Influence of Zinc Doping on the Structural, Morphological, Optical and Electrical Properties of Copper Oxide Thin Films Prepared by Jet-Nebulizer Spray Pyrolysis Technique

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Abstract. This research details the deposition and characterization of adding zinc (Zn) impurities with different doping concentrations (1%, 3%, and 5%) into copper oxide (CuO:Zn) by using a jet nebulizer spray pyrolysis system. The impact of zinc doping on the different copper oxide properties was investigated. The structural studies confirm that pure copper oxide and zinc doped copper oxide thin films are matched with monoclinic structure. High resolution Schottky field emission scanning electron microscopy and Energy dispersive spectrum analysis identifies the surface structure and chemical composition of pure CuO and CuO:Zn thin films. EDS spectra reveal the occupancy of Cu, O, and Zn elements in the pure CuO and CuO:Zn thin films. The highest transmittance was observed as 66.91% for 5% Zn concentration. The absorption studies clearly indicated that the absorbance of the films was decreased when Zn doping concentration increase. The energy band gap value (Eg) is calculated as 2.01eV for pure CuO and the value of Eg for CuO:Zn thin films are varied from 2.07 to 2.26 eV. Keithley high resistance and low current electrometer was used to measure direct current conductivity of both pure CuO and CuO:Zn thin films and maximum conductivity value was observed for CuO:Zn (5%) thin film.

1. Introduction

Copper oxide consider as an important p-type semiconductor with narrow bandgap, categorized into nanostructures of metal oxide group. Monoclinic structured based CuO contains various characteristics such as chemical, physical and thermal properties [1]. It can be act as solar absorber due to its high solar absorption capability [2]. Furthermore, CuO involved in the fabrication of solar photovoltaic cells since it has suitable optical properties [3]. CuO provides favourable applications in the field of sensors, detectors, capacitors and energy based materials [3-8]. In recent years, influence of various metal oxides such as cadmium (Cd), nickel (Ni), manganese (Mn), zinc (Zn), cobalt (Co) etc., on the characteristics of CuO have been investigated by different researchers. Batuayr et al. investigated the impact of Ni doping with CuO and reported on the significant modification of optical and electrical properties of the CuO films [9]. Bayansal et al. examine that the CuO nanostrucres grain size was decreased with increasing Co doping concentration [10]. Rejith et at. reported that the energy band gap is decreased while doping with Cd in nanostructured CuO thin films [11]. Among different transition metals, CuO: Zn thin films have been reported very few. It can be a useful material for optoelectronic application.
Both physical and chemical deposition techniques were involved in the formation of CuO thin films such as pyrolysis deposition, oxidation process, sol-gel, jet nebulizer spray pyrolysis [12-19]. In present work pure CuO and CuO:Zn thin films were deposited via low cost jet-nebulizer spray pyrolysis system (JNSP). It is examined that pure CuO thin film deposited at the fixed temperature 450°C with 0.2M molar concentration have preferred properties. Similarly, CuO:Zn thin films are deposited with Zn concentration 1%, 3% and 5% at the same temperature. In this work the influence of adding Zn impurities with CuO has been studied using properties analysis. To the best of our knowledge CuO: Zn thin films had not yet been reported deposited using JNSP system.

2. Experimental procedures

2.1. Deposition of pure CuO and CuO:Zn

Jet- nebulizer spray pyrolysis system is very simple and cost effective. This system does not require sophisticated apparatus. It consists of only nebulizer with “L” shaped glass tube, hot furnace with temperature controller and compressor. Ultrasonic cleaned glasses were utilized as a base substrate to deposit pure CuO and CuO:Zn. Substrate cleaning is an important method in all kind of thin and thick film deposition. Initially, base glass substrates were soaked in the well blended double distilled water and nitric acid solution for 20 min. After 20 min, these substrates were taken from the solution and clean up with double distilled water. After primary cleaning method, ultrasonic bath cleaner in 30 min timer operation used to clean substrates with acetone solution. This ultrasonic bath cleaning method protects the glass surface from the damage caused by strong alkali and acid. Consequently, dust and alkali-free substrates were produced and taken from the ultrasonic bath. Finally, these substrates are preserved at room temperature.

