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Cu Doping: An Effective Method For Improving Optoelectronic Properties Of Sprayed SnS Thin Films

Gisa Grace Ninan[1], V. G Rajeshmon[2], C. Sudha Kartha[1] and K.P. Vijayakumar[1,*]

[1]*Department of Physics, Cochin University of Science and Technology, Cochin-682022, India*
[2]*St.Paul's College, Kalamassery, Cochin-682022, Kerala, India*
[*]*E-mail: kpv@cusat.ac.in*

Abstract. SnS thin films were deposited using Chemical Spray Pyrolysis (CSP) technique at a substrate temperature of 415 °C. Resistivity of pristine SnS thin film was 120 Ω.cm. In order to decrease resistivity, in-situ copper doping was done and its effects on the structural, optical and electrical properties were studied. Percentage of Cu was varied as 2%, 4%, 6%, 8% and 10% of tin in the precursor solution. Resistivity decreased with minimum resistivity of 1.6 Ω.cm for the sample doped with 6% copper. Beyond 6 % doping, resistivity increased. All the films were n type irrespective of doping.

Keywords: Spray techniques, Optical properties, Electrical properties, Thin films
PACS: R81.15 Rs, 78.66Qn, 73.61.Ph, 73.50 Fq

INTRODUCTION

Tin monosulphide (SnS) belongs to IV-VI group semiconductors and crystallizes with orthorhombic layer structure [1]. SnS thin films is one among the most promising materials for low-cost thin film solar cells due to its near-optimal direct band gap of 1.3 eV and high absorption coefficient of ~ 10^4-10^5 cm^{-1} [2]. High natural abundance of tin and sulfur could potentially enable scaling of SnS photovoltaics manufacturing to terawatt levels. SnS thin films can be deposited on any kind of substrate, by simple, economic and environmentally approved technique through various physical and chemical means of thin film deposition such as Vacuum evaporation [3], Chemical vapor deposition [4], Chemical bath deposition [5], Chemical spray pyrolysis [6] etc. In the present work we report effect of Cu doping on sprayed SnS thin films.

EXPERIMENTAL DETAILS

The films were prepared on glass substrates by chemical spray pyrolysis (CSP) method. Aqueous solution containing stannous chloride ($SnCl_2.2H_2O$) and thiourea ($CS(NH_2)_2$) was sprayed at a rate of 2 ml/min onto the substrate kept at 415 °C, using compressed air (pressure~1.5 bar) as the carrier gas. Total volume of solution sprayed was 30 ml. Effect of copper doping on the structural, electrical and optical properties of the films was studied by varying the percentage of Cu keeping the ratio of tin and sulphur at 1:2. Copper doping was done by including the required percentage of cuprous chloride ($CuCl_2.2H_2O$), to the aqueous pristine solution. Doping percentage of Cu was varied as 2%, 4%, 6%, 8%, 10% of the tin concentration in the precursor solution and these samples were referred as SnS_2%, SnS_4%, SnS_6%, SnS_8%, SnS_10% respectively. Structural analysis of the films were performed using X-ray diffraction studies using Rigaku(D. Max.C) automated X-Ray diffractometer and diffraction pattern is recorded using filtered Cu Kα (λ =1.5405 A°) radiation and Ni filter operated at 30 kV and 20 mA. Bandgap of the films was measured using UV-VIS-NIR spectrophotometer (JASCO V 570 model). Electrical characterization was done employing using Two-Probe method, hot probe technique and Hall effect. Conductivity type (n type or p type) was confirmed using hot probe technique. Hall measurment was done using Ecopia model No HMS-53000,magnetic field = 0.57 T and capable of current measurement in the range (1nA-20 mA).

RESULTS AND DISCUSSIONS

XRD pattern of pristine as well as Cu doped films are shown in Figure 1. This reveals the presence of traces of other phases along with predominant SnS

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phase. Preferential orientation was along the (111) plane corresponding to a 2θ value of 31.5^0. No peaks were observed corresponding to the phase SnS_2.

