Effect of Annealing on Sensing Properties of ZnO: CuO Nanocomposite Thin Films by the Sol-gel Method

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Abstract

The zinc oxide (ZnO) - copper oxide (CuO) n-p junctions are a promising material for detecting ammonia gas. In this work, nanocomposite of ZnO: CuO thin films were deposited by using sol-gel spin coating method on a glass substrate. The search aimed to study the effect of annealing at 500°C on the physical properties and the effect of annealing on the sensing properties of the prepared films. The characterization of thin films before and after annealing treatment was studied by X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) for the morphology of the surface and grain size of particles also, UV-Visible analysis for optical properties. Sensing properties were also studied before and after annealing. The results showed the films were polycrystalline in nature with a monoclinic phase and the crystalline size was 5.4 nm and 9.9 nm before and after annealing. The results of SEM and AFM showed the surface uniformly and particle size was 25nm to 32 nm before and after annealing. The results of sensing properties for ammonia gas showed the sensitivity was enhancement after annealing treatment.

Key Words: Composite Films, Sol-gel Method, Optical Properties, Response and Sensitivity %, Sensing Properties.

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Introduction

The gas sensor is used for detection and effectively on harmful gases for human health such as CO_2, H_2S, NO_2, and NH_3. Metal oxides semiconductor (MOS) are the promising material to manufacture a gas sensor (Li et al., 2018; Moumen, Hartiti, Thevenin, & Siadat, 2017). MOS-based gas sensors are widely used because of it have a good characterization as like, a high sensitivity, low cost, fast response, small size, and long life (Peng et al., 2020). There are two main types of MOS such as P-type (the charge carrier is holes) and the n-type (the main charge carrier is electrons), For the purpose of producing gas sensors and very high efficiency, many semiconductors there are many nanostructures MOS such as SnO_2, ZnO, WO_3, CuO, Fe_2O_3 (Nadargi et al., 2020). Zinc oxide is an n-type semiconductor having band gap 3.37 eV consider one of important semiconductors used to producing gas sensors because has specifications such as easy and cheap manufacture, chemical stability, good reaction selectivity, thermal stability, and non-toxicity that make it a friend of environment (Bhati, Hojamberdiev, & Kumar, 2020). For the purpose of obtaining a distinctive properties of semiconductors materials are doped with other materials or metals to improve some of its mechanical and electrical properties (Sakib et al., 2019). Copper oxide (CuO) has a narrow and direct band gap and p-type semiconductor, so it is considered the most semiconductors used in the sensing applications.

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CuO has many properties suitable for many physical applications, such as catalytic activity, photoelectric, antibacterial activity, it is stable under exposure to various gases, and relatively low resistance. It is a less expensive materials compared to other semiconductors substances used in gas sensing applications (Rydosz, 2018). In this work, n-ZnO: p-CuO thin film was prepared by Sol-Gel spin coating technique for used as a gas sensor to detect ammonia (NH_3) and study the effect of annealing on the characterization and sensing properties of the obtained films.

Experimental Details

1. Materials

The materials used to obtain the thin films in this work were bought from a company Sigma-Aldrich Chemical Limited with a purity of 99.99. The material are zinc acetate hydride [$Zn(OOCCH_3)_2.2H_2O$] as starter materials, 2-methoxy ethanol (MOE: $CH_3OCH_2CH_2OH$) as a solvent, mono ethanol amine (MEA): $COCH_2CH_2NH_2$) as stabilizer material of solution, Copper(II) acetate monohydrate [$Cu(OOCCH_3)_2.H_2O$] as doping materials, 2-Propanol [$(CH_3)_2CHOH$ (IPA): C_3H_7OH] as cleaning materials, polyethylene glycol 400 [$H(OCH_2CH_2)_n$ OH (PEG) for viscosity of solution and non-ionized water (DI) for cleaning.

