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Layers of xCuS–$SiO_2 \cdot n H_2O$ Nanocomposite, Synthesized by the Layer-by-Layer Technique

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Abstract—For the first time conditions were determined for the synthesis of $Cu_xSiO_{2+x} \cdot nH_2O$ nanostructured layers by consecutive adsorption of copper ammine cations and adagulation of colloidal SiO_2 particles and also for the synthesis of xCuS–$SiO_2 \cdot nH_2O$ nanocomposite layers by consecutive surface adsorption of copper cations and HS^- anions. These layers were studied by means of UV and visible transmission spectroscopy, X-ray spectral microanalysis, and scanning electron microscopy. Schemes of the surface reactions were constructed on the basis of this experimental material.

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Presently the layer-by-layer synthesis of nanolayers and nanostructures attracts increasing attention. The corresponding results are summarized in the monographs [1, 2] and reviews, for example [3, 4], that describe syntheses with molecules, ions, and colloidal particles as reagents. In [4], the diversity of such reactions has been suggested to subdivide into special groups in terms of the nature of the reagents, and to define the procedures of synthesis, in particular, as ionic, ionic–colloid, and colloid layering. The necessity in such subdivision is connected with the fact that each of these procedures is underlain by its specific processes. Thus, ionic layering involves adsorption reactions yielding inner- and outer-sphere surface complexes, colloidal layering involves adagulation reactions, etc.

The aim of the present work was to apply the ionic–colloid and ionic layering procedures for the synthesis of a nanocomposite consisting of CuS semiconductor nanoparticles in a dielectric support (SiO_2). Earlier [5] new quantum-dimensional electrophysical and optical properties were predicted to appear in such systems. Therewith, such nanocomposites were synthesized by filling the interior volume of nanoporous materials, for example Zeolites or MCM materials, with semiconductor nanoparticles. This known approach, however, has limitations in the case of the synthesis of nanocomposite layers on the surface of various supports of arbitrary complicated shapes.

Nano- and mesoporous SiO_2 supports were synthesized by consecutive adsorption of copper ammine cations and adagulation of colloidal SiO_2 particles by the ionic–colloid layering procedure. It follows from Fig. 1 that multiple and alternate treatment of the

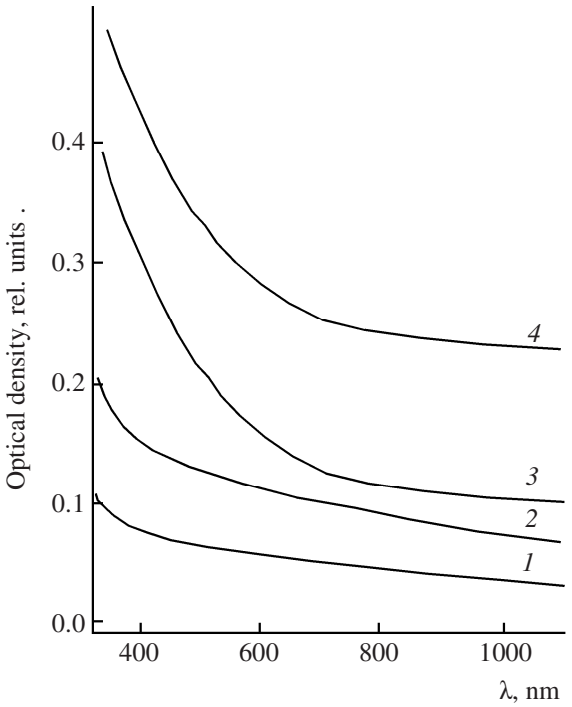

Fig. 1. Transmission spectra of: (*1, 2*) $Cu_xSiO_3 \cdot nH_2O$ and (*3, 4*) xCuS–$SiO_2 \cdot nH_2O$ nanolayers synthesized on a surface of fused quartz as a result of (*1*) 6 and (*2*) 12 cycles of ionic–colloid layering and of (*3*) 1 and (*4*) 3 cycles of ionic layering. {C[$Cu(NH_4)_2(OAc)_2$] 0.01, C(Na_2SiO_3) 0.02 M}. {C[$Cu(OAc)_2$] 0.01, C(Na_2S) 0.001 M}.

substrate surface by this procedure results in the formation of a layer on the surface, which absorpbs light in the range of 200–400 nm with an intensity increasing with the number of ionic–colloid layering cycles. As follows from X-ray spectral microanalysis data for a sample synthesized on a corundum surface, the Cu/Si concentration ratio in the layer is 0.1. Scanning elec-tron microscopy showed that the synthesized layer (Fig. 2) consists of nanoparticles with a size of about 10–20 nm, which is close to the size of colloidal particles in the SiO_2 solution.

