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# Structural and optical characterization of Cu doped ZnO thin films deposited by RF magnetron sputtering

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Cu doped transparent ZnO thin films (CZO) were sputtered on soda lime glass substrates at three different distances between substrate and target. The effects of copper doping on the structural and optical properties were investigated by X-ray diffraction (XRD) and transmittance measurements. The XRD results indicated that CZO thin films have a preferential crystallographic orientation along the hexagonal wurtzite (002) axis. With increasing the distance between substrate-target, from 4 cm to 8 cm, the refractive index of the CZO films decreased. In the visible wavelength region, the average value of the transmittance was above 80%. Thus, significant changes in the structural and optical properties have occurred due to the decrease of the distance between the target-substrate and the residual compressive stress at the film-substrate interface arising during deposition.

K e y w o r d s: Cu doped ZnO, thin films, RF magnetron sputtering, XRD, optical properties

## 1 Introduction

The need for reliable energy, non-polluting and efficient technologies have led to new areas of applied electronics research. The scientific and technical methods developed so far have first created the need to manufacture electronic components that have characteristics associated with high performance. Thus, the use of multifunctional materials that can perform different tasks with a single component has become an extremely useful innovation in the energy field. Due to technological advances in the field of photovoltaic technology, thin film deposition technology has become more and more varied and precise. ZnO remains one of the most important (II-VI) semiconductors with large exciton binding energy ($E \sim 60$ meV) that is known for its many potential applications [1-8]. It has a wide and direct band gap ($E_g = 3.37$ eV) and good chemical and thermal stability. Furthermore, ZnO is cheaper, non-toxic and more abundant in nature, thus, having more advantages compared to ITO films (indium tin oxide). Due to the fact that it has chemical stability to hydrogen plasma processes, doped-ZnO thin films have various applications, such as solar cells [1], gas sensors [2-4], diodes [5], display devices [6], spintronics [7], photocatalytic activity [8] and so on. These dopants act as impurities in the ZnO structure. They can work as a donor for the metallic ZnO when it replaces an occupied $Zn^{2+}$ state or a state in between the zinc oxide composition structures, the donor offering the optical transparency. Among dopants, Cu element is of great interest in substituting into the ZnO lattice at $Zn^{2+}$ sites due to almost an equal ionic radius to $Zn^{2+}$ (0.74 Å) [9]. Also, the similar electronic shell structure between Cu and Zn is a further advantage to consider Cu as a good doping material option.

In this work, we present the structural and optical characterization of CZO thin films obtained by RF magnetron sputtering. This technique is often used to deposit thin films because it allows growth of uniform thin films at low temperature, strong adhesion to substrates over large area surfaces and good reproducibility [10,11].

## 2 Experimental details

To prepare the target, a total of 5 g of chemical compound was needed, from which 97% *wt* percentage of ZnO powder of 99.99% purity and 3% *wt* percentage of CuO powder of 99.98% purity was used. The two substances were homogenized by manual milling. Then, the mixed powders were pressed at 490 MPa and heat treated in ambient air at 930 °C for two hours to eliminate any residues. Following the solid phase reaction, the chemical composition of the target was $Cu_{0.03}Zn_{0.97}O$. The films were deposited on commercial soda lime glass substrates that were cleaned in an ultrasonic bath for 5 minutes in ethanol and water. The film deposition was performed on soda-lime glass substrates heated at a constant temperature of 150 °C, plasma power $P = 100$ W, deposition time $t = 90$ minutes, deposition pressure $p = 2.8 \times 10^{-2}$ mbar.

