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Preparation and Characterization of CuO Thin Films Prepared by Spray Pyrolysis Technique for Ethanol Gas Sensing Application

[1]C. Ravi Dhas, [1]Dinu Alexander, [1]A. Jennifer Christy, [2]K. Jeyadheepan, [3]A. Moses Ezhil Raj and [4]C. Sanjeevi Raja

[1]Department of Physics, Bishop Heber College (Autonomous), Tiruchirappalli, 620 017, Tamil Nadu, India
[2]School of Electrical and Electronics Engineering, SASTRA University, Thanjavu, 613 401, Tamil Nadu, India
[3]Department of Physics, Scott Christian College, (Autonomous), Nagercoil, 629 001, Tamil Nadu, India
[4]Department of Physics, Alagappa Chettiar College of Engineering and Technology, Karaikudi, 630 003, Tamil Nadu, India

Corresponding Author: C. Ravi Dhas, Department of Physics, Bishop Heber College (Autonomous), Tiruchirappalli, 620 017, Tamil Nadu, India

ABSTRACT

The biomedical, chemical, drug and food industries have great demand of an alcohol sensor with high sensitivity and selectivity which can operate at low temperature. In this study, CuO thin films were deposited on well cleaned glass substrates by spray pyrolysis technique for 0.1, 0.2 and 0.3 molar concentrations of copper chloride precursor solutions and at a substrate temperature of 300°C and at an air pressure of 0.4 kg cm^{-2}. X-ray diffraction patterns of the prepared films revealed the formation of CuO thin films having monoclinic structure with a grain size ranging from 35 to 54 nm. The microstrain and dislocation densities are found to decrease with increase in molar concentration. The surface morphology and the elemental composition of the deposited samples were analyzed using SEM and EDAX. The change in resistivity of the films was studied with respect to the change in temperature using two probe method. From Laser Raman spectral studies, the characteristic Raman peaks of the prepared samples were observed. The ethanol gas sensing properties of the prepared films were studied for 100 and 200 ppm ethanol vapour.

Key words: Spray pyrolysis, concentration, copper chloride

INTRODUCTION

Due to the emerging applications of metal oxides in technical fields, it is essential to characterize the physical and chemical properties of metal oxides (Ueda *et al*., 1998; Liu *et al*., 2007; Zhu *et al*., 2007; Ferreia *et al*., 1996). The application of metal oxide semiconductor sensors in toxic and inflammable gas detection leads to advanced research in this area. Current research in the field of gas sensors has been focused on the fabrication of sensors which are low cost with rapid response, high sensitivity and good selectivity. Copper oxide can be used as a candidate material for gas sensing application.

Copper oxide commonly crystallizes in two forms such as cupric oxide or tenorite (CuO, a band gap of 1.1-1.9 eV and a monoclinic structure) and cuprous oxide or cuprite (Cu_2O, a band gap of 2.1-2.6 eV and a cubic structure) (Ray, 2001; Pierson *et al*., 2003). Due to the copper vacancies in

the structure, Cu deficient CuO exhibits native p-type conductivity. CuO thin films could be employed in solar cells, photo sensor applications, photo thermal application, high temperature super conducting materials (Balamurugan and Mehta, 2001; Chen *et al*., 2009; Zhu *et al*., 2005), diodes, lithium-copper oxide electrochemical cell, field emission devices etc. Copper oxide based sensors have applications in the fabrication of gas sensing devices because of the conductivity changes induced by the reaction of gases with surface adsorbed oxygen (Saito *et al*., 1985; Traversa, 1995).

Conventional methods for depositing Copper oxide thin films are thermal oxidation (Gong *et al*., 1995; Huang *et al*., 2004), electro deposition (Brown and Choi, 2006), dip coating (Serin *et al*., 2005), chemical vapour deposition (Maruyama, 1998), plasma evaporation (Santra *et al*., 1992), reactive sputtering techniques (Drobny and Pulfrey, 1979) and spray technique (Rajaram *et al*., 2013). Referring to the spray pyrolysis technique, assorted parameters like air pressure, deposition rate, substrate temperature and Substrate to Nozzle Distance (SND) have effect on the various material properties of thin films. Owing to its simplicity in the making of the films over a large area and its inexpensiveness, the spray pyrolysis technique is a better suited method among the other methods which are in practice. This method is convenient for preparing pinhole free, homogenous, smoother thin films.

In the present study, the CuO films have been deposited by chemical spray pyrolysis technique on to the glass substrates kept at a temperature of 300°C. The prepared films were characterized by different techniques and an attempt has been carried out to examine the feasibility of CuO thin films for gas sensing applications.

EXPERIMENTAL METHODS

Spray pyrolysis setup: The spray pyrolysis apparatus setup constructed for the deposition of CuO thin film is shown in Fig. 1.

The main parts of the system setup are an atomizer that converts the spray solution to fine droplets and a furnace reaction chamber for producing pyrolytic action. A tubular vertical cylindrical furnace of diameter 15 cm and length of 32 cm has been fabricated and used as the reaction chamber. With an on build heating coil arrangement powered by AC voltage, a

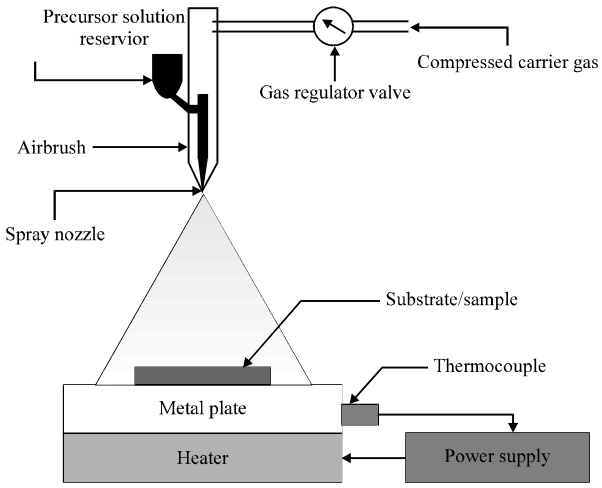

Fig. 1: Spray pyrolysis set up

Table 1: Parameters for CuO thin film deposition by spray pyrolysis.

