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Synthesis, structural and optical characterizations of cadmium oxide (CdO) thin films by chemical bath deposition (CBD) technique

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Thin films of cadmium oxide (CdO) were synthesized and characterized using chemical bath deposition (CBD) technique. The XRD studies revealed amorphous CdO thin films which upon annealing at 623K transformed to polycrystalline structure. The optical studies showed that the CdO films have high average transmittance over 60% in the visible region and direct optical bandgaps of 2.02 ± 0.05 eV, 2.03 ± 0.05eV and 2.05 ± 0.05eV for samples X, Y, Z respectively. These characteristics make them good candidates for applications in photodiodes, phototransistors, photovoltaics, transparent electrodes, liquid crystal displays, IR detectors and anti-reflection coatings.

Key words: Thin films, chemical bath method, cadmium oxide, characterizations, bandgap.

INTRODUCTION

Metallic oxides are becoming prominent and important group of materials due to their versatile physiochemical, structural, and optical characteristics which include high temperature superconductivity, ferroelectricity, ferromagnetism, piezoelectricity, semiconductivity, optical, opto-electronic, magnetic, electric, thermal, electrochemical, catalytic and sensor properties (Jia et al., 2004; Vayssieres, 2004). Other attractive optical properties are low bandgap, high transmission, coefficient, invisible spectral domain, remarkable and luminescence characteristics (Ortega et al., 1999; Rusu and Rusu, 2005). The diversity emanates from the more complex crystal and electronic structures of metal oxides in comparison to other classes of materials. The elegancy of the metal oxides are found in the oxidation states, coordination numbers, symmetry, crystal-field stabilization, density, stoichiometry and acid-base surface properties that they exhibit. These characteristics made them to find applications in photodiodes, phototransistors, photovoltaics, transparent electrodes, liquid crystal displays, IR detectors and anti-reflection coatings (Dhawale et al., 2008).

The cadmium oxide (CdO) thin films are n-type semiconductor that exhibits rock salt structure (FCC) with wide optical bandgap of 2.2 eV, high conductivity and high transmission in VIS region (Ortega et al., 1999; Henriguez et al., 2008). The thin films have attracted attention in recent years due to their attractive properties and wide range of technical applications in transparent electrodes, photovoltaics and display devices, saucers and others (Dhawale et al., 2008). The films also have been used as transparent contact in CuInSe2 and Si Solar Cells (Ortega et al., 1999).

Different techniques have been used by researchers in the past ten years for synthesizing the thin films such as spray pyrolysis, sputtering, pulsed laser deposition,

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sol-gel spin coating, electrochemical, activated reactive evaporation, metal organic chemical vapour deposition (MOCVD) and chemical bath method or solution growth methods (Henriguez et al., 2008; Caglar and Yakuphanoglu, 2009). In this study chemical bath method (CBD) was used in synthesizing cadmium oxide (CdO) and the synthesized samples were characterized using XRD, SEM and UV-VIS spectrophotometric techniques in order to find their possible areas of applications.

MATERIALS AND METHODS

The starting chemicals used in this work without further purification include cadmium chloride ($CdCl_2.4H_2O$) (AR chemicals grade), ammonia ($NH_3.H_2O$) and double distilled water (DDW). PVA and PVP cadmium chloride ($CdCl_2.4H_2O$) was used as precursor for the preparation of CdO thin films as a Cd^{2+} ionic source.

A detail of chemical bath deposition (CBD) has been discussed elsewhere (Ezekoye and Okeke, 2006; Ezema and Osuji, 2008). Stock solution (5 ml) of $CdCl_2$ was poured in a beaker followed by addition of 4 ml of 30% NH_3, with slight shake gave a whitish solution which is odourless. More of 30% NH_3 was poured into the set-up until it was clear by a total of 4 ml of NH_3. Double distilled water (H_2O, 34 ml) was added to the set-up which gave a fair whitish colour. The set-up was kept into an open conical flask where a good amount of oxygen was sufficiently supplied to it. A whitish film was deposited on the glass slide after 45 h, which turned clearly whitish when rinsed with distilled water.