Cupric nitrate trihydrate [Cu (NO₃)₂·3H₂O] taken as a starting material to produce pure CuO thin film. Zinc acetate dihydrate [(CH₃COO)₂Zn·2H₂O] taken as a dopant to provide CuO:Zn thin films. To prepare pure CuO, cupric nitrate was blended with double distilled water and magnetically stirred for 60min. similarly, cupric nitrate and zinc acetate were mixed well with double distilled water to prepare CuO:Zn. The quantity of cupric nitrate and zinc acetate were regulated in atomic weight percentage and 1%, 3%, and 5% of Zn concentration taken to deposit CuO:Zn thin films. Pure CuO and CuO:Zn precursor solution was sprayed onto ultrasonically cleaned glass substrate at a fixed temperature of 450°C with 0.2M mole concentration and 4ml volume of solution which was kept on a hot furnace. The hot furnace substrate temperature regulated and fixed at 450°C using a thermocouple. The nozzle of the glass tube attached with the jet nebulizer was fixed at a 5 cm distance from the glass substrate. The air compressor’s flow rate has been fixed at 2 bar. After sprayed, all deposited films were kept on the hot furnace plate for 5 min and then cooled naturally at ambient temperature.

2.2. Characterization approach

The crystal structural studies were examining using Shimadzu X-ray diffractometer (XRD) in the 2-theta range from 20° to 60°. XRD has been used to determine the crystalline phase and to study the structural properties. The surface structure and chemical composition were carried out by High-resolution Schottky Field Emission Scanning Electron Microscopy and Energy Dispersive Spectrum. The optical studies of the films were examined using an Ultraviolet (UV) -visible spectrophotometer (JASCO-570). Keithley high resistance and low current electrometer (6517-B) was used to measure direct current conductivity of both pure CuO and CuO: Zn thin films.

3. Result and analysis

3.1. Structural analysis

Figure 1 shows typical structural analysis of XRD patterns for pure CuO and CuO:Zn thin films with different Zn concentrations. The XRD profiles of all the films observed at 2-theta between 20 ° and 60°. The obtained XRD data of pure CuO thin film reveals that the film was a crystal in a monoclinic system (JCPDS No. 89-5899) [20]. The strongest peaks were observed with diffraction angle 2-theta and favorable orientation planes of 35.5° (-111), 38.7° (111), and 53.5° (020). Similar to pure CuO, XRD data for CuO: Zn thin films were also monoclinic crystal structures. Despite this, no
other peaks compatible with Zn elements is recognized by XRD data. The reason is XRD system might be challenging to find a small amount of Zn impurities that may present in the cluster form in CuO:Zn. Meantime, increasing doping concentration causes reduced peak intensity in diffraction angle of 53.5° and disappeared completely for the 5% CuO: Zn thin film. The structural analysis revealed that the peak intensity of all the films was decreased with increasing Zn doping concentration.

Figure 1. X-ray diffraction peaks of pure CuO and CuO:Zn thin films

The average crystallite size estimated from the following Debye-Scherrer’s equation with the help of full width half maximum (FWHM) value which strengthens the structural analysis [21]

\[ D = \frac{0.9\lambda}{\beta \cos(\theta)} \]  

Where \( \beta \) FWHM of the diffraction peak at diffraction angle \( \theta \), \( \lambda \) is the X-rays radiation wavelength, and \( D \) is the estimated average crystallite size. The following equations are used to calculate micro-strain (\( \varepsilon \)) and dislocation density (\( \delta \)) values [22] which is listed in the table 1.

