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Nanoscale Oxide Surface Modification of Inorganic Materials

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Abstract—A method of synthesis of metal oxide films by carboxylate pyrolysis on a substrate surface is developed. The optic physical properties of the obtained films are studied by spectrophotometry using special-design fiber-optic probes.

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INTRODUCTION

In terms of materials research, the surface of a material is qualified as its phase nano component (by composition, structure, defects, etc). Of particular importance for nanoscale chemical structural modification are amorophous and nonequilibrium states arising in chemical reactions under extreme conditions and extending the isomorphism limit by forming homogeneous multicomponent phases [1].

The principal engineering approaches to surface modification are based on chemical and physical methods of deposition of thin-film coatings. The most widespread technologies are based on physical physical principles: vacuum ion plasma sputtering, electric spark alloying, finish plasma strengthening, etc. Modification by laser or plasma tempering is also applied. The use of the above-mentioned technologies is limited by their specific field, and their realization is associated with large investments.

Among chemical modification technologies, a particular place belongs to the carboxylate technology [2–6] which is capable of producing nanoscale film coatings of different compositions. This technology was used to success to produce high-temperature superconductors, magnetic materials, segnetoelectrics, active materials for lithium power sources, solid electrolytes, and tin dioxide films for gas sensors. Nanocrystalline films on different substrates for gas sensors and magneto-optic films for current sensors were produced. Research on protection and strengthening of surfaces has also been reported [2, 4].

The main advantages of the carboxylate technology are the simplicity of its instrumentation and the possibility to obtain homogeneous final products. This technology allows production of functional materials and films of various applications with various mechanical and electrophysical properties [4].

Here we present the results of experimental studies of the formation of nanoscale layers of amorphous and nanocrystalline phases (nano scales 10–150 nm and 150–600 nm) on the surfaces of quartz glass and metal alloys.

Fabrication of Oxide Films

Over the past 10–15 years increasing interest has been attracted to nanotechnologies and design and research of nano objects. New materials with unique properties are being developed on the basis of nanolayered structures.

Nanosized objects are presently recognized as a separate class of substances, which is explained by the fact that, as the size of solid or liquid particles decreases to 100 nm and lower, they start to exhibit quantum size effects, and changes primarily occur in the atomic and crystal structure and physicochemical properties of the disperse phase [7].

All methods of preparation of thin films and coatings for microelectronics and other fields can arbitrarily be divided into physical and chemical. Combinations of these methods are also applied.

Physical methods of film fabrication generally make use of film-forming substances (targets). When the target is sputtered, its particles condense onto a substrate to form a film and, at so doing, they undergo no chemical transformations. A big group of physical methods is formed by vacuum film deposition methods which make use of different energy sources to induce transfer of a target substance onto a substrate surface. These are versatile and widely used methods. An important advantage of this group of methods is that they allow almost all parameters to be controlled during the process of film deposition.

Chemical methods of film fabrication are based on the processes of layer growing, which occur during chemical reactions. The most common chemical methods are pyrolysis of complex compounds with concurrent film formation from the decomposition products, as well as solid-phase synthesis.

Chemical methods of film fabrication offer a number of advantages: (a) the composition of films can be widely varied, (b) no complex vacuum equipment is required, (c) the process is easily engineered, (d) each process chain unit can be controlled, and (e) coatings can be deposited on surfaces of any shape. Non-vacuum methods of film fabrication include electrophoretic film deposition, liquid-phase epitaxy, as well as sol–gel method and pyrolysis of solutions.

Among the up-to-date chemical methods of surface modification we would like to dwell on those which allow fabrication of nanoscale oxide films. First of all, this is the method of liquid-phase epitaxy from melts at atmospheric pressure. Due to the temperature equilibrium, mechanical tensions in growing films are reduced. Under these conditions, the process of film growth in monocrystalline substrates with different lattice parameters is easy to control. The methods of epitaxial film deposition, which allow variations in the composition and structure of deposited materials (cathode sputtering and organometallic epitaxy) form a separate group. The key stages of such film deposition processes are as follows: pre-evacuation of the chamber with a substrate, feeding a reactant or carrier gas, and chemical reaction on the support. The disadvantages of the methods of epitaxial film fabrication by vacuum deposition include, along with that they require a complicated and costly equipment, the difficulty in their combining with other operations of the process cycle, possibility of contamination of the evaporated substance with the evaporation source material, and insufficient reproducibility of patterns on complex-shaped surfaces.

