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Magnetron sputtered nanostructured cadmium oxide films for ammonia sensing

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ABSTRACT

Nanostructured cadmium oxide (CdO) films were deposited on to glass substrates by reactive dc magnetron sputtering technique. The depositions were carried out for different deposition times in order to obtain films with varying thicknesses. The CdO films were polycrystalline in nature with cubic structure showing preferred orientation in (1 1 1) direction as observed by X-ray diffraction (XRD). Field-emission scanning electron microscope (FE-SEM) micrographs showed uniform distribution of grains of 30–35 nm size and change in morphology from spherical to elliptical structures upon increasing the film thickness. The optical band gap value of the CdO films decreased from 2.67 to 2.36 eV with increase in the thickness. CdO films were deposited on to interdigitated electrodes to be employed as ammonia (NH_3) gas sensor. The fabricated CdO sensor with thickness of 294 nm has a capacity to detect NH_3 as low as 50 ppm at a relatively low operating temperature of 150 °C with quick response and recovery time.

1. Introduction

NH_3 is colourless, highly irritating and pungent smelling gas. In the atmosphere, natural NH_3 is present in low (1–5 ppb) levels. About 80% NH_3 is produced by industry and it is used in numerous applications such as manufacturing of plastics, textiles, explosives, pesticides and in agriculture [1]. The Occupational Safety & Health Administration (OSHA) has set a limit of 25 ppm in the workplace during an 8-h shift and a short-term limit (15 min) of 35 ppm. The exposure of NH_3 above its threshold level values is highly dangerous to health and life. Due to this cause there is an increase in demand for NH_3 gas sensor. Current research is focused on the development of low-cost NH_3 sensors which can provide high sensitivity and low detection limit. Several metal oxide films were used to detect NH_3 such as ZnO [2], WO_3 [3], TiO_2 [4] and SnO_2 [5], etc. The literature available on CdO based NH_3 sensor is limited.

CdO is an n-type wide band gap semiconductor with high carrier concentration. It shows high electrical conductivity due to existence of shallow donors caused by interstitial cadmium atoms and oxygen vacancies [6]. CdO is known to have very strong surface activity and high thermal stability and hence used as a catalyst [7]. These properties of CdO make it an attractive candidate for gas sensing studies. It has a wide range of applications ranging from optics to electronics such as solar cells, photovoltaic cells, transparent electrode, liquid crystal display, IR detectors, gas sensor, etc. [8,9].

Knowing the importance of low-cost NH_3 sensors, in the present work, CdO thin films were deposited for different deposition times on to glass substrates patterned with interdigitated electrodes using reactive dc magnetron sputtering and their structural, optical, morphological and NH_3 sensing properties were studied.

2. Experimental

2.1. Fabrication of interdigitated electrodes

The electrodes were prepared by thermal evaporation technique using shadow mask on to the glass substrates. The detailed description of fabrication of interdigitated electrode is described in our previous work [8]. Prior to deposition, the glass substrates were immersed in the surfactant (Titron X) and ultrasonicated for 10 min to remove oily residues. Ultrasonication with Titron X helps to removes the oily residues and provide well adherence of the film over the glass substrate during deposition. This is followed by ultrasonication with deionized water, ethanol, acetone and finally the substrates were dried in hot-air oven maintained at 80 °C for 20 min. The cleaned substrates were placed in the thermal evaporation chamber. The electrodes were deposited by evaporating aluminium (Al) (99.99% purity) by resistive type heating. The distance between the two electrodes was 0.2 cm.

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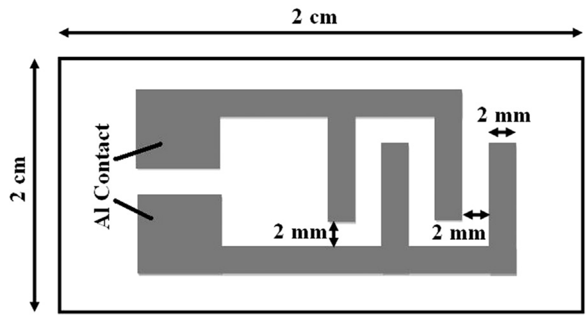

Fig. 1. Schematic diagram of fabricated interdigitated electrode.

Finally, the deposited electrodes were annealed at 250 °C for 3 h. The schematic diagram of the fabricated interdigitated electrode is shown in Fig. 1. CdO films with different thicknesses were deposited on glass substrates with interdigitated electrodes. The deposition of CdO films is explained in Section 2.2.

