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Synthesis on Silica Surface by the Ionic Deposition Technique of Nanolayers of Heteropolycompounds on the Basis of Phosphomolybdic Acid

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Abstract—Layers of a "hybrid" iso- and heteropolycompound of the composition $Zr_{2.6}(OH)_xPMo_{8.0}Sn_{1.9}O_y \cdot nH_2O$ were obtained on silica surface by ionic deposition. Heating in air at 200–400°C results in removal from the layer of water molecules, oxidation of Mo^{5+} to Mo^{6+}, and formation of Mo–O–Zr and Mo–O–Sn chemical bonds.

Heteropolycompounds have found application as catalysts, proton carriers, and electron- and ion-exchangers. The scope of their applications may prove still more extended, provided thin-layer structures of heteropolycompounds would be synthesized on various supports. However, synthesis of such structures is a challenging problem, since, in particular, they are thermally unstable and cannot be prepared by vacuum vapor deposition. Heteropolycompounds are also difficult to layer from reagent solutions in view of the fact that certain features of the "cluster" structure of these compounds make their sorption energy on most supports insufficiently high for a thick monolayer to be formed. Moreover, the sorbed heteropolycompound layer have no sorption centers for a further layer to form.

The aim of the present work to explore the feasibility of the ionic deposition technique for synthesis of thin-layer structures of heteropolycompounds. This technique involves synthesis of thin layers of inorganic compounds by successive sorption on the surface of a support of anions and cations, whose surface reaction gives rise to a sparingly soluble compound.

For the anion, in principle, one can take a heteropolyacid anion, whereas for the cation, any cation that gives with it a sparingly soluble compound. According to [1], the suitable cations for phosphomolybdic acid are ammonium and heavy alkaline metal cations. However, we failed to find reasonable conditions for ionic deposition on silica surface of a film containing these cations and the heteropolyacid anion. Probably, the compound formed by the anion and cation on the surface is fairly well soluble and removed in the stage of solvent washing. At the same time, as shown in [1], $H_3PMo_{12}O_{40} \cdot nH_2O$ can be fairly easily reduced to $[PMo_{12}O_{40}]^{n-}$ which may prove to be more reactive in the synthesis of films by ionic deposition. On the other hand, it is known [2] that the reduced form of phosphomolybdic acid forms the most sparingly soluble compound with Zr^{4+}. As the supports for the synthesis of nanolayers we used fused quartz of KU brand and a <100> single-crystal silicon of KEF-7.5 brand (14th degree of surface finish). The reagents were aqueous solutions of $Zr(CH_3COO)_4 \cdot nH_2O$, $SnCl_2 \cdot 2H_2O$, and phosphomolybdic acid $H_3PMo_{12}O_{40} \cdot nH_2O$. The solution of $SnCl_2$ was prepared by the procedure in [3]. The solution of the reduced phosphomolybdic acid was prepared by adding an equivalent amount of a solution of Sn^{2+} to aqueous $H_3PMo_{12}O_{40} \cdot nH_2O$. Once the reagents had been mixed, the solution got blue and had pH 3. Relying on data in [1] we can suggest that in the reagent mixture Sn(IV) ions are incorporated into the heteropolyanion via substitution of one or two molybdenum atoms. The solution of $Zr(CH_3COO)_4 \cdot nH_2O$ was prepared immediately before use by dissolving the salt in distilled water in the cold. The resulting solution had pH 3.5. At such pHs hydrolysis occurs and, as a result, zirconium(IV) exists mostly as trimers and tetramers $Zr_3(OH)_5^{7+}$ and $Zr_4(OH)_8^{8+}$ [4, 5].

To find reproducible synthetic conditions, we measured the concentrations and pHs of the reagent solutions and washings. The following conditions were recognized as optimal: $c[Zr(OAc)_4]$ 0.01, $c(H_3PMo_{12}O_{40})$ 0.01, and $c(SnCl_2)$ 0.05 M. As the washing liquid for removal of excess reagents we used distilled water acidified with AcOH to pH 4. At such a pH, neither zirconium(IV) hydroxide formation nor

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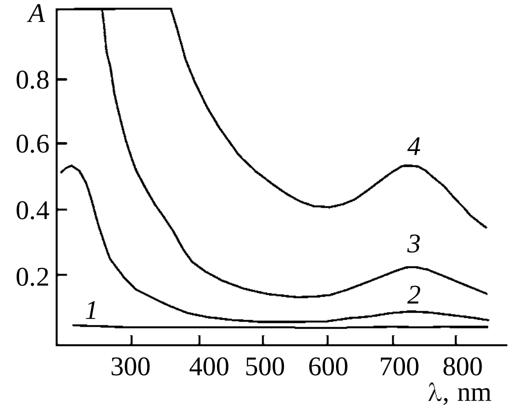

Fig. 1. Transmission spectra of the Zr–P–Mo–Sn–O-containing nanolayers synthesized on (*1*) fused quartz surface as a result of (*2*) 10, (*3*) 20, and (*4*) 30 cycles of ionic deposition.