Sample Y was post-treated at 200°C for 1 h which gave a whitish colour after the annealing. Sample X was post-treated at 400°C for 1 h, forming a brownish colour after the annealing. Sample Z was as-deposited, that is, no treatment given.

For the complex formation, an excess ammonium hydroxide solution (NH_3+H_2O) was added (30%) till a clear solution was obtained. The clear solution was kept under unstirred condition and glass substrate was dipped in it for 45 h. Whitish films due to the $Cd(OH)_2$ were formed on glass substrate. The CdO films were annealed in oxygen air-tight container at 473 and 673K for 1 h which generally facilitates decrease in dislocations, stresses, and inhomogeneities (Dhawale et al., 2008). The change in colour from whitish to brown films during annealing confirmed the formation of CdO. The equations for the reactions are as follows:

$$CdCl_2 + NH_3 + H_2O \longrightarrow [Cd(NH_3)_4]^{2+} + 2OH^- + 2Cl^- \quad (1)$$

$$2OH^- + Cd^{2+} \longrightarrow CdO + H_2O \quad (2)$$

RESULTS AND DISCUSSION

Thickness measurement

Film thickness (d) was determined by gravimetric weight difference method using high precision electronic balance given by the relation (Ezekoye and Okeke, 2006):

$$d = \frac{M}{(\rho \ x \ A)} \quad (3)$$

where M is the mass of the film deposited on the substrate in gram, A is the area of the deposited film and ρ, the density of the deposited material. The maximum thickness obtained for CdO thin film was 180 *n*m. This thickness is greater than the nano range classification of materials.

Optical studies

Optical properties of cadmium oxide (CdO) thin films were investigated by UV–VIS spectrophotometric technique. The absorption coefficient(α) is related to incident photons by the relation $\alpha hv = A(hv - E_g)^n$ (Caglar and Yakuphanoglu, 2009; Ezema and Osuji, 2008; Mohamed and Ali, 2008), where *A* is a constant and *n* is an index that characterizes the optical absorption process and is theoretically equal to 1/2, 2, 3/2 and 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively. Since CdO is a direct band gap semiconductor, the $(\alpha hv)^2$ versus the *hv* diagram is depicted in Figure 1. The straight line on the curve at horizontal axis shows the energy band gap of the CdO thin films and is corresponding to 2.02 ±0.05eV (Sample Z) for the as-grown film. By annealing at 200 and 400°C, the band gap increased to 2.03 ± 0.05eV (Sample Y) and 2.05 ± 0.05eV (Sample X), respectively.

Figure 2 shows absorption spectra of CdO. The variation of optical absorbance (α) with wavelength (λ) of CdO film is shown in Figure 2. These spectra reveal that as-grown CdO films have low absorbance in the visible region. Figure 3 shows the transmittance spectra for CdO films. The increase in transmittance with increasing wavelength in ultra-violet (UV) region is fairly sharp. The absorption coefficient (α) was determined from the relation, $\alpha = \left(\frac{1}{d}\right)\ln\left(\frac{1}{T}\right)$, where d is the thickness of the film and T is the transmittance (Caglar and Yakuphanoglu, 2009; Mohamed and Ali, 2008) (Figure 3). This indicates that the absorption band gap transitions, which is characteristic of CdO and the fundamental absorption, which corresponds to electron excitation from the valence band to conduction band can be used to determine the nature and value of the optical band gap. The optical studies showed that the CdO films have high average transmittance over 60% in the visible region.

