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Investigation and comparison of electrical and optical properties of RF sputtered Cu doped ZnO and ZnO/Cu/ZnO multilayer films

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Abstract
This study presents the comparison of structural, electrical and optical properties of Cu doped ZnO films and ZnO/Cu/ZnO multilayer films before and after annealing, they are produced via radio frequency magnetron sputtering. the results showed that all films has a good crystalline properties after annealing, ZnO/Cu/ZnO multilayer films showed low resistivity of 1.8 × 10 $^{-3}$ Ω.cm and an average transmittance of 75%, these parameter values indicate that films are a potential candidate for high-quality electrodes in various displays.

Keywords: ZnO:Cu , multilayers, resistivity, transmittance, sputtering

1. Introduction

Zinc oxide (ZnO) as a semiconductor with a large direct gap (3.3 eV) and an hexagonal wurtzite structure is used in many applications especially on optoelectronic devices for example it's used as anode on organic light emitting diode (OLED)[1], also as a detector on gas sensor[2] and on flat panel devices [3], it's an abundant material on earth's crust, non-toxic and have a low cost. The electrical resistivity of ZnO has a wide range, extended from 10^{-4} to 10^{12} Ω.cm depending on the deposition methods, conditions [4-7] and doping [8-10]. ZnO thin films can be deposited using various technique such as sol-gel process [11], Pulsed laser deposition [12], spray pyrolysis [13] and RF magnetron sputtering [14-15].

Among the broad range of methods, sputtering technique offered much more advantages, it's perform high deposition rate [16], it is relatively a simple method with low cost, easy to deposited material on large scale glass substrates [17], during deposition, there are no toxic gas emission, good adhesion on variety of substrates [18]. Synthesizing via RF magnetron sputtering produces high quality ZnO films with good electrical and optical properties has much interesting one, well, ZnO is a degenerate n-type semiconductor which conductivity's can be enhanced by native donors (intrinsic doping) such as interstitial metal atoms or oxygen vacancies, or extrinsic doping by additional donor atom which increase carrier concentration. A number of dopant elements have been used to produce conducting ZnO films such as F, B, Al, Ga, Sn, Cu and Ag. Between these dopants, silver (Ag) has the lowest resistivity of all metals (about 1.59 × 10^{-8} Ωm at 20°C) [19]; despite it has a high cost. Copper (Cu) is an excellent conductor with 2 μ Ω.cm of resistivity, and the price is relatively low compared with Ag. Increasing carrier concentration may increase source of scattering which reducing the transparency in visible region, it's caused by a shift from absorbing infrared wavelengths to visible light. These two parameters affect and limit the doped ZnO resistivity, in addition, single layer doped ZnO shows limited chemical and thermal stabilities in various environments [20]. To solve this problems, one of many approach that has been proposed is the used of multilayer films structure (ZnO/Me/ZnO) by introducing a thin metal layer between two films of ZnO, these structures show very lower resistivity and high optical transmittance on visible region by suppressing reflection from the metal layer [21]. In this work, we deposited Cu doped ZnO films and

ZnO/Cu/ZnO multilayer films by RF magnetron sputtering using the same deposition conditions (power, deposition time, annealing temperature) to investigate and compare electrical and optical properties obtained for the different structures.

2. Experimental and procedure

The Cu doped ZnO single layer films and ZnO/Cu/ZnO multilayer films were deposited onto glass substrates with co-sputtering RF magnetron for Cu doped ZnO films and RF magnetron sputtering layer by layer deposition for the multilayer of ZnO/Cu/ZnO. Ceramic ZnO target (99.99% purity) and Cu target (99.99% purity) were used at room temperature. Before depositing films, the glass substrates (1.7×2.5 cm^2) were cleaned in an ultrasonic bath with acetone for 10 min, Ethanol for 5min, deionized water for 15 min and finally dried in a N_2 flux gas, the conditions operating were kept at low pressure less than 10^{-6} mbar inside the chamber before inserting the argon gas with a fixed flow rate of 20 sccm, and a working pressure of 0.5 Pa, the target was pre-sputtered for 15 min to clean its surface. The ZnO and Cu were deposited with RF powers of 200 w for 8 min and 10 w for 5 min respectively and annealed at 300°C for 1h, the thickness of the Cu doped ZnO was 150 nm and 158 nm for ZnO/Cu/ZnO multilayer films. The thickness of the single-layer films and multilayer films were determined with profilometer. The crystal structure of samples was determined with X-ray diffraction and the surface morphology was characterized with atomic force microscopy, AFM images have been scanned in contact mode over an area of 5 μm×5μm, and Gwyddion software was employed for surface roughness. Hall measurements were performed with the Van der Pauw method using a magnetic field of 1 T, the four-point-probe technique was used to measure the sheet resistances of the samples. The transmittance of the single-layer and multilayer films was measured with a Safas UV-Vis spectrophotometer using glass substrate as reference when measuring the optical transmittance of the films.

