of the surface. In comparison to that it is shown, that the zirconium dioxide coating (curve 2) protects the glass against damaging and the additional ion-beam treatment (boron mixing) ensures the durability enhance by almost 4 times (curve 1).

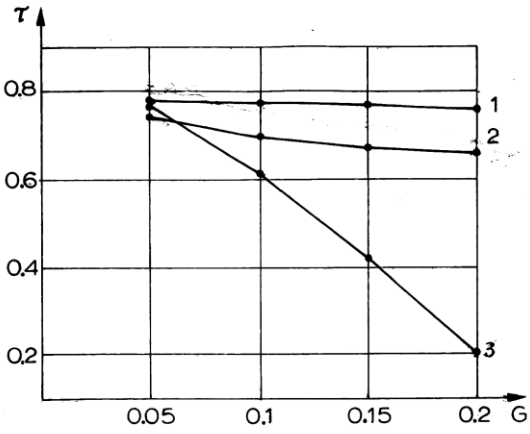

Fig.1. Plot of directional transmissivity (λ=0.633 μm) vs the produced material mass G for calcium-aluminate glass, subjected to ion-beam modification 1 – ZrO_2 coating after mixing of B^+ (E=100 keV, F=3·10^{17} cm^{-2}); 2 - ZrO_2 coating before mixing; 3 – standard (glass with conventional SiO_2 coating)

The strengthening effect grows when the fluence increases up to 3·10^{17} cm^{-2} but above this value the durability recedes probably because of partial scattering of the formed coating. It is found out that there is an optimal number of layers and the coating properties deteriorate if this number is increased.

"Needle on a disk" technique was used for steel substrates. The abrasive wearing degree was assessed through the quantity of the shaving and the parameters of the groove, such as depth and length, width, produced on the sample surface by the abrasive material exposure [4]. We used a replaceable ball of tungsten carbide (∅ =3 mm) as an abrasive needle to perform back-and-forth motion on the sample surface with the velocity of 0.02 m/s. We have also calculated the friction factor with reference to the number of cycles.

The steel (1.4301) samples protected with the zirconium dioxide coating possess a significantly higher durability than the non-coated samples. The experimental results are given in [4].

Table 1 contains experimental results on the durability of a sample with the coating and without it. For the given number of cycles (40 000 and 80 000) the abrasive wear is not observed on the coated sample unlike the initial one. The friction factor of the coated sample is twice smaller than the non-coated sample.

Table 1 - Abrasive wear parameters of steel samples 1.4301 before and after the protective coating

Number of cycles	Groove parameters	Initial sample	Coated sample (N6/1)
40000	Volume losses, μm^3	0,68	-
	Depth, μm	0,57	-
	Width, μm	122	-
	Length, μm	1693	1854
	Area, μm^2	40	-
80000	Volume losses, μm^3	1,02	-
	Depth, μm	0,72	-
	Width, μm	153	-
	Length, μm	1846	1822
	Area, μm^2	55	-

2.3 Corrosion resistance

The corrosive characteristics of the coating were studied through the potentiodynamic polarization method. The 0,05 M solution of H_2SO_4 was used as the electrolyte. The potential change rate was 10 mV/s. The area of the sample surface region under study was 0.07068 cm^2.

Fig.2 and Table 2 contain corrosion resistance measurement results for steel samples with coatings obtained at various conditions.

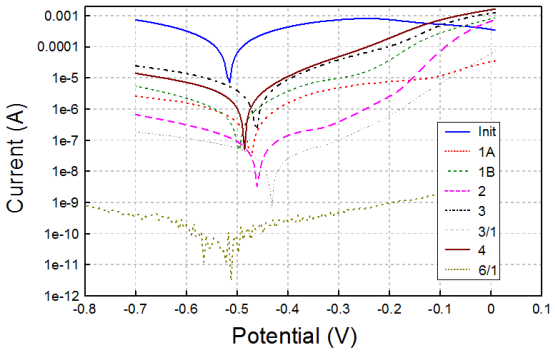

Fig. 2. Corrosion velocity for steel 1.4301 samples with coatings obtained at various conditions (see Table 2) and without coating (to compare)

The best result is achieved for the sample 6/1, though its coating thickness is still 30 nm. The corrosion current density for this sample is 5.678·10^{-9} A/cm^2, in comparison to 1.333·10^{-2} A/cm^2 for the non-coated sample. The sample 6/1 possessed the highest durability (as seen from Table 1).