2. Synthesis Thin Films

ZnO solution was produced by mixing zinc acetate dihydride (2.6 g) with MOE (19.28 mL) and MEA (0.72 mL). These mixture solutions were stirred at 300 rpm for 60 minutes at 60°C. On the other hand, CuO solution was formed by mixing copper(II) monohydrate (0.99 g) with IPA (17.6 mL), 1 mL PEG, 1 mL MEA, these mixture solutions were stirred at 300 rpm for 90 minutes at room temperature. The two solutions were mixed with 0.6 M for ZnO solution and 0.25 M for CuO solution. The ratio mixture of the two solutions was a 1:1 volume ratio. The mixed solution was aged 24 hours (Sakib et al., 2019). The dimension of the substrate was (1.5 x 2.5) cm^2. The substrate was washed in individual measuring cups with IPA in an ultrasonic device and then cleaning with DI water and dried utilizing N2 gas. The technique of deposition was a spin-coating, using Covered with a standard spinner (Laurel Technologies Corporation), the outriggers spin at 3000 rpm for 30 seconds. Then the prepared samples were dried with 60^oC at oven for 15 minute. This process returned three times to get the required thickness. The obtained samples were examined using a light microscope to ensure that they were free of cracks and defect. The mask of the used in test of sensor is shown in the fig. (1).

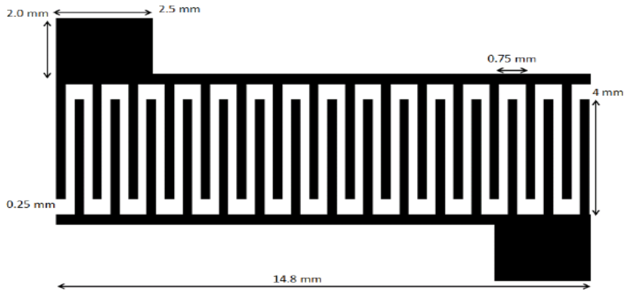

Figure 1. The mask design used for the configuration sensor film

The thickness of the thin films for all samples was 300 ± 10 nm. Thickness measurements were performed by the Mini-Test 3000 Microprocessor Coating Thickness, made in Germany. A schematic diagram of the system used for sensor checks is shown in Fig. (2). The sensor's supply voltage was 60 V and the ammonia gas concentration was 500 ppm. The sensor current was measured with a high-sensitivity galvanometer.

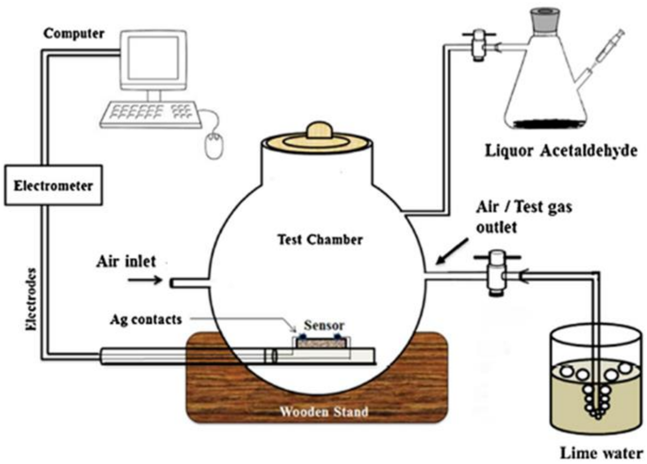

Figure 2. The system used to measure the gas sensing properties in this work

3. Characterization

For the purpose of studying the structural properties use a device is Shimadzu-6000, made in Japan. The target is copper, wavelengths λ = 1.5406 0A, current 300 A, voltage 40 Kv, angle range (10-80) degrees with velocity (5 days/min). Atomic force microscopy (AFM) (SPM Nitegra NT. MDT) made in Russia. JEOL JSM-67001 Scanning Electron Microscopy used to study the surface morphology and Sensor Characteristic done by Systems (Home-made) with 1500 W heater.

