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$In_{0.22}SnS_{0.33}(OH)_4$ Nanolayers Synthesized by the Layer-by-Layer Technique

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Abstract — The possibility of the synthesis of $In_{0.22}SnS_{0.33}(OH)_4$ nanolayers on the silica surface by the layer-by-layer technique was demonstrated. The synthesized layers were studied by ellipsometry, X-ray spectral microanalysis, and electronic and IR Fourier spectroscopy.
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Much attention is given today to the problem of the synthesis of nanolayers of various compounds on substrate surfaces by the layer-by-layer technique. To obtain nanolayers of metal sulfides, the techniques of molecular layering (ML) [1], atomic layering (AL) [2], and ionic layer deposition (ILD) [3–7] are used. Each of these techniques has its own area of the most efficient application as regards the synthesis conditions and the range of synthesized compounds. For example, ML and AL techniques are used to prepare layers of those sulfides for which volatile metal compounds used as reagents exist in the field of the thermal stability of surface functional groups. The ILD technique is applicable to the synthesis of nanolayers of metal sulfides that are difficultly soluble in aqueous solutions; in this case, solutions of a salt of the corresponding metal and Na_2S [4–5] or H_2S [6–7] are used as reagents.

The preparation of nanolayers of double sulfides and hydroxosulfides of metals on a surface is also of considerable interest. It was found previously [8] that a layer of Ag_7SbS_6 can be prepared by the ILD technique with solutions of Ag^+ and Sb(V) (Na_3SbS_4) salts used as reagents.

The aim of this work was the synthesis of $In_xSn \cdot S_y(OH)_z$ nanolayers. These layers find application as semiconducting and optical materials.

To synthesize indium- and tin-containing layers, we used 0.01 M solutions of Na_4SnS_4 and $In(NO_3)_3$ or $InCl_3$ with an equilibrium pH. However, the first experiments showed that a layer is formed on the silica surface only when $In(NO_3)_3$ solutions are used in the synthesis. To account for this result, we calculated the equilibria in solutions of indium salts at various pH values using the Visual Minteq 2.40b program [9]. The results obtained show that, at the equilibrium pH 2.5, fairly stable complexes $InCl^{2+}$ and $InCl_2^+$ ($\log K$ 2.75–4.37) are formed in the $InCl_3$ solution. These complexes are probably inert with respect to the reaction with tin-containing compounds on the substrate surface. At the same time, the $In(NO_3)_3$ solution contains $In(OH)^{2+}$ and In_{aq}^{3+} complexes which enter into such reaction and are adsorbed on the surface.

The layer synthesized using $In(NO_3)_3$ and Na_4SnS_4 is characterized by the UV spectrum (Fig. 1) with a broad absorption band in the range 200–450 nm and the IR spectrum (Fig. 2) with an absorption band at 1640 cm^{-1} belonging to bending vibrations of the O–H groups of water molecules, bands of bending vibrations of O–H groups of metal hydroxides (1400 and 1200 cm^{-1}), and a broad absorption band in the range 600–300 cm^{-1}, which should be assigned to stretching vibrations of Sn–O and In–O bonds [10].

The spectra essentially change on heating. After heating at 400°C, the bands at 1400–1200 cm^{-1} disappear from the IR Fourier spectrum and a more structured absorption band in the range 600–300 cm^{-1} appears, which suggests the decomposition of the hydroxides with the formation of the corresponding oxides. The absorption in the range 400–850 nm decreases, which is probably due to partial removal of sulfur atoms from the layer on heating.

It follows from the ellipsometry data that a layer of thickness 0.4 nm is formed on the surface in one ILD cycle. According to the data of the X-ray spectral microanalysis, the layer synthesized by 25 ILD cycles contains In, Sn, and S atoms in the ratio of 2 : 9 : 3.

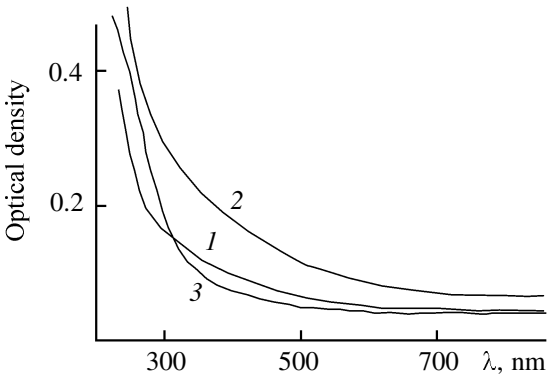

Fig. 1. UV–visible absorption spectra of $In_{0.22}SnS_{0.33}\cdot(OH)_4$ layers on the quartz surface, synthesized by (*1*) 10 and (*2*) 15 ILD cycles from $In(NO_3)_3$ and Na_4SnS_4 solutions; (*3*) the same as *2*, after heat treatment in air at 300°C for 30 min.

Thus, the formula of the synthesized compound can be written as $In_{0.22}SnS_{0.33}(OH)_4$, and after heating in air, as $In_{0.22}SnO_{2.33}$.

