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Effect of annealing on the properties of nanostructured CuO thin films for enhanced ethanol sensitivity

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Abstract

Copper oxide (CuO) thin films were grown on glass substrates by low cost spray pyrolysis technique for three different molar concentrations (0.05 M, 0.10 M and 0.15 M), at a substrate temperature of 350 °C, and subsequently annealed at 400 °C for 2 h. The effects of precursor concentration and annealing on the structural, electrical and morphological properties of the crystallized films were investigated. X-ray diffractograms of the films showed the formation of single phase CuO with tenorite structure. The electrical properties of the films like carrier concentration, Hall co-efficient (R_H), mobility and conductivity were studied from Hall effect measurements. The positive values of R_H confirmed the p-type conductivity of the films. Resistivity decreased drastically by two orders of magnitude for the annealed films. The microstructures characterized by a scanning electron microscope for 0.15 M concentration of the precursor revealed that the morphology of the films was substantially affected by annealing. The film surface revealed uniformly distributed cluster of peanut shaped grains after annealing. The response of the as deposited and annealed CuO sensor to low concentration of ethanol (10 ppm) was compared. The annealed CuO film showed higher sensor response than the as-deposited CuO film did. The result suggested that annealing causes significant effect on the sensing performance of CuO to ethanol.

Keywords: C. Electrical properties; CuO films; SEM; Ethanol sensor

1. Introduction

Ethanol is the most important alcohol owing to its diverse applications. It is widely used in food industry, brewing process control, medical and clinical applications and bio-medical technological processes. Those working on ethanol synthesis have great chances of being victims of respiratory and digestive track cancer. Hence, there is a great demand for monitoring ethanol gas at trace level. Semi-conductor metal-oxide based gas sensors are commonly used for environmental monitoring and industrial applications, due to their advantages such as small dimension, low cost and convenient operation. To date, n-type metal oxides are widely investigated, such as ZnO [1], In_2O_3 [2], and SnO_2 [3], due to their extensive sensing performance. Recently, increasing interest has been taken in gas sensors based on p-type semi-conductors. Among a variety of p-type semi-conductors, copper oxide (CuO) has proved itself to be one of the most attractive materials for gas sensor applications, from the point of view of gas sensitivity as well as chemical stability. CuO has been found to be sensitive to HCHO, NO_2, H_2S and CO [4]. However, research on p-type CuO based ethanol sensor and the effects of annealing on the sensing properties of CuO to ethanol is not satisfactory.

There are two well-known copper oxides: Cu_2^+O (cuprite) and $Cu^{2+}O$ (tenorite). A meta-stable copper oxide, Cu_4O_3 (paramelaconite), which is an intermediate compound between the previous two, has also been reported [5]. Cu_2O has a cubic structure with the lattice parameters of 4.27 Å, and Cu_4O_3 has a tetragonal structure with the lattice parameters $a=5.837$ Å and $c=0.9932$ Å. CuO crystallizes in monoclinic structure with the lattice parameters $a=4.684$ Å, $b=3.425$ Å, $c=5.129$ Å and $\beta=99.28^\circ$, in which CuO_2 units are chained and Cu forms four coplanar bonds with O [6]. CuO is unique amongst the monoxides of 3D transition elements having a square planar co-ordination of copper by oxygen in the monoclinic structure [7]. A variety of deposition techniques were used for depositing CuO films, which include electro-deposition [8], CVD [9], plasma evaporation [10], and RF sputtering techniques [11].

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In most of the techniques, a mixture of different phases like CuO, Cu_2O, and Cu were obtained generally at room temperature. This is a major drawback of all these methods for utilizing CuO films as a semiconductor. Spray pyrolysis technique has been extensively used nowadays in depositing nano-structured metal oxide films. The CuO films prepared using this technique are well compacted and the surface to volume ratio of the drops is large, which may make thin film useful for device applications [12]. The film surface is uniform and stoichiometry of the film is easy to control in this technique. In the present study, the CuO films were deposited by spray pyrolysis on glass substrate kept at a temperature of 350 °C for three different molar concentrations, and subsequently annealed at 400 °C. As a part of the comprehensive work on preparation of highly crystalline, single phase CuO films with good electrical properties, for application in the detection of low concentration of ethanol at low temperature, we have developed a novel spray pyrolysis deposition route to CuO with a specially designed spray nozzle. In order to get reproducible film and facilitate the ethanol sensing properties, the growth parameters like substrate temperature, thickness, solution flow rate and concentration of the solution were optimized during deposition.

