Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 840–843. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 899–903.
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Synthesis of Ag_7SbS_6 Nanolayers on the Silica Surface by Ionic Layer Deposition

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Received July 4, 2000

Abstract—Nanolayers of Ag_7SbS_6 were prepared for the first time by ionic layer deposition. The influence of reactant solution concentrations and number of ionic layer deposition cycles on the layer growth kinetics was examined, and conditions were determined under which the layer formation occurs on the support surface by the reaction between ions sorbed from the reactant solutions, occurring in the layer. The layers were studied by transmission and diffuse reflection spectroscopy, X-ray spectral microanalysis, X-ray photoelectron spectroscopy, and powder X-ray diffraction.

Recently there has been a great deal of interest in precision synthesis of thin films of various compounds on support surfaces. Nanolayers of metal sulfides are mainly prepared by three methods: molecular layer deposition [1], atomic layering epitaxy [2], and ionic layer deposition [3–7]. From the viewpoint of the synthesis conditions and range of compounds being synthesized, each of these methods has its specific fields of efficient application. For example, molecular layer deposition is used to prepare sulfides for which there exist volatile metal precursor compounds stable in the range of thermal stability of the surface functional groups, whereas atomic layering epitaxy is a suitable route to sulfides whose evaporation temperature exceeds that of the precursors by several hundred degrees. Ionic layer deposition is used to prepare nanolayers of metal sulfides from a solution of appropriate metal salt and an Na_2S [4, 5] or H_2S [6, 7] solution. However, it should be noted that, in the papers cited, the indicated synthesis conditions correspond to synthesis of nanolayers of individual metal sulfides or of their so-called “superlattices.”

Of considerable interest is also preparation of supported nanolayers of double sulfides. This is apparently a complex problem, in view of the above-mentioned specific features of each synthetic procedure. Here we report the synthesis by ionic layer deposition of Ag_7SbS_6 nanolayers using as one of reactants a solution of an Sb^{5+} thio salt.

As supports we chose KU grade fused quartz polished to the 14th finish grade and KSKG grade silica gel (specific surface area 270 $m^2\,g^{-1}$), as the surface chemistry of these materials had been extensively studied. Before synthesis, all the supports were specially pretreated and cleaned as described in [8].

In the course of the synthesis, a support (or a weighed portion of dispersed silica) was successively treated with a silver salt solution, water, an Na_3SbS_4 solution, and again water. This sequence comprised one ionic layer deposition cycle, which was repeated the required number of times. Some samples on the fused quartz surface were prepared in an automatic mode using a computer-controlled apparatus described in [8]. The time of treatment with each reactant was 0.5–2.0 min for fused quartz samples and 30 min for silica gel. Excess salt solution was washed out from the silica surface by treatment with four portions of water followed by decanting. The completeness of reactant removal was confirmed by the negative reaction of the wash water for the corresponding cation and anion.

The samples were examined by diffuse reflection spectroscopy in the UV, visible, and IR ranges, transmission spectroscopy, X-ray photoelectron spectroscopy, X-ray spectral microanalysis, and powder X-ray diffraction. The spectra were taken as described in [8], and the X-ray spectral microanalysis was performed as described in [6]. The X-ray diffraction patterns of silica gel samples were recorded with a DRON-3.0 X-ray diffractometer, CuK_α radiation.

Among the most important factors determining the success of ionic layer deposition on a support surface are appropriate pretreatment of the support and proper choice of conditions for the first ionic layer deposition cycle (treatment with a solution of an Ag^+ salt), involving Ag^+ sorption. In the course of subsequent washing of the sample to remove excess salt from the surface, the sorbed Ag^+ ions should be retained. To find conditions for the first cycle of ionic layer deposition, we studied the compounds that are formed on the surface at silver sorption by chemical analysis and diffuse reflection spectroscopy in the UV, visible, and near IR ranges.

To determine the amount of silver ions sorbed on the silica gel surface, we analyzed the samples after sorption and dissolution of sorbed ions. The silver content on the surface was determined as the difference between its amount in the initial solution before sorption and the total amount in the solution after sorption and in wash waters. Analysis was performed by Mohr precipitation titration with potassium chromate as indicator [9].

