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Chemically deposited cubic structured CdO thin films: Use in liquefied petroleum gas sensor

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ABSTRACT

Cadmium oxide (CdO) thin films have been synthesized by chemical bath deposition (CBD) method. The deposition is carried out at room temperature (300 K). The surface morphology of the CdO thin films showed interconnected prism-like structure. The CdO thin films are oriented along (1 1 1) plane with the cubic crystal structure. The sensing properties of nanostructured CdO thin films have been studied for liquefied petroleum gas (LPG) at operating temperature of 573 K. The CdO thin films exhibited maximum gas response of 44% upon the LPG exposure of 1040 ppm.

1. Introduction

The development of gas sensors to monitor combustible gases is imperative due to the concern for safety requirements in homes and for industries, particularly for the extensively used liquefied petroleum gas (LPG). LPG can be potentially hazardous, when it explodes upon leakage accidentally or by mistake. Hence, the detection of LPG is necessary in domestic appliances. In the recent years, the synthesis of oxide materials has become critical point of research activities in the area of nano materials owing to the quest for their technological applications [1–5]. It is known that the charge carriers on the surface of a semiconductor are sensitive to the composition of surrounding atmosphere and therefore, considerable research has been carried out on novel solid-state gas sensors based on semiconducting metal oxides. Among the metal oxides, semiconducting oxides such as SnO_2 [6], ZnO [7], CdO [8] and WO_3 [9] have been studied. However, these materials are still not as selective as one would expect since they sense other gases like hydrogen, carbon monoxide, ethanol, and NO_2. Among these, CdO received less attention because of its narrow energy band gap [10]. However, CdO films show higher mobility values necessary for high conductivity transparent conducting oxide materials, especially when low free carrier absorbance is desired.

The sensor performance is strongly dependent on the microstructural features such as crystallite size, and size grain boundary characteristics and thermal stability [11]. Therefore, one can improve the sensitivity by controlling the grain size and surface morphology. The effect of the different surface treatments on active sensor surface causes the change in morphological properties of material and hence on the sensor performance [12–14].

In the recent years, synthesis of CdO has been reported in the literature by physical and chemical methods such as sputter deposition [15], metal organic chemical vapour deposition (MOCVD) [16] and pulsed laser deposition [17]. These preparative methods need special equipments, complex process controls and high deposition temperature. In contrast, chemical bath deposition (CBD) a soft chemical method is used to deposit polycrystalline thin films of many metal chalcogenides. In CBD method, small degree of supersaturation of the solution causes the heterogeneous nucleation of the metal oxide on the substrate [18]. The solubility of the solutes changes as a result of chemical reactions in the solution. When the solution reaches supersaturation, solid particles are formed through the nucleation and crystal growth process.

In the present paper, synthesis of CdO thin films using CBD method at room temperature is reported. The cadmium hydroxide ($Cd(OH)_2$) films are deposited onto glass substrate and annealed at 723 K to eliminate hydroxide inclusion. The stabilization of the CdO

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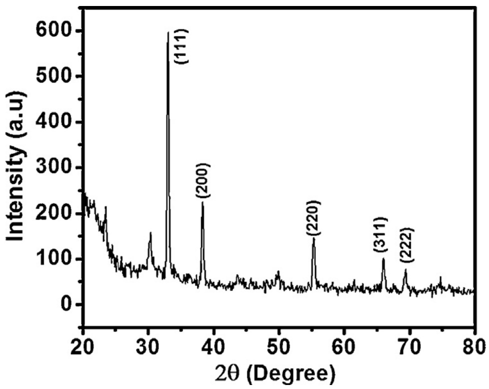

Fig. 1. The XRD pattern of the CdO thin film deposited glass substrate.

thin films, the effect of operating temperature and LPG concentration on gas response are studied.

2. Experimental details

In the present experiments, nanostructured CdO films are synthesized by CBD method. In typical synthesis, the bath was prepared by adding ammonia solution drop by drop to aqueous 0.1 M $CdCl_2$ solution, with the constant stirrering thereby forming the precipitate of $Cd(OH)_2$. Further, precipitate of $Cd(OH)_2$ was dissolved by addition of excess ammonia solution and to obtain a clear solution. The pH of resultant solution was adjusted 12 ± 0.1. The solution was transferred into another beaker containing ultrasonically cleaned glass substrates inclined vertically at 20° to the walls of the beaker. After a predetermined time of 72 h the glass substrates coated with $Cd(OH)_2$ were removed, washed with double distilled water and dried in air. Further, these films were air annealed at 673 K for 2 h to remove hydroxide content in the film. The X-ray diffraction study was carried out using Philips PW-1710 with Cu-Kα radiation in the 2θ range from 20° to 80°. The surface morphology was visualized using a JEOL-JSM 6360 scanning electron microscope (SEM). The LPG sensing properties were studied using a computer controlled gas sensor unit.