2. Experimental details

All reagents were purchased from Alfa Aesar and were used as received without further purification. The CuO films were prepared by spray pyrolysis method. The glass substrates were first cleaned by dipping it in hot chromic acid, in order to remove the impurities. Then, they were cleaned ultrasonically in successive baths of deionized water, soap solution and acetone. The solution was prepared by dissolving copper chloride ($CuCl_2 \cdot 2H_2O$) in de-ionized water. The resulting solution was mixed for 20 min using a magnetic stirrer and then filtered. The final solution, with concentration of 0.05 M, was dark blue and clear, without any suspension of particles. The solution was sprayed onto glass substrates kept at a temperature of 350 °C for 60 min, and the solution flow rate was controlled by a flow meter and kept at 5 ml min^{-1}. Compressed purified air was used as the carrier gas (0.4 kg/cm^2). The substrates were heated by a tube furnace, and the substrate temperature was measured using a thermocouple. The distance between the nozzle and the substrate was maintained at 30 cm. A similar procedure was followed to obtain copper oxide films for two more concentrations (0.1 M and 0.15 M). The as deposited films of three molar concentrations were annealed in a muffle furnace at 400 °C for about 2 h. The thickness of the films was measured using a Mitutoyo (SJ 301) surface profilometer. The crystalline structure of the copper oxide films was studied by X Pert Pro X-ray diffractometer (XRD), with CuK_α radiation. The Ecopia HMS-3000 version 3.51.3 Hall effect measurement system was used to measure the Hall-coefficient, charge carrier concentration, mobility, resistivity and conductivity of the films. The surface morphologies of the films were examined by SEM (Philips XL 30 SFEG) and AFM (Nano Surf Easy Scan 2). The CuO films optimized with deposition conditions were used to fabricate the gas sensor with two thick silver pads on two sides of the film to take out electrical contacts. A schematic of the gas sensing setup used for ethanol sensing is discussed in detail by the authors elsewhere [13]. Ethanol was injected into the container and gasified by heating. Air in the atmosphere was used as the diluting gas, which afforded 10 ppm tested vapor.

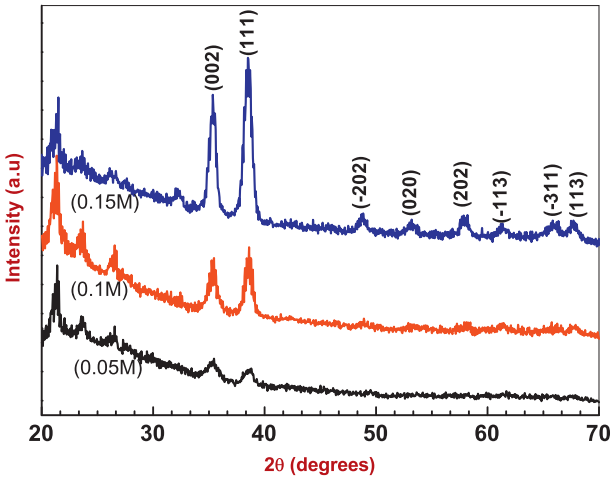

Fig. 1. XRD patterns of as deposited CuO films for three different concentrations: (a) 0.05 M, (b) 0.1 M and (c) 0.15 M.

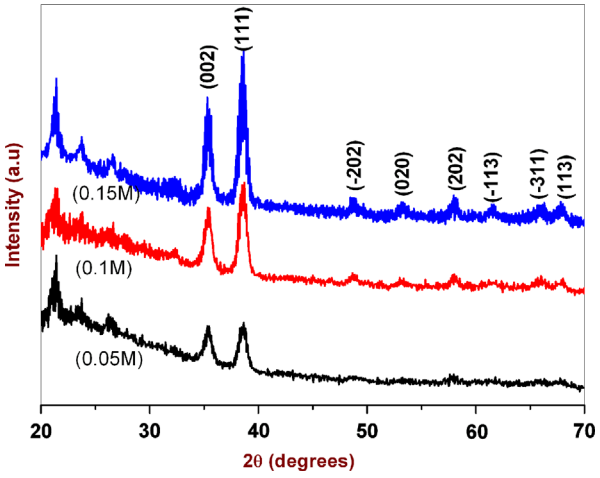

Fig. 2. XRD patterns of CuO films annealed at 400 °C for three different concentrations: (a) 0.05 M, (b) 0.1 M and (c) 0.15 M.