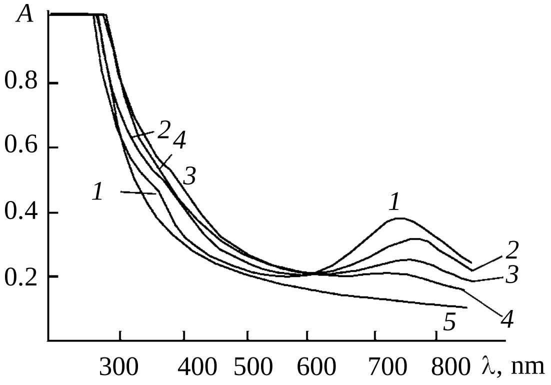

Fig. 2. Transmission spectra of the Zr–P–Mo–Sn–O-containing nanolayer synthesized on fused quartz surface as a result of (*1*) 20 cycles of ionic deposition followed by heating at (*2*) 200, (*3*) 300, (*4*) 350, and (*5*) 400°C.

structural changes in the heteropolyanion occurred on the support surface in the washing stage.

The synthetic procedure was as follows. Supports were successively immersed into solutions by a certain scheme (zirconium acetate solution, washing liquid, reduced phosphomolybdic acid solution, and washing liquid) forming an elementary cycle of ionic deposition. The time of treatment with each reagent was 0.5 min. One cycle formed on the support surface one nanolayer.

Ultraviolet and visible transmission spectroscopy (Fig. 1) were used to show that repeated treatment increases the layer thickness on fused quartz surface, as evidenced by the fact that increasing number of cycles enhances the absorption bands at 200–500 and 730 nm. According to [1], the first band is formed by Sn^{4+} and Mo^{6+} ions incorporated in the layer and the second, by Mn^{5+} ions that are probably formed by the partial reduction of Mo^{6+} by the reaction $Sn^{2+} + 2Mo^{6+} \rightarrow Sn^{4+} + 2Mo^{5+}$.

Figure 2 shows the transmission spectra of the layer synthesized on fused quartz surface and heated in air at various temperatures. It can be seen that the absorption band at 730 nm attenuates with increasing temperature until it disappears completely upon heating at 400°C. These changes can unambiguously be related to the decrease in the concentration of Mo^{5+} ions, resulting from reaction of the layer with atmospheric air at elevated temperatures.

The IR spectrum of the layer obtained after 20 cycles of ionic deposition on the surface of single-crystal silicon is represented in Fig. 3, spectrum *1*. The IR spectrum of phosphomolybdic heteropolyacid contains three groups of bands, cm^{-1}: $\nu(PO_4)$ 800–1100, ν(Mo=O) 900–1000, and ν(Mo–O–Mo) 200–900 [6]. Zirconium and tin hydroxides give characteristic strong bands at 300–600 cm^{-1} [6]. In view of these data, in the experimental spectrum of the synthesized layer we can identify bands at 1051, 958, and 792 cm^{-1}, belonging to the heteropolyacid anion, as well as bands at 300–540 cm^{-1}, presumably belonging to Zr(IV) and Sn(IV) oxohydroxides. Noteworthy is the presence in the layer of water molecules that reveal themselves by the absorption bands at 3550–3200 (OH stretching vibrations) and 1630–1600 cm^{-1} (HOH deformation vibrations).

Heating of the samples in air at 200–300°C produces considerable changes in their IR spectra. Thus the absorption bands of water get weaker, but they do not disappear completely upon heating at 300°C. Furthermore, the PO_4 absorption maximum shifts to 1085 cm^{-1}, the band at 958 cm^{-1} gets weaker and then disappers, the band at 780–800 cm^{-1} gets stronger and broader, and the band with maxima at 540 and 358 cm^{-1} gets weaker. In our opinion, these changes may suggest cleavage of Mo=O bonds and formation of new bonds, for example, Mo–O–Zr or Mo–O–Sn.

The element concentration ratio in the synthesized layer was determined by X-ray photoelectron (XPE) spectroscopy. As seen from the XPE spectrum in Fig. 4, the layer contains Zr(IV), P(V), Mo(V, VI), Sn(IV), and O(II) ions at a 2.6 : 1 : 8.0 : 1.9 : 57.4 ratio. The formula of the obtained compound can be written as $Zr_{2.6}(OH)_xPMo_{8.0}Sn_{1.9}O_y \cdot nH_2O$. This notation does not place emphasis on the concentration of various forms of oxygen in the layer, since it is obvious that oxygen can be incorporated in water molecules, OH grous, and metal oxide compounds. Unfortunately, we failed to estimate the concentration of Mo^{5+} ions from the XPE spectra, probably, because of the low concentration of these ions and close location of their bands to those of Mo^{6+} ions.

