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Study of Ethanol sensing properties of spray deposited CdO thin films

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ABSTRACT

The objective of this work is to study the influence of deposition temperature on morphological and ethanol sensing properties of the CdO thin films prepared by spray pyrolysis technique. These films were characterized for morphological by means of scanning electron microscopy (SEM). As deposited CdO films are polycrystalline with (111) preferential orientation. The relationship between the surface morphology and the sensing properties to ethanol sensing properties of the CdO thin films is newly established. The CdO films exhibited the maximum response of 21% at 300 °C upon exposure to 0.2 vol.% LPG.

Key words: CdO films, LPG, spray pyrolysis technique.

INTRODUCTION

Metal oxides possess a broad range of electrical, chemical and physical properties that are often highly sensitive to changes in their chemical environment. Because of these properties, metal oxides have been widely studied, and most commercial sensors are based on appropriately structured and doped oxides [1]. Among the metal oxides, wide band gap semiconducting oxides such as SnO₂, ZnO and In₂O₃ have been extensively studied. Other well known sensors include Fe₂O₃ [2], WO₃ [3], CuO-BaTiO₃ [4-6].

CdO is an n-type semiconductor with a rock-salt crystal structure (FCC) and possesses a direct band gap of 2.2 eV [7]. Besides, the CdO will be attractive in the field of optoelectronic devices by making heterostructures with ZnO which has band gap energy of 3.3 eV. CdO thin films have been prepared by various techniques such as sol-gel, DC magnetron sputtering, radio-frequency sputtering, spray pyrolysis, pulsed laser deposition, chemical vapor deposition, and chemical bath deposition [8-14]. Further, among these methods, the spray pyrolysis is unique and cost effective compared to other methods requiring high vacuum environment. It is one step method operating at atmospheric pressure with very short production time [15]. This can be used to tune the band gap of materials. Due to these economical and flexible experimental conditions, spray pyrolysis has been employed to deposit CdO thin films and to study various properties of the films. The LPG sensing properties of these CdO thin films have been studied.

METHODOLOGY

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. The amorphous glass substrates supplied by Blue Star Mumbai, were used to deposit the CdO thin films. Before the deposition of CdO thin films, glass slides were cleaned with detergent and distilled water, then boiled in chromic acid (0.5 M) for 25 min, then slides washed with double distilled water and further ultrasonically cleaned for 15 min. Finally the substrates were degreased in AR grade acetone and used for deposition.

Thin film preparation

CdO films were prepared on preheated glass substrate using a spray pyrolysis technique. Spray pyrolysis is basically a chemical process, which consists of a solution that is sprayed onto a hot substrate held at high temperature, where the solution reacts to form the desired thin film. The spraying solution was prepared by mixing the appropriate volumes of 0.5 M cadmium

sulphate (CdSO₄) and distilled water. The CdO films were deposited at different substrate temperatures of 250, 300, 350 400 and 450 °C. Samples deposited at various substrate temperatures are denoted by C250, C300, C350, C400 and C450, where numbers stand for substrate temperatures. The optimized values of important preparative parameters are shown in bracket viz. airflow rate which is used as carrier gas (1.2 kg/cm²), spray rate (3 ml/min), distance between substrate to nozzle (30 cm), solution concentration (0.5 M) and quantity of the spraying solution (30 ml). After the deposition, the films were allowed to cool naturally at room temperature. All the films were transparent and well adherent to the substrate, were further used for morphological and LPG sensing properties.

The LPG sensing properties of CdO films were studied in gas sensor assembly. For electrical measurements, silver paste contacts (1mm) were formed on the CdO sample of area 1 cm \times 1 cm. The electrical resistance of CdO films in air (Ra) and in the presence of LPG (Rg) was measured to evaluate the gas response, S, defined as follows:

 $S(\%) = [(Ra - Rg)/ Ra] \times 100$

RESULTS AND DISCUSSIONS

Sensor resistance stabilization

Stabilization of sensor resistance prior to gas exposure is important, because it ensures sable zero level, for gas sensing applications. From SEM and XRD studies the sample deposited at 450 °C was chosen for various gas sensing performances. Fig. 1 shows the typical initial stabilization curve of resistance of selected film sample. Initially, when the temperature of 400 °C was attained, the resistance was decreased rapidly with few seconds and then raised and exhibited a stable value. This can be attributed to the generation of electrons due to thermal excitation. However, some of these electrons from the conduction band of CdO are extracted by the oxygen adsorbed undergoes the following reactions [15]

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$$O_{2(gas)} \leftrightarrow O_{2(ads)}$$
 $O_{2(ads)} + e^{-} \leftrightarrow O_{2(ads)}$
 $O_{2(ads)} + e \leftrightarrow 2O_{2(ads)}$

Thus, the equilibrium of the chemisorptions process results in stabilization of surface resistance.

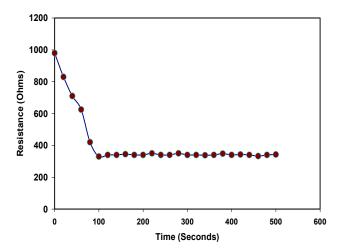


Fig. 1. Resistance stabilization curve for with time for CdO film maintained at 400 $^{\circ}\text{C}$

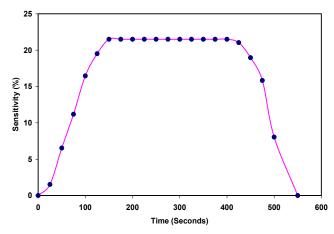


Fig. 2 Dynamic response transient curve of CdO film for Ethanol.

Ethanol sensing properties

Electrons are drawn from the conduction band of CdO by adsorbed oxygen, and a potential barrier to charge transport is developed. The response of a semiconductor oxide gas sensor to the presence of a

given gas depends on the speed of chemical reaction on the surface of the grains and the speed of diffusion of the gas molecules to the surface, which are activation processes.

The dynamic response transients of CdO films is depicted in Fig. 2 with operating temperature at 400 °C. When ethanol gas was introduced in the gas chamber, the response increased with operating time. As the it is turned off, the response of the same film fall rapidly

CONCLUSION

CdO thin films are successfully synthesized by spray method. The sensing properties were studied at low concentrations of ethanol, the gas response is increased as time increased and reached to 22%. The maximum response of 22% at the operating temperature of 400 °C was found under the exposure of 500 ppm concentration. The CdO thin films exhibited good sensitivity and rapid response-recovery characteristics to ethanol.

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