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THIN TIN MONOSULFIDE FILMS DEPOSITED WITH THE HVE METHOD FOR PHOTOVOLTAIC APPLICATIONS

TANKA PLAST HVE KOSITROVEGA MONOSULFIDA ZA UPORABO V FOTOVOLTAIKI

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In the present study, thin films of SnS photo-absorbers with two different thicknesses of 0.5 μm and 1 μm were deposited onto molybdenum-covered soda-lime-glass substrates using high-vacuum evaporation (HVE). The changes in the structural, phase-composition, morphological and photo-electrochemical properties depending on the film thickness were studied. The films showed a polycrystalline orthorhombic SnS crystal structure with (040) as the preferred orientation. It was observed that the films showed improved crystallinity with the increase in the film thickness. Raman analysis confirmed the presence of single phase SnS without any other binary phases. Photoconductivity measurements revealed that the layers have the p-type conductivity. The SnS layers grown at a thickness of 1 μm showed a high photosensitivity and could be considered as an absorber layer for solar-cell applications.

Keywords: SnS, thin films, HVE, photo-electrochemical, solar cell

V tej študiji je bila z visokovakuumskim naparevanjem (HVE) nanesena tanka plast SnS fotoabsorberja z dvema debelinama 0,5 μm in 1 μm na z molibdenom prekrito podlago iz natrij-kalcijevega stekla. Preučevane so bile spremembe v strukturi, sestavi faz, morfološke in fotoelektrokemijske lastnosti v odvisnosti od debeline plasti. Te plasti so pokazale polikristalno ortorombično kristalno strukturo SnS z (040) kot prednostno orientacijo. Opaženo je bilo, da se s povečanjem debeline plasti izboljša njena kristaliničnost. Ramanska analiza je potrdila prisotnost samo ene faze SnS brez drugih binarnih faz. Meritve fotoprevodnosti so odkrile, da imajo plasti prevodnost p-tipa. Plasti SnS, ki so zrasle na debelino 1 μm, imajo veliko fotoobčutljivost in so lahko uporabne pri sončnih celicah kot absorpcijska plast.

Ključne besede: SnS, tanke plasti, HVE, fotoelektrokemičen, sončna celica

1 INTRODUCTION

Tin monosulfide (SnS) is a layered compound semiconductor that crystallizes in an orthorhombic structure with the lattice parameters of a = 0.4329 nm, b = 1.1193 nm and c = 0.398 nm.[1] It has a high absorption coefficient with a photon energy threshold of 1.3 eV and exhibits the p-type conductivity.[2] Besides, its constituent elements Sn and S are earth-abundant and nontoxic. SnS has been used in photocondutors,[3] photovoltaic conversion,[1] holographic recording media,[4] solar control,[5] near-infrared detector,[6] etc. Owing to these advantages SnS has to be the promising material in the fabrication of thin-film solar cells. So far, the best reported conversion efficiency for SnS solar cells is about 4.4 %,[7] which is a very low value when compared to CIGS (about 21.7 %)[8] and CZTS (12.6 %) solar cells.[9] The reason for the low efficiency of the SnS solar cells so far has not been understood. In the present study, SnS thin films with two different thicknesses of 0.5 μm and 1 μm were grown on molybdenum (Mo) covered soda-lime-glass substrates and the influence of the preparative parameters of deposition on the microstructural parameters and photocurrent response of the films is reported.

2 EXPERIMENTAL WORK

Thin films of SnS were deposited onto Mo-covered soda-lime-glass substrates with the high-vacuum evaporation technique using BOC EDWARDS Auto 500 systems. The films with two different thicknesses of 0.5 μm and 1 μm were deposited at a constant substrate temperature (T_s) of 300 °C, with a deposition rate of 0.5 nm/s. The deposition was carried out in a vacuum chamber at a pressure of around 1.33×10^{-6} mbar with a deposition source-to-substrate distance of ≈ 25 cm. The crystalline-phase identification and phase-composition determination were done with a Bruker D5005 X-ray diffractometer and a Horiba LabRam HR spectrometer, respectively. The surface morphology of the as-deposited layers was observed using high-resolution scanning electron microscopy (HR-SEM Zeiss ULTRA 55) and an atomic force microscope (AFM, Bruker Nanoscope V controller with the application module MultiMode 8.10). The type of conductivity of the prepared SnS films was identified by performing the photo-electrochemical measurements in a background electrolyte solution of 0.1 M H_2SO_4.

