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Silver Nanoribbons Synthesized on a Silicon Surface by the "Layer-by-Layer" Technique

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Abstract—Conditions for the synthesis of silver nanoribbons on a silicon surface by the "layer-by-layer" technique were determined for the first time. The synthesized structures were studied by scanning electron microscopy, energy-dispersion microanalysis, and X-ray diffraction. A conclusion on the sequence of possible reactions occurring on the surface during the synthesis was drawn on the basis of the experimental data.

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The synthesis of 1D and 2D inorganic nanostructures is one of the major problems of modern preparative chemistry, as it opens new possibilities for creating promising functional materials based on such nanostructures. A number of publications [1–3] is devoted to the procedures of synthesizing metal nanoparticles in solutions and to the study of their properties and prospects of application. The reviews [4, 5] describe the creation of reproducible procedures of the synthesis and stabilization of silver nanoparticles of various morphology (ribbons, rods, globules, spheres, etc.) in solutions. The synthesis of silver nanoparticles on the surfaces of various solids represents an actual problem, as it allows modifying properties of materials and expanding boundaries of their application. In the present paper we present the results of the synthesis of silver nanoparticles on the surface of single-crystal silicon by the "layer-by-layer" procedure [6]. The basic feature of this approach is the possibility of obtaining silver nanoribbons of various sizes immediately on a substrate surface, the particle size being governed by a number of surface treatment cycles in such method of the synthesis.

Multiple and alternate treatment of single-crystal silicon plates by the "layer-by-layer" technique results in the formation of nanoparticles on a surface, the particle size being governed by the number of the treatment cycles (Fig. 1).

The photograph of silver nanoparticles on a silicon surface synthesized as a result of 8 treatment cycles is presented in Fig. 1a.

The nanoribbons reach 2.5 μm in length and ~100 nm in width. After 12 synthesis cycles (Fig. 1b) the size of nanoparticles reaches 4 μm in length and ~300 nm in width.

The combination of reactions, which can take place during the synthesis, is presented in Eqs. (1)–(5).

$$AgNO_3 + NH_4OH \underset{}{\overset{NH_4NO_3}{\rightleftharpoons}} [Ag(NH_3)_2]NO_3 + H_2O, \quad (1)$$

$$Cu(OAc)_2 + 2N_2H_4 + 3OH^- \xrightarrow{NH_4OAc} Cu(N_2H_4)OAc + N_2 + AcOH + 3H_2O, \quad (2)$$

$$Cu(N_2H_4)^+ + O_2 \rightarrow Cu^{2+} + N_2 + 2H_2O, \quad (3)$$

$$[Ag(NH_3)_2]^+ + Cu(N_2H_4)^+ + OH^- \xrightarrow{NH_4OH} Ag + Cu^{2+} + 1/2N_2 + 3NH_3 + H_2O, \quad (4)$$

$$Cu^{2+} + NH_4OH \xrightarrow{NH_4NO_3} Cu(NH_3)_4^{2+}. \quad (5)$$

Equilibrium (1) is established in a silver ammine aqueous solution, whereas, according to [7], Cu^{2+} ions are reduced in a copper salt solution to form a Cu^+ complex with hydrazine (2). A partial oxidation of the complex by air oxygen should not be excluded (3). After the sorption of silver ammine on the surface, $\equiv SiOAg(NH_3)_2$ complexes are formed [8], which play the role of centers for reduction reaction (4) resulting in the oxidation of copper ions leaving the surface to form complexes [reactions (2, 5)]. The energy-dispersion analysis confirms the fact that the nanoribbons do not contain copper, nitrogen, or carbon atoms, which would be able to enter into their composition from the reducing agent solution. The weak diffraction maximum at 2θ 38.8 corresponding to

