Sn Doping Effect on the Structural, Optical and Electrical Properties of Cu$_2$O Thin Film Prepared by Nebulizer Spray Technique

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ABSTRACT

This study was mainly examined by the influence of the Sn doped concentration on the structural, optical and electrical properties of undoped and Sn-doped cuprous oxide (Sn:Cu$_2$O) with different Sn percentage (0%, 1% and 2%) thin films coated on glass substrates using a simplistic Nebulizer spray technique. The samples were characterized by X-ray diffraction, UV-visible spectroscopy, Atomic force microscopy, Hall Effect measurements. The band gap trended downward from 2.2 to 1.95 eV with increasing Sn doping content. The crystallite size of the films decreased with increasing Sn doping content from 46 to 35 nm. The carrier concentration, Hall mobility and resistivity of the Sn: Cu$_2$O films were $9.14 \times 10^{15} - 1.08 \times 10^{16}$ cm$^{-3}$, $7.14 - 12$ cm$^2$/Vs and $65 - 10^3$ Ω cm, respectively. The results showed that SnO$_2$ doping strongly affects the structural, optical and electrical properties of the films.

KEYWORDS: Cuprous oxide, nebulizer spray deposition, AFM, UV-visible spectroscopy, Hall Effect.

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1. INTRODUCTION

In recent years, copper oxide (Cu$_2$O) thin films have attracted great interest due to their important applications in many technological fields. This is due, firstly, to the low cost, the non-toxicity and the availability of copper in the nature, secondly to the simplicity of the deposition process of its components. Copper oxide is known to have two stable forms, namely CuO and Cu$_2$O with different properties. Cu$_2$O is a p-type semiconductor with a monoclinic structure; it has a relatively low band gap of 1.2 -1.9 eV $^{1,2}$. Copper oxide thin films are reasonably good electrical and optical properties $^3$. There are two well-known copper oxides: Cu$_2$O (cuprite) and CuO (tenorite) $^4$. Several techniques have been employed to prepare CuO thin films for example: sol-gel$^5$, electrode position $^6$, chemical vapor deposition $^7$, thermal oxidation$^8$ and reactive sputtering $^9$. Among these techniques CuO thin films have been grow typically by Nebulizer spray pyrolysis. It is a simple and easy technique for deposition of various metal oxide thin films. Copper oxide films have been reported to have band gap energy values, which make them suitable for application as windows for solar energy conversion $^{10,11}$.

In this study Sn doped Cu$_2$O thin films with the desired properties can be obtained in this technique by optimizing various deposition parameters such as the molar concentration of the precursor solution, spray rate, nozzle to substrate distance and air pressure. In particular, crystalline property and formation of nanostructures depend mainly on the molar concentration of the precursor $^{12,13}$. Further, temperature plays an important role in the growth of thin films, as it determines the nucleation and further growth of nanostructures.

2. EXPERIMENTAL DETAILS

2.1. Preparation of the Samples

Undoped and Sn doped cuprous oxide thin films have been deposited on glass substrates by using the method of Nebulizer spray technique with different doping concentrations of copper (II) acetate monohydrate (C$_4$H$_6$O$_4$·H$_2$O), high pure glucose (C$_6$H$_{12}$O$_6$) both with the molar concentration of 0.04 M and 20% volume of Propanol was dissolved in 10 ml of distilled water. For this Precursor solution, the required quantity of precursor salt was made to dissolve in the distilled water by continuous stirrer for 15 minutes using a magnetic stirrer. The final solution, with different doping concentrations of Tin oxide of 1% and 2% was dark blue and clear, without any suspension of particles. The solution was sprayed onto the ultrasonically cleaned glass substrates. The substrate temperature was maintained at 280°C using temperature controller. The air pressure was maintained by pressure meter and kept at 1.5 Kg/cm$^2$ and the distance between the nozzle to the substrate is 6
cm. The crystalline structure of the copper oxide thin films was studied by X Pert Pro X-ray diffractometer (XRD), with CuKα radiation. The optimized parameters as shown in Table 1.

The crystalline structure of the cuprous oxide thin films was confirmed by X-ray diffracted (XRD) with CuKα radiation (Rigakumodel, λ = 1.5406Å). The surface properties of all films were investigated using Atomic force microscope (AFM). Optical transmittance and absorptions of the films were recorded by a Perkin Elmer UV/vis Lambda 2S spectrometer (double-beam) range from 200 to 1100 nm. Hall Effect measurement was used to study the electrical properties of the Sn doped copper oxide thin films with the use of four probe method.

