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Nanostructured Copper Oxide Thin Film for Ethanol Vapor Sensing

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Abstract: Nanostructured copper oxide (CuO) thin films have been deposited onto thoroughly cleaned glass substrates by spray pyrolysis technique. The structural, morphological, optical and electrical properties of the CuO thin films deposited at different concentrations of precursor solution as a function of substrate temperature around 373 K were investigated using XRD, FE-SEM and electrometer respectively. The nanostructured CuO thin films showed significant response towards various concentrations of ethanol vapor and hence this material can used as an effective sensor element to detect ethanol.

Key words: Cerium oxide, spray pyrolysis, gas sensor, volatile organic compounds

INTRODUCTION

Among various metal oxides CuO thin films have attracted researchers due to their potential applications in the fields of solar cells and gas sensors (Akimoto *et al*., 2006; Frietsch *et al*., 2000; Jeong *et al*., 2008; Shishiyanu *et al*., 2006). Presence of copper vacancies in the crystal structure, CuO and Cu_2O materials are known to be a p-type semiconductors (Jeong *et al*., 2008) and hence this material is very much useful for designing junction devices (Muhibbullah *et al*., 2003). CuO is also has received special attention in the design of photovoltaic devices (Nova, 1986; Hu *et al*., 2003). The earlier studies on CuO was mainly focused on their potential use as cathodes in lithium primary cells (Frietsch *et al*., 2000; Samarasekara *et al*., 2006), electrochromic devices (Derin and Kantarli, 2002) nanoscale quantum dots (Nachimuthu *et al*., 2003; Lyubinetsky *et al*., 2004; Balamurugan and Mehta, 2001) and low-friction materials (Goto *et al*., 2004). CuO has also been widely used in semiconducting gas sensors (Rodriguez *et al*., 2003; Berezin and Weichman, 1981) due to its higher activity and selectivity in oxidation and reduction reactions. Due to the availability of CuO with nontoxic nature and low cost CuO thin films are found to be more attractive for different applications.

Among, various deposition techniques, CuO thin films like reactive sputtering (Pierson *et al*., 2003), reactive evaporation (Balamurugan *et al*., 2001), thermal evaporation (Huang *et al*., 2004), sol-gel (Armelao *et al*., 2003; Ray, 2001) chemical, thermal and anodic oxidation (Ray, 2001; Rakhshani, 1986; Musa *et al*., 1998), electrochemical (Niesen and de Guire, 2001; Mahalingam *et al*., 2004) and chemical deposition (Mathew *et al*., 2001), spray pyrolysis (Ristov and Sinadinovski, 1985; Morales *et al*., 2005), is found to be in-expensive and efficient technique. Since, nanostructured CuO thin film as one of the potential materials for chemical sensing have not explored, structural, morphological and sensing behavior of spray deposited nanostructured CuO thin films were studied and reported in the present work.

MATERIALS AND METHODS

CuO thin films were deposited over the glass substrate, using spray pyrolysis technique. The optimized experimental set-up and deposition parameters were reported in our earlier work (Sivalingam *et al*., 2012a, b). Cupric mono acetate ($Cu(C_2H_3O_2)_2.H_2O$) of 99.9% purity from Fisher Scientific, India was used as precursors. The deposition temperature was fixed at 493 K since films deposited below this temperature were found to be less adhesive and powdery in nature.

X-ray powder diffractometer (XRD) (D8 Focus, Bruker, Germany) that radiates Cu K_α of wavelength 1.5418 Å at 2θ range between 20 and 70° was used to study structural properties of CuO films. The surface morphology of CuO films were studied using field emission scanning electron microscope (FE-SEM, 6701F, JEOL, Japan). Further, the sensing behaviour of the nanostructured CuO thin films were studied, using an electrometer (6517A, Keithley, USA) connected to Volatile Organic Compound (VOC) testing chamber of 5 L capacity. The chamber is equipped with digital thermostat

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coupled compact heater and a septum provision for injecting the desired concentration of VOCs.

