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Ammonia, acetone and ethanol gas sensing characteristics of CuO thin films grown by sputtering

Anju Anna Jacob[1], L. Balakrishnan[2,*], S. R. Meher[3], R. Sivacoumar[4], K. Shambavi[5], and Z. C. Alex[4]

[1]School of Electronics Engineering, VIT University, Vellore 632 014, India.
[2]Department of Physics, Government College of Technology, Coimbatore 641 013, India.
[3]Department of Physics, School of Advanced Sciences, VIT University, Vellore 632 014, India.
[4]Department of Sensor and Biomedical Technology, School of Electronics Engineering, VIT University, Vellore 632 014, India
[5]Department of Communication, School of Electronics Engineering, VIT University, Vellore 632 014, India.

*Email: bslv85@gmail.com

Abstract. Here, we have reported the sensing characteristics of CuO thin films towards volatile gases like ammonia, acetone and ethanol. The CuO films were deposited on glass substrate by RF magnetron sputtering at 350 ºC and 400 ºC. The characteristics of CuO thin films grown at both temperatures were analyzed using X-ray diffractometer (XRD), UV-Vis spectrometer, atomic force microscope (AFM), scanning electron microscope (SEM) and Fourier transform infrared spectrometer (FTIR). The thin films showed mesoporous morphology with average crystallite size of 78 nm and 36 nm for films grown at 350 ºC and 400 ºC, respectively. As the film grown at 400 ºC showed better properties, it has been preferred for the gas sensing analysis. Gas sensing properties of the film towards different concentration (50-250 ppm) of ammonia, acetone and ethanol were studied in chemi-resistive mode. As expected, an increase in resistance with concentration of gases was observed due to the p-type nature of CuO thin films. Further, the film showed comparatively better sensitivity towards ethanol than other gases.

Keywords: Thin film, CuO, sputtering, Gas sensor, Ethanol sensing.

1. Introduction

Novel gas sensors development are of great concern due to its widespread applications in automobiles, safety, environmental control, indoor air quality, food, medicine etc., [1–5]. For the past few decades, semiconducting metal oxide (SMO) based gas sensors are extensively studied and developed. SMOs strike as being best candidate for gas sensing materials, considering their high sensitivity along with easy fabrication, low cost, miniaturized dimension, reliability etc.,

A wide range of SMOs like SnO2, ZnO, CuO, TiO_2, WO_3, Fe_2O_3 etc., have been reported as gas sensing materials[6–11]. Cupric oxide (CuO) is one among the SMOs that exhibits p-type conductivity with a narrow band gap of 1.2 eV and has widespread applications in the field of gas sensors,

catalysis, electrochemical cells, field emission displays, etc. Considerably good electrical properties, high absorption coefficient, catalytic reactivity, stability in air and earth abundance make it a promising candidate for the fabrication of gas sensors[12–14]. Taking up the advantages as sensing material, p-type SMOs are prone to well exchange of lattice oxygen with target gas. Furthermore, the conductivity of p-type oxides are remarkably less dependent on temperature at higher ranges. Also, CuO is a prominent catalytic material. All these benefits for the betterment of sensitivity, stability and life time of the sensors[15–17].

CuO thin films for gas sensing can be grown using various methods like chemical vapor deposition, thermal oxidation, solvo-thermal technique, DC or RF magnetron sputtering etc.,[8,12,18–20]. Among these the film properties like thickness and uniformity can be effectively controlled using RF magnetron technique. Also, it has the advantages of better tuning of grain morphology, stoichiometry and crystallinity of the film[21,22].

In this work, we have reported the deposition of uniform and crystalline CuO thin films by RF magnetron sputtering technique and its sensing response towards acetone, ammonia and ethanol gases.

2. Materials and Methods

CuO thin films were deposited on glass substrate of size 2×2 cm^2 by RF reactive magnetron sputtering technique using metallic Cu target. Oxygen and argon were used as the reactive and sputtering gases with gas pressure 0.02 mbar and 0.01 mbar, respectively. The substrates were fixed on a substrate holder at a distance of 7 cm above the target. For deposition of CuO thin films sputtering was done for 20 minutes at 350 ºC and 400 ºC.