Results and Discussion

Fig. (3) showed the XRD diagrams of ZnO: CuO thin films before and after annealing. The diffraction peaks in the diagrams correspond to the values in (JCPDS 36-451) for ZnO and (JCPD 5.05-00661) for CuO. Fig. (3) showed that the film is polycrystalline structures and monoclinic phases before and after annealing. The site separation of the angels was visible confirming between ZnO and CuO. The ZnO diffraction peaks were shown in the plan (100, 002, 101, 102, 110, 103 and 201) and (201, 111, and 220) for CuO, which follow the angles 31.31°, 33.96°, 35.79°, 46.52°, 54.71°, 60.45° degrees and 66.14° for ZnO and 35.05°, 38.29° and 65.25° for CuO. The intensity of these peaks increases with annealing to 500°C. After annealing treatment, a strong trend is observed along (101) and (100). Other peaks, such as (002), (102), (110), (103), (201), (201), (111), and (220), were also observed, but their intensity is very small compared to (101) and (100) peaks. From this result, we can see that the amorphous phase decreases after the annealing. To determine the crystal size, Scherer's equation used (Ramanathan & Murali, 2017).

$$D = 0.9\,\lambda / \beta\cos\theta \qquad (1)$$

Where D: crystalline size nm, β: full-width rad and λ is the wavelength of x-ray and θ is Bragg angle. Dislocation density δ(lin/nm²) and stacking fault probability α (nm) also calculated by equations (Zur Loye, 2001).

$$\delta = \frac{1}{D^2} \qquad (2)$$

$$\alpha = \frac{2\pi D(2\theta)}{45\sqrt{3}tantan\,\theta} \qquad (3)$$

Table (1) summarizes the XRD data, we notice the crystal size increases from 3.1 nm before annealing to 6.7 nm after annealing, and the dislocation density decreases from 0.102 line/nm² to 0.022 line/nm², and the stacking error probability also decreases from 0.036 nm to 0.016 nm. We can conclude that annealing at 500 °C improved the structural properties, the dislocation intensity and stacking error probability decreased, and the crystal size also increased.

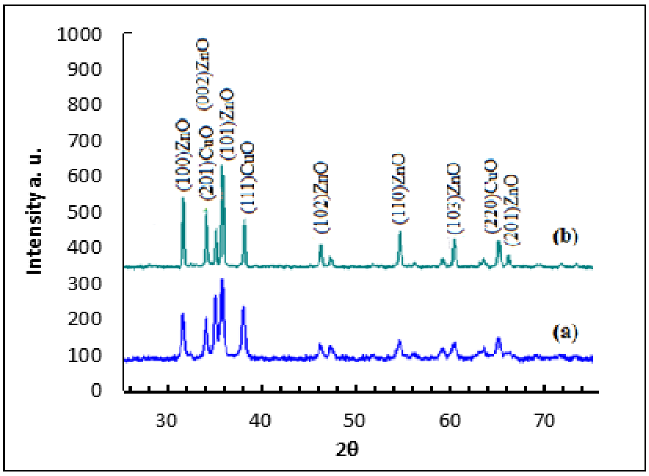

Figure 3. XRD diagrams of ZnO: CuO films, (a) before annealing and (b) after annealing

Table 1. The structural parameters of ZnO: CuO thin films before and after annealing treatment

Samples name	2θ	FWHM deg	D_{hkl} Exp.(°A)	hkl	D nm	δ (lin/nm)	α nm
Before annealing	31.31°	1.534	2.8546	100	5.4	0.0343	0.0241
	35.97°	2.673	2.4948	101	3.1	0.10227	0.03637
After annealing	31.28°	0.8360	1.646	100	9.9	0.0101	0.01318
	35.91°	1.2431	1.483	101	6.7	0.02212	0.01691

Fig. (4) showed the atomic force microscopy images of ZnO: CuO films with dimensions (2,3) before and after annealing. The surface of the films showed uniformly, and the grain size distribution decreased from 29.5 nm to 13.2 nm after annealing also the roughness and the RMS decreased from 2.328 nm, 2.883 nm to 0.619 nm, 0.864 nm, respectably. The reason is due to the positive effect of annealing treatment on the structural properties and also to remove the stress of the surface, which is agree with the results of the researcher (Haque & Ranjan, 2014).

