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# Microstructural and optical properties of Cu doped ZnO thin films prepared by magnetic spin coating

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**Abstract.** Undoped and Cu doped ZnO (ZnO:Cu) thin films have been prepared by magnetic spin coating technique. Magnetic spin coating technique is a novel thin film deposition technique in which a sol-gel solution is used and the substrate rotation is made magnetically. Influence of Cu doping on structural, morphological and optical properties of ZnO thin film was investigated. The crystallinity of ZnO thin films was found to be degraded by the Cu doping. Both crystallite size and surface morphology were affected by doping. The grain size values decreased with increase in doping concentration. It was observed a change in the optical band gap value with doping. This change has been realized as a decrease depending on the increase in doping. It was determined that structural and optical properties of ZnO films could be controlled by Cu doping.

## INTRODUCTION

Zinc oxide (ZnO) thin films, which have unique properties such as high optical permeability [1] and whose electrical properties can be enhanced by doping with different metal elements [2], are frequently used in technological applications such as photodetectors [3], spintronic devices [4], high photocatalytic performance materials [5-6], photovoltaic cells [7] and antimicrobial activities [8]. Copper (Cu) is an important luminescence activator in ZnO and by doping Cu element to ZnO, its electrical and optical properties can be improved [9].

As an alternative to costly and complex techniques used in ZnO thin film production, sol-gel magnetic spin coating technique was developed and more economical, simple and convenient Cu doped ZnO thin films was produced with sol-gel magnetic spin coating technique which is used for the first time in the literature. Undoped and 1%, 3%, 5% Cu doped ZnO thin films were produced and their structural, morphological and optical properties were examined.

## EXPERIMENTAL DETAILS

Undoped and Cu doped ZnO thin films were prepared by sol-gel method using magnetic spin coating technique onto glass substrates. 0.5 M zinc acetate dihydrate was used as a starting material. 2- methoxyethanol, monoethanolamine (MEA), copper acetate hydrate were used as a solvent, stabilizer and dopant source, respectively. The molar ratios of MEA to zinc acetate dihydrate and copper acetate hydrate were maintained at 1:1. The nominal molar ratio of the Cu/Zn was 0, 1, 3 and 5% and series named as shown in the Table 1.

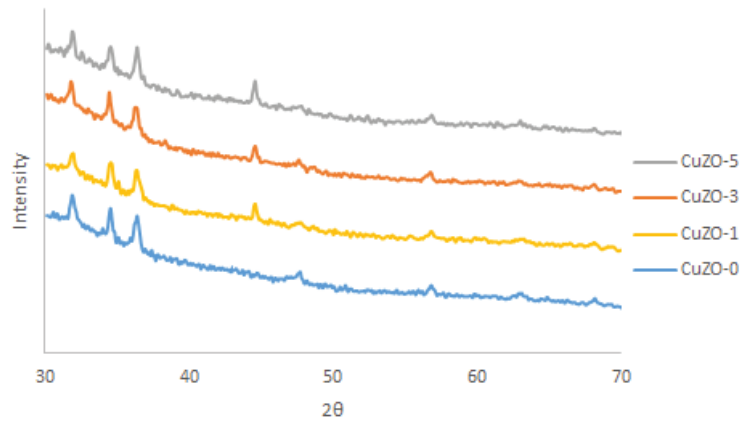
**TABLE 1:** Nomenclature of series.

Dopant ratio (%)	Series
0	CuZO-0
1	CuZO-1
3	CuZO-3
5	CuZO-5

The precursor sol was spin coated with a speed of 2000 rpm for 30 s onto the glass substrate. Then the films were dried at 150 °C for 10 min. This coating/drying procedure was repeated for 9 times. The films were finally annealed at 500 °C for 1 h in air for crystallization. Structural, morphological and optical characterizations of 3 series with 1%, 3% and 5% Cu doping were obtained by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and UV-Vis spectroscopy respectively, and the effects of doping were examined by comparing with the undoped ZnO series.

## RESULTS AND DISCUSSION

Panalytical Empyrean X-Ray Diffractometer was used to investigate the structural properties of the films. Obtained thin films were examined at  $30^{\circ} \leq 2\theta \leq 70^{\circ}$  limit values, using a  $\text{CuK}\alpha$  beam with a scanning speed of 2 degrees/minute and a wavelength of 1,5406 Å, at 45 kV voltage and 40 mA current. The structures found were compared with ICDD (International Centre for Diffraction Data): 98-003-1052 for ZnO in hexagonal structure and 98-009-6699 cards for  $\text{CuO}_2$  in monoclinic structure. XRD analysis spectra of undoped and Co doped ZnO thin films are shown in Fig. 1.

**FIGURE 1.** XRD spectra of CuZO thin films.

All series were observed to be polycrystalline in XRD spectra. In the undoped ZnO series films (CuZO-0), 5 peaks of the hexagonal ZnO structure are observed as (010), (002), (011), (012) and (110). With the increase of the doping amount, the peak belonging to monoclinic  $\text{CuO}_2$  structure (026) at  $44.57^{\circ}$  was observed in CuZO-1 series alongside the peaks belonging to ZnO series. In CuZO-3 and CuZO-5 series, by increasing the doping amount to 3% and 5%, the peak intensity of (026) monoclinic  $\text{CuO}_2$  peak was increased.