We believe that the reactions occurring on the surface can be presented by Eqs. (1) and (2).

$$\geqslant SiO^- + In^{3+}_{aq} \longrightarrow \geqslant SiOIn^{2+}_{aq}[In(NO_3)_3]_{ads,x}, \quad (1)$$

$$\geqslant SiOIn^{2+}_{aq}[In(NO_3)_3]_{ads,x} + H_2O \text{ (washing)} \longrightarrow \geqslant SiOIn(OH)_{2,aq}. \quad (2)$$

As a result of reaction (1), a layer of chemically and physically adsorbed $In(NO_3)_3$ is formed on the surface in the first operation cycle. After removing the substrate from the $In(NO_3)_3$ solution and washing with water [reaction (2)], the layer of physically adsorbed ions is washed off, whereas the more strongly adsorbed layer of In^{3+}_{aq} aqua complexes forms a layer of indium hydroxide $\geqslant SiOIn(OH)_{2,aq}$ on the surface. Then, in the stage of the treatment with a SnS_4^{4-} solution and washing to remove its excess, a complicated negatively charged hydroxosulfide complex of indium and tin is formed on the surface. It is a center of the adsorption of indium cations in the following ILD cycle. However, the treatment of this complex with an $In(NO_3)_3$ solution does not result in complete hydrolysis of the Sn–S bonds, and a part of sulfur atoms is incorporated in the growing layer.

Thus, we have demonstrated for the first time the possibility of preparing $In_{0.22}SnS_{0.33}(OH)_4$ nanolayers by the ILD technique.

EXPERIMENTAL

The IR Fourier transmission spectra of the synthesized layers were obtained on a Perkin-Elmer 1760X spectrophotometer at a resolution of 4 cm^{-1} from 20 scans. The UV–visible absorption spectra were recorded on a Perkin–Elmer Lambda-9 spectrophotometer at a scanning rate of 50 nm min^{-1} and the 2 nm slit program. Ellipsometric measurements were carried out on an ellipsometer with a light wavelength of 632.8 nm and the light incidence angle of 45°. The X-ray spectral microanalysis was carried out at the accelerating voltage of 20 kV on a CAMSCAN-4 scanning electron microscope combined with an AN-10000 semiconducting spectrometer of characteristic X-ray radiation. The data were processed by the ZAF 4-FLS program.

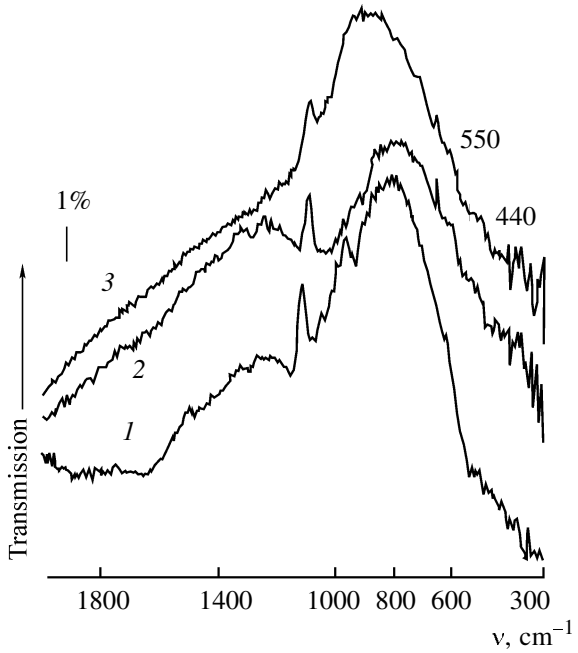

Fig. 2. IR Fourier transmission spectra of an $In_{0.22}Sn\cdot S_{0.33}(OH)_4$ layer synthesized by 20 ILD cycles on the silicon surface from $In(NO_3)_3$ and Na_4SnS_4 solutions: (*1*) initial sample; (*2, 3*) samples heat-treated in air for 30 min at 200 and 400°C, respectively.

As substrates for the synthesis of nanolayers we used KDB-40-grade single-crystalline silicon of the <100> orientation and KB-grade quartz polished to surface finishing class ⟨14⟩. The technique of the preparation of substrates prior to the synthesis has been described in [11].

To synthesize the layers by dissolving the corresponding salts in water, we prepared 0.01 M solutions of $Na_4SnS_4\cdot 18H_2O$ and $In(NO_3)_3$ or $InCl_3$ with the equilibrium pH values. $Na_4SnS_4\cdot 18H_2O$ was prepared according to [12] from $Na_2Sn(OH)_6$ and $Na_2S\cdot 9H_2O$ as reagents.

The time of the treatment of substrates in the reagents and in water was 0.5 min. In the first stage of the synthesis, the substrate was kept in an indium salt

solution, washed with water to remove the excess solution, and placed in a Na_4SnS_4 solution. After keeping the substrate in it, the excess salt was washed off with water. These operations constituted one ILD cycle. This sequence of treatments was multiply repeated.

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