3. Results and discussion

The XRD patterns of Cu doped ZnO and ZnO/Cu/ZnO before and after annealing are presented on fig (1). All films exhibit strong (002) peak at 34,2 ° and its harmonic peak (004) at 71,5° indicating that the Cu-doped ZnO and ZnO/Cu/ZnO multilayer films were highly textured along the c-axis perpendicular to the substrate surface because It is easier to grow c-axis oriented ZnO films by sputtering technique and the surface free energy of (002) plane is the lowest in ZnO films. Also the films crystallize in hexagonal wurtzite phase [22]. In addition, no other crystalline phases such as Cu and CuO are detected on Cu doped ZnO, indicating that some Cu^{2+} ions substitute into the Zn^{2+} sites without any defects, for ZnO/Cu/ZnO multilayer films, XRD patterns show a small (111) peak of Cu. The intensity of (002) peak increases after annealing at 300°C which indicate an improvement in crystalline quality of films. In the other hand, the position of (002) peak shifts towards higher values of 2θ (Δ2θ=0.404 for Cu doped ZnO and Δ2θ=0.082 for ZnO/Cu/ZnO) after annealing, the shift of diffraction peaks towards higher diffraction angle is probably due to the cell contraction.

The average crystallite size (D) of single layer (Cu doped ZnO) and multilayer films of ZnO/Cu/ZnO before and after annealing was estimated from the most intense peak (002) using the Debye-Scherrer formula [23]:

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

Where λ is the wavelength of the X-ray (Cu kα = 0.15406 nm), β is the full width at half maximum (FWHM) of the peak measured in radians, and θ is the Bragg diffraction angle.

The average crystallite size of the films are shown in table (1)

Table 1: The average values of crystalline size and roughness surface of Cu-doped ZnO and ZnO/Cu/ZnO films as grown and after annealed at 300°c for 1h

	Cu doped ZnO		ZnO/Cu/ZnO	
	Before annealing	Annealed at 300°C	Before annealing	Annealed at 300°C
Crystallite size (nm)	20	25	19	20
Roughness (nm)	2.52	3.92	2.29	2.40

It's observed that the crystallite become larger after annealing, the large grains adsorb the small one because it has enough of thermal energy. The origin of this energy is the annealing process of samples at 300°C. [24], if the material is defective, heat treatments cause the recrystallization of distorted lattice in the bulk [25].