2.2. Film deposition

The fabricated interdigitated electrodes with proper masking for depositing the CdO sensing layer (1×1 cm^2) on to it were loaded on the sample holder in the deposition chamber. The schematic representation of deposition chamber is already reported earlier [9]. The deposition chamber was evacuated to a base pressure of 2×10^{-5} mbar using diffusion pump coupled with rotary pump. Cadmium (Cd) metal target (99.995% purity) of 50 mm diameter and 3.2 mm thickness was used as the source. Argon (Ar) (99.9995% purity) was used as sputtering gas. Initially the target was pre-sputtered in the Ar atmosphere in order to remove contamination on the target surface. After this step, Ar and Oxygen (99.9995% purity) were flown in to the deposition chamber controlled by mass flow controllers to maintain the process pressure at 3.8×10^{-3} mbar. The cathode power was maintained at 25 W. No intentional substrate heating or substrate bias was applied during the film growth. The depositions were carried out for different deposition times viz., 5, 10 and 15 min in order to obtain films with different thicknesses and the thickness values as measured by stylus probe measurement (Mitutoyo SJ 301).

2.3. Film characterization

Nanostructured CdO films with different thickness were coated on to the glass substrates. And the films were characterized for their structural, optical, morophological and gas sensing properties. The structural properties were studied by XRD (Bruker, D8 Focus) using Cu*K*α radiation of wavelength 1.5418 Å recorded in the 2θ range from 30 to 60°. The surface morphology of the films was studied using FE-SEM (JEOL JSM 7601F) with 3 kV electron beam power and at a working distance of ~7 mm in secondary electron imaging mode. The samples were coated with a thin gold layer in order to make the sample surface conducting. The optical properties such as optical band gap and transmittance were calculated from the data obtained from UV–Visible spectrophotometer (Perkin Elmer, Lambda 35) in the wavelength range of 200–800 nm.

2.4. Gas sensing system

Gas sensing experiment was carried out in a custom built gas sensing chamber [10]. The schematic diagram of gas sensing set up is shown in Fig. 2. The gas sensing chamber consists of double-walled stainless steel chamber of volume 30 l containing a hot stage upon which the sample is mounted. The sample can be heated up to 500 °C at a rate of 6 °C/min. Temperature was controlled by PID controller (Eurotherm 2404). Chilled water was circulated between the walls of the stainless steel chamber in order to keep it at ambient temperature. Gas flow is set from mass flow controllers which are regulated through valves which operate pneumatically. The sensor response upon exposure to gas is manifested as resistance change and is recorded using a multimeter (Agilent 34401) through data acquisition software. CdO films with different thickness were exposed to NH_3 at different operating temperature. The change in resistance of the sensor upon exposure to NH_3 is recorded against time.

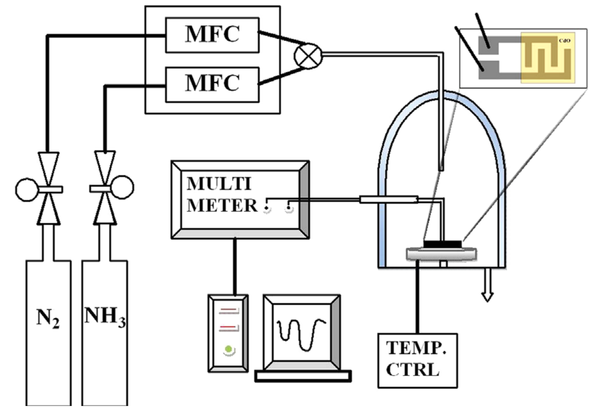

Fig. 2. Schematic diagram of gas sensing set up.

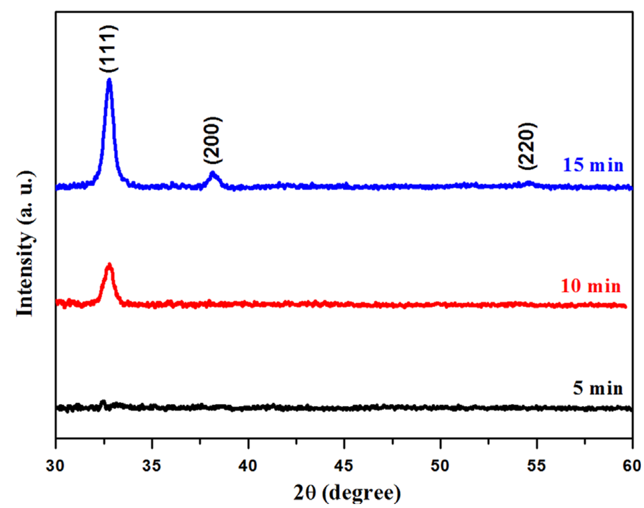

Fig. 3. XRD patterns of CdO films deposited at different deposition time.

3. Results and discussion

3.1. Thickness measurement

The thickness of the films were 122, 204 and 294 nm for deposited at 5, 10 and 15 min, respectively. It very obvious that as the deposition time increased the number of particles arriving to the substrate to form a film is higher its leads to increase the thickness of the film. The growth rate of the thin films was ~20 nm/min.

3.2. Structural properties

Fig. 3 shows the XRD diffractograms of nanostructured CdO films deposited at different deposition times. The CdO thin film