OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 7, July 2010, p. 968 - 972

Effect of molar concentration on the optical and surface properties of CdO thin film deposited by spray pyrolysis

M. M. ISLAM, J. PODDER*, M. R. ISLAM
Department of Physics, Bangladesh University of Engineering & Technology, Dhaka-1000, Bangladesh

Cadmium oxide (CdO) thin films have been deposited onto glass substrates from different molar concentration of cadmium acetate precursor solution using a simple spray pyrolysis technique. The surface morphology, structural and optical properties of the films has been characterized by Scanning Electron Microscopy (SEM) attached with an EDX, X-ray diffraction study and UV spectroscopy. From EDX data, atomic weight % of Cadmium and Oxygen are found to be 41.11% and 58.89% respectively. The SEM micrographs of as-deposited film show uniform deposition over the substrate. On annealing, the surface roughness increases and reveals sprayed particles (atoms) are adsorbed onto the glass substrate to form clusters as the primary stage of nucleation. At higher annealing temperature growing nuclei come into contact to form island stage and appears as spheroid shape. The crystal structure of the as deposited and annealed films were found to be polycrystalline with cubic structure and the lattice constant is a=4.65Å. The absorption coefficient is obtained in the order of 10^4 cm^{-1}. For different molar concentrations (0.1M ~ 0.5M), the direct band gap is found to be in the range 2.40 ~2.53 eV and indirect band gap in the range 1.70~ 2.14 eV. The band gap energies depend on molar concentration of solution.

(Received March 01, 2010; accepted July 14, 2010)

Keywords: Spray pyrolysis, CdO, Molarity, Optical band gap

1. Introduction

Cadmium oxide (CdO) belongs to the family of transparent conducting oxide films whose extremely wide range of physical and chemical properties makes them important materials both for technological and industrial applications, especially in the field of optoelectronic devices such as solar cells [1-2], photo transistors [3], diodes [4], transparent electrodes [5], and solid state gas sensors [6], etc. CdO thin films exhibit high transmission in the visible and UV regions, as well as a high ohmic conductivity. Bulk CdO shows n-type conductivity mainly due to oxygen vacancies. In the recent years, many different techniques such as thermal evaporation [7], sputtering [8], solution growth [9], pulsed laser sputtering [10], activated reactive evaporation [11] and spray pyrolysis deposition (SPD) [12-14], etc. have been used for the preparation of CdO thin film. Among the various methods SPD technique provides a simple route of synthesizing thin films because of its simplicity, low cost experimental setup from an economical point of view. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. This method has good control over the thickness uniformity and good adherence to the substrate. CdO thin films were deposited by thermal evaporation [7] under vacuum onto glass substrates at 300 and 473K respectively. The optical energy band gap was found 2.4 eV [15]. Thin films of CdO were deposited onto amorphous and fluorine-doped tin oxide (FTO) glass substrate using SPD technique [16] and direct band gap energy was found 2.26 eV.

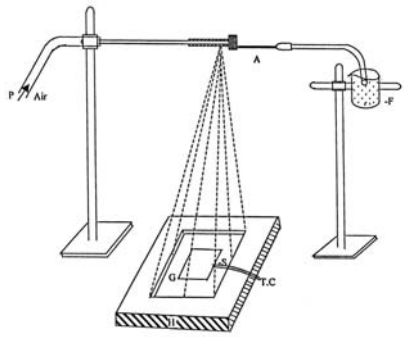
Surface roughness, inhomogenity and intrinsic defects, etc. are the cause of the optical losses. From the practical point of view, these properties can severely degrade or modify the performances of a component. Overall, the structural and optical properties of the thin films depend on the method of the preparation. The properties of the films are influenced by the geometry of the experimental setup.

From industrial application point of interest, we have deposited CdO thin films with larger grains under optimum conditions and studied their structural and optical properties more precisely for various molar concentrations of precursor solution by a locally developed SPD system, so as to reduce the preparation cost and make it economically more viable. The influence of annealing temperatures on the film characteristics has also been investigated and we have compared the results of our as-deposited CdO thin films with others reported values [15-16].

