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Preparation of thermally deposited $Cu_x(ZnS)_{1-x}$ thin films for opto-electronic devices

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ABSTRACT

Zinc sulfide thin films have been doped with copper atoms to investigate their efficiency as transparent conductor layers. $Cu_x(ZnS)_{1-x}$ thin films were deposited on glass substrate using thermal evaporation technique by varying the Cu concentration ($x = 0.01$, 0.02, 0.03, 0.05, 0.10 and 0.25). The prepared thin films were characterized using XRD, FE-SEM, EDS and UV–Vis spectroscopy. The X-ray diffraction studies revealed that the films are crystalline in nature and well oriented along (111) direction with the cubic crystal structure. Crystallite size increases with increase in Cu concentration. FE-SEM studies showed that the films are homogenous and pin-hole free. All the films exhibited p-type conductivity. It was also observed that the band gap of the $Cu_x(ZnS)_{1-x}$ films vary from 3.48 eV to 2.60 eV when the copper content varies from 0 to 0.25. At a Cu concentration of $x = 0.03$, the hole conductivity increases to 1.9×10^3 S/m retaining an optical transparency of ~73% in the visible spectra. This combination of optical transparency and hole conductivity of $Cu_x(ZnS)_{1-x}$ thin films for such low Cu concentration is, to our knowledge, the best reported to date.

1. Introduction

In recent years, transparent conducting materials (TCMs) are becoming important in opto-electronic applications such as light emitting diodes, photovoltaics, organic electronics, etc. There are many n-type wide band gap materials such as ZnS, ZnO, SnO_2, etc. which are widely used for transparent electronics. There are relatively fewer reports on successful fabrication of p-type transparent conducting films. In the area of photovoltaics, p-type TCMs can be used for cost-effective synthesis of heterostructured thin film devices with intrinsically n-type materials. Also, the performance of multi-junction solar cells could be enhanced by using p-type TCMs which would facilitate the collection of photogenerated charges independently from each absorber layer and thus improving the overall efficiency. In practical applications, the crucial challenge in using p-type TCMs is performance, particularly the combination of transparency and hole conductivity. Considerable efforts have been made to fabricate p-type ZnO [1,2], ZnS [3] and ZnSe [4], but the reliability of p-type doping still remains controversial [5]. In addition to the above binary compounds, p-type transparent ternary and quaternary compounds have begun to attract attention. In 1997, the first p-type ternary TCM $CuAlO_2$ was reported which had a hole conductivity of ~1 S cm^{-1} and an average optical transparency of 70% [6]. Since then, significant efforts have been made to improve the performance of p-type TCMs [7,8]. In spite of these efforts, properties of these materials are quite inadequate for the device application, and fabrication of transparent p-type materials still remains a major challenge.

Recently, chemical bath deposition and pulsed laser deposition of p-type Cu_xZn_yS thin films were reported [9–11], respectively. The band gap of Cu_xZn_yS thin films varies from 2.1 to 3.5 eV depending upon x and y ratio which makes Cu_xZn_yS another interesting candidate for p-type TCMs as well as buffer/window layer in solar cells.

In the present study, $Cu_x(ZnS)_{1-x}$ thin films have been deposited by thermal evaporation technique. The Cu concentration in $Cu_x(ZnS)_{1-x}$ thin films has been varied and its effect on thin film properties has been studied in detail.

2. Experimental procedure

For the preparation of $Cu_x(ZnS)_{1-x}$ ($x = 0$, 0.01, 0.02, 0.03, 0.05, 0.10 and 0.25) thin films, a mixture of Cu (purity 99.999%, Alfa

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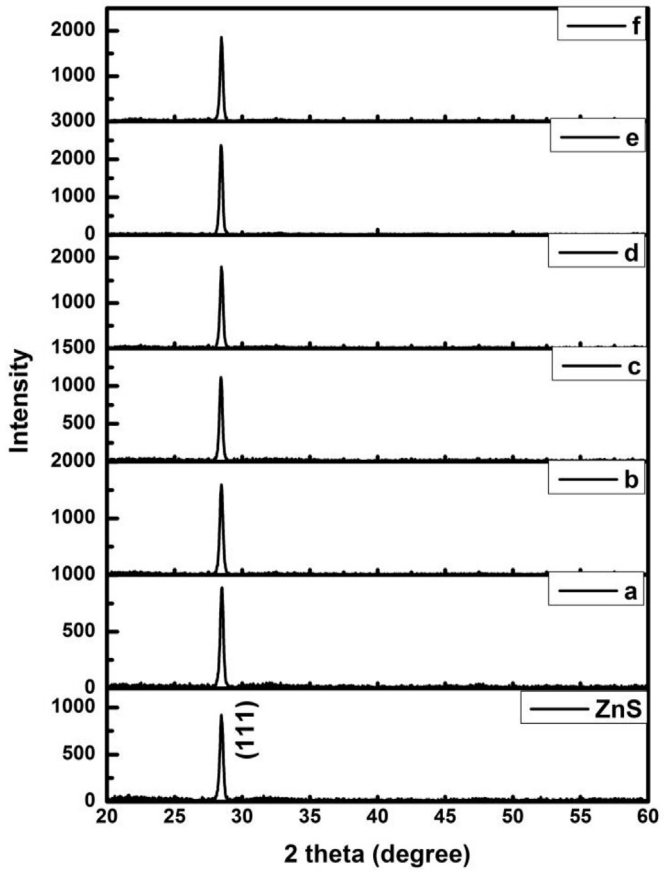

Fig. 1. XRD patterns of $Cu_x(ZnS)_{1-x}$ thin films: a) x = 0.01, b) x = 0.02, c) x = 0.03, d) x = 0.05, e) x = 0.10 and f) x = 0.25.