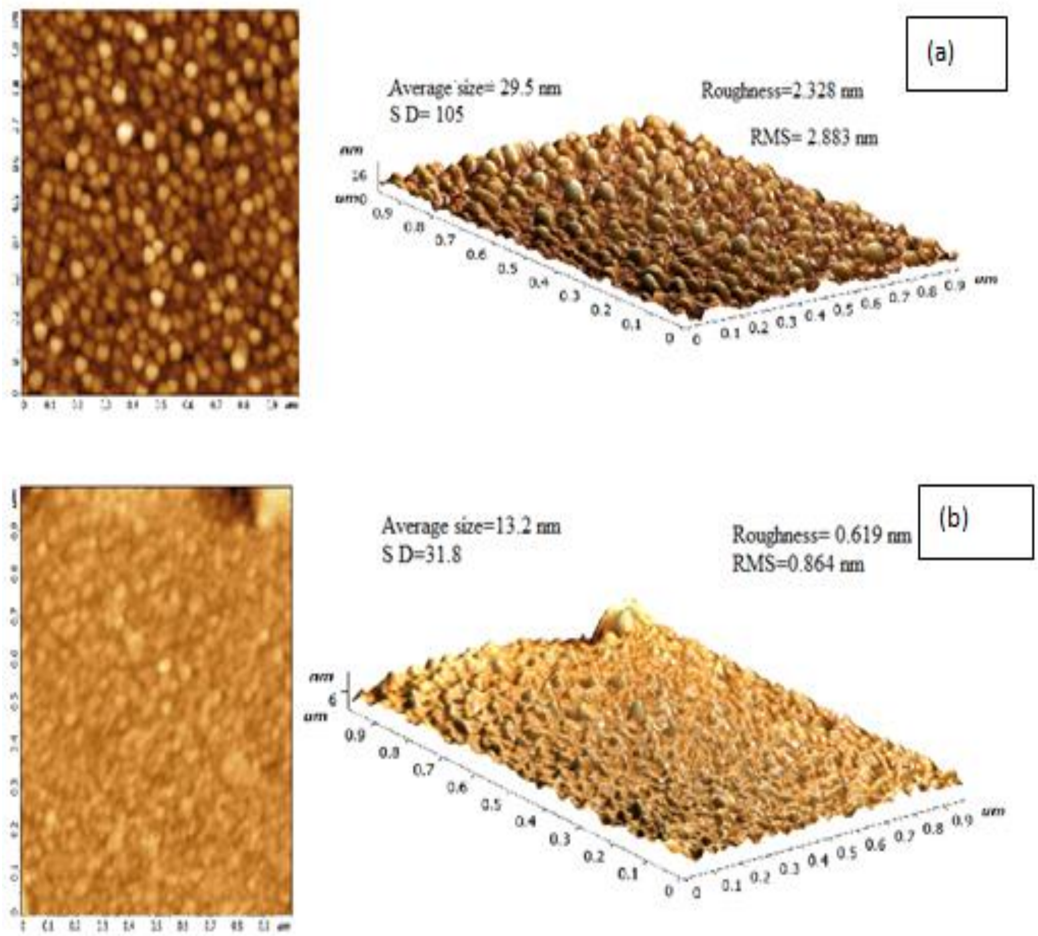

Figure 4. AFM images of ZnO: CuO films, (a) before annealing, (b) after annealing

Fig. (5) showed the scanning electron microscopy images of ZnO: CuO films before and after annealing. The formation of the different particle shapes and particles distributions of the ZnO: CuO films were confirmed. From the results, we can see that the surface changes and is affected by annealing, where the average particle size was 25 nm before annealing, after annealing it becomes 32 nm and becomes quieter, the increase in grain size is due to heat treatment (Sakib et al., 2019).