Precursor	$CuCl_2.2H_2O$
Solvent	Double distilled water
Substrate	Glass
Carrier Gas	Compressed air
Substrate to nozzle distance	30 cm
Substrate temperature	300°C
Pressure	0.4 kg cm^{-2}
Flow rate	10 mL min^{-1}

temperature of 300°C has been attained. A plate of diameter 12 cm and of thickness 0.5 cm has been mounted in the uniform zone of the furnace to serve as the substrate holder. The substrate temperature has been measured using a thermocouple placed just below the substrate holder. The temperature of the furnace has been maintained by a temperature controller. The spraying of the solution has been carried out using a specially designed atomizer made of glass material. The flow of solution through the tube has been controlled by the stop cock of the burette connected to the inner glass tube of the atomizer which in effect controls the flow of solution through the nozzle.

Film deposition: CuO thin films have been deposited on glass substrates by the method of spray pyrolysis technique with different molar concentrations of copper chloride ($CuCl_2.2H_2O$) for 0.1 M, 0.2 and 0.3 M. To prepare 100 mL of precursor solution, the required quantity of precursor salt was made to dissolve in distilled water by continuous stirring by a magnetic stirrer for 15 min. Before deposition, substrates were cleaned well. The deposition parameters of the spray pyrolysis setup such substrate to nozzle distance, substrate temperature, pressure and precursor flow rate were optimized and kept at constant to obtain pin hole free and well adherent films. The deposition parameters are given in the Table 1.

The precursor solution was sprayed using a glass jet nozzle using air as the carrier gas on to the pre-heated, cleaned glass substrates (2×1.4 cm of geometric area). The basic reaction involved in the film formation is given below.

$$CuCl_2+H_2O \rightarrow CuO+2HCl$$

Sensing system for measuring gas response: We have adopted static system,for sensitivity measurement of deposited films,which comprises an airtight chamber with air admittance and gas inlet valves as shown in Fig. 2. The sensor element was placed inside the chamber of volume 57,000 cm^3. Multi meter was connected to sensor films which is having ohmic contacts. Intially the sensitivity measurements were performed at the room temperature in air ambient and is taken as the reference response to calculate the sensitivity. After noting the reference response, the ethanol liquid was placed in a beaker above the heater inside the chamber and the base pressure maintained at 10^{-3} m bar using a rotary pump.

During measurements all the valves were closed to avoid the leakage of the test gas. The resistance of the sensor is measured for different exposure time in ethanol vapor-air ambient. After completing the measurements, the gas is wiped off completely by operating the rotary pump again and by injecting fresh air into the chamber.

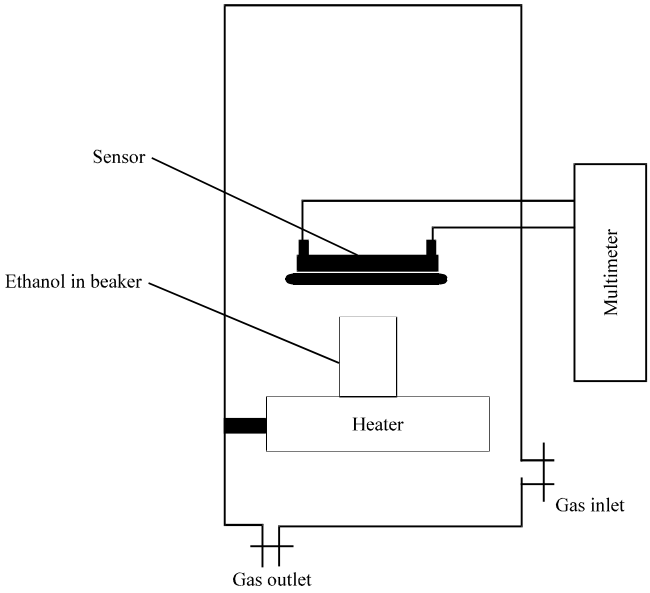

Fig. 2: Sensing system

RESULTS AND DISCUSSION

X-Ray diffraction (XRD) analysis: The prepared CuO thin films were characterized by XRD to obtain the structural parameters as a function of deposition parameters. All the peaks, indexed and matched with JCPDS card (JCPDS card no: 01-089-2529), confirm that the deposited films are polycrystalline in nature having monoclinic CuO structure. The recorded patterns show the pre-dominent peak (111) of CuO located at '2θ' value of 38.6° with 'd' value 2.33 Å (Table 2). Another high intensity peak corresponding to (-111) plane of CuO present at '2θ' value of 35.5° has also been observed. The peak positions and 'd' values of the diffraction peaks for CuO are in good agreement with the earlier reports of the spray deposited CuO thin films.

It is emphasized that no peak corresponding to Cu_2O phase has been appeared in the XRD pattern of the films deposited at various precursor molar concentrations. But the results of earlier reports on the spray deposited films have both CuO and Cu_2O phases (Kose *et al*., 2008; Morales *et al*., 2004).

Effect of molar concentration on crystallization: Figure 3 indicates the XRD patterns of CuO thin films deposited at 0.1, 0.2 and 0.3 M mentioned as samples a, b and c, respectively. Copper chloride with 0.1 M concentration (sample a) give rise to two highly oriented peaks at '2θ' equal to 35.58° and 38.63° which corresponds to the reflections from (-111) and (111) planes respectively. When the molar concentration increased to 0.2 M, the CuO peaks corresponding to (-111) and (111) orientations also enhanced. It was found that when the molar concentration of copper chloride was increased to 0.3 M, there was an enhancement in the intensity of corresponding peaks.