Film structure

Figures 4 (X), 4 (Y) and 4 (Z) show the XRD spectra of the grown CdO thin films. The film structure was studied by X-ray diffraction (XRD) technique using the CuK$_\alpha$ a radiation (λ = 0.1790 nm) and the grain size or crystallite size D was obtained using the Debye Scherrer relation (Barman et al., 2005):

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta}, \quad (4)$$

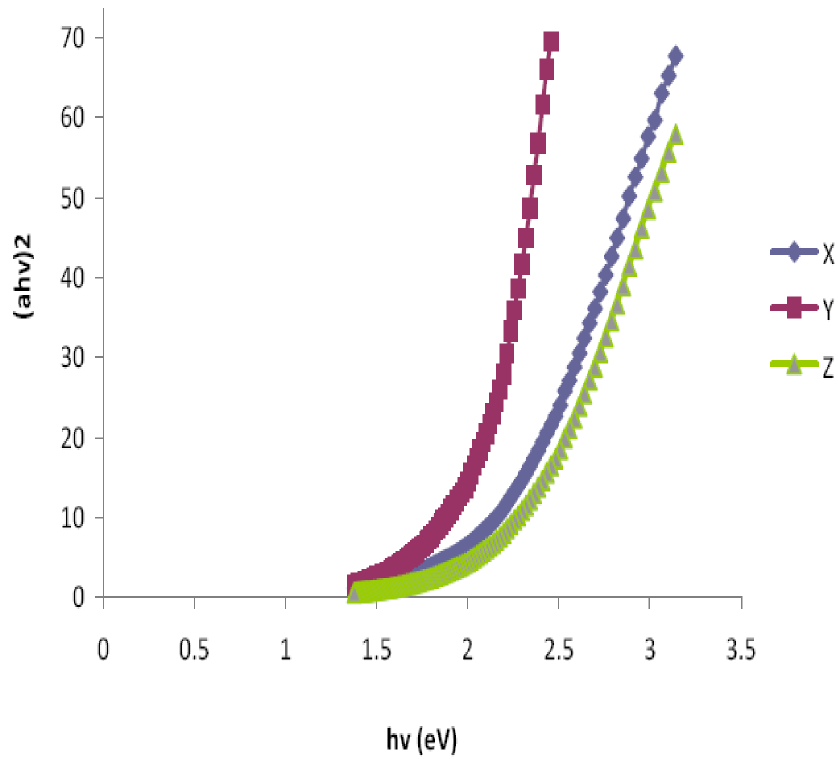

Figure 1. Plot of (α h ν)^2 against photon energy h ν (eV).

