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Improving the optical and electrical properties of Zinc Oxide thin film by Cupric Oxide dopant

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Abstract : *ZnO and ZnO/CuO nanocomposite were successfully synthesized by Sol-Gel technique. The crystal structure was investigated by X- ray diffraction technique and the molecular structure was studied by Fourier transformation infrared. Atomic force microscopy was used to study the topological properties of the prepared thin films. The optical properties were studied and the optical band gap were evaluated from the x-axis intercepts at $(\alpha h\upsilon)^2=0$ and found to be decreased from 3.27 to 3.26 eV as the dopant increased. ZnO and ZnO/CuO nanocomposite were used as interfacial layer on schottky diode. The technical parameters such as ideality factor and the barrier height were found to be increased from 3.7 to 6.5 and from 0.59 to 0.62 eV respectively as the dopant were increased.*
Keywords: *ZnO; CuO; Composite; optical Properties; Schottky diode;*

I. Introduction

Nanostructured metal-oxide semiconductor materials have been widely studied due to their electronic, optical, optoelectronic properties and potential applications in nanoscale devices. These materials offer many new opportunities to study fundamental surface processes in a controlled manner and this, in turn, leads to fabrication of new devices. Great interest has been shown in the preparation of nanomaterials, particularly oxides. Transparent conductive oxides (TCOs) such as Zinc Oxide (ZnO), Cadmium Oxide (CdO), Tin Oxide (SnO_2), Titanium Oxide (TiO_2), etc. those are both transparent in the visible region and electrically conducting [1].

ZnO is a II–VI group compound semiconductor with a hexagonal wurtzite crystal structure [2]. It has a wide and direct band gap of 3.37 eV at 300 K and a large free exciton binding energy of 60 meV [3]. It has unique physical and chemical properties [4], low-dimensional volume, high aspect ratio, light-matter interaction, cost-effectiveness and can be synthesized by various chemical and physical methods [5–11]. ZnO has become one of the most popular materials for electrical and optical applications over the time. It is promising material for many optoelectronic applications such as ultraviolet lasers, light-emitting diodes, p–n junction devices, thin-film transistor, solar cells, acoustic devices, chemical and biological sensors [12]. In order to obtain better crystallization quality and better optical and electrical properties, researchers have performed doping in metal oxides. Zinc is an important transition metal element and Zn^{2+} has close ionic radius parameter to that of Cu^{2+}, which means that Zn can easily penetrate into CuO crystal lattice or substitute Cu position in the crystal [13].

In this work, ZnO and CuO/ZnO nanocomposite thin films were fabricated by spin coating technique. The structural properties of the thin films were characterized using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy, the topological properties were studied by Atomic force microscope (AFM), the optical properties of the samples were studied and the optical band gap were estimated. Finally, schottky diodes were fabricated and the technical parameters were calculated.

II. Experimental Details

II.1. Synthesis Of The Samples

All reagents used in our experiments were of analytical grade and were used without further purification. Zinc acetate, 2-metoxyethanol, and diethanolamine, DEA, were used as starting material, solvent and stabilizer respectively. The dopant source of Cu was copper acetate dehydrate. The choice of acetate coming from the fact that hydrolysis of acetate group give products which are soluble in the solvent medium and get easily decomposed into volatile compounds under heat treatment [14]. In a typical synthesis, two different solutions of 0.5 M of zinc acetate and copper acetate was slowly dissolved in 2-metoxyethanol followed by addition of DEA. The molar ratio of DEA to zinc acetate and copper acetate was 1. The resulting mixture was stirred for 2 h at 60°C to yield a clear homogenous solution. 60 µl and 90 µl of CuO Sol-Gel were added to 3 ml of ZnO Sol-gel, respectively. These samples were stirred for 2 h at 60°C. The synthesized ZnO and CuO/ZnO nanocomposite were deposited on glass and p-Si/Al for optical and electrical studies, respectively, by using Spin Coating technique. The glass substrates were firstly cleaned by methanol and acetone baths for 10 min using an ultrasonic cleaner and then, the substrates were rinsed with deionized water and dried with nitrogen gas. The coating solution was dropped into a glass substrate, which was rotated at 1000 rpm for 20 s. After the spin coating, the film was dried at 80 °C for 10 min on a hot plate to evaporate the solvent and to remove organic residuals. This coating/drying procedure was repeated for five times and after this process, the obtained solid films were annealed in a furnace at 450°C for 1 h.

