

Surface Topography, Physical and Optical Properties Studies of Cadmium Oxide (CdO) Thin Film Fabricated by Spray Pyrolysis Technique

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Abstract: Cadmium oxide (CdO) thin films were fabricated by spray pyrolysis technique from aqueous solution of cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) with substrate temperature at 300°C. Here two different volume of solution were taken to fabricate the films. The X-ray diffraction (XRD) study indicates the formation of polycrystalline (FCC crystal structure) CdO phase with preferential orientation along (111) plane. The film thickness, refractive index, absorption coefficient, roughness was measured by Ellipsometry spectroscopy. From these result thickness was increased with roughness by increasing volume of solution. The surface topography was determined by AFM which indicate that surface electron mobility is high. The direct band gap energy of the film was 2.39 eV.

Key words: CdO, Ellipsometry, AFM, Spray pyrolysis.

1. Introduction

Transparent conductive oxides (TCOs) are a type of non-stoichiometric semiconductor oxides of high conductivity arising from structural metal interstitials and oxygen vacancies. They have widespread use in many advanced technology applications. It is well known that high carrier mobility is essential for TCOs with good quality electro-optical properties. The TCOs have attracted much attention due to their importance in optical and electrical applications like in displays, gas sensors, solar cell technology [1, 2].

Cadmium oxide is a good transparent conductive material because their high transparency coefficient in visible region, high electrical conductivity and high optical transmittance in the visible region of solar spectrum along with a moderate refractive index make it useful for various applications, such as photodiodes, gas sensors, etc. The CdO based materials could be widely used in high performance solar cells which contain a large amount of Cd [3, 4]. It has n-type semiconducting property with a rock-salt crystal structure (FCC) and an optical band gap lies between 2.2-2.7 eV [5- 7]. The CdO semiconducting gas sensors is spreading more to detect the pollutants, toxic gases, alcohol and food freshness and used in moisture detectors, electronic sensors [8- 11]. The morphology, the particle size and surface area are the important role in sensing materials.

In the present work, preparation of CdO thin films deposited by simple and low cost spray pyrolysis technique. Compared to other deposition technique, spray pyrolysis offers several advantages like non-vacuum use of inexpensive equipment, ease of large scale adoption and possibility of automation for industrial use. More ever using spray pyrolysis one can control the basic structural and morphological characteristic of the as-grown material through the growth conditions, leading to films exhibiting the required functionality for particular applications, substrate temperature, concentration of precursor solution, type and pressure of the carrier gas, geometric characterization of the spraying system and spraying rate are the parameters that can significantly affect the properties of the as grown films.

2. Experimental details

The CdO solution was prepared with 0.1N using $(\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O}$ as a precursor salt and deionised water as a solvent (50 ml). Cadmium oxide thin films were fabricated on glass substrate using spray pyrolysis technique. Two different type of sample were fabricated based on solution volume sample 1 was coated with 15 ml and sample 2 was coated with is 35 ml. The temperature of the substrate was maintained around 300°C . The spray rate was kept constantly by 0.25 to 0.5 ml/s using air as a carrier gas. The each spray time was 3 seconds continuously and time interval between each spraying was 90 seconds. The solution was deposited onto the substrate through a nozzle fixed at 30 Cm from the substrate. The XRD study reveals the face centre cubic and the thin film is grown crystalline in nature. Surface morphology and roughness of the film was studied using AFM. The physical properties of the film were measured by ellipsometry spectroscopy. The optical properties of cadmium oxide (CdO) thin films were investigated by UV-VIS spectrophotometric technique.

3. Result and discussion

3. 1. X- ray diffraction pattern of CdO thin film

The XRD patterns of CdO films are shown in Fig.1. According to XRD, the grown CdO films are highly oriented in (1 1 1) plane and the position of X-ray diffraction peaks fit well with face centre cubic (FCC) structure of CdO thin film (ICSD collection code: 60764). The crystalline size ($D = 850\text{\AA}$) was calculated using Scherer's formula $D = 0.9\lambda/\beta \cos\theta$. Where D is the crystalline size, β is the broadening of diffraction line measured at half of its maximum intensity and λ is the X- ray wavelength. When crystallites size are less than approximately $1,000\text{\AA}$ in size, appreciable broadening in the x-ray diffraction lines will occur.

