Studies on the brush plated SnS thin films

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Tin sulfide (SnS) is one of the IV-VI layered semiconductor compounds of the form MX where M is Sn and X is the chalcogen S. SnS finds wide applications in optoelectronic devices and window material for heterojunction solar cells [1]. It is cheaply available and has band gap in the region of 1.0 to 1.2 eV [2], matching the highest intensity of the solar spectrum. Hence studies are made to use SnS in the photoelectrochemical (PEC) solar cells. Crystalline SnS is usually a p-type semiconductor [3] and the acceptor levels are created by the tin vacancies normally present in the lattices. The orthorhombic structure of SnS can be regarded as a small distortion of NaCl structure, results in a considerable reduction of bond strength along one end leads to the layered nature of SnS [4]. The objective of this paper is to study the structural, morphological and optical properties of SnS films obtained by the brush plating technique for the application in PEC solar cells.

Brush plating is one of the electrochemical methods of synthesizing thin films. This technique has been adopted for the first time to coat SnS film on tin oxide conducting substrates. It is a simple, convenient and low cost method for obtaining large area films. Details regarding equipments and solutions engaged in the deposition of metals and alloys are given by Norris [5, 6]. Brush plating equipment includes power packs, solutions, plating tools, anode covers and auxiliary equipments. The schematic of brush plating system is given in Fig. 1. Microprocessor controlled Selectron Power Pack Model 150 A–40 V was used to transform A.C. current to D.C. current. Layers of SnS were brush plated on tin oxide coated conducting glass substrates of about 50 cm^2 which is the negative electrode. The stylus, consisting of a carbon rod wrapped in cotton wool served as the anode. The cotton wool was held in position by a porous sleeve. The electrolyte bath contained 5.0 mM of $SnCl_2$ and 2.5 mM of $Na_2S_2O_3$. The pH and temperature was maintained at 1.5 and 28 °C (RT) respectively throughout the experiment. Prior to plating, the stylus was wired to the power supply and the cotton wool was soaked in the electrolyte. The stylus was then brought into contact with the substrate and moved at uniform speed. An electrical current was found passing whenever the stylus was in contact with the substrate. This is associated with the acceleration of ions in the electrolyte trapped within the cotton wool which was subsequently reduced at the substrate to form SnS layer. The current density was maintained at 80 mA cm^{-1}. SnS films of thickness up to 2 μm were obtained after 5 min. The films were annealed at 250 °C in vacuum for 30 min under a controlled rate of heating and cooling.

Structural characterization was carried out by X-ray diffraction (XRD) studies using Cu K_α radiation. Morphological studies were carried out using JSM 6400 Jeol scanning and electron microscope. A Nanoscope$^{(R)}$ E scanning probe microscopy 3138 J was used for AFM analysis to observe fine structure. A VG MK11 ESCA Spectrometer coupled with Ar^+ etching was used for XPS measurements. Light transmission was measured as a function of the wave length from 400-1400 nm on a double beam Hitachi UV-VIS-NIR U3400 spectrophotometer. Resistivity of the films was measured with an Agronic digital microohm meter, model 53 C.

The XRD pattern of the vacuum annealed SnS film on a conducting glass substrate is shown in Fig. 2. The polycrystalline nature of the films is evident from the presence of the strong peaks corresponding to the planes (101), (040), (131) and (141) of orthorhombic phase. Elemental Sn or S is not detected in the diffractogram. The interplanar spacings (d values) as calculated from these patterns were found to agree well with those reported in the literature [7]. The crystallite size was calculated from FWHM of the XRD pattern and found to be in the order of 30 nm. Surface chemical composition of the as-prepared SnS film was determined by XPS analysis. The more intense lines obtained in the survey XPS spectrum as given in Fig. 3

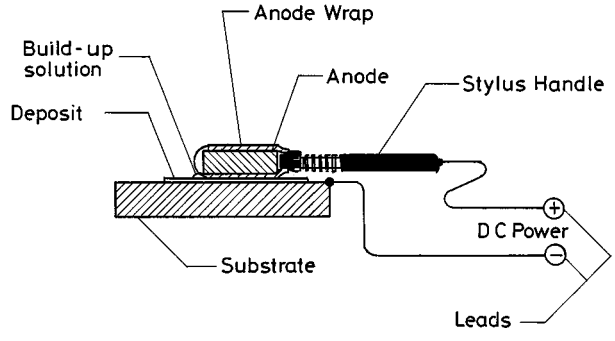

Figure 1 Schematic of brush plating system.