Preparation of CuO thin film: The precursor solution was prepared by dissolving cupric mono acetate $(Cu(C_2H_3O_2)_2.H_2O$ in 50 mL of distilled water with different molar concentration 0.02, 0.04, 0.06, 0.08 and 0.1 M; each of these cases are represented as C1, C2, C3, C4 and C5 further reference. The thin films were deposited at an optimized deposition temperature of 493 K.

The As-deposited CuO thin films were found to be well adherent on the glass substrate. During pyrolytic process, when fine mists arrive very near to the preheated glass substrates, the mists undergo thermal decomposition which lead to the formation of highly uniform copper oxide film. During the pyrolytic process, possible reaction mechanisms is as follows:

$$Cu(CH_3COO)_3.H_2O+H_2O \rightarrow CuO+2CH_3COOH+H_2O$$

RESULTS AND DISCUSSION

Structural and morphological characterization: The crystallinity and structure of CuO thin film samples, C1, C2, C3, C4 and C5 were analyzed using powder X-ray Diffractometer (XRD). From the XRD profile, sample C1, C2 and C3 does not have any noticeable peaks, it showed that 0.02, 0.04 and 0.06 M concentrations, CuO metal oxide formation of thin films as amorphous nature, shown in Fig. 1a-c. The sample C4 and C5 shown in Fig. 1-e, were found to be polycrystalline in nature with a monoclinic structure of CuO. An increase in the peak intensity with an increase from 0.08-0.1 M molar concentration of the precursor solution was observed in Samples C4 and C5. The peak positions were found to be in well agreement with the JCPDS of CuO (card no. 48-1548).

SE micrograph of samples C1, C2, C3, C4 and C5 are shown in Fig. 2a-e. The films were found to have homogenous nanostructured film with spherical shape nano grains of different size. It is observed that as the concentration increases the grain size were also increased and where found to be in agreement with the grain size calculated from XRD profile of the samples using Scherrer's formula. From the XRD and SE micrograph observations, C4 and C5 samples were taken into consideration for further sensing characteristics.

P-type conductivity of the nanostructured CuO thin films samples C4 and C5 was observed using hot probe method (Golan *et al*., 2006).

Sensing characteristics: Among various VOCs, ethanol is found to be a good marker for quality discrimination for highly perishable products like milk (Ampuero and Bosset, 2003; Marsili, 1999). Hence, the sensing behaviour of CuO thin film samples at various concentrations of ethanol carried out. The response of CuO thin films were calculated using (Varghese and Grimes, 2004). For p-type metal oxide in the presence of a reducing gas response or sensitivity (S) is defined as:

$$S = \frac{(R_g - R_0)}{R_0} \approx \frac{R_g}{R_0}$$

$$\text{if } R_0 << R_g$$

where, R_0 and R_g are the electrical resistance of the film in the absence and presence of VOCs, respectively.

The stabilization of surface resistance of the sensing element under ambient conditions is important to fix R_0 and to calculate the response (Mitra *et al*., 1998). Hence, the initial stabilization of C4 and C5 samples were carried out by placing the sample at 373 K and found to be stabilized around the resistance of 8.27×10^4 Ω and 2.03×10^6 Ω (Fig. 3).

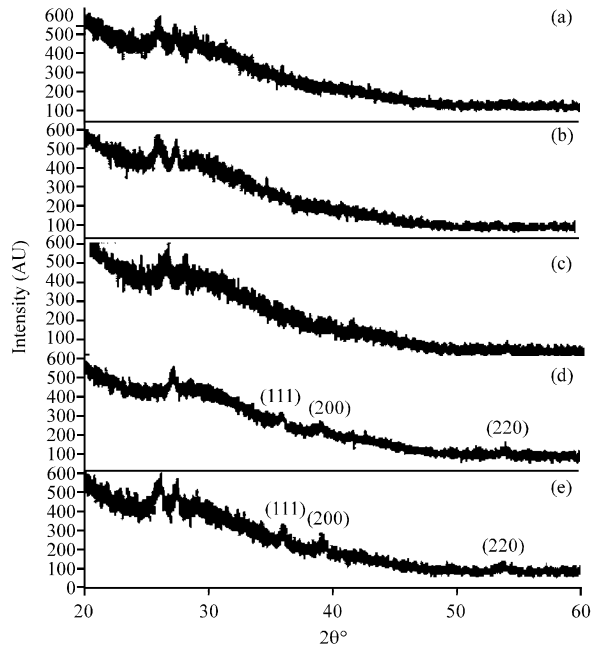

Fig. 1(a-e): XRD patterns of CuO thin film samples prepared by different molar concentrations (a) C1: 0.02, (b) C2: 0.04, (c) C3: 0.06, (d) C4: 0.08 and (e) C5: 0.1 M of precursor solution