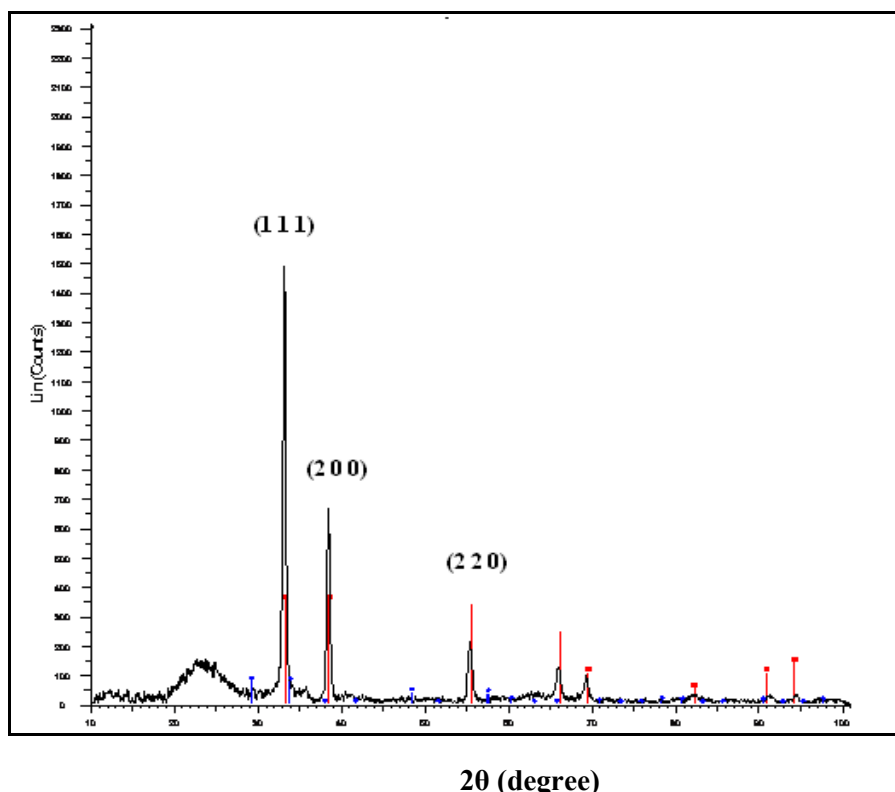


Fig. 1. The XRD pattern of CdO thin film.

3. 2. Surface topography study by Atomic force microscope

The surface topography and roughness of grown CdO thin film was studied by AFM with constant height mode (distance between probe and sample) shown in Fig.2. The film was composed of spherical particles. It is seen that each grain comprises several small crystallites appearing as grains on the surfaces of the films shown in Fig. 2. From the cantilever deflection image, on the film surface the mobility of charge carrier is

high and the film surface is almost perfectly smooth with nano size grains distributed and are well connected. The root mean square (rms) roughness was measured as 70 nm.

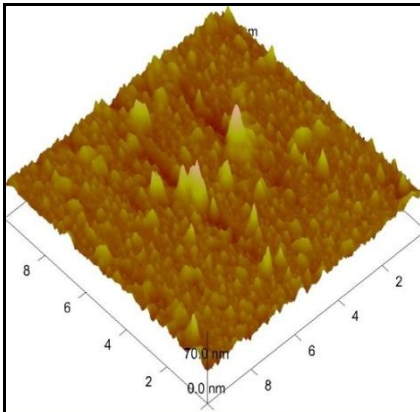


Fig. 2. AFM image of CdO thin film.