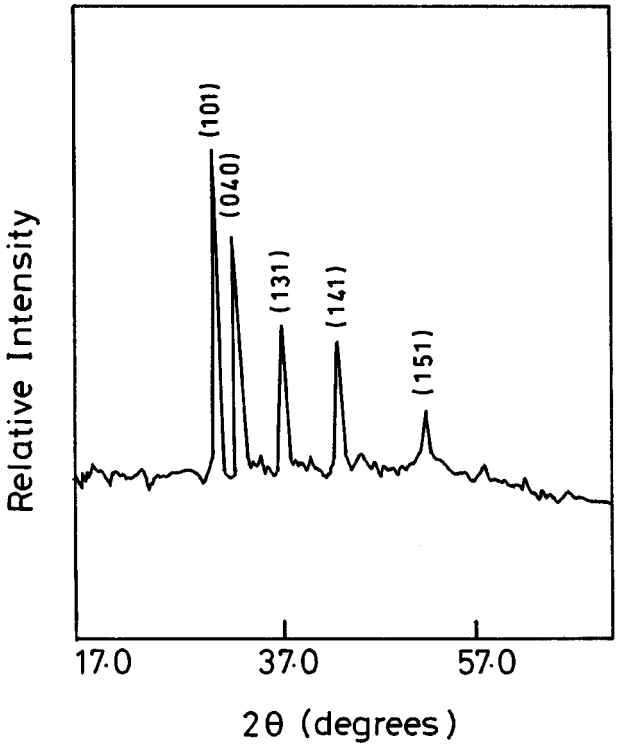

Figure 2 An X-ray diffractogram of a brush plated SnS film.

allowed one to identify Sn, S, O and C on the surface of the film. The spectrum obtained for the surface analysis corresponding to Sn 3d level reveals the signals at 485.4 and 494.2 eV coincide with the characteristic binding energy for 3d 5/2 and 3d 3/2 electrons in SnS [8]. Quantitative analysis of the elements shows a surface atomic concentration of 39.9% for Sn, 38.4% for S, 12.5% for C and 9.2% for 0. After $2 + 2$ min sputtering with argon ion, the atomic concentration is changed to 40.9% for Sn and 40.1% for S, which confirms the nearly stoichiometric or slightly Sn-rich film. XPS data rule out the presence of any SnS_2 or Sn_2S_3 in our brush plated SnS samples.

Fig. 4 indicates the surface morphology of the heat-treated SnS film. As-prepared SnS film showed a granular morphology. The efficiency of unannealed SnS films for solar energy conversion was limited by the small grain size and low electrical conductivity. Annealing the films in vacuum for 30 min has improved the surface smoothness and increase in grain size, leading to coalescence of the grains. The average size of the microcrystallites was determined by Cottrell's method [9] from SEM picture. It was found to be ~320 nm.

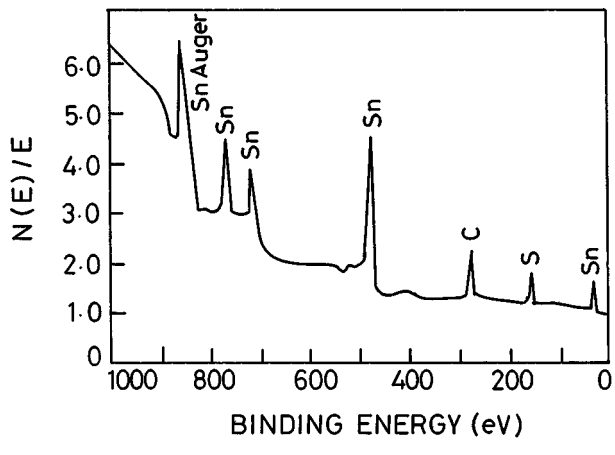

Figure 3 Survey XPS data for a SnS film after $2 + 2$ min sputtering with argon ion.

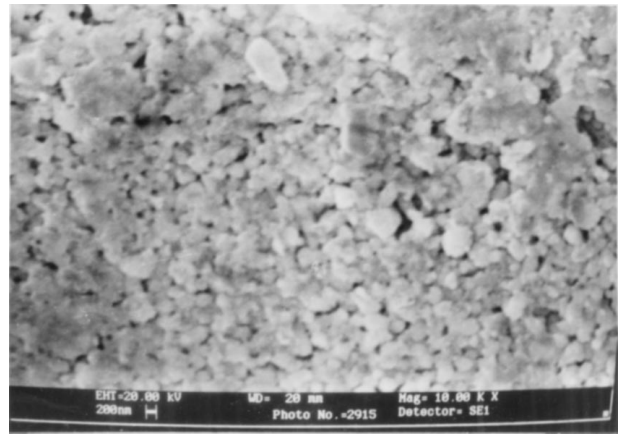

Figure 4 Scanning electron micrograph of orthorhombic SnS film.

The microstructure of the annealed film can be observed for its minute details by AFM, as illustrated in Fig. 5a and b for scanned areas of 10 μm × 10 μm and a corresponding 1 × 1 μm zoom for SnS film with thickness of 1.2 μm respectively.

