Russian Journal of General Chemistry, Vol. 74, No. 3, 2004, pp. 323–326. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 3, 2004, pp. 360–363.

Synthesis of "Hybrid" $Ag^0_x \cdot Mno_2 \cdot nH_2O$ Metal Oxide Nanolayers by Ionic Deposition

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Received December 30, 2002

Abstract — So-called "hybrid" metal oxide nanolayers were obtained by the ionic deposition method. The effect of solution pH, reagent concentrations, and the number of ionic deposition cycles on the kinetics of layer growth was studied using $Ag^0_x \cdot MnO_2 \cdot nH_2O$ nanolayers on quartz and silicon surfaces as examples.

One of the methods for synthesing nanolayers of inorganic compounds on a solid surface is ionic deposition that involves repeated sorption of anions and cations from reagent solutions on the support surface, resulting in formation of a sparingly soluble compound [1]. In the synthesis of nanolayers by this method optimal conditions are chosen for each compound, which requires controlling over up to 10 different parameters, for example, the concentration and pH of several reagent solutions, the pH of washings, etc. Earlier [2, 3] we found conditions for synthesizing nanolayers of different classes of inorganic compounds, such as metal oxides, hydroxides, sulfides, and fluorides. At the same time, the potential of the method seems far from being exhausted, since its very essence gives the possibility for precisely specifying the thickness of the synthesized layer, its composition, and, as a consequence, for synthesizing inorganic "artificial" structures, so-called "hybrid" structures comprising layers of inorganic substances of different classes.

The aim of this work was to study regularities of the synthesis of the "hybrid" metal oxide compound $Ag^0_x \cdot MnO_2 \cdot nH_2O$ by ionic deposition. The choice of this compound was defined by the fact that the conditions for synthesizing Ag^0 [4] and MnO_2 [5] nanolayers by ionic deposition were determined previously.

Among the possible synthetic routes to such compounds the most preferable is a method based on redox reactions that occur successively on the surface in each ionic deposition cycle. A similar method we used earlier in the synthesis of MnO_2 and Ag nanolayers [4, 5].

The available experience of the synthesis of nanolayers by ionic deposition showed that the main problem is to determine conditions for irreversible sorption of layer-forming cations and anions on the support surface from reagent solutions. On the other hand, for successful synthesis it is imperative to remove excess reagents and reaction products by solvent washing of the support after treatment with each reagent solution. However, in the majority of the systems considered, solvent washing or treatment of the support with any of reagent solutions in further cycles of ionic deposition resulted in removal of the deposited cation layer, implying lack of layer growth in the course of the synthesis.

To solve the problem of irreversible sorption of metal cations on the surface and to attain their irreversible sorption upon repeated treatment with reagent solutions, in our previous works [5, 6] we proposed to oxidize cations after their sorption and removal of their excess by washing. In this case we took advantage of the known tendency of metal cations in the highest oxidation states for enhanced sorption at a given pH. In the synthesis of $Ag^0_x \cdot MnO_2$ layers, one can use a solution of an Mn^{2+} salt as reagent and a solution of an Ag^+ salt, as oxidant, in view of the fact that these reagents have a pH region where the reaction products on the surface, namely MnO_2 and Ag^0, are sparingly soluble. These were the properties of the compounds under study, which served as the basis for choosing the reagents for synthesizing "hybrid" metal oxide layers.

As reagents in the synthesis of Ag^0–Mn–O nanolayers we used aqueous solutions of analytical grade $Mn(Oac)_2 \cdot 4H_2O$ and $AgNO_3$. Water served as washing liquid. The ionic deposition reactions were carried out on the surfaces of fused quartz of KU brand, a <100> single-crystal silicon of KEF-7.5 brand, and silica gel of KSKG brand. The optimal conditions for the synthesis of Ag^0–Mn–O nanolayers were determined by varying the pHs and concentrations of the solutions of manganese(II) and silver(I)