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

\[ \alpha = \frac{1}{D^2} \]  

The comparison of average crystallite size and FWHM are also illustrated in the figure 2. The result shows that the average crystallite size is increased with increase of Zn impurities. Accordingly, adding Zn impurities into CuO shows an important role in the crystal size regulating process. The comparison of micro-strain variations and average crystallite size for pure CuO and CuO:Zn is illustrated in the figure 3. The average crystallite size is varied from 17 to 28 nm for pure CuO and CuO:Zn thin film which is listed in the table 1. The comparison plot clearly indicate that the strain values are degreased while increase in the average crystallite size. Similarly, dislocation density values are degreases with increase of Zn impurities.
Table 1. Variation of structural parameters of pure CuO and CuO:Zn thin films

| Thin films   | 2θ (degree) | FWHM (Degree) | Crystallite size (D) (nm) | Micro strain (Ԑ) | Dislocation density (δ) (×10^{15} lines m^{-2}) |
|--------------|-------------|---------------|--------------------------|------------------|-----------------------------------------------|
| Pure CuO     | 38.7131     | 0.4809        | 17                       | 0.0019           | 3.25719                                       |
| CuO: Zn (1%) | 38.7516     | 0.3942        | 21                       | 0.0016           | 2.18919                                       |
| CuO: Zn (3%) | 38.7583     | 0.3533        | 23                       | 0.0012           | 1.64718                                       |
| CuO: Zn (5%) | 38.8094     | 0.3188        | 28                       | 0.0010           | 1.38985                                       |

Figure 2. Comparison of crystallite size and FWHM for Pure CuO and Zn doped thin films

Figure 3. Comparison of crystallite size and micro strain for Pure CuO and Zn doped thin films

3.2 Surface morphological analysis

FESEM is a useful technique to determine the surface structure of thin films. The surface structure images of pure CuO and CuO:Zn thin films with various concentrations are shown in figure 4. Figure 4 (a) shows spherical shape morphology of pure CuO thin and Figure (b)-(d) exhibits the flower-like structure which confirm the presence of Zn impurities in the CuO:Zn [23]. The morphology of the figure (b)-(d) was observed as flower kind of structure. However, the density of the flowers is seen to change, significantly and the aggregation is spotted only for CuO: Zn (1%). Further, elementary composition analysis is carried out to examine the ‘Cu’, ‘O’ and ‘Zn’ in the synthesized materials using Energy Dispersive Spectra (EDS). CuO: Zn (5%) sample was examined to identify the
presence of chemical composition in the synthesized material. Figure 5 shows EDS spectra which reveal the occupancy of Cu, O, and Zn elements in the pure CuO and CuO:Zn thin films.

**Figure 4.** Surface structure images of (a) Pure (b) 1% (c) 3% and (d) 5% CuO: Zn

**Figure 5.** EDS spectra and data of elemental analysis for Zn doped CuO thin film
3.3. Optical analysis

The optical analysis of pure CuO and CuO:Zn thin films deposited by JN spray pyrolysis system were studied. The influence of adding Zn impurities on CuO were investigated. Figure 6 shows the optical transmittance studies exhibited the amount of energy transmitted by the material sprayed on the substrate. The pure CuO thin film exhibited an optical transparency of 49.83%. When increasing Zn doping concentration, the optical transmittance increases from 53.19% to 66.91. CuO: Zn thin films exhibit high transparency in the near-infrared (NIR) region. The maximum transparency is 66.91% for CuO:Zn 5%. As a result it is well know that adding Zn impurities were strongly influences on the optical properties of CuO thin films. The absorption spectra of pure CuO and CuO: Zn thin films deposited by JN spray pyrolysis as shown in figure 7. The spectra reveal that absorption of the entire films exhibit high ultra violet field. From the absorption spectral analysis, absorption capability of the films was reduced when increasing the percentage of Zn impurities. The energy bandgap of the pure CuO and CuO:Zn thin films were evaluated from the absorption values. As CuO is a direct band gap material, the absorption coefficient can be relevant to the energy bandgap (E_g) through Jan tauc’s relationship by using following formula [24]

\[ \alpha h\nu = \beta (h\nu - E_g)^n \]  

