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Layer-by-Layer Synthesis and Study of Nanostructured $Pb_4SbS_{6.5}$ Layers

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Abstract—Conditions for the layer-by-layer synthesis of nanostructured $Pb_4SbS_{6.5}$ layers on a silica surface, using reagent solutions, were determined. The synthesized layers were studied by X-ray photoelectron spectroscopy, UV and visible transmission spectroscopy, X-ray spectral microanalysis, and scanning electron microscopy.

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One of important directions in creating semiconductor materials with a new set of properties is synthesis of materials consisting of nanoparticles and nanolayers with quantum size effects.

In the present work one of such materials, double lead and antimony sulfide, was synthesized by the ionic colloid layering (ICL) method. A review of applications of this method is presented in [1]. The essence of the synthesis of Pb–Sb–S-containing layers consists in successive and multiple treatment of a support with a lead salt solution and by a colloidal solution containing $\{[H_xSb_2S_5]^{m-}\}mNa^+$ nanoparticles, which react with each other to form a layer of a sparingly soluble compound on the support surface. An indispensable condition for successful synthesis is to remove excess reagents in each stage by, in particular, solvent washing. Owing to a preset sequence of treatments and to a choice of other conditions of the synthesis, for example, pH and reagent concentrations, the resulting layer can be expected to consist of nanoparticles with a size corresponding to the size of colloidal particles.

The transmission spectrum of the nanolayer formed on a fused quartz surface by multiply repeated ICL cycles shows an absorption band in the region of 300–550 nm (Fig. 1), and the intensity of this band increases with increasing number of ICL cycles. Based on the intensity of the transmission band (Fig. 2) we chose optimal concentrations of the reagent solutions [$C(Pb(OAc)_2$ 0.01 M and $C(Na_3SbS_4)$ 0.01 M].

The synthesized layers were studied by X-ray photoelectron (XPE) spectroscopy, X-ray spectral microanalysis, and scanning electron microscopy (SEM). According to XPE data (not shown in figures), the layer contains the following ions: Pb^{2+} (137.4 eV, $4f_{7/2}$ peak), Sb^{5+} (528.9 eV, $3d_{5/2}$ peak), and S^{2-} (160.5 eV, $2p$ peak [2]). Other cations or anions which could pass into the layer from the reagent solutions are absent from the layer composition. According to the X-ray spectral microanalysis, the Pb/Sb/S ratio in the Pb–Sb–S-containing nanolayers synthesized by 20 ICL cycles was 4.0/1.0/6.5.

The morphology of the synthesized layer was studied by SEM (Fig. 3) to show that the layer consists of 15–20-nm nanoparticles. This size seems to

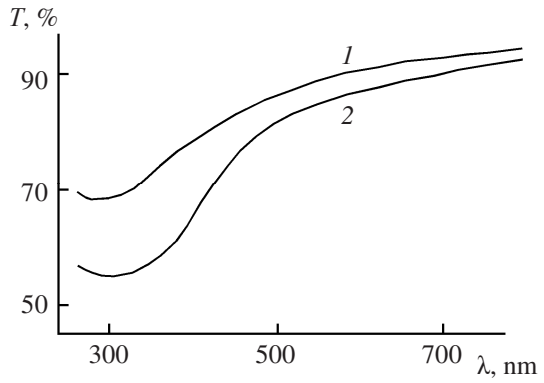

Fig. 1. Transmission spectra of Pb–Sb–S-containing nanolayers synthesized on a fused quartz surface as a result of (*1*) 20 and (*2*) 40 ICL cycles [$C(Pb(OAc)_2$ 0.01 M, $C(Na_3SbS_4)$ 0.01 M].