The experimental results are listed in the table. The amount of Ag^+ ions per unit surface area of silica gel is given in relation to the composition and pH of the initial Ag-containing solutions and washing liquids.

It is seen that the Ag^+ content on the silica gel surface depends on the solution composition, its pH, and pH of the washing liquid. For example, the lowest silver content on the surface is observed in samples treated with aqueous $AgNO_3$ and washed with water. Treatment with a solution of $AgNO_3$ in aqueous ammonia results in a larger amount of sorbed silver. This may be due to the fact that treatment of silica gel with a weakly alkaline solution of the silver ammine complex results in formation of $\equiv SiOAg(NH_3)_{2aq}$ complexes in which silver is bound to the surface more strongly than in the hydrated form, so that these complexes are not broken down when excess silver is washed out. The largest content of sorbed silver was attained when sorption was performed from a solution of the silver ammine complex and washing with aqueous ammonia. Apparently, when excess silver is removed by washing with water, the surface ammine complex is broken down, and part of silver is washed out. With aqueous ammonia as washing liquid, the ammine complex is probably preserved, which is confirmed by examination of the surface by IR and UV diffuse reflection spectroscopy (Fig. 1).

The choice of this method was governed by the fact that measurement of the reflection spectrum in the UV, visible, and near IR ranges in one experiment furnishes information both on metal sorption (from the intensity of the absorption band of the sorbed metal cation) and on interaction of $\equiv SiOH$ groups with salt solutions (from the intensity and position of bands in the 1300–1500 nm range corresponding to overtones of stretching vibrations of free and hydrogen-bonded hydroxyls). Note that, in the range of overtones, the intensity of the absorption band of molecular water (1450 nm) is considerably lower than the intensity of the SiOH bands (1370 and 1405 nm), which, according to our experience, allows observation of the absorption band of $\equiv SiOH$ overtones in silica gel samples dried for 1 day in a desiccator over $CaCl_2$ and then for 1 day over P_2O_5, with subsequent recording of the spectrum in a quartz cell in air, whereas spectroscopic studies in the range of the fundamental OH stretching vibrations (3750–3400 cm^{-1}) require a vacuum.

Degree of filling of the silica gel surface Θ in sorption of Ag^+ ions

Solution (c_{Ag} 0.01 M), pH	Washing liquid, pH	Θ, at. nm^{-2}
$AgNO_3$, 4.8	H_2O, 5.7	0.54
$Ag(NH_3)_2NO_3$, 8.8	H_2O, 5.7	1.36
$Ag(NH_3)_2NO_3$, 8.8	$H_2O + NH_4OH$, 8.5	2.28

The diffuse reflection spectrum of the silica gel sample after silver sorption from $AgNO_3$ solution (Fig. 1, *2*) exhibits an absorption band in the range 350–450 nm and a narrow "transparent" range with an absorption minimum at 320 nm. This pattern,

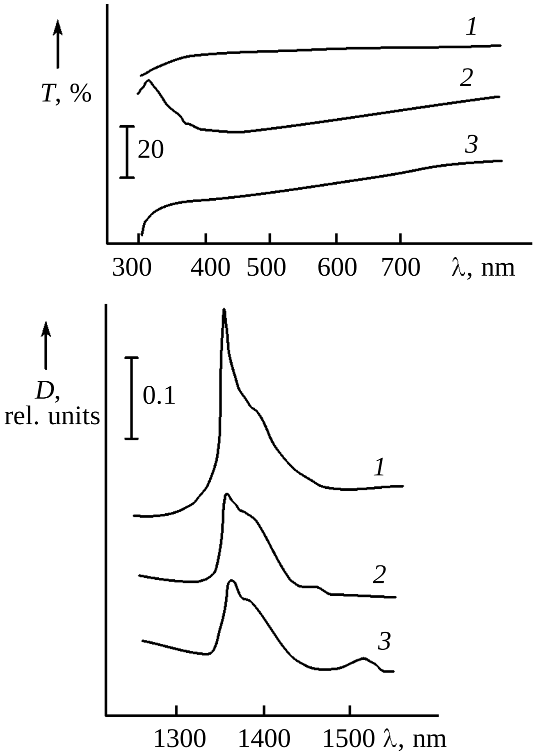

Fig. 1. Diffuse reflection spectra of silica gel samples treated for 10 min in various media: (*1*) water; (*2*) 0.01 M $AgNO_3$ solution, with subsequent washing with water to remove excess $AgNO_3$; and (*3*) 0.01 M $Ag(NH_3)_2NO_3$, with subsequent washing with aqueous ammonia.