2. Experimental details

Spray pyrolysis is basically a chemical process involves spraying aqueous solution onto a substrate held at high temperature, where the substrate provides the thermal energy for the thermal decomposition and subsequent recombination of the constituent species followed by sintering and recrystallization of the clusters of crystallites giving rise to a coherent film. A simple glass nozzle was fabricated to give a fine and very small droplets of precursor solution which is driven by air from the compressor. The precursor solution was prepared by dissolving a known quantity of cadmium acetate [$Cd(CH_3COO)_2.2H_2O$] in deionized water and methanol in the ratio 1 : 1. The deposition set up consists of four

sections, which include (a) the precursor solution and carrier gas (air) assembly connected to the spray nozzle, (b) the reaction chamber in which the substrate is heated, (c) the pumping and exhausting gas scrubbing systems, and (d) temperature controller with a Copper-Constantan thermocouple to control the substrate temperature. The experimental arrangement is shown in Fig. 1.



F (aqueous solution), A (nozzle), P (air pressure), G. S (glass substrate), T. C (thermocouple), H (heater)

Fig. 1. Spraying aqueous solution on a glass substrate by the carrier air pressure.

In this study, precursor solutions of 0.1M, 0.2M, 0.3M, 0.4M and 0.5M concentration of cadmium acetate was used as raw material to deposit CdO thin films. The glass substrates were cleaned ultrasonically in acetone and methanol respectively for 10 minutes in each case. The solution was sprayed onto pre-cleaned glass substrate. The substrate temperature was maintained constant at 573K. The normalized distance between the spray nozzle and the substrate was fixed at 29 cm. The pressure of the carrier gas (air) was kept constant at 1 bar. The solution flow rate was maintained 0.5 ml min^{-1} throughout the experiment. The films of various thicknesses were prepared through different molar concentrations for fixed deposition time.

The possible chemical reaction that takes place on the heated substrate to produce CdO may be as follows: when the droplets of the aqueous solution reached the heated substrate, chemical reaction of cadmium acetate with water vapor of solutions, stimulated by the temperature, takes place providing the formation of CdO films with the formation of carbon dioxides through some intermediate products.

$$Cd(COOH_3)_2 2H_2O \xrightarrow[\text{deposited to}]{300^{\circ}C} CdO + CO_2 + CH_4 + Steam$$

2. 1 Characterization

The surface properties of the films were examined by using HITACHI S-3400N model Scanning Electron Microscope (SEM) attached with an EDX to measure quantitatively the sample stoichiometry. The Optical transmission measurements were carried out within the wavelength range 300 to 1100 nm using UV-1601 PC SHIMADZU scanning double beam spectrophotometer. The experimental accuracy of the transmittance is (±0.005%) and wavelength is (±0.005%). The observed transmittance data were corrected relative to optically identical uncoated glass substrate. The thicknesses of the films were determined by using Fizeau-fringes method.

A Philips PW3040 X'Pert PRO X-ray diffractometer was used to characterize the materials and to determine the lattice parameters. The monochromatic (using Ni filter) CuK_{α} radiation was used whose primary beam power was 40 kV and 30 mA. All the samples were irradiated over 2θ range from 20° to 80° to get possible fundamental peaks of the sample with the sampling pitch of 0.02° and time for each step data collection was 1.0 sec. All the data of the samples were analyzed by using computer software "X'PERT HIGHSCORE" from which structural parameters was determined.

3. Results and discussion

3.1 Compositional studies

The quantitative analysis of the as-deposited CdO films carried out by EDX is shown in Fig. 2. Two strong peaks corresponding to Cd and O were found in the spectrum, confirms the high purity of the CdO thin film.

Table 1. Elemental analysis of the as-deposited thin film.

