International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2020): 7.803

SILAR Synthesized CdO Thin Film for Ethanol Sensing

Md. Naiyar Perwez

Department of Physics, R. N. College, Hajipur, Vaishali, Bihar, India – 844101
Email: *mnperwez78[at]gmail.com*

Abstract: ***The effect of number of depositions on structural and gas sensing properties of CdO thin films prepared by low-costand effective successive ionic layer adsorption and reaction (SILAR) method. The structural, morphological and optical characterization of the deposited films were done using X-ray diffraction, SEM, TEM, UV-Vis spectroscopy etc. XRD patterns reveals that CdO thin film shows poly crystalline cubic cadmium oxide structure. The XRD analysis reports that crystallite size increases with number of deposition and also thickness increases.TEM shows particle size ~ 24-30 nm. SEM studies reveal increase in surface roughness and porosity with increase in thickness. Optical data shows band gap decreases with increase in thickness. Semiconducting metal oxides (SMO) are broadly used in gas sensors for sensing different gases. Their sensitivity can be increased by varying different parameters involved in deposition process. The gas sensing ability of CdO thin film shows that increasing of number of depositions enhances the sensitivity bizarrely for ethanol.***

Keywords: Cadmium Oxide, thin film, SILAR, ethanol, gas sensing.

1. Introduction

Transparent conducting oxides (TCOs) mainly semiconductor material is becoming widely popular amongst researcher due to its different applications in semiconductor and electronics industries [1]. Cadmium oxide (CdO) is one of the first testified TCO with wide application in electronic industry, optoelectronic sectors, organic and chemical sensors devices irrespective of its high toxicity [2].CdO is reported as n-type semiconductor with direct band gap value of ~2.23 eV at room temperature [1]. The high electrical conductivity and high optical transmittance of CdO makes it a perfect material for application in solar cell, photodiodes, gas-sensors, etc. [3]. Numerous works have been done by different 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 Bath Deposition (CBD) [6] etc. Among all those different methods, SILAR is a unique technique due to its ability to deposit uniform, adherent, large area stoichiometric thin film at room temperature with low operational cost.

In our day-to-day life, we use many simple organic materials such as ethanol. It is a colorless liquid material with wide application in bio-medical, 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 disorder including cancer [8]. Augmented usage of ethanol increases the issues of water pollution [7]. So, it is very much vibrant to have an effective method for sensing ethanol at trace level [8].The semiconductor metal oxide (SMO) based gas sensing materials are becoming fecund due to its large scale 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 surface morphology plays an important role in sensing properties of thin films. Those interactions result in a alteration of charge carrier concentration of that material which further varied its resistivity.

Influence of thickness (due to change in number of dipping) in structural, morphological and optical properties of CdO thin film has been described by different researchers [1, 6, 9]. A group of researcher have tried to analysis the variation of gas sensing properties of cadmium oxide thin film prepared by spray pyrolysis with increasing thickness depending on deposition time [3].But detail study of impact of number of deposition on structural, optical, morphological and gas sensing properties of CdO thin film prepared by low-cost method is scarce. 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 detail idea about the influence of number of dipping(maybe change of thickness) on structural, optical, morphological and gas sensing properties in SILAR synthesized CdO thin film. We have tried to fabricate effectively CdO thin films using SILAR method with varying the number of dipping. The structural and optical properties of obtained nano-structured thin films have been investigated and compared. The sensing properties of this material for ethanol was studied deeply to explore the effect of thickness on sensing ability.

2. Experimental

CdO thin films were deposited on glass substrates using SILAR technique. The substrate cleaning process was done properly before deposition. The cationic precursor used was 0.1 M of cadmiumacetate [$Cd(CH_3COO)_2{\cdot}H_2O$] which was further made alkaline (pH 12) by mixing ammonium hydroxide (NH_4OH) at room temperature. The anionic precursor used was double distilled water maintained at a temperature 75°C. A complete cycle of SILAR consist of the following steps: (1) First of all, immersion of the glass substrate into the cationic precursor for 15 sec for complex absorption on the substrate (2) then in double distilled water maintained at 75°C for 15 sec and rinsing in distilled water keep at room temperature for another 15 sec. This cycle was repeated for 100 (CdO1), 150 (CdO2), and 200(CdO3) number of dipping and at the end of a complete cycle, the deposited films were rinsed properly with distilled water. Finally, the deposited films were annealed in air at 200°C for 1hour.The mass of the film was determined using an electronic high-precision balance and thickness is measured precisely by galvanometric method. The thickness of the films were ~ 250 nm (CdO1), 315 nm (CdO2) and 360 nm (CdO3).

