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Temperature dependent grain-size and microstrain of CdO thin films prepared by spray pyrolysis method

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Abstract. **CdO thin films on glass substrate were prepared by home built spray pyrolysis unit from aqueous solution of $Cd(CH_3COO)_2{\cdot}2H_2O$ at different substrate temperatures. X-ray diffraction (XRD) studies indicate the formation of polycrystalline cubic CdO phase with preferential orientation along (111) plane. X-ray line broadening technique is adopted to study the effect of substrate temperature on microstructural parameters such as grain size and microstrain. Scanning electron microscopy (SEM) shows that the film prepared at 250°C consists of spherical shape grains with size in nanometer range and is comparable with the XRD studies.**

Keywords. **Spray pyrolysis; line broadening; microstructural parameters.**

1. Introduction

Spray pyrolysis technique (Chopra *et al* 1982) has been used for several decades in glass industry and in solar cell production to deposit electrically conducting electrodes. Thin film formation using this technique involves spraying a metal salt solution onto a heated substrate. The sprayed droplet reaching the hot substrate surface undergoes pyrolytic decomposition and forms the desired product. The other volatile by-products escape in the vapour phase. The quality and properties of the films depend largely on substrate temperature, precursor solution concentration, atomization type and substrate (Chamberlin and Skarman 1966; Patil 1999; Chen *et al* 1996). Recently nanostructured metal oxide materials are being used for microelectronic applications which are widely prepared using spray technique. CdO is one such semiconducting material having wide range of applications such as transparent conducting oxide (TCO), solar cells, smart windows, optical communications, flat panel display, phototransistors, etc. (Su *et al* 1984; Zhao *et al* 2002). CdO thin film is prepared by various methods such as activated reactive evaporation (Phatak and Lal 1994), spray pyrolysis (Gurumurugan *et al* 1994; Sanatana *et al* 1999), chemical bath deposition (Verkey and Fort 1994), pulsed laser deposition (Yan *et al* 2001), RF sputtering (Ueda *et al* 1998) and Sol-gel technique (Ghosh *et al* 2004). In the present work spray pyrolysis technique is chosen due to its simple and relatively cost-effective method, especially regarding equipment cost. Moreover this technique does not require high quality substrates or chemicals. The physical properties of the film prepared by spray pyrolysis technique depend on the microstructural parameters like grain size and microstrain which depend largely on the process parameters. Hence the objective of the present study is to deposit CdO thin film on glass substrate by home built spray pyrolysis technique. Effect of substrate temperature and precursor concentration on microstructural parameters is analysed and discussed.

2. Experimental

Cadmium Oxide thin films have been deposited on glass substrate from aqueous solution of cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$) in concentration range from 0·02 to 0·1 M in steps of 0·04 M using spray pyrolysis technique. A home made spraying system shown in figure 1 has been developed to obtain high quality thin films. It consists of (i) spray gun (ii) plate heater with thermostat and (iii) glass chamber with exhaust system. Spray gun is made up of two co-axial glass nozzles of length 15 cm. The inner nozzle of tip diameter 0·52 mm is connected to the precursor solution reservoir via flow meter and outer nozzle of 0·78 mm air gap to inner nozzle is connected to an air compressor. Electric plate heater was made from nichrome coil of 1500 W wound parallel with a separation gap of 1 cm on ceramic base of 15 cm diameter and 3 cm thickness. The free ends of coil were connected to 230V/16A power supply through a digital thermostat. A 304 grade stainless steel plate of 20 × 20 cm area with

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12 mm thickness is placed 1 cm above the ceramic base so that the glass substrate placed on it can be heated uniformly. The spray gun fitted in stand and plate heater were kept inside a glass covered wooden chamber (3 × 2 × 2·5 ft) with an exhaust fan of 40W/1800 rpm kept above the heater.