The resulting data suggest formation on silica surface in the course of ionic deposition on successive treatment of the support with solutions of reduced phosphomolybdic acid and of zirconium(IV) acetate of a “hybride” compound comprising structural fragments both of the starting heteropyacid and of Zr(IV) polyhydroxycations. The latter, along with Sn^{4+} cations serve as a kind of “bridges” that bind anions; as a result, a 3D network of chemical bonds is formed on the surface. Evidence for these suggestions comes from the fact that the layer synthesized on quartz or silicon surface possesses a high mechanical strength. After drying, it withstands the simplest abrasion test.

EXPERIMENTAL

The UV and visible transmission spectra were measured on a Perkin–Elmer Lambda-9 spectrophotometer, scan rate 50 nm/min, slit width 2 nm. The Fourier IR spectra were taken on a Perkin–Elmer-1760X spectrophotometer. The XPE spectra were obtained on a Perkin–Elmer-5400 spectrometer with MgK_{α} excitation.

Quartz supports were washed with acetone, held at 90–100°C for 10 min in concentrated nitric acid, and then washed in succession with distilled water, KOH solution (pH 9), and water. Single-crystal silicon supports were first calcined at 750°C for 1 h to form on their surface of a silicon oxide layer and then treated for 0.5 h at 90–100°C in twice distilled water.

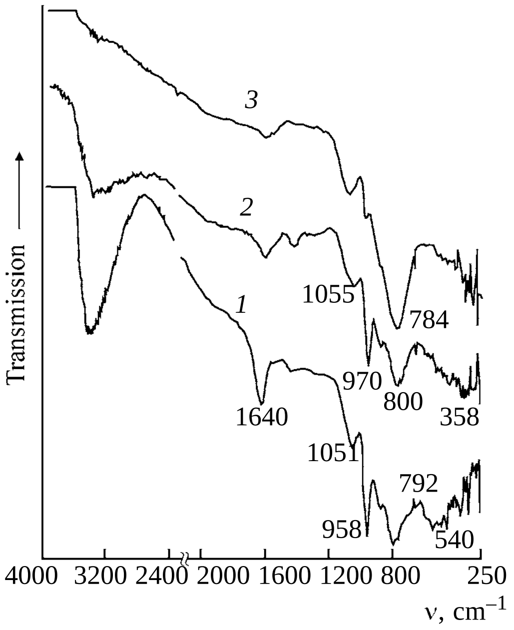

Fig. 3. Fourier IR spectra of the Zr–P–Mo–Sn–O-containing monolayer synthesized on single-crystal silicon surface as a result of (*1*) 20 cycles of ionic deposition followed by heating in air at (*2*) 200 and (*3*) 300°C.

After standard treatment the supports were fixed in the holders of an automated computer-controlled device for synthesis and subjected to treatment by the scheme forming an elementary cycle of ionic deposi-

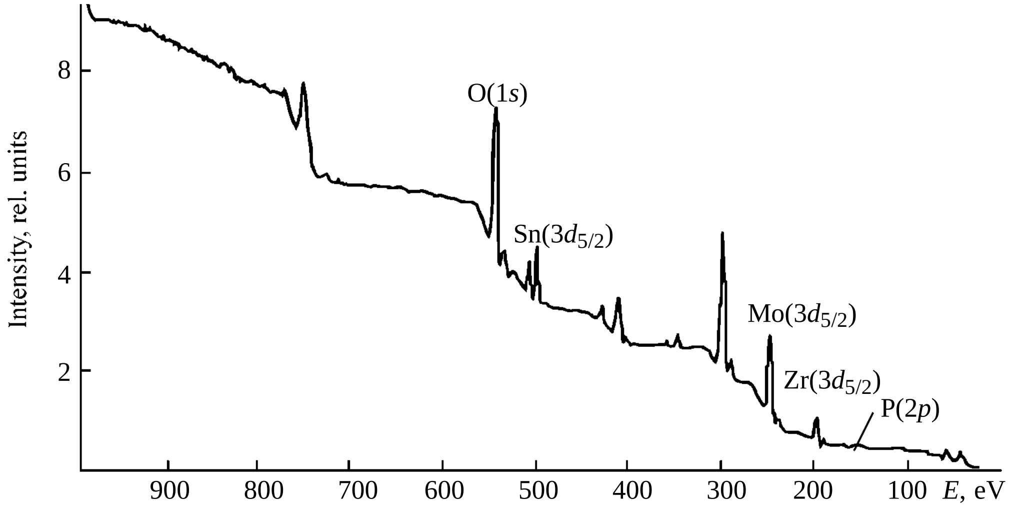

Fig. 4. X-ray photoelectron spectrum of the Zr–P–Mo–Sn–O-containing nanolayer synthesized on single-crystal silicon surface as a result of 20 cycles of ionic deposition.

tion. The successive layers were synthesized by repeating the deposition cycles.

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