The properties of films were studied using X-Ray diffractometer (XRD), atomic force microscope (AFM), scanning electron microscope (SEM), Fourier transform infra-red (FTIR) spectrometer and UV-Vis spectrometer. For gas sensing characteristics, aluminum interdigitated electrodes were made on the films using metal evaporation technique. The electrical characteristics of the films for gas sensing analysis were studied using Agilent B2901A Precision Source/Measure Unit. The gas sensing characteristics of the film was studied in chemi-resistive mode. The change in resistivity due to the variation in concentration of free electrons through the reaction with the target gas can be monitored for the detection and quantification of gases[23].

3. Results and Discussion

The X-ray diffraction pattern of CuO thin films grown by sputtering at substrate temperature of 350 ºC and 400 ºC are shown in Fig. 1a and 1b respectively. The patterns confirm that the films deposited were polycrystalline in nature with monoclinic structure and the film coated at 400 ºC shows better crystallinity. Both the films exhibited a single diffraction peak at $2\theta = 37.73$ corresponding to (111) orientation of CuO thin film which conveys the preferential orientation of the films along (111) plane. The grain size of the films (D) was evaluated from the full width half maximum (FWHM) intensity of X-ray diffraction peak of CuO using Scherrer's relation,

$$D = \frac{k\lambda}{\beta cos\theta}$$ (1)

where, k is shape factor generally it has been taken as 0.89 for spherical shape, β is the FWHM of the (111) peak measured in radians. The calculated grain sizes of the films are 78 nm and 36 nm for substrate temperatures 350 ºC and 400 ºC, respectively.

The UV-Vis transmission and absorption spectra of the cupric oxide thin films deposited on glass substrates by RF magnetron sputtering is shown in Fig. 2a and 2b. Both the films showed approximately 57% of transmittance in the visible region. Sharp fall in the optical transmittance at shorter wavelengths resulted from the excitation of charge carriers across the optical band gap.

To determine the optical band gap, absorption coefficient (α) of the film was calculated using the following relation,

$$\alpha(\nu) = 2.303\left(\frac{Abs}{t}\right) \tag{2}$$

where, Abs is the optical absorbance and t is the film thickness. The optical band gap of the films was estimated by using Tauc's equation,

$$\alpha h\nu = C\left(h\nu - E_g\right)^{\frac{1}{2}} \tag{3}$$

where, $h\nu$ is the energy of the incidence photon, C is a constant and Eg is the optical band gap.
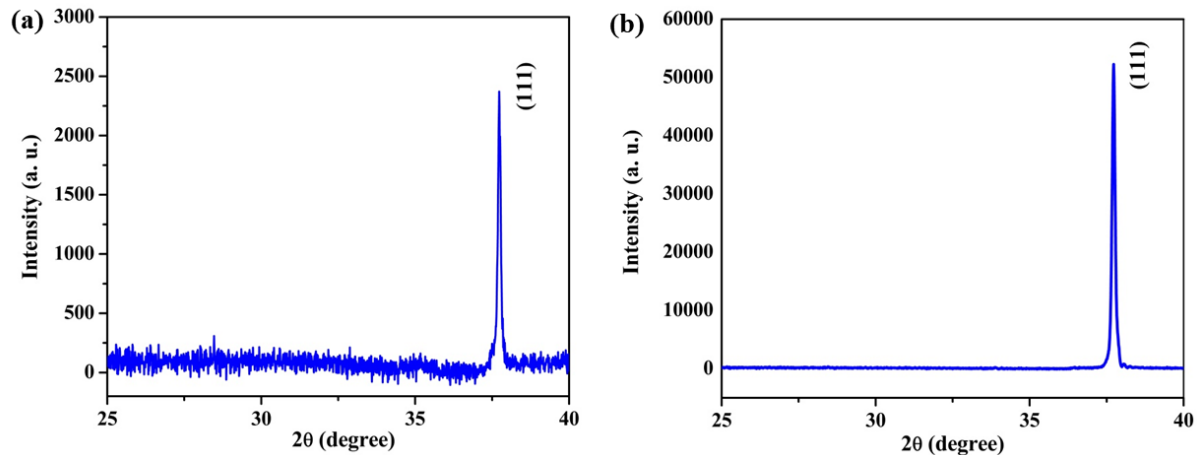
Figure 1. XRD pattern of CuO film at (a) 350 ºC and (b) 400 ºC.