Fig. 5a shows the film morphology of granular grains with uniform size of about 350 nm. This is consistent with the SEM morphology results as discussed earlier. Fig. 5b presents a very close look at the

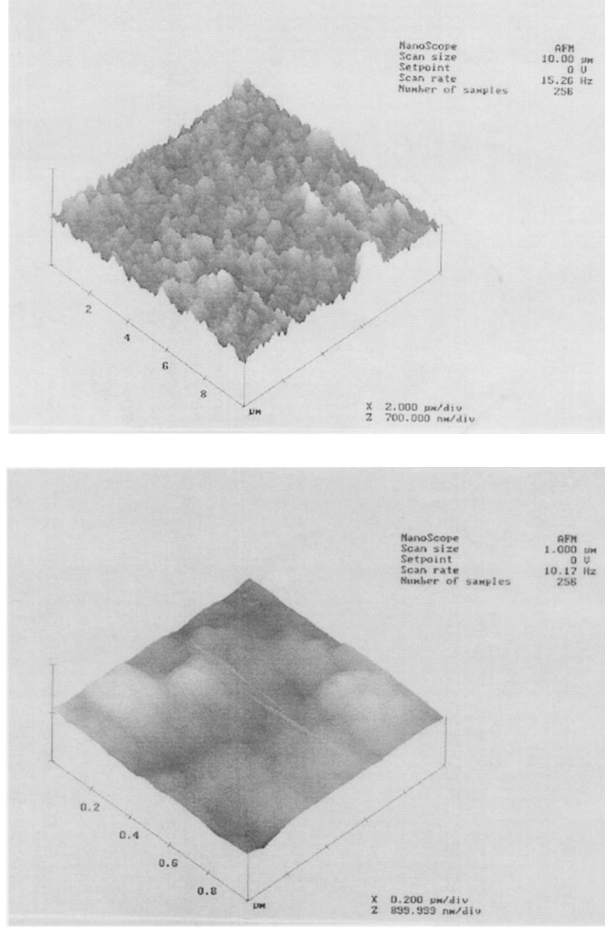

Figure 5 AFM image of the surface of brush plated SnS film.

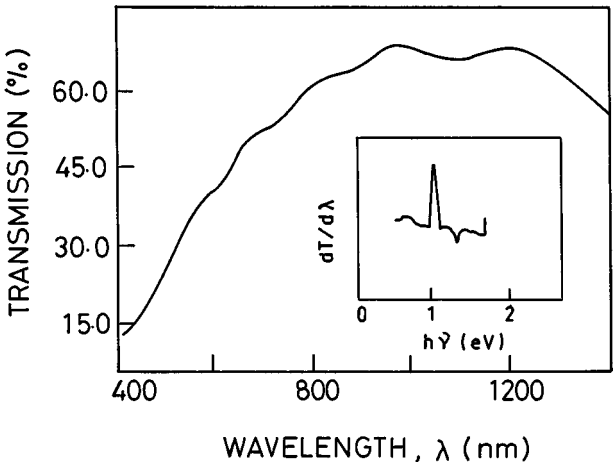

Figure 6 Optical transmittance spectra for brush plated SnS film and the variation between dT/dλ and hν.

individual grains. Each grain is found to be consisting of several crystallites of size varying in the range 20–40 nm. This observation on crystallite size corroborates the XRD results already given in this paper. The density and height of the hills on top of a homogeneous granular background surface is found increased for higher thickness of about 1.6 μm of the deposit. It reveals that the growth of SnS film on conducting glass substrate by brush plating is associated with the formation of three dimensional grains in the perpendicular direction without lateral diffusion of adatoms on the surface parallel to the substrate. This may be attributed to the preferentially oriented crystalline nature of the tin oxide substrate over which SnS film is brush plated.

Fig. 6 shows the optical transmission T of the vacuum annealed SnS film on conducting glass substrate as a function of wave length. The absorption coefficient α was calculated from this curve, and was found to be of the order of 10^4 cm^{-1} near the band edge. The average thickness of the films has been calculated from the successive maxima of the interference pattern observed in the transmittance curve as 1.18 μm. A graph is drawn between differential transmittance for different wave lengths, very close to the region near the absorption edge and hν (inset to Fig. 6). A peak is obtained corresponding to the band gap value of 1.1 eV. The band gap value is in good agreement with the value obtained from the usual plot of $(\alpha h\nu)^{1/2}$ vs hν reported in the literature [10]. The indirect nature of optical transition is observed for brush plated SnS films. The continuous differential descent method [11] has been used to determine the refractive index of the material. A maximum refractive index value of 3.0 at a wave length of 1100 nm corresponds to the band gap of SnS is obtained.

TABLE I Structural, optical and electrical properties of SnS thin films brush plated on SnO_2

Crystal structure	Orthorhombic
Grain structure	Spherical
Grain size (nm) from SEM	320
Thickness range (μm)	1.0 to 2.0
Optical band gap (eV)	1.1
Transmittance (%)	65
Absorption coefficient (cm^{-1})	10^4
Refractive index near band gap wave length	3.0
Resistivity (Ωcm)	5.0 to 15.0
Nature	p-type

Using hot-probe method, it was observed that as-prepared and annealed films have p-type conductivity. The cross-plane resistivity was found to be in the range of 10–15 Ω cm and the in-plane resistivity was found to be 5–8 Ω cm. The silver paint forms an ohmic contact to these films.

In conclusion, SnS semiconductor films have been deposited for the first time by the brush plating technique. The films are polycrystalline and adherent well to tin oxide substrate. The structural and optical properties are summarized in Table I for a low resistance SnS sample. A study of the use of brush plated SnS film as photocathode in photoelectrochemical solar cells is in progress.

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