Table 1 Showing the optimizes parameters used in the preparation of Cu$_2$O thin film

<table>
<thead>
<tr>
<th>Spray Parameters</th>
<th>Optimal Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of Copper Acetate</td>
<td>0.04 M</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.04 M</td>
</tr>
<tr>
<td>Propanol</td>
<td>20%</td>
</tr>
<tr>
<td>Sn doping concentration</td>
<td>0%, 1%, 2%</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>280 °C</td>
</tr>
<tr>
<td>Distance of Nozzle from substrate</td>
<td>6 cm</td>
</tr>
<tr>
<td>Air Pressure</td>
<td>1.5Kg/cm$^2$</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1 Structural properties

![XRD pattern of Sn: Cu$_2$O thin films of different doping concentrations](image)

Fig. 1 XRD pattern of Sn: Cu$_2$O thin films of different doping concentrations

It was seen in the XRD patterns shown in Fig.1 that the patterns appear there include peaks which have different intensities and widths. The presence of different peaks such as Sn: Cu$_2$O on the XRD patterns of copper oxide thin films prepared using undoped, 1% and 2% with different concentration of precursor are shown in Fig. 1 indicates that all copper oxide films have
polycrystalline structures, and shows the characteristics peaks corresponding to Cu$_2$O phase. The diffraction data were collected at width over a 20 range from 0° to 80°. Further the XRD diffractogram of Cu$_2$O films deposited at different doping concentration with constant temperature 280°C are shown in which is matching to the observed and the standard (h k l) planes confirm that the deposited films are polycrystalline having cubic Cu$_2$O. The XRD pattern has shown the prominent (1 1 1) peak copper oxide located at 20 value of (36.61) with d value 2.5211 Å. Another high intensity peak corresponding to (2 0 0) atomic plane of copper oxide located at 20 value of (42.77°) with d value 2.3221Å and (0 2 0) atomic plane of copper oxide located at 20 value of (61.26)° with d value 1.7094Å has also been observed.

No XRD peaks of SnO$_2$ were observed, which indicated that SnO$_2$ had entered the crystal lattice of Cu$_2$O. The intensities of the major peaks is increased with increasing Sn doping concentration, suggesting an increase in the degree of crystalline with increasing Cu$_2$O solution concentration. This is due to expansion of the Cu$_2$O lattice due to the Sn$^{4+}$ ions occupied in the interstitial position of Cu$_2$O lattice sites. Generally, if Sn$^{4+}$ interstitial position for Cu$^{2+}$, then the lattice should decompression because the ionic radius of Sn$^{4+}$ and Cu$^{2+}$ in tetrahedral coordination was 0.69 and 0.72 Å, respectively. The observed and the standard (h k l) planes that confirm that the deposited films are cubic of undoped and Sn doped Cu$_2$O as confirmed by standard JCPDS data (card no. 77-0199).

The position and the d values of the diffraction peaks for Cu$_2$O films are in good agreement with those reported earlier for the spray deposited Cu$_2$O thin films. The intensity of prominent peak was maximum when films have been deposited at different doping concentration with constant temperature 280°C. The average grain size (D), strain (ε) and dislocation density (δ) were calculated for all the samples. Dislocation density value shows the amount of defects in the structure. Higher dislocation density (δ) values indicate lowers crystalline levels for the films.

The dislocation density was found to decrease with increase in doping concentration and was lowest for 2% doped film owing to high crystalline nature of the film as obtained from XRD analysis.

The decrease in strain in Table 2 with respect to increase in doping concentration indicates the decrease in imperfection and formation of high quality film and it can be attributed to the increase in crystalline size of the film with increase in doping concentration.

XRD analysis shows that precursor molar concentration plays a vital role in the microstructure and the structural properties of undoped and Sn: Cu$_2$O films and the optimized 2% Sn film for the most suitable for thin film solar cell fabrication.
Table 2 Micro structural parameters of Sn: Cu₂O thin films at (111) plane

<table>
<thead>
<tr>
<th>Sample Doping (%)</th>
<th>Crystallite size (D) (nm)</th>
<th>Dislocation Density (δ) (10¹⁵) lines/m²</th>
<th>Strain (ε) (10⁻³) lines² m⁻⁴</th>
<th>Texture Coefficient (TC)</th>
<th>Cell Volume (a³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>2.12</td>
<td>2.22</td>
<td>1.63</td>
<td>2.985</td>
<td>79.683</td>
</tr>
<tr>
<td>1%</td>
<td>1.41</td>
<td>5.02</td>
<td>2.45</td>
<td>0.454</td>
<td>79.685</td>
</tr>
<tr>
<td>2%</td>
<td>2.83</td>
<td>1.24</td>
<td>1.22</td>
<td>0.205</td>
<td>79.172</td>
</tr>
</tbody>
</table>