The sample possesses a direct band gap of 2 eV for the films coated at 350 ºC and 2.4 eV for the films coated at 400 ºC. The change in band width is mostly due to increase in growth temperature, which results in improved crystallinity. Also, the deviation from bulk optical band gap may be attributed to the Burstein-Moss effect and quantum confinement[15,24].
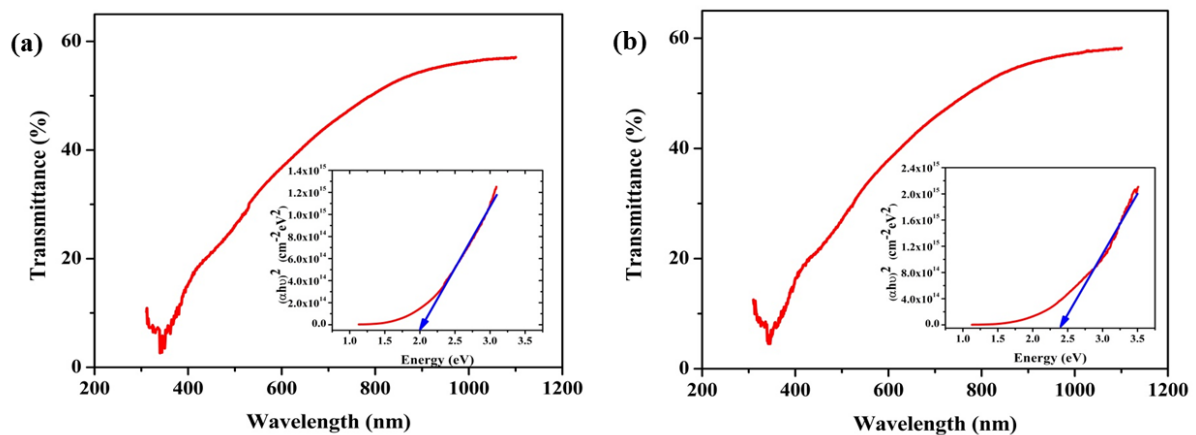

Figure 2. UV-Spectrum of CuO film at (a) 350 ºC and (b) 400 ºC.

Surface morphology of the CuO thin films were studied by atomic force microscopy (AFM). Figures 3a and 3b shows the three dimensional AFM morphology of CuO thin films deposited at different temperatures. The peak to valley roughness of the CuO thin films grown at 350 ºC and 400 ºC are 86.96 and 44.75 nm, respectively and the average roughness of the films are found as 6.41 and 3.83 nm. It was observed that films are polycrystalline and consisted of smaller grains. The results do exhibit apparent evolution in film grain morphologies with increasing substrate temperatures. The

deposited CuO thin film at 400 ºC exhibits much smoother surface morphology as compared to the film grown at 350 ºC.