3 RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction (XRD) profiles of the SnS thin films deposited onto Mo-coated glass substrate at a substrate temperature of 300 °C and a detailed XRD pattern of the (040) peak is shown in the inset. XRD profiles of all the layers had diffraction peaks at $2\theta \approx$ (26.12°, 31.96° and 39.04°), corresponding to the polycrystalline orthorhombic crystal structure of SnS with (040) as the dominant peak and being in agreement with the JCPDS data (card no. 39-0354). The strong-characteristic (040) diffraction peak could be due to the fact that most of the SnS crystallites grew preferentially along the (010) crystal plane that has the lowest surface energy,[10] with its orientation parallel to the substrate. At a thickness of 1 µm, the (040) plane of the as-deposited SnS film showed an enhanced intensity. The average crystallite size of the films was calculated using the full width at half maximum (FWHM) of the (040) plane with Scherrer's relation.[11] The FWHM of the (040) peak decreased with the film thickness, which indicates that the film crystallinity had improved. The evaluated average crystallite size of the prepared SnS films was found to be 18.9 nm and 58.9 nm for the thicknesses of 500 nm and 1 µm, respectively. The observed increase in the crystallite size at the higher thickness may be due to a decrease in the disorderness and microstrain in the thicker films. Analogous results for nanocrystalline SnS thin films prepared with electron-beam evaporation were also reported by Shaaban et al.[12] The microstrains of SnS thin films were calculated from equation[13] and the calculated values are 0.00183 and 0.00061 for the thicknesses 500 nm and 1 µm, respectively.

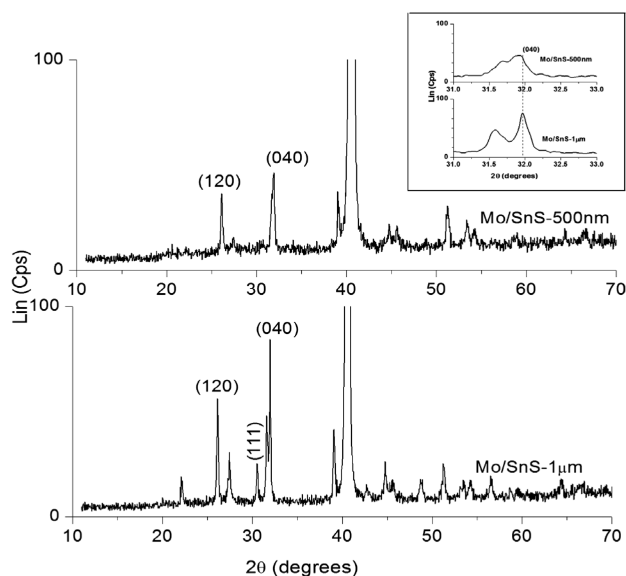

Figure 1: XRD patterns of SnS thin films (the inset: detailed (040) peak profiles)
Slika 1: XRD-posnetka tankih plasti SnS (vložek: podrobnejši profil vrhov (040))