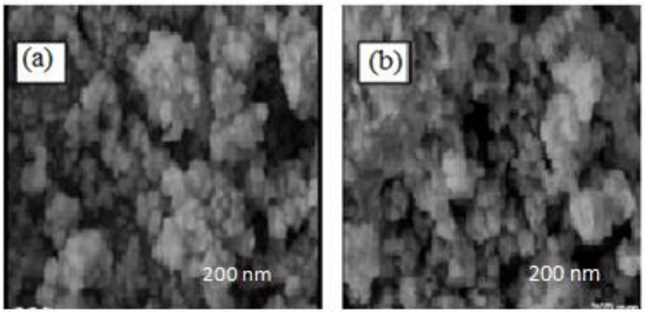

Figure 5. SEM images of ZnO: CuO films, (a) before annealing, (b) after annealing

The spectra of absorption for ZnO: CuO films deposited on a glass substrate before and after annealing were studied. Fig. (6) showed the absorption spectra (A) with wavelength (λ) on the range 200-1100 nm. After annealing the absorption increased slightly. This is probably due to the increase in crystal size and the decrease in the number of defects. Also the absorption edge turns red from the treated film. This shift indicates a decrease in the optical energy gap, where the energy gap was calculated using the following relationship (Haque & Ranjan, 2014).

$$\alpha = A\,(h\nu - E_g)^{n}/h\nu \qquad (4)$$

Where A and n are constants, n = 1/2 for direct band gap semiconductors and α, hυ absorption coefficient, energy of incident photon, respectively. The estimated energy gaps of $(\alpha h\nu)^2$ versus hυ cut-offs are shown in Fig. (7) of ZnO: CuO films. Fig. (7) showed the linear nature indicates a direct transition and the energy gap of the prepared films was determined by extrapolating the straight part of the energy axis at α = 0. The results showed that the value of the energy gap was 3.28 eV before annealing and becomes 2.95 eV after annealing. The decrease in the energy gap after annealing leads to a strong "redshift" in the absorption spectra (Moumen et al., 2017). It is known that while the lattice parameters and grain size are increased, the optical energy gap is decreasing (Moumen et al., 2017). Also, blue/red shift' has been suggest in energy gap values of films have a smaller thickness and crystal sizes.

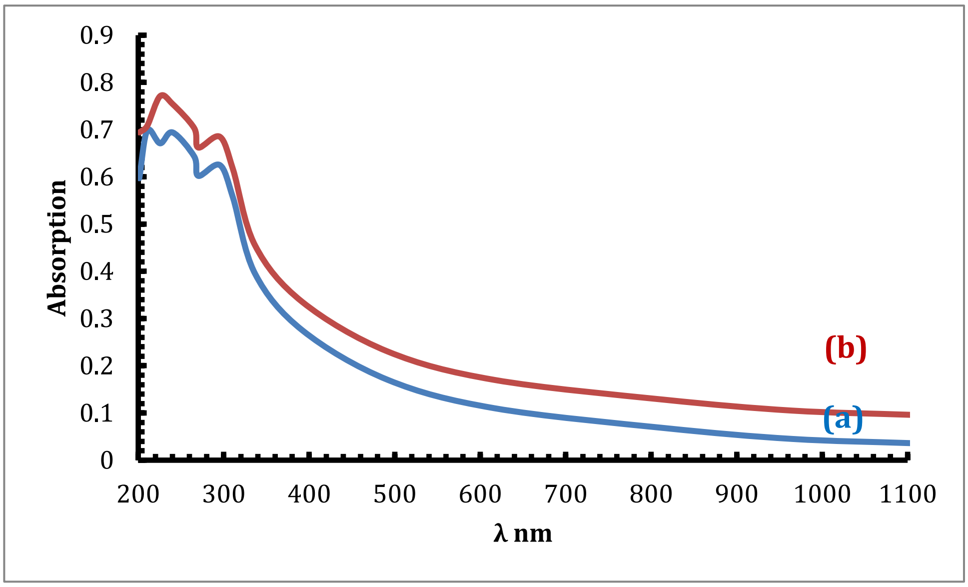

Figure 6. Absorbance spectra of ZnO: CuO films, (a) before annealing, (b) after annealing