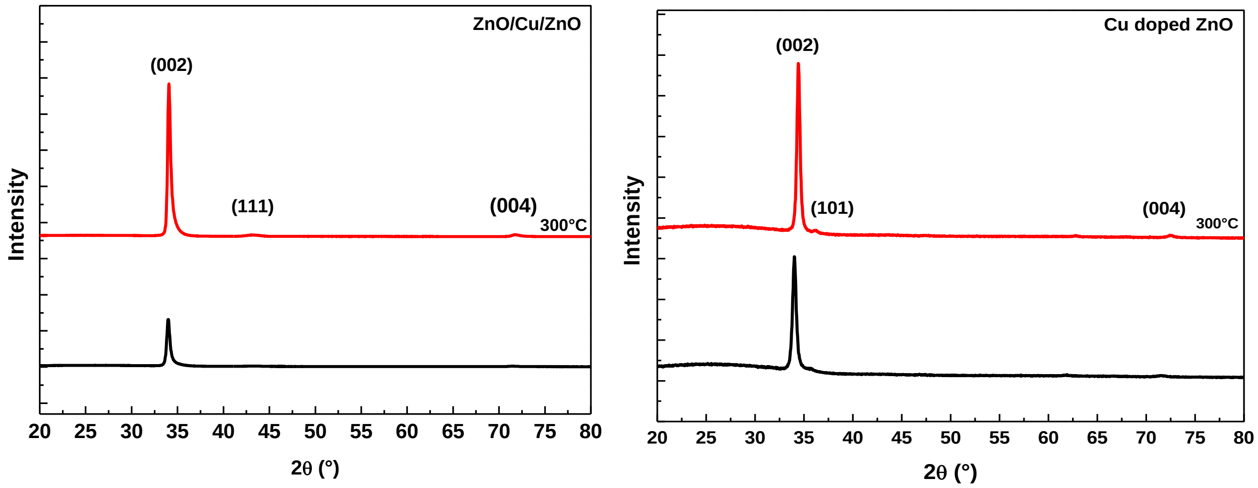
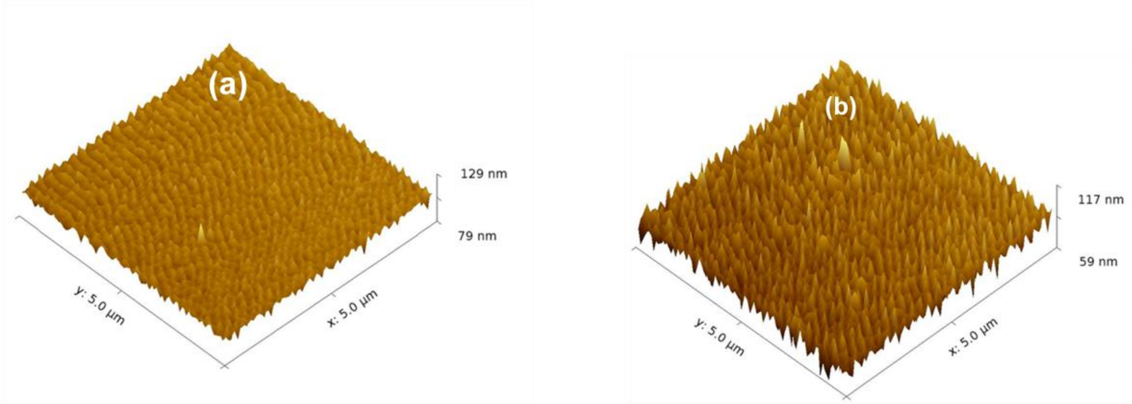


Figure 1. XRD patterns of the Cu doped ZnO and ZnO/Cu/ZnO multilayer films.

3.1. Morphological properties

Fig (2) shows the 3-dimensional image of the surface topography of Cu-doped ZnO and ZnO/Cu/ZnO multilayer films before and after annealing, the surface roughness of all films and multilayer films determined by the AFM software is tabulated in table (1). It's observed that the surface roughness of films increase after annealing. Hence, the as-grown films are much smoother than the films annealed at 300°C; this is attributed to the heat treatment which increase diffusion energy of the smaller crystallites [26], inducing coalescence of these smaller grains, enhances its growth, thus, resulting in increase in surface roughness of the films.



