Volatile organic compound sensing using copper oxide thin films: Addressing the cross sensitivity issue

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ARTICLE INFO

ABSTRACT

We have investigated the sensing characteristics of ethanol, methanol, acetone, and 2-propanol using wet chemical synthesized copper oxide (CuO) thin films deposited on fused quartz substrates. As compared to the volatile organic component (VOC) sensing characteristics of CuO films reported in recent literatures, our thin film sensors offer relatively higher response (%), lower optimized temperature (corresponds to highest response%), better stability, and faster response time. In order to address the cross-sensitivity towards these VOC sensing we had performed fast Fourier transformation (FFT) analyses of the resistance transients. The resultant data matrices extracted from these FFT analyses were used as input parameter in a linear unsupervised principal component analysis (PCA) pattern recognition technique. We have demonstrated that FFT combined with PCA is an excellent tool for differentiating these reducing gases.

1. Introduction

For stringent environmental monitoring for human safety, detection of toxic and flammable volatile organic compounds (VOCs) has received immense attention in recent times [1—4]. The permissible exposure limits for ethanol, methanol, and acetone have been prescribed to be 1000 ppm, 200 ppm, and 1000 ppm respectively [5]. Apart from environmental monitoring, detection of VOCs is also important for industrial process control, medical diagnosis and agricultural industries. Nano-structured 'n' type semiconducting oxides (viz. SnO_2, In_2O_3, ZnO etc) have popularly been used for various types of VOC detection. However, most of these 'n' type oxides are plagued with relatively higher sensor operating temperature (>300 °C), and poor selectivity [6—10]. Mainly due to their extreme sensitivity towards hazardous gases (such as H_2S) and better selectivity to some VOCs, 'p' type semiconducting oxides (viz. CuO, Co_3O_4, MnO, NiO etc) are currently being studied for VOC detection [11—14]. Among these oxides, the band gap of 'p' type CuO is reported to be in the range of 1.2—1.9 eV and its acceptor levels are attributed due to the presence of copper vacancies [15,16]. It is one of the most attractive materials for solar

cells, and electro-chromic devices [17,18]. Recently there are some reports of the detection of a few test gases (such as NO_2, H_2S, NH_3, C_2H_5OH etc) using various nano-structured CuO including nanowires, nano-tubes, nanoflowers, nanobelts, nanoleaves, nanoplates, nanofibers, nanoparticulates etc [11,19—24]. Reviewing these literatures it is apparent that using 'p' type CuO, the gas sensing characteristics of various VOCs has not extensively studied. More research works are required to improve the response (%), sensitivity, stability, and speed of response of CuO sensor towards VOC sensing. Additionally, to the best of our knowledge no work has been reported to address the cross-sensitivity of CuO towards various types of VOC sensing.

In the present work we have synthesized CuO thin film on fused quartz substrate using an economic wet chemical synthesis route. Using CuO sensors, the sensing properties of ethanol, methanol, acetone, and 2-propanol were investigated systematically by varying the operating temperature and gas concentration. We have demonstrated that as compared to other nano-structured CuO sensors used for VOC sensing, CuO thin film sensors offer relatively higher response (%), lower optimized temperature (corresponds to highest response%), better stability, and faster response time. Unfortunately, the thin film CuO sensor is not fully selective to any one of the VOCs studied in the present work. In order to address the cross-sensitivity towards these VOC sensing the data matrices extracted from the fast Fourier transformation (FFT) analyses of the

resistance transients were used as input parameter in a linear un-supervised principal component analysis (PCA) pattern recognition technique. We have demonstrated that FFT combined with PCA is an excellent tool for the differentiation of these reducing gases.

2. Experimental

A wet chemical synthesis route was adopted to deposit CuO thin film on fused quartz substrate. Copper (II) acetate monohydrate (Cu $(COOCH_3)_2$, H_2O) of 99% purity was used as precursor. Copper (II) acetate monohydrate (0.025 mol) was dissolved in 2-propanol solvent. Subsequently 0.025 mol of mono-ethalomine (MEA) and 4 ml of (poly) ethylene glycol (PEG) were added into the solution and stirred for 45 min at 70 °C.The solution for thin film deposition was homogeneous and dark blue in colour. The concentration of the precursor sol for thin film deposition was 0.25 M.

Optically flat quartz substrates were used for CuO film deposition. Prior to film deposition the substrate were cleaned ultrasonically in trichloro-ethylene for 5 min followed by subsequent ultrasonic cleaning in acetone and deionized water (for 3 min each). Subsequently, the cleaned substrates were dried in flowing nitrogen and used for thin film deposition. A spin coating unit (SCU 2007, Apex instruments Co. India) was used for thin film deposition maintaining a spinning speed ~3000 rpm for 20 s. Just after coating the films were heated at 300 °C for 5 min to remove the organic moieties. The coating and firing sequence was repeated for 15 times to attain films about 0.36 μm thick. After final coating films were annealed at 600 °C for 1 h in air for crystallization.