3. Results and discussion

3.1. Variation in structure of CuO films with annealing

Figs. 1 and 2 show the glancing angle XRD patterns of copper oxide films deposited at 350 °C for three different molar concentrations, and subsequently annealed at 400 °C for 2 h. XRD pattern of as deposited film for 0.05 M concentration revealed the formation of single phase CuO with tenorite structure. The peaks at 2θ angle 35.58° and 38.72°, with d_{hkl} 2.52 Å and 2.32 Å, correspond to diffraction planes (002) and (111), respectively of CuO (JCPDS 05-6661 for CuO). In comparison to this, Balamurugan and Mehta [14] reported a

Table 1
Crystallite size, dislocation density, strain and number of crystallites of the as deposited and annealed CuO film (400 °C).

Stage	Diffraction angle (deg)	d_{hkl} (Å)	Crystallite size (nm)	Microstrain $\times 10^{-3}$	No. of crystallites $\times 10^{17}$
As deposited	38.60	2.3304	15	1.83	1.164
	38.69	2.3253	12	2.28	1.262
	38.72	2.3236	12	2.24	1.936
Annealed	38.68	2.3254	10	2.71	1.875
	38.67	2.3261	17	1.62	2.389
	38.67	2.3261	17	1.62	0.033

Table 2
Hall effect studies of the as deposited and annealed CuO film (400 °C).

Stage	Concentration	Thickness (μm)	Hall co-efficient R_H($\times 10^2$ cm^3/°C)	Resistivity ρ (Ω cm)	Conductivity σ (Ω^{-1} cm^{-1})
As deposited	0.05	0.20	4.13	0.3111	3.21
	0.10	1.22	81.91	0.2871	3.48
	0.15	1.67	318.30	4.0420	0.24
Annealed	0.05	0.20	1.69	0.0579	17.25
	0.10	1.22	9.51	0.0680	14.69
	0.15	1.67	34.25	0.0519	19.24

mixture of Cu_2O and CuO phase by an activated reactive evaporation technique. Nair et al. [15] could only achieve a deposition of Cu phase along with a minority Cu_2O phase at room temperature by the chemical deposition technique. It is important to note that in the present method of spray pyrolysis technique with specially designed spray nozzle, copper oxide thin films with a predominant CuO phase were grown successfully at 350 °C. As the concentration was increased, the intensity of the peaks increased due to the increase in thickness of the film during the formation of CuO, which is consistent with the results reported by Morales et al. [16], Senthil Kumar et al. [17] and Cho et al. [18] for CuO films prepared by spray pyrolysis technique. At 0.15 M concentration eight XRD peaks at $2\theta = 35.58°$, 38.69°, 49.08°, 51.95°, 58.19°, 61.65°, 66.04° and 67.95° appeared, owing to the diffraction of the (002), (111), (−202), (020), (202), (−113), (−311) and (113) planes, repectively, of CuO. The (002) and (111) diffraction peaks of CuO was intensified in the process of increasing the concentration. Further, the presence of multiple peaks of the CuO phase at 0.15 M concentration revealed the polycrystalline nature of the films. All the peaks in the XRD pattern could be assigned with monoclinic structure of CuO. Fig. 2 reveals that the films sintered at 400 °C for 2 h increased the crystalline quality of CuO, as indicated by the enhancement in the intensity of the most prominent (002) and (111) peaks of CuO. Thus, it is clear that the annealing treatment provided the atoms with enough thermal energy to properly arrange into the final crystalline product. It was reported earlier that the CuO phase may transform into Cu_2O phase after annealing [19]. However, in the present work the single phase CuO was retained even after annealing to 400 °C. The crystallite size (D) were calculated using Scherrer's formula [20]

$$D = (0.94\lambda)/(\beta cos\ \theta) \quad (1)$$

The average crystallite size was found to be ~13 nm for the as deposited CuO film, and it increased to ~17 nm after annealing at 400 °C. The increase in D value after annealing might be due to decrease in grain boundaries, and hence the amount of defects in the films. The thermal energy produced by annealing led to enhancement of mobility of active species by filling the micro-voids or defects in the structure and formation of more packed and large crystalline films. Park et al. [21] reported the effect of annealing on the crystallite size of CuO film prepared by rf sputtering. The dislocation density (δ), strain (ε) and the number of crystallites (N) are calculated using the relation