Figures 4a and 4b shows the SEM images of the films grown at 350 ºC and 400 ºC, respectively. The average particle sizes calculated from SEM images were 67 nm and 31.6 nm for the films grown at 350 ºC and 400 ºC respectively. The SEM image shows the spongy porous appearance and randomly disperses particles on the surface of the thin film. Both the films showed slight mesoporous surface morphology which can enable them to use efficiently for gas sensor applications.
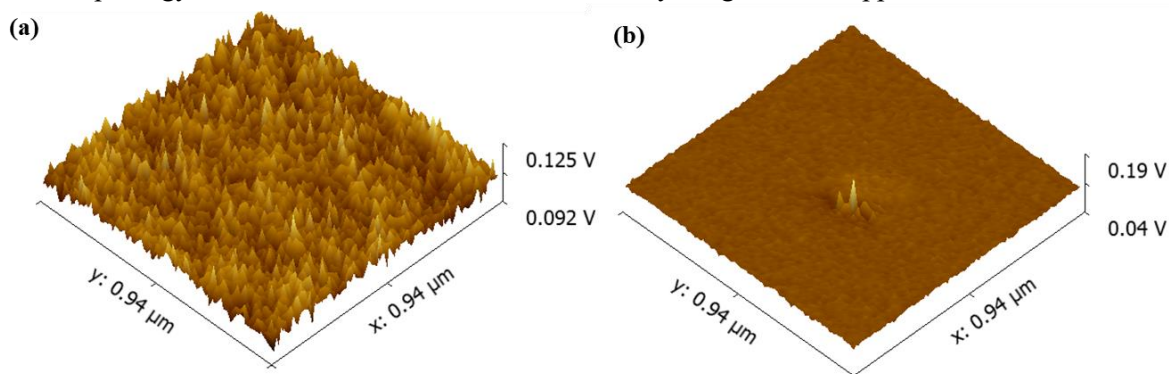

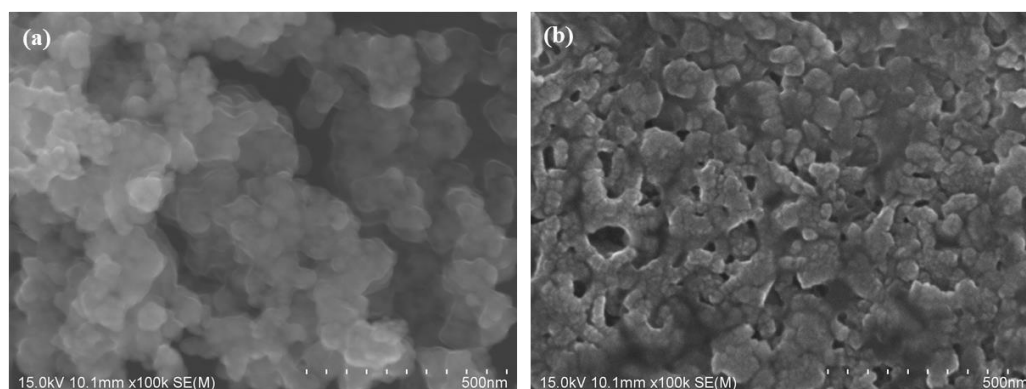**Figure 3.** AFM images of CuO film at (a) 350 ºC and (b) 400 ºC.

Figure 4. SEM images of CuO film at (a) 350 º C and (b) 400 º C.

Figures 5a and 5b shows the room temperature Fourier transform infrared (FTIR) spectra of CuO thin films on glass substrate deposited by sputtering. The FTIR spectrum of CuO thin films shows three characteristic strong peaks associated with the Cu-O vibrations of monoclinic CuO. At 350 ºC the peaks are at 442, 467 and 560 cm^{-1}, whereas at 400 ºC, the peaks are at 416, 442 and 558 cm^{-1}. The strong band located at about 558 cm^{-1} in both films is due to the Cu-O stretching along (111) direction.

From the XRD, AFM and SEM analysis it has been found that the film grown at 400 ºC shows better properties compared to the film grown at 350 ºC, hence it has been selected for further sensing studies. The sensitivity of the film towards ammonia, acetone and ethanol gases were analyzed in chemi-resistive mode and are shown in Fig. 6.