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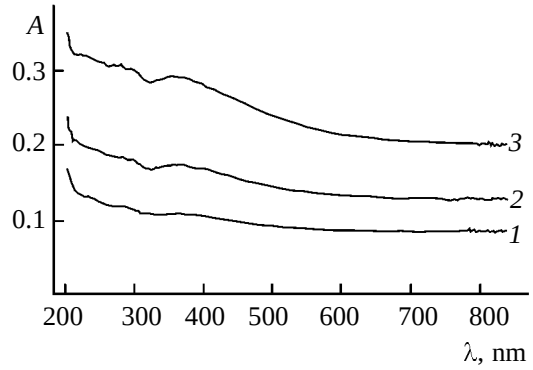

Fig. 1. UV and visible transmission spectra of Ag^0–Mn–O nanolayers on fused quartz surface as a function of the number of ionic deposition cycles n = (*1*) 5, (*2*) 10, and (*3*) 15.

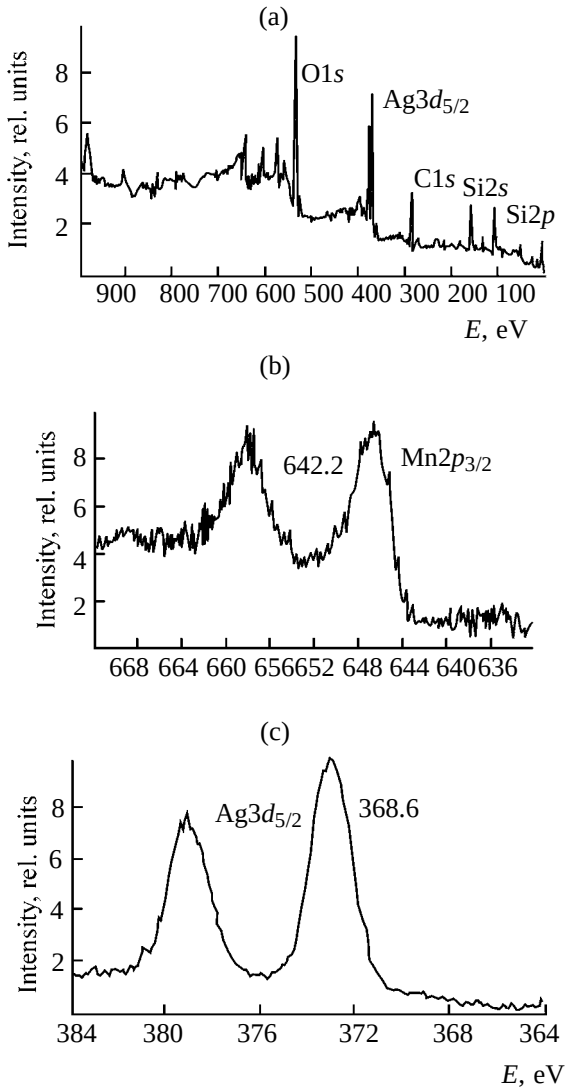

Fig. 2. XPE spectrum of the Ag_x^0–Mn–O layer synthesized on silica surface by 6 ionic deposition cycles. (a) Overall spectrum, (b) manganese region, and (c) silver region.

salts. It was found that layer growth is observed in 0.01 M aqueous solutions of $Mn(OAc)_2$ (pH 7.5) and $AgNO_3$ (pH 8.5–9). The $Mn(Oac)_2$ and $AgNO_3$ solutions were made alkaline using sodium acetate and ammonia solutions, respectively. On the one hand, reagent sorption at these solution pHs is stronger than at equilibrium pHs and, on the other, Mn^{2+} oxidation and Ag^+ reduction occur irreversibly. As seen from Fig. 1, in the electronic transmission spectra of the samples synthesized under these conditions, the optical density at 200–800 nm increases with increasing number of ionic deposition cycles. This observation suggests reproducible growth of layer thickness in each cycle.

