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AFM examination of nanolayers synthesised by the molecular layering method on the surface of manufacturing glasses

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The surface topography of glass matrixes has been investigated before and after oxide coatings caused by molecular layering method. The conductance of synthesised nanolayers has been investigated.

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1. Introduction

The problem of preparing high-voltage electronic devices with high electric strength is still acute now [1–3]. In the devices designed for operating at tens and hundreds kV, the dielectric glass shell is the most important element which determines electrical strength of the device [4]. Examination of initiation of a voltage failure in X-ray tubes has revealed emersion of a parasitic secondary auto electronic emission from the electrodes, much reducing the strength of the glass balloons. One of the reasons specified is, apparently, accumulation of static charge on microcracks at the glass shell interior surface of X-ray tubes [2].

One of the expedients of raising high-voltage X-ray devices electric strength, making concerning „thick“ (tens micron) dielectric coats of oxides on an interior surface of glass shells is now in use [5]. At the same time, modern demands to X-ray tubes compel to search for more effective methods of preparing oxide overlay with optimal thickness and uniformly coating tubes of any geometrical shape.

In order to solve the above problem, the use of precision synthesis of surface nanostructures by the method of molecular layering seems to be promising [6–8]. Compared to the traditional thin-film technologies, the method of molecular layering offers a number of advantages, such as the accuracy in specifying the composition and thickness of the layer on the atomic and molecular levels, the formation of strong (chemical) bonds between the coating and the surface of the matrix, and a uniform distribution of modifying materials over the surface irrespective of its geometric configuration [8,9]. The developed approaches were implemented earlier when using the molecular layering method for synthesising titanium oxide nanolayers in order to heal microdefects of glass microspheres [10] and pores in silica glasses [11,12], which ensured a considerable decrease in the number of surface defects and an enhancement of the hydrostatic strength, respectively.

In the present work we study the surface topography of glass matrixes before and after oxide coatings caused by molecular layering method, and investigate the conductance of synthesised nanolayers.

2. Experimental part

The investigations were carried out at borosilicate glass of the molybdenum group S 52-1, which has been used for manufacturing X-ray tube bulbs. Element-oxide nanocoatings were synthesised using a flow-vacuum unit under the conditions that excluded uncontrollable side of chemical transformation [13]. The thickness of the layer was controlled by varying the number of cycles of sequential processing of the matrix with $TiCl_4$ or CrO_2Cl_2 and H_2O or C_2H_5OH vapours [7].

The check of the process of forming element oxide layers we spent on laboratory zero-ellipsometer with He–Ne-laser ($\lambda = 632.8$ nm). Sensitivity of the device made $< \pm 0.1$ nm.

The condition of the initial surface and transformations of its topography after deposition of nanocoatings were examined on a Solver-P47-Pro scanning probe microscope (NT-MDT, Russia).[1] The measurments were performed in air with an AFM scanning head in trapping mode.

The conductance of synthesised coatings determined by two-contact method on a direct current at pressure 10^{-1} Pa in the temperature interval $30-90$°C on the vacuum plant descrybed in-process [14].

3. Results and discussion

The AFM examination of topography of initial matrix has shown, that on the glass surface alongside with rather smooth rections (the roughness, determined according to DIN-4768 is about $3-4$ nm) there are observed chaotically distributed particals bounded with a surface (ungeometrical form with sizes from $0.5 \times 0.5 \times 0.15$ up to $1.5 \times 1.5 \times 0.4\,\mu$m) (Fig. 1, a) and melted microcracks the width of which lies in the range $100-200$ nm and the depth varies from 2 to 40 nm (Fig. 1, b). The average surface roughness of initial glass is $20-50$ nm. Emersion on a surface of similar cracks, apparently, can occur during manufacturing balloon of an X-ray tube.

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[1] The investigations were carried out at the TsKP „Chemical Assembling of Nanomaterials“, St. Petersburg State Technological Institute, Russia.