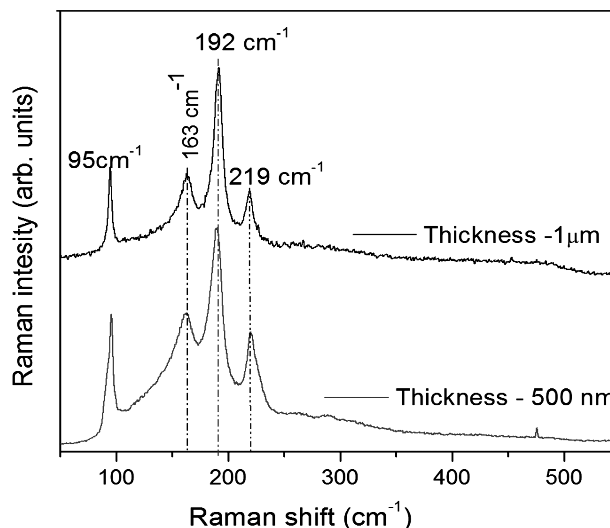

Figure 2: Raman spectra of SnS films at the thicknesses of 500 nm and 1 µm
Slika 2: Ramanska spektra plasti SnS pri debelinah 500 nm in 1 µm

Raman measurements were performed to get detail information of the phase composition of the films. The room-temperature Raman spectra of the SnS thin films were measured in a wavenumber range of 50–550 cm^{-1} and are shown in **Figure 2**. The peaks at (96, 163, 192

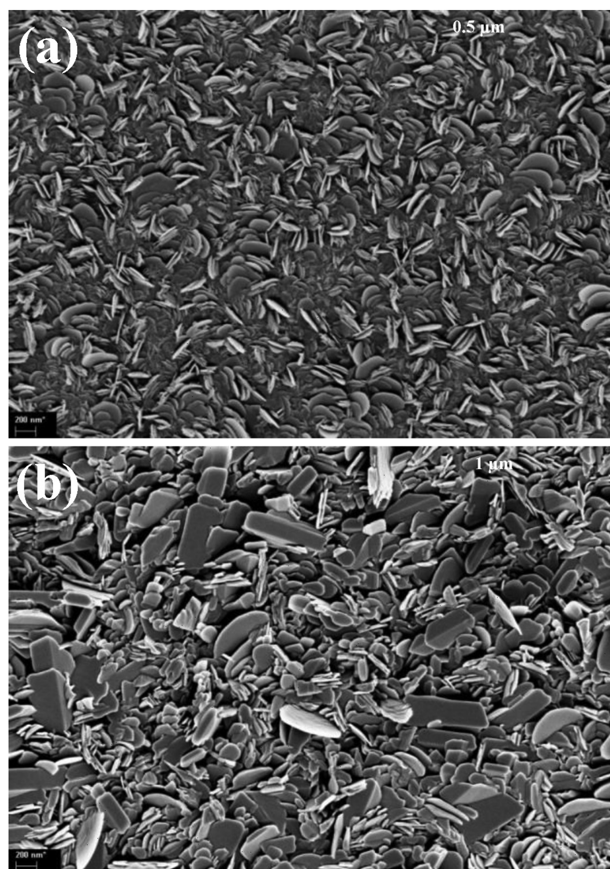

Figure 3: SEM pictures of SnS thin films
Slika 3: SEM-posnetka površine tanke plasti SnS

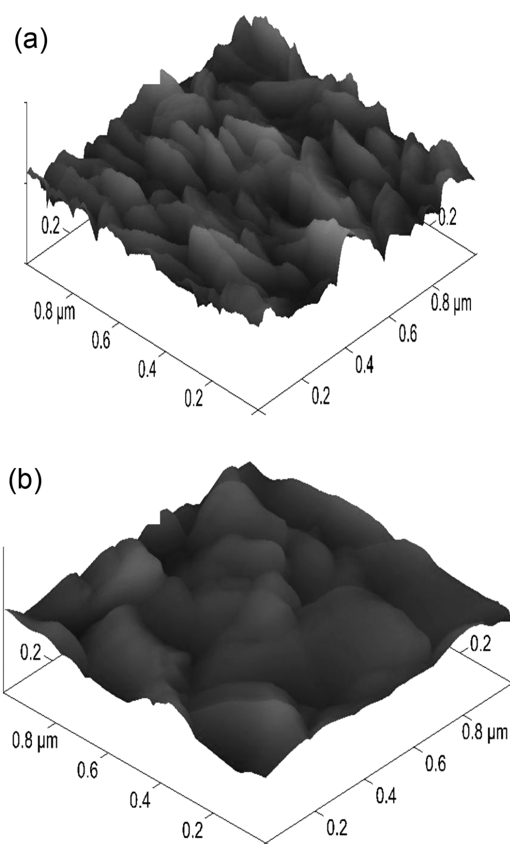

Figure 4: AFM images of SnS films of: a) 0.5 µm and b) 1 µm
Slika 4: AFM-posnetka plasti SnS: a) 0,5 µm in b) 1 µm