The sol–gel method based on hydrolysis of metal compounds is widely used for fabrication of complex oxide functional materials. The starting materials here are organometallic compounds and organic and mineral metal salts. This method is simple to implement, and it makes possible to fabricate ordered films and control their composition, is fairly cheap, and can be performed at low temperatures. The key factors affecting the film formation process are the concentration of the solution, rate of film formation, and temperature of thermal treatment.

Quite widespread is the method of oxide film deposition from organic solutions. The characteristic feature of thin films deposited from carboxylate solutions is their homogeneous phase composition, as well as the presence of a prevailing orientation of crystallites, which is quite important for microelectronic applications. The quality of oxide films depends on the purity of the substrate surface: Thorough pretreatment of the surface ensures a high adhesion of the film to substrate.

Technology of Film Deposition from Solutions

There are three principal technologies of the deposition of oxide films from solutions [9].

(1) Immersion of a sample into a film-forming solution and withdrawing the sample from the solution. This is a universal and an economically efficient method of film deposition onto large surfaces. The thickness of the resulting layer depends primarily on the rate of sample withdrawal from the solution, inclination angle of the surface being coated, and the concentration of the solution. Other parameters (solution viscosity and surface tension) are included into a coefficient specific of each film-forming solution. The temperature dependence of this coefficient should also be taken into account. The advantage of the immersion method consists is that it requires simple equipment and that the operation can be fully automated.

(2) Centrifuging the sample for uniform distribution of the solution over the surface. This is applied with small round substrates and allows fairly thin films to be deposited on flat plates or plates with a shallow surface relief. This method does not destroy the quality of layers at the plate edges.

(3) Spraying the film-forming solution onto a hot substrate. The method is applied with solutions which give films exclusively at high temperatures. It is widely used in industry for depositing oxide coatings on various materials: electroconducting, optical, and protective coatings on glasses, dielectric coatings on metals and alloys, etc.

To approach the problem of fabrication of nanoscale oxide coatings, in our work we made use of the carboxylate method. This method involves the decomposition of organic compounds, specifically salts of higher iso acids (higher iso carboxylates, HIC), to the corresponding oxides and the subsequent synthesis of complex oxide films in the course of thermal treatment [3–6]. The density of monoxide and multicomponent films markedly increases with temperature due to caking. Their thermal treatment at 300–600°C leads to gradual decrease of porosity and pore size. Such thermal treatment provides multiple film deposition.

Fabrication of Optical-Quality Oxide Films

Of particular interest in terms of functional application are the optical and optic-physical properties of nanoscale coatings. The technology of glass clarification by silica film deposition from solutions is well known [8, 9]. In [10, 11], a technology of oxide film deposition from solutions of hydrolyzing compounds was developed. This technology is used for fabrication of protective coatings in electronics.

The technologies of fabrication of semiconductor devices and integrated circuits using glassy SiO_2 and various silicate films deposited from tetraethoxysilane solutions have found wide application [12].

The sol–gel method was used to deposit films with excellent optical characteristics. For example, Garuz and Fujihashi [13] prepared $Ba_2NaNb_5O_{15}$ films on platinum and quartz substrates. Optically transparent thin films were synthesized on quartz. Popova and Popovich synthesized luminophores on the basis of yttrium oxyorthosilicate activated by rare-earth metal salts [14]. The lighting characteristics of these luminophores were enhanced by 10–30%. Toshio [15] prepared optical oxide films (for example, TiO_2, SiO_2, and Al-doped ZnO films and PbO and GeO_2 dielectric films) from alkoxides by the sol–gel method.

