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Sprayed CdO thin films for liquefied petroleum gas (LPG) detection

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ABSTRACT

Nanocrystalline cadmium oxide (CdO) thin films were deposited onto glass substrates by a chemical spray pyrolysis method using an aqueous solution of cadmium acetate. These films were characterized for their structural and morphological properties by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The CdO films are oriented along (1 1 1) plane with the cubic crystal structure. These films were utilized in liquefied petroleum gas (LPG) sensors. The dependence of the LPG response on the operating temperature, LPG concentration and CdO film thickness was investigated. The CdO film showed selectivity for LPG over N_2 compared to CO_2 ($S_{LPG}/S_{N_2} = 11.3$ and $S_{LPG}/S_{CO_2} = 1.88$). The maximum LPG response of 34.11% for the film of thickness 0.97 μm at gas concentration of 0.16 vol.% at 698 K was achieved. Additionally, the stability of films has been studied.

1. 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]. Thus, ZnO, SnO_2 and In_2O_3 have been employed in different forms to sense the gases such as hydrogen, carbon monoxides, ethanol and NO_2. In spite of considerable efforts, good sensors for LPG have not been found hitherto, the problem being of vital importance for industrial as well as domestic purposes. The leakage of LPG is a serious problem as lower explosive limit (LEL) of LPG is 1.8 vol.%. Considerable research has been carried out for development of reliable and efficient LPG sensors. Wide band gap semiconductors such as SnO_2 and ZnO have been studied for making efficient gas sensors with noble metal additives such as palladium and platinum [2–8]. However, the above mentioned materials are still not as selective as one would expect since they sense other gases. In addition, the stability of some of the materials is not very good, resulting in poor reliability due to aging and humidity induced effects. Moreover, when the sensors are used in the array configuration for electronic nose application, the lack of stability and reliability deteriorates the performance of the whole device. Among the oxides cadmium oxide received less attention due to its narrow energy band gap [9]. However, these films show higher mobility values which are necessary for high conductivity transparent conducting oxide materials, especially when low free carrier absorbance is desired [10].

CdO thin films have been prepared using various physical as well as chemical deposition methods [11–16]. Among these, deposition of CdO thin films by simple and low cost chemical spray pyrolysis method has been reported by Bhosale et al. [17] and Gurumurugan et al. [18]. Due to stability of spray method doping of different materials to improve the conductivity of CdO films for solar cell application has been carried out [19]. Deokate et al. [20] have studied effect of fluorine doping on structural properties of CdO thin films. Influence of post-thermal annealing on the properties of sprayed CdO thin films has been studied by Vigil et al. [21]. Recently, Guo et al. [22] reported the use of porous CdO nanowires obtained by hydrothermal route for NO_x detection. We showed that SILAR and CBD synthesized CdO films exhibited LPG response of 18% [23] and 23% [24], respectively. To the best of our knowledge, the sprayed CdO thin films have not been used in LPG sensors.

In the present work, we adopted spray pyrolysis method which provides one step stable CdO films and report on the thickness dependant LPG sensing characteristics of CdO thin films at gas concentration as low as 10% of lower explosive level (LEL), after characterizing these films by XRD, SEM and AFM techniques. Initially, the selectivity of CdO films towards LPG has been studied.

2. Experimental details

In the spray pyrolysis method, a precursor solution was pulverized by means of a neutral gas so as to reach a substrate in the form of very fine droplets. The constituents reacted to form a chemical compound onto the substrate. The experimental setup for

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spray deposition is reported earlier [25]. Cadmium oxide films were deposited using an aqueous solution of cadmium acetate (Loba Chemie Pvt. Ltd. (99% pure)). The solution was sprayed through a glass nozzle onto the ultrasonically cleaned glass substrates kept at temperature of 648 K. The spray rate of 5 cm^3/min was maintained using air as the carrier gas. The thickness was obtained using the formula:

$$t = \frac{M}{A\rho} \quad (1)$$

$$M = m_1 - m_2 \quad (2)$$

where t is film thickness, M is mass of the film material (in g), A is area of the film (cm^2), m_1 is mass of the substrate with film, m_2 is mass of the substrate without film and ρ is bulk density of the film material (g/cm^3). The films obtained by spraying the cadmium acetate solution of quantity less than 25 ml were very thin and non-uniform whereas the films obtained with above 125 ml quantity were powdery. Therefore, the films were deposited by varying the quantity of solution from 25 to 125 ml. The films so obtained by spraying quantity of 25, 50, 75, 100 and 125 ml are denoted by A, B, C, D and E, respectively.

To study the structural property of CdO films, XRD patterns were obtained on a Philips (PW3710) diffractometer with a Cu Kα (λ = 1.5409 Å) target. Microstructural study was carried out using SEM and AFM. The SEM micrographs were obtained with a Cambridge stereoscan 250 MK-3 assembly. The AFM images were recorded in contact mode with a Nanoscope III (digital instruments using commercial n^+ silicon cantilever with spring constant 0.2 N/m). The LPG sensing properties of CdO films were studied in a home-made gas sensor assembly reported earlier [25]. The two-probe technique was used to measure the electrical resistance in air and in the presence of LPG. For electrical measurements, silver paste contacts (1 mm) were used to form Ohmic contacts on the CdO sample of area 1 cm × 1 cm. The electrical resistance of a CdO film in air (R_a) and in the presence of LPG (R_g) was measured to evaluate the LPG response defined as follows:

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100 \quad (3)$$

3. Results and discussion

3.1. CdO film formation and thickness measurement

Aqueous solution of cadmium acetate when sprayed over the hot substrate, pyrolytic decomposition of solution takes place and results into formation of solid cadmium oxide. The possible chemical reaction of CdO film formation is as follows [26],

$$Cd(CH_3COO)_2 + 3H_2O \xrightarrow{Heat} CdO + CH_4\uparrow + 3CO_2\uparrow + 4H_2\uparrow \quad (4)$$

Thickness of CdO film was measured by the gravimetric weight difference method using the density of CdO in bulk form (ρ = 8.150 g/cm^3 for CdO) [27]. Yellowish coloured, uniform and well adherent CdO films were deposited on the glass substrate. The colour of film changed from yellowish to dark brown with film thickness, as shown in Fig. 1. The variation of film thickness with the quantity of the sprayed solution is shown in Fig. 2. The film thickness increased with increased quantity of the spray solution up to 100 ml (t = 1.39 μm) and then decreased. Such behavior may be attributed to the powdery film formation at large solution quantity, analogous to Shinde et al. [25].

3.2. X-ray diffraction studies

Fig. 3(A–D) shows the XRD patterns for the CdO samples. The diffraction peaks show the formation of nanocrystalline crystal-

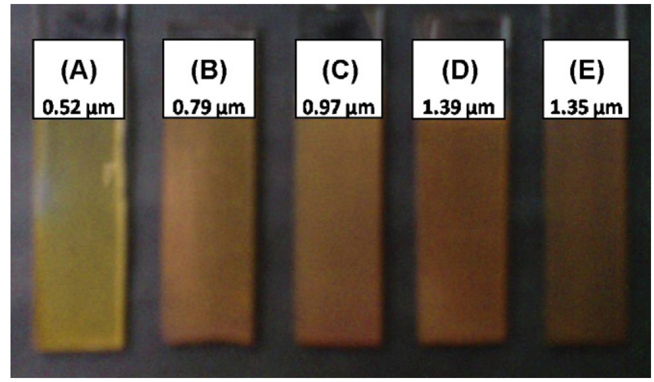

Fig. 1. Photograph of CdO thin films of different thicknesses (A) 0.52 μm, (B) 0.79 μm, (C) 0.97 μm, (D) 1.39 μm and (E) 1.35 μm.

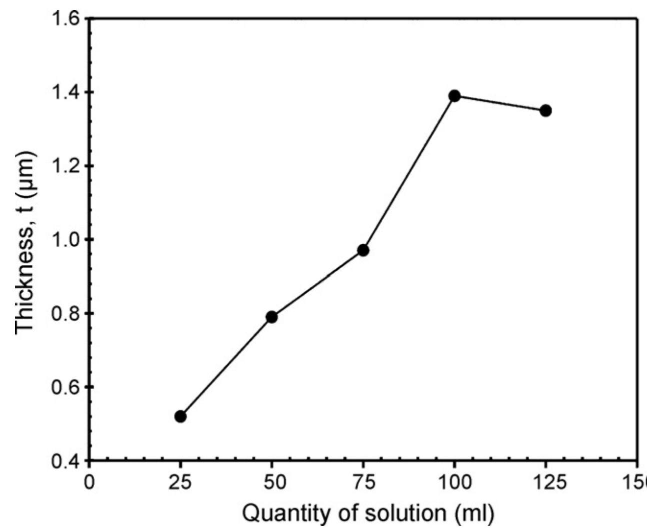

Fig. 2. The variation of CdO film thickness with quantity of cadmium acetate solution sprayed at 648 K.

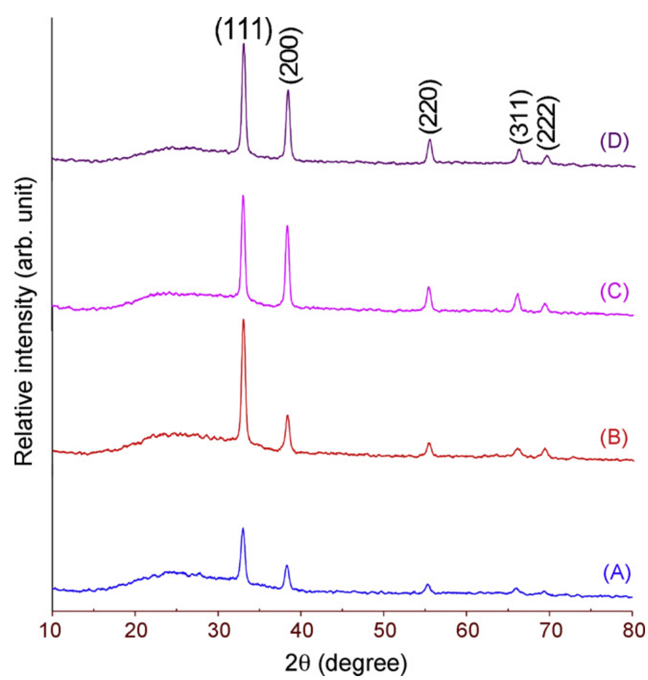

Fig. 3. The XRD patterns of CdO films of different thicknesses obtained by spraying different quantity of 0.1 M of cadmium acetate solutions, (A) 0.52 μm, (B) 0.79 μm, (C) 0.97 μm and (D) 1.39 μm.