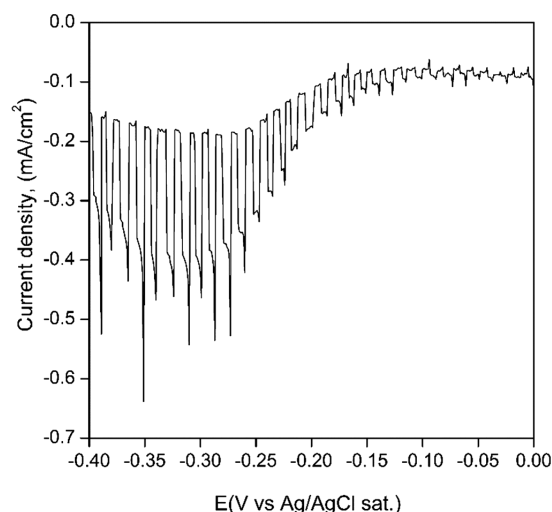

Figure 5: PEC measurements of a SnS film deposited with a thickness of 1 µm
Slika 5: PEC-meritev nanesene plasti SnS z debelino 1 µm

and 220) cm^{-1} can be attributed to the orthorhombic SnS. The Raman modes observed at (96, 192 and 220) cm^{-1} belong to the A_g mode whereas the band line at 163 cm^{-1} can be ascribed to the B_2g mode.[14] The spectra do not indicate the presence of traces of SnS_2 or Sn_2S_3 phases in the films.

The HR-SEM images of the SnS thin films deposited at the thicknesses of 0.5 µm and 1 µm are presented in **Figure 3**. The surfaces of the films are composed of densely packed flake-like particles with the average diameters of about 179 nm and 429 nm for the thicknesses of 500 nm and 1 µm, respectively.

Figure 4 shows the AFM micrographs of the SnS thin films that were scanned over an area of 1 µm × 1 µm. It is clear from the images that the thinner films (500 nm) have smoother surfaces compared to the thicker films (1 µm). The root-mean-square roughness (R_q) and the mean-value roughness (R_a) for the film with the 500 nm thickness are 20.6 nm and 16.7 nm, whereas for the thicker film (1 µm) the values of R_q and R_a are about 25.8 nm and 20.3 nm, respectively. The average grain size of the as-deposited SnS films increased from 24 nm to 60 nm with the increase in the film thickness.

Figure 5 shows the photocurrent response of the SnS thin films, taken under illumination in the background electrolyte. The photocurrent was found to be increased towards the negative region of the applied potential, confirming that the films exhibit the p-type electroconductivity. The results indicate that the best photosensitivity was obtained with the SnS absorber layer with a thickness of 1 µm.

The above studies revealed that the SnS thin films deposited at a thickness of 1 µm showed a larger crystallite size of 58.9 nm with a surface roughness of 25.8 nm and a high photosensitivity. These results are promising for the fabrication of complete solar-cell structures based on a SnS photo-absorber.

4 CONCLUSIONS

Thin films of SnS were successfully deposited onto a Mo-coated soda-lime-glass substrate using the HVE technique with two different thicknesses of 500 nm and 1 µm. The XRD and Raman analysis showed that the films have a single-phase SnS orthorhombic crystal structure without any other binary traces of SnS_2, Sn_2S_3, etc. The layers deposited with a thickness of 1 µm compared with the layers with a thickness of 0.5 µm show an improved crystallinity, a uniform and densely packed surface morphology and a high surface roughness. They exhibit the p-type conductivity and high photosensitivity. Therefore, the prepared SnS photo-absorber layers could be applied in complete solar-cell structures.

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