Thin transparent indium–tin oxide coatings on glass show a good electrical conductivity, high transparency is the visible range, and high reflectivity in the IR range [16]. Planar film waveguides were prepared from zinc oxide using acetic acid. The reversible response of films on acid–base pairs opens up wide possibilities for their application as waveguides for optic sensors. The sol–gel method was used for fabrication of high-temperature superconducting films [18].

In terms of the fabrication of optical films, of interest is the carboxylate method of formation of universal oxide coatings, which is favored by the availability of the methods of synthesis of many starting metal carboxylates. The specific feature of the developed technologies of film deposition is that the chemical processes at pH < 7 differ radically from those involved in the alcoholate, sol–gel, and other processes. At the same time, the potential of the carboxylate technology in fabrication of nanoscale oxide films of the optic quality has not yet obtained sufficient experimental evidence.

Study of Nanoscale Oxide Films

Measurement of Film Thickness

In the development of a technology for fabrication of oxide nanocoatings, one has to solve a separate task to develop a procedure for measuring film thickness. Below we describe the procedures for measuring the thickness of oxide coatings, which were applied in our work.

Micro Weighing

The substrate is weighed before and after the deposition of an oxide film. The weight difference gives the film weight and, knowing the metal content in the carboxylate, geometric parameters of the substrate, and film density, we can calculate the film thickness. Therewith, the acceptable degree of approximation of the relative density of the formed oxide was $\rho_x/\rho_{tab} \approx 1.0$.

Radiolabeling

As the label we used a solution of highly enriched ^{235}U.

α-Particles emitted by the ^{235}U-labeled nanocoating are counted by means of a radiometer comprising two blocks: a remote block with a detector sensitive to α-particles and a main block with electronic units for amplification, formation, and registration of pulses received from the remote block. We used a BZD-2 detector with a PSO2-4 counter unit.

Samples are sequentially placed into the detector block. The measurement time for each sample is 100 s,

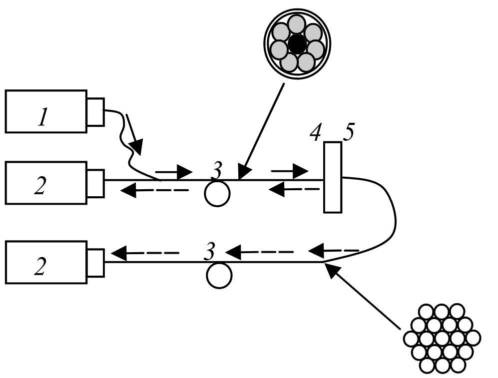

Fig. 1. Schematic diagram of the installation for spectral analytical control of oxide films: (*1*) light source, (*2*) spectral analyzer, (*3*) optic bundle, (*4*) film, and (5) substrate. (Solid arrows) Light propagation from the source over the fiber-optic bundle; (top dashed arrows) propagation of light reflected from the film–substrate system in the reflection study, and (bottom dashed arrows) light propagation over the fiber-optic bundle in the transmission study.

number of measurements ≥ 5. The number of pulses for each sample is calculated as the mean of the radiometer readings minus the background reading obtained before sample measurements. The quantity of ^{235}U in the nanoscale layer is calculated in accordance with the radioactive decay law. Correction for the concentration of a ^{234}U admixture is introduced. Knowing the ^{235}U concentration in the starting solution, one can calculate the film weight. Further on calculations are performed like in the micro weighing procedure, specifically, the substrate geometry is taken into account.

Fiber-Optic Spectrophotometry

This is an optical method for contactless nondestructive control. It is an important element of control at different stage of the coating fabrication process. In our work we used an AvaSpec-1050 fiber-optic spectrophotometer equipped with combined fiber-optic bundle modules.

The structural scheme of the installation for research on nanolayers is presented in Fig. 1.

If a broad-spectrum incandescent lamp is used as the light source, the spectrum analyzer detects reflection spectra which contain absorption bands and reveal features of interference in the film. After analysis of the reflectance spectra, film transmission is studied. To this end, the second optic bundle is connected to the spectrum analyzer (as shown in the bottom part of the scheme).