Name of the film	Percentage of atoms present in the film	
	Cd	O
CdO	41.11	58.89

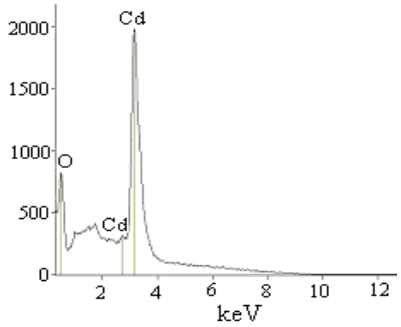


Fig. 2. Element analysis of as-deposited CdO film on glass substrate.

3.2 Surface morphology

Surface morphology of the as-deposited films was studied by Scanning Electron Microscope (SEM) under 1K magnification. Figs. 3 and 4 show the SEM micrographs of the CdO films of different molar concentrations deposited on glass substrate at temperature 573 K and annealed at 623 K and 673 K for 1 hour. Fig. 3 (a) shows uniform surface and deposition covers the substrate well. Fig (b) and (c) show annealed samples at different temperatures. After annealing the surface roughness is increased. It means that sprayed particles (atoms) are adsorbed onto the substrate to form clusters as the primary stage of nucleation. Clusters have a higher energy than the individual atoms, so at higher annealing temperature growing nuclei come into contact to form island stage and appears as spheroid shape.

For higher molar concentration of precursor solutions the thickness of the films increases. Freshly deposited films are assumed to be associated with the formation of highly unstable phases along with imperfections and defects. On annealing some of these defects will diffuse out with time and leads to a stable phase. At higher temperature the cluster migration mechanism also starts. Hence the smaller clusters move randomly and some of them are absorbed by the larger clusters to increase their radius and height [Fig.4 (a-b)]. Fig. 4(c) shows the reduced grain boundary of spheroid shape. This is caused due to coalescing of neighbor islands to the film to decrease its total energy by growing large grains for increasing substrate temperature.

The SEM micrographs show that a polycrystalline structure is formed with a well defined circular grain and grain boundaries. This shows that the disorder of the grain boundary increases as the thickness of the film increases. By comparing the micrographs it can be observed that the grain size increases with the increase in film thickness.

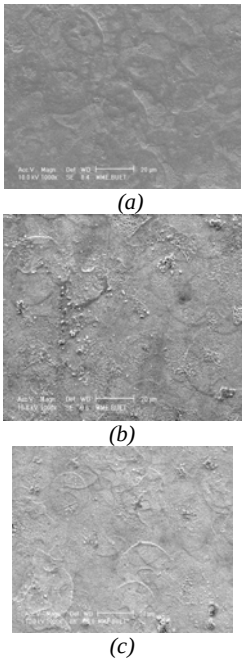


Fig. 3. SEM micrograph of CdO film of 0.1M concentration (a) as-deposited at 573 K for 10min, and (b) annealed at 623 K for 1 hour and (c) annealed at 673 K for 1 hour.

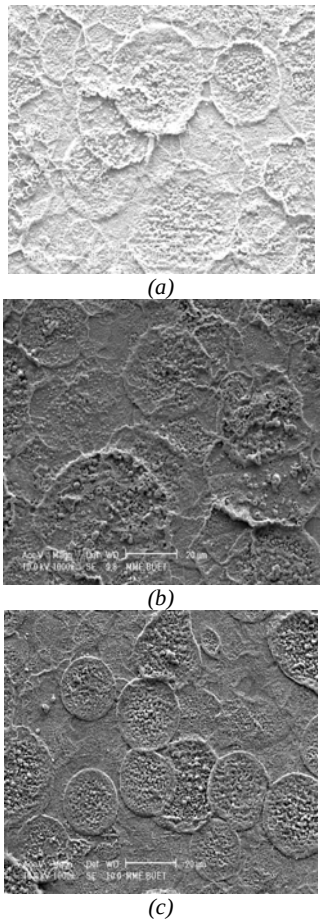


Fig. 4. SEM micrographs of CdO film 0.5M concentration (a) as-deposited at 573K for 10min (b) annealed at 623 K for 1 hour and (c) annealed at 673 K for 1 hour.