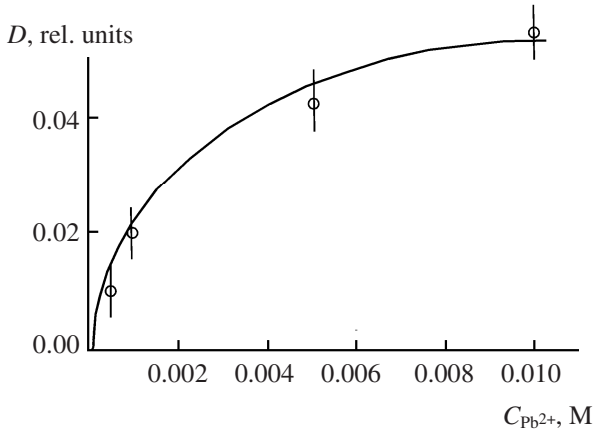

Fig. 2. Changes in the optical density D (λ 400 nm) in the transmission spectra of the Pb–Sb–S-containing nanolayers synthesized on a quartz surface by 10 ICL cycles vs. concentration of the $Pb(OAc)_2$ solution [$C(Na_3SbS_4)$ 0.01 M].

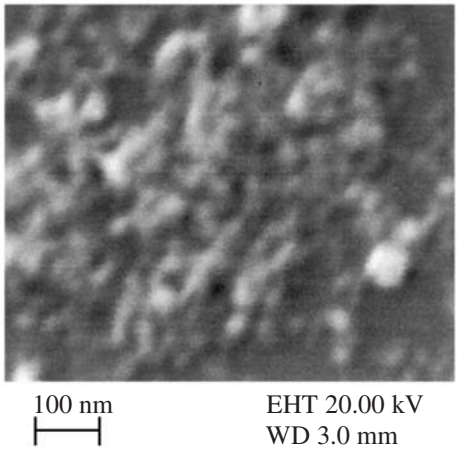

Fig. 3. Scanning electron microscopy image of the surface of the Pb-Sb-S layer synthesized by 10 ICL cycles on a silicon surface [$C(Pb(OAc)_2$ 0.01 M, $C(Na_3SbS_4)$ 0.01 M].

correspond to the size of colloidal Sb_2S_5 particles in the Na_3SbS_4 solution.

On the basis of the foregoing data on the synthesis of a Pb–Sb–S-containing nanolayer we can offer the following scheme of the processes that occur on the surface. After the adsorption of Pb^{2+} cations on the support surface and the removal of their excess by washing with water, the compound ≡Si–OPbOH is formed on the surface and enters in reaction with $\{[H_xSb_2S_5]^{m-}\}mNa^+$ colloidal particles from the Na_3SbS_4 solution to form a new compound. This Pb–Sb–S-containing compound adsorbs lead cations in the second ILC cycle, thus reproducing the cyclic layer growth process. Therewith, when the $H_xSb_2S_5$ colloidal particle adsorbed on the support surface is treated with an excess of the lead salt, lead cations substitute a part of antimony atoms to form lead sulfide and to dissolve antimony in the form of $Sb(OH)_5$.

EXPERIMENTAL

The XPS spectra were obtained on a Perkin–Elmer 5400 spectrometer, exciting radiation MgK_α. The UV and visible transmission spectra were recorded on a Perkin–Elmer Lambda-9 spectrophotometer, scan rate 50 nm min^{-1}, slit width 2 nm. The surface images were taken using a Zeiss EVO-40EP scanning electron microscope, LaB_6 cathode. X-ray spectral microanalysis was carried out on this microscope at an accelerating voltage of 20 kV by using an INCA 350 energy dispersion analyzer (Oxford Instruments).

A KDB-40 single crystal silicon of <100> orientation and a KB quartz polished up to 14 surface finish class were used as supports for the synthesis of nanolayers. The procedure of preparation of the supports before synthesis is described in [3].

The layers were synthesized using 0.01 M aqueous solutions of Na_3SbS_4 and $Pb(OAc)_2$ purchased from Vekton. The pH of the lead salt solution corresponded to an equilibrium solution, and the pH of the Na_3SbS_4 solution was adjusted to 8.5 with acetic acid. At this pH, a light yellow colloidal solution of Sb_2S_5 stable within one day formed.

The treatment time of supports in reagents and water was 0.5 min. In the first stage of the synthesis, a support was exposed to the lead salt solution, washed with water to remove salt, exposed to the Na_3SbS_4 solution, and, finally, washed with water to remove an excess of the latter salt. This treatment comprises one ICL cycle. This treatment sequence was multiply repeated. Earlier we used a similar procedure to synthesize Ag_7SbS_6 layers [4].

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