Fiber-optic bundles include several types of wave guides: The first-type bundles contain fibers of different compositions and the second-type bundles contain fibers of the same composition.

The central waveguide in the first-type bundles transmits UV and visible light. It has a fluorosilicate reflecting shell and a high-purity synthetic fused quartz core, which allow such a waveguide to be used for transmission of a probe light with minimal losses.

The second bundle which comprises fiber of the same composition is fabricated from quartz germinate

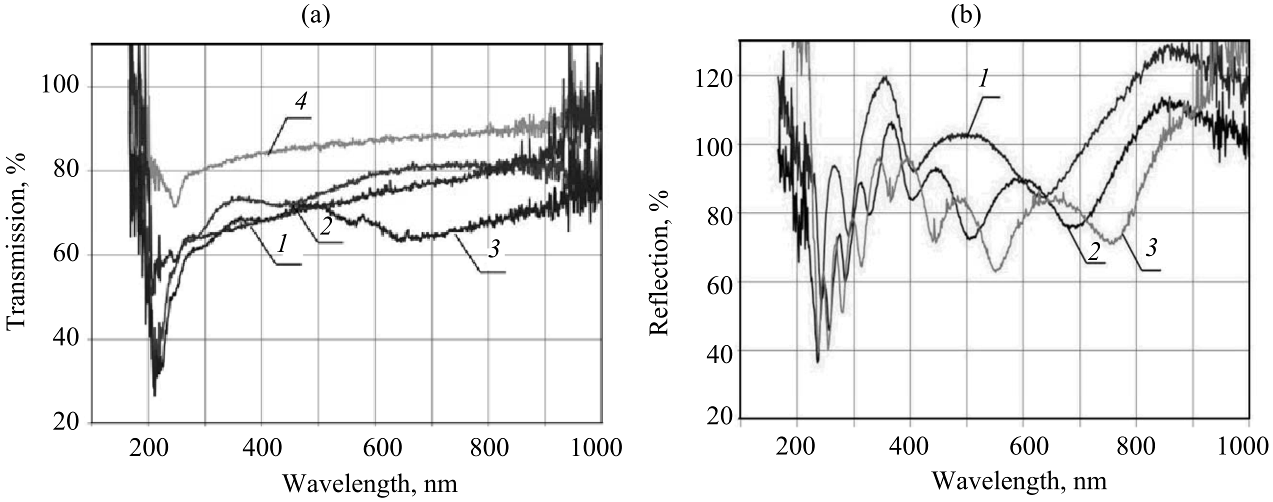

Fig. 2. (a) Transmission and (b) reflection spectra of zirconium oxide on (a) monocrystalline quartz and (b) stainless-steel substrates: (*1*) one oxide layer, (*2*) two layers, (*3*) three layers, and (*4*) substrate.

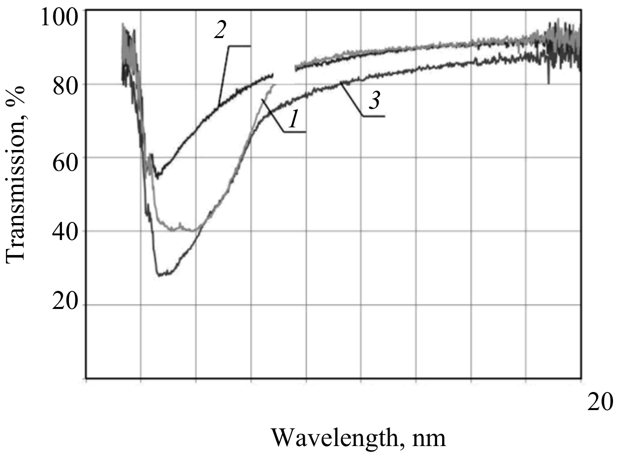

Fig. 3. Transmission spectra of nanocoatings on the basis of (*1*) uranium, (*2*) zirconium, and (*3*) cerium oxides.

