Copper oxide thin films for ethanol sensing

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Abstract. The present is a study of a new active layer for ethanol (C₂H₅OH) vapour sensing devices based on copper oxide (CuO). CuO films were prepared by spray ultrasonic pyrolysis at a substrate temperature of 350 °C. Films microstructure was examined by X-ray diffraction and atomic force microscopy. Vapour-sensing testing was conducted using static vapour-sensing system, at different operating temperatures in the range of 100°C to 175°C for the vapour concentration of 300 ppm. The results show a high response of 45% at relatively low operating temperatures of 150°C towards ethanol vapour.

1. Introduction

Gas sensors based on semiconducting metal oxides are widely studies for solving applications spanning from the detection of toxic, dangerous and pollutant gas. They are having several advantages such as easy and low cost production, controlled size and simple measure electronics [1, 2]. However the performance of such gas sensors is considerably influenced by the proprieties of sensing materials such as the morphology and structure. Among the used sensing materials, copper oxide have been the subject of interest for the detection of many different gas such as H₂ [3], NO₃, CO and C₅H₁₀OH [4]. CuO is generally p-type semiconductor with bad gap in the range of 1.21 to 1.51 eV [5, 6]. Several researches in the field of gas sensing have been reported, they are based on the association of metal oxide with CuO, and forming of the p-n heterojuction such as CuO/ZnO, CuO/Cu₂O and CuO/SnO₂. These structures have achieved a high sensitivity and selectivity [7–9]. CuO films have been deposited by various conventional deposition methods; with include electrodeposition [10]; dip coating [11]; chemical vapor deposition [12] and reactive sputtering [13]. Ultrasonic spray pyrolysis technique has been used extensively because it is very attractive method to deposit adherence and stochiometric thin films. The important features of this technique are the low cost and the simplicity of equipments.

In this work, we have synthesized CuO films by ultrasonic spray pyrolysis technique and investigate their ethanol vapor sensing performance.

2. Experimental

2.1. Preparation of CuO thin film

Copper oxide thin film has been prepared on glass substrates by ultrasonic spray pyrolysis. The precursor solution was prepared by dissolving 0.05 M copper chloride (CuCl₂·2H₂O) in distilled water. Then, the precursor solution sprayed in fine droplets of 40 μm in diameter, by an ultrasonic generator.
on heated glass substrate. Film was formed by pyrolytic reaction. During deposition, the substrate temperature is kept at 350°C. The deposition time was fixed 10 min. Films structural properties were determined by XRD using Philips X’Pert system with Cu K\textsubscript{α} radiation (\(\lambda_{\text{Cu}} = 0.154056\) nm). The reflections were taken at room temperature and at 2\(\theta\) value ranged from 20° to 80°. The film surface morphology was characterized by using atomic force microscopy (AFM) was carried out in air at ambient condition (300 K) using Nanosurf easy scan 2.

2.2 Sensing system for measurement of vapour response

The vapour-sensing studies were carried out using a static gas chamber to ethanol vapor detection in air ambient. The CuO thin film deposited at 350°C was used as the sensing elements. Two gold interdigitated electrodes were evaporated on the top surface of the sensing layer. A thermocouple is mounted to measure the temperature. The output of the thermocouple is connected to a temperature indicator. Gas concentration inside the system is achieved by injecting a known volume of test vapor.

The electrical response of the sensing layer was investigated under two atmospheres: synthetic air and a mixture of air + vapour ethanol (300 ppm) by registering the variations in resistance with Keithley 617 programmable electrometer as a function of time. The response of the sensor was calculated using the expression given in the literature [14]:

\[
\text{Sensitivity} = \left| \frac{R_v}{R_{\text{air}}} \right| / R_{\text{air}} \times 100
\]  

(1)

Where \(R_{\text{air}}\) is the reference resistance in the presence of air and \(R_v\) is the measured resistance in the presence of ethanol.

3. Results and discussion

3.2 Structural characterization of CuO thin films

The XRD study was primarily carried to determine the structure and orientation of deposited thin films CuO. Figure 1 shows the XRD diffraction pattern of the sensitive CuO thin film. The presence of intense peaks in the XRD patterns of the film indicates that the CuO film is polycrystalline in nature. Two most prominent peaks can be clearly seen at 2\(\theta\) value 35.5° and 38.7° corresponding to atomic planes (002) and (111), respectively of CuO phase. No peak corresponding to Cu2O phase of copper oxide has appeared in the XRD pattern thereby indicating the formation of pure CuO films.

![Figure 1. XRD pattern of the sensitive layer CuO thin film.](image)
Atomic force microscopy (AFM) has been proved to be a unique method to analyze surface morphology of a film. Figure 2(a and b) shows typical two dimensional (2-D) and three dimensional (3-D) AFM image of CuO film deposited on glass substrate. The (3-D) image indicate that the surface evolution of the film shows hills and valley like structures, which are uniformly distributed over the entire substrate surface. The 2-D images of the deposits show compact and granular morphology with presence of pores in the surface this is a good argument to increase the sensitivity of the gas sensor. It is recognized that porous materials have been extensively investigated due to high surface area and accordable pore size in the fields of catalysis and gas sensing.

![Figure 2. (a) The AFM 2-D image, (b) the AFM 3-D image of the deposited CuO film.](image)

3.3 Ethanol sensing characteristics of CuO thin films

The response of semiconducteur based on sensor is greatly influenced by its operating temperature. In fact, the adsorption of gases is directly related to the temperature at the surface of the sensing layer. In order to determine the operation temperature for the sensor based on CuO thin film to vapor ethanol, it was exposed to 300 ppm of ethanol at different operation temperature between 100 and 175 °C and the resultant responses are showing in figure 3. A typical operation temperature correspond to maximum response is widely reported in literature. In our case, the evolution of the response of the layer shows that this maximum is located around 150°C.