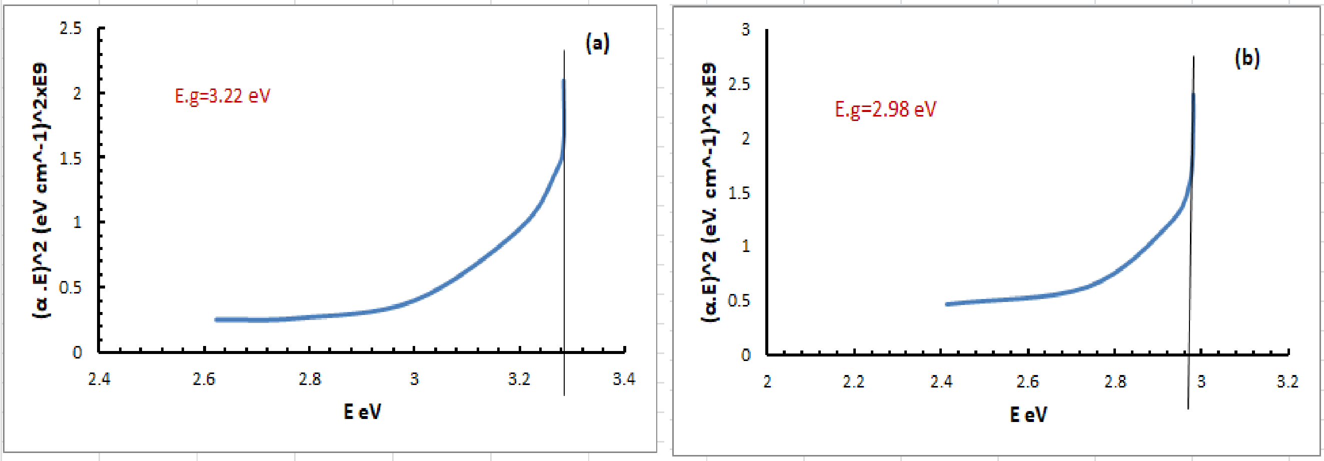

Figure 7. Plots of $(\alpha h\nu)^2$ versus photon energy of ZnO: CuO films, (a) before annealing, (b) after annealing

Fig. (8) showed the change of sensor resistance over time after exposure to NH_3 gas at room temperature of the ZnO: CuO films before and after annealing. Fig. (8) Indicated that the resistance of the films is affected by the presence of gas before and after annealing treatment, whereas the resistance of films increased with the increasing in the exposure time to the gas. The reason for an increase in resistance of films can be return to the ammonia gas reduced for oxygen atoms from the surface of the films because it is a reduce gas. The sensitivity % is shown in the fig. (9). The sensitivity % is measured by equation (2) (Mani & Rayappan, 2013):

$$S\% = \frac{Ra-Rg}{Ra} x100\% \quad (5)$$

Where Ra, Rg: the resistance of the thin films before and after exposure to the gas, respectively. The response time and recovery time of the sensor before exposure to NH_3 gas at 500 ppm concentration was 36-56 s and after exposure to NH_3 gas was 42-41 s, respectively. See Table (2). It's a clear the annealing effect on the sensitivity % where the sensitivity increased from 63.28604% to 68.27853 % after annealing.

Table 2. The sensing characterize of ZnO: CuO gas sensors of NH_3 gas

State of sample	Response time (s)	Recover time (s)	Sensitivity %
Before annealing	36	56	63.28604
After annealing	42	41	68.27853