The adsorbed oxygen on the surface of the thin film traps electrons from p-type CuO film which thereby increases the hole concentration. When the gases ethanol, acetone and ammonia are introduced, which interacts with adsorbed oxygen or lattice oxygen, releases electrons which in turn decreases the hole concentration and hence reduces conductivity. This change is resistivity/conductivity of film, with varying sensing gas concentration is obtained from the I-V characteristics to measure the sensitivity. Sensitivity is calculated using the following relation,

$$S = \left[\frac{R_{gas} - R_{air}}{R_{air}} \right] \times 100 \qquad (4)$$

where, R_{air} is the resistance of the film in air ambience and R_{gas} is the resistance of the film upon gas exposure.
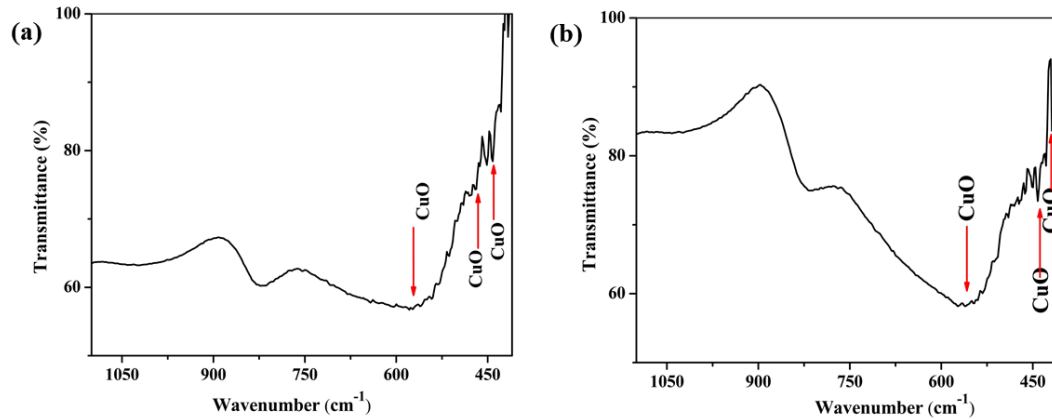

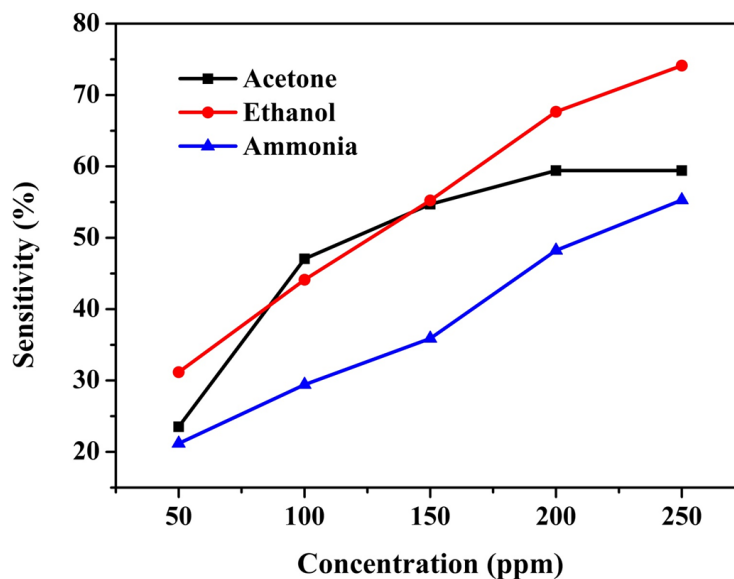**Figure 5.** FTIR Spectrum of CuO film at (a) 350 ºC and (b) 400 ºC.

Figure 6. Sensitivity response of CuO thin film sensor towards different concentration of acetone, ethanol and ammonia gases.

Further, it has been found that the film showed better sensitivity towards ethanol compared to acetone and ammonia due to the enhanced catalytic activity towards ethanol. The good sensitivity of the film can be attributed to its porous morphology and also in the case of CuO film, both adsorbed oxygen and lattice oxygen will take part in sensing reaction.