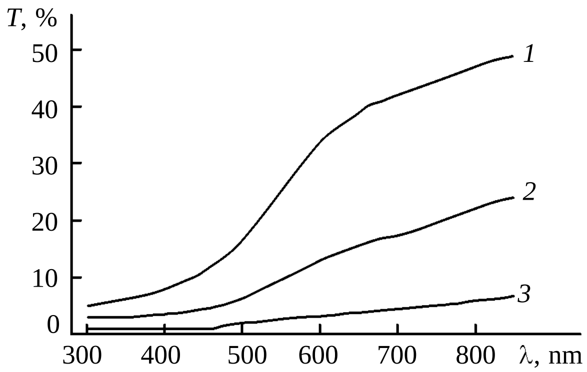

Fig. 2. Diffuse reflection spectra of silica gel samples with an Ag–Sb–S-containing nanolayer synthesized by (*1*) one, (*2*) three, and (*3*) five cycles of ionic layer deposition (c_{AgNO_3} = $c_{Na_3SbS_4}$ 0.01 M).

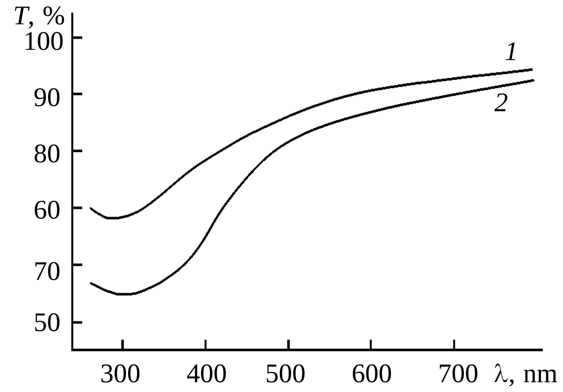

Fig. 3. Transmission spectra in the UV and visible ranges of Ag–Sb–S-containing nanolayers prepared on the surface of fused quartz by (*1*) 20 and (*2*) 40 cycles of ionic layer deposition (c_{AgNO_3} = $c_{Na_3SbS_4}$ = 0.01 M).

according to [10], corresponds to Ag^0 clusters on the surface. Apparently, washing of the sample with water to remove excess $AgNO_3$ and its drying in air were accompanied by formation of photochemically unstable silver hydroxo complexes decomposing to Ag^0 under UV irradiation of the spectrophotometer in the course of recording the spectrum. The diffuse reflection spectrum of silica gel after sorption of the metal from the $Ag(NH_3)_2NO_3$ solution and washing with aqueous NH_4OH exhibits in the UV range only the absorption maximum. The near-IR spectrum of this sample contains a band at 1530 nm belonging to an overtone of NH stretching vibrations (Fig. 1, *3*), and the intensity of the band at 1370–1400 nm decreases approximately by half. The latter fact is indicative of decreased content of OH groups on the silica gel surface.

The whole set of data on silver sorption suggest formation of the following sorption compounds on the surface:

$$\mathrm{SiOH} + \mathrm{AgNO_3} \xrightarrow{\mathrm{H_2O}} \mathrm{SiOAg_{aq}},$$

$$\mathrm{SiOH} + \mathrm{Ag(NH_3)_2NO_3} \xrightarrow{\mathrm{H_2O}} \mathrm{SiOAg(NH_3)_2}.$$

After treating with an Na_3SbS_4 solution the samples with sorbed silver ions and removing excess thio salt by washing with water, the silica gel sample turns brown. Its diffuse reflection spectrum contains an absorption band in the range 300–600 nm (Fig. 2).

These changes suggest formation of a surface nanolayer containing Ag, Sb, and S. After repeated ionic layer deposition cycles, a layer is formed with the color changing from dark brown at $n \le 4$ to black with a strong luster at n = 5–10. Significant changes are also observed in the diffuse reflection spectrum: With increasing number of ionic layer deposition cycles, the intensity of the band at 300–600 nm increases, and after 5–10 cycles the absorption in the UV and visible ranges becomes virtually continuous.