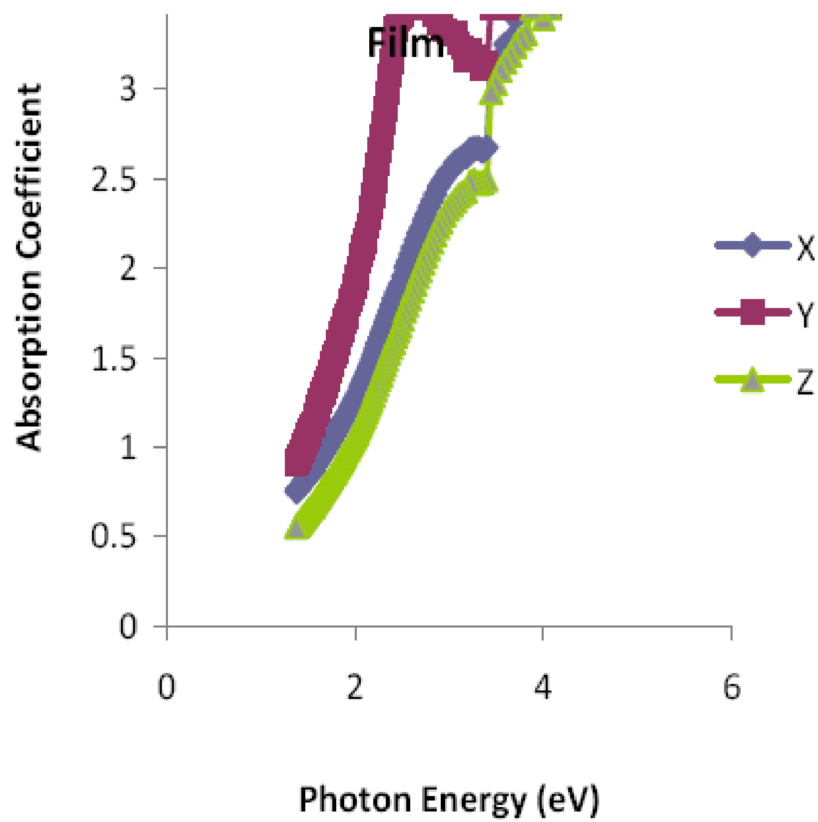

Figure 2. Plot of absorption coefficient against photon energy hv (eV).

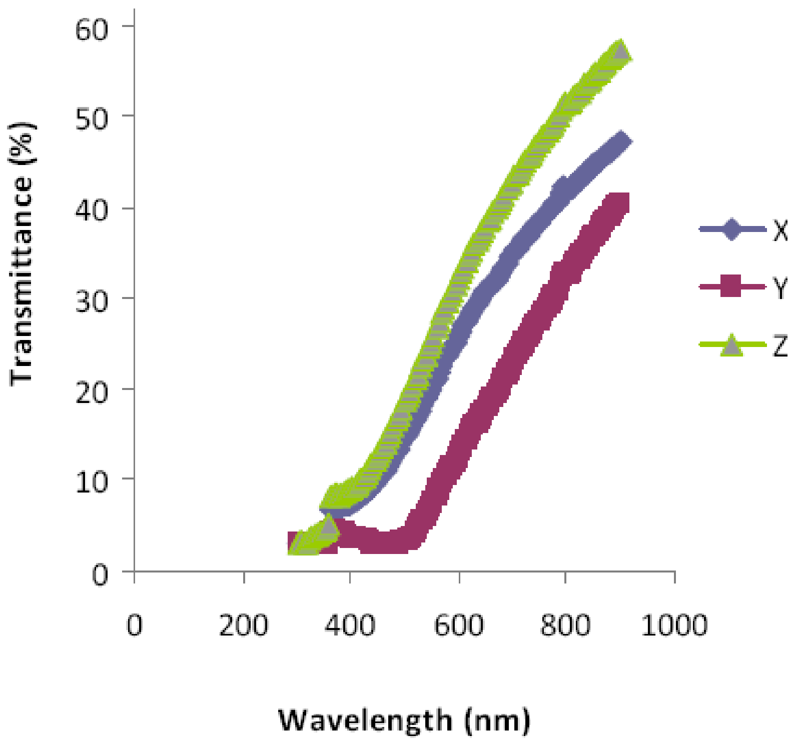

Figure 3. Plot of Transmittance (%) against photon energy hν (eV).