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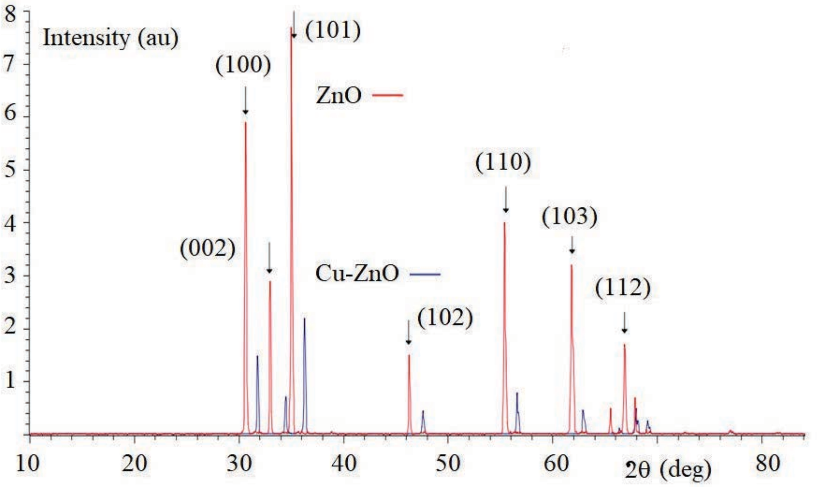


**Fig. 1.** XRD spectra of pristine ZnO and CZO targets

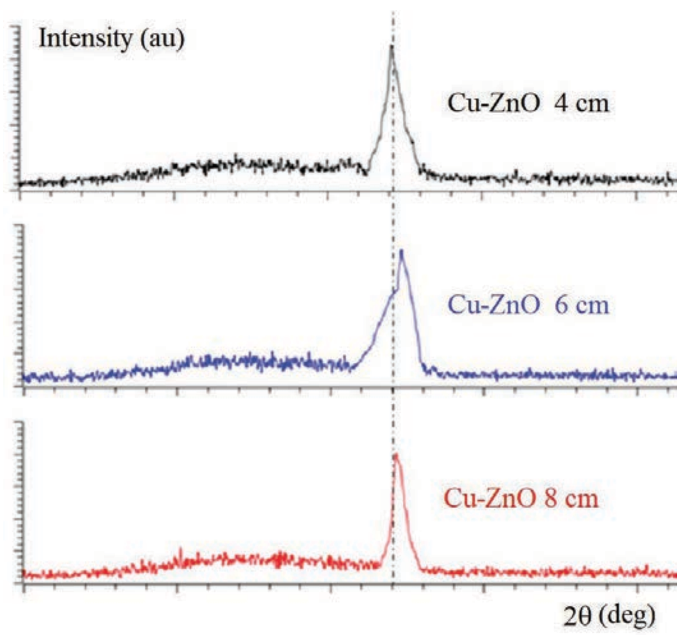


**Fig. 2.** XRD pattern of CZO thin films deposited at 4 cm, 6 cm and 8 cm

By modifying the distance between substrate-target for 4 cm, 6 cm and 8 cm, the films CZO4, CZO6 and CZO8 were obtained. For easier notation we will use these abbreviations each time we refer to one of the films as follows: CZO4 for 4 cm deposition distance, CZO6 for 6 cm deposition distance and CZO8 for 8 cm deposition distance. The crystal phases were identified by comparing the $2\theta$ values and intensities of reflections on X-ray diffractograms with JCP data base using the Diffraction AT-Brucker program. The diffractometer uses a Cu-Ka anode radiation in a Bragg-Brentano geometry configuration. Measurements were made using X-ray wavelength $\lambda = 1.506$ nm , in the range $10°– 90°$with a step of $0.05°$/second. From the transmission spectra, the optical constants were calculated using the program PARAV-V2.0 [12]. To evaluate the electro-optical characteristics we used an ellipsometer J. A. Wollam M2000V.

## 3 Results and discussions

### *3.1 Structural characterization*

*a) Target diffraction*

Figure 1 shows the difference in peak positions and intensities of pristine ZnO and Cu doped ZnO target. The shift of the maximum peak obtained for the CZO ceramic target is caused by the presence of Cu dopant that influences the crystalline lattice constants. The peaks obtained were used to determine the Miller indices (100), (002), (101), (102), (110), (103), (112), that are specific to the crystalline planes of ZnO material. The decrease in the peak intensities of CZO target is most likely caused by the interstitial location of copper atoms.

*b) Thin film diffraction*

The variation of the distance between substrate-target might influence the collisions between the spreading gas ions and the dislocated metal atoms in the target, thereby affecting their kinetic energy. The adhesion of the particles to the substrate depends on this size which affects the growth and orientation of the crystalline structure of thin films. Fig. 2 shows the XRD results of the RF sputtered thin films deposited at three different distances.