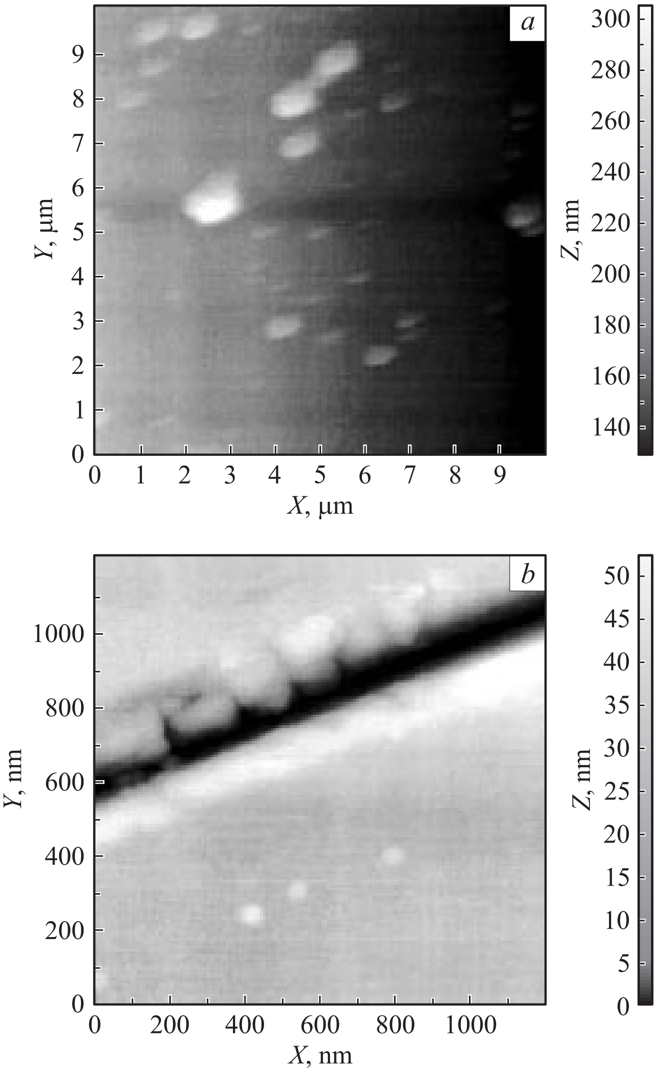

Figure 1. AFM reconstruction of the initial glass surface: microparticles (*a*), and microcrack (*b*).

Therefore, the AFM data indicate that the surface of the initial glass has a srtucture with many defects characterised by both nanosized cracks and volume microdefects in the form of irregular-shaped particles. It is evident that their presence on the inner surface of the glass bulbs can be responsible for the accumulation of an excess charge [1].

For exclusion of charge accumulation at the glass surface the opportunity of forming a super-thin chrome oxide coatings by molecular layering (ML) method at the glass has been considered. A synthesis of chrome oxide structures was carried out in the temperature interval $T_S = 160-220°\mathrm{C}$. The experiments have shown that the dependence of synthesised coating thickness on T_S was obviously expressed at minimum 170°C. If at $T_S = 160°\mathrm{C}$ greater nanolayer thickness can be caused by possible hydrolysis of $\mathrm{CrO_2Cl_2}$ with water physically adsorbed on the glass surface [15,16], at $T_S \gtrsim 180°\mathrm{C}$ the thickness increase is caused probably by a thermal decomposition of $\mathrm{CrO_2Cl_2}$ vapours and precipitation of the received products (compounds type as $\mathrm{(CrO_2)_3Cl_2}$, $\mathrm{Cr_5O_9}$, $\mathrm{CrO_2}$, etc.) at the surface carrier to analogously CVD processes [17].

The AFM-examination of topography of a surface of the synthesised nanolayers has shown, that at 170°C the uniform coats of chrome oxide structures with lateral size up to 50 and 1.0 nm in height (Fig. 2, *a*) are formed on the glass surface. The processing at $T_S \gtrsim 180°\mathrm{C}$ result in irregular coating at the surface, described formation particles with diameter up to 250 nm which adhesion performances sharply differ from properties of other surface that is evidently visible when a sample is scanned in a phase contrast regime (Fig. 2, *b*). The received effects confirm a leakage at $T_S \gtrsim 180°\mathrm{C}$ for CVD-processes, resulting in precipitation on a surface of a matrix of the irregular coatings. Therefore the synthesis of chrome oxide nanolayers on glass was carried out at $T_S = 170°\mathrm{C}$ in the requirements which have been