3.3 Structural properties

X-ray diffraction has been taken on as-deposited cadmium oxide thin film and the spectrum obtained is shown in Fig. 5. Spectrum shows well defined peaks, which indicates that the studied films are polycrystalline consisting of single phase CdO and no other phase could be detected. The structure was found to be cubic. Strong characteristic peaks at $2\theta = 32.90°$, 38.24^0 corresponding to (111) and (200) respectively along with weaker reflection at $2\theta = 55.24^0$ were observed in the spectrum.

It is also clear from the spectrum that the deposited films have the <111> preferred orientation and this is in agreement with the result obtained by others on film prepared by sputtering [17], vacuum evaporation [7] and spray pyrolysis [12]. Lattice constant for cubic CdO has been calculated using (100) reflection and the value obtained is a = 4.65Å and this is also in good agreement with the value obtained by others [8, 11, 12, 13].

Crystallite size of the prepared CdO has been calculated from the peak width of half the maximum intensity by using the Scherrer formula [18]

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

where t is the diameter of the crystal particle, λ is the wavelength used and B is the broadening of diffraction line measured at half its maximum intensity. The calculated diameter of the crystal particle was found to be 2.52 nm for as-deposited film. From the result it may be said that nano-crystalline CdO material can be grown by our locally developed spray pyrolysis method.

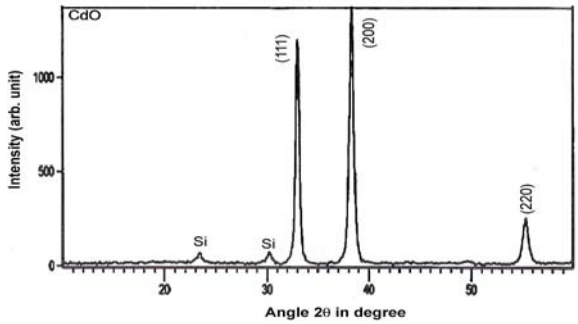


Fig. 5. The X-ray diffraction pattern of CdO for as-deposited and annealed films.

3. 4 Optical properties

The transmission spectra for as-deposited and annealed CdO thin films in the wavelength range (300-1100nm) are shown in Fig. 4. The as-deposited film onto heated substrate shows high transmittance and the annealed film results in a small decrease of transmittance due to Cd precipitation in the transition from amorphous into polycrystalline structure. At higher temperatures, the film surface became powdery because of homogeneous nucleation and reaction. Variation of optical absorption coefficient with photon energy for various molar concentrations is shown in Fig. 5. The absorption coefficient (α) is calculated from the transmittance spectrum using the relation

$$\alpha = \frac{\ln(1/T)}{t}$$

where T is the transmittance and t is the thickness of the film. It shows that the absorption coefficient increases slowly at the higher wavelength region and then increases sharply near the absorption edge. The band gap was determined using the following relation:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$$

where A is a constant, α is the absorption coefficient and $n = \frac{1}{2}$ for allowed direct transition and $n = 2$ for allowed indirect transition.

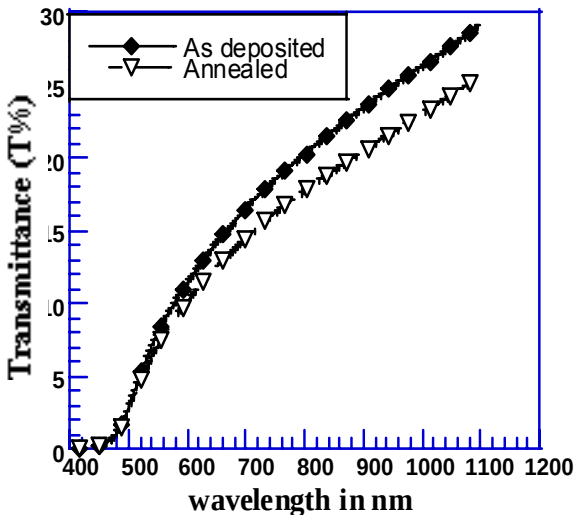


Fig. 6. Variation of optical transmittance with wavelength of as deposited and annealed film CdO film for thickness 360nm.

