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OPTICAL AND AFM STUDIES ON p-SnS THIN FILMS DEPOSITED BY MAGNETRON SPUTTERING

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Tin sulfide thin films were prepared by DC magnetron sputtering of a nanostructured SnS target in argon. The obtained samples were analyzed using atomic force microscopy (AFM), radio frequency glow discharge optical emission spectroscopy (RF-GD-OES) and UV-vis spectrophotometry. The thickness, roughness and surface porosity were evaluated using module software for AFM data visualization and analysis Gwyddion. A thin film growth mechanism was suggested based on the analysis of the AFM images.

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Keywords: SnS thin films, Magnetron sputtering, Atomic force microscopy

1. Introduction

Scientific interest in excellent semiconductor and optical properties of tin sulfide (SnS) thin films determines a promising outlook for photovoltaics [1]. This material has also a good potential as a non-toxic and eco-friendly alternate to photovoltaic materials containing toxic buffer elements like CdS. In the literature, most reports have been focused on methods for synthesis of tin sulfide films such as pulse electro-deposition [2], electron-beam evaporation [3], thermal evaporation [4], and spray pyrolysis [5]. Among them, DC-magnetron sputtering has been developed for last few years and has been characterized by a lack of scientific works devoted to SnS films despite its simple equipment, low operation cost and high deposition rate for achieving high quality thin films [6].

This paper suggests a study of p-type SnS films which were prepared using DC mode magnetron sputtering in argon from a nanostructured target. The method of self-propagating high-temperature synthesis was used for fabrication of SnS nanostructured powders as a raw material for magnetron sputtering target. The research work is focused on structural parameters, elemental composition and optical properties of p-SnS thin films deposited on a glass substrate by DC magnetron sputtering. Our observations of morphology and optical properties were performed using atomic force microscopy and radio frequency glow discharge optical emission spectroscopy.

2. Experimental

A SnS target was prepared from a nanostructured powder produced by self-propagating high-temperature synthesis described in [7-9]. Samples were deposited onto ceramics and glass

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substrates by magnetron sputtering in the direct current mode with a sputtering power 40 W. The deposition time was 3 min. Argon was used as a working gas at a pressure 2–2.5 Pa. The distance between the substrate and the target was about 55 mm. The sputtering chamber was pumped down to $6 \cdot 10^{-3}$ Pa. The surface microstructure of the samples was analyzed using an atomic force microscope (AFM) «Ntegra-Aura» in the intermittent contact mode.

Radio frequency glow discharge optical emission spectroscopy (RF-GD-OES) was employed for elemental analysis of SnS samples on a GD Profiler2 with a polychromator f=0.5 m. Argon was used as a discharge gas. Transmission spectra of SnS films were obtained using a spectrophotometer APEL PD-303UV in the ultraviolet-visible and infra-red range.

3. Results and discussion

Fig.1 shows the AFM images and 3D-visualisations of the tin sulfide film fabricated by DC magnetron sputtering. The AFM results allowed us to propose island-type SnS film growth (Volmer-Weber growth mechanism). The Volmer–Weber mode provides equilibrium conditions of a newly formed crystal of the SnS film staying in contact with the glass or ceramic substrate. At the same time, there is no condensed SnS matter in some other areas on the substrate surface. Such kind of film nucleation is observed by the atomic force microscope in the intermittent contact mode. The number and the size of nuclei then increase, interact with each other and ready to produce a continuous thin film.

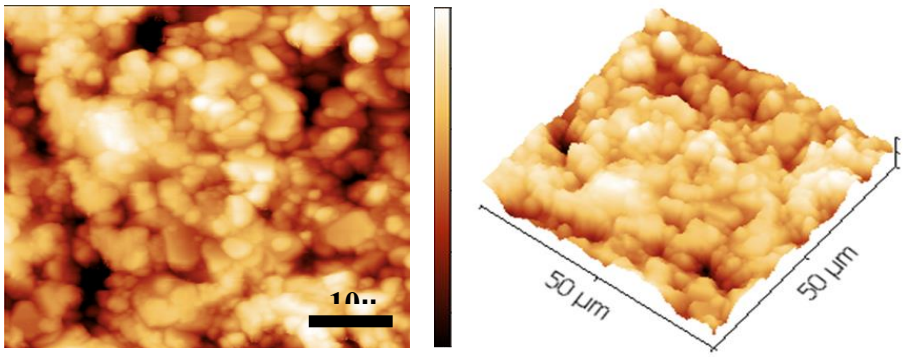

Fig.1. 2D and 3D-visualisation of the SnS film.

AFM-images adaptation and next evaluations was performed using the Gwyddion modular software. Based on functional possibilities of Gwyddion, the following parameters were determined: average roughness R_q, surface porosity P_{surf} and average pore size D_{por}. According to [10], surface porosity determines as:

$$P_{surf} = \frac{S_{por}}{S_{scan}},$$

where S_{por} – image area of pores, S_{scan}– area size of image.

The average profile R_z, average roughness R_q, surface porosity P_{surf} and average pore size D_{por} of the films were measured using the modular program Gwyddion and are presented in Table 1.

The modular program Gwyddion allows researchers to estimate thickness of the samples, which valuation comes up approximately to 40 nm. Also, the 2D and 3D-topographies of samples in the 50µm×50µm area are characterized by the presence of small hills on the top of surface. This fact is concerned with significant uniformity of ceramic. According to AFM-image,tin sulfide films are evaluated by small roughness, which valueis of 56 nm.Total pore size for SnS is 1.85µm, surface porosity is 18%.