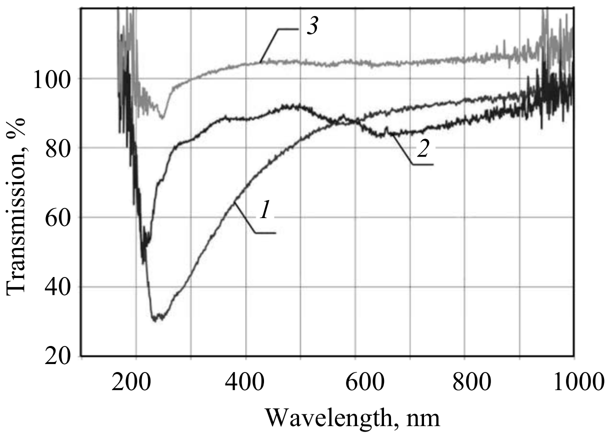

Fig. 4. Transmission spectra of nanocoatings on the basis of (*1*) ZrO_2 and (*2*) $ZrO_2–YO_{1.5}$. (*3*) Substrate spectrum.

fibers, so that in transmission measurements one can also gain information from the near IR range. Analysis of light propagation from the central, lightning waveguide is performed with account for the data in [19]. The signal reflected from film and received by the polyfiber modules contains information on the film composition and thickness. The information on a linear dependence of transmitted light intensity on admixture concentration is reflected as selective absorption bands. In fact, a transmission spectrum of the analyzed medium is recorded. The reflection and transmission spectra also show interference effects which relate to film thickness.

Figure 2 present the transmission and reflection spectra for nanoscale ZrO_2 coatings on monocrystalline quartz and stainless-steel substrates. The reflection spectra show a well-defined interference pattern. Film thickness is calculated from the positions of interference minima and maxima. The characteristic feature of the method of determination of nanofilm thickness from the interference pattern is that it provides a superposition of a substrate reflection spectrum and a film absorption spectrum: The film absorption band superpimposes on the interference pattern. This fact should be borne in mind in the analysis of such spectra.

Spectroscopy of Nanoscale Oxide Films

From the materials science viewpoint, oxide nanocoatings can be divided into several groups.

One-component oxide coatings {ZrO_2, Al_2O_3, CeO_2, uranium oxide (UO_2, U_3O_8), Nd_2O_3, Gd_2O_3, HfO_2, etc.}.

Such coatings were fabricated by pyrolysis (at 500°C under argon) of metal HICs applied on degreased monocrystalline quartz plates. Figure 3 shows the transmission spectra of zirconium, cerium, and uranium oxide nanocoatings. As seen, transmission at 200–400 nm regularly decreases, which is associated with absorption of metal oxides in this range. As the number of nanolayers increases from 1 to 3, transmission tends to decrease in proportion to the thickness of nanolyers. The dependence of the absorptivity on the number of metal oxide layers near the absorption maximum of metal oxide groups is, as expected, close to linear.

The nanofilms obtained at varied metal contents in HICs but fixed pyrolysis temperatures and times still showed a high transmission in the visible range, but the UV absorption band grew with increasing molar concentration of the metal.

The fundamental absorption bands of Zr, U, and Ce oxide layers mach differ from each other (Fig. 3). This fact was taken into account in the research on multicomponent oxide coatings.

Multicomponent coatings with solid-solution compositions. Films on the basis of ZrO_2 oxide doped with 10 mol % of $YO_{1.5}$ (Fig. 4), as well as compositions in the $UO_2–CeO_2$ system were studied.

The transmission spectra of multicomponent nanocoatings are not a simple superposition of the spectra of individual zirconium and yttrium oxides, and the $UO_2–CeO_2$ system, This finding implies formation of mixed phases, initially as amorphous solid solutions with the fluorite structure and then as metastable nanocrystals.