II.2. Photodiode Fabrication

Prior to fabrication of Schottky diodes, the substrate p-type silicon wafer of orientation (111), thickness 600 µm and resistivity 5-10 Ω·cm. the Si-wafer was chemically etched by the solution of hydrofluoric acid for 1 min and then rinsed in distilled water using an ultrasonic bath for 10-15 min. Aluminum was evaporated on the unpolished side of Si-wafer by thermal evaporation technique followed by a thermal treatment at 570ºC for 5 min in N_2 atmosphere for ohmic contact. The films were grown onto the front side of Si-wafer by spin coating with a rotation speed of 1000 rpm for 20 s. The previous process was followed by heating the samples at 150ºC for 10 min to evaporate the solvent and remove organic residuals. Before the final process was achieved the structure the incomplete devices were annealed at 450ºC for 1 h in electrical furnace [15]. Finally, the top contact was made by evaporating silver, Ag, using physical mask to have a contact area 3.14 cm^2.

II.3. Structure Techniques

The prepared samples were characterized by X-ray diffraction, XRD, using X-ray diffractometer model-Empyrean with CuKα radiation λ=1.54 Ǻ and generator settings 30 mA, 45KV. Fourier-transform infrared spectroscopy, FTIR, spectra of the samples were obtained using a Bruker, Vector 22 infrared spectrophotometer in the infrared spectral range 400-4000 cm^{-1}. The Surface topographical properties of the grown thin films after sintering at 450ºC were investigated using a PARK system XE-100E atomic force microscopy, AFM. The UV–Vis spectra of the films were recorded from 200 nm to 1000 nm wavelength using SHIMADZU UV-3600 UV–Vis–NIR spectrophotometer at room temperature. Under dark conditions, The (I-V) characteristics of the fabricated schottky diodes were investigated and measured by using 4200-keithley semiconductor characterization system.

III. Results And Discussion

III.1. Structural Characterization

Fig. 1 shows the XRD pattern of the thin films. All the peaks are indexed to the hexagonal wurtzite structure of ZnO which indicates that copper atoms replaced zinc atoms in the hexagonal lattice. The obtained data were found to be in agreement with the JCPDS Card No. 01089-0510. The pattern shows that the peaks have low intensities because the thicknesses of the films are quite thin. The grain size have been calculated from Scherrer's equation [16] and found to be increased by increasing the percentage of CuO dopant. Table 1 shows the calculated grain size and the lattice parameters for the samples. Fig. 2 shows FT-IR spectra of ZnO and ZnO/CuO nanocomposites. The peak at 472 cm^{-1} is the characteristic absorption peak of Zn–O bond [17]. The peak observed at 3451and 1041 cm^{-1} are may be due to O-H stretching and deformation, respectively assigned to the water adsorption on the metal surface [18]. The topological properties of the thin films have been studied by atomic force microscope (AFM). Fig. 3 shows the AFM images of the thin films at different magnifications.

III.2. Optical Characterization

UV–Vis absorption spectroscopy is a powerful technique to explore the optical properties of semiconducting nanomaterials [14]. Fig. 4 indicates the transmittance plot of ZnO and ZnO/CuO nanocomposites. The samples show high optical transparency ranging from 80 to 90 % approximately. As it is well known, the high transmittance of the deposited films mainly results from the low film thickness [19]. For a crystalline and amorphous semiconducting material, the analysis of optical absorption near the absorption band edge is a standard method for determining the types of transitions and calculation of the optical band gap. The energy dependence of the interband absorption coefficient for direct and indirect allowed transitions is given by the following expression [20]:

For allowed direct transitions

$$\alpha(h\upsilon)=A_{direct}(h\upsilon-E_{gd})^{1/2}, \quad (1)$$

For indirect allowed transitions

$$\alpha(h\upsilon)=A_{indirect}(h\upsilon-E_{gin})^{2}, \quad (2)$$

where E_{gd} and E_{gin} represent the band gap energy, A is a characteristic constant parameter, independent of photon energy, for direct and indirect transition, respectively. Fig. 5 shows the plots of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for

ZnO and ZnO/CuO nanocomposites thin films. The optical band gap energy for ZnO and ZnO/CuO nanocomposites thin films are evaluated from the x-axis intercepts at $(\alpha h\upsilon)^2=0$. The values of the corresponding energies were found to be 3.28, 3.275and 3.269 eV for ZnO, 60µl CuO/3 ml ZnO and 90µl CuO/3 ml ZnO, respectively.

