Study On The Doping Effect Of Cu-Doped ZnO Thin Films Deposited By Co-Sputering Technique

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Abstract. Cu-doped ZnO thin films with variation power at 0, 3, 5, and 10 W were prepared by DC/RF magnetron sputtering technique. The thin films have been deposited onto the soda lime glass (SLG) substrates at room temperature. The XRD peaks of the Cu-doped ZnO thin films identified as hexagonal wurtzite structure ZnO. The surface morphology of Cu doped ZnO thin films was investigated through a scanning electron microscope, which indicated the grain size slightly decreased by doping Cu. The transmittance significantly decreases accompanying increasing the Cu concentration. The optical band gaps Cu-doped ZnO thin film were estimated to be 3.30, 3.25, 2.87, and 2.31 eV when the powers of Cu target were 0, 3, 5, and 10 W respectively. The 15\% of the Cu content show the best data in our experiment.

1. Introduction
The development of thin oxide film research was undergoing a significant improvement, especially zinc oxide (ZnO) material. ZnO is a multi-functional material of the $n$-type II-VI group semiconductor with a direct wide band-gap of $\sim 3.3$ eV at room temperature and a free-exciton binding energy of 60 meV [1, 2]. High transparency, wide band-gap, abundance in nature and absence of toxicity attract people’s interesting in the last few years. ZnO is the promising material for the application of optoelectronic devices such as organic LEDs [7], solar cells [3-6], gas sensors [8-11], also it can be used as photocatalysts and antibacterial agents in biomedical applications [12, 13].

The morphological, structural, optical, electrical, and photodetector properties of the ZnO have been investigated, while the doping effect is still under exploration. The undoped ZnO thin films usually are not stable due to changes in the surface conductance under oxygen chemisorptions and adsorptions [14]. The doping strategy is an effective manner to tune the surface state, transport performance or carrier and energy level in the semiconductor. ZnO thin films are doped or alloyed with many elements such as Ag [15, 16], Al [1, 5, 7, 11, 17, 18], Co [19], Cr [20], Cu [21], Fe [22], Ga [23, 24], Li [25], Mg [26, 27], and Sn [14, 28, 29].
The metal group IB, such as silver and copper are considered as the fast-diffusing impurities in the semiconductor compound [21]. The doping of both metals into ZnO can affect its morphological, structural, optical, and electrical properties. The Cu doping has an advantage due to the cost cheaper than Ag. Cu-doped ZnO thin films can be prepared by any different methods like spray pyrolysis technique [21], radio frequency (RF) sputtering [30], chemical vapor deposition method [31], and co-precipitation method [32]. In this research, we report the Cu-doped ZnO thin films at different concentrations. We have used DC/RF magnetron sputtering to deposit the pure ZnO and Cu-doped ZnO thin films. We synthesized the Cu-doped ZnO thin films with atomic Cu alloy concentrations at the [Cu]/([Cu]+[Zn]) percentages of 0%, 15%, 30% and 40%. The variations of morphology, structure, optical and electrical properties were investigated in our study and defect mechanism was derived.

2. Experimental procedure
Copper-doped ZnO material was prepared in the form of the thin film by the co-sputtering method. Cu-doped ZnO thin films in this experiment were produced in a direct current (DC) magnetron sputtering for the copper metal target, and an RF magnetron sputtering for ZnO target. The metal target of Cu was operated with varying power at 0, 3, 5, and 10 W under DC sputtering, while the cermet ZnO target was proceed at 100 W under RF sputtering. The films have been deposited onto the soda lime glass (SLG) substrates at room temperature. The composition and growth morphology of films were characterized by field-emission scanning electron microscopy (FESEM, JSM 6500F, JEOL, Japan). We used the Energy dispersive spectrometer equipped on SEM for composition analysis. The X-ray diffractometry was used to analyze the crystal structure. We used the Ultraviolet-Visible (UV–vis) Spectrometer to measure the absorption spectra for thinned films which were deposited on glass substrates.

3. Result and Discussion
The surface morphologies of Cu-doped ZnO thin films at different concentration of Cu are shown in Fig. 1. The images were performed at 30,000 magnifications. From the observations of cross-sectional images (Fig 1.b), all Cu-doped thin films had a thickness of ~280 nm, and they adhered very well to the SLG substrates without any pores. As seen in Fig. 1, the grain size slightly decreases with increasing Cu content. The compositions of the Cu-doped ZnO with power at 3 W under DC sputtering for the Cu metal target were carried out by EDS analysis and elemental composition (%) of Zn, O and Cu elements in the films with was listed in Fig. 1e. The elemental composition of Cu were 0, 15, 30, and 40% when the powers of Cu metal target were 0, 3, 5, and 10 W, respectively.