![Figure 3. Sensor response curves of the CuO based sensor towards ethanol (300 ppm) at different operating temperatures](image)
Figure 4 shows the resistance transient of CuO layer recorded at the optimum temperature of 150 °C. The decrease in resistance when vapor of ethanol is injected reveals that \( R_v \) is lower than \( R_{air} \). The response is found to be 45% for 300 ppm of ethanol concentration at operation temperature. The CuO based sensor fabricated by Mitesh.al [15] shows a relatively sensor response of 8.3% towards 700 ppm ethanol vapor at operation temperature of 400 °C. It is observed that our thin film CuO based sensor has the lowest operating temperature (150 °C) as well as the highest response (45%). The higher response of sensor in this case may be attributed to the large amount of porosity in the material as suggested by Jimenez et al. [16]. The response and recovery time are respectively the duration by which the sensor response reaches to almost 90% of the saturation value and the time to recover its initial value when the vapor is evacuated. The sensing layer exhibits response and recovery times of 2.98 min and 2.11 min respectively. The long response and recovery time observed is probably the result of a complex mechanism of adsorption and desorption of molecules when the layer is exposed to vapor of ethanol. The kinetics of each of this mechanism is strongly influenced and controlled by the morphology and deposition conditions of the film. Modification of these conditions to obtain more porosity and decrease of the layer thickness may be a suitable method to improve the response time.

![Figure 4](image.png)

**Figure 4.** Resistances change vs. time during 300 ppm of ethanol sensing at the operation temperature.

4. **Conclusion**

A CuO thin film was tested for ethanol vapour sensing. This film was deposited by spray ultrasonic pyrolysis on heated glass substrate. Two gold interdigitated electrodes were used for gas-sensing measurement. The optimal response was obtained at a temperature of 150°C with a value of 45%. These results obtained with a simplified test device are very promising due to the low operating temperature and the high sensitivity of the material. These characteristics are promising for industrial applications, especially in gas and vapour related chemical sensing.

**References**

[1] Tomchenko, A.A.; Harmer, G.P.; Marquis, B.T.; Allen, J.W. Semiconducting metal oxide sensor array for the selective detection of combustion gases. *Sens. Actuat. B* 2003, 93, 126-134.
[2] Kanan, S.M.; El-Kadri, O.M.; Abu-Yousef, I.A.; Kanan, M.C. Semiconducting metal oxide based sensors for selective gas pollutant detection. *Sensors* 2009, 9, 8158-8196.
[3] S.A. Patil, L.A. Patil, D.R. Patil, G.H. Jain, M.S. Wagh, CuO-modified tin titanate thick film resistors as H2gas sensors, Sens. Actuators B: Chem. 123 (2007) 233–239.
[4] P. Samarasekara, N.T.R.N. Kumara, N.U.S. Yapa, J. Phys.: Condens. Matter 18 (2006) 2417
[5] Marabelli F, Parraviciny GB, Drioli FS. Phys Rev B 1995;52:1433.
[6] Ghijsen J, Tjeng LH, Elp JV, Eskes H, Westerink J, Sawatzky GA, Czyzyk MT. Phy Rev B 1988;38:11322.

[7] S.J. Appleyard, Simple photovoltaic cells for exploring solar energy concepts, Phys. Educ. 41 (5) (2006) 409–419.

[8] V.R. Katti, A.K. Debnath, K.P. Muthe, Manmeet Kaur, A.K. Dua, S.C. Gadkari, S.K. Gupta, V.C. Sahni, Mechanism of drifts in H2S sensing properties of SnO2/CuO composite thin film sensors prepared by thermal evaporation, Sens. Actuators B 96 (2003) 245–252.

[9] S. Aygun, D. Cann, Hydrogen sensitivity of doped CuO/ZnO heterocontact sensors, Sens. Actuators B 106 (2005) 837–842.

[10] E.R. Kari, K.S. Brown, Choi, Electrochemical synthesis and characterization of transparent nanocrystalline Cu2O films and their conversion to CuO films, Chem. Commun. (2006) 3311 3313.

[11] N. Serin, T. Serin, S. Horzum, Y. Celik, Annealing effects on the properties of copper oxide thin films prepared by chemical deposition, Semicond. Sci. Technol. 20 (5) (2005) 398.

[12] T. Maruyama, Copper oxide thin films prepared from copper dipivaloylmethanate and oxygen by chemical vapor deposition, Jpn. J. Appl. Phys. 37(1998) 4099–4102.

[13] V.F. Drobny, D.L. Pulfray, Properties of reactivity-sputtered copper oxide thin films, Thin Soild Films 61 (1979) 89–98.

[14] S. Kar, B.N. Pal, S. Chaudhuri, D. Chakravorty, One-dimensional ZnO nanostructure array: synthesis and characterization. J. Phys. Chem. C 110, 4605–4611 (2006).

[15] Mitesh Parmar and K.Rajanna Copper (II) oxide thin film for methanol and ethanol sensing vol. 4, December 2011 710-725.

[16] I. Jimenez, M.A. Centeno, R. Scotti, F. Morazzoni, J. Arbiol, A. Cornet, J.R. Morante, NH3 interaction with chromium-doped WO3 nanocrystalline powders for gas sensing applications, J. Mater. Chem. 14 (2004) 2412–2420.