Table 1.The average profile R_z, average roughness R_q, surface porosity P_{surf} and average pore size D_{por} of the SnS films

Parameters	Sample
R_z	≈40 nm
R_a	56 nm
P_{surf}	18%
D_{por}	1.85 μm

The qualitative profile of tin sulfide is presented in Fig.2. According to Fig.2, well-formed shelf allows us to propose about Sn_xS_y phase formation. The intensity of curves for Al and O, which are performed as substrate elements, increases with an increase in the argon sputtering time and, thus, with penetration to cross-sectional of the samples. The low intensity of the lines for Sn and S elements can be related to the low thickness of the samples which was determined by AFM images in the Gwyddion modular program.

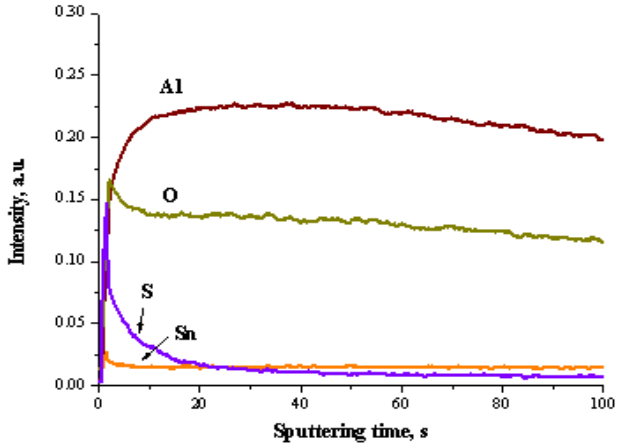

Fig.2. The qualitative profile of the SnS thin film on the ceramic substrate

Fig.3 illustrates the total transmittance spectrum for the SnS film in the wavelength range of 300–1000 nm. Transmittance of the sample is low till the wavelength value of 370 nm. In the range of 370–450 nm transmittance grows up rapidly and achieves 95%.

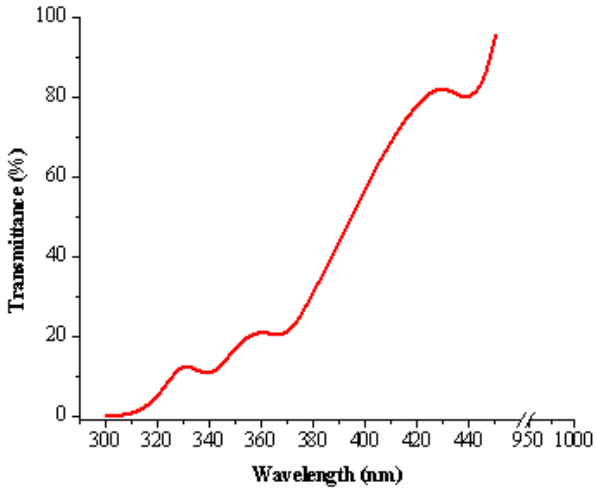

Fig.3. The transmittance spectrum of the SnS film

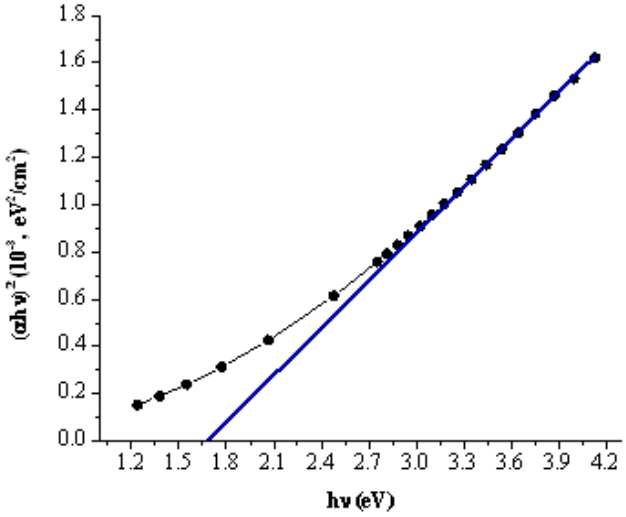

Fig.4. Plot of $(\alpha h\nu)^2$ vs. hν for the SnS films.

According to the results, the plot's behavior (Fig.4) has a straight line, that points at the direct optical transition near the absorption edge [11].The energy bandgap was calculated using the plot presented in Fig.4 by extrapolating it onto the hν axis. In this study the E_g value is 1.65 eV, which is in good correlation with works [12, 13].

4. Conclusions

SnS films were deposited by DC-magnetron sputtering of a nanostructured target prepared from tin sulfide produced by self-propagating high-temperature synthesis. The AFM results have identified island-type growth of the samples (the Volmer-Weber mode). Tin sulfide with the thickness of 40 nm has good uniformity (56 nm), small porosity (18%). Elemental analysis indicates the Sn_xS_y phase formation. The transmittance spectra showed a rapid increase in the range of 370–450 nm. The direct band gap is evaluated to be 1.65 eV which is comparable with the data published in works [12, 13]. DC magnetron sputtering is therefore viable technique to produce SnS thin films with appropriate morphology and optical properties.

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