4. Conclusion
Polycrystalline CuO thin films were deposited using RF magnetron sputtering technique at 350 ºC and 400 ºC growth temperatures. After detailed structural, morphological and compositional study the film grown at 400 ºC which exhibited more advantageous properties was selected for further sensing

studies. The film showed good sensitivity towards ethanol compared to other gases. The enhanced catalytic activity towards ethanol and porous structure makes CuO thin films preferable candidates for the fabrication of ethanol gas sensors.

References

[1]   Afzal A, Cioffi N, Sabbatini L and Torsi L 2012 *B Chem.* **171**–**172** 25–42
[2]   Kanan S M, El-Kadri O M, Abu-Yousef I A and Kanan M C 2009 *Sensors* **9** 8158–96
[3]   Kim Y S, Hwang I S, Kim S J, Lee C Y and Lee J H 2008 *Sensors Actuators, B Chem.* **135** 298–303
[4]   Hu P, Du G, Zhou W, Cui J, Lin J, Liu H, Liu D, Wang J and Chen S 2010 *ACS Appl. Mater. Interfaces* **2** 3263–9
[5]   Nam J M, Stoeva S I and Mirkin C A 2004 *J. Am. Chem. Soc.* **126** 5932–3
[6]   Bhanjana G, Dilbaghi N, Kumar R, Umar A and Kumar S 2015 *Electrochim. Acta* **169** 97–102
[7]   Rai P, Raj S, Ko K J, Park K K and Yu Y T 2013 *Sensors Actuators, B Chem.* **178** 107–12
[8]   Yang C, Su X, Xiao F, Jian J and Wang J 2011 *Sensors Actuators, B Chem.* **158** 299–303
[9]   Bayata F, Saruhan-Brings B and Ürgen M 2014 *B Chem.* **204** 109–18
[10]   Hubner M, Simion C E, Haensch A, Barsan N and Weimar U 2010 *Sensors Actuators, B Chem.* **151** 103–6
[11]   Tang H, Yan M, Zhang H, Li S, Ma X, Wang M and Yang D 2006 *Sensors Actuators B Chem.* **114** 910–5
[12]   Parmar M and Rajanna K 2011 *Int. J. Smart Sens. Intell. Syst.* **4** 710–25
[13]   Rakhshani A E 1986 *Solid State Electron.* **29** 7–17
[14]   Liu X-W, Wang F-Y, Zhen F and Huang J-R 2012 *RSC Adv.* **2** 7647
[15]   Korotcenkov G 2007 *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **139** 1–23
[16]   Lu Y-M, Chen J-Y and Wey T-S 2004 *Mater. Res. Soc. Symp. Proc.* **822** 55–64
[17]   Heiland G 1954 *Phys.* **138** 459–64
[18]   Barreca D, Comini E, Gasparotto A, Maccato C, Sada C, Sberveglieri G and Tondello E 2009 *Sensors Actuators, B Chem.* **141** 270–5
[19]   Raksa P, Gardchareon A, Chairuangsri T, Mangkorntong P, Mangkorntong N and Choopun S 2009 *Ceram. Int.* **35** 649–52
[20]   Zoolfakar A S, Ahmad M Z, Rani R A, Ou J Z, Balendhran S, Zhuiykov S, Latham K, Wlodarski W and Kalantar-Zadeh K 2013 *Sensors Actuators, B Chem.* **185** 620–7
[21]   Ogwu A A, Bouquerel E, Ademosu O, Moh S, Crossan E and Placido F 2005 *Acta Mater.* **53** 5151–9
[22]   Pierson J F, Thobor-Keck A and Billard A 2003 *Appl. Surf. Sci.* **210** 359–67
[23]   Wetchakun K, Samerjai T, Tamaekong N, Liewhiran C, Siriwong C, Kruefu V, Wisitsoraat A, Tuantranont A and Phanichphant S 2011 *Sensors Actuators, B Chem.* **160** 580–91
[24]   Kamat P V, Dimitrijevic N M and Nozik A J 1989 *J. Phys. Chem.* **93** 2873–5

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