3.3. Thickness and physical property measurement by Ellipsometry spectroscopy

Determining the refractive index (n), the absorption coefficient (k), film thickness of a coating are important parameters in thin film research. Because optical devices performs are depend upon number of film layers and the difference in the refractive index. For this purpose we are using **Spectroscopic Ellipsometer** (Make: J AWoolam, USA). Woollam's new patented B-Spline model is an easy to use method of fitting mathematical functions to get optical constants. Complete EASE also includes our Generalized Oscillator model with a comprehensive library of mathematical functions.

Ellipsometry measures two values, Ψ and Δ , which are related to the polarization change in the light that interacts with a sample. Figure 3, 4 illustrates ellipsometric data on $\Psi(\lambda)$ (red colour line in spectrum) and $\Delta(\lambda)$ (green colour line spectrum) for the indicated incidence angles (60° , 65° , 70°), for a film on glass.

The film thickness is determined by interference and the interference involves both amplitude and phase information. The phase information is very sensitive to films down to sub-monolayer thickness. There are large variations in Δ , while the reflectance for each film is nearly the same. The excellent agreement to the experimental data, evident from figures 3, 4 was obtained for fitted values of the cadmium oxide thin film. From the Fig.3. (15 ml coating), film thickness (d) = 83.59 nm, refractive index (n) = 1.6249, existence coefficient (k) = 0.07223, roughness (r) = 6.28 nm. From the Fig. 4 (35 ml coating), the film thickness (d) = 426.18 nm, refractive index (n) = 1.5779, existence coefficient (k) = 0.06461, roughness (r) = -8.35 nm.

The optical properties of the materials can be described in terms of their spectrally dependent complex refractive index, $N = n + ik$, or, alternatively, in terms of their complex dielectric function, $\epsilon = N^2$. Also determination of complex refractive index gives access to fundamental physical properties which are related to a variety of sample properties including morphology, crystallinity, chemical composition and electrical conductivity.

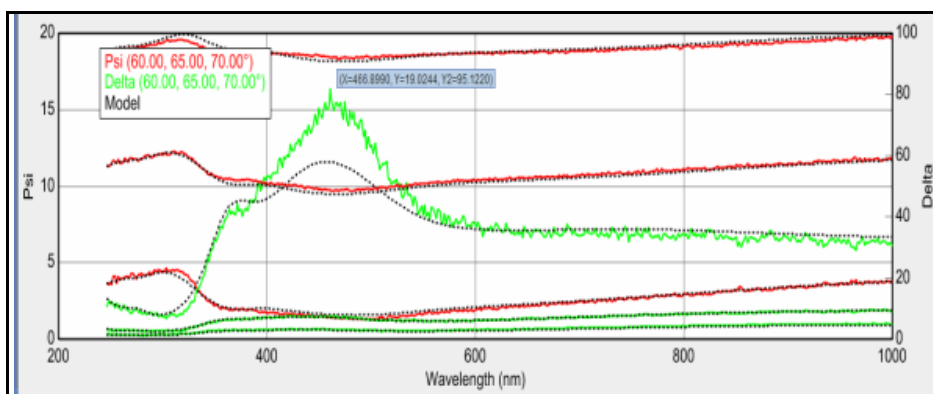


Fig. 3. Ellipsometry spectrum of CdO thin film (15ml).

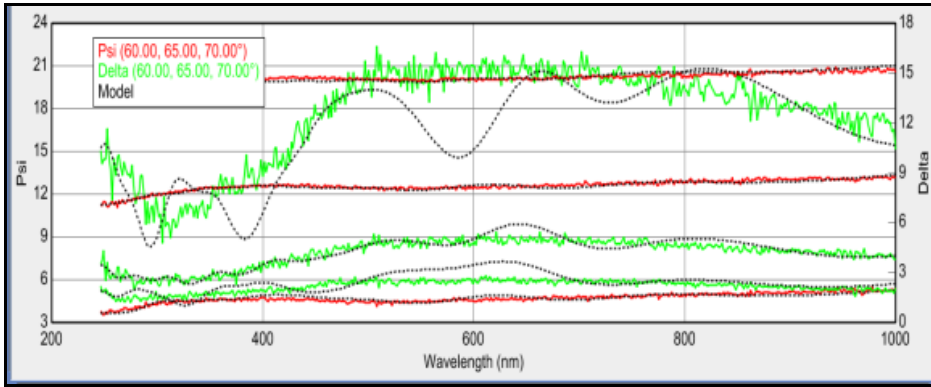


Fig. 4. Ellipsometry spectrum of CdO thin film (35 ml).

