PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 3, 03TF05 (2pp) (2012)

As_2S_3 Thin Films Synthesized in "Soft Chemistry" Conditions and Microtubules From Them

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(Received 20 June 2012; published online 13 July 2012)

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.

PACS numbers: 68.55.ag, 68.37.Hk

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].

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, Raman, SEM, and EPMA.

X-ray diffraction (XRD) patterns were recorded using a DRON-3.0 X-ray diffractometer with Cu K_α radiation, and the morphology were determined using scanning electron microscopy (Zeiss EVO-40EP) and optical microscopy (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). Raman spectra were obtained on a SINTERRA Raman microscope.

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 (Figs. 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'.

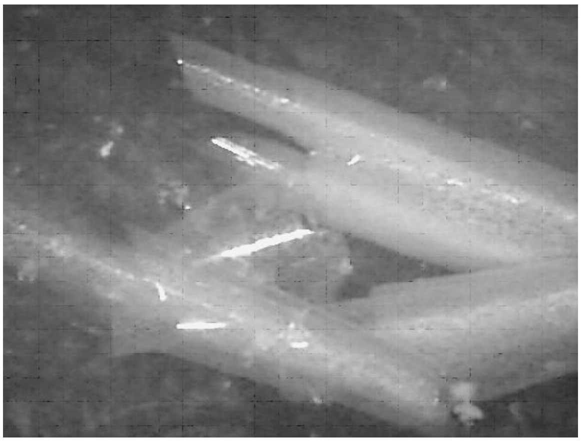

Fig. 1 – Photo image of As_2S_3 microtubes obtained at 200-fold magnification.

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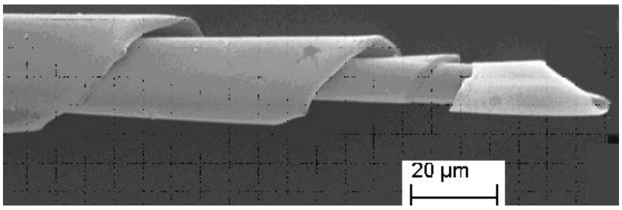

Fig. 2 – SEM image of As_2S_3 microtube.

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 [8], to the As-S bonds.

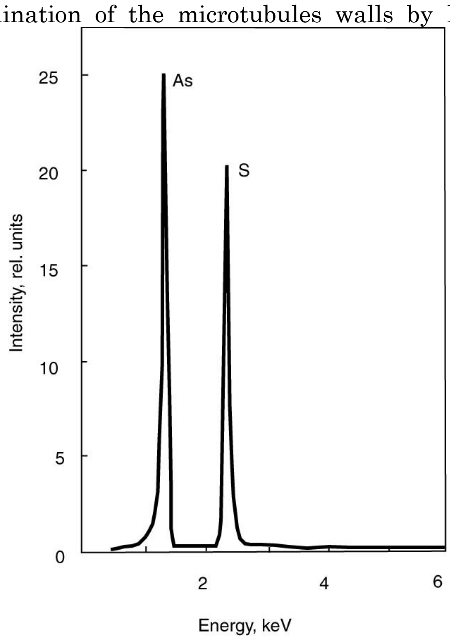

Fig. 3 – EPMA spectrum of As_2S_3 microtube wall.

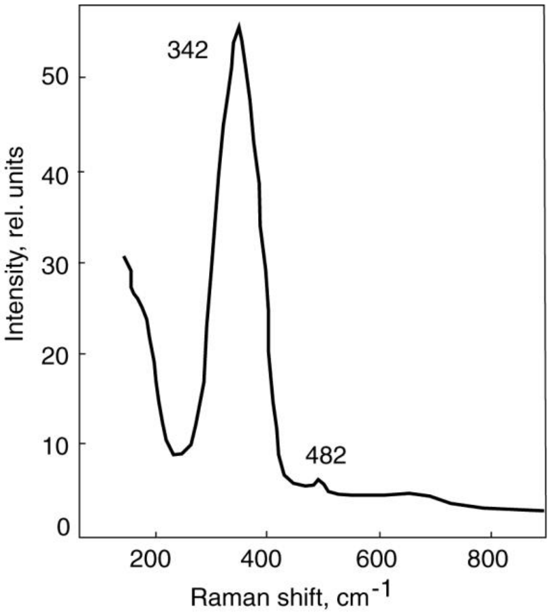

Fig. 4 – Raman spectrum of As_2S_3 microtube wall.

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 – 3 µm thickness leads to a formation of microtubules.

AKNOWLEDGEMENTS

This work was supported by RFBR grant # 12-03-00805-a.

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