Sol–Gel-Derived Cu-Doped ZnO Thin Films for Optoelectronic Applications

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ABSTRACT: Pristine and Cu-doped ZnO thin films were deposited on Si(100) and quartz substrates by the sol–gel method, followed by post annealing at 450 °C. Structural analysis shows that all grown films are polycrystalline in nature and the crystallite size of the doped film increases with the doping concentration. Narrowing of the band gap is seen with Cu doping, and electrical analysis shows an increase in the conductivity and carrier concentration with Cu doping. As compared to pristine ZnO, Cu-doped thin films show p-type conductivity with a maximum carrier concentration of $1.34 \times 10^{15}$ cm$^{-3}$ for 6% doping at room temperature. The p-type conductivity in these films easily degraded with time, which may be due to the interaction of films with ambient conditions or may be due to the diffusion of indium inside the material. After 15 days, ambient-exposed films were totally converted into n-type, whereas the vacuum-placed film still shows p-type behavior with good mobility. This study shows that sol–gel-derived Cu-doped thin films show low electrical resistivity, p-type conductivity, and high transmittance and can be used for optoelectronics devices if these films were well prepared, protected, and properly passivated.

1. INTRODUCTION

ZnO is a superior wide band gap semiconducting material for manufacturing optoelectronic devices. Although the optical band gap of ZnO is wide enough for fabricating window layer solar cells, liquid crystal displays, heat mirrors, and other optoelectronic device applications, there are some other devices such as high brightness white and UV LED, laser diodes, UV photodetector, and so forth which require much lower band gaps than that of ZnO. Furthermore, lower band gap materials are also required to realize the core-barrier layer, core-cladding layer, and quantum well structures in optoelectronic and photonic applications. The other major challenge faced by researchers is the non-availability of efficient p-type dopants for ZnO, which is considered as the vital building block for any quantum well-based optoelectronic device. The main hindrance in attaining p-type doping arises due to the amalgamation of the self-compensating effect with low solubility of the acceptors. Many researchers have reported p-type behavior in ZnO by using group-IA elements, which substitutes the O sites. Generally, the radius of group-IA elements is smaller than of Zn, so achieving p-type ZnO doping with the required hole mobility, conductivity, and carrier concentration is difficult. On the other hand, group V elements are also considered not suitable candidates as the basis of group V elements does not directly replace the O sites. Therefore, transition metal atoms can be used for p-type doping (p-ZnO) with good structural, optical, electronic, and electrical properties. Among all, Cu is one of the best p-type dopants whose ionic radii (Cu$^{2+}$ 0.73 Å) is nearly equal to the Zn$^{2+}$ (0.74 Å) ion. Cu also exhibits a similar electronic structure; this makes it a suitable candidate for doping ZnO, p-type. Cu-doped ZnO thin films are reported by many authors.

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in the literature. In all published reports, p-type behavior with good hole mobility is not significantly explained, so in the present work, Cu-doped ZnO is considered for the study to understand the behavior of Cu-doped ZnO in different doping concentrations.

2. METHODOLOGY OF THIN-FILM DEPOSITION

Among all growth techniques, we have selected the sol–gel technique which is an eco-friendly and comparatively cheaper technique. ZnO sol was prepared using zinc acetate dihydrate ([Zn(CH₃COO)₂·2H₂O, Alfa Aesar] as zinc source and copper(II) acetate using anhydrous copper source. For solvent and stabilizer, 2-methoxy ethanol [(CH₃OCH₂CH₂OH, Alfa Aesar) and ethanolamine (MEA) [H₂NCH₂CH₂OH, Alfa Aesar] were used. For pristine ZnO solution, 1.0973 gm of zinc acetate dihydrate was dissolved in 10 mL of 2-methoxy ethanol. For 3 at. % of Cu doping, 0.0272 g of copper(II) acetate dihydrate was dissolved in 10 mL of 2-methoxy ethanol. For 6 at. % of Cu doping in ZnO, 0.0562 g of copper(II) acetate anhydrous was dissolved in previously prepared pristine ZnO solutions. Then, the stabilizer is added to the prepared solution and the solution was stirred for 2 h continuously until transparent homogeneous solutions are obtained. Finally, Whatman’s filter papers were used to filter all the above solutions. All prepared sols were placed at room temperature for 24 h for aging.

