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New Way of As_2S_3 Microtubules Preparation by Roll Up Thin Films Synthesized at the Air-Solution Interface

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For the first time the conditions of synthesis As_2S_3 microtubules were defined. Investigation of the synthesized scroll-like structures was carried out by optical microscopy, scanning electron microscopy, electron microprobe analysis, X-ray diffraction, and Raman spectroscope.

Keywords: Arsenic sulfide, Microtubules, Scanning electron microscopy, Optical microscopy, EMPA analysis, Raman spectroscope.

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1. INTRODUCTION

Much attention is being paid lately to synthesis of nano- and microtulules of inorganic compounds. The potential of their practical application gives rise to new prospects in the development of nanomaterials with a novel set of numerous practically valuable properties. Results of research work in this direction have been reported in a number of reviews, for example in [1, 2], where conditions of the synthesis and some properties of the nano- and microtubules are considered.

According to the reports, in most cases nanotubular structures can be produced in the conditions of solvo- or hydrothermal synthesis using compounds with layered crystal structure. Being subjected to these conditions separate nanosheets of these compounds roll up into nanotubes [3, 4].

Nano- and microtubes can be obtained also if the synthesis of thin layers of inorganic substances is carried out on the surface of a template having regular porous structure with penetrating pores or on the surface of fibers with subsequent dissolution of the substrate [5-7].

New possibilities concerning the synthesis of the nanotubular structures provides the method offered in the work of V.Ya. Prinz [8]: multi-nanolayer comprising at least two layers with different mechanical properties is formed on a substrate, then the under-layer is dissolved and the upper-layer rolls up into a certain 3-dimentional structure, in some cases a nanotubule.

For as sulphides the tubular structures were obtained earlier as a product of chemical bath deposition [9] and via the reduction of As (V) and $S_2O_3^{2-}$ under anaerobic conditions [10].

In the present work it is shown for the first time that microtubules of As_2S_3 can be obtained from the thin films, which grow in "soft chemistry" conditions from the aqueous solution of $NaAsS_2$ salt at solution – air interface.

2. EXPERIMENTAL SECTION

The synthesis procedure was as follows. 2 ml of the $NaAsS_2$ 0.01 M solution were poured into a flat vessel and put into a glass line chemical reactor. Then a mixture of air with HCl was fed from one side into the reactor.

The experiments have shown that after the treatment of the solution surface by the HCl flow a yellow-colored layer was formed on the surface that was next transferred carefully to the surface of pure distilled water in order to remove extra solution from the layer-solution interface. The film was transferred in the same way to the surface of single crystalline silicon, then dried and analyzed by X-ray diffraction (XRD), Raman spectroscopy, Scanning Electron Microscopy (SEM), and Electron Microprobe Analysis (EMPA).

X-ray diffraction patterns were recorded using a DRON-3.0 X-ray diffractometer with Cu K_α radiation, and the morphology were determined using scanning electron microscope Zeiss EVO-40EP with LaB_6 cathode and USB optical microscope Penscan. Chemical composition of the samples (As/S ratio) was determined by EPMA analysis using scanning electron microscope equipped with an INCA 350 Energy EDX analyzer (Oxford Instruments) and 30 mm^2 Si(Li) detector. Raman spectra were obtained on a SINTERRA Raman microscope. Vibrational modes were excited by a laser with $\lambda = 785$ nm.

3. RESULTS AND DISCUSSION

The SEM and Photo images of the thin films formed at the interface of $NaAsS_2$ solution-air and then placed on the surface of single crystalline silicon and dried in air show that for a number of samples microtubules 20-100 μm in diameter and up to 2-3 mm long can be seen on their surface (Fig. 1 and 2). For a sample prepared by 10 minutes HCl treatment the wall thickness of a microtubule is approximately 3 μm. Extension of the treatment results in a growth of the layer thickness up to 10 μm. However, for samples with the wall thickness less than 1 μm and more than 4 μm the formation of microtubules no longer occurs in course of drying of the synthesized layer. Most likely, when the thickness is less than 1 μm microtubules do not form due to a comparatively low mechanical strength of the synthesized layers and, on the contrary, for thicker layers excessive stiffness hampers their 'rolling up'.