Morphological properties of thin films were investigated by using ZEISS Supra 40VP field emission scanning electron microscope (FESEM). FESEM images of undoped and Cu doped ZnO thin films with 100kx magnification were given in Figure 2. As seen on FESEM images, the surface characteristics of all samples are same, only the crystallite size are changing. The grain size values decreased with increase in doping concentration. In Fig. 3 elemental mapping images of CuZO films were shown. The yellow dots in the image represent the Copper (Cu) atoms. As seen from the images there are no dots in CuZO-0 series. With the increase of the doping concentration, Cu dots in the images were increased. This result prove that the doping procedure has been made successfully.

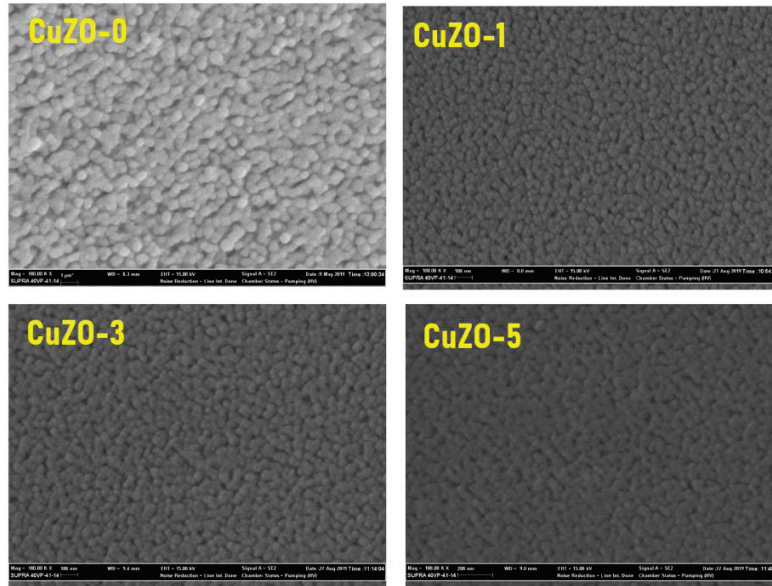


FIGURE 2. FESEM images of CuZO thin films.

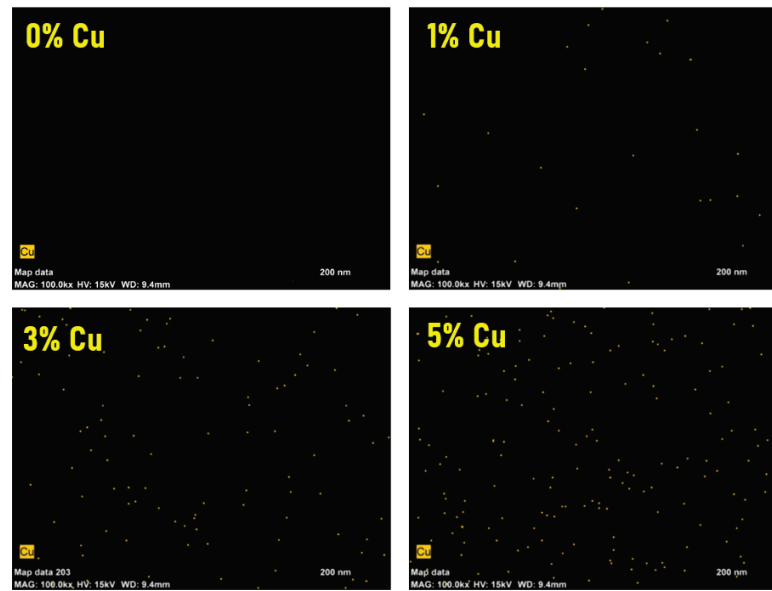


FIGURE 3. Elemental mapping images of CuZO thin films.

Absorption spectra of films obtained by Perkin Elmer Lambda 25 UV-Vis spectrophotometer in the wavelength range 300 - 1100 nm were examined. By using absorption spectrum data, the band gap values of the CuZO thin films were determined using the Tauc Method [10]. The band gap values of thin films are given in Table 2. As shown in the table, band gap values vary from 3.31 eV to 3.13 eV with Cu doping.

TABLE 2: Band gap values of CoZO thin films.

Series	Band Gap (eV)
CuZO-0	3.31
CuZO-1	3.28
CuZO-3	3.22
CuZO-5	3.13

## CONCLUSION

Undoped and Cu doped ZnO thin films have been deposited by magnetic spin coating method which was developed as an alternative to thin film production techniques and used for the first time in the literature. Influence of Cu doping on structural, morphological and optical properties of ZnO thin film was investigated. The microstructure of ZnO thin films was found to be degraded by the Cu doping. Both crystallite size and surface morphology were affected by doping. The grain size values decreased with increase in doping concentration. When the optical properties of Cu-doped ZnO thin films were examined, it was determined that the band gap values decreased with increasing amount of doping. These results are consistent with the characteristics of Cu doped ZnO thin films produced by different techniques in the literature. As a result of these investigations, with this technique, used for the first time in literature, Cu-doped ZnO thin films could be produced more easily and economically.

## ACKNOWLEDGMENTS

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