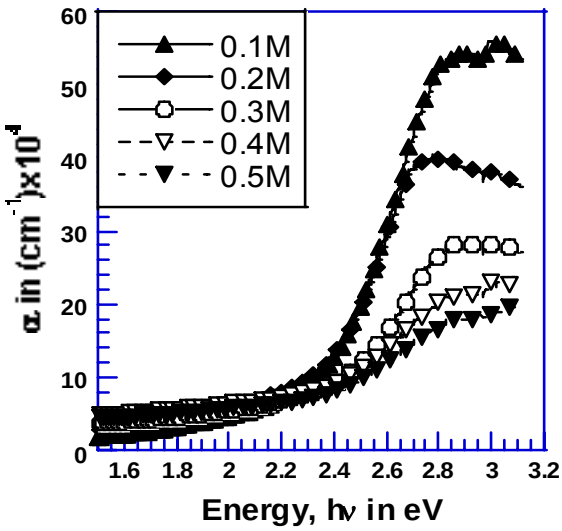


Fig. 7. Variation of absorption coefficient as a function of photon energy for CdO films for different film molarity.

Plots of $(\alpha h\nu)^2$ versus hν are shown in Fig. 8. The direct band gap energy of CdO has been obtained from the intercept of the straight line drawn from $(\alpha h\nu)^2$ versus hν curve on the energy axis. Fig. 9 shows $(\alpha h\nu)^{1/2}$ versus hν. The indirect band gap has been determined by the similar way. The values of optical band gap obtained for direct and indirect transitions are shown in Table 1, which indicates that both direct and indirect band gap decreases with increase of molar concentration of the precursor material (Fig. 10). It could be due to the increase of density of localize state in the conduction band. From figure it is seen that the energy gap decrease slightly with increase of molar concentration and the direct band gap energy is slightly higher than the indirect band gap energy.

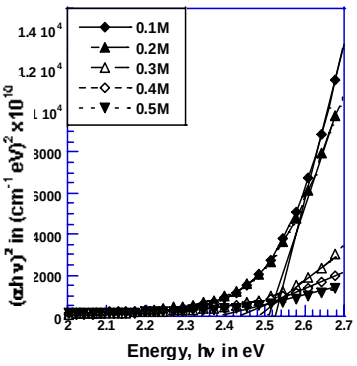


Fig. 8. Variation of $(\alpha h\nu)^2$ with photon energy for CdO films of different molarity.

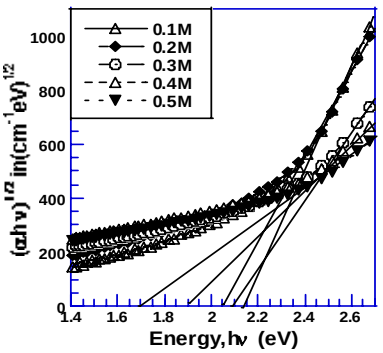


Fig. 9. Variation of $(\alpha h\nu)^{1/2}$ with photon energy for CdO films of different molarity.

Table 1. Values of direct and indirect band gap energy for CdO thin films for different molar concentration.