The chemical composition of the layers was studied X-ray photoelectron (XPE) spectroscopy and IR Fourier transmission spectroscopy. The XPS spectra (Figs. 2a–2c) show a peak at 642.2 eV corresponding to the Mn^{4+} ions (2*p*) in MnO_2 and a peak at 368.6 eV corresponding to Ag^0 (3*d*) [7]. The Ag^0-to-MnO_2 ratio in the layer of about 0.7 was determined from the intensities of these peaks. The Fourier IR spectra (Fig. 3) contain absorption bands at 3700–3200 and 1640 cm^{-1}, which points to the presence of water molecules in the layer, as well as bands at 430–500 cm^{-1}, assignable Mn–O stretching vibrations in MnO_2. The diffuse reflection spectra of the layers synthesized on silica surface (Fig. 4) display broad bands at 400–500 nm in the region characteristic of metallic silver clusters [8]. According to powder X-ray data, metallic silver incorporated in a layer gives a peak at 2θ 64.48°, which, according to [9], provides evidence for its crystal structure.

Our experimental results allow us to describe the synthesis of the $Ag_x^0MnO_2$ nanolayer by the following schemes of surface reactions. The first stage involves treatment of the support with the $AgNO_3$ ammonia solution and results in sorption of Ag(I) complexes.

$$\equiv Si\text{–}OH + Ag(NH_3)_2^+ \longrightarrow \equiv Si\text{–}OAg(NH_3)_2 + H^+.$$

Then, when excess silver(I) salt is washed out with water, the ammonia complex is destroyed and a layer of hydrated silver(I) oxide is formed.

$$\equiv Si\text{–}OAg(NH_3)_2 + H_2O \longrightarrow \equiv Si\text{–}OAg_{aq} + 2NH_4OH.$$

On treatment with the manganese acetate solution, the silver(I) oxide enters a redox reaction to give Ag^0 and manganese ions in an oxidation state higher than Mn^{2+}, most likely Mn^{4+}.

$$\equiv Si\text{–}OAg_{aq} + Mn(OAc)_2(H_2O) \rightarrow \equiv Si\text{–}OMn(OH)_3 \cdot Ag^0.$$

The latter compound is not dissolved, when the sample is washed to remove excess manganese acetate solution. Provided the describe scheme is realized, the reaction should form on the surface a layer of a "hybrid" compound with a 2:1 Ag:Mn ratio, since the oxidation $Mn^{2+} \rightarrow Mn^{4+}$ involves transfer of two electrons, whereas the reduction $Ag^{+} \rightarrow Ag^{0}$, of one electron only. In practice, however, the observed ratio was 0.7. Probably, the synthesis gives rise to Mn^{3+} ions, and the latter are oxidized with air oxygen to Mn^{4+} in the washing stage.

One more problem to be solved is the morphology of the synthesized layer. In fact, according to the above scheme, the silver atoms formed by the reaction must be present on the surface in the atomic state and must be evenly distributed over the manganese(IV) oxide matrix. However, the peak of crystalline Ag^0 is already observed in the X-ray pattern of the sample synthesized on silica surface by six ionic deposition cycles. Apparently, formation of atomic silver from its larger size clusters is favored by energy and driven by high mobility of silver atoms on the surface. Unfortunately, the size of these clusters is presently impossible to determine. This problem will be considered in a special publication.

EXPERIMENTAL

The Fourier IR transmission spectra were measured on a Perkin–Elmer-1760X spectrophotometer (scan number 300, resolution 4 cm^{-1}). The diffuse reflection spectra in the UV–VIS region were recorded on a Perkin–Elmer Lambda-9 spectrophotometer (scan rate 50 nm/min, slit setting 2 nm). The X-ray patterns were obtained on a DRON-3 diffractometer (CuK_α radiation, chart speed 2400 cm/h, sample speed 2 rpm, current 18 mA, voltage 36 kV). The XPE spectra were taken on Perkin–Elmer-5400 spectrometer (MgK_α radiation).

Before synthesis supports were treated as described in [6]. One ionic deposition cycle involved successive treatment of the supports with an $AgNO_3$ solution, distilled water, an $Mn(OAC)_2 \cdot 4H_2O$ solution, and distilled water. The time of treatment with each reagent was 1 min for fused quartz and silicon samples, and 30 min for silica gel. Excess reagent solutions were removed from silica surface by washing four times with distilled water by the decantation technique.