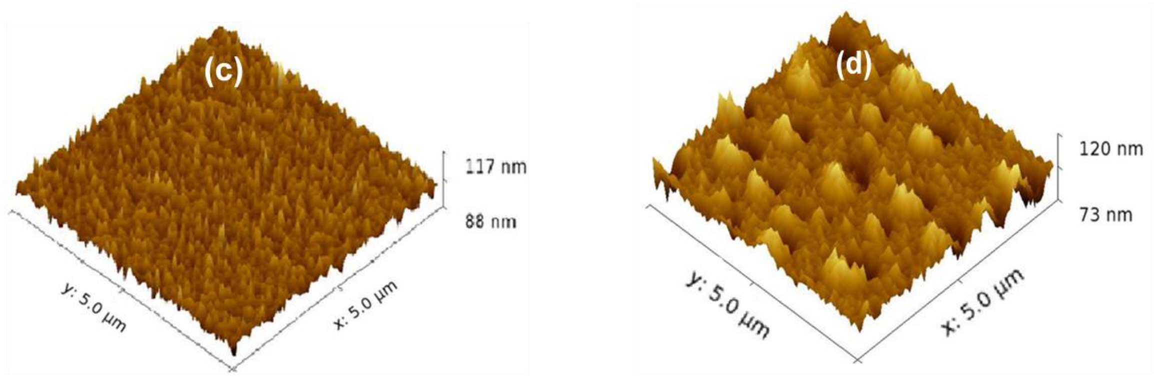


Figure 2. AFM images of Cu-doped ZnO films ((a) as grown, (b) annealed at 300°c) and ZnO/Cu/ZnO multilayer films ((c) as grown, (d) annealed at 300°c).

3.2. Electrical properties

Table (2) shows the resistivity, the carrier concentration and mobility of Cu-doped ZnO films and ZnO/Cu/ZnO multilayer films before and after annealing.

Compared to ZnO/Cu/ZnO multilayer film annealed at 300°C, the Cu doped ZnO annealed at 300°C showed high resistivity of 8.1×10^{-2} Ω.cm , due to the low carrier concentration and low mobility, the introduction of Cu thin layer between two layer of ZnO led to a reduction in resistivity by two order and increases of carrier concentration and mobility because the Cu layer could produce and inject directly electrons into both bottom and top ZnO layers.

Table 2 : Carrier concentration, mobility and resistivity of Cu-doped ZnO and ZnO/Cu/ZnO multilayer films as grown and after annealed at 300°c for 1h.

Films	Carrier concentration (cm^{-3})	Mobility ($cm^{2}.V^{-1}.s^{-1}$)	Resistivity (Ω.cm)
Cu-doped ZnO	1.049×10^{19}	0.232	2.5
Cu-doped ZnO (300°C)	2.910×10^{20}	2.01	8.1×10^{-2}
ZnO/Cu/ZnO	5.123×10^{19}	3.41	3.45×10^{-2}
ZnO/Cu/ZnO (300°C)	7.821×10^{20}	7.659	1.8×10^{-3}

3.3. Optical properties

The optical properties of Cu doped ZnO films and ZnO/Cu/ZnO multilayer films is also very important, The transmittance spectra as a function of wavelengths in visible range (300-800 nm) are shown in fig (3)

The Cu doped ZnO films show the lowest transmittance, the color of the films also dark brown.

In the other hand, ZnO/Cu/ZnO multilayer films have a transmittance of 70% on the visible range, after annealing at 300°C, transmittance increase to 75%. It's observed that the transmission of ZnO/Cu/ZnO in the visible region increase at short wavelength near the ultraviolet range for multilayer film annealed at 300°C.