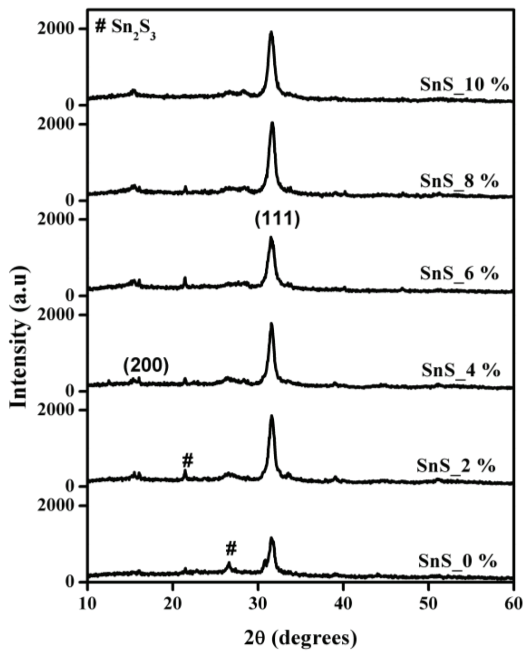

FIGURE 1. X-ray diffractograms of pristine and Cu doped SnS thin films.

It is seen that peak intensity of (111) plane is enhanced as the percentage of doping is increased. The (111) orientation of SnS thin films is generally preferred for PV applications, as the maximum efficiency SnS based solar cell is having SnS with (111) plane [7]. Even for 10 % doping there is no peaks corresponding to the formation of Cu_xS phase. Crystallite size was calculated using Scherer's formula and there is not much variation in crystallite size with Cu doping. The average grain size was 11 nm.

Absorption spectra of Cu doped and pristine samples were given in (Figure 3). From the $(\alpha h\upsilon)^2$ Vs hυ plot, optical band gap of the films were determined. Linearity of the plot confirmed the direct band gap of the material. We can see that, Eg at first decreases from 1.3 eV to a minimum value of 1.2 eV for Cu-doping 2% and then increases. Similar observations were reported before in thermally evaporated SnS:Cu thin films [8]. The band gap value was obtained between 1.2eV and 1.3eV and the absorption coefficient was found to be > 10^4 cm^{-1}.

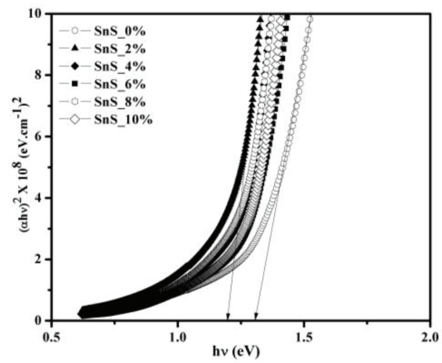

FIGURE 2. Absorption spectra of pristine and Cu doped SnS thin films.

Resistance of the sample is measured using Two-Probe method. The resistance and hence resistivity showed a decrease of two order in magnitude due to Cu doping and the minimum was obtained for 6% doping.(Table 1) Hot probe and Hall measurement were carried out on the samples to determine the conductivity type and this proved that all the film were n type.

TABLE 1. Resistivity of pristine and Cu doped SnS thin films.

Sample Name	Resistivity (Ω cm)
SnS_0%	120
SnS_2%	3.2
SnS_4%	1.76
SnS_6%	1.68
SnS_8%	4.4
SnS_10%	4.0

CONCLUSIONS

Effect of Cu doping on the properties of sprayed SnS thin films were studied. The doped as well as pristine films showed similar structure and common preferred orientation (111). All the films were of n type conductivity. The band gap value varied from 1.2eV to 1.3eV. Cu-doped SnS films with low resistivity and high absorption coefficient can be an alternative material for thin film solar cells.

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