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Short communication

# Influence of Cu dopant on the optical and electrical properties of spray deposited tin sulphide thin films

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ABSTRACT

Copper doped tin sulphide (SnS: Cu) thin films have been prepared by the spray pyrolysis technique at the substrate temperature of 350 °C. The optical and electrical properties of the films were studied as a function of copper dopant concentration (up to 10 at.%). The optical measurements showed the energy band gap, refractive index and extinction co-efficient values varied with increase in Cu concentration and the PL spectra showed the strong emission peak around at 765 nm. The film has the lowest resistivity while higher carrier concentration and mobility were obtained at 8 at.% of Cu.


Optical investigation of solid constituents is very much essential to estimate its suitability for various applications. To enhance the economic feasibility of thin coatings a study is made of potentially low cost coatings. Thin films are used to create optical coatings like anti reflective coatings on the glasses, reflective baffler on car head lights high precision optical filters and mirrors. The optical properties of semiconductor materials are tunable varying their shapes and sizes [1,2]. The recent investigations are directed towards the development of cost effective and non toxic optical materials that can be synthesized by a simple and robust technology. In this direction, attention has been focused on new materials, which are abundant in nature and can be easily processed without posing any environmental issues. The semiconducting chalcogenide thin films like SnS have received much attention due to its novel property [3,4]. It has direct band gap (1.2–1.6 eV) [5,6] and high optical absorption co-efficient (>$10^4$ $cm^{-1}$) for photons with energies greater than the band gap such that only a few microns of SnS are needed to absorb most of the incident light [7]. In addition, the elemental constituents of this material are cheap, non toxic and abundant in nature.

SnS thin films have been prepared using different techniques such as chemical bath deposition [8,9], vacuum evaporation [10], rf sputtering [11], dip deposition [12], chemical spray pyrolysis [13,14], etc. Among these, spray pyrolysis technique is very advantageous for large scale production of thin films with lower cost and also for preparing pin hole free, homogeneous deposits of the required thickness [15]. Doping in semiconductor material can improve its optical and electrical properties. Therefore it is necessary to study doped tin sulphide thin films for different applications. In this aspect Copper is identified as suitable dopant for optical and electrical properties, so we have tried to prepare Cu doped SnS thin films by spray pyrolysis technique.

Cu doped tin sulphide thin films (SnS: Cu) were deposited onto 75 × 25 $mm^2$ microscopic glass substrates by the spray pyrolysis technique. A detailed description of optimized parameters, precursor concentration for formation of single-phase tin sulphide thin films and automated spray-coating unit has been discussed before [16,17]. Copper was doped with SnS thin films using $CuSO_4$ as the dopant source in the ratio of [Cu/Sn] = 2–10% added to starting solution.

Optical measurements were carried out using a JASCO V-670 UV–Vis–NIR double-beam spectrophotometer in the wavelength range of 400–1200 nm. The photoluminescence (PL) spectra were

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recorded at room temperature using a FluoroLog spectrofluorometer with an excitation wavelength of 650 nm. The electrical resistivity, carrier concentration and mobility were measured by automated Hall Effect system (ECOPIA HMS-3000) measured at room temperature.

The spectra of transmission for SnS thin films obtained at various doping concentrations of Cu are shown in Fig. 1(a). This figure exhibits a cut off region on transmittance spectrum at shorter wavelengths indicating the onset of the intrinsic inter-band absorption in SnS: Cu thin films and possessed high absorption coefficient (>$10^5$ $cm^{-1}$) which means that the films were good for absorbing sunlight from the visible to near-infrared band. The absorption edge shifted to higher wavelength region with increase in doping concentration which indicated the decrease of optical band gap. The decrease of transmittance at higher doping concentration may be due to the increased scattering of photons by crystal defects. The similar behavior of Cu doping in SnS thin films was observed and reported by Manoj et al. (2007) [18].

Fig. 1 (b) illustrates the variation of $(\alpha h\nu)^2$ with hν for copper doped tin sulphide thin films. It can be seen that the band gap value was found to decrease from 1.55 eV to 1.37 eV for doped films upto 8 at.% of copper; this value was nearly equal to the optimum value (1.40 eV) of efficient light absorption; and then the energy band gap increased slightly for further increase of doping concentration. The decrease in optical band gap might be attributed to the band shrinkage effect because of increasing carrier concentration [19]. Also, the unsaturated bonds that might be present in the layers are responsible for the formation of some defects, while produce localized states in the band structure reducing the optical band gap [20]. By increasing the doping concentration above 6 at.%, the band gap value increased and it was due to an effective incorporation of dopant into the SnS lattice, since more copper atoms were placed at the substitutional sites, therefore the occupied states and the band gap were incremented [21]. These results clearly suggested that the optical properties of SnS thin films were affected by copper doping [22].