The ellipsometry spectra of CdO thin film was shown the volume of the solution increasing while increasing in the film thickness and decreasing in refractive index, roughness, absorption coefficient. Also decrease of roughness of the film increasing light reflection and decreasing in light absorption in the visible region of the solar spectrum in solar cells.

3. 4.Optical study of CdO thin film

The Fig.5 shows the optical absorption spectra of CdO thin films (coated with 15 ml solution) in the wavelength range of (200-1100) nm. It is clear that the films have high absorption at short wavelength. The absorption coefficient α is calculated from the absorption spectrum of the film using Lambert’s law $\alpha = 2.303 (A/t)$.

Where, A is the absorption and t is film thickness here 83 nm coating with 15 ml solution. Assuming that transition becomes constant at the absorption edge, the absorption coefficient α for directly allowed transition for simple parabolic scheme can be as described as a function of incident photon energy as $(\alpha h\nu)^2 = hv$.

The optical band gap has 2.39 eV. The optical energy gap is determined by plotting $(\alpha h\nu)^2$ as a function of photon energy as shown in Fig. 6.

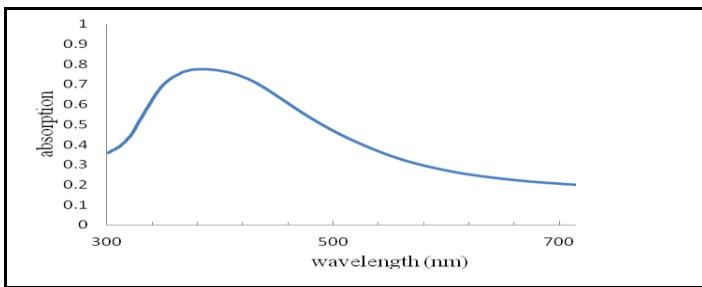


Fig. 5. UV-Vis absorption spectrum of CdO thin film.

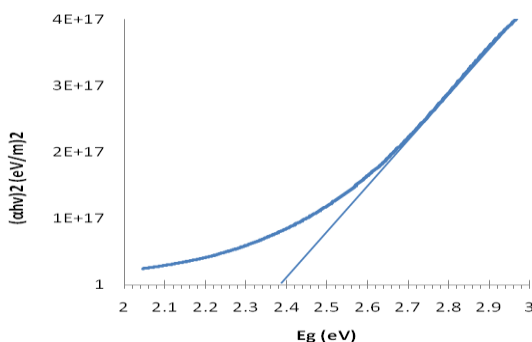
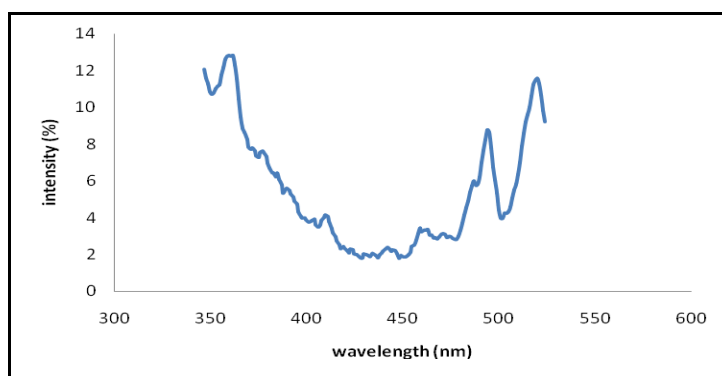


Fig. 6. Tauc's graph for thin films $(\alpha h\nu)^2$ Vs photon energy.**3.5. Photoluminescence spectrum of CdO thin film**