Table 1. The lattice constants and volume of unit cells of Cu-doped ZnO thin films at different dopant concentration.

| Sample (Cu-doped ZnO) | 2θ (002) peak | a (Å) | c (Å) | Volume (Å³) |
|-----------------------|---------------|-------|-------|-------------|
| 0 at %                | 34.440        | 3.179 | 5.204 | 45.55       |
| 15 at %               | 34.287        | 3.240 | 5.228 | 47.53       |
| 30 at %               | 32.253        | 2.932 | 5.548 | 41.30       |
Fig. 2 shows XRD patterns related Cu-doped ZnO thin films with different dopant concentration. As observed from Fig. 2, the diffraction peaks of the Cu-doped ZnO thin films could be identified as hexagonal wurtzite structure ZnO, which can be indexed with JCPDS data file (80-0075) [33]. As the figures show, the XRD patterns shift to lower 2θ values, bigger d-spacing, with increasing Cu content due to the small ionic radii of Zn$^{2+}$ size (0.62 Å) replacing the bigger ionic radio of Cu$^+$ size (0.77 Å). Based on the higher peak (002) shift for Cu-doped ZnO, a subsequent calculation of the lattice parameter $a$ and $c$ can be made to study the defect behavior. Table 1 shows the variations of XRD-derived lattice parameters ($a$ and $c$) of ZnO thin films with varying concentration of Cu content. The lattice parameters were calculated according to the Bragg equation for the hexagonal structure ($a = b \neq c$) and the lattice spacing of (103) and (002) peaks were obtained with the help of Diffrac plus EVA software and

![Fig. 1 SEM surface images of Cu-doped thin films with various Cu doping: (a) pure ZnO, (b) ZnO:Cu 15%, (c) ZnO:Cu 30%, (d) ZnO:Cu 40%, and (e) elemental compositions conducted from EDS measurement for the ZnO:Cu 15%.

The transmittance spectra of Cu-doped ZnO thin films at different dopant concentration are shown in Fig. 3. The pure ZnO thin film exhibits up to 80% transmittance in the visible region. The transmittance of the Cu-doped ZnO found to decrease with the increasing of Cu concentration. The lattice defects increase with the increasing the number of Cu concentration on ZnO thin films. The replacing of Cu ion to the ZnO lattice site causes the increase in the absorption of light. The transmittance significantly decreases accompanying increasing the Cu

| 40 at %   | 31.796 | 2.912 | 5.624 | 41.30 |
concentration. The percentages of transmittance for doped thin films with Cu≥15% decreased and significantly dropped, which should be attributed to the presence of more defects due to Cu doping in ZnO thin film. The 15% of the Cu content show the best data in our experiment.

Fig. 2 XRD patterns of ZnO thin films with different dopant concentration.

Fig. 4 shows the $(\alpha h\nu)^2$ versus $h\nu$ plots of Cu-doped ZnO thin films with various Cu doping. The absorption coefficient ($\alpha$) was calculated according to the relation $\alpha(\lambda) = (1/d)\ln[(1-R(\lambda))/T(\lambda)]$, where $d$ is the thickness of the thin film, and $T(\lambda)$ and $R(\lambda)$ is the transmittance and reflectance, respectively [34]. The optical band gaps Cu-doped ZnO thin film were estimated to be 3.30, 3.25, 2.87, and 2.31 eV, when the powers of Cu target were 0, 3, 5, and 10 W respectively, by extrapolating the linear region of the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$).

Fig. 3 Optical transmittance of ZnO thin films with different dopant concentration.
Fig. 4 The optical band-gap of ZnO thin films with different dopant concentration.

4. Conclusion
Cu-doped ZnO semiconductor thin films were successfully prepared onto soda lime glass. The structural and optical of ZnO thin films were affected by Cu doping. The optimum concentration of Cu dopant is about 15 at.% in producing thin films containing the best in our experiment. The percentages of transmittance for doped thin films with Cu \( \geq 15\% \) decreased and significantly dropped, which should be attributed to the presence of more defects due to Cu doping in ZnO thin film.

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