As a result of this work it was found out that increasing the number of layers of the coating results in the steel corrosion resistance receding and the corrosion resistance depends on the temperature and the duration of annealing for the equal number of layers.

Table 2 - Corrosion resistance of steel (1.4301) samples with coatings obtained at various conditions

Samples	Number of ZrO_2 layers	Annealing temperature, C	Annealing duration, s	Corrosion current density, A/cm^2
Initial	-	-	-	1.333·10^{-2}
1A	3	600	10	1.373·10^{-5}
1B	7	630	10	1.513·10^{-5}
2	3	510	24	3.491·10^{-6}
3	4	600	10	9.959·10^{-5}
3/1	4	540	20	2.264·10^{-7}
4	6	650	15	5.705·10^{-5}
6/1	3	630	15	5.678·10^{-9}

2.4 Discussion

The research literature on zirconium dioxide coatings as well as the experimental data obtained in this work testify that as a result of the thermolysis process the transparent heat resistant coatings of 10-30 nm in thickness and corresponding to the general formula $(ZrO_2)_x \cdot (Y_2O_3)_y$ are formed on the surface of glass and metal substrates.

Increase of durability and corrosion resistance of the samples of both kinds can be explained through formation of surface of ZrO_2 monoclinic phase and its cubic modification as a result of thermal treatment process, as it was reported in [1, 3]. The strengthening effect growth after the additional ion-beam processing might be caused by zirconium dioxiboride formation within the coating as a result of solid-state ion-beam synthesis.

In order to verify these hypothesizes we used the IR reflection spectrometry and the atomic force microscopy (AFM).

Surface microrelief of the samples studied through AFM technique revealed nanocrystal formations (Fig. 3). The crystal average size is 950×625×163 nm^3. Preliminarily it was seen that the number of crystals on the sample surface depends on the thermal treatment mode, number of formed layers and solution concentration. It was noted that the highest corrosion resistance and durability are observed when the size of crystals is of the same order and their distribution on the surface is uniform.

It was found out that there is an optimal number of layers and if it is exceeded the coating properties deteriorate. AFM pictures show disruptions of the film in this case.

Additional ion-beam processing of samples (bore implantation) resulted in surface crystals size decrease and sample strength properties growth.

In order to clarify the impact of ion-beam processing of coatings onto samples strength properties growth, as mentioned above, we hypothesized that the strengthening effect is ensured by zirconium dioxiboride within the formed coating as a result of solid-phase ion synthesis induced by ion bombardment.

In order to verify this hypothesis the pure zirconium dioxiboride was thermally synthesized, its IR reflection spectrum was studied and compared to IR reflection spectrums of the samples under study with the coating before and after bore implantation.

It is evident from Fig. 4 that bore implanting into ZrO_2 coated glass induces two new bands (curve 3) typical for the pure zirconium dioxiboride compound (curve 1). These bands are missing in the spectrum of the coated sample before bore implantation (curve 2).

Subsequently the impact of the ion-beam modification parameters, such as kind of ions, energy, fluence, onto the nanocrystal size (hence the properties of the formed coatings) should be ascertained.

Targeted impact onto phase transformation process in $(ZrO_2)_x \cdot (Y_2O_3)_y$ films will make possible to control a lot of utilization characteristics of metals and glasses.

The coatings formed under the described technique have self-organizing structure as a result of their chemical composition changing first in the solution, then during the film forming on the substrate, in the course of the thermal treatment process and at last - during ion-beam modification.

The advantage of the described coating forming technique is a wide range of oxide thickness – from tens of nanometers to several microns.