$$\delta = (1/D^2) \quad (2)$$

$$\varepsilon = (\lambda/D\ sin\ \theta) - (\beta/tan\ \theta) \quad (3)$$

$$N = (t/D^3) \quad (4)$$

where λ is the wavelength of the incident X-ray ($\lambda = 1.5418$ Å), θ is the Bragg angle, β is the full width at half-maximum (FWHM) in radians, D is the average crystallite size and t is the thickness of the film. Table 1 reports the crystallite size, dislocation density, strain and number of crystallites for as deposited CuO films, and films annealed at 400 °C. The dislocation density in our case was found to be less for the annealed CuO films. It was observed that the lattice spacing of the preferential orientation of the films slightly changed with annealing, which may be attributed to the decrease in strain in the CuO films. From these results, it was confirmed that the fundamental effect of increase in crystallite size is related to decrease in strain. The decrease in strain indicates the decrease in lattice imperfections and formation of high quality films.

3.2. Variation in electrical properties of CuO with annealing

The electrical properties were estimated from the Hall measurements in Vander Pauw configuration for the as deposited and annealed CuO films. To carry out the Hall measurements, copper oxide films with 2.5×1 cm^2 area were used. Contacts were made using gold coated clips on the

surface of the film by spring action, and the distance between the two points was 0.5 cm. Measurements were carried out under a magnetic field of 1070 G. The different electrical parameters are summarized in Table 2. The variation in mobility and carrier concentration with the Cu precursor concentration for as deposited and annealed CuO films is shown in Figs. 3 and 4, respectively. The positive sign of the Hall co-efficient (R_H) revealed that the deposited CuO film is p-type in nature. It was observed that resistivity (ρ) of the film varies with concentration of the precursor,which may be attributed to the variation in the stoichiometric changes induced by copper ion vacancies and neutral defects in the film [22]. Drobny and Pulfrey [23] observed an initial increase in resistivity in films which is a mixture of CuO and Cu_2O and then obtained CuO films with low resistivity which they associated with non-stoichiometry [23]. Shokr et al. [24] reported that the relatively low resistivity observed for the SnO_2 film is attributed to the deviation from stoichiometry due to oxygen vacancies, which act as electron donors and increase the free carrier concentration. Resistivity (ρ) decreased drastically by two orders of magnitude for the annealed films. Nair et al. [15] reported that the electrical resistance of CuO films deposited by chemical deposition decreased by an order of magnitude after annealing. The larger crystallite size after annealing reduces grain boundary scattering, increasing the mobility and carrier concentration of the films. The increase in mobility may also be due to the improvement in crystallinity of the films with annealing. Wang and Gong [25] observed a significant increase in the conductivity of copper oxide films after annealing in air. This may be another experimental proof of the p-type conduction caused by excess oxygen. Maximum carrier concentration of 1.96×10^{18} was obtained for the sample prepared with 0.15 M concentration, which is one order of magnitude higher than that reported by Figueiredo et al. [26].

3.3. Variation in morphology of CuO with annealing

Surface morphology studies of the CuO films were carried out using SEM. Fig. 5(a) and (b) shows the SEM images of as deposited and annealed CuO films optimized for 0.15 M concentrations, respectively. The surface of the as deposited films is very smooth and well packed with quasi-spherical grains and peanut shaped particles. The growth of CuO in a spray pyrolysis process goes from a heterogeneous phase of precipitating in the solution. Heterogeneous growth yields a dense, conformal buffer layer, but the homogeneous growth deposits a layer with adherent CuO precipitates [27]. After annealing at 400 °C for 2 h, it was observed that the grain size increased and surface showed uniformly distributed cluster of grains. This is due to the fact that annealing increases the crystalline quality of the films. Moreover, the adsorbed species might progressively acquire a higher surface mobility, providing a more favorable path for the formation of the observed anisotropic structure which possess large grains, as seen in Fig. 5(b). This is also evident from the atomic force microscope (AFM) images of the CuO films shown in Fig. 6(a) and (b) (scan area, 10 μm × 10 μm), which revealed that some of the small grains had merged to form large grains after annealing (Fig. 6(b)). The surface becomes rough as the crystal grains cluster together with annealing. For the as deposited films, the root mean square roughness (RMS) was 19 nm. Upon annealing to 400 °C, the RMS roughness increased to 43 nm. The increase of RMS roughness of CuO films with annealing leads to significant effect on its sensing performance.