(4)

\[ \beta \] referred as energy-independent constant, \( h\nu \) referred as incident photon energy and \( n \) referred as constant that determines the type of optical transition. \( \alpha \) is the absorption coefficient which can be calculated using below formula [24]

\[ \alpha = \frac{2.303A}{t} \]  

(5)

Where \( A \) and \( t \) referred as absorbance value and thickness of the CuO films. The relationship between \( (\alpha h\nu)^2 \) and \( h\nu \) showed in the fig. The energy bandgap (E_g) value is estimated from the value of intercept of the straight line at \( \alpha = 0 \) by plotting \( (\alpha h\nu)^2 \) against \( h\nu \) [25]. According to Jan tauc plot energy band gap value is calculated 2.01eV for pure CuO and value of E_g for Zn: CuO thin films are varied from 2.07 to 2.26 eV. From the figure 8, it is seen that the value of E_g raising with the increase of Zn impurities.
3.4 Direct Current (DC) Electrical analysis

The direct current electrical conductivity for pure CuO and CuO:Zn thin films were evaluated using Keithley high resistance and low current electrometer under ambient temperature. Current Vs voltage (I-V) characteristics of pure CuO and CuO:Zn thin films exhibited in figure 7 (a). The current values were measured by varying applied DC voltages. From figure 7 (a), it is noted that an increase in applied voltage leads to a gradual increase in the current value. Similarly, an increase in Zn impurity percentage leads to an increase in the current value. The results show that CuO: Zn (5%) thin films have the highest current value. The DC conductivity for pure CuO and CuO:Zn thin films were determined using the below formula [26]

$$\sigma = \frac{V}{I} \times \frac{d}{A}$$

Where ‘V’ referred as applied voltage, ‘I’ referred as current, ‘d’ referred as distance and ‘A’ referred as cross sectional area of the film. Average conductivity of pure CuO and CuO: Zn thin films depicted in the figure 7 (b). The studies showed that the conductivity value is increased when increasing Zn doping concentration. CuO:Zn (5%) thin film shows the highest conductivity of $7.87 \times 10^{-10}$ Siemens per centimeter (S/cm). The results reveal that adding Zn impurities with CuO tends to increase the conductivity value.
4. Conclusion

In this paper, we reported on the deposition of pure CuO and CuO: Zn thin films with varied Zn impurities (1%, 3%, and 5%) via the JNSP system. The characteristic analysis of pure CuO and CuO: Zn thin films evaluated to study the impact of Zn incorporation with CuO. XRD results reveal that all the films are crystal in a monoclinic structure and agree with JCPDS No. 89-5899. From XRD results, no corresponding peak is observed related to Zn impurity and Zn-based oxide compounds at even CuO:Zn (5%). The intensity of the peaks gets reduced and crystallite size was increased when increasing the Zn doping concentration. FESEM results show spherical-shaped structure for pure CuO and flower-like structure for CuO: Zn thin films. It establishes the presence of Zn impurities in CuO:Zn thin films. EDS analysis certifies the presence of ‘Cu’, ‘O’, and ‘Zn’ elements in the CuO: Zn thin film. The pure CuO thin film exhibited optical transparency of 49.83%. When increasing Zn doping concentration, the optical transmittance increases from 53.19% to 66.91%. The highest transparency is 66.91% for 5% CuO:Zn. The absorption spectra indicate that the absorbance of the films was decreased when Zn doping concentration increase. In agreement with Jan tauc plot, the value of energy bandgap value is calculated at 2.01 eV for pure CuO, and the value of Eg for Zn: CuO thin films are varied from 2.07 to 2.26 eV. The DC electrical conductivity of pure CuO and CuO: Zn thin films were measured. It is observed that the current value is increased gradually with increasing applied voltage and the current value is increased when increasing the Zn doping concentration. CuO:Zn (5%) thin film shows the highest conductivity of 7.87 x 10^-10 Siemens per centimeter (S/cm). The results reveal that adding Zn impurities with CuO tends to increase the conductivity value. At last, we presume that adding Zn impurities assumed an imperative part in the modification of structural, optical, morphological, and electrical properties of CuO thin films.

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