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n-type SnS:Cu Thin Films with High Surface Energy (111) Plane: Optimization of its Substrate Temperature

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Abstract

Using Chemical Spray Pyrolysis (CSP) Technique n- type Copper doped SnS (SnS:Cu) thin films were successfully deposited onto soda-lime glass substrate. According to earlier reports (111) orientation of SnS is suggested to be the preferred orientation for PV applications. This paper reports the preparation of SnS:Cu films with (111) orientation by varying the substrate temperature which is an important parameter of CSP technique. Using X-ray diffraction, Scanning electron microscopy, UV-Vis-NIR spectroscopy and Hall measurements the Structural, Morphological, Optical and Electrical properties of SnS:Cu films are studied. The substrate temperature of 375^{0}C is found to be the best for preparing good quality SnS:Cu thin films with preferred orientation in plane (111).

Keywords: Spray techniques, Optical properties, Electrical properties, Thin films.

1. Introduction

The binary semiconductor Tin sulfide (SnS) belonging to IV-VI group semiconductors, with earth abundant components, orthorhombic structure and having a band gap of around 1.4eV makes it a potential candidate for photovoltaic studies [1] [2]. SnS can be prepared as single crystals, thin films or nanostructures using various physical and chemical methods such as chemical bath deposition [3] spray pyrolysis [4], thermal evaporation [5] sputtering [6] etc according to required applications [7]. Properties of the thin film prepared by CSP technique is very much connected with the substrate temperature, as this parameter provides energy for pyrolytic reduction. With very high temperature, anionic species get re-evaporated where as with very low temperature proper pyrolytic reduction will not take place. Hence the substrate temperature is so critical to prepare an uniform thin films with required opto-electronic properties. The present study report the changes in Copper doped SnS thin films on varying the substrate temperature from 300^{0}C to 450^{0}C.

2. Experimental Details

SnS:Cu thin films were synthesized over glass substrates using CSP technique. Stannous chloride ($SnCl_2.2H_2O$), Thiourea ($CS(NH_2)_2$) and Cuprous Chloride ($CuCl_2.2H_2O$) is used as the precursors for the above study. The substrate temperature is varied as 300^{0}C, 350^{0}C, 375^{0}C, 400^{0}C and 450^{0}C. The samples are named as C300, C350, C375, C400 and C450 respectively. Compressed air is used as the carrier gas and the opto-electronic studies were carried out keeping all the spray parameters unchanged with Sn:S ratio at 1:2. Copper doping is fixed as 4% of tin concentration as reported elsewhere [8].

X-ray diffraction studies were carried out using Rigaku (D. Max.C) automated X-Ray diffractometer and diffraction pattern is recorded using filtered Cu Kα (λ = 1.5405 A^o) radiation and Ni filter operated at 30 kV and 20 mA.UV-VIS-NIR spectrophotometer (JASCO V 570 model) is used for optical studies. Surface morphology is studied using ZEISS Scanning electron microscopy.Ecopia model No HMS-53000, magnetic field = 0.57 T and capable of current

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measurement in the range (1nA-20 mA) Hall system is used for electical studies.

3. Results and Discussions

Figure 1 depicts the XRD patterns of SnS:Cu films deposited at different substrate temperatures. All the samples except those prepared at very low and very high pyrolysis temperature had SnS phase crystallized in Orthorhombic structure (JCPDS 75-0925). At lower temperature 300⁰C presence of Sn_2S_3 phase (JCPDS 14-0619) is observed along with SnS phase and at higher temperature 450⁰C the SnS_2 phase (JCPDS 23-0677) become prominent.

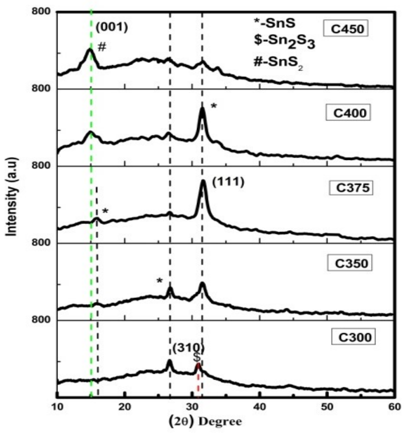
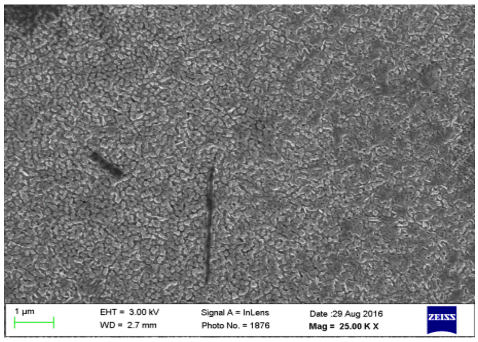
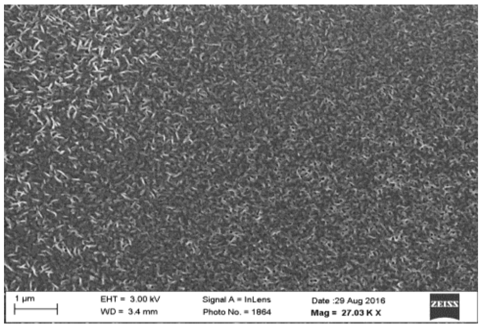