To explain the results obtained, we constructed schemes of surface reactions that occur in the course of the ionic-colloid layering synthesis (Fig. 3). According to these schemes, after adsorption of copper cations on the support surface (Fig. 3b) this latter acquires a positive charge at the pH of the colloidal SiO_2 solution and can react with colloidal particles to form the compound shown in Fig. 3c. This compound reacts with copper cations in the stage of treatment in a copper ammine solution, as a result of which the surface again acquires a positive charge, providing the possibility for adagulation of colloidal SiO_2 particles in the following ionic-colloid layering cycles, etc.

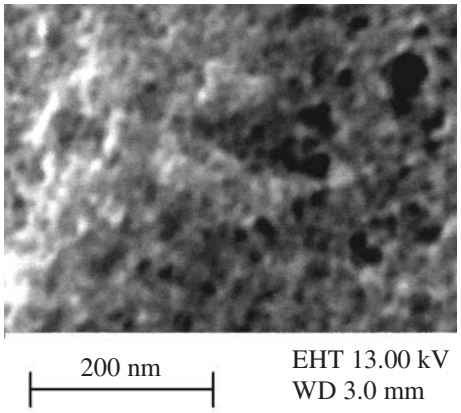

Fig. 2. Scanning electron microphotograph of the $Cu_xSiO_{2+x} \cdot nH_2O$ layer on a silicon surface. The layer was synthesized as a result of 10 cycles of ionic–colloid layering. {C[$Cu(NH_4)_2(OAc)_2$] 0.01, C(Na_2SiO_3) 0.02 M}.

If the resulting layer is consecutively treated in Na_2S and $Cu(OAc)_2$ solutions by the ionic layering procedure, then, as follows from the transmission spectra in Fig. 1 (curves *3* and *4*), its optical properties