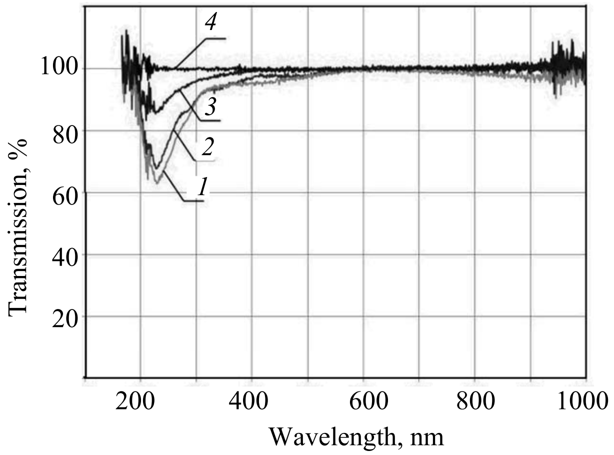

Fig. 5. Transmission spectra of nanocoatings on the basis of (*1*) yttrium oxide, (*2*) yttrium–aluminum garnet, and (*3*) aluminum oxide. (*4*) Substrate spectrum.

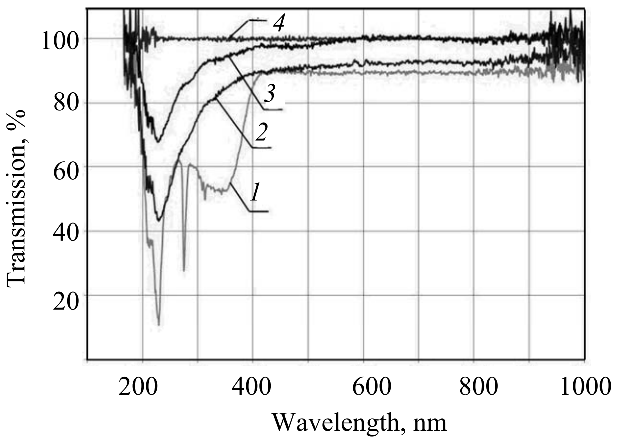

Fig. 6. Transmission spectra of samples with (*1*) gallium–gadolinium garnet nanolayer and (*2*) ten and (*3*) five nanolayers of yttrium–aluminum garnet. (*4*) Substrate spectrum.

Multicomponent coatings with garnet compositions. An aluminum–zinc oxide composition on a monocrystalline quartz substrate was synthesized by pyrolysis of a mixture of aluminum and yttrium HIC solutions at 500°C. The Y and Al contents in the starting carboxylates corresponded to the stoichiometric composition of the yttrium–aluminum garnet $Y_3Al_2(AlO_4)_3$. Caution was taken that the starting carboxylates were protected from atmospheric moisture after their synthesis to mixing.

The multicomponent composition of gallium and gadolinium oxides was synthesized under analogous conditions. The mixture of gallium and gadolinium HICs was prepared so that their Ga and Gd contents corresponded to the $Ga_3Gd_5O_{12}$ garnet composition.

Figure 5 shows the transmission spectra of monocrystalline quartz samples with nanocoatings of aluminum oxide, yttrium oxide, and a binary aluminum–yttrium oxide composition (garnet). The spectra of garnet and aluminum and yttrium oxide nanolayers resemble each other in that they show similar UV absorption bands and contain no selective absorption bands in the visible and IR ranges. However, there are some characteristic differences, specifically, the principal absorption band of garnet has two well-defined bends at 270–280 and 310–320 nm.

The spectrum of a monocrystalline gallium–gadolinium garnet (Fig. 6) contains resolved selective absorption bands ($\lambda_{\max}$ 230 and 275 nm), which is characteristic of crystalline structures, as well as a less intense broad band at 310–380 nm. Certain correlation is observed between the transmission spectra of yttrium–aluminum and gallium–gadolinium garnet nanofilms. The crystallographic structures and, consequently, principal UV and IR absorption bands of these two garnets are identical to each other. At the same time, these bands in the spectra of the garnet compositions are scarcely resolved. This observation suggests that the crystallization processes are limited by the initial stage of the transition of amorphous phases into the nanocrystalline state.