The nanolayers synthesized on silicon surface were studied by Fourier IR transmission spectroscopy, on quartz surface, by UV–VIS spectrophotometry, and on silica surface, by UV–VIS diffuse reflection spectroscopy, powder X-ray analysis, and XPE spectroscopy.

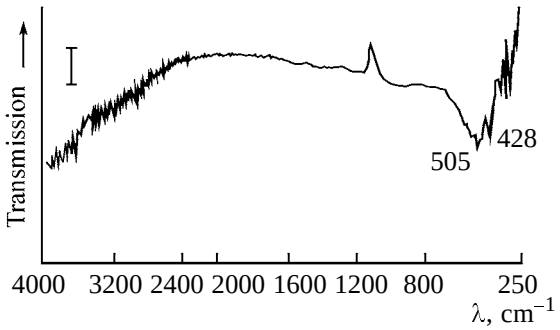

Fig. 3. Fourier IR transmission spectrum of the Ag_x^0–Mn–O nanolayer synthesized on single-crystal silicon surface by 40 ionic deposition cycles.

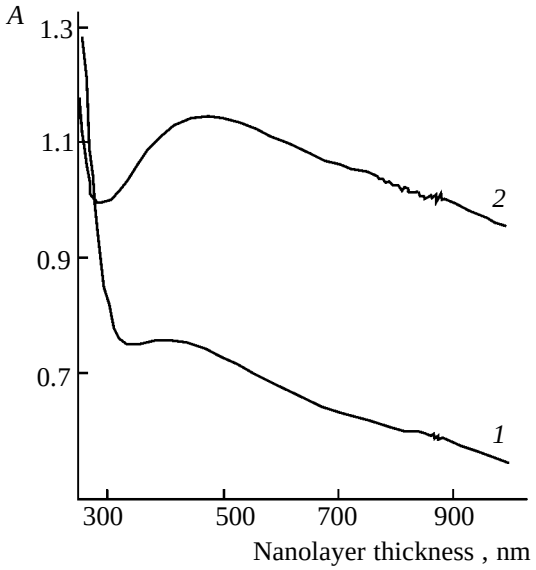

Fig. 4. Diffuse reflection spectra of Ag_x^0–Mn–O nanoayers synthesized on silica surface by (*1*) 1 and (*2*) 2 ionic deposition cycles.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project number 01-03-32427) and by the Program for Support of Young Researchers, St. Petersburg State University (PD02-1.3-229).

REFERENCES

1. Tolstoi, V.P., *Usp. Khim.*, 1993, vol. 62, no. 3, p. 260.
2. Tolstoi, V.P., *Zh. Neorg. Khim.*, 1993, vol. 38, no. 7, p. 1146.

3. Gulina, L.B. and Tolstoi, V.P., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 6, p. 899.

4. Tolstoi, V.P., Tolstobrov, E.V., and Gulina, L.V., *Vestn. S.-Peterb. Gos. Univ., Ser. 4: Fiz., Khim.*, 2002, issue 3, p. 120.

5. Tolstoy, V.P., Murin, I.V., and Reller, A., *Appl. Surf. Sci.*, 1997, vol. 112, p. 255.

6. Tolstoy, V.P. and Ehrlich, A.G., *Thin Solid Films*, 1999, vol. 307, nos. 1–2, p. 60.

7. Nefedov, V.I., *Rentgenoelectronnaya spektroskopiya khimicheskikh soedinenii* (X-ray Electron Spectroscopy of Chemical Compounds), Moscow: Khimiya, 1984.

8. Kharlamov, G.V., Ivan'kin, I.A., Bogdanchikova, N.E., Anufrienko, V.F., and Davydov, A.A., Abstracts of Papers, *X Vsesouyznyi Seminar "Primenenie opticheskoi spectroskopii v adsorbtsii i katalize"* (X All-Union Seminar "Application of Optical Spectroscopy in Adsorption and Catalysis), Leningrad, 1988, p. 109.

9. *Index to Crystallographic Data Compilations*, ASTM N 41-1402.