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Structural and morphological properties of spray deposited CdO thin films

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ABSTRACT *The objective of this work is to study the influence of deposition temperature on structural and surface morphological properties of the CdO thin films prepared by spray pyrolysis technique. These films were characterized for the structural and morphological properties by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). As deposited CdO films are polycrystalline with (111) preferential orientation. The information on crystallite size, microstrain and dislocation density is obtained from the full width-at half- maximum (FWHM) of the diffraction peaks. Texture coefficient and lattice constant have been calculated. The surface morphology of the films has been analyzed.*

1. Introduction

Transparent conducting metal oxide semiconductor materials have attracted much attention owing to their potential applications in flat panel display, smart windows, light emitting diodes, heat reflectors, electronic, photovoltaic devices and solar cells [1–4]. Its high electrical conductivity and high optical transmittance in the visible region of the solar spectrum along with a moderate refractive index make it useful for various applications such as transparent electrodes, phototransistors, photodiodes, gas sensors, etc. [5-6]. CdO is an n-type semiconductor with a rock-salt crystal structure (FCC) and possesses a direct band gap of 2.2 eV [7]. Besides, the CdO will be attractive in the field of optoelectronic devices by making heterostructures with ZnO which has band gap energy of 3.3 eV. CdO thin films have been prepared by various techniques such as sol–gel, DC magnetron sputtering, radio-frequency sputtering, spray pyrolysis, pulsed laser deposition, chemical vapor deposition, and chemical bath deposition [8-11].

Further, among these methods, the spray pyrolysis is unique and cost effective compared to other methods requiring high vacuum environment. It is one step method operating at atmospheric pressure with very short production time [12]. This can be used to tune the band gap of materials. Due to these economical and flexible experimental conditions, spray pyrolysis has been employed to deposit CdO thin films and to study various properties of the films. The crystalline structure and optical properties of the films were studied as a function of the substrate temperature (Ts) from 250 to 450 ^{0}C.

2. Experimental details

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. The amorphous glass substrates supplied by Blue Star Mumbai, were used to deposit the CdO thin films. Before the deposition of CdO thin films, glass slides were cleaned with detergent and distilled water, then boiled in chromic acid (0.5 M) for 25 min, then slides washed with double distilled water and further ultrasonically cleaned for 15 min. Finally the substrates were degreased in AR grade acetone and used for deposition.

2.1. Thin film preparation

CdO films were prepared on preheated glass substrate using a spray pyrolysis technique. Spray pyrolysis is basically a chemical process, which consists of a solution that is sprayed onto a hot substrate held at high temperature, where the solution reacts to form the desired thin film. The spraying solution was prepared by mixing the appropriate volumes of 0.5 M cadmium sulphate ($CdSO_4$) and distilled water. The CdO films were deposited at different substrate temperatures of 250, 300, 350 400 and 450 ^{0}C. Samples deposited at various substrate temperatures are denoted by C250, C300, C350, C400 and C450, where numbers stand for substrate temperatures. The optimized values of important preparative parameters are shown in bracket viz. airflow rate which is used as carrier gas (1.2 kg/cm^2), spray rate (3 ml/min), distance between substrate to nozzle (30 cm), solution concentration (0.5 M) and quantity of the spraying solution (30 ml). After the deposition, the films were allowed to cool naturally at room temperature. All the films were transparent and well adherent to the substrate, were further used for structural and morphological characterizations.

2.2. Characterization of thin films

The film thickness of the as-deposited films was measured by a well-known gravimetric weight difference method using sensitive microbalance and assuming bulk density of CdO (8.15 g/cm^3). The structural characterization of the films was carried out by analyzing the X-ray diffraction (XRD) patterns obtained using Philips PW-3710 X-ray diffractometer with CuKα radiation (λ = 1.5406 Å), within the 2θ range of angles between 20 and 80^0. The surface morphology of the spray-deposited CdO thin films on glass substrate was carried out using JOEL-JSM 5600.