Photoluminescence spectrum of the CdO thin film was shown in Fig.7, it can be used to determine the band gap energy as well as the energy levels of different defect levels in the band gap region in semiconductors. The strong emission was observed at 355 nm (3.4 eV) in UV region and low emission peaks 493nm (2.5 eV), 517 nm (2.4 eV) are observed in visible region. The visible light emission was observed at 517 nm due to green band emission corresponding to the crystal defects. This green emission originated from the recombination of the holes with the electrons occupying the single ionized oxygen vacancies. Intensity of the UV emission was related to the crystal quality of deposited materials with fewer structural defects and impurities. The CdO thin film has good optical properties and promising candidate for the UV optical devices.

**Fig. 7. Photoluminescence spectrum of CdO****4. Conclusion**

CdO thin film was fabricated by spray pyrolysis deposition technique. The XRD pattern confirms CdO phase with FCC structure with preferential orientation along (002) plane. The surface topography and electron mobility on film surface was studied by AFM constant height mode. From the AFM result given well surface topography image and shows electrons mobility on the film surface. Changing the volume of solution, it made variation in the film thickness and the optical properties as refractive index, absorption coefficient are decreasing when film thickness is increasing was measured by ellipsometry spectroscopy. The direct band gap energy of the CdO thin film was 2.39 eV calculated from UV-Vis absorption spectrum. Photoluminescence study shows the film have less structural defect and impurities due to light emission of film in UV region.

References

1. H. Kim, C.M. Gilmore, A. Pique, J.S. Horwitz, H. Mattoussi, H. Murata, Z.H. Kafafi, D.B. Chrisey, Electrical, optical, and structural properties of indium-tin-oxide thin films for organic light-emitting devices, *J. Appl. Phys.* 1999, Vol. 86, pp. 6451-6461.
2. T. Minami, H. Tanaka, T. Shimakawa, T. Miyata, H. Sato, High-Efficiency oxide hetero junction solar cell using Cu₂O sheets. *Jpn.J. Appl. phys.* 2004, Vol. 43, L917-L919.
3. M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Noufi, Progress toward 20% efficiency in Cu(In,Ca)Se₂ polycrystalline thin-film solar cells, *Prog. Photovoltaics*, 1999, vol. 7, pp. 311-316.
4. O. Niitsoo, S.K. Sarkar, C. Pejoux, S. Ruhle, D. Cahen, G. Hodes, Chemical bath deposited J. *Photochem.photobiol.*, A, 2006, vol. 181, no. 306.
5. M. Ortega, G. Santana, A. Morales-Acevedo, *Solid State Electron*, 2000, vol. 44, no. 1765.
6. R. S. Rusu, G. I. Rusu, *J. Optoelectronics and Advanced Materials*, 2005, vol. 7, no. 1511.
7. A. A. Dakhel, *J. Material Science*, 2004, vol. 46, no. 6925.
8. A. Dakhel, A. Y. Ali-Mohamed, *J. Sol-Gel Sci. Technol.* 2007, Vol. 44, no. 241.
9. S. Yu-Sheng and Z. Tian-Shu, "Preparation, structure and gassensing properties of ultramicro ZnSnO₃ powder," *Sensors and Actuators B*, 1993, vol. 12, no. 1, pp. 5-9.

10. T. Zhang, Y. Shen, and R. Zhang, "Ilmenite structure-type β - CdSnO₃ used as an ethanol sensing material," *Materials Letters*, 1995, vol. 23, no. 1-3, pp. 69-71.
11. W. Xing-Hui, W. Yu-De, L. Yan-Feng, and Z. Zhen-Lai, "Electrical and gas-sensing properties of perovskite-type CdSnO₃ semiconductor material," *Materials Chemistry and Physics*, 2003, vol. 77, no. 2, pp. 588-593.
12. X.-H.Wu, Y.-D.Wang, Z.-H.Tian, H.-L. Liu, Z.-L. Zhou, and Y.- F. Li, "Study on ZnSnO₃ sensitive material based on combustible gases," *Solid-State Electronics*, 2002, vol. 46, no. 5, pp. 715-719.