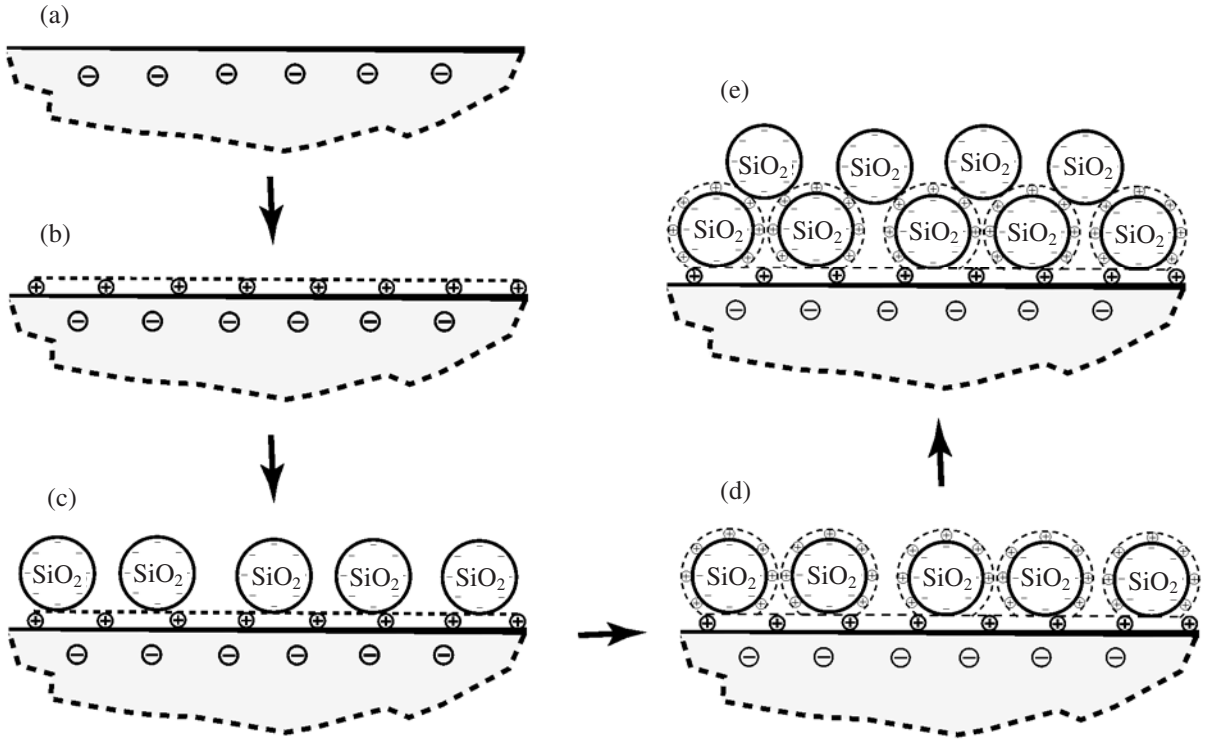

Fig. 3. Scheme of formation of a $Cu_xSiO_{2+x} \cdot nH_2O$ layer in the course of the ionic–colloid layering synthesis: (a) initial substrate, (b, d) stages of adsorption of copper ammine cations, and (c, e) stages of adagulation of colloidal SiO_2 particles.

sharply change, and it turns dark brown. The X-ray spectral microanalysis of this layer shows that the Cu/S concentration ratio is one, implying formation of a CuS layer. It is essential that, according to scanning electron microscopy data (not shown in Fig. 2), the morphology of the initial layer does not change essentially, which provides evidence showing that the CuS layer is formed in meso- and nanopores of the SiO_2 support.

Thus, using the synthesis of $Cu_xSiO_{2+x}\cdot nH_2O$ and xCuS–$SiO_2\cdot nH_2O$ layers as an example, we have proposed and experimentally substantiated the way of the synthesis of nanolayers of inorganic substances by the ionic–colloid and ionic layering procedures.

EXPERIMENTAL

The UV and visible transmission spectra were recorded on a Perkin-Elmer Lambda-9 spectrophotometer at the scan rate 50 nm min^{-1} and the slit program 2 nm. The images of sample surfaces were obtained on a Zeiss EVO-40EP scanning electron microscope with a LaB6 cathode. The X-ray spectral microanalysis was carried out on this microscope at the accelerating voltage of 20 kV using an INCA 350 (Oxford Instruments) energy dispersion analyzer.

As substrates for the synthesis of nanolayers we used KDB-40 grade single-crystal silicon of the <100> orientation and KB-grade quartz polished up to the 14 surface finish class. The technique of the preparation of supports before synthesis has been described in [6].

The colloidal SiO_2 solution was obtained from a freshly prepared 0.02 M Na_2SiO_3 solution in twice distilled water by its acidification with HCl to pH 7 and exposed at room temperature for 1 day before synthesis. According to [7], colloidal SiO_2 particles in such solutions are about 10 nm in size. The copper ammine solution (C 0.01 M) was prepared by dissolving $Cu(OAc)_2$ and NH_4OAc (1 : 12) in twice distilled water. Its pH was made 9.2–9.3 by adding conc. NH_4OH. The 0.001 M Na_2S solution (pH 9.0) was prepared in twice distilled water.

The synthesis was performed as follows. Before synthesis the support was prepared by a standard procedure, placed in a holder of an automated device, and successively treated in a copper salt solution, distilled water, a colloidal SiO_2 solution, and again in distilled water. This treatment formed one cycle of ionic–colloid layering. After the synthesis of the $Cu_xSiO_{2+x}\cdot nH_2O$ layer, the samples were dried in air at 100°C and then treated in a Na_2S solution, distilled water, a $Cu(OAc)_2$ solution, and again in water. This sequence of operations comprised one cycle of ionic layering. The duration of treatment by each of the reagents was 30 s.

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