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Ensuring The Homogeneity OF Spray Pyrolised SnS Thin Films Employing XPS Depth Profiling

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Abstract. SnS thin films were prepared using chemical spray pyrolysis (CSP) technique. p-type SnS films with direct band gap of 1.33 eV and having very high absorption coefficient were obtained with the optimized deposition conditions. In this paper we focus on investigating the uniformity and phase purity of the hence deposited SnS films employing Raman and X-ray Photoelectron Spectroscopy (XPS) analysis. Raman Spectra of the films had only single peak corresponding to the Raman active Ag mode at 224 cm^{-1} which is characteristic for phase-pure SnS thin films. Detailed XPS analysis on these samples were performed by scanning the peaks for Sn, S, and O with high resolution to estimate the chemical states and composition. Employing Ar-ion sputtering, the depth profiles showing variation in concentration and binding energies of S, Sn, O over the sample thickness were obtained and the uniformity in composition along the thickness has been discussed in detail.

Keywords: Solar cell material, thin films, homogeneity, depth profile

PACS: 81.15 Rs, 82.80 Gk, 78.30-j

INTRODUCTION

Tin monosulfide (SnS) is one among the Tin chalcogenide (IV-VI group) compounds having layer structure. It has direct band gap of 1.33 eV and an absorption coefficient of 10^5 cm^{-1} which make the material an ideal solar cell absorber layer [1]. Theoretically predicted light conversion efficiency of this material is 25% [2] and its electro-optical properties can be controlled by doping with suitable dopants. In addition, its constituent elements Sn and S are abundant and less toxic in nature.

In spite of possessing the aforementioned good qualities, conversion efficiency of the SnS solar cell is quite low compared to the theoretical predictions [3-5]. The major parameters that pull back from attaining higher efficiency may be the uniformity of SnS films and/the existence of other binary sulfides of Sn such as Sn_2S_3 and SnS_2 . Another problem of this class of materials is the poor control over the stoichiometry; i.e., metal to chalcogen ratio in the film. Because of large difference in the vapor pressures of Sn and S, the stoichiometry is generally controlled by means of sophisticated vapor-monitoring techniques. In contrast to Physical Vapor Deposition (PVD) techniques, in CSP technique, ratios of the constituents are directly

linked to their concentrations in the spray solution. Moreover, this technique is ideally suited for deposition of large area films with controlled dopant profiles [1].

By optimizing the deposition parameters, we could obtain SnS thin films having high absorption coefficient and optimum band gap for maximum photovoltaic conversion [1]. The present study structure and composition of the hence deposited SnS films were probed employing Raman and XPS analysis. It demonstrates the potential and suitability of the technique to deposit stoichiometric, SnS thin films with good phase purity, which are quite difficult to obtain employing other techniques.

EXPERIMENTAL DETAILS

Pristine SnS thin films were deposited on Soda-lime glass substrates using CSP technique. Spray solution, consisting of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CS}(\text{NH}_2)_2$ in required molarities was sprayed on to the substrate kept at a temperature $375 \pm 5^\circ\text{C}$ at the rate of 2 ml/min. Total volume of the solution sprayed was 30 ml and the thickness of the hence obtained SnS film was $0.8\text{ }\mu\text{m}$. The detailed report on the deposition and characterization of SnS film was reported elsewhere

[1]. Structural analysis was performed employing X-ray diffraction (XRD) using Rigaku X-ray diffractometer (Model D.Max.C; $\lambda=1.5405 \text{ \AA}$; Ni filter operated at 30 kV and 20 mA). Raman analysis was performed in the back scattering mode at room temperature using micro Raman system from Jobin Yvon Horibra LABRAM-HR visible (400 -1100 nm) with a spectral resolution of 1cm^{-1} . Argon ion laser of wavelength 488 nm was used as the excitation source. Optical absorption studies were carried out using UV-Vis-NIR (190 - 2500 nm) spectrophotometer (Jasco V-750). Atomic concentration and compositional details were studied with the help of X-ray Photoelectron Spectroscopy (XPS), (ULVAC- PHI unit, Model: ESCA 5600 CIM). Here Ar-ion sputtering was used to obtain the depth profile and atomic ratio of the films.

RESULTS AND DISCUSSIONS

XRD

Figure 1 shows XRD pattern of the SnS film deposited at optimized condition. The films were, crystallized in 'Herzenbergate' orthorhombic structure, as observed from the XRD pattern with SnS phase orientated along (111) plane having lattice parameters $a=4.329 \text{ \AA}$, $b= 11.19 \text{ \AA}$, $c=3.983\text{\AA}$, at $2\theta =31.53^\circ$ (JCPDS data card 39-0354).

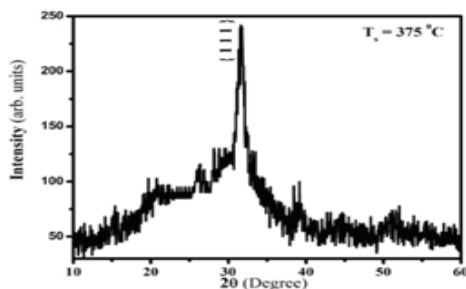


FIGURE 1. XRD pattern of SnS thin film.

Grain size of the films were calculated from the peak at $2\theta = 31.53^\circ$ using the Debye-Scherrer formula. The films had grain size of 10 nm.

Raman Analysis

Raman analysis was performed on the samples as it is more sensitive to the structural and compositional changes of the material [6]. Raman spectrum has distinct peaks for each binary sulfides of Sn (SnS , Sn_2S_3 , SnS_2), which is otherwise very difficult to distinguish from the XRD pattern.