Response of sensing element: The sensitivity of the sensing element C4 and C5 towards various concentrations of ethanol were observed and plotted as

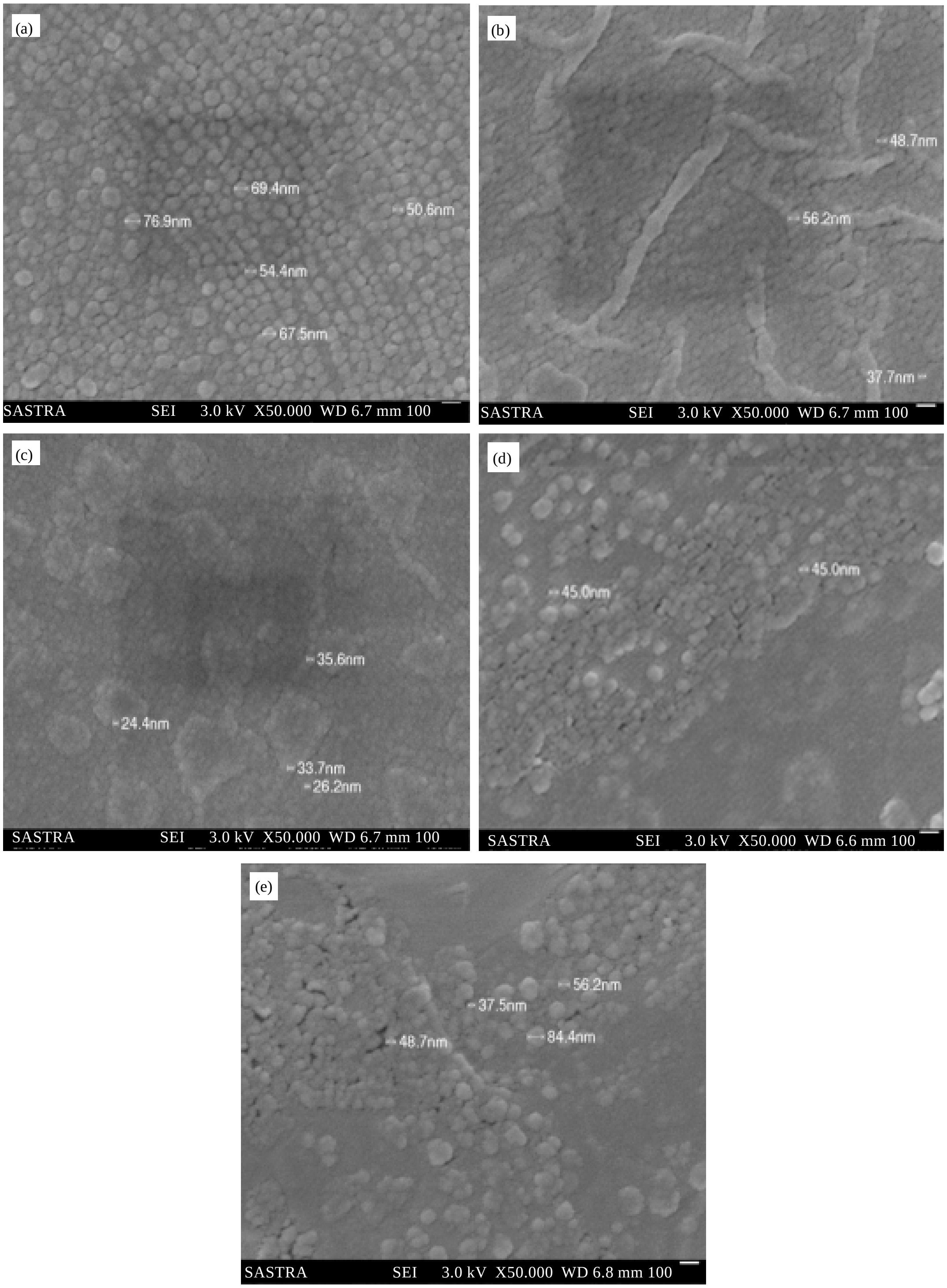

Fig. 2(a-e): SE Micrographs of CuO thin film samples prepared by different molar concentrations (a) C1: 0.02, (b) C2: 0.04, (c) C3: 0.06, (d) C4: 0.08 and (e) C5: 0.1 M of precursor solution