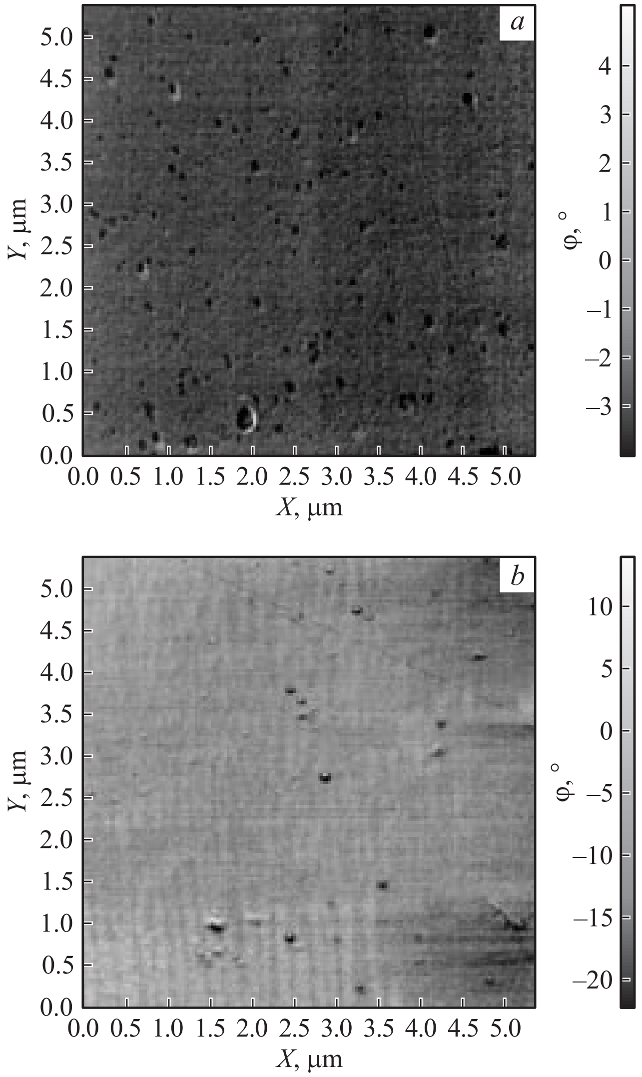

Figure 2. AFM reconstruction of chrome oxide coatings surface ($n = 5$). Regime of the phase contrast. Temperature of syntesis T_S, °C: *a* — 170, *b* — 218.

Table 1. Geometrical sizes of chrome oxide nanostructures

Number of processing cycles, *n*	Size of synthesised chrome oxide structures (by AFM dates), nm		Thickness of chrome oxide nanolayers (by ellipsometry dates), nm
	lateral	height	
5	50–100	0.7–1.2	1.0
10	130–200	1.8–2.1	1.8
50	250–400	6–10	8.4

Table 2. Geometrical sizes of titanium oxide nanostructures (according to AFM dates)

Number of processing cycles, *n*	Size of synthesised titanium oxide structures, nm	
	lateral	height
4	10–20	1–2
8	25–40	2–2.5
12	100–200	4–8

not complicated by a leakage of uncontrollable secondary processes.

The AFM-research in phase contrast and Kelvin probe regimes of samples with chrome oxide nanolayers show, that after the first ML cycle at $T_S = 170°\mathrm{C}$ all the surface has flown down uniformly. It was covered without any extended defects by chrome oxide structures. The further nanolayer growth up to 50 nonolayers is accompanied by forming on the surface distinctly expressed chrome oxide clusters (which sizes are given in the Tabl. 1), densely overlapping an initial matrix. The good conformity of thickness of synthesised coatings calculated from ellepsometry dates and experimentally fixed height of chrome oxide structures (see Table 1) also can testify to uniformity of covering of an initial matrix surface.

It should be noted that the chrome oxide nanostructures cover not only smooth sections of the glass. Thus, filling and smoothing the existing cracks and microdefects but also the surface of the volume microinclusions composed of glass particles. That is, the syntheses performed according to the molecular layering method ensures the deposition of the conformal coating regardless of the relief of the initial surface.

Alongside with chrome oxide layers the certain interest from the point of view of electric strength represents also coating based on titanium dioxide [5]. High thermal stability of TiO_2 [18] allows the shape titanium oxide coating with the given chemical and phase composition in wide interval of synthesis temperature (up to 600°C) [19].