For the spray solution with low molar concentration 0.1 M, the net heat absorbed by the droplet, may not sufficient enough to vaporize the entire droplet due to fast travel of droplet to the substrate. As a result precipitation and sublimation has taken place on the substrate. So, the reaction appears to be of homogeneous one and the film had low crystalline (sample a). When the molar concentration of $CuCl_2$ was increased to 0.2 M, the intensities of the peaks of CuO got

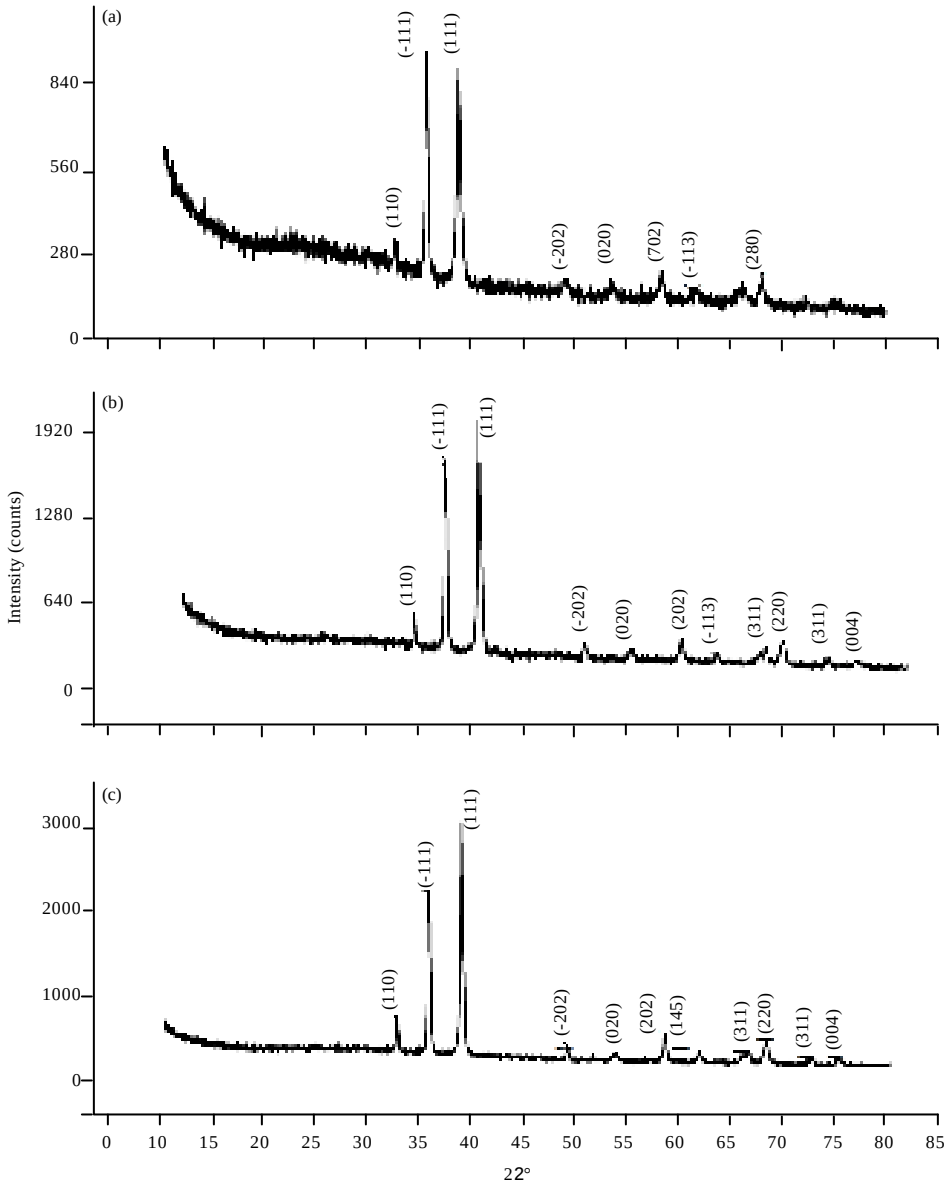

Fig. 3(a-c): XRD pattern of CuO thin films (a) 0.1 M, (b) 0.2 M and (c) 0.3 M

Table 2: Molar concentration, position of the observed XRD peaks (2θ°), observed d (Å) spacing, reflecting planes (hkl) and observed relative intensity of peaks (I)

Molar concentration	2θ°	d-spacing (Å)	Miller indices (hkl)	Intensity I (%)
0.1 M	38.6370	2.33039	(111)	100.00
	35.5860	2.52287	(-111)	98.49
0.2 M	38.6435	2.33001	(111)	100.00
	35.5185	2.52752	(-111)	78.07
0.3 M	38.6656	2.32873	(111)	100.00
	35.5780	2.52342	(-111)	61.47

Table 3: Value of grain size (D), strain (ε) and dislocation density (δ) for the CuO thin films.

Properties	0.1 M	0.2 M	0.3 M
Average grain size (nm)	35.325	49.657	54.51
Non uniform strain (ε)	0.0014	0.00104	0.0008
Dislocation density (δ) (10^{14}/unit area)	22.110	10.526	5.744

enhanced (sample b) which indicates that the crystallinity of crystallites had been improved. The increase in crystalline nature is due to the enhancement in oxidation process and reduced atmosphere. At this 0.2 M concentration might have a reaction transition from homogenous type to heterogeneous type. Referring to 0.3 M concentration (sample c), the entire droplet would have evaporated in the hot space above the substrate before reaching the surface of the substrate. Thus the film with 0.3 M concentration had the highest crystalline nature (Rajaram *et al*., 2013). The optimized characteristics have been obtained at 0.3 M concentration of CuO thin film.

The average grain size (D), strain (ε) and dislocation density (δ) were calculated for all the samples. The films deposited at 0.3 M precursor concentration exhibited maximum crystallinity.

Dislocation density value indicates the amount of defects in the structure. Higher dislocation density (δ) values indicate lower crystallinity levels for the films. The dislocation density was found to decrease with increase in molar concentration and was lowest for 0.3 M film owing to the high crystalline nature of the film as obtained from XRD analysis.

The decrease in strain (Table 3) with respect to increase in molar concentration indicates the decrease in lattice imperfection and formation of high quality film and it can be attributed to the increase in grain size of the film with increase in molar concentration.

XRD analysis showed that precursor molar concentration plays a vital role in the microstructure and the structural properties of CuO films and the optimized 0.3 M film was the most suitable film for ethanol gas sensing application.

