



Chemical Vapour Deposited CdO thin film for ethanol sensing

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Abstract— Herein we report the formation of cubic-phased Cadmium Oxide thin films using the aerosolassisted chemical vapor deposition (AACVD) technique which gives high-quality, uniform thin film. The structural, morphological, and optical characterization of the deposited films was done using X-ray diffraction, SEM, TEM, UV-Vis spectroscopy, etc.The XRD analysis reports that crystallite size increases with film thickness. TEM shows particle size ~ 30 nm. SEM studies reveal an increase in surface roughness and porosity with the increase in thickness. Optical data shows band gap decreases with an increase in thickness. Semiconducting metal oxides (SMO) are broadly used in gas sensors for sensing different gases. Their sensitivity can be increased by varying the different parameters involved in the deposition process. The gas sensing ability of CdO thin film shows that increasing of number of depositions enhances the sensitivity bizarrelyfor ethanol.

Keywords— Cadmium Oxide, thin film, CVD, ethanol, gas sensing.

I. INTRODUCTION

In recent times, transparent conducting oxides (TCOs), mainly semiconductor materials, have become widely popular among researchers due to their different applications in the semiconductor and electronics industries[1]. Cadmium oxide (CdO) is one of the first testified TCOs with very wide application in the electronic and optoelectronic industry, organic and chemical sensors devices, and energy storage devices, irrespective of their high toxicity [2]. As per the report of several researchers, CdO is an n-type semiconductor with a direct band gap value of ~2.24 eV at room temperature [1]. The high electrical conductivity and high optical transmittance of CdO make it a perfect material for application in solar cells, photodiodes, gas sensors, etc. [1,3]. Several works have been done by researchers on CdO thin film prepared by various methods such as sol-gel [1], thermal evaporation [2], spray pyrolysis [3], sputtering [4], successive ionic layer adsorption and reaction(SILAR) [5], Chemical Vapour Deposition (CVD) [6], etc.Among all those different methods, CVD is a unique technique due to its ability to deposit pure, uniform, adherent, largearea thin film at low operational cost.

In our day-to-day lives, we use many simple organic materials such as ethanol. It is a colorless liquid material widely applied in biomedical, chemical, and food processing industries. Ethanol is also the intoxicating constituent of many alcoholic drinks such as beer, wine, and distilled spirits. Leakages of volatile ethanol can make people more victims of various respiratory as well as digestive disorders including cancer [8]. Augmented usage of ethanol increases the issues of water pollution [7]. So, it is very vibrant to have an effective method for sensing ethanol at a trace level [8]. Semiconductor metal oxide (SMO) based gas sensing materials are becoming fecund due to their large application in diverse ecological and industrial sectors [8]. The specific target gas completely interacts with the metal oxide surface usually through surface adsorbed oxygen ions. The gas-sensing ability of any material is important for them to be used as sensors [9]. There is plenty of scope to develop room-temperature Ethanol sensor.

A group of researchers have tried to analyze the variation of gas sensing properties of cadmium oxide thin film prepared by spray pyrolysis with increasing thickness depending on deposition time [3].But detailed study of the

impact of the number of depositions on structural, optical, morphological, and gas sensing properties of CdO thin film prepared by low-cost method is scarce. Here we have tried to prepare the thin film in low-cost but efficient process. Aerosol Assisted Chemical Vapor Deposition (AACVD) technique has been employed to prepare the deposited films. The performance of a sensing material mostly depends on its surface roughness, porosity, and structural growth. So, in our current study, we have tried to get a detailed idea about the influence of deposition time on structural, optical, morphological, and gas sensing properties in CVD-synthesized CdO thin films. We have tried to fabricate CDO thin films effectively using the CVD technique with varying deposition times. The structural and optical properties of obtained nanostructured thin films have been investigated and compared. The sensing properties of this material for ethanol were studied deeply to explore the effect of thickness on sensing ability.

II. EXPERIMENTAL

CdO thin films were deposited on substrates using the CVD technique. The cationic precursor used was 0.1 M of cadmium acetate [Cd (CH₃COO)₂·H₂O] dissolved in 100 ml double distilled water. It was further made alkaline (pH 12) by mixing ammonium hydroxide (NH_4OH) at room temperature. This mixture is kept on a magnetic stirrer for 20 min until it is all clear. The solution was placed in two necked 200 ml round bottom flasks. One neck was connected to the air compressor, to provide air as the gas carrier, and the other was fitted to a glass column where the substrates were placed. The two necked flasks were placed in a water bath above an ultrasonic humidifier to generate the aerosol. The generated aerosol was carried into the reaction zone by air. The glass column containing the substrate was placed into a horizontal tubular furnace where the temperature was fixed at 320°C. The flow rate of the air was fixed at 4L/min and the process takes 60-90 min. After the precursor had been consumed, the films were allowed to cool down to room temperature. The deposition time was varied for 60 min, 75 min, and 90 min. The samples are marked as CdO1, CdO2, and CdO3, respectively.