III.3. I–V Characteristics Of The Fabricated Photodiodes

The electrical properties of Schottky diode junctions were analyzed by I–V measurements. Fig. 6 shows the semi–logarithmic I–V characteristic curve of the fabricated photodiodes. Fig. 6 indicates that the I–V characteristic of the samples shows rectifying behavior in dark. Such behavior can be analyzed by thermionic emission theory [21]. According to this model, the current through such diode could be expressed as [21, 22]:

$$I = I_0 \exp\left(\frac{q(v - IR_s)}{nKT}\right)[1 - \exp\left(\frac{q(v - IR_s)}{KT}\right)] , \quad (3)$$

where Io is the reverse saturation current, q is the electronic charge, V is the applied voltage, RS is the series resistance, n is the ideality factor, k is the Boltzmann constant and T is the Kelvin temperature. The ideality factor was determined from the slope of the linear region of forward bias ln(I)-V plot. The ideality factors of the fabricated Schottky diodes were found to be 3.7, 4.9 and 6.5 for ZnO, 60µl CuO/3 ml ZnO and 90µl CuO/3 ml ZnO, respectively. The higher value of the ideality factor shows the presence of inhomogeneities of Schottky barrier height and existence of interface states, and series resistance [23, 24]. The reverse saturation current (I0) is expressed by the following relation [22]:

$$I_0 = AA^* \exp\left(\frac{-q\varphi}{KT}\right) , \quad (4)$$

where A is the diode contact area, $A^*$is the effective Richardson constant (equal to 32 A/cm^2 K^2 for p-type silicon) and φ is the barrier height. The calculated barrier heights of the fabricated devices were found to be 0.59, 0.62 and 0.61 for ZnO, 60µl CuO/3 ml ZnO and 90µl CuO/3 ml ZnO, respectively.

IV. Figures And Tables

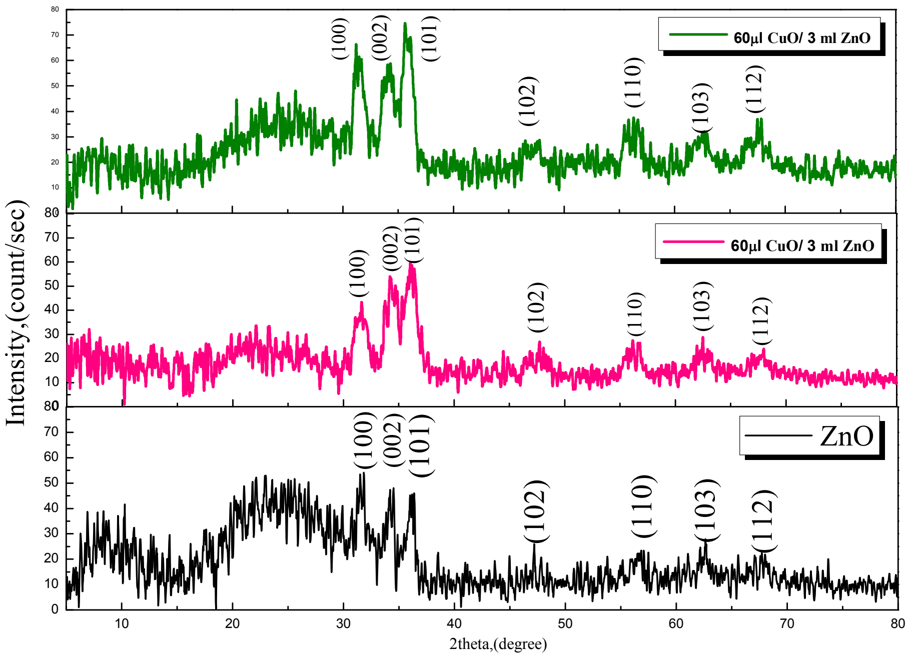

Fig.1 XRD pattern of ZnO and ZnO/CuO Nanocomposites.