Scanning electron microscopy (SEM) analysis: SEM images of CuO thin films prepared by chemical spray pyrolysis were shown in Fig. 4a-c with different magnifications. The microstructure of the thin film prepared at 0.1 M shows needle like appearance and it is interesting to note that the microstructures for thin films prepared at 0.2 and 0.3 M were shown with porous structure. As shown in figures, CuO films at 0.2 and 0.3 M were composed of aggregated particles with porous structure and it is clear that the amount of pores increases as the molar concentration increases and is highest for 0.3 M film. From XRD calculations it was also confirmed that the grain size is highest for 0.3 M film and the increase in pore size for 0.3 M film may be due to the increases in grain size of the film (Patrocinio *et al*., 2009).

Energy dispersive X-ray analysis (EDAX): Energy Dispersive X-ray Analysis (EDAX) is one of the versatile techniques used for determining the chemical composition of unknown material, by identifying the peaks in EDAX Spectrum which is unique to an atom and therefore corresponds to a single element. Figure 5 shows the EDAX spectrum of CuO thin films. The K_{α} radiation shown in figure indicates the electronic transition from L-shell to K-shell. The EDAX spectrum proves that synthesized samples are composed of Cu and O elements by the representation of different copper and oxygen peaks. The atomic percentage of Cu and O is 66.14/33.86 for 0.1 M, for 0.2 M it is 67.78/32.22 and for 0.3 M it is 68.77/31.25 (Table 4). The elemental composition analysis shows that the surface of the samples were rich in copper for molar concentrations 0.1, 0.2 and 0.3 M.

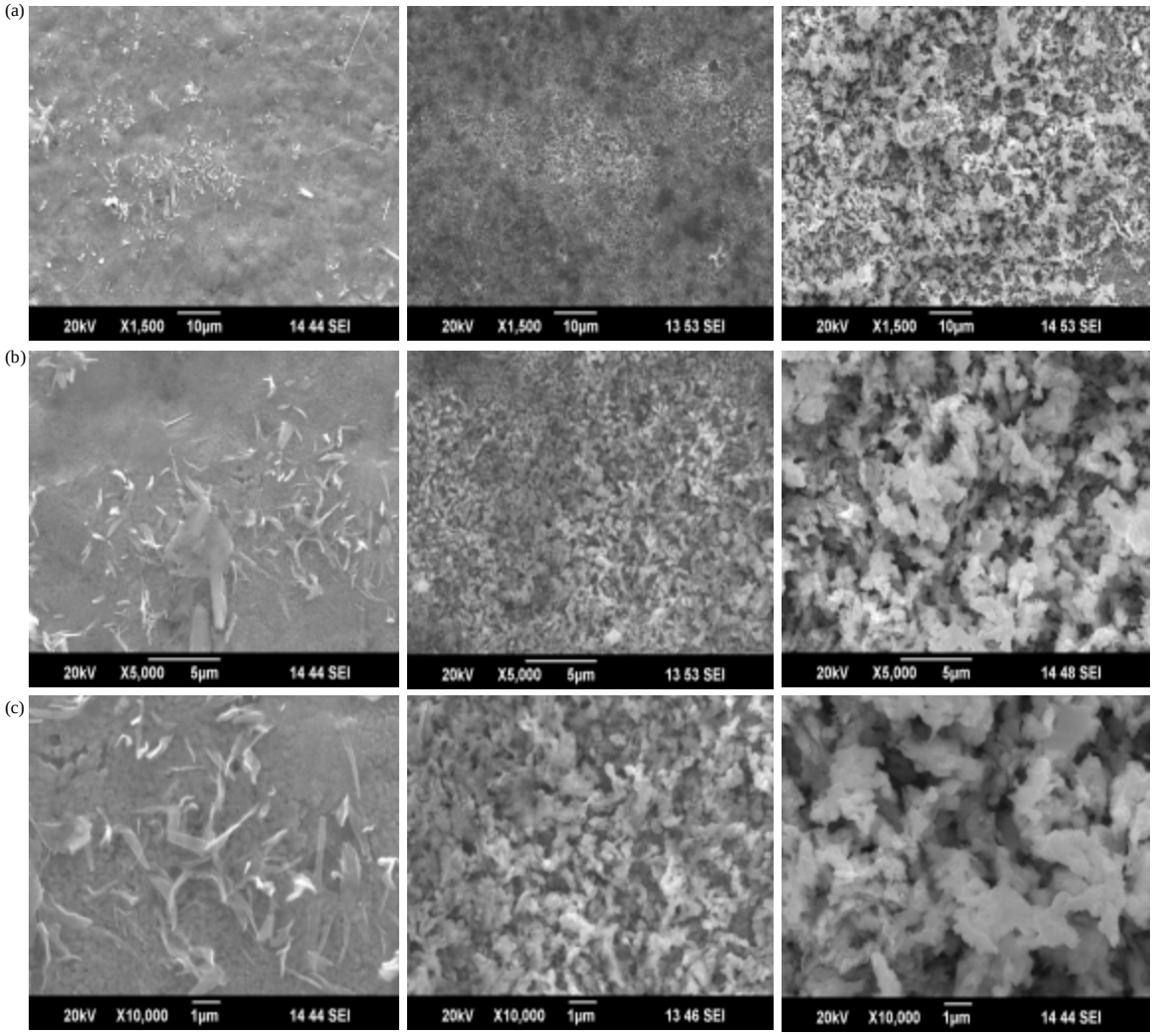

Fig. 4(a-c): (a) SEM image for 0.1, 0.2 and 0.3 M CuO thin film (X1500), (b) SEM image for 0.1, 0.2 and 0.3 M CuO thin film (X5000) and (c) SEM image for 0.1, 0.2 and 0.3 M CuO thin film (X10000)

Table 4: EDAX results of CuO thin film for 0.1 to 0.3 M

Mole M	Element (K)	Wt (%)	At (%)
0.1	O	11.42	33.86
	Cu	88.58	66.14
0.2	O	10.69	32.22
	Cu	89.31	67.78
0.3	O	10.26	31.25
	Cu	89.74	68.77

Electrical properties: The electrical characterization of the CuO thin films can give a clear idea regarding the transport mechanism related to electrical conduction which gives the value of electrical resistivity (ρ) and conductivity (σ) of films. There are various models to explain the

