RESEARCH PAPER | Physics | Volume : 5 | Issue : 8 | August 2015 | ISSN - 2249-555X

Effect of Cu Doping on Lpg Sensing Properties of Spray Deposited Cdo Thin Films

KEYWORDS: Thin films; Cu:CdO films; spray pyrolysis; LPG sensing.

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ABSTRACT *The present study deals with the influence of Cu doping on liquefied petroleum gas 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 depositedCdO films are polycrystalline with (111) preferential orientation. The effect of Cu doping on the surface morphology and the sensing properties to liquid petroleum gas (LPG) of the ZnO films is newly established. The Cu:CdO films exhibited the maximum response of 32% at 300 0C upon exposure to 0.2 vol.% LPG at 2% Cu doping.*

1. Introduction

The charge carrier concentration on the surface of a semiconductor is sensitive to the composition of surrounding atmosphere, considerable research has been carried out on the development of novel solid state gas sensors based on semiconducting metal oxides. The past few decades have seen the development of a multitude of simple and robust solid-state sensors whose operation is based on the transduction of the binding of an analyte on the active surface of the sensor to measurable signal that most often is a change in the resistance, capacitance or temperature of the active element [1].

Transparent conducting metal oxide semiconductor materials have attracted much attention owing to their potential applications in flat panel display, smart windows, light emitting diodes, heat reflectors, electronic, photovoltaic devices and solar cells [2–4]. Its high electrical conductivity and high optical transmittance in the visible region of the solar spectrum along with a moderate refractive index make it useful for various applications such as transparent electrodes, phototransistors, photodiodes, gas sensors, etc. [5-6]. 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].

In the present study, we report use of a Spray Pyrolysis method to form thin films of Cu doped CdO, which were further utilized for studying liquefied petroleum gas (LPG) sensing properties.

2. Experimental details

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

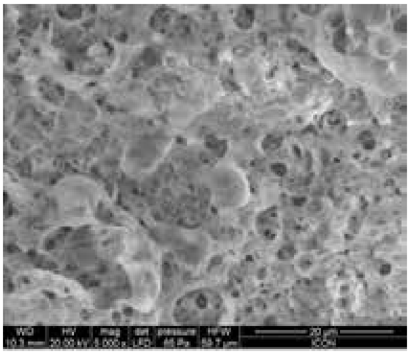
CdO films were prepared on preheated glass substrate using a spray pyrolysis technique. The spraying solution was prepared by mixing the appropriate volumes of 0.5 M cadmium sulphate ($CdSO_4$) and $CuSO_4$ and distilled water. The Cu:CdO films were deposited at substrate temperatures 400 ^{0}C with 1%, 2% and 3% of Cu. Samples deposited at various mole % are denoted by X_0, X_1, X_2 and X_3, where numbers stand for mole %. The optimized values of important preparative parameters are shown in bracket viz. airflow rate which is used as carrier gas (1.2 kg/cm^2), 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 Cu:CdO films were studied in gas sensor assembly. For electrical measurements, silver paste contacts (1mm) were formed on the Cu:CdO sample of area 1 cm × 1 cm. The electrical resistance of Cu:CdO films in air (Ra) and in the presence of LPG (Rg) was measured to evaluate the gas response, S, defined as follows:

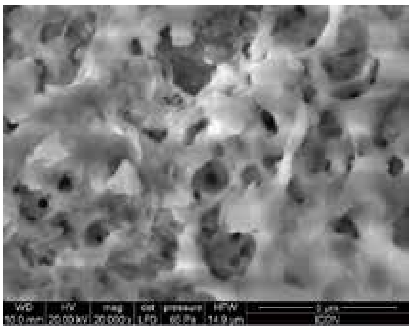
$$S(\%) = [(Ra - Rg)/ Ra]\times 100.$$

3. Results and discussion

The surface morphologies of the Cu doped CdO films were performed by using SEM. Before SEM studies, all films were covered with a very thin layer of gold for better definition. Fig. 1 shows the SEM micrographs 0 mole % and 2 mole % Cu doped CdO films. It can be obviously seen from Fig. 1 that all films have not a smooth and homogeneous surface morphology with a holes and cracks. But also, all the films are compact, dense and adhered well to the substrates. The surface properties of the CdO films appear to change significantly as a Cu mole %. Coalescence of different shapes and size grains into a bigger flat grain can be noticed. At some favorable nucleation centers overgrown grains and cloudy splashes are also seen. The 2 mole % Cu:CdO films have more porous nature.