Molar concentration	Direct band gap energy E_g in eV	Indirect band gap energy E_g in eV
0.1M	2.53	2.14
0.2M	2.52	2.05
0.3M	2.49	2.01
0.4M	2.45	1.90
0.5M	2.40	1.70

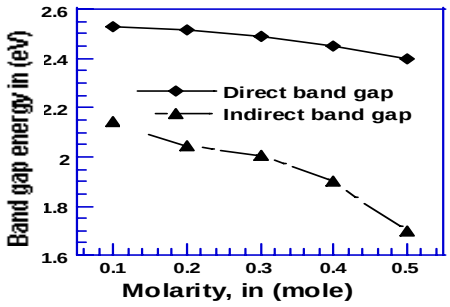


Fig. 10. Variation of direct and indirect band gap energy for different molar concentrations.

4. Conclusions

CdO thin films have been prepared from the different molar concentrations of cadmium acetate onto glass substrate keeping the substrate temperature 573K using a simple spray pyrolysis method. Different physical properties such as optical and surface properties as well as surface morphology have been studied. With the variation of molar concentrations (0.1M~0.5M) the thicknesses of the deposited film changes from 115nm to 390 nm. The SEM micrographs of as-deposited film show homogenous deposition over the substrate. SEM micrographs exhibit clear grains and grain boundary formation. It is observed that the band gap decreases with the increase of the molar concentration of the cadmium acetate aqueous solutions. The optical band gap was found to vary from 2.40~2.53 eV. The band gap could be tuned by controlling the molar concentration of the precursor solutions. The optical results show the suitability of these thin films as optical window material for photovoltaic applications. These results are in good agreement with other reported values. In conclusion, we can state that the spray pyrolysis could be a good and convenient method for the preparation of suitable thin films for scientific studies and technological applications.

References

[1] T. Trindade, P. O'Brien, N. L. Pickett, Chem. Mater., **13,** 3843 (2001).
[2] C. Sravani, K. T. R. Reddy, O. Md. Hussain, and P. J. Reddy, J. Solar Energy, Soc. India, **1,** 6 (1996).
[3] L. M. Su, N. Grote, F. Schmitt, Electron. Lett, **20,** 716 (1984).
[4] R. Kondo, H. Okimura, Y. Sakai, Jpn. J. Appl. Phys. **10,** 1547 (1971).
[5] F. A. Benko, F. P. Koffyberg, Solid State Commun. **57,** 901 (1986).
[6] A. Shiori Jpn. Patent **7,** 909 (1997).
[7] A. A. Dakhel, F. Z. Henari, Cryst. Res. Technol. **38**(11), 979 (2003).
[8] T. K. Subramanyam, S. Uthanna, B. Sinivasulu Naidu, Materials Letters **35,** 214 (1998), Appl. Surface Science **169,** 529 (2001).
[9] A. J. Varkey, A. F. Fort, Thin Solid Films **239,** 211 (1994).
[10] I. I. Shagnov, B. P. Kryzhanovskii, V. M. Dubkov, Sov. J. Opt. Technol. **48**, 280 (1981).
[11] K. T. Ramakrishna Reddy, C. Sravani, R. W. Miles, J. Cryst. Growth **184/185,** 1031 (1998).
[12] M. D. Uplane, P. N. Kshirsagan, B. J. Lokhande, C. H. Bhosale, Materials Chemistry and Physics **64,** 75 (2000).
[13] L. C. S. Murthy, K. S. R. K. Rao, Bull. Mater. Sci. **22**, 953 (1999).
[14] M. Kul, M.Zor, A.Senol Aybek, S. Irmak, E. Turan, Thin Solid Films **515**, 8590 (2007).
[15] R. S. Rasu, G. I. Rusu, J. Optoelectron. Adv. Mater. **7**(2), 823 (2005).
[16] C. H. Bhosale, A. V. Kamble, A. V. Kokate, K. Y. Rajpure, Materials science and Engineering B **122,** 67 (2005).
[17] T. L. Chu, S. S. Chu, J. Electron Mater. **19**, 1003 (1903).
[18] B. D. Cullity, Elements of X-ray diffraction, Addison-Wesley Publishing Company, London, 1967.

*Corresponding author: jpodder@phy.buet.ac.bd