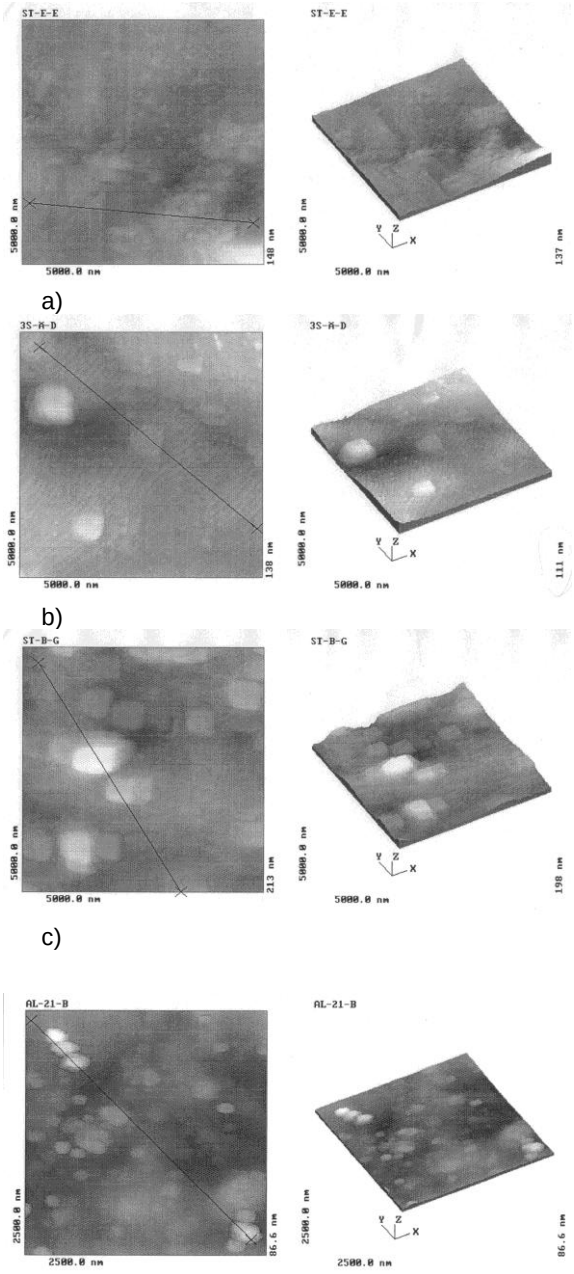

Fig. 3. AFM images of the surface microrelief of steel 1.4301 samples before (a) and after coating formation (b – for sample N3, c – for sample N6/1) (formation conditions as given in Table 2) and of silicon glass with ZrO_2 coating after ion-beam mixing B^+ (E=100 keV, F=$3 \cdot 10^{18}$ cm^{-2}) (d)

3. Conclusions

1. The transparent heat-resistant coatings of 10-30 nm in thickness are formed on the surface of glasses and metals by thermolysis technique. The composition of the coatings corresponds to general formula $(ZrO_2)_x$ $(Y_2O_3)_y$.

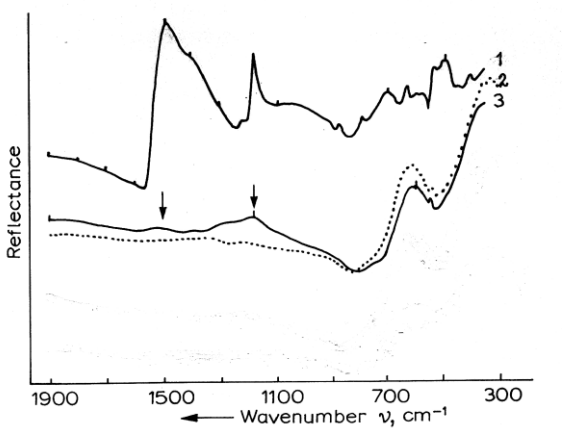

Fig. 4. IR reflection spectra of zirconium oxiboride (1) and calcium-gallium glasses with ZrO_2 coating before (2) and after (3) ion mixing (B^+ions, E=100 keV, F=$3 \cdot 10^{17}$ cm^{-2})

2. The obtained coatings possess a good adhesion strength, high corrosion and abrasion resistance. These properties are ensured as a result of nanocrystalline particles formation on the sample surface. The number of particles depends on the solution concentration, number of layers and treatment mode.