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 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 details the optical properties of the samples at room temperature using a double-beam spectrophotometer (Shimadzu, UV–1800).The gas sensing ability was measured using simple home-made arrangement with help of Keithley 6514 DMM electrometer for measuring resistance value.

3. Result and Discussion

X-ray diffraction (XRD) pattern of CdO thin film is shown in figure 1. According to the XRD pattern the CdO1sample (film produced by 50 dipping cycle) 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 matches to cubic phased cadmium oxide [JCPDS file no. 05-0640]. The plane (111) is the maximum intense one. The lattice constant for CdO1is ~ 0.458 nm and it slightly decreases with increase in number of dipping as thickness increases. The crystallite size was estimated from the X-ray diffraction data using the Debye–Scherrer equation as given by

$$d = \frac{0.89\lambda}{\beta \cos\theta} \qquad (1)$$

where β denotes FWHM intensity of the concerned peak. The average crystallite size is ~ 20.2 nm for CdO1 sample where margin of error for calculation is within ± 5% limit. Figure 2 shows variation of thickness with number of deposition cycle. The particle size is of the order of 24-30 nm as measured from TEM images [figure 3] using Image J software [10].The SEM images of CdO thin film for 100 and 200 deposition cycle was shown in figure 4(A) and 4(B) respectively. The surface roughness along with porosity increased with increase in number of dipping cycle. The change in surface roughness may further increases the ability of a material to sense target gas.

The band gap energy (E_g) was calculated using Tauc's relation for direct band gap of CdO [11]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (2)$$

where h is the Planck's constant, ν is the frequency and A denotes function of index of refraction and hole/electron effective masses. Figure 5epitomizesthe plot of $(\alpha h\nu)^2$ as a function of photon energy $h\nu$ for all samples CdO1, CdO2 and CdO3. The value of band gap decreases from ~2.14eV to ~2.02 eV with increasing thickness (also with increase in dipping cycle) of CdO thin film. This may be is due to quantum confinement effect with agreement of crystalline size.

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

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

Figure 6shows plotting of percent sensitivity with operating temperature for 1000 ppm ethanol gas. The maximum sensitivity attained at 250° C for all samples. The amount sensitivity increases with deposition cycle which may be due to increase in surface roughness and porosity with deposition cycle. The increase in porosity increases the effective surface area for reaction of target gas molecules with chemisorbed species [12]. As the 200 dipping cycle sample shows maximum porosity than others, so it shows highest response for ethanol. The sensing capability of any sensing material depends largely on temperature. At a specific temperature sensing material attains a 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 reached maximum efficiency. The maximum operating temperature greatly depends on structure, roughness, porosity and material.

4. Conclusions

In this work, we have mainly discussed the structural, morphological and optical properties of CdO thin films of different thickness synthesized using simple, low-cost SILAR method by varying the number of deposition cycle. The band gap energy decreases with increase in film thickness. XRD study strongly confirms the presence of cubic phased cadmium oxide with (111) as most intense peak.SEM micrograph shows the increase in porosity and surface roughness with thickness as well as number of deposition cycle. The thickness greatly affect the sensing ability of CdO thin film for ethanol target gases. Such clear increase in sensitivity may be due to enhancement of both surface roughness and porosity with increase in thickness. In

Future, we plan for modification of these sensing materials in a systematic way.

5. Acknowledgments

The author acknowledges the Department of Physics, R.N.College, Hajipur for their help to carry out the work. The author is also thankful to Babasaheb Bhimrao Ambedkar Bihar University, Bihar, India for success of this work.

References

[1] Z. A. Alahmed, H. A. Albrithen, A. A. Al-Ghamdi, F. Yakuphanoglu, Optical band gap controlling of nanostructure Mn doped CdO thin films prepared by sol-gel spin coating method, Optik126 (2015) 575–577.

[2] R. Chandiramouli, B.G. Jeyaprakash, Review of CdO thin films, Solid State Sciences 16 (2013) 102-110.

[3] R. H. Bari, S. B. Patil, Nanostructured CdO thin films for LPG and CO2 gas sensor prepared by spray pyrolisis technique, International Letters of Chemistry, Physics and Astronomy Online 37 (2014) 31-46. DOI:10.18052/www.scipress.com/ILCPA.37.31

[4] T.K. Subramanyam, S. Uthanna, B. Srinivasulu Naidu, Preparation and characterization of CdO films deposited by dc magnetron reactive sputtering, *Materials Letters* 35 (1998) 214-220.