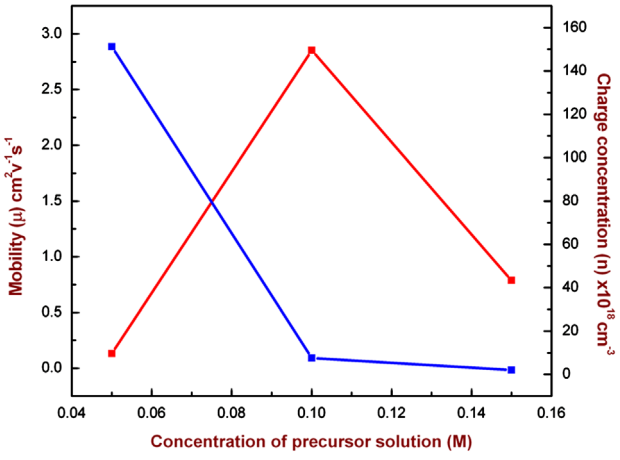

Fig. 3. Variation in mobility and charge concentration of as deposited CuO films for different Cu precursor concentrations.

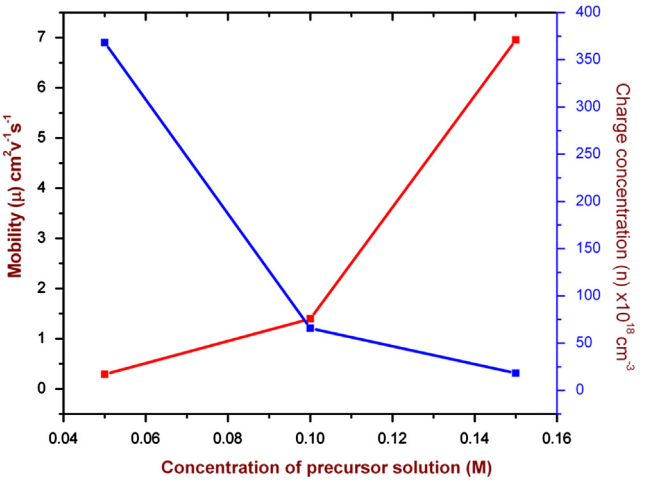

Fig. 4. Variation in mobility and charge concentration of annealed CuO films for different Cu precursor concentrations.

3.4. Variation in response time and sensitivity of CuO film sensor

After having optimized the film for precursor concentration and annealing, the response of annealed CuO film for 0.15 M concentration was investigated for its performance toward ethanol. Fig. 7(a) and (b) shows the dynamic resistance of the as deposited and annealed CuO sensor (0.15 M concentration) with time, for 10 ppm of ethanol. Upon exposure to ethanol vapor, the resistance of the sensor decreased upto 200 s, as seen from Fig. 7(a). The reason for decrease in the resistance may be due to the oxidation of the ethanol vapors upon coming in contact with the oxide semi-conducting surface, which liberates

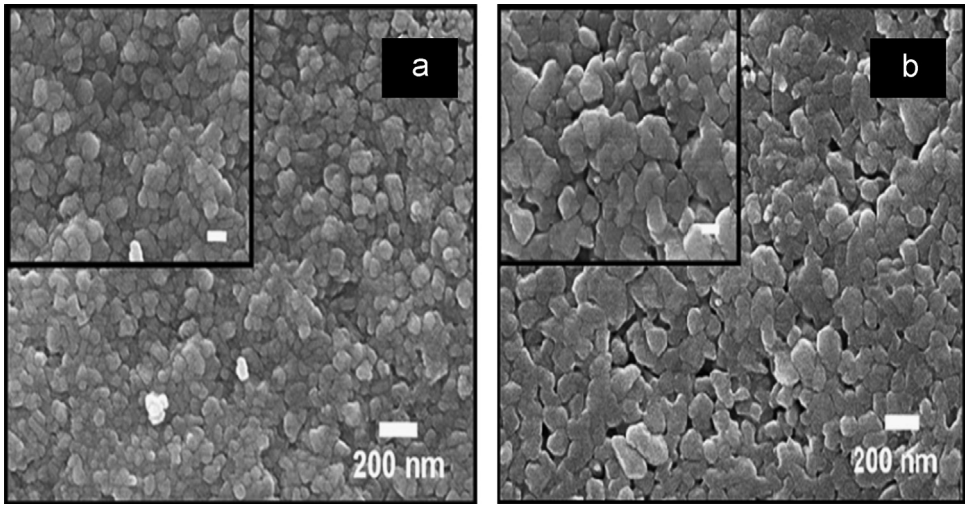

Fig. 5. SEM images of (a) as deposited and (b) annealed CuO film (400 °C), for 0.15 M Cu precursor concentration (inset: magnified image).