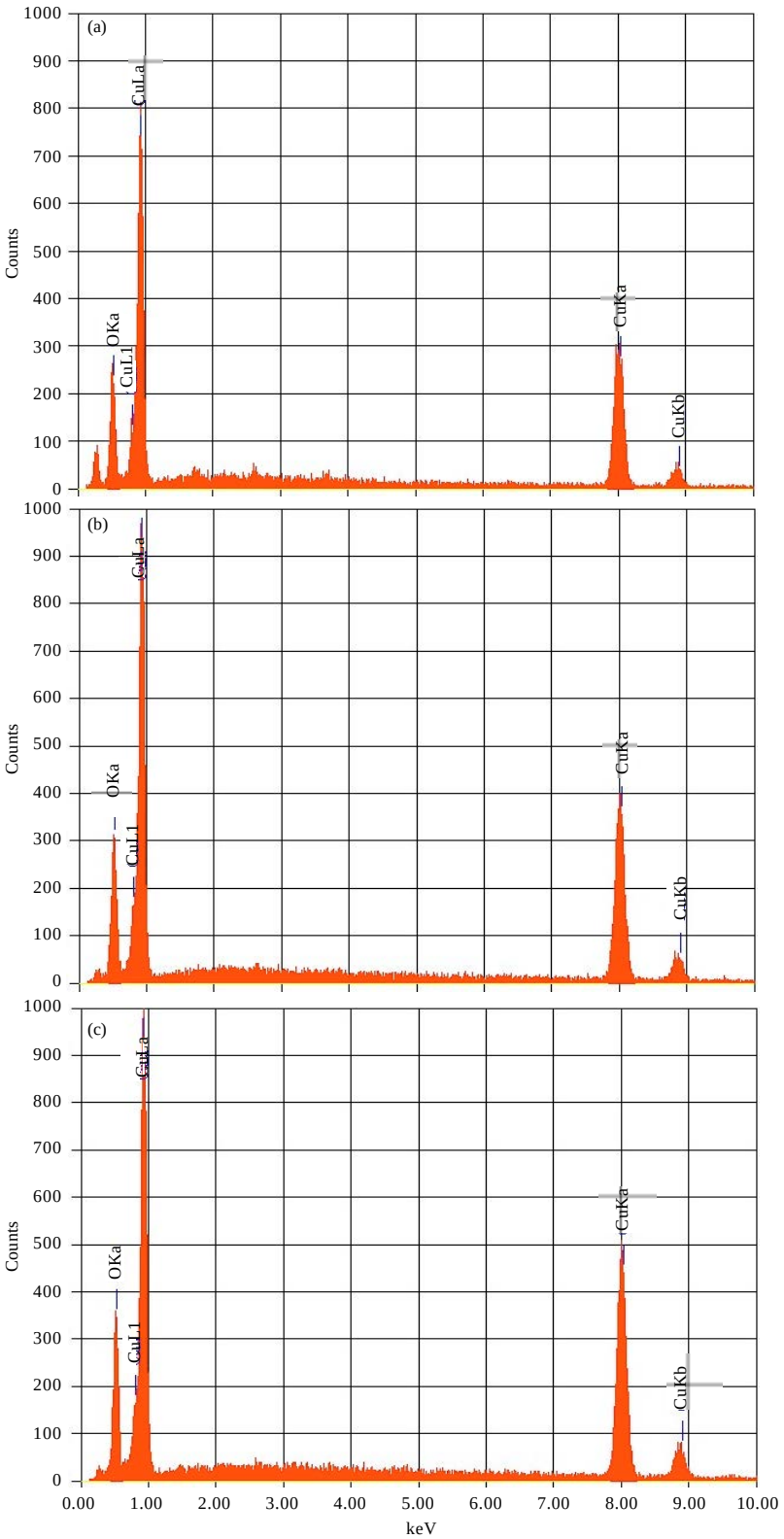

Fig. 5(a-c): EDAX spectra of the CuO thin films (a) 0.1 M (b) 0.2 M (c) 0.3M

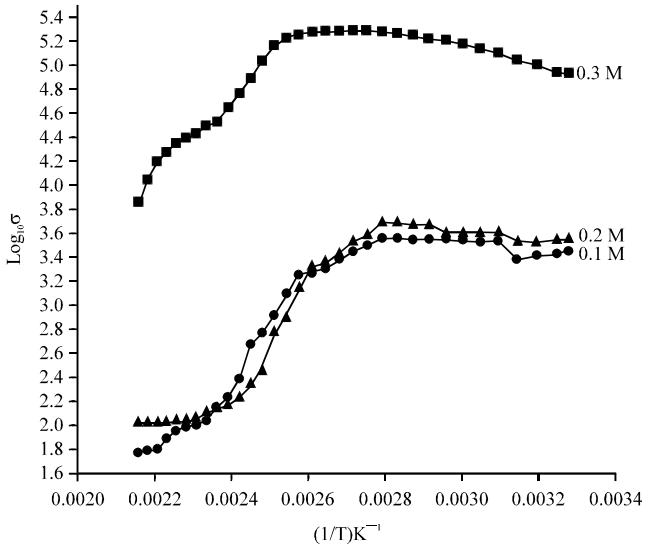

Fig. 6: Variation of electrical conductivity as a function of temperature T of CuO thin film

Table 5: Variation of activation energy of 0.1, 0.2 and 0.3 M CuO thin films

Concentration (M)	Activation energy (eV)
0.1	1.58
0.2	1.07
0.3	0.81

conduction process in poly crystalline films based on different scattering mechanisms. The film resistivity, however, may be due to a combination of three mechanisms, namely (1) Due to scattering from phonon, impurities and point defects, etc. (2) From film surface, (3) Due to grain boundaries which would be predominant in poly crystalline films. Figure 6 reports in σ vs 1000/T curves for 0.1, 0.2 and 0.3 M films. The variation in conductivity with temperature indicates the semiconducting behaviour of the films suggesting a thermally activated conduction mechanism.

In the present study 0.3 M film had the highest electrical conductivity and lowest electrical resistivity. This may be due to the highest grain size of 0.3 M film. The increase of grain size may be due to the improved crystallanity of 0.3 M film. The growth in grains leads to the reduction of grain boundary scattering which decreases the resistivity for the films and eventually the increase in the conductivity of the films (Mustafa, 2008).