Multiphase nanoscale coatings were synthesized on the basis of the binary and ternary systems $Li_2O–SiO_2$ and $Li_2O–SiO_2–ZrO_2$ on quartz glass substrates. The principal target criterion was a good adhesion of the coating.

Study of the Microstructure of Nanomodified Quarz Glasses

The study was performed using an OptiTech microscope in the transmission mode (magnification ×400). Rectangular plates (15×15×0.4 mm) were cut out of a quartz band. Several compositions which characterize the potentialities of nanoscale surface modification of quartz glass were studies. The microstructures of nanomodified surfaces of quartz glass are shown in Fig. 7.

The nanoscale surface modification of quartz glass by the pyrolysis on its surface of a solution of zirconium HIC at 600°C (5 min) followed by fast cooling to room temperature forms a uniform transparent film (Fig. 7a) in the case of single- and multilayer coatings 30–600 nm thick. As the pyrolysis temperature is elevated to 900°C, a characteristic network appears on the surface (Fig. 7b), which implies development of

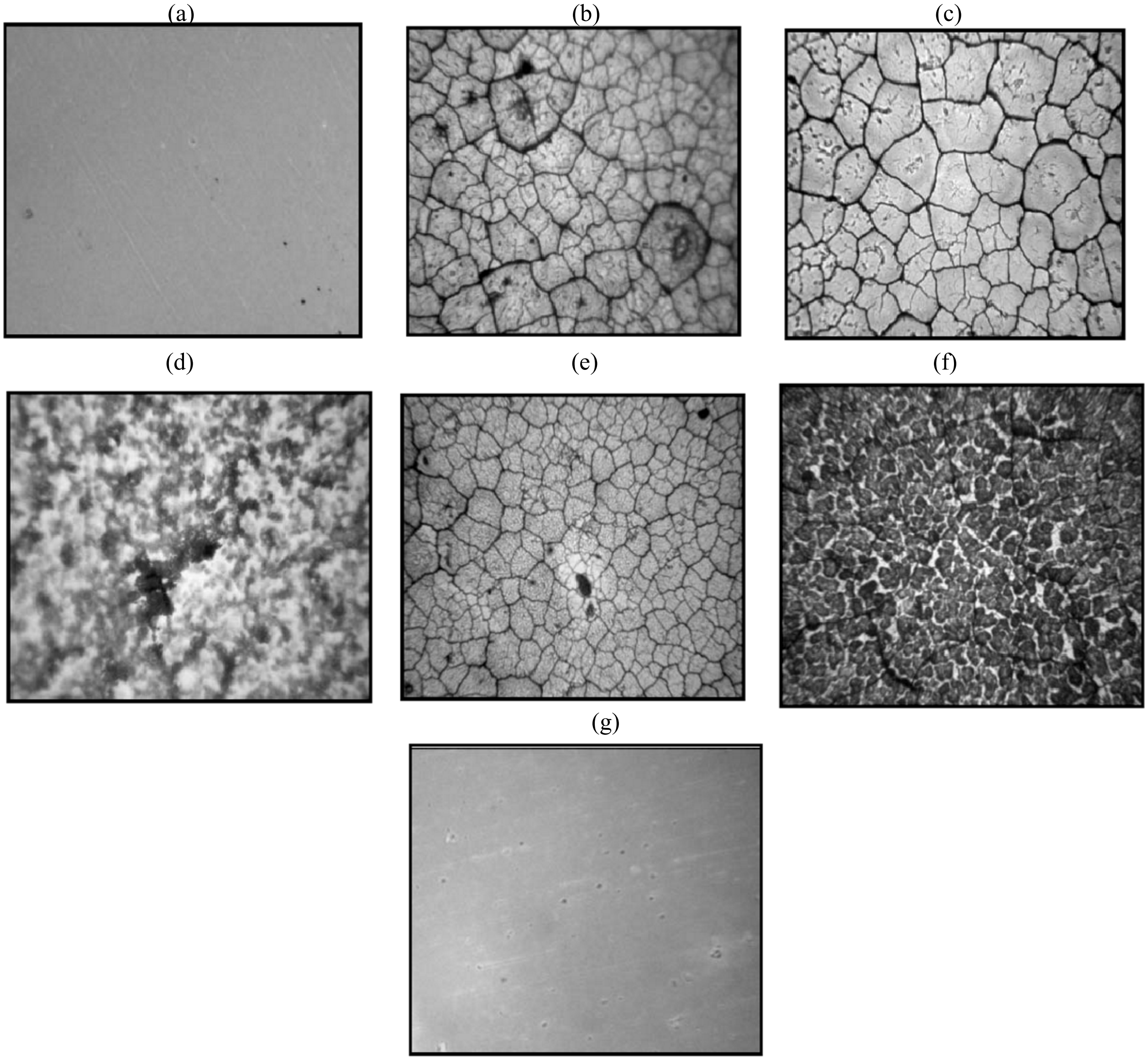

Fig. 7. Mocrostructures of nanomodified quartz glass surfaces. Nanocoating: (a, b) ZrO_2, (c) Li_2O, (d) SiO_2, (e) $Li_2O + SiO_2$, and (f, g) Li_2O–ZrO_2–SiO_2.

crystallization processes and formation of microcracks due to a sharp difference in the thermal expansion coefficients of the quartz glass and ZrO_2 nanocoating.

The same picture is observed in the pyrolysis of lithium HIC at 900°C (5 min; fast cooling) (Fig. 7c). The presence of a Li_2O nanocoating on the surface of quartz glass is hardly possible, on account of reaction diffusion which forms lithium silicate nanolayers or lithium silicate glasses. In any case the difference in the expansion coefficients destroys, in the long run, the uniformity of the nanoscale reactive layer.

A different picture is observed in the pyrolysis of silicon HIC (900°C, 5 min, fast cooling). No film is formed (Fig. 7d). Nontransparent white flakes showing no signs of adhesive interactions are formed on the surface of quartz glass. However, on addition to a solution of silicon HIC of an equimolar amount of lithium HIC, a uniform lithium silicate layer (with micricracks) with rare flaky silica microinclusions is formed (Fig. 7e).