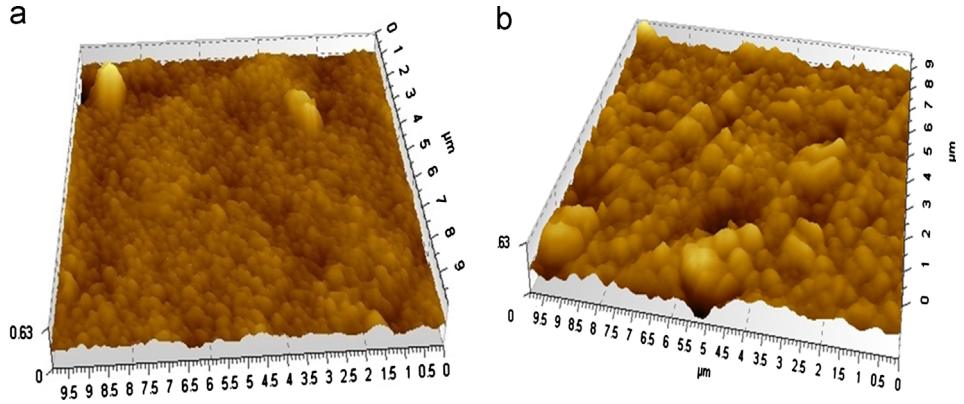

Fig. 6. AFM images of (a) as deposited and (b) annealed CuO film (400 °C) in a scan area of 10 μm × 10 μm, for 0.15 M Cu precursor concentration.

free electrons and H_2O. The atmospheric oxygen chemisorbs on the surface of the oxide semi-conductor as O^{2-} or O^{-}, removing an electron from the conduction band of the semi-conductor. Ethanol vapors react with the chemisorbed oxygen and reinject the carrier thereby reducing the resistance of the material. This interaction of oxygen ions on the surface of CuO with ethanol molecules can be described by the following reactions [28]:

$$O_{2\ (ads)} + e^{-} \leftrightarrow 2O^{-}_{(ads)} \quad (5)$$

$$C_2H_5OH_{(ads)} + 3O_2 \rightarrow 2CO_{2(g)} + 3H_2O_{(g)} + 3e^{-} \quad (6)$$

The free electrons liberated move into the conduction band of CuO resulting in a decrease in the resistance of CuO film. The response time (the time taken by the sensor to reach to 90% of its final value) of the CuO sensor was found to be 200 s (Fig. 7(a)). After 200 s the resistance started increasing as the gaseous species on the surface desorbed. However, it took longer time for the sensor response to reach its original value, as the ethanol vapors do not easily desorb. Because of the water liberation, the surface got saturated after sometime, which required cyclic heating and flushing the chamber with hot air. The resistance of the as deposited CuO film was 0.48 MΩ, while for the annealed film it is only 0.39 MΩ, after exposure to ethanol. It was also observed that the sensor shows much lower resistance for annealed films (Fig. 6(b)), and the response time of the ethanol was 180 s, indicating that as the grain size increased with annealing, the CuO sensor shows higher response. The behavior of CuO based sensor to ethanol is based on changes in electrical resistance induced by adsorption or desorption of the gas on its surface [29]. The sensitivity of CuO sensor has been calculated using the expression [30]

$$S = (R_{gas} - R_{air}/R_{air}) \quad (7)$$

where R_{air} was the sample resistance in dry air, and R_{gas} was the resistance in the presence of test gas. The CuO films were tested under very low concentration of ethanol as compared to what is reported in the literature up to now i.e. 10 ppm of ethanol, in order to determine the sensitivity. Fig. 8(a) and (b) shows the variation in sensor response of CuO sensor with time for 10 ppm of ethanol. The sensitivity obtained for as deposited and annealed films was 23% and 37%, respectively. These values are high for CuO films compared to the ones reported by