From the slope of plots in Fig. 6 the activation energy for CuO thin film at different molar concentration was calculated and is listed in the Table 5. The decrease in activation energy with increase in molar concentration can be due to the increase in grain size.

Laser raman studies: Raman Spectroscopy can be used to find the Raman Active normal modes of CuO which belongs to C^{6}_{2h} group with two molecules per primitive cell. There are three acoustic modes, six IR active modes and three Raman active modes for CuO.

Figure 7 represents Raman spectra of the prepared CuO thin films of 0.1, 0.2 and 0.3 M, respectively. It was found that the intensity of Raman peaks increases with the molar concentration. The peaks at 300 and 610 cm^{-1} corresponds to Cu-O stretching vibrations. The peak at 610 cm^{-1} corresponds to the first order scattering from the expected (B_g) modes and the peak at

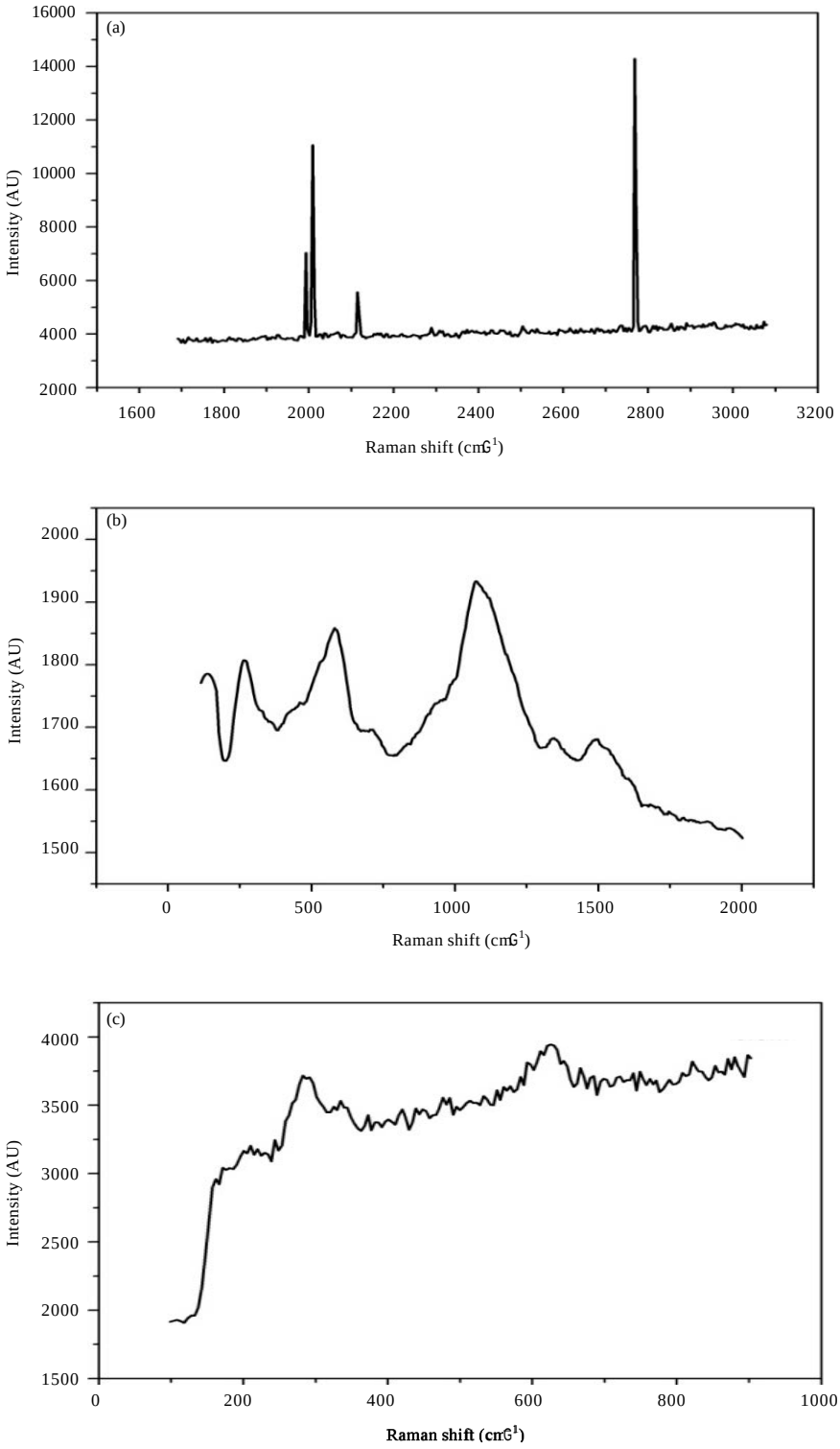

Fig. 7: Raman spectra for (a) 0.1M (b) 0.2M and (c) 0.3M CuO thin film

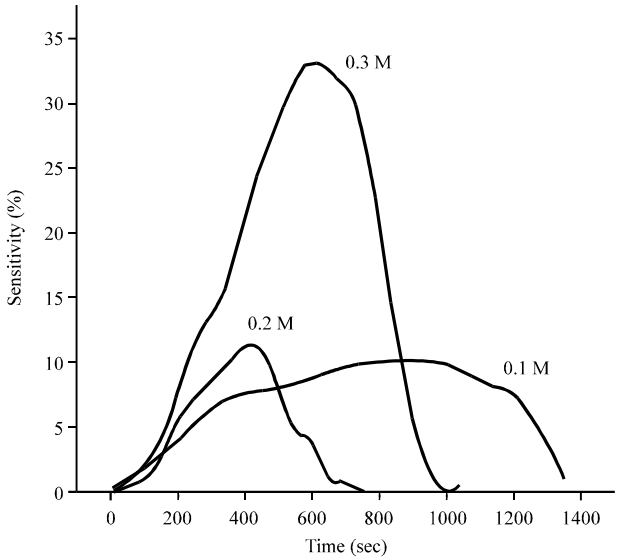

Fig. 8: Gas sensing graph of CuO film for 100 ppm

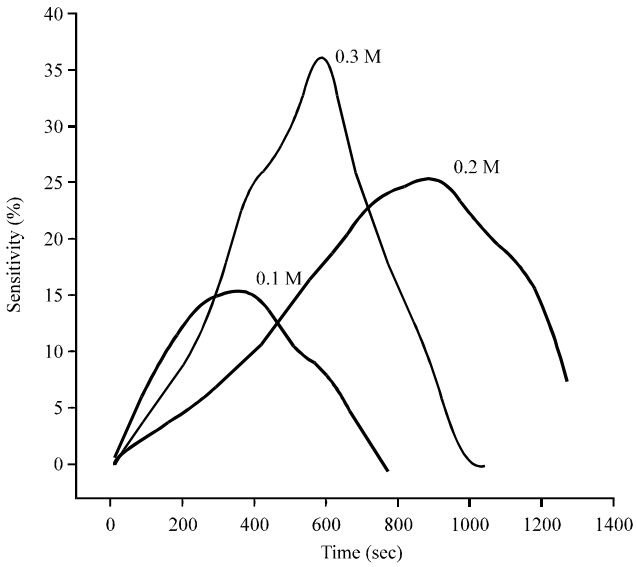

Fig. 9: Gas sensing graph of CuO film for 200 ppm ethanol

1274 cm^{-1} corresponds to two phonon scattering. The peak at the energy range 2000-2800 cm^{-1} was due to multi-phonon scattering. The multi phonon scattering is attributed to the fact that, beyond 640 cm^{-1} the density of phonon states of CuO is zero, so that at least 4 phonons are needed to produce a multi phonon scattering at the energy range 2000-2800 cm^{-1} (Swankar *et al*., 2009).

Ethanol response: The responses of the films prepared at different molar concentration for 100 ppm and 200 ppm ethanol vapor are summarized in Fig. 8 and 9. The gas sensing mechanism depends on the amount of oxygen adsorbed (O^-, O^{2-}) on the sensor surface. The charge exchange interactions of sensing can be concluded from Eq. 1-4 (Bari *et al*., 2013):

$$O_2(gas) \leftrightarrow O_2(ads) \quad (1)$$

$$O_2(ads) + e^- \leftrightarrow O^-_{2(ads)} \quad (2)$$

$$O^-_{2(ads)} + e^- \leftrightarrow 2O^-_{(ads)} \quad (3)$$

$$O^-_{(ads)} + e^- \leftrightarrow O^{2-}(ads) \quad (4)$$

The interaction of ethanol molecules, with pre adsorbed oxygen is represented by Eq. 5-7:

$$C_2H_5OH_{(gas)} \rightarrow C_2H_5OH_{(ads)} \quad (5)$$

$$C_2H_5OH_{(ads)} + O^- + DH_2 \rightarrow e^- + CH_3CHO_{(gas)} + H_2O + D\,H \quad (6)$$

$$C_2H_5OH_{(ads)} + O^{2-}(ads) \rightarrow 2e^- + CH_3CHO_{(gas)} + H_2O + D\,H \quad (7)$$

The changes in the resistance of sensor film is caused by releasing of free electrons due to the reaction between ethanol vapour and pre-adsorbed oxygen.