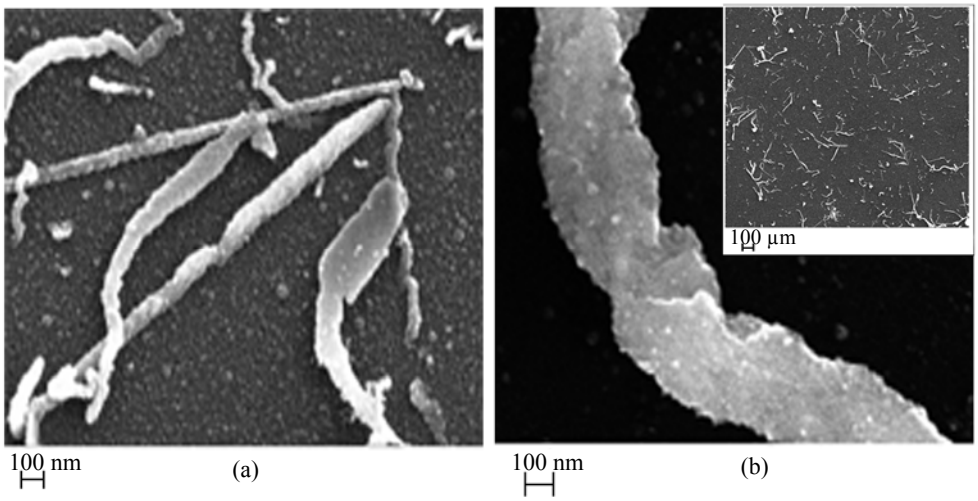

Fig. 1. Microphotographs of silver nanoparticles synthesized on a silicon surface as a result of (a) 8 and (b) 12 cycles of treatment by the "layer-by-layer" scheme.

the reflection from the (111) plane of the cubic modifications of silver crystals [9, 10] was found in the X-ray pattern of the sample (Fig. 2) synthesized as a result of 12 cycles of the "layer-by-layer" treatment.

Thus, it has been found experimentally that silver nanoparticles are formed as a result of the synthesis, the morphology of the nanoparticles depending on the composition of solutions used. In particular, conditions for the formation of silver "nanoribbons" of length 1.5–4.0 μm and width 50–300 nm have been determined, their size depending on the number of treatment cycles.

EXPERIMENTAL

Plates of single-crystal KDB-40 grade silicon of the <100> orientation polished up to the 14 surface finish class were used as substrates for the synthesis of nanolayers. To remove organic impurities, the substrates were washed with acetone, with dilute (1:10) hydrofluoric acid, and with water. After that, to form an oxidized hydroxylated surface, they were held within 0.5 h under the action of ultrasonic sound (60 W) in a "piranha" solution, which represents a mixture of 30% H_2O_2 and concentrated H_2SO_4 (the 3:7 volume ratio), and then carefully washed out with water.

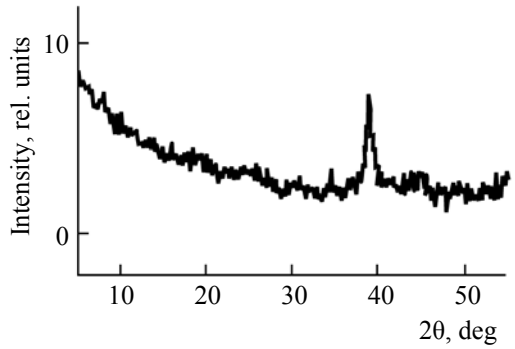

Fig. 2. Differential (in relation to the initial silicon surface) diffractogram of silver nanoparticles synthesized on a silicon surface as a result of 12 "layer-by-layer" treatment cycles.

A solution of $Ag(NH_3)_2NO_3$ prepared according to the procedure [8] was the precursor of silver nanoparticles. A solution of Cu(I) stabilized by hydrazine was used as a reducing agent. To prepare a reducing agent solution, NH_4OAc was added to a 0.01 M $Cu(OAc)_2$ aqueous solution up to the concentration 0.5 M and a 20% N_2H_5OH solution up to the formation of a light-yellow solution; pH of the resulting solution did not exceed nine.

Synthesis of nanolayers. After the standard treatment, substrates were fixed in holders for samples in an automated computer-operated installation intended for the synthesis and were sequentially treated by plunging in solutions according to the certain scheme: in a silver salt solution, in a washing liquid, in a copper(I) salt solution, and again in a washing liquid. The time of sample treatment by each reagent was 0.5 min. This sequence of treatments comprised one cycle. Samples were synthesized as a result of 4–12 treatment cycles.

Electron microphotographs were taken on a Zeiss EVO-40EP scanning electron microscope with a LaB_6

cathode at the accelerating voltage of 20 keV. The composition of synthesized nanoparticles was determined with the use of an Oxford INCA 350 energy-dispersion analyzer with a Si(Li) detector of 30 mm^2 in area. The X-ray diffractograms of samples were taken on a Thermo ARL X'TRA diffractometer (CuK_α radiation) in a θ–θ scanning mode with the fixed angle of incidence of X-rays 2°.

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