The microstructure of a nanomodified surface of quartz glass radically changes in going to the Li_2O–

ZrO_2–SiO_2 oxide composition with a 1 : 1 : 1 Li : Zr : Si atomic ratio (Fig. 7f). The increased number of components in this system increases the possibility for chemical reaction between the components and microflake formation. The formation of a finely dispersed two-phase "pseudoeutectic"-type structure can be associated either with decreased melting point of the nanosized multicomponent amorphous solid solution or with phase stratification in the nanoscale layers of the lithium–zirconium–silicate glass compositions formed on the substrate surface. The two-phase structure of the nanocoatings (Fig. 7f) is formed upon fast cooling of the samples. However, even if the time of pyrolysis is prolonged only slightly (for example, when the sample is cooled together with the oven), the nanolayer becomes transparent and uniform.

Thus, a great variety of composite materials with different compositions and structure can be developed, depending on the optic physical and engineering requirements to nanofilm coatings.

CONCLUSIONS

The technology of the deposition of nanoscale oxide coatings by carboxylate pyrolysis holds a great promise for fabrication of functional materials. Such materials can be used in antireflection coatings (SiO_2, Al_2O_3, ZrO_2) and interference filters (SiO_2 + GeO_2, Al_2O_3 + ZrO_2); strengthening, antifriction, and protective coatings (Zr, Y)O_2, Al_2O_3, SiO_2; radio-optical coatings doped with neutron-sensitive (Li, U, Hf, or Gd isotopes) and luminescing ions (Ce, Nd, or Er); magnetically sensitive films (on the basis of Fe, Co, Bi, and garnets); and chemically sensitive films (SnO_2, In_2O_3, TiO_2, or Ta_2O_5).

Thus, the universal, fairly inexpensive, and well-proven pyrolytic technology for fabrication of nanoscale oxide films from metal HICs creates a wide functional field for practical application of such films.

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