(a)



(b)

Fig. 1 SEM micrograph Cu doped CdO thin films (a) at 0% and (b) at 2%

LPG sensing properties

Before exposing to LPG gas, the Cu:CdO films were allowed to be stable for electrical resistance for 30 min and the stabilized resistance was taken as *R*a. In the present study, initially the gas response to 0.1 vol. % of LPG was measured as a function of operating temperature for a Cu:CdO film. Fig. 2 shows the response of a Cu:CdO film A as a function of LPG concentration at 300 °C. The figure indicates that the gas response increased from 12.5 to 21.5% as the LPG concentration increased from 0.05 to 0.2 vol. %. For film X_0. The response increased rapidly for X_1, X_2, and X_3 However, at higher concentrations the increase in gas response was gradual and saturated at LPG concentrations more than 0.15 vol.%. The response of a sensor depends on removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. For a small concentration of gas, exposed to a fixed surface area of a sample, there is a lower coverage of gas molecules on the surface and hence lower surface reaction occurred [16].

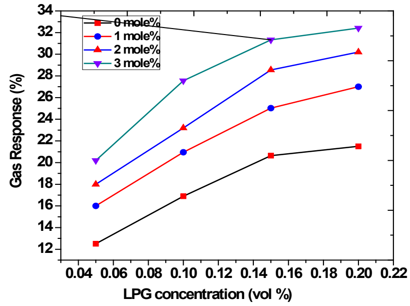


Fig. 2. The variation of gas response of a Cu doped CdO film at 300 °C to LPG of different gas concentrations.

Dynamic Gas response studies

The dynamic variation of sensitivity of samples X_0, X_1, X_2 and X_3 with operating time at 300° C for the exposure of 0.2 vol % LPG is shown in Fig. 3. When the LPG gas was introduced in the gas chamber, the sensitivity was increased with the operation time. As the LPG gas was turned-off the sensitivity of the same film only fell rapidly, indicating that the good recovery of the resistance was obtained. We observed from SEM micrograph of sample porous network was connected deep inside the structure. So, this kind of morphology helps relevant gases to react on the outer surface as well as inside porous surface more efficiently. Thus, the effective surface area for gases to react increases, and the response evidently increases.

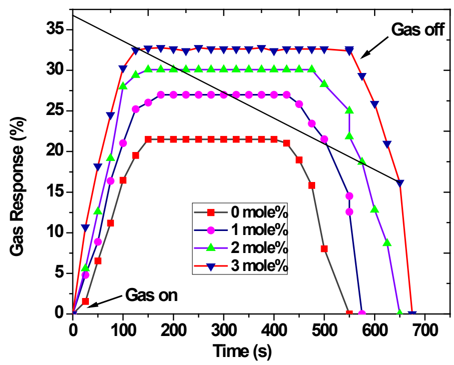


Fig.3. Dynamic response transients of Cu doped CdO films deposited by spray pyrolysis

4. Conclusions

The effect of Cu doping in CdO films on the LPG sensing characteristics of Cu:CdO films prepared by spray pyrolysis was studied The sensing properties were studied at low concentrations of LPG, and it was found that the film shows the highest response of 32.5% under the influence of 0.2 vol.% of LPG at 300 °C for 3 mole %. The response of a sensor depends on removal of adsorbed oxygen molecules by reaction with a target gas and generation of electrons. In dynamic gas response good recovery of the resistance was obtained.

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