The structural properties as shown in Table 2. The crystallite size (grain diameter) $D$, of the deposit was determined using the Debye-Scherer’s equation

$$D = \frac{k\lambda}{\omega \cos \theta}$$ \hspace{1cm} (1)

Where $\lambda$ is the wavelength of X-rays, $\theta$ the Bragg angle and $\omega$ the full width half maximum (FWHM) in radian. $K$ varies with $(h k l)$ values. The Crystallite size was found to be varying between 1.41 and 2.83 nm for the samples. The lattice constant of the Nebulizer spray coated copper oxide films were calculated using the formula

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$ \hspace{1cm} (2)

Where ‘$d$’ is the inter planar distance, $(h k l)$ are the Miller indices, ‘$a$’ is the lattice constant for the cubic structure, they are evaluated as in Table 2 which is well in agreement with the standard values of JCPDS data.

### 3.2 Optical Properties

(a) Absorption spectrum

![Absorption spectrum of undoped, 1% and 2% Sn: Cu₂O thin film](image-url)
Fig. (2) shows the optical transmission spectra of the three films undoped, 1% Sn and 2% Sn. From figure (3) it can be noticed that at high absorbance at ultraviolet region, then it decreases rapidly in the visible near infrared region from 300 nm to 1100 nm, the absorption studies reveals that the films are very low absorptive at the visible region and is more suitable for the production fabrication of solar cells \(^{22,23}\).

(b) Absorption coefficient

From the absorbance data, the absorption coefficient \(\alpha\) was calculated in the fundamental absorption region using Lambert law \(^{24, 25}\)

\[
L_n \left(\frac{I_0}{I}\right) = 2.303\alpha d = \alpha d \quad \text{(3)}
\]

Where \(\alpha = \frac{4\lambda}{\alpha}
\]

\(I_0\) and \(I\) are the intensity of incident and transmitted light respectively and \(A\) the optical absorbance and \(d\) the film thickness. Fig. (4) shows the variation of absorption coefficient with photon energy for all the undoped and Sn:Cu\(_2\)O thin films. The figure also shows the variation of absorption coefficient in the low energy range was its value increase rapidly beyond absorption edge region. It can evidently see that undoped and Sn: Cu\(_2\)O thin films have high value of absorption coefficient (\(\alpha > 104 \text{ cm}^{-1}\)) which is more conducive to increasing the probability of direct transitions occurrence.

(c) Extinction coefficient

Extinction coefficient \((k)\) of prepared films was calculated by using the relation \(^{26, 27}\)

\[
K = \frac{\alpha\lambda}{4\pi} \quad \text{(4)}
\]
Where $\lambda$ is the wavelength of the incident photon. Variation of extinction coefficient as a function of photon energy is shown in fig. (5), the extinction coefficient of prepared film has values in the range (0.033 - 0.155) for undoped, the range (0.0350 - 0.1869) for 1% Sn and the range (0.0757 – 0.2205) for 2% Sn. The rise and fall in the extinction coefficient are directly related to the absorption of light \textsuperscript{27, 28}. This leads to non-zero value of $k$ for photon energies smaller than the fundamental absorption edge.

(d) Reflectance

Fig. 5 Reflectance of undoped, 1% and 2% Sn: Cu$_2$O thin film

Fig. 5 Show the optical reflectance spectra for undoped and Sn: Cu$_2$O thin films. The reflectance has been found by using the relationship \textsuperscript{27}

$$R + T + A = 1 \ldots \ldots \ldots \ldots \ldots (5)$$

The figure also shows that the film reflectance increases rapidly at low energies and then decreases at photon energy less than the energy band gap.
(e) Refractive index

![Fig. 6 Refractive index of undoped, 1% and 2% Sn: Cu$_2$O thin film](image)

From the reflectance data, the refractive index (n) was calculated by using the following relationship

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad \text{(6)}$$

Fig. 6 shows the variation of refractive index with photon energy of various concentrations of Sn doped Cu$_2$O thin films. The refractive index increases rapidly at the low energies and decreases at the photon energy which is larger than energy gap because of the increasing direct electronic transition at those energies. The results show that the refractive index values of prepared films varies with small changes.