The maximum diffraction peak was around 34° value. This peak corresponds to the zinc oxide crystalline structure (002) Miller index that is specific for the hexagonal wurtzite structure. Furthermore, the absence of other peak intensities indicates a preferential orientation along the $c$-axis, perpendicular to the surface of the substrate.

The main peak (002) of the films CZO8 and CZO4 is symmetric. The (002) peak of CZO6 ($d = 6$ cm) film becomes asymmetric and is shifted towards the left side. This shift is associated with the decrease of the height of unit cell, c. The shoulder of the (002) peak of CZO6 film is in the same position as the peak of CZO8 film. This result suggest that in CZO6 film, the growth of crystal on the direction normal to substrate leads to two different values of the unit cell's height. The change in (002) peak of CZO6 film suggests that a moderate quantity of Cu atoms can exist at interstitial sites and confirms the structural modification of ZnO matrix. According to literature [13-16], similar results were obtained for Al doped ZnO films.

A consequence of the variation in the distance between the substrate and target may result in differences in intensity values due to the different number of interstitial localized Cu atoms. The change in the shape of the maximum peak could also mean that the presence of Cu dopant that influences lattice of the ZnO structures. Using the Scherrer equation as in references [17-19] we determined the average size of crystals. There was a small change in the grain size for the CZO films deposited at 6 cm and 8 cm (see Table 1). However, if we compare the film deposited at 4 cm with the other two films, there is a large difference in grain size. This difference shows that during the process of deposition the ejected atoms from the target do not have enough time to balance their kinetic energy when arriving on the substrate that is placed at 4 cm. While for the 8 cm distance between target-substrate, the atoms have enough time to balance their energy and rearrange on the substrate surface resulting the best crystallinity.

### 3.2 Optical characterization

Transmittance measurements for CZO thin films were performed in ambient atmosphere, as a function of wavelength in the range of 375 – 1000 nm. Results are illustrated in Fig. 3 and Fig. 4. By ellipsometry measurements we determined the optical band gap and the thickness of CZO thin films, while optical constants were determined from reflection. Fig. 3 emphasizes the difference of transmittance in ZnO thin films doped with 3% Cu. For the films deposited at $d = 4$ cm and 8 cm the transmittance value is around 78.8% in the visible range, while for CZO layer deposited at the distance of 6 cm we observe a higher transmittance, reaching a maximum of 90% for the visible range 535 – 586 nm.

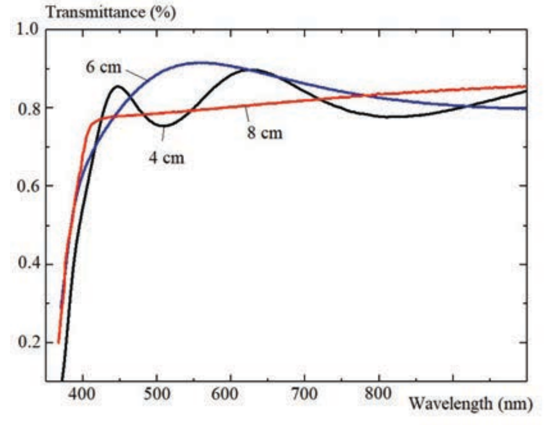


**Fig. 3.** Transmittance spectra of CZO thin films deposited at 4 cm, 6 cm and 8 cm

The variation in the distance between the substrate and target influenced the location of Cu atoms in the ZnO structure. We obtained an average transmittance of 78.7% for CZO film deposited at 4 cm, 85.2% for the film deposited at 6 cm and 80.6% for the one deposited 8 cm substrate-target distance. These values highlight a better transparency for the film deposited at 6 cm compared to the two others. However, because in the XRD spectra, the CZO6 film shows a shoulder and a visible shift in the (002) orientation results in a disordered crystalline structure that is not suitable for applications.

To determine the energy of the optical band gap we plotted the dependency of $(\alpha h\nu)^2$ upon the energy $hc/\lambda$ of the incident photons. Fig. 4 shows the Tauc linear fit representation in determining the optical band gap value.