3. Results and discussion

3.1 Film thickness

Film thickness has a strong impact on the structural, optical and electrical properties of the device. Film layer thickness was measured by gravimetric weight difference method using the relation,

$$t = \frac{m}{\rho A} \qquad (1)$$

where, m is the mass of the film deposited onto the substrate, A is the area of the deposited film and ρ is the bulk density of CdO (8.15 g/cm^3). Thicknesses of as-deposited thin films were found to be in the range from 310 nm to 425 nm and listed in Table 1.

3.2. X-ray diffraction analysis

The XRD patterns of as-deposited CdO thin films as function of deposition temperatures are shown in Fig. 1. All the films are observed to be well grown with polycrystalline textures having cubic CdO phase. For all films, major crystalline texture is (1 1 1)-oriented one (JCPDS card No.: 75-0592) at 2θ~33.08^0. The intensity of the major reflex increased with increase in deposition temperature up to 400 ^{0}C and further intensity decreased. For the CdO films, the main characteristic peaks are assigned to the (1 1 1), (2 0 0), (2 2 0) (3 1 1) and (2 2 2) planes. A light preferential orientation in the (1 1 1)

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plane is observed for the CdO films and similar behavior has also been reported by other researchers [13].

The grain size, strain, lattice parameter, dislocation density and texture coefficient were estimated form the XRD pattern. The grain size was estimated using Scherrer's equation [14]

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad (2)$$

where λ is the wavelength of incident X-ray, β is the full width at half maximum (FWHM) measured in radians and θ is the Bragg's angle of diffraction peak.

The strain and dislocation density values were calculated using the standard relations [15]:

$$\text{Strain}\ (\varepsilon) = \frac{\beta \cos\theta}{4} \qquad (3)$$

$$\text{Dislocation density}\ (\delta) = \frac{1}{D^2} \qquad (4)$$

where 'D' is the grain size. The strain values varied in the range of 1.17×10^{-3} to 0.67×10^{-3}. The dislocation density value was around 1.173×10^{15} lines/m^2. The calculated grain size, strain values and dislocation densities are tabulated in Table 1.

The texture coefficient defined by Barret and Massalski [16] has been used to describe the preferred orientation.

$$\mathbb{C} = \frac{I(hkl)/I_0(hkl)}{1/N \sum I(hkl)/I_0(hkl)} \qquad (5)$$

where TC(h k l) is the texture coefficient of the (h k l) plane, I the measured intensity, I_0 the ASTM standard intensity of the corresponding powder and N is the number of reflections observed in the X-ray diffraction pattern. It is clear that the deviation of the texture coefficient from unity implies the preferred orientation of the growth. Table 1 shows the texture coefficient of the (1 1 1) plane for different deposition temperature. From Table 1, it is clear that TC (1 1 1) increase initially with deposition temperature and become maximum at 400 0^C, then reduce for further deposition temperature. This is a consequence of reorientation effect in crystalline structure of CdO with deposition temperature.

3.3. Morphological studies

It is known that the surface properties of the TCO films influence their optical and electrical properties which are important factors for applications in optoelectronic devices. For example, the increase in surface roughness of the films leads to an increase in the propagation loss for surface acoustic wave (SAW) devices and a decrease in the efficiency for photovoltaic solar cells. Therefore, it is very important to investigate the surface morphology of the films. In this study, the surface morphologies of the CdO films were performed by using SEM. Before SEM studies, all films were covered with a very thin layer of gold for better definition. Fig. 2 shows the SEM micrographs of deposition temperature dependent CdO films. It can be obviously seen from Fig. 2 that all films have not a smooth and homogeneous surface morphology with a holes and cracks. But also, all the films are compact, dense and adhered well to the substrates. The surface properties of the CdO films appear to change significantly as a function of deposition temperature. Coalescence of different shapes and size grains into a bigger flat grain can be noticed. At some favorable nucleation centers overgrown grains and cloudy splashes are also seen (for C400). This is one of the uniqueness found in spray pyrolysis technique and such type of film morphology is useful in sensing properties.