The structural analysis was done by X-ray diffraction (XRD) method with the help of a Bruker (D8 advance) X-ray diffractometer using Ni-filtered CuK_{α} radiation (λ =1.5418 Å). The diffraction data were recorded in the range of 20°–70° scattering angle and plotted for all samples. The experimental obtained peak positions were compared with standard Joint Committee of Powder Diffraction System (JCPDS) files. Transmission electron

microscopy (TEM) investigation was done using Tecnai F30 G2, FEI, Hillsboro, Oregon. microscope which operates at 200kV. The micrograph obtained from TEM was used for particle size estimation using image J software. Surface morphology was studied using SEM micrograph. UV–VIS spectrophotometry process was used to study in detail the optical properties of the samples at room temperature using a double-beam spectrophotometer (Shimadzu, UV–1800).The gas sensing ability was measured using a simple homemade arrangement with the help ofa Keithley 6514 DMM electrometer for measuring resistance value.

III. RESULT AND DISCUSSION

The X-ray diffraction (XRD) pattern of the CdO thin film is shown in Figure 1. According to the XRD pattern,the CdO1 sample (film produced by deposition time of 60 min)is polycrystalline in nature. Prominent diffraction peaks of CdO thin films are observed at ~33.13°, ~38.41°,55.38° and 66.20° corresponding to the (111), (200), (220) and (311) diffraction planes respectively which well match cubic phased cadmium oxide [JCPDS file no. 05-0640]. The plane (111) is the maximum intense one.The lattice constant for CdO1 is ~ 0.458 nm, and it slightly decreases with an increase in deposition time. The crystallite size was estimated from the X-ray diffraction data using the Debye–Scherrer equation as given by

$$d = \frac{0.89\lambda}{\beta\cos\theta} \tag{1}$$

where β denotes the FWHM intensity of the concerned peak. The average crystallite size is ~ 20.2 nm for the CdO1 sample where the margin of error forcalculation is within ± 5% limit. The particle size is of the order of 30-35 nm as measured from TEM images [figure 2] using Image J software [10].The SEM images of CdO thin film deposited for 75 min in Figure3.The surface roughness plays a vital role in modifying the ability of a material to sense target gas.

The measurement of gas sensing characteristics of all samples (CdO1, CdO2 and CdO3) is carried out for 1000 ppm ethanol in the presence of air. The sensing characteristic of CdO thin films of different deposition times but for a fixed concentration of ethanol was performed. The samples were properly electroded using well-graded conducting carbon paste on a single side keeping an equal gap for all samples. The percent sensitivity for the material can be expressed as

$$S\% = \frac{R_{air} - R_{gas}}{R_{air}} \times 100 \,(3)$$

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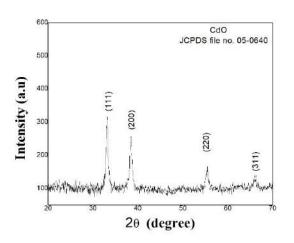


Fig.1. X-ray powder diffraction patterns of CdO

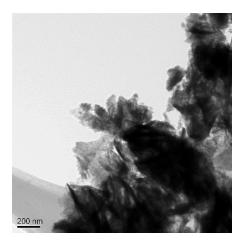


Fig.2: TEM image of CdO

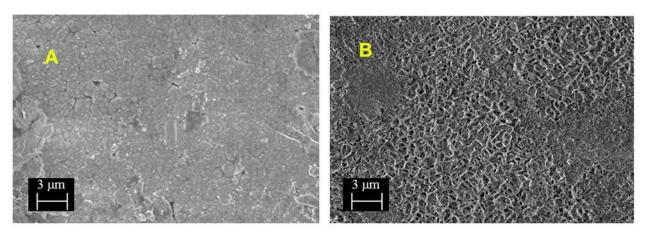


Fig.3 SEM images of (A) CdO1 and (B) CdO3

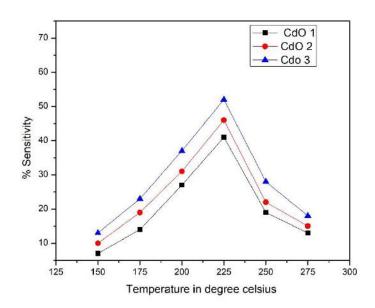


Fig.4: Sensitivity vs Operating Temperature curve for CdO thin films for ethanol.

Figure 4 shows the plotting of percent sensitivity with operating temperature for 1000 ppm ethanol gas. The maximum sensitivity was attained at 225° C for all The amount sensitivity increases with the samples. deposition time which may be due to an increase in surface roughness and porosity with deposition time. The increase in porosity increases the effective surface area for the reaction of target gas molecules with chemisorbed species [12]. As the 90-minute deposition timing-based sample shows maximum porosity than others, it shows the highest response for ethanol. The sensing capability of any sensing material depends largely on temperature. At a specific temperature sensing material attains sufficient energy to overcome the barrier of activation energy. Over and below which sensitivity is low. That specific temperature is called maximum operating temperature in which the sensor performance reaches maximum efficiency. The maximum operating temperature greatly depends on structure, roughness, porosity, and material.

IV. CONCLUSIONS

This work mainly discusses the structural, morphological, and sensing properties of CdO thin films synthesized using a simple, efficient CVD method by varying the deposition time. XRD study strongly confirms the presence of cubicphased cadmium oxide with (111) as the most intense peak. SEM micrograph shows the increase in porosity, surface roughness with thickness, and deposition time. The thickness greatly affects the sensing ability of CdO thin film for ethanol target gases. Such a clear increase in sensitivity may be due to the enhancement of surface roughness and porosity.In the future, we plan to modify these sensing materials systematically.

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