The responses of the films prepared at different molar concentration for 100 and 200 ppm ethanol vapor are summarized in Fig. 8 and 9. All the sensors showed a decrease in resistance upon exposure to ethanol vapor and an increase in resistance when ethanol vapor was removed. From Fig. 8 and 9, it is clear that 0.3 M films shows highest sensitivity compared to 0.1 and 0.2 M films. It is interesting to note that, there is an increase in the sensitivity of 0.3 M film from 33.66 to 36.84 as ethanol concentration increases. The above result indicates the dependence of sensitivity on ethanol concentration (Parmar and Rajanna, 2011).

During sensing the reversible interaction of gas with the surface of the material can be influenced by many factors, including internal and external causes, such as natural properties of base material, surface areas and microstructure of sensing layers, surface additives, temperature and humidity. In addition to the above mentioned factors, the prime factor that determines the gas response is the amount of oxygen adsorbed by thin film surface and it in turn depends on operating temperature, particle size and specific area of the sensor (Wang *et al*., 2010).

The grain size and pores of deposited CuO films affect the sensing capability. The transport of ethanol gas through the pores takes place by diffusion equation (Terry *et al*., 1998).

$$D_k = 4r/3(2RT/3.14M)^{(1/2)}$$

where, r is the pore radius, M is the molecular weight of the gas, R is the gas constant and T is the temperature. It follows that D_k is proportional to r which would depend on the grain size of the metal oxide used. Thus 0.3 M CuO sensor film which possesses highest grain size with highly oriented crystalline nature and more amount of pores revealed largest gas response compared to 0.1 and 0.2 M CuO films.

CONCLUSION

CuO thin films were deposited on glass substrates by Spray pyrolysis technique for 0.1, 0.2 and 0.3 molar concentrations. X-ray diffraction patterns of the films revealed the formation of polycrystalline CuO thin films having monoclinic structure with a grain size ranging from

35 to 54 nm. Crystalline nature of deposited films increases with increase in molar concentration. The microstrain and dislocation density were found to decrease with increase in molar concentration. The microstructure of the thin film prepared at 0.1 M exhibited needle like appearance while 0.2 M and 0.3 M CuO films had a porous structure. It is interesting to note that 0.3 M CuO thin film had larger number of pores compared with 0.2 M film. The presence of copper and oxygen in the prepared samples was confirmed from EDAX spectra. The elemental composition analysis confirmed the enrichment of copper in the prepared samples with increase in molar concentration. Electrical study of prepared samples revealed that 0.3 M film had the highest conductivity and lowest activation energy. The characteristic Raman peaks at 300, 610 and 1274 cm^{-1} observed from Laser Raman spectral results for the prepared samples confirmed the formation of copper oxide. Ethanol gas sensing measurements were performed on CuO thin films. It was observed that the film prepared at 0.3 M exhibited highest gas sensing property for 100 and 200 ppm ethanol vapour compared to 0.1 and 0.2 M CuO thin films.