3. Ion-beam modification of the obtained coatings in the mixing mode ensures the abovementioned properties enhance due to zirconium dioxiboride forming as a result of ion-beam synthesis of the coating.

In conclusion the authors express their gratitude to the researchers of the Institute of ion-beam physics and materials research in Rossendorf (Germany) A. Schneider and R. Hüller for the technical assistance.

References

1. *Lynkov L.M., Soloviev V.V., Shishakova L.I. , Prischepa S.L.* // Proceedings of the Academy of Science BSSR. - 1993. - Vol. XXXVII, N 3. - P. 45-47.
2. *Deshkovskaya A., Yanishevski V., Gritsai S., Lynkov L., Skornyakov I.* // Nucl. Instr. and Meth in Phys. Res. B. – 1993. - 80/81. – P. 1230-1232.
3. *Deshkovskaya A., Nagibarov L., Glybin V.P.* The protection coating forming technique. Patent BY. N 5135 reg. 2003.01.21.
4. *Deshkovskaya A., Lynkov L., Nagibarov L., Pham M., Richter E.* // Doklady BSUIR; Electronics, Materials, Technology, Informatics. – 2003. - Vol. 2. - P. 73-80.

ANNEALING EFFECTS ON PHOTOLUMINESCENCE OF SiN_X FILMS GROWN BY PECVD

F.F. Komarov[1)], I.N. Parkhomenko[1)], L.A. Vlasukova[1)], O.V. Milchanin[1)],
A.K. Togambayeva[2)], N.S. Kovalchuk[3)]
[1)]*Belarusian State University*
4, Nezavisimosti Ave., 220030 Minsk, Belarus, +375(17)212 48 33, e-mail: komarovf@bsu.by
[2)]*Al-Farabi Kazakh National University*
71, Al-Farabiy Ave., 050038 Almaty, Kazakhstan,
+7(727)377 33 30 (1137), e-mail: Altynay.Togambayeva@kaznu.kz
[3)]*"Integral" Joint Stock Company,*
121 A, Kazintsa Str., 220108 Minsk, Belarus, (+375 17) 398 20 40, 7033696@mail.ru

Si-rich and N-rich silicon nitride films were deposited at low temperature 300 °C by using plasma-enhanced chemical vapor deposition (PECVD). The optical and structural properties of these films have been investigated by ellipsometry, Rutherford backscattering (RBS), transmission electron microscopy (TEM), Raman spectroscopy (RS) and photoluminescence (PL). The formation of silicon clusters in both Si-rich and N-rich silicon nitride films after annealing at 900 °C and 1000 °C for hour in N_2 ambient has been revealed by TEM. Dependency of PL spectra on stoichiometry and post-annealing temperature was analyzed. The contribution of Si and N-related defects in emitting properties of Si-rich and N-rich SiN_x has been discussed.

Introduction

The creation of light emitter based on silicon technology is still actual problem. Well-known as insulating layer silicon nitride is promising candidate for Si-based full-color light-emitting devices. In spite of numerous works devoted to investigation of light-emission properties of silicon nitride, nature of PL is still not unambiguously understood. Some authors assign PL to the quantum confinement effect of Si nanoclusters in silicon nitride [1,2], while others attribute it to radiative defects [3,4] or band tail recombination [5,6]. The most of these works are devoted to investigation of Si-rich SiN_x ($x<4/3$), because it is an initial material for formation of system "Si nanocrystals in dielectric matrix". The aim of this paper is to study of structural and optical properties of both Si-rich and N-rich silicon nitride films. The comparison of properties of such types of SiN_x will be useful for understanding nature of PL.

Experimental

In this study, SiNx films were deposited on n-type Si(100) substrates by PECVD using the gases of monosilane (SiH_4) and ammonia (NH_3) as the precursors. The deposition temperature was 300 °C. The stoichiometric composition depended on the ratio NH_3/SiH_4 in the gaseous mixture. The thickness and refractive index were measured by ellipsometry. Then the samples were annealed in N_2 at 900 - 1100 °C for 1 hour using resistance furnace. The depth distribution of N and Si atoms and stoichiometric composition SiNx were analyzed with RBS spectrometry using 1.3 MeV He+ ions. Raman spectra in a back-scattering geometry were