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DEPENDENCE OF STRUCTURAL, ELECTRICAL, OPTICAL AND SURFACE MORPHOLOGICAL PROPERTIES OF SOL-GEL SPIN COATED CdO THIN FILMS ON THE PROCESS TEMPERATURE

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Transparent conducting Cadmium Oxide thin films have been prepared on glass substrates by the simple sol-gel spin coating technique. The structural, electrical, optical and surface morphological properties of the deposited films have been studied with a view to investigate the effect of process temperature on the different physical properties of the films. It has been found that the process temperature has a strong influence on the properties of the CdO *films and highly conducting poly crystalline* CdO *films with good transmittances have been obtained by controlling the deposition temperature and the results have been reported.*

Keywords: *SOL GEL SPIN COATING, THIN FILMS, CADMIUM OXIDE, