NANOLAYERS OF THE $Au^0_x \cdot SnO_2$ NANOCOMPOSITE SYNTHESIZED BY SUCCESSIVE IONIC LAYER DEPOSITION METHOD

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Abstract: We studied possibilities of SILD (successive ionic layer deposition) technology for depositing nanocomposite $Au^0_x \cdot SnO_2$ nanolayers. This new method of layer deposition is of high interest, because of the method's simplicity, cheapness, and ability to deposit thin nano-structured films on rough surfaces. Aqueous 0.01 M solutions of $SnCl_2$ and $HAuCl_4$ were used as precursors for synthesis of the nanocomposite layers on the surface of silica and Si. Optical spectra of such layers are characterised by a band at 200–300 nm consistent with the electronic absorption of the Sn–O polyhedrons and a band at 560–570 nm due to a plasmon generated in the gold nanoparticles, while the FTIR spectra exhibit a band at 580 cm^{-1}, characteristic for the Sn–O stretchings. Based on the spectral dependences on the sample heating in the 200-400°C range, chemico-structural transformations of the layers were inferred.

Key words: nanolayers, nanocomposites, SnO_2, Au^0 nanoparticles, SILD

1. INTRODUCTION

At present, incorporation of second component in metal oxide as bulk doping or surface modification is becoming one of the most perspective methods of optimization of gas sensing properties of conductometric solid state gas sensors [1, 2]. For these purposes various additives may be used. Depending on the required result, noble metals (Ag, Pd, Pt), transition metals (Fe, Mn, Co, Ni, Cu), oxides (SiO_2, Al_2O_3), and so on were used. These additives can act as promoters, catalysts, surface sites for adsorption of oxygen and detected gas with following spillover of adsorbed species, or as elements promoting to improvement of porosity of gas sensing matrix and thermal stability of gas sensing characteristics. According to results of many research, the change of grain size of metal oxide and concentration of free charge carriers may affect on gas sensing characteristics of these materials so strong as the change of their surface properties.

In this report we discuss the possibility of SnO_2 modification by Au^0. For this purpose we used successive ionic layer deposition (SILD) method. As we have shown earlier [3-5] SILD

technology is a promising method for deposition of metal oxide nanolayers on shaped surfaces, for example on the surface of porous materials. SILD technology allows depositing with high precision via the composition control of used solutions and the number of ionic deposition cycles.

2. EXPERIMENT

The SILD method essentially consists in repeated successive treatments of the substrate in solutions of various salts, anions and cations that can form upon adsorption poorly soluble compounds [3]. Then the substrate is washed with distilled water to remove excess of the salt. The 0.01M aqueous solutions of $SnCl_2$ and $HAuCl_4$ were used as a precursor. The duration of each treatment was 1 min. One such treatment comprised one deposition cycle. We used in our experiments from 1 to 20 deposition cycles. The substrates were plates of fused quarts or crystalline Si <111>. The synthesized layers were studied by FTIR and UV-Vis spectroscopies, as well as by electron microprobe (SEM).

3. RESULTS AND DISCUSSIONS

The Au:SnO_2 layers obtained after 5 and 10 cycles of SILD are characterized by the transmission spectra shown in Fig. 1. These spectra are characterized by a band at 200–300 nm consistent with the electronic absorption of the Sn–O polyhedrons and a bands at 560–570 nm due to plasmons generated in the gold nanoparticles. The SEM analysis revealed that the Sn:Au ratio in the layer is 1. According to Ref. [6], this position of the plasmon band corresponds to the particle size greater than 3.5 nm, while the red shift upon increasing the number of the SILD cycles testifies to increasing content of larger particles in the layer.

Heating at 200 and 400 °C resulted in substantial changes in the spectra (see Fig. 1, curves 3 and 4). The background absorption in the 200–800 nm increases, while the plasmon band shifts from 570 to 620 nm and broadens. These observations can be attributed [7, 8] to aggregating the Au nanoparticles and increasing the dielectric constant of the matrix they are immersed in. We explain these changes by increasing density of the SnO_2 layer upon heating.

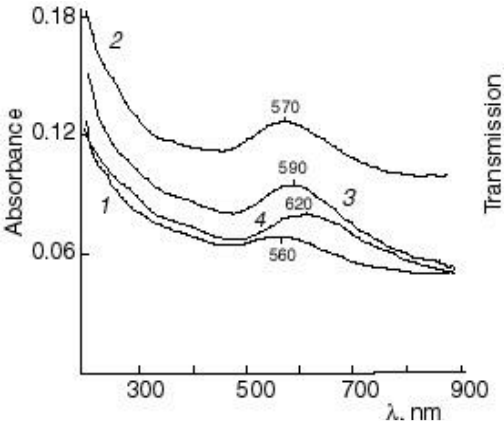

Fig.1. UV-Vis spectra of $Au^0_x \cdot SnO_2$ nanolayers synthesized on the surface of fused quartz. *1*- the number of deposition cycles n = 5; *2* – n = 10; *3* - sample *2* after heating in air at T = 200 °C, *4* – at T = 400 °C; $t_{heat.}$ = 20 min.

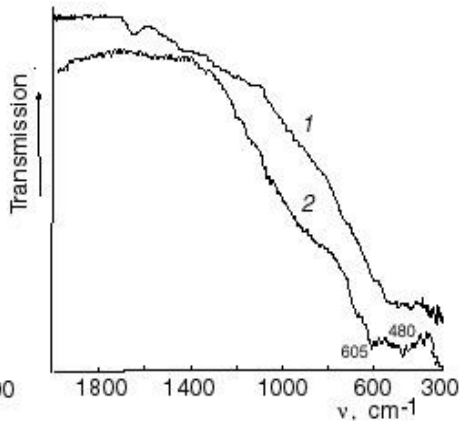

Fig.2. FTIR spectra of $Au^0_x \cdot SnO_2$ nanolayers synthesized on the surface of silicon after 20 SILD cycles. *1*- initial state; *2* – after heating in air at temperature equaled 200 °C; *3* - at T = 400 °C; $t_{heat.}$ = 20 min.

As regards the layer structure, the FTIR spectra (Fig. 2) show that the layers are amorphous, as the maximum of the Sn–O band is at 580 cm^{-1}. After heating at 400 °C, the 1640 cm^{-1} band, which is due to bending OH vibrations of incorporated water molecules and possibly SnOH groups, disappears. At the same time the Sn–O band broadens and develops additional components at 605 and 480 cm^{-1}. Nevertheless, complete splitting into the latter two components, which is typical for the crystalline form, is not observed.

4. CONCLUSIONS

It was shown that SILD can be used for synthesizing nanolayers of the $Au^0 \cdot SnO_2$ nanocomposite. The thickness of the nanolayers can be controlled by the number of the SILD cycles. The Au:Sn ration in the layer is 1. The SnO_2 matrix has amorphous structure. Heating at 400 ˚C brings about aggregating gold clusters and increasing the layer density.

5. ACKNOWLEDGEMENT

This work was supported by CRDF in the frame of Cooperative Grant Program (Grant # MOE2-2588-CH-04).

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