Figure 1. The X-ray diffractograms of SnS:Cu thin films by varying the substrate temperature

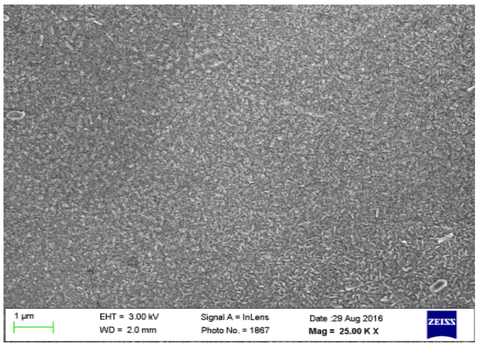
It is quite clear from our XRD data that, at substrate temperature 375⁰C, the impurity phases are almost absent and has better crystallinity with prominent SnS (111) plane. It is already reported that for PV applications the (111) orientation of SnS is generally preferred because out of all the SnS based solar cells the maximum efficiency is for SnS with these orientation [9]. Even with the doping no peaks corresponding to Cu_xS phase is formed. According to reports the surface energies (σ) of orthorhombic structure increases as σ (100) < σ (001) < σ (010) < σ (111) and it is also mentioned that the (111) plane will grow only when an optimum number of Sulfur atoms is present around Sn atoms [7]. Hence at temperature 375⁰C we could successfully synthesis SnS:Cu thin films with this high energy (111) plane.



(a)



(b)



(c)

Figure 2. SEM images of SnS:Cu thin films prepared at (a) 300⁰C, (b) 375⁰C, (c) 450⁰C

The Surface morphology of the temperature varied samples showed a noticeable difference as temperature changes. This change is clearly observed in Figure 2. The samples at low temperature (300⁰C) showed spherical grains where as samples at 375⁰C showed typical SnS:Cu needle like structure and as

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the temperature is increased further to 450⁰C the morphology changed partially as that of SnS_2 granules.

Optical band gap for films prepared at different substrate temperatures were determined using '$(\alpha h\nu)^2$ versus hν' plot (Figure 3). The absorption coefficient (> 10^5 cm^{-1}) is obtained for all the samples. The film synthesized at 375⁰C has got optimum band gap around 1.4 eV. For lower and higher temperature the band gap is found to be greater than that of C375. The variation in band gap shows its tunability by merely changing the temperature alone.

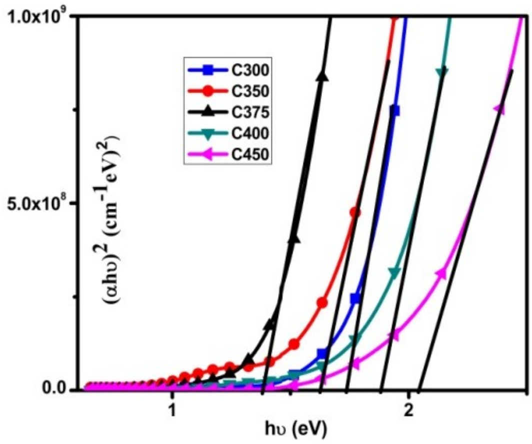

Figure 3. The band gap obtained for SnS:Cu thin films by varying the substrate temperature

The high band gap value obtained for lower and higher temperature is probably due to the presence of other phases like Sn_2S_3 and SnS_2 respectively [10].

The resistivity of all the samples were calculated using Hall measurement and found to be decreasing as temperature increases with minimum value for samples prepared at 375⁰C; further increase in temperature resulted in increase of resistivity due to the formation of SnS_2. The minimum resistivity obtained for C375.

4. Conclusions

SnS:Cu thin films were deposited using CSP technique over glass substrate by varying the substrate temperature. The optimum temperature for fabricating phase pure SnS:Cu is determined to be 375⁰C and its band gap is found to be around 1.4eV. These properties are quite promising for a good absorber layer in solar cell fabrication. This optimized film showed n-type conductivity with minimum resistivity. This work also shows the possibility of tuning the resistivity and band gap of SnS:Cu films by controlling the substrate temperature without any change in its conductivity type. All these superior properties are achieved without employing any post deposition treatments and hence it is quite useful for the development of low-cost thin film solar cells.

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