REFERENCES

Balamurugan, B. and B.R. Mehta, 2001. Optical and structural properties of nanocrystalline copper oxide thin films prepared by activated reactive evaporation. Thin Solid Films, 396: 90-96.

Bari, R.H., S.B. Patil and A.R. Bari, 2013. Spray-pyrolized nanostructured CuO thin films for H_2S gas sensor. Int. Nano Lett., Vol. 3 10.1186/2228-5326-3-12

Brown, K.E. and K.S. Choi, 2006. Electrochemical synthesis and characterization of transparent nanocrystalline Cu2O films and their conversion to CuO films. Chem. Commun., 31: 3311-3313.

Chen, L.B., N. Lu, C.M. Xu, H.C. Yu and T.H. Wang, 2009. Electrochemical performance of polycrystalline CuO nanowires as anode material for Li ion batteries. Electrochim Acta, 54: 4198-4201.

Drobny, V.F. and D.L. Pulfrey, 1979. Properties of reactively-sputtered copper oxide thin films. Thin Solid Films, 61: 89-98.

Ferreia, F.F., M.H. Tabacniks, M.C.A. Fantinia, I.C. Fariab and A. Goren, 1996. Electrochromic nickel oxide thin films deposited under different sputtering conditions. Solid State Iconics, 86-88: 971-976.

Gong, Y.S., C. Lee and C.K. Yang, 1995. Atomic force microscopy and Raman spectroscopy studies on the oxidation of Cu thin films. J. Applied Phys., 77: 5422-5425.

Huang, L.S., S.G. Yang, T. Li, B.X. Gu, Y.W. Du, Y.N. Lu and S.Z. Shi, 2004. Preparation of large-scale cupric oxide nanowires by thermal evaporation method. J. Cryst. Growth, 260: 130-135.

Kose, S., F. Atay, V. Bilgin and I. Akyuz, 2008. Some physical properties of copper oxide films: The effect of substrate temperature. Mater. Chem. Phys., 111: 351-358.

Liu, H., X. Zhang, L. Li, Y.X. Wang and K.H. Gao *et al*., 2007. Role of point defects in room-temperature ferromagnetism of Cr-doped ZnO. Appl. Phys. Lett., 91: 0725111-0725113.

Maruyama, T., 1998. Copper oxide thin films prepared from copper dipivaloylmethanate and oxygen by chemical vapor deposition. Japanese J. Applied Phys., 37: 4099-4102.

Morales, J., L. Sanchez, F. Martin, J.R. Ramos-Barrado and M. Sanchez, 2004. Nanostructured CuO thin film electrodes prepared by spray pyrolysis: A simple method for enhancing the electrochemical performance of CuO in lithium cells. Electrochimica Acta, 49: 4589-4597.

Mustafa, O., 2008. Influence of grain size on electrical and optical properties of InP films Chin. Phys. Lett, Vol. 25.

Parmar, M. and K. Rajanna, 2011. Copper (II) oxide thin film for methanol and ethanol sensing. Int. J. smart Sensing Intell. Syst., 4: 710-725.

Patrocinio, A.O.T., L.G. Paterno and N.Y. Murakamilha, 2009. Layer-by-layer TiO2 films as efficient blocking layers in dye-sensitized solar cells. J. Photochem. Photobiol. A: Chem., 205: 23-27.

Pierson, J.F., A. Thobor-Keck and A. Billard, 2003. Cuprite, paramelaconite and tenorite films deposited by reactive magnetron sputtering. Applied Surf. Sci., 210: 359-367.

Rajaram, K., E. Savarimuthu and S. Arumugam, 2013. Structural, surface morphological and electrial properties of spray pyrolysis made Cu/Cu2O composite films for different molar concentration of Cu (OAc)2. Res. J. Mater. Sci., 1: 18-21.

Ray, S.C., 2001. Preparation of copper oxide thin film by the sol-gel-like dip technique and study of their structural and optical properties. Solar Energy Mater. Solar Cells, 68: 307-312.

Saito, S., M. Miyayama, K. Koumoto and H. Yanagida, 1985. Gas sensing characteristics of porous ZnO and Pt/ZnO ceramics. J. Am. Ceramic Soc., 68: 40-43.

Santra, K., C.K. Sarkar, M.K. Mukherjee and B. Ghosh, 1992. Copper oxide thin films grown by plasma evaporation method. Thin Solid Films, 213: 226-229.

Serin, N., T. Serin, S. Horzum and Y. Celik, 2005. Annealing effects on the properties of copper oxide thin films prepared by chemical deposition. Semiconductor Sci. Technol., Vol. 20. 10.1088/0268-1242/20/5/012

Swankar, R.K., S.C. Singh and R. Gopal, 2009. CTAB assisted oxidation of copper nanoparticles synthesized by pulsed laser ablation and its characterization. Proceedings of International Conference 1st International Conference on Nanostructured Materials and Nanocomposites, April 6-8, 2009, Kottayam, India, pp: 23-29.

Terry, P.A., M. Anderson and I. Tejedor, 1998. Catalytic dehydrogenation of cyclohexane using coated silica oxide ceramic membranes. J. Porous Mater., 6: 267-274.

Traversa, E., 1995. Intelligent ceramic materials for chemical sensors. J. Intell. Mater. Syst. Struct., 6: 860-869.

Ueda, N., H. Maeda, H. Hosono and H. Kawazoe, 1998. Band-gap widening of CdO thin films. J. Applied Phys., 84: 6174-6177.

Wang, C.X., L.W. Yin, L.Y. Zhang, D. Xiang and R. Gao, 2010. Metal oxide gas sensors: Sensitivity and influencing factors. Sensors, 10: 2088-2106.

Zhu, H., F. Zhao, L. Pan, Y. Zhang, C. Fan, Y. Zhang and J.Q. Xiao, 2007. Structural and magnetic properties of Mn-doped CuO thin films. J. Appl. Phys., 101: 09H1111-09H1113.

Zhu, Y.W., T. Yu, F.C. Cheong, X.J. Xu and C.T. Lim *et al.*, 2005. Large-scale synthesis and field emission properties of vertically oriented CuO nanowire films. Nanotechnology, 16: 88-92.