Spin-coating was used for depositing thin films on Si(100) substrates. The solution was spin-coated on a glass substrate at 2500 rpm for 30 s; then, the film was dried in an environment maintained at 200 °C for 10 min to evaporate the solvent. The spinning, deposition, and curing processes were repeated 10 times to obtain the desired thickness. The samples were then annealed at 200°C for 24 h for aging.

Deposited thin films were characterized for structural, morphological, optical, and electrical properties to check the possibility of optical device fabrications. The thickness of the deposited films was measured by step surface profiler and found to be 210 nm, 197 nm, and 206 nm for pristine, 3, and 6 at. % samples, respectively. The structural and surface morphological properties were determined using field emission scanning electron microscopy (FESEM) (Zeiss Ultra-60) and X-ray diffraction (XRD) (Philips XPert Pro-diffractometer, respectively). The optical transmittance and band gap were determined using a UV–vis–NIR spectrophotometer (Agilent Technologies, Cary 5000), and electrical properties were studied by using two probe electrometers (Keithley 4200-SCS) at bias voltage between −5 and +5 V. p-type conductivity of the grown samples was studied by the hall effect measurement in four-point van der Pauw configuration using indium contacts.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis. The XRD graphs of pure and Cu-doped ZnO thin films are shown in Figure 1. All the grown films are polycrystalline in nature. The characteristic peak positions in data were identified by comparing with JCPDS card no 36-1451. All peak positions for undoped ZnO and doped ZnO samples were indexed with wurtzite hexagonal symmetry and labeled in the graph. No other peaks related to Cu compounds or other oxides are observed in the XRD pattern, which confirms that all of the doped Cu ions are fully inhabited inside the substitutional site of the ZnO wurtzite structure. No other impurity peaks or phases exist in the doped and undoped ZnO films.

3% Cu-doped ZnO films show a little smaller value of lattice parameters “a” in comparison to undoped ZnO, but for 6% Cu, “a” is larger than undoped ZnO, whereas the inter planer distance “d” decreases with Cu doping. Othman et al. also got a similar type of results in Cu-doped ZnO films. The diffraction peaks slightly shift toward higher 2θ with an increase in Cu doping. The valence state of the Cu ion plays a significant part in the variation of the lattice constant along the c-axis (002). The ionic radius of Cu⁺ (0.077 nm) ions is slightly greater than Zn²⁺ (0.074 nm) ions, and Cu²⁺ (0.073 nm) is slightly less than Zn²⁺. Therefore, the increase in 2θ diffraction peak confirms that the Cu²⁺ ion has been substituted into the congregation lattice at Zn²⁺ position, which also justifies the earlier report in literature by Joshi et al. The variation in crystallite size can be predicted by measuring the width of the (002) peak. With Cu doping, the crystallite size increases, predicting an increase in crystallinity with the increase in concentration. The calculated lattice constant and crystallite size are listed in Table 1.

3.2. Surface Morphological Analysis. The FE-SEM images of ZnO, 3% Cu-doped ZnO, and 6% Cu-doped ZnO are shown in Figure 2. SEM pictures of pristine ZnO shows a homogeneous surface with densely packed spherical and hexagonal nanoparticles. The grain size of Cu-doped ZnO increases with the doping concentration. The difference in crystallite size can be due to the difference in the crystal growth rate with Cu concentration. The surface roughness and inhomogeneity in the sample increase with doping and small voids start appearing probably due to a mismatch in the size of Zn and Cu. Due to Cu doping, the average particles size also increases.