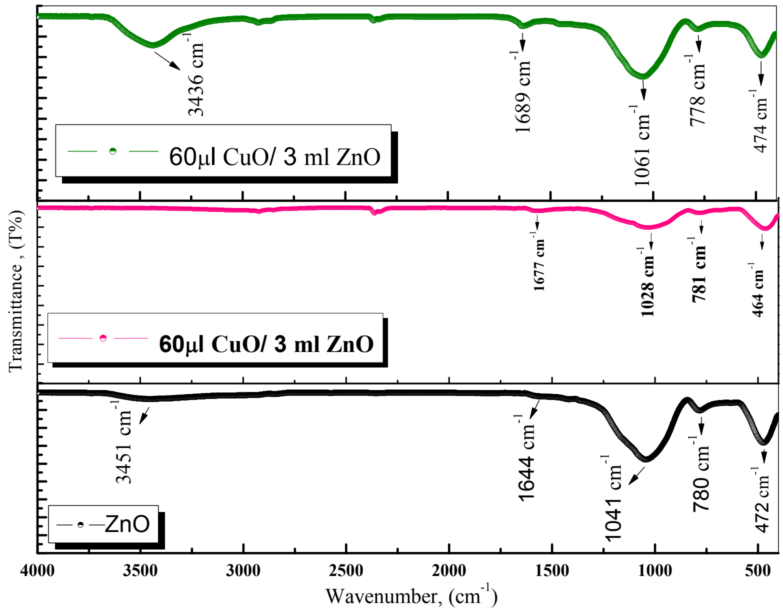

Fig.2 FT-IR spectra of ZnO and ZnO/CuO Nanocomposites.

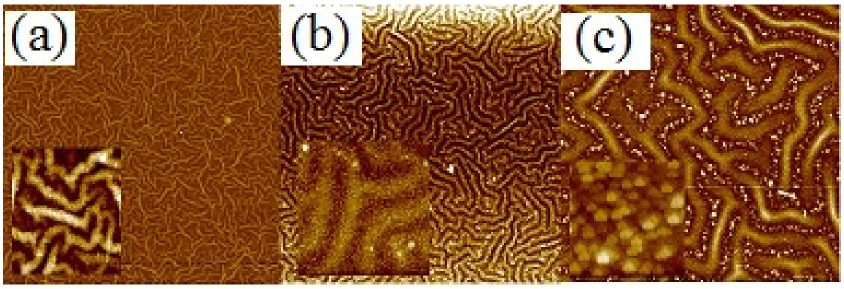

Fig. 3 AFM images at 40µm×40µm and 1µm×1µm (a) pure ZnO, (b) 60µl CuO/ 3ml ZnO and (c) 90µl CuO/ 3ml ZnO.

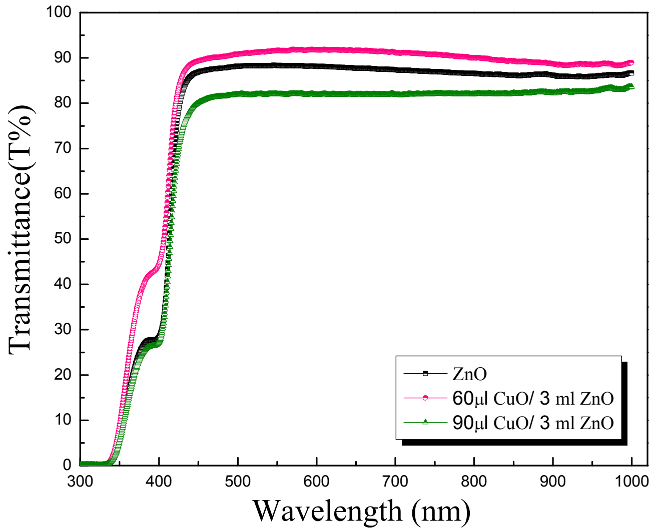

Fig. 4 Transmittance spectrum for ZnO and ZnO/CuO Nanocomposite thin films.