The solution was sprayed at an angle of 45° onto the preheated glass substrate kept at a distance of 50 cm from the spray gun. Prior to deposition, the substrate was chemically cleaned. Compressed dry air at a pressure of 2 kg/cm^2 from an air compressor via an air filter-cum regulator was used as the carrier gas and spray rate of the solution was maintained at 3 ml/min. To avoid excessive cooling of substrates, successive spraying process was used with time period of 15 s between successive bursts. Substrate temperature was controlled by a chrome-nickel thermocouple fed to a temperature controller with an accuracy of ± 1°C. The temperature on top side of the substrate is measured by placing a thermocouple on a reference glass substrate kept near the coating substrate so as to measure the exact temperature. Large number of films were prepared by varying solution concentration, volume of solution and substrate temperature to analyse the optimum growth condition for nanocrystalline grains of CdO thin films. For all the above varying parameters, solution flow rate (3 ml/min) and air pressure were kept constant. The overall reaction process can be expressed as heat decomposition of cadmium acetate to form cadmium oxide in presence of water as:

$$Cd(CH_3COO)_2.2H_2O_{(aq)} \rightarrow$$
$$CdO_{(s)} + CH_3COCH_{3(g)} + CO_{2(g)} + 2H_2O_{(g)}.$$

Film thickness was estimated by weighing method and verified with cross-sectional view of SEM image. To study the microstructural detail of the film, PANalytical X-ray diffractometer (Model X'per PRO) using Ni-filtered CuKα radiation (λ = 1·5148 Å), was employed with generator setting of 30 mA and 40 kV. Continuous scanning was applied with a speed of 10°/min. A range of 2θ from 10–100° was scanned from a fixed slit type, so that all possible diffraction peaks could be detected. X-ray line broadening technique is adopted to determine microstructural details. Surface morphology of the films was studied using HITACHI Scanning Electron Microscope (Model S-3000H) with an accelerating potential of

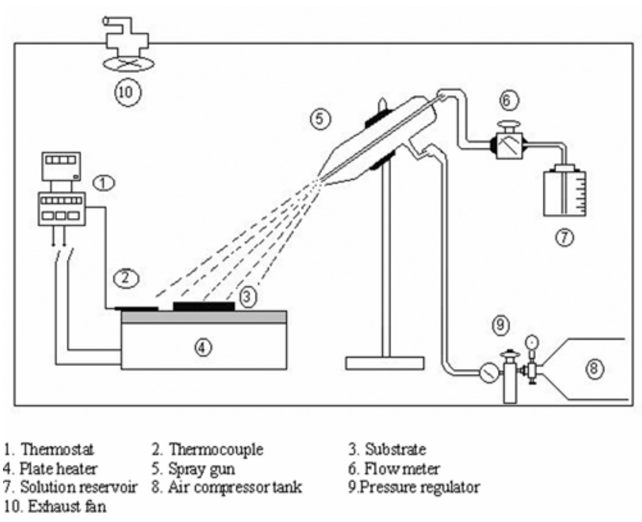

Figure 1. Schematic diagram of home built spray pyrolysis unit.