3.3. UV–Visible Analysis. ZnO is a direct band gap semiconductor, and its band gap can be determined easily by measuring the direct transition between the conduction band and valance band. Figure 3 shows the optical transmittance of deposited samples measured at 300–800 nm wavelengths using a UV–visible spectrometer. All deposited films exhibit intense optical transmittance within the visible spectrum. For a
transparent conducting oxide material, high transmittance is an important property that can reveal the morphological homogeneity and crystalline quality of the deposited films for the optical applications.\(^{28}\) The optical transmittance in Cu-doped ZnO thin films is smaller than pristine ZnO, which may be due to the increase of absorbing and scattering centers with the incorporation of Cu\(^{2+}\) ions. The Cu 3d orbital is much shallower than the Zn 3d orbital, and when a Cu atom occupies a Zn site inside the ZnO lattice, it introduces two strong effects: first, the strong d–p interaction between Cu and O moves O 2p up, which narrows the direct fundamental energy gap, and second, the Cu 3d orbital creates impurity bands above the ZnO valance band. These impurity levels act as a strong absorption site in the UV–visible regime and are hence responsible for the decreases in transmittance in doped films.

All deposited films exhibit a single transmission slope and hence the optical transmission spectrum can be used to predict their band gaps by Tauc’s formulation. Figure 4 shows Tauc’s plot of undoped and doped thin films. The calculated band gap of all deposited films is listed in Table 1. The optical band gap for pristine films is around 3.14 eV and with the increase in doping concentration decreases the band gap (~3.07 eV). The reduction in band gap can be due to the increase in tensile stress (reducing in c/a ratio) with Cu doping. Rao et al. reported that tensile stress in films can cause a red shift in the band gap and compressive in blue shift band gap values of doped ZnO films.\(^{29}\) Furthermore, this variation of band gap values can be very much understood by the Burstein–Moss
The increasing Cu concentration decreases the free electron concentration and increases in holes concentration, and due to this, the Fermi level shifts toward a lower energy state and apparently decreases the band gap in Cu-doped ZnO films. The net shift in the optical band gap can be ascribed to the combined effect of the stress factor and BM shift.

3.4. Electrical Properties. Resistivity ($\rho$) of all deposited thin films were calculated using equation

$$\rho = \frac{RA}{L} \ \Omega \ \text{cm}$$

(1)

where $R$ is the resistance, $A$ is the cross-sectional area, and $L$ is the distance between probes. The room-temperature (RT) $I$–$V$ characteristics of Cu-doped and undoped ZnO thin films are shown in Figure 5. Subsequently, the resistivity of all deposited thin films is listed in Table 2. The RT resistivity of Cu-doped films only lasts for few days after the deposition, and when we repeated the measurement after 15 days, all Cu-doped films show a n-type behavior with high resistivity. This might be due to the diffusion of indium inside the material or due to degradation of films under ambient conditions. Microscopic analysis of the films suggests the degradation and evaporation of thins films from certain area of the sample. Furthermore, new Cu-doped thin film were deposited under the same condition, initially tested, and then placed under vacuum 15 days. Table 3 shows the day 1 and after 15 days hall effect measurement of the deposited sample. After 1 month, vacuum-placed Cu-doped sample still show p-type conductivity, and the carrier concentration falls by half time than the initial conditions, whereas samples under normal ambient show n-type behavior with higher mobility and carrier degradation. This confirms that sol–gel-derived Cu-doped thin films cannot stand for long-term usage under normal ambient conditions and these films must be properly protected and passivated before using in any applications.

4. CONCLUSIONS

Pristine and Cu-doped ZnO films were synthesized by the sol–gel method, followed by using the spin-coating technique and post-deposition annealing. XRD results show the polycrystalline nature of the deposited thin film, where the size of crystallite increases with the doping concentration. The increase in crystallite size is also confirmed by SEM analysis. The doped thin films exhibit narrowing in the band gap with a decrease in the transparency. The electrical analysis shows an increase in the conductivity and carrier concentration with Cu doping. Cu-doped thin films exhibit p-type conductivity at room temperature. Films with low electrical resistivity, p-type conductivity, and high transmittance are likely to present high optical and electrical quality and thus can be used for fabricating, TCO, window layers for the solar cells, p–n junction, photodetectors, solar cells, and LEDs. However, due to low stability, these Cu-doped thins films must be well

![Image of I–V measurement](https://doi.org/10.1021/acsomega.2c02040)
prepared, protected, and properly passivated before using in any of the above-mentioned applications.

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