[5] M. R. Das and P. Mitra, SILAR-synthesized CdO thin films for improved supercapacitive, photocatalytic and LPG-sensing performance. *Chemical Papers*, *73*(7) (2019) 1605-1619.

[6] R. A. Ismail, H. H. Ahmed, A. M. E. Al-Samarai, S. J. Mohmed. (2014) Effect of pH on the structural and optical properties of nanostructured CdO films grown by chemical bath deposition technique. *Micro & Nano Letters* **9** (12) (2014) 935-939.

[7] Freitas, J. G., Fletcher, B., Aravena, R., and Barker, J. F. (2010). Methane production and isotopic fingerprinting in ethanol fuel contaminated sites. Ground Water 48, 844–857. doi: 10.1111/j.1745-6584.2009.00665.x

[8] M R Das, A Mukherjee, P Maiti, S Das and P Mitra. Studies on Multifunctional Properties of SILAR Synthesized CuO Thin Films for Enhanced Supercapacitor, Photocatalytic and Ethanol Sensing Applications. Journal of Electronic Materials. 2019; 48, 2718–2730. DOI: https://doi.org/10.1007/s11664-019-06940-1

[9] C. Yusuf, B. Derya, B. Silan, Optical and electrical properties of Ni-doped CdO thin films by ultrasonic spray pyrolysis. Journal of Materials Science: Materials in Electronics 29 (2018). 9841.

[10] W. Rasband, ImageJ [Software], U. S. Natl. Institutes Heal. Bethesda, Maryland, USA. (2015) //imagej.nih.gov

[11] J. Tauc, *Amorphous and Liquid Semiconductor*, Plenum Press, New York, 1974, 159-220.

[12] P A Terry, M Anderson and I Tejedor. Catalytic Dehydrogenation of Cyclohexane Using Coated Silica Oxide Ceramic Membranes. J. Porous Mater. 1999; 6, 267-274.