The kinetics of the growth of Ag–Sb–S-containing nanolayers on the fused quartz surface was studied by transmission spectroscopy. For example, as the concentration of the silver salt solution is increased from 0.0005 to 0.01 M, the optical density in the transmission spectra of the nanolayers (n = 10) considerably increases, whereas increase in the concentration of the silver salt solution above 0.01 M exerts no further effect on the optical density. This fact gives good grounds to believe that the reaction product is formed in the layer of ions sorbed on the support surface, rather than in the bulk of the solution. With 0.01 M solutions of $AgNO_3$ and Na_3SbS_4, the optical density is a linear function of the number of ionic layer deposition cycles, which indicates that the layer is synthesized in steps. The transmission spectra of Ag–Sb–S-containing nanolayers prepared by 20 and 40 cycles of ionic layer deposition are shown in Fig. 3; it is seen that the absorption intensity in the range 300–600 nm increases as the number of ionic layer deposition cycles is increased.

The X-ray photoelectron spectrum of the layer prepared on silica gel by 10 ionic layer deposition cycles (Fig. 4) contains lines corresponding to the electron binding energies of 368.0, 529.3, and 161.4 eV, which, according to [11, 12], belong to Ag^+, Sb^{5+}, and S^{2-}, respectively.

X-ray spectral microanalysis gave the following ratio of the elements in the layer prepared on silica

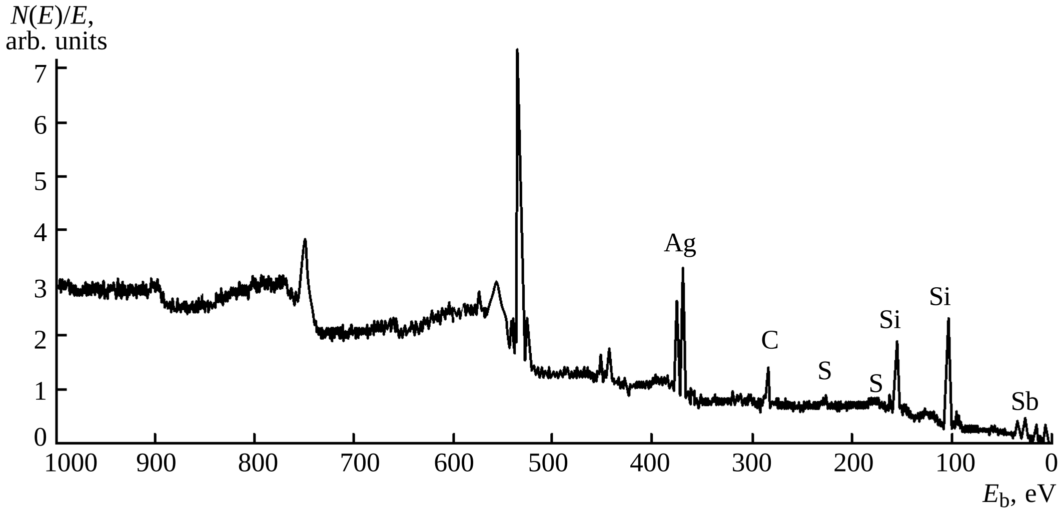

Fig. 4. X-ray photoelectron spectrum of an Ag–Sb–S-containing nanolayer prepared on the silica gel surface by ten cycles of ionic layer deposition.

gel by ten cycles of ionic layer deposition: Ag/Sb/S = 8.2/1.0/7.2. These data, taking into account the experimental error, are best consistent with the composition of the compound Ag_7SbS_6. The formation of this compound was also confirmed by powder X-ray diffraction. Although the layer as a whole was X-ray amorphous, a weak peak was detected art $2\theta = 30.34°$, corresponding to Ag_7SbS_6 according to the ASTM data base [13].

Thus, nanolayers of Ag_7SbS_6 are formed on the silica surface in the course of ionic layer deposition by alternating treatments with aqueous solutions of $AgNO_3$ and Na_3SbS_4. The layer thickness can be set with a high precision by the number of ionic layer deposition cycles.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 98-03-32 583).

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