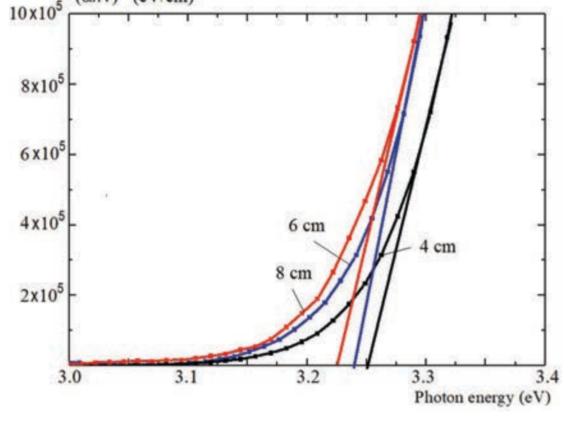


**Fig. 4.** Tauc plot graph of the optical band gap energy calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ versus $(hc/\lambda)$

**Table 1.** Optical band gap and refractive index of CZO thin films

| Sample | Distance $d$ (cm) | Optical band gap $\Delta E_g$ (eV) | Wavelength $\lambda$ (nm) | Refractive index $n$ (–) | Thickness $h$ (nm) | Grain size $D$ (nm) |
|---|---|---|---|---|---|---|
| CZO4 | 4 | 3.25 | 545 | 1.96 | 614 | 14.5 |
| CZO6 | 6 | 3.24 | 550 | 1.77 | 459 | 21.5 |
| CZO8 | 8 | 3.22 | 550 | 1.52 | 304 | 23.2 |

The band gap, $E_g$, was determined from transmittance data by using the Tauc formula [20]:

$$(\alpha h\nu)^2 = A^2(h\nu - E_g) \tag{1}$$

where $A$ is a proportionality constant that depends on the electron-hole mobility, $h$ is Plancks constant. According to references [21,22], constant $A$ represents the square root ratio between the linear part $(\alpha h\nu)^2$ over $(h\nu - E_g)$. By using the slope of the Tauc plot graph (Fig. 4), the value of constant $A$ can be approximated to $4 \times 10^3$ eV/cm$^2$ The optical absorption coefficient is defined as:

$$\alpha = \frac{1}{t}\ln\frac{(1-R)^2}{T} \tag{2}$$

where $t$ is the thickness of the thin films. The band gap $E_g$ was estimated by extrapolating the linear portion to the energy axis in the $(\alpha h\nu)^2$ vs. $h\nu$ graph (see Fig. 4). The change of value in the refractive index was determined using the program PARAV-V2.0. The same program was used to calculate the thickness of the deposited layers. The table below summarizes the calculated values for all three CZO thin films.

Table 1 shows the electro-optical characteristics of the obtained thin films. The thickness of the deposited layers decreases by increasing the distance between substrate-target. Also, this parameter influences other properties of CZO thin film however the distance between substrate-target has a weak influence upon the optical band gap energy. We can observe from spectroscopic measurements a decrease of the refractive index by increasing the distance between target and substrate (Table 1). These results suggest the existence of a minimum number of Cu atoms located interstitially in the deposited CZO layer deposited at 8 cm distance [23-26].

## 4 Conclusions

To entail, copper doped ZnO thin films were obtained by RF magnetron sputtering technique under the same deposition conditions. The variation in substrate-target distance and the 3% *wt* Cu-doping were chosen to improve the structural, optical and electrical properties of zinc oxide. To investigate the properties of the CZO films XRD and transmittance measurements were performed.

The XRD measurements indicated an epitaxial growth following the (002) perpendicular direction of the thin films and a variation of the crystallites size due to deposition at different target-substrate distances. The best crystallite size is obtained for $d = 8$ cm. The shoulder of the (002) peak present in the film obtained for $d = 6$ cm suggests that the growth of crystal on the direction normal to substrate leads to two different values of the unit cell's height.

The thickness of CZO thin films increases with decreasing the distance between target-substrate and, also, due to the variation in kinetic energy during deposition. All CZO thin films exhibited a transmittance above 80% in the visible range.

The distance target-substrate has a weak influence upon the optical band gap energy. The spectroscopic measurements suggest that in CZO layer deposited at 8 cm distance the number of Cu atoms located interstitially is minimal.

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