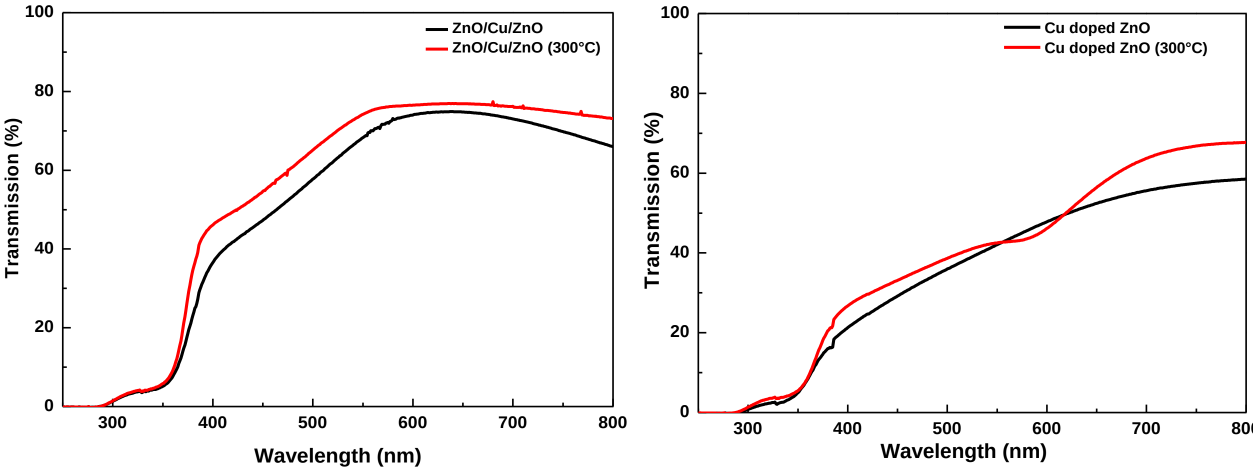


Figure 3. Optical transmittance spectra of Cu doped ZnO and ZnO/Cu/ZnO multilayer films

The band gap energy were evaluated using the derivative of the transmittance (T) with respect to energy (E) [27], our analysis shows that the estimated optical band-gap energies (Eg) of Cu doped ZnO films and ZnO/Cu/ZnO multilayer films dependent significantly on the annealing temperature, the Eg for the Cu doped ZnO before and after annealing at 300°C are 3.42 eV and 3.38 eV respectively, and for ZnO/Cu/ZnO multilayer films before and after annealing are 3.3 eV and 3.34 eV respectively, the Eg for the annealed multilayer films is wider than that of the as-deposited multilayer film. The augment of Eg can be explained by the Burstein-Moss effect [28], according to the discussion in electrical properties part, the resistivity of ZnO/Cu/ZnO annealed at 300°C has the largest carriers concentration, so, the occupied state in the valence band lead to a wider band gap. Concerning Cu-doped ZnO, the reduction of Eg after annealing at 300°C can be probably attributed to the donor level coming from the metal atoms segregation.

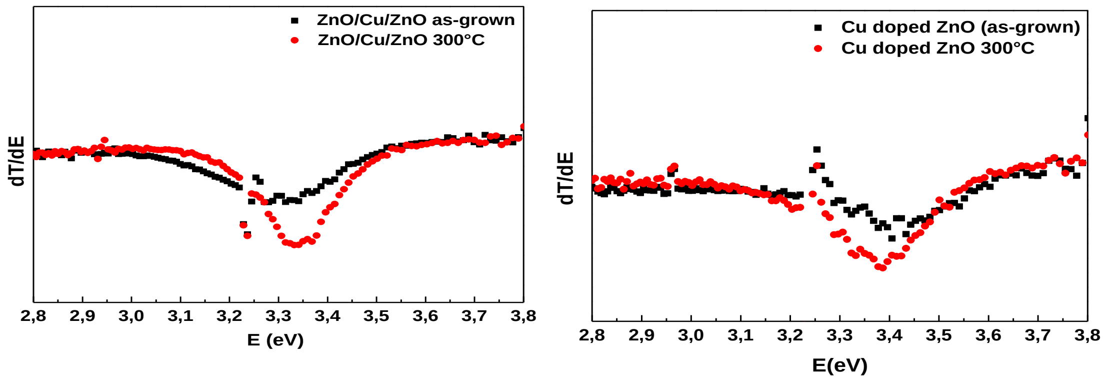


Figure 4 Plots of the derivative of transmittance with respect to energy of Cu doped ZnO and ZnO/Cu/ZnO multilayer films

4. Conclusion

Cu-doped ZnO and ZnO/Cu/ZnO multilayer films were deposited by magnetron sputtering at room temperature and annealed at 300°C for 1h, the structural, morphological, electrical and optical properties of all films and multilayer films with annealing temperature at 300°C were systematically investigated, the results indicate that the insertion of Cu interlayer between ZnO layer improve electrical properties than doped with Cu, after annealing at 300°C, conductivity and transparence of films become better, the very low resistivity of 1.8×10^{-3} Ω.cm and a transmittance of 78% were obtained for ZnO/Cu/ZnO annealed at 300°C which demonstrate that ZnO/Cu/ZnO multilayer films is an excellent candidate as a TCO electrode for optoelectronics applications.

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