(f) Optical conductivity

![Fig. 7 Optical conductivity against photon energy for undoped, 1% and 2% Sn: Cu$_2$O thin film](image)

From the below relation we can calculate the optical conductivity $\sigma$:

$$\sigma = \frac{\alpha n c}{4\pi} \quad \text{(7)}$$
Where $c$ is the velocity of light. The optical conductivity versus photon energy curve is shown in figure (8).

(g) Energy gap

![Energy gap figure](image)

Fig. 8 Band gap energy for undoped, 1% and 2% Sn: Cu$_2$O thin film.

The nature of transition (direct or indirect) is determined by using the relation [30, 31]

$$\alpha h\nu = A (h\nu - E_g)^n \quad \text{......... (8)}$$

Where $h\nu$ is the photon energy, $E_g$ the band gap energy, $A$ and $n$ are constants. For allowed direct transition, $n = 1/2$ and for allowed indirect transition, $n = 3/2$. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ are shown in fig. (9), for undoped and Sn:Cu$_2$O thin films. The linear nature of the plot indicates the existence of direct transitions. The direct allowed energy gap could be determined which was found to be 2.1eV undoped to 1% and 2%Sn and 1.75eV. By increasing the concentration of the solution the band gap is slowly decreased. This result was good agreement with the results mentioned reference 32-35.

3.3 AFM

![AFM images](image)

Fig. 9 AFM 2D images of undoped, 1% and 2% Sn: Cu$_2$O thin film.

As in fig. 9 (a,b,c), the AFM images of 2D undoped and Sn doped Cu$_2$O thin films with different doping concentrations of 0%, 1% and 2% Sn are represented as a, b, and c. The deposited
films are found to be smooth and well packed with little grains. From the morphology of the films it is seen that there are little cracks with roughness is increased while the doping concentration of Sn increased, which indicates that the films thickness is increased. The grains are clearly visible for the film prepared with a solution concentration of 2% Sn.

### 3.4 Electrical Studies

**Table 3** Electrical properties of copper oxide thin films

<table>
<thead>
<tr>
<th>Sn Doping Concentration (%)</th>
<th>Resistivity ((\Omega \text{ cm}) \times 10^2)</th>
<th>Carrier Concentration ((\text{cm}^{-3}) \times 10^{16})</th>
<th>Hall Mobility (\text{cm}^2/\text{vs})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1000</td>
<td>1.08</td>
<td>7.14</td>
</tr>
<tr>
<td>1</td>
<td>455</td>
<td>55.5</td>
<td>9.26</td>
</tr>
<tr>
<td>2</td>
<td>65.23</td>
<td>91.4</td>
<td>12</td>
</tr>
</tbody>
</table>

![Fig. 10 Electrical resistivity (\(\rho\)), carrier concentration (\(n\)) and carrier mobility (\(\mu\)) of the copper oxide thin films](image)

Fig. 10 gives the electrical resistivity, carrier concentration, Hall mobility and for undoped and Sn: Cu\(_2\)O thin films which were measured by a Hall Effect measurement and the results are listed in Table 3. All the three sample shows p-type conductivity. Hall effect studies show a positive Hall constant at room temperature and all the samples can be considered p-type having carrier concentrations in the range around 1.08 x 10\(^{16}\) to 91.4 x 10\(^{16}\) \(\text{cm}^{-3}\). The carrier concentration increases with increasing precursor volume from undoped to 2% Sn. The resistivity decreased along with increase of Sn doping upto 2% which indicates the insufficient copper vacancies of copper oxide films. The resistivity values vary from 10 x 10\(^2\) to 65.23 (\(\Omega\) cm).

### 4. CONCLUSION

In this paper, the feasibility of fabricating the Tin doped Copper oxide thin film (at a constant temperature of 280°C using a simplified Nebulized spray pyrolysis technique, was investigated as it is useful in many applications particularly, in thin film solar cell application. The
effects of the substrate temperature on structural, optical and surface properties were studied and reported with suitable results. The response of the undoped, 1% and 2% Sn: Cu$_2$O thin films was studied and compared with earlier reports. The optical characterization shows a strong absorbance in the visible range with values of optical gap varied from 1.75 to 2.2 eV. The Hall Effect studies shows that increase in mobility, carrier concentration and conductivity of Copper oxide thin films for increasing doping concentration and it confirms that the grown films are P type conductivity in nature for all the film. Hence we conclude that Sn doped Cu$_2$O thin film deposited at 280°C seems to be suitable for efficient thin film for solar cell application.

ACKNOWLEDGEMENTS

The authors acknowledge the authorities of the Arul Anandar College, Karumathur – 625 514, Madurai District for their support and encouragement during the course of this work.

REFERENCES