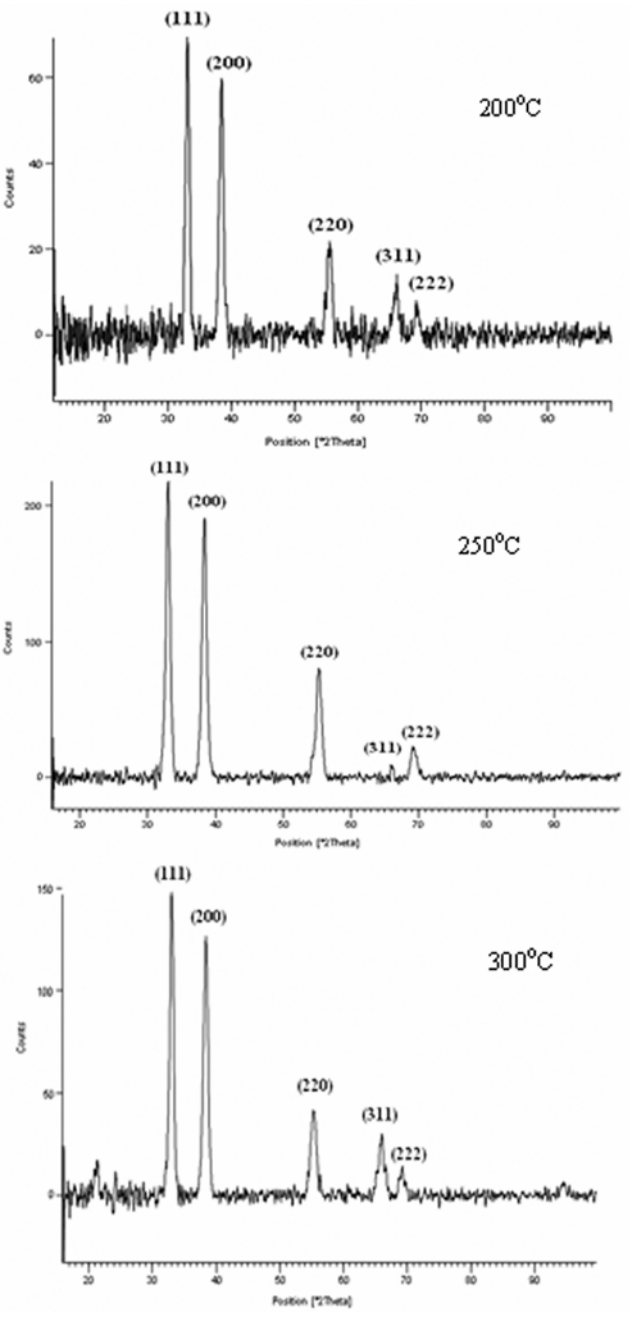

Figure 2. XRD pattern of CdO thin films prepared at different substrate temperatures from the precursor solution concentration of 0·06 M.

18 kV. Prior to imaging, the films were sputtered with thin gold film to enhance the emission of secondary electron for better imaging.

3. Results and discussion

3.1 *Structural studies*

Figure 2 shows the XRD pattern of the film prepared at different temperatures from precursor solution concentration of 0·06 M. It shows presence of different strong diffraction peaks which confirm polycrystalline cubic CdO phase formation. All the diffraction peaks of the films are indexed to (111), (200), (220), (311) and (222) as compared with standard bulk CdO [JCPDS: 05-0640]. Crystalline nature increases as substrate temperature increased to 250°C. This is clear from the increase in peak intensity. But the film prepared at 300°C has lesser peak intensity due to lesser deposition. This can be confirmed from the observed film thickness which decreases from 870 nm to 610 nm prepared at 250°C and 300°C respectively. The decrease in film thickness at higher temperature is due to vaporization of precursor before it reaches the substrate (Perednis and Gauckler 2005). No appreciable difference is observed in the XRD pattern of the film prepared at various concentrations. This indicates the crystalline nature strongly depends on substrate temperature alone. Texture coefficient (TC) is used to quantify the preferential orientation of the film deposited at different substrate temperature using the following relation (Hadouda *et al* 1995):

$$T_c = \frac{I_{(hkl)}/I_{o(hkl)}}{(1/N)\left[\sum_N I_{(hkl)}/I_{o(hkl)}\right]},$$

where I is the measured intensity, I_o is the Joint Committee on Powder Diffraction Standards, (JCPDS) standard intensity and N is the number of diffraction that peaks. It is maximum for (111) plane for all the films deposited at different temperatures. This indicates no orientation and phase change in the CdO film.

3.2 *Microstructural details*

XRD lines are usually broadened in their shape. These effects can be classified into instrument and specimen broadening. Instrument broadening originates from the non-ideal optical effects of the diffractometer and from the wavelength distribution of the radiation. In the present work instrumental broadening is corrected by using a standard defect free silicon sample.

Specimen broadening arises due to small crystallite (grain) size and strain (lattice distortion). Grain size causes the radiation to be diffracted individually (Williamson and Hall 1953). The prepared CdO film is polycrystalline in nature, and hence large number of grains with various relative positions and orientations cause variations in the phase difference between the wave scattered by one grain and the others. The total intensity scattered by all grains is the sum of individual intensities scattered by each grain. On the other hand, lattice strain broadening is caused by varying displacement of the atoms with respect to their reference-lattice positions. A uniform compressive or tensile strain (macrostrain) results in peak shift (Sciti *et al* 2007) of X-ray diffraction lines, whereas a non-uniform tensile and compressive strain results in broadening of diffraction lines (microstrain). Thus grain size and microstrain effects are interconnected in the line broadening of peaks, which makes it difficult to separate. Many approaches exist for the evaluation and separation of size and strain parameters from the occurring line broadening. Williamson-Hall technique (Williamson and Hall 1953) is adopted in the present work where grain size D and micro strain ε is related as:

$$\frac{\beta_C \cos\theta}{\lambda} = \frac{1}{D} + \varepsilon\left(\frac{\sin\theta}{\lambda}\right),$$