Figures

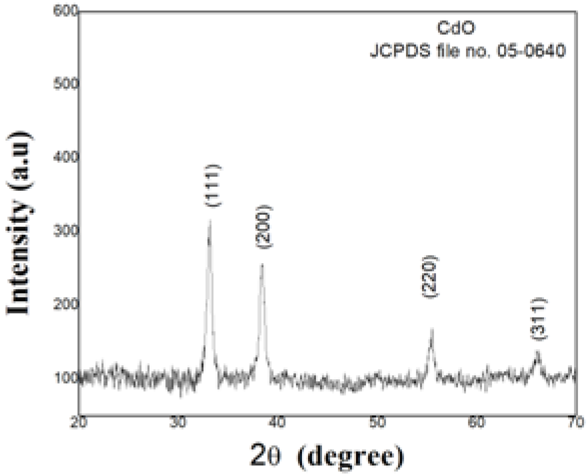

Figure 1: X-ray powder diffraction patterns of CdO

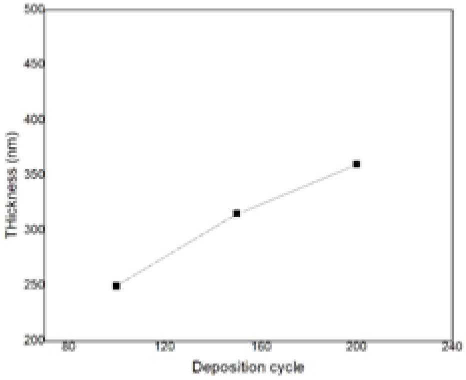

Figure 2: Variation of thickness of CdO thin films

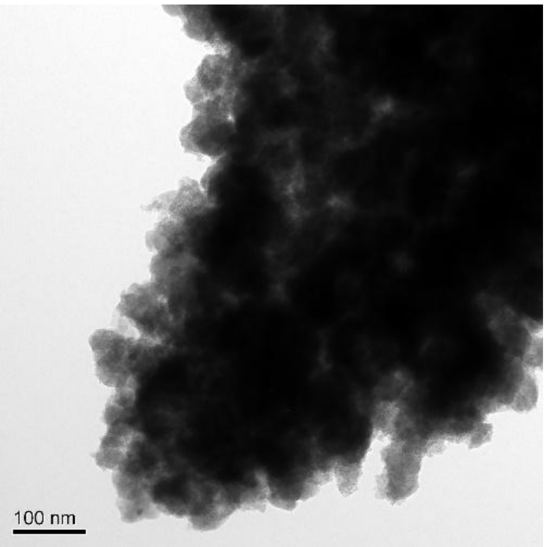

Figure 3: TEM image of CdO1

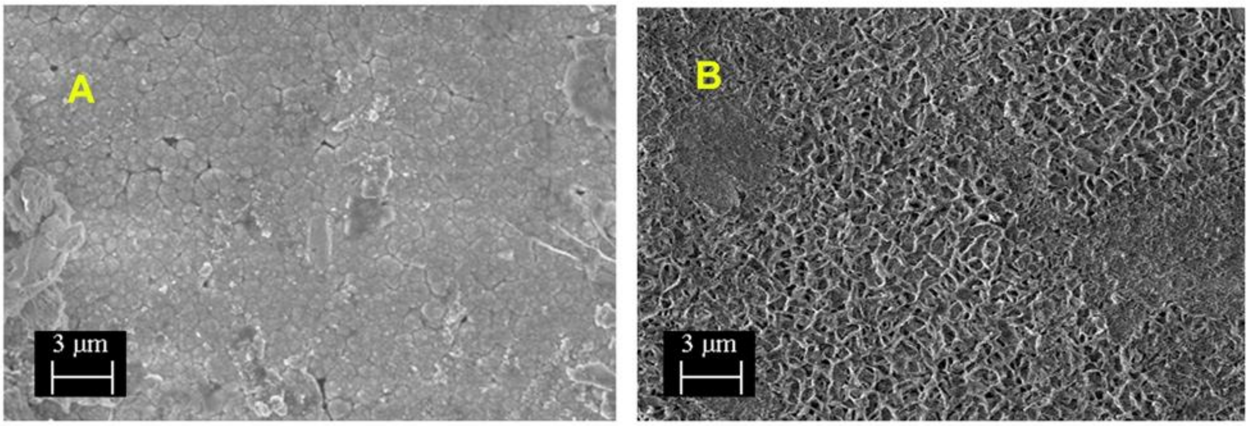

Figure 4: SEM images of (A) CdO1 and (B) CdO3

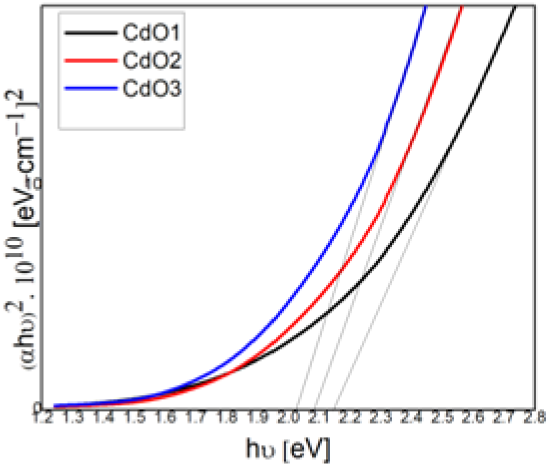

Figure 5: Plot of $(\alpha h\nu)^2$ vs. $h\nu$ forCdO1, CdO2 and CdO3 thin films

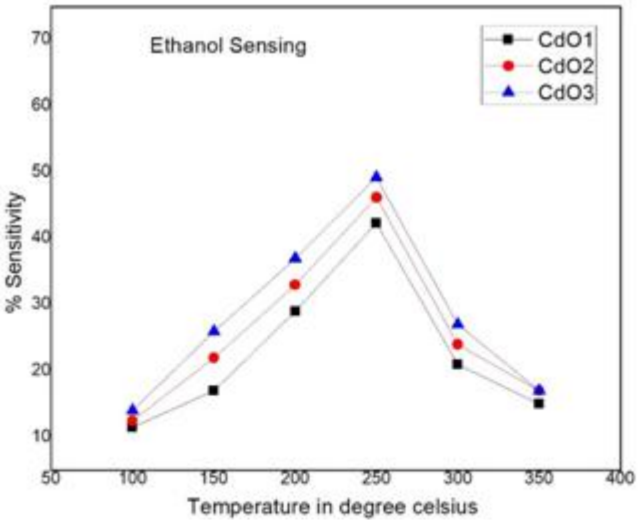

Figure 6: Sensitivity vs Operating Temperature curve for CdO thin films for ethanol.