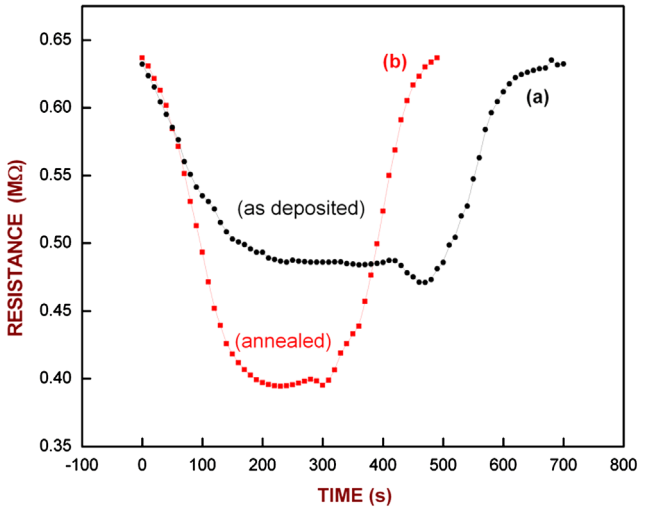

Fig. 7. The response of (a) as deposited and (b) annealed CuO sensor prepared at 0.15 M concentration, upon exposure to 10 ppm of ethanol gas at room temperature.

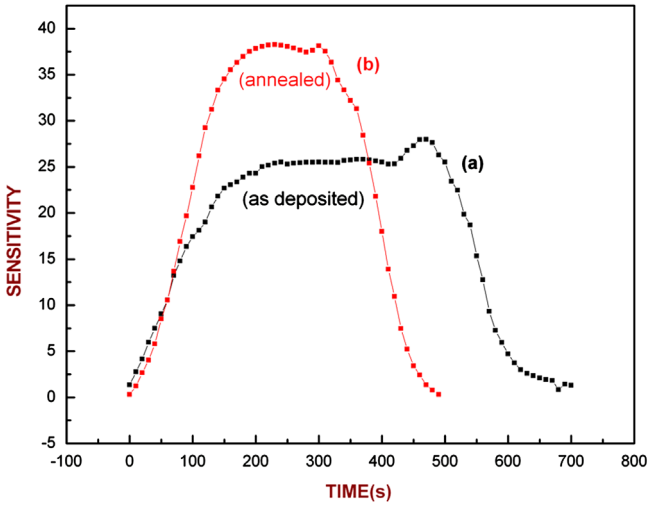

Fig. 8. Variation in sensitivity with time for (a) as deposited and (b) annealed CuO sensor prepared at 0.15 M concentration, toward 10 ppm of ethanol.

Parmar and Rajanna [31], for example, who found only 29% sensitivity for 2500 ppm of ethanol at high temperature. The sensitivity of CuO based sensor to specific gases is dependent on the grain size of the film. The grain size of CuO in gas sensors ranges from a few nm to several tens of nm in mean diameter, so that the sensing body includes pores between the grains. The transport of gas through these pores takes place by Knudsen diffusion equation [32], $D_k = 4r/3(2RT/\pi M)^{1/2}$, where r is the pore radius, M the molecular weight of the gas, R the gas constant and T the temperature. It follows that D_k is proportional to r, which would depend on the grain size of oxide used. Thus, the annealed CuO sensor which possesses well-defined microstructure with uniform grain size, revealed large gas response compared to as deposited CuO. It is suggested that this tendency mainly reflects an increasing order of the mesopore size or Knudsen diffusion co-efficient (D_k) involved among the films.

4. Conclusion

Nanocrystalline copper oxide thin films were prepared by spray pyrolysis technique. The preparation process with enhanced pyrolysis spray disposal resulted in the formation of phase pure CuO films, with good crystal quality. Post-deposition annealing of the films was found to result in a predominant CuO phase in the films. The average crystallite size was found to vary from ~13 to 17 nm with annealing. The Hall effect studies revealed a significant increase in conductivity, mobility and carrier concentration of CuO films after annealing. The surface morphology studies revealed that the grain size increased after annealing, and the surface showed uniformly distributed cluster of grains which is confirmed from the increase in roughness of the films with annealing. The gas sensing performance of the as deposited and annealed CuO films to 10 ppm of ethanol at room temperature was investigated. The annealed film revealed higher response as the grain size of CuO increased, suggesting the contribution by an increase in mesopore size. This study will be useful for the optimization of deposition parameters, such as concentration of the precursor and annealing, and the response time of CuO sensor for enhanced ethanol sensitivity.

Acknowledgments

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