β_C is the instrumental effect corrected full width at half maximum of the peak measured in radian, θ the diffraction angle and λ the wavelength of X-ray. The slope of the plot between $\beta_c \cos\theta/\lambda$ and $\sin\theta/\lambda$ gives the microstrain and the inverse of intercept on y-axis gives grain size value. Figure 3 shows the Williamson-Hall plot of CdO thin film prepared from precursor solution concentration of 0·06 M with different substrate temperatures. It shows grain size increases from 32 nm to 49 nm as substrate temperature increases but strain value decreases from $0{\cdot}22 \times 10^{-3}$ to $0{\cdot}10 \times 10^{-3}$.

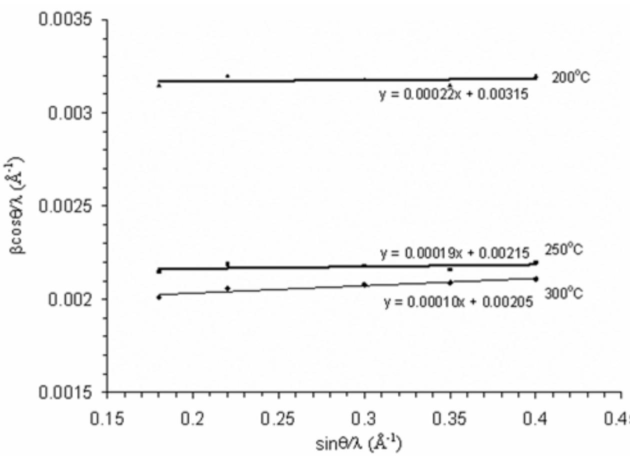

Figure 3. Williamson–Hall plot to determine grain size and strain of CdO film prepared at different substrate temperatures.

3.2a *Grain size analysis*: Figure 3 shows that the grain size is lesser for the film deposited at a lower temperature of 200°C. This is because droplets splash onto the substrate and decompose to yield smaller grains. But the surface morphology of the film prepared at this temperature shown in figure 4a has cracks. This is because a thin, wet layer is present on the film during deposition. Too fast drying of this layer results in stresses and subsequent cracking (Chen *et al* 1996). Figure 4b shows the SEM image of the film prepared at 250°C. It consists of closely packed uniform spherical shape grains without cracks. This indicates that the film is well adherent with substrate. The grain size as seen from the image is comparable with the XRD studies. At 300°C the deposited spray droplets are almost dry. Therefore, discrete particles are formed on the surface due to slow spreading. This can be explained that at higher temperatures the precursor vapourizes before it reaches the substrate and consequently solid particles are formed as powdery and non-adherent deposits (Perednis and Gauckler 2005). Also figure 5 shows that the grain size increases as precursor solution concentration is increased. This is due to increase in the number of species involved in the formation of CdO film.