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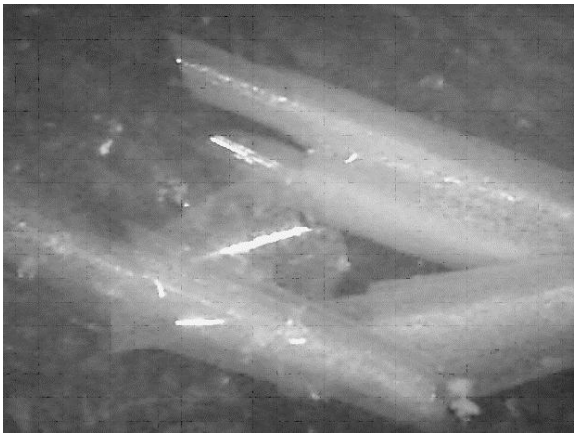

Fig. 1 – Photo image of As_2S_3 microtubes obtained at 200-fold magnification

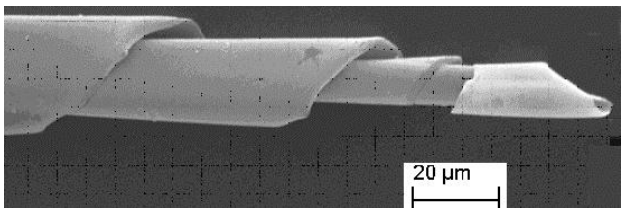

Fig. 2 – SEM image of As_2S_3 microtube

Examination of the microtubules walls by EMPA (Fig. 3) indicated, that the substance of the walls contains As and S atoms. Results of the X-ray diffraction study proved that the structure of nanoparticles forming the layer is amorphous. These results were confirmed by the Raman spectroscopy data (Fig. 4), i.e. the spectra in which the bands at 342 cm^{-1} could be found corresponding, according to [11], to the As-S bonds. The second group, with peaks having much low intensity, is at 482 cm^{-1} and may be due to S-S bonds [11].

In our opinion, there is the following reaction at the interface after treatment of $NaAsS_2$ solution by HCl : $2NaAsS_2 + HCl \rightarrow As_2S_3 + NaHS + NaCl$.

As_2S_3 layer is hydrophobic and does not sink in the solution. At the interface of layer-solution are adsorbed anions AsS_2^- and this leads to a gradient across the sheet properties and roll up after drying.

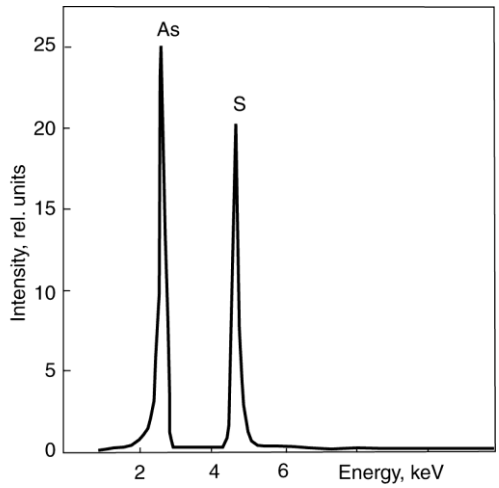

Fig. 3 – EMPA spectrum of As_2S_3 microtube wall

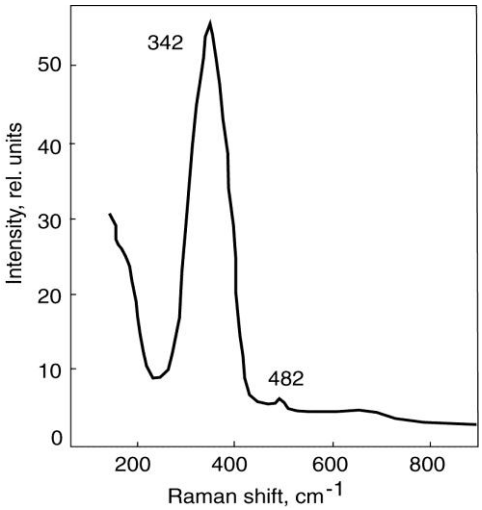

Fig. 4 – Raman spectrum of As_2S_3 microtube wall

To explain the observed phenomenon of the microtubules formation one can speculate that in course of drying of the As_2S_3 film at the air-layer interface arise greater a surface tension than on the side of the layer-solution.

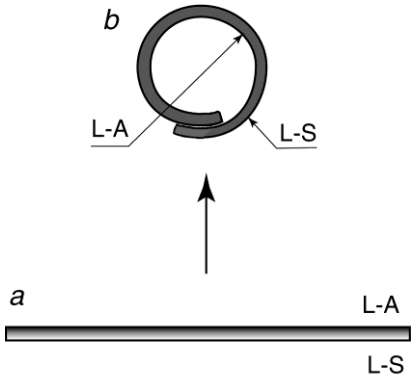

Fig. 5 – Hypothetical scheme of formation of microtubules in course of drying (L-S – Layer-Solution interface, L-A– Layer-Air interface) *a* – the sample synthesized at the solution-air interface after removal of extra solution by its flushing with distilled water, *b* – the same sample after drying in air.

4. CONCLUSIONS

As a result of interaction of the aqueous solution of $NaAsS_2$ with HCl delivered by the air flow to the interface solution-air an As_2S_3 layer is formed on the surface of the solution. For the first time it has been demonstrated that subsequent drying in air conditions of the layers having 1-4 μm thickness leads to a formation of microtubules.

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