Fig. 2(a) depicts the variation of refractive index with different wavelength and it was interesting to note that the $n_{max}$ was shifted to higher wavelength region (lower photon energy) with increasing doping concentration upto 8 at.% and then shifted to lower

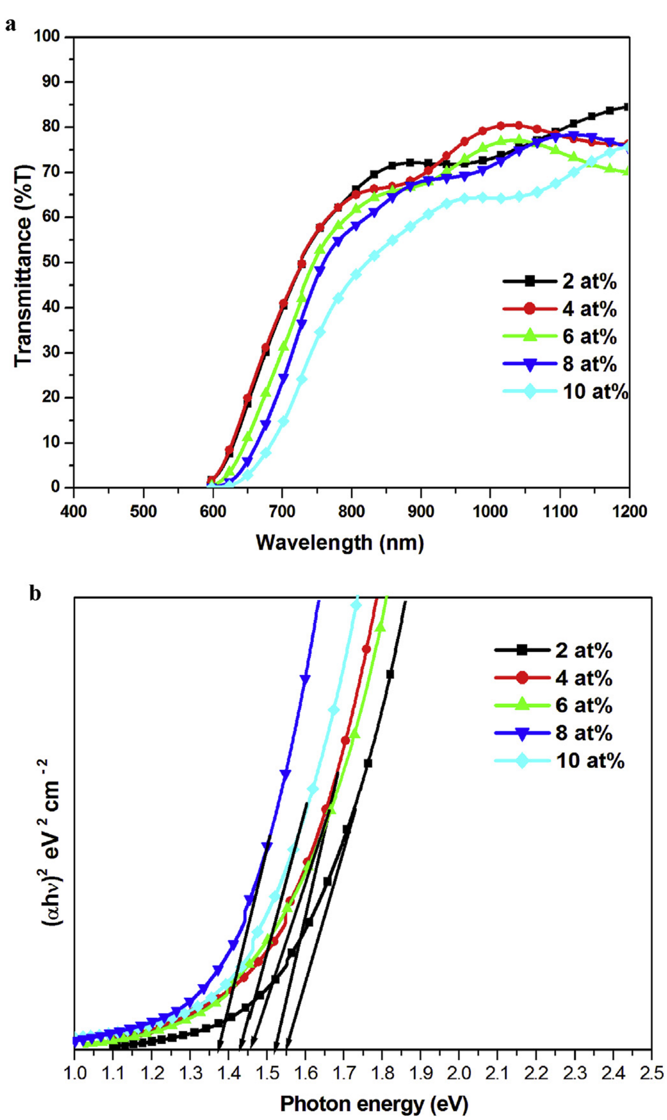


**Fig. 1.** (a) Transmittance spectra and (b) Plots of $(\alpha h\nu)^2$ versus photon energy (hν) for Cu doped SnS thin films prepared at various doping concentrations.

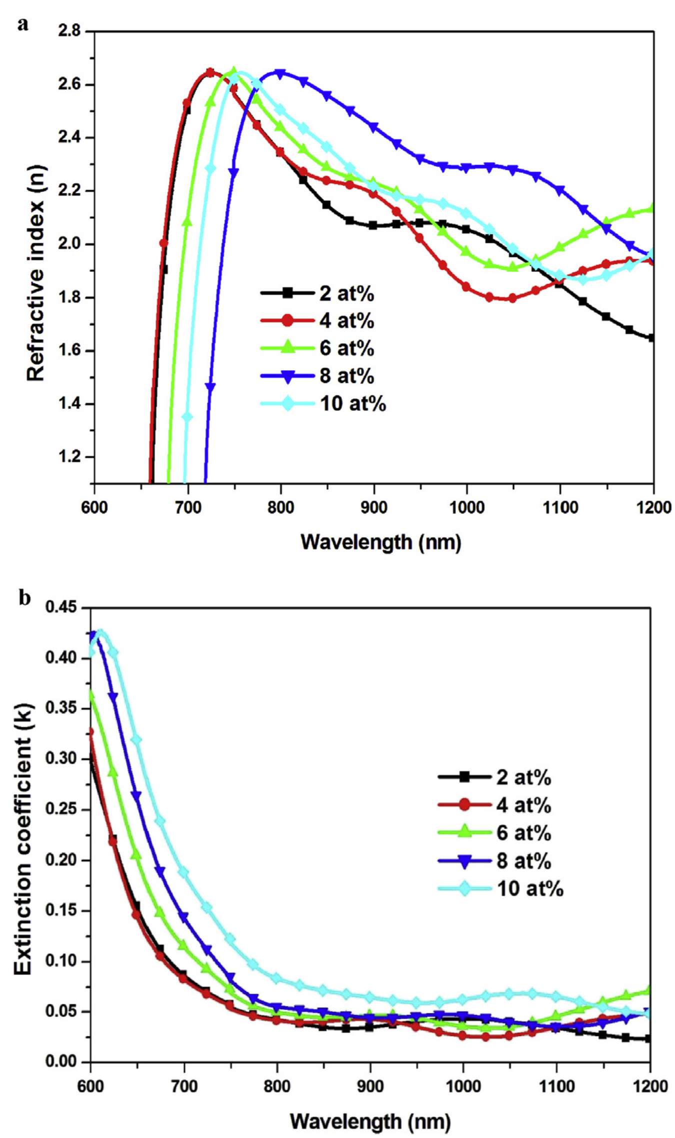


**Fig. 2.** (a) Variation of refractive index (n) and (b) Variation of extinction coefficient (k) with wavelength for Cu doped SnS thin films prepared at various doping concentrations.