The phase formation behaviour of the annealed thin films were studied by X-ray diffraction (XRD) (Ultima III, Rigaku, Japan) analyses using Cu K_α radiation. XRD data were recorded (in the 2θ range 20—80°) utilizing a scanning speed 3° min^{-1} unless specified otherwise. For X-ray diffraction measurements, the accelerating voltage and current were maintained at 40 kV and 30 mA respectively. The X-ray diffractometer was calibrated using standard silicon powder. The standard powder was prepared from ultra-high purity silicon boules that were crushed and jet milled to a median particle size of 4.1 μm. The resulting powder was then annealed in argon ambient at 1000 °C for 2 h and stored in argon. For selected samples, X-ray diffractograms were also recorded in specific 2θ range using step size of 0.05° and scan speed 0.05°sec^{-1}. The residual stress measurement was performed using a Bruker diffractometer with CuKα source. In all our measurements a flat graphite monochromator and proportional counter was used. The diffractometer was aligned with silicon standard. The specimen was offset to record data at different ψ angles. The Bragg peak from intense (111) plane was obtained for each ψ angle. The lattice spacing (d_r) of the film was estimated from these measurements. The micro structural characteristics of the films were investigated using field emission scanning electron microscope (FESEM) (SUPRA-40, Carl Zeiss, Germany). The elemental analysis was carried out by the X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versa probe II) at a pressure of <10^{-6} Pa; pass energy of 58.700 eV, electron take off angle 45° and overall resolution 0.51 eV (X-ray source: monochromatic Al K_α radiation). The energy calibration of XPS spectra was done by setting the hydrocarbon C1s line at 284.6 eV. Room temperature UV—Vis absorption spectra of CuO thin film were measured using a spectrophotometer (LAMBDA750, PerkinElmer, USA). Thin film resistivity, mobility, carrier concentration and Hall coefficient as a function of temperature were studied using a Hall measurement system (HMS-5300, Ecopia, South-Korea).

Gas sensing characteristics of the annealed films were investigated by using a quasi-static system developed by us in our laboratory. The setup is equipped with a humidity sensor (model SY-HS-220, Syhitech) to measure the relative humidity of the sensor ambient. Un-saturated sodium chloride solutions at various temperatures were used to maintain the ambient humidity in the range of 40—95% [25]. Gold finger electrodes (electrode separation ~1 mm) were sputter deposited on CuO thin film and the electroded films were used as the sensing element. The thin film sensing elements were placed on a thermal stage and its temperature was controlled using an external temperature controller. A known load resistance (R_L) is connected in series with the sensing element. A constant voltage (~5 V) is applied across the sensor and the output voltage across the load resistance is measured using Atmel ATMEGA 32 micro-controller based data acquisition circuit developed in our laboratory [26]. The data acquisition set up is connected to a pc through RS232 interface for the data storage and further analyses.

To test the VOC sensing characteristics, the sensing element was placed on the thermal stage with its temperature maintained in the range of 200—300 °C. The sensing chamber is equipped with two small fans (fixed in opposite direction) to introduce and take out dry air/gas from the chamber. At a constant operating temperature, first, the base resistance of the sensing element was stabilized in ambient air. Subsequently, measured quantity of a typical VOC (ethanol, methanol, acetone, and 2-propanol) was injected into the static chamber by a micro-syringe. The injected liquid got immediately evaporated due to the radiant heat of the thermal stage (usually maintained at 200 °C or above). Knowing the volume of the injected liquid and static chamber we estimated the test gas concentration. For the VOCs studied in the present work, the test gas concentration was varied in the range of 50—300 ppm. Since CuO is a 'p' type semiconductor, the sensor resistance is found to increase up on gas injection. Knowing the output voltage (V_o), input voltage (~5 V) and load resistance (100 kΩ and 1MΩ), we recorded the resistant transient (resistance as a function of time) of the sensing elements for response and recovery cycles. The response% (S) was measured using the following relation

$$S(\%) = (R_g - R_a)/R_a \tag{1}$$

where R_g and R_a are the equilibrium resistances measured in presence of test gas and air respectively. The response (τ_{res}) and recovery (τ_{rec}) times (s) were estimated from the respective resistance transients where the base resistance is raised to 90% of the maximum resistance (τ_{res}) or fall to 90% of the equilibrium resistance in air (τ_{rec}).

3. Results and discussion

3.1. Characterization of CuO thin film

Fig. 1(a) shows the X-ray diffraction pattern of calcined CuO thin film deposited on fused quartz substrate. Using the same precursor sol we have also prepared CuO powder and the XRD pattern of this powder, calcined at 600 °C for 1 h is shown in Fig. 1(b). The powder XRD spectra is Rietveld refined by using MAUD software [27] and the refined spectra (solid line) is also shown in Fig. 1(b). Analysing the X-ray diffraction pattern we have confirmed that the diffraction peaks could be indexed to a monoclinic phase of CuO. The refined lattice parameters, crystallite size, unit cell volume and theoretical density are tabulated in Table 1. The refined lattice parameter matches well with the one reported in standard X-ray diffraction pattern (JCPDS 05-0661) [28]. The thin film pattern matches well with the powder X-ray diffractogram shown in Fig. 1(b). As compared to the powder XRD, the right shift of the thin film diffraction peaks could be due to retained strain [29]. The relative shift of (002) and (111) diffraction peaks of CuO thin film and powder is shown separately in the inset of Fig. 1. Usually the strain