3. Results and discussion

3.1. CdO film formation

Initially, due to the cadmium chloride and the ammonia, $Cd(OH)_2$ is formed as follows

$$CdCl_2 + 2NH_4OH \rightarrow Cd(OH)_2 + 2NH_4Cl \quad (1)$$

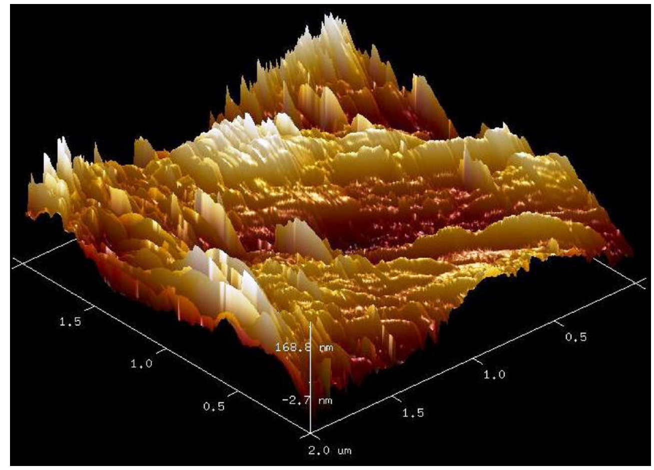

Fig. 3. Three dimensional AFM image of CdO thin film.

Further, to remove hydroxide phase and to improve the crystallinity of films, the films were air annealed at 673 K for 2 h.

$$Cd(OH)_2 \xrightarrow{\Delta} CdO + H_2O \uparrow \quad (2)$$

3.2. Structural and morphological studies

Fig. 1 shows the XRD pattern of CdO thin film on glass substrate. The CdO thin film showed polycrystalline nature. The peaks assigned as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes are of cubic structure of CdO (JCPDS card no. 5-0640) for CdO [19,20]. Fig. 2(a, b) shows surface morphology of the deposited CdO films at different magnifications. The interconnected hierarchical triangular nanoplates with high surface area were obtained and these interconnected nanoplates form prism-like structure. The average thickness of the nanoplates is ∼160 nm as shown in Fig. 2(a) with height of the prism is ∼5 μm as shown in Fig. 2(b). The pores of diameter 1–2 μm are observed between the prisms, as seen in Fig. 2(a, b). Chemical bath deposition is the "bottom-up" approach method based on the formation of a solid phase upon transformation of a supersaturated solution to the saturated state [21]. This transformation incorporated with various distinct steps as (i) nucleation, (ii) aggregation, (iii) coalescence, and (iv) subsequent growth by stacking of the particles.

$Cd(OH)_2$ ions come closer to each other to start nucleation process in the bath. After nucleation of $Cd(OH)_2$ molecules are aligned in one direction. This multiple joining of alignment $Cd(OH)_2$ molecules lead to the formation of aggregation. Consequently in

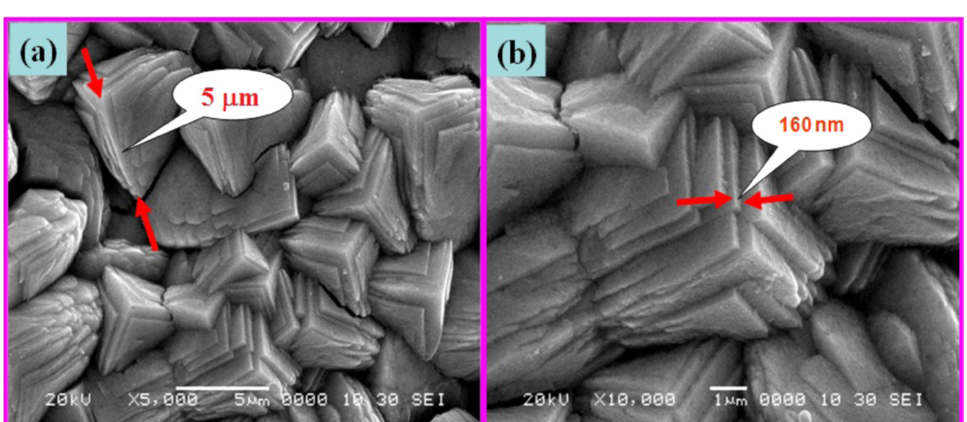

Fig. 2. Scanning electron micrographs of CdO film at two different magnifications (a) 5000×, and (b) 10,000×.