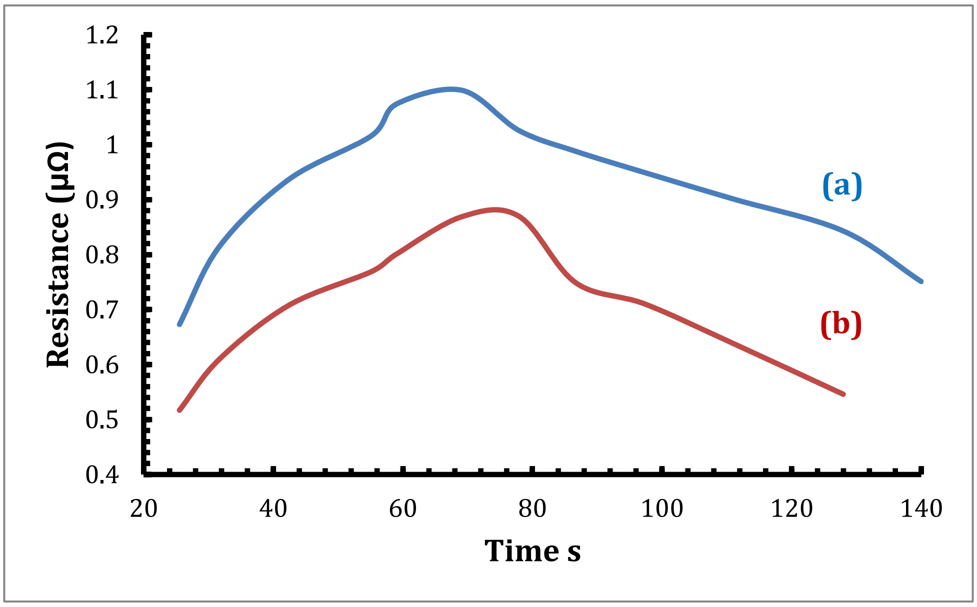

Figure 8. The resistance of ZnO: CuO films for NH_3 gas, (a) before annealing, (b) after annealing

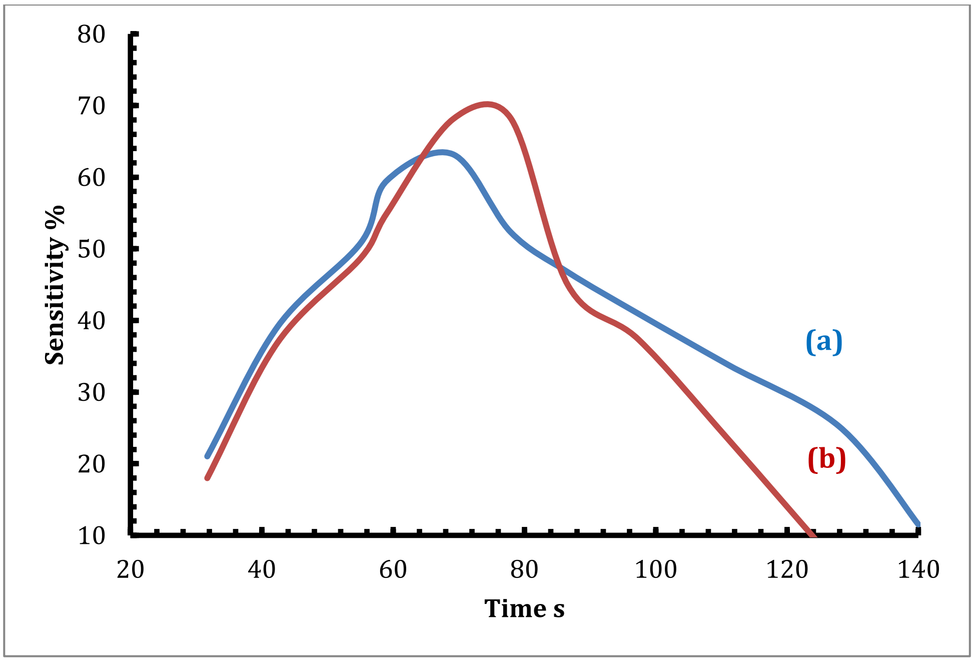

Figure 9. The sensitivity % of ZnO: CuO films, (a) before annealing, (b) after annealing

Conclusions

ZnO: CuO thin films have been successfully prepared by the Sol-Gel spin coating method. The effect of annealing at 500°C on the structural, optical, and sensing properties was evident. The structure was polycrystalline with monoclinic phase and the crystal size increased from 5.4 nm to 9.9 nm after annealing. The AFM and SEM results showed that the surface of the thin films was homogeneous, and the particle size also increased from 25 nm to 32 nm. The energy gap was reduced from 3.22 eV to 2.98 eV and the absorbance (A) was increased after annealing. The sensitivity % increased from 63.28604 % to 68.27853 % after annealing.

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