Titanium oxide nanolayers of different thickness were synthesised on the surface of the initial glass at a temperature of 200°C by sequential processing with $TiCl_4$ and H_2O vaporous (4, 8, and 12 cycles). The AFM investigations of the samples thus obtained revealed that, already after four cycles, there arises a continuous uniform coating composed on titanium oxide nanostructures. The linear sizes of these nanostructures are presented in the Tabl. 2. An increase of the number of processing cycles to eight leads to an increase of the mean sizes of individual titanium oxide nanostructures (see Table 2). In this case, the boundaries between clusters manifest themselves in the AVM images.

After 12 processing cycles, the roughness of the glass surface decreases significantly. The sample is coated with a continuous layer composed of titanium oxide nanostructures (Fig. 3), whose lateral sizes are as large as 100–200 nm and height varies from 4 to 8 nm. The analysis of the AFM images of the sample surface demonstrates that an individual titanium oxide cluster has a dome-shaped form and is surrounded by six or eight adjacent structures; however, we could not reveal the formation of periodic structures with a mutually ordered arrangement of individual particles of the surface of the glass. The boundaries of the contact between individual nanoclusters are observed at a level of 2.0–3.5 nm. This also indicates that the clusters intergrow together below this level and that a continuous titanium oxide coating free from defects is formed on the surface of the glass.

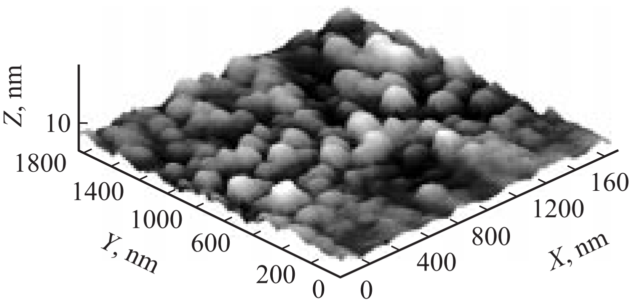

Figure 3. AFM reconstruction of topography of surface titanium oxide coating ($T_S = 200°\mathrm{C}$, number of processing cycles $n = 12$).

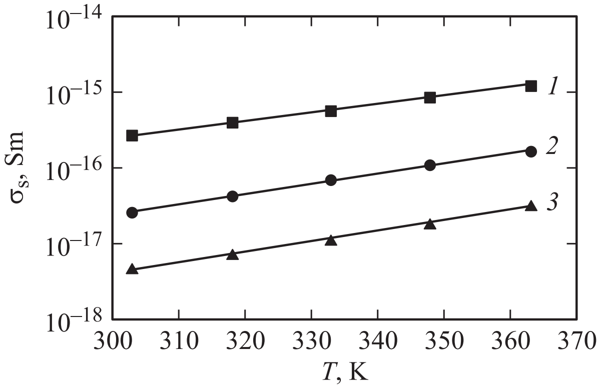

Figure 4. Dependences of conductivity σ_S from temperature for coats: *1* — manufacturing chrome oxide, *2* — synthesised by ML method titanium ($T_S = 200°\mathrm{C}$, $n = 12$), *3* — chrome oxide ($T_S = 170°\mathrm{C}$, $n = 50$).

The measuring of the reseived chrome and titanium oxide coating conductance has shown that their surface conductance on air at 25°C is close and in within the interval $1.0-5.5 \cdot 10^{-16}$ Sm. At the same time, considering, that in real exploration conditions of X-ray tubes coats is high-vacuum, and that the surface conductivity of high-resistance materials can increase essentially due to adsorption of water vapour [20,21]. For removal of adsorbed water the sample was pumped in the measuring unit at 90°C and pressure 10^{-1} Pa within 1 h. The results of surface conductivity measuring are given in Fig. 4.

The comparison of super-thin conducting coatings received by ML method with properties of manufacturing conducting based on chromium (III) oxide has shown (Fig. 4), that nanolayer conductivity is comparable to properties of the coats applied now. At the same time the coatings received by ML method are characterised by essentially smaller thickness and absence of defects.

4. Conclusion

Thus, the result of the inversigation performed have demonstrated that the use of molecular layering method allows to prepare conformal covers at the matrix surface, and cover conductance is comparable to properties of manufacturing protective layers based on chromium oxide.

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