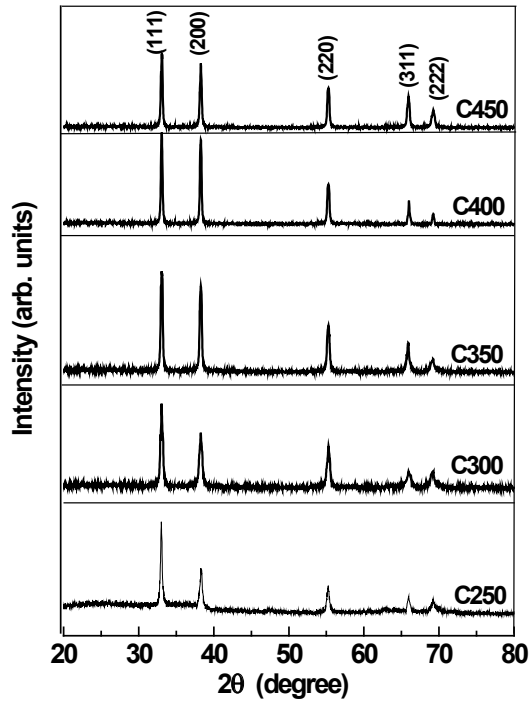

Fig. 1. XRD patterns of CdO thin films grown at different substrate temperatures.

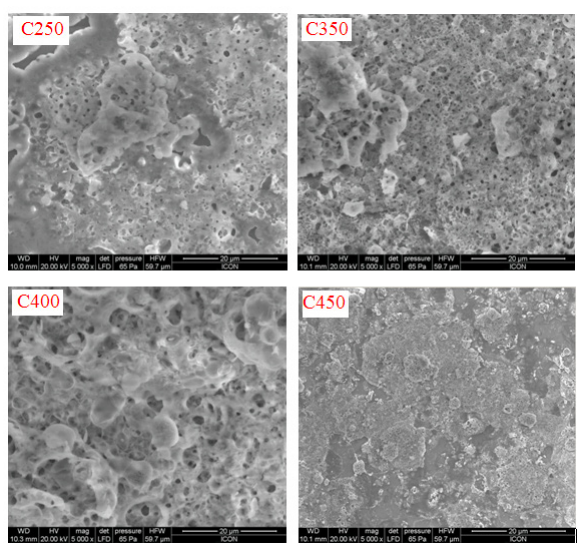

Fig.2. Scanning electron micrographs of CdO thin films prepared with different substrate temperatures.

4. Conclusions

In this study, the influence of the deposition temperature on the structural and surface morphology properties of CdO thin films grown on amorphous glass substrates by spray pyrolysis was investigated. From the X-ray diffraction (XRD) pattern, it was observed that the CdO thin films were polycrystalline with cubic structure. SEM analysis revealed the surface morphology of the films is uniform and morphology of the film varying with the deposition temperature.

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Table 1. Values of film thickness, lattice parameter, grain size, dislocation density, strain and energy band gap of the CdO films for different deposition temperatures.

Deposition Temperature (^{0}C)	Thick. (nm)	Lattice Para. (Å)	Grain Size (nm)	Strain ($\times 10^{-3}$)	Dislocation density ($\times 10^{15}$)	TC (111)	E_g (eV)
250	310	4.6957	21	1.178	2.225	0.348	2.46
300	360	4.6902	24	0.925	1.682	0.385	2.41
350	395	4.6874	27	0.724	1.424	0.508	2.38
400	**425**	**4.6872**	**29**	**0.672**	**1.173**	**0.612**	**2.34**
450	390	4.6905	25	1.093	1.626	0.421	2.37

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