Aesar) and ZnS (purity 99.995%, Sigma Aldrich) was deposited on clean glass substrates by the thermal evaporation technique at a pressure of ~10^{-6} Torr. The substrate temperature was maintained at 100 °C and post deposition annealing was carried out at the same temperature for 1 h. The thickness of the deposited films was determined by the gravimetric method and was maintained at ~500 nm for different compositions. The structural characterization of the films was carried out by X-ray diffractometer (Rigaku Mini-Flex 600) using Cu Kα radiation with a wavelength of 1.5418 Å. The surface morphology and elemental composition of the grown thin films were analyzed using scanning electron microscope (Carl Zeiss FE-SEM) with a linked electron dispersion X-ray (EDX) detector which was operating at an accelerating voltage of 5 kV. The optical absorbance and transmittance spectra of the prepared thin films were measured at room temperature in the spectral range 300–800 nm using spectrophotometer (SpectraPro 2300i). The electrical characteristics of the thin films were studied using a sourcemeter (Keithley sourcemeter 2400) and a multimeter (Keithley multimeter 2002) with indium (In) as an ohmic contact.

3. Results and discussion

3.1. Structural studies

X-ray diffraction (XRD) studies were carried out on the deposited thin films and the diffraction patterns were analyzed to gather information about its various structural features. The X-ray diffraction (XRD) patterns of $Cu_x(ZnS)_{1-x}$ (x = 0, 0.01, 0.02, 0.03, 0.05, 0.10 and 0.25) thin films is shown in Fig. 1. According to the XRD pattern, the reflection labeled as (111) at 28.46° corresponds to the cubic structure (zinc blende) of the undoped ZnS thin film (JCPDS card no. 01-077-2100). No significant shift in the (111) peak position was observed even at higher Cu concentration. This might be due to the reason that the ionic radii of copper in the +1 valence state and zinc in the +2 valence state with IV coordination are both 74 pm [11,12]. Moreover, no additional peak(s) corresponding to any phase of Cu or Zn was observed, as previously reported [11].

The d-values for the various diffraction peaks were calculated using Bragg's relation:

$$n\lambda = 2d_{hkl} \sin\theta \quad (1)$$

The obtained 'd' values were found to be in a good agreement with the standard JCPDS data, shown in Table 1.

The crystallite size 'D' (nm) of the investigated films was calculated by using the Scherrer's formula:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

where 'λ' is the wavelength of the X-ray used and 'β' is the full width at half maximum of the diffraction peak at 2θ, where θ is the Bragg diffraction angle.

The lattice constant 'a' for cubic phase was determined by the following relation:

$$a = \frac{d}{\sqrt{(h^2 + k^2 + l^2)}} \quad (3)$$

3.2. Scanning electron micrographs

The SEM images of the $Cu_x(ZnS)_{1-x}$ films are shown in Fig. 2. A uniform, homogeneous and pin-hole free surface throughout the deposited area can be observed for the films deposited at various Cu concentration. EDAX spectra confirm the presence of Cu, Zn and S in the deposited thin films as shown in Fig. 3a. Fig. 3b–d shows the elemental mapping images of Cu, Zn and S on the grown film. It can be observed that all the elements (Cu, Zn and S) are homogeneously distributed throughout the film. The atomic compositions of various films are tabulated in Table 2.

3.3. Optical properties

The optical absorbance and transmission spectra of the films

Table 1
X-ray diffraction data of $Cu_x(ZnS)_{1-x}$ thin films.

Sample	2θ	Inter planar spacing, d (Å)	Crystallite size, D (nm)	Lattice parameter, a (Å)
$Cu_{0.00}(ZnS)_{1.00}$	28.46	3.1333	26.52	5.4270
$Cu_{0.01}(ZnS)_{0.99}$	28.47	3.1325	27.63	5.4256
$Cu_{0.02}(ZnS)_{0.98}$	28.44	3.1362	27.63	5.4321
$Cu_{0.03}(ZnS)_{0.97}$	28.42	3.1384	30.05	5.4358
$Cu_{0.05}(ZnS)_{0.95}$	28.46	3.1331	29.54	5.4267
$Cu_{0.10}(ZnS)_{0.90}$	28.43	3.1369	31.60	5.4328
$Cu_{0.25}(ZnS)_{0.75}$	28.44	3.1360	32.82	5.4317