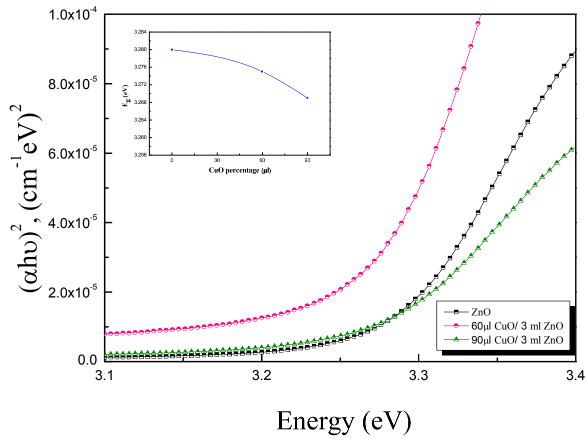

Fig. 5 The plots of $(\alpha h\upsilon)^2$ versus (hυ) for ZnO and ZnO/CuO Nanocomposites thin films.

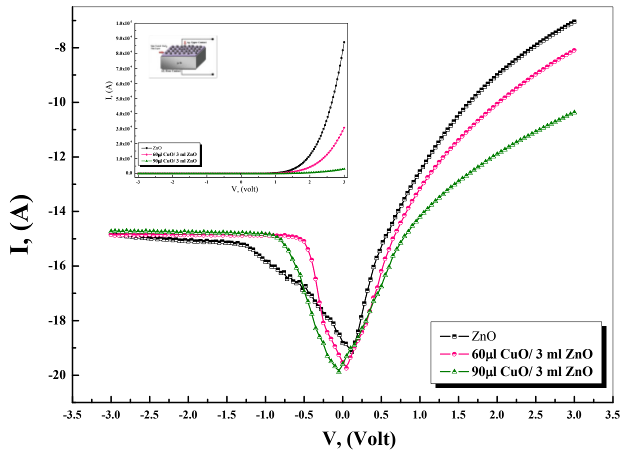

Fig. 6 I–V characteristic curve of the fabricated photodiodes.

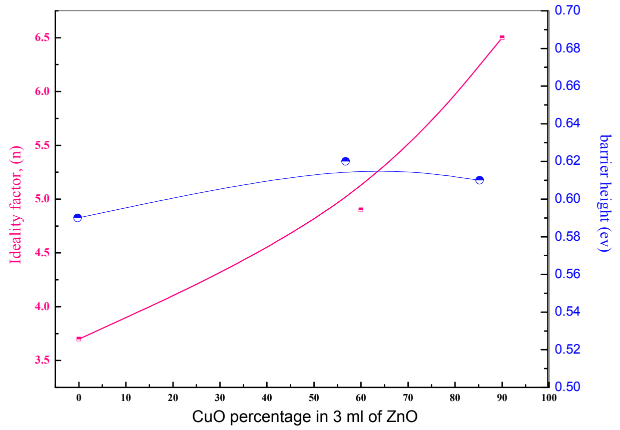

Fig. 7 The variation of ideality factor and barrier height

Table 1 variation of the grain size and lattice parameters with the percentage of CuO dopant

Nanocomposite	Grain Size [nm]	Lattice parameters	
		a[Å]	c[Å]
ZnO	10.62	3.24	5.19
30 µl CuO/ 3ml ZnO	13.48	3.25	5.24
60 µl CuO/ 3ml ZnO	15.34	3.31	5.26

V. Conclusion

ZnO and ZnO/CuO nanocomposites have been successfully synthesized by Sol-Gel technique. The crystal structure have been investigated by X-ray diffraction technique and it was found that all the peaks are indexed to the hexagonal wurtzite structure of ZnO which indicates that copper atoms replaced zinc atoms in the hexagonal lattice. FT-IR technique was used to investigate the molecular structure. The peak at 472 cm^{-1} is the characteristic absorption peak of Zn–O bond. The optical properties were studied ZnO and ZnO/CuO nanocomposites thin films. The energy band gap was estimated and found to be decreased as the CuO percentage was increased. ZnO and ZnO/CuO nanocomposites were used as interfacial layers for Schottky diodes. The technical parameters such as ideality factor and barrier height were calculated. The calculated barrier heights of the fabricated devices were found to be 0.59, 0.62 and 0.61 eV for ZnO, 60µl CuO/3 ml ZnO and 90µl CuO/3 ml ZnO, respectively. So, CuO modificate the barrier height of the fabricated schottky diode.

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