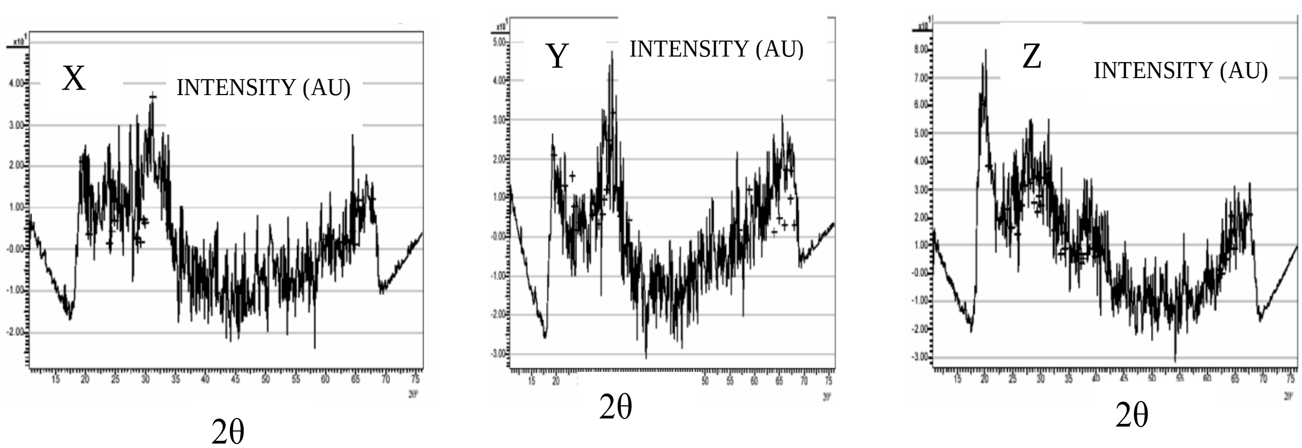

Figure 4. XRD spectra of the cadmium oxide thin film (X) annealed at 400°C (Y) annealed at 200°C and (Z) as-grown.

where K = 0.94, is the shape factor, $\lambda = 15408\dot{A}$, θ is the diffraction peak angle (Bragg's angle) in degrees and β is the full width at half maximum (FWHM) in radians, of the corresponding diffraction peak. Table 1 shows the various parameters of the grown film at 298, 473 and 673K. By increasing the annealing temperatures, the grain size of the crystallite was found to increase which is in agreement to Barman et al. (2005). Figure 5 shows the micrographs of the as-grown films (Z), and the annealed at 200°C (Y) and annealed at 400°C (X). The as-grown is amorphous while the annealed became crystalline as can be seen by increase in grain-size in Table 1.

Conclusion

Thin films of cadmium Oxide (CdO) were synthesized and characterized using CBD technique. The XRD

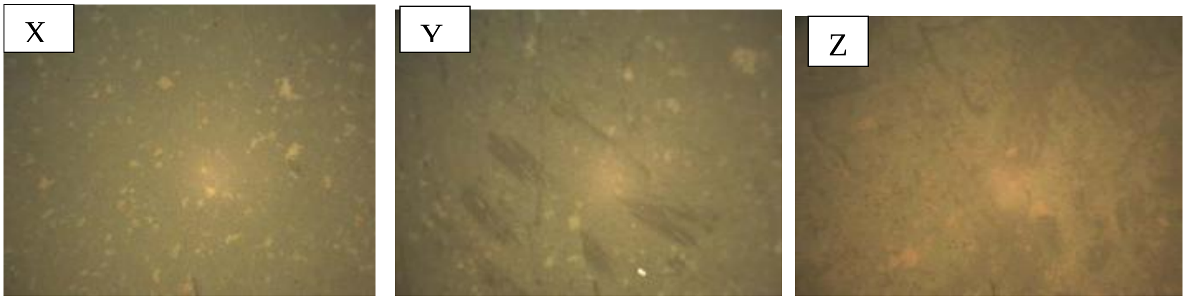

Figure 5. SEM image of samples X, Y, Z of the cadmium oxide thin films.

Table 1. XRD Parameters of the grown cadmium oxide (CdO) thin films.

Sample	Peak type	Peak position	Grain size (nm)	FWHM (°)	Bandgap (eV)
Z(278K)	(111)	31.19	28.675	1.4259	2.05 ± 0.05
Y(473K)	(111)	30.11	29.6749	0.96616	2.03 ± 0.05
X(673K)	(111)	20.64	43.0241	0.78548	2.02 ± 0.05

studies revealed amorphous CdO thin films which upon annealing at 623K transformed to polycrystalline structure. The optical studies showed that the CdO film has a high average transmittance of about 60% in the visible region with presence of direct bandgaps values of 2.02 ± 0.05eV, 2.03 ± 0.05eV and 2.05 ± 0.05eV for samples X, Y, Z, respectively. These characteristics make them good candidates for applications in photodiodes, phototransistors, photovoltaics, transparent electrodes, liquid crystal displays, IR detectors and anti-reflection coatings.

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