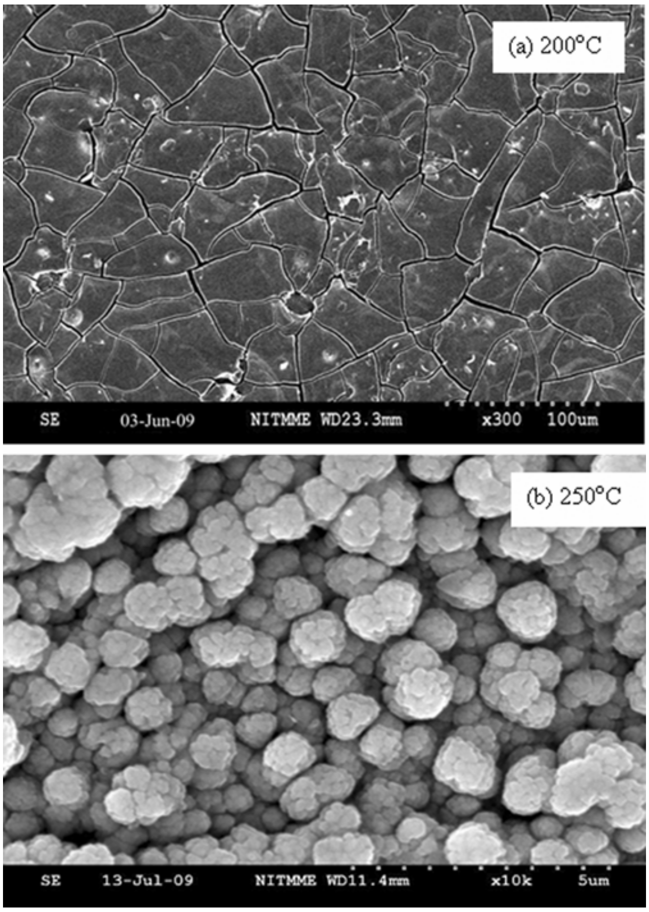

Figure 4. SEM image of CdO thin film prepared from precursor solution concentration of 0·06 M.

3.2b *Microstrain analysis*: XRD pattern for the films deposited at different temperatures do not show significant peak shift but the lines are broadened as the function of diffraction angle. This indicates the presence of microstrain rather than macrostrain. As is seen from figure 3, the microstrain is higher for the film prepared at low temperature and at higher temperature the linear dependence of Williamson-Hall plot is weaker indicating that the broadening is due to grain size. Figure 6 shows that as precursor solution concentration increases the microstrain also increases. This observation may be related to the temperature miss-match between the formed under layer and the newly sprayed solution accompanied with film relaxation due to slower spreading of droplet at higher concentration.

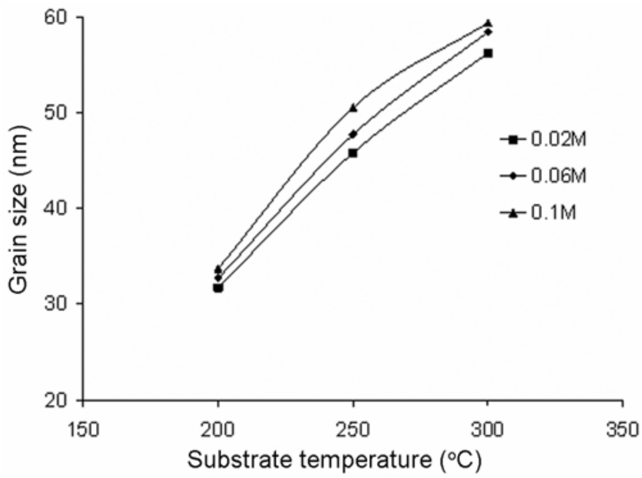

Figure 5. Plot of grain size vs substrate temperature for different precursor solution concentrations.

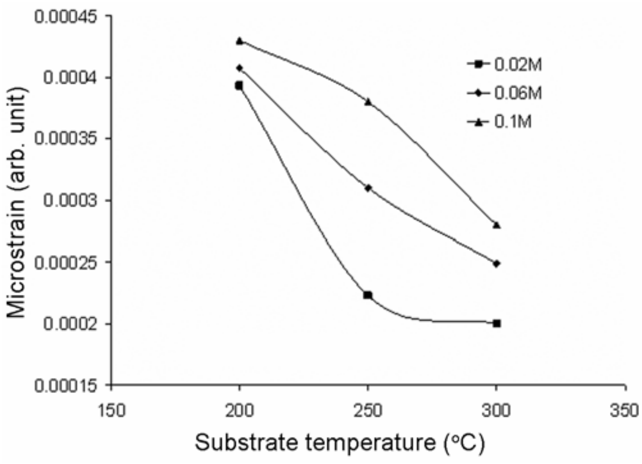

Figure 6. Plot of microstrain vs substrate temperature for different precursor solution concentrations.

4. Conclusion

Thin film of CdO on glass substrate is prepared by home built spray pyrolysis unit. XRD pattern confirms CdO phase with preferential orientation along (111) plane. Grain size and microstrain is obtained using Williamson–Hall plot method. As substrate temperature increases grain size increases and microstrain decreases. The film prepared at 200°C has microcracks and at 250°C has spherical shaped grains with size lying in the range 46 nm without cracks and were adherent with substrate. Thus 250°C is an optimum deposition temperature to obtain nano size grains of CdO thin film with lesser microstrain.

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