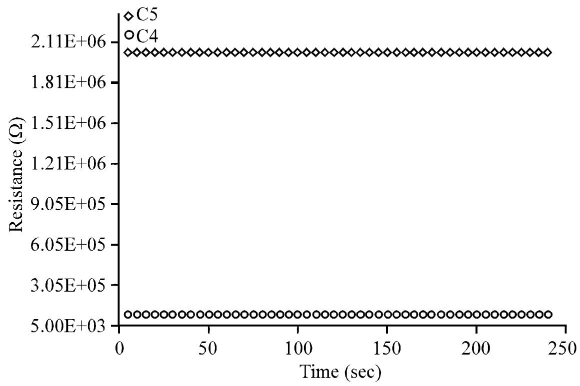

Fig. 3: Baseline of the sensor elements C4 and C5

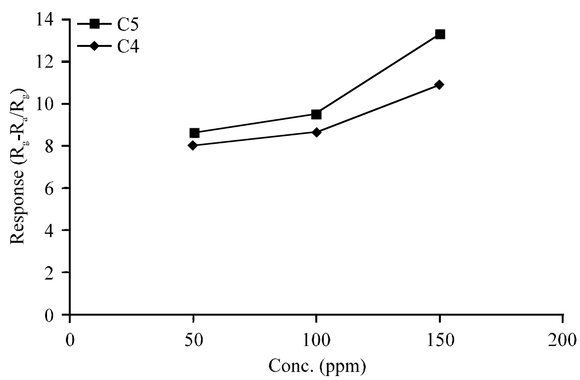

Fig. 4: Sensitivity of CuO thin film samples C4 and C5 towards various concentrations of ethanol

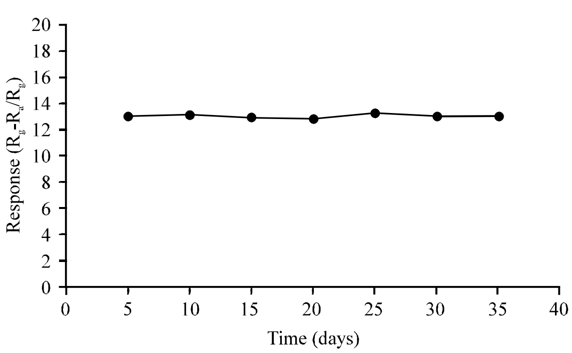

Fig. 5: Stability and Reproducibility of the senor element's response towards 150 ppm of ethanol

shown in Fig. 4. An increase in sensitivity with an increase in precursor solution concentration and in turn the charge carrier. From these observations C5 sample deposited with 0.1 M of cupric mono acetate was found to have appreciable sensitivity towards ethanol. Hence the C5 sample can be effectively used as a sensor element to sense ethanol in an array of electronic-nose sensors.

Sensing element stabilization: The stability and reproducibility of C5 sample stored over a period of 6 months was determined by studying the response repeatedly in the presence of 150 ppm of ethanol at an operating temperature of 373 K over a period of 35 days with the time interval of 5 days. The observed response data shown in Fig. 5 substantiates the stability and reproducibility of the sensing characteristics with a response ~13.

CONCLUSION

Nanostructured CuO thin films were deposited with various precursor concentrations of cupric mono acetate and the film deposited with the precursor concentrations of 0.08 (C4) and 0.1 M (C5) were found to be polycrystalline in nature. From the response of C4 and C5 samples at an operating temperature of 373 K it is noted that the nanostructured CuO thin film deposited with 0.1 M of cupric acetate is found to be a suitable sensing element for ethanol.

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