Figure 2 shows room temperature Raman spectrum of Sn_xS_y films. Here, Raman mode was observed at 224 cm^{-1} . Based on the previous report on Raman spectra of SnS single crystal, the observed Raman modes were assigned to Ag mode [7]. In accordance with Raman spectra of GeS also, the Raman mode at 224 cm^{-1} was assigned to Ag mode [8]. Therefore, both Raman and XRD results were complimentary to each other. Both the analyses confirmed that deposition temperature to obtain single phase SnS thin films is 375°C .

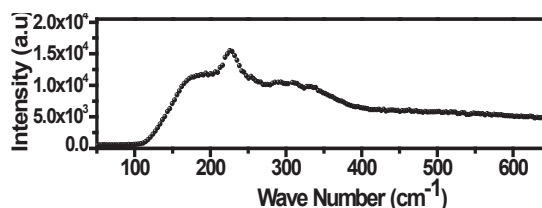


FIGURE 2. Raman spectra of the SnS film

The large background noise observed in the Raman spectra while comparing to that of single crystal is due to the small grain size of the samples. Also the Raman modes of SnS thin films show broadening and are shifted towards lower wave number side as compared to the Raman modes of single crystal counterpart. This is due to 'phonon confinement' effect. Liu et al. et al. [9] observed 2Ag modes at 223 cm^{-1} for SnS nano-wires and Gou et al. [10] observed only 2Ag modes at 189 and 220 cm^{-1} for SnS nano particles. Similar observations were observed by other workers also [11].

XPS Analysis

XPS analysis were performed on the sample to estimate chemical states and composition. The XPS spectrum is shown in Figure 3. Incorporation of O in the films could have occurred during their deposition and come from carrier gas and ambience. Oxygen and carbon were predominantly surface bound; a situation which may result from the handling and storage of the films in air. Hence before taking the XPS spectrum a few surface layers were etched out. Presence of the elements Sn, S and O were checked by doing detailed high resolution scan. Binding energies (BEs) were calibrated with that of C contaminant present on the sample surface (BE of C 1S is 285 eV).

BE for S was observed at 161.5 eV. This value is characteristic of S in a metal sulfides. Sulfur has a large range of binding energy from 161.7 eV (for compounds with oxidation state of S is 2) to 171 eV (for compounds with oxidation state of S is 4). Binding energies of S at 161.5 eV obtained for the sample corresponds to that of S(II) and indicates the formation

of SnS. It is reported that the BE of Sulfur in the nano crystalline SnS was among the lowest recorded for sulfur [12]. As far as the B.E of Sn is concerned, the samples had Sn 3d 5/2 (B.E at 485.2 eV) which agreed well with the Sn 3d 5/2 peak reported for SnS of 485.6 eV [12, 13].

Oxygen observed in the bulk of the material had binding energy of 533.4 eV which was not due to a metal oxide for which the characteristic BEs are in the region 529 - 532 eV (for tin(IV) oxide BE is 530.6 eV). Other molecular oxygen species also have binding energies in this vicinity. It suggests that the O arises during the reaction, possibly adsorbed from the ambience. The BE of Sn 3 d5/2 in Tin (II) oxide is 486.9 eV and in Tin(IV) oxide is 486.6 eV; both these peaks were absent in the samples [12].

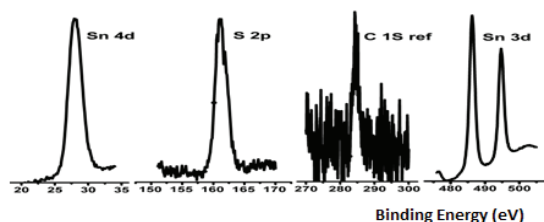


FIGURE 3. XPS spectra of the sample showing the BEs of S, Sn and O.

Depth-wise XPS analysis of the sample is carried out to check the composition of Sn, S and O along the thickness. As in the above case here also the spectra were calibrated against shifts due to machine errors, using the C 1s line of the hydrocarbon contamination on the films as the standard (Binding energy of C 1s is 284.5 eV). Employing Ar-ion sputtering, the depth profiles showing variation in concentration and binding energies of S, Sn, O along the sample thickness were obtained (figure 4). At the end of sputtering, the glass substrate was exposed. It is evident from the figure that, although the surface was heavily contaminated with carbon and oxygen, the bulk composition showed less oxygen and almost no carbon.

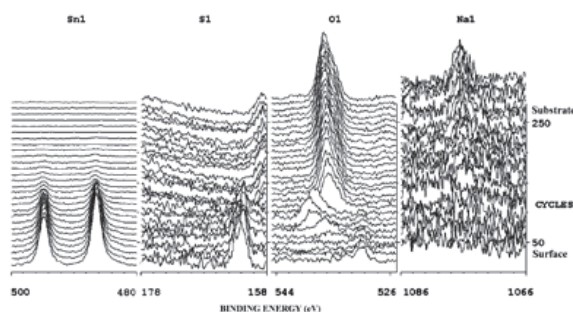


FIGURE 4. XPS depth profile of SnS thin films.

The B.E at 25 eV is corresponding to the elemental Sn present in the film. This peak could be a result of preferential sputtering of S during etching leaving

some exposed Sn metal. This effect has been observed in an XPS study of tin nitride films where preferential sputtering caused all the N to be removed, leaving Sn metal [14].

CONCLUSION

Raman and XRD analysis confirmed the presence of phase-pure SnS crystallized in 'Herzenbergate' orthorhombic structure in the sample. It is evident from the XPS depth profile spectra of SnS that, although the surface was heavily contaminated with carbon and oxygen, the bulk composition showed less oxygen and almost no carbon. Throughout the depth of the film the B.Es of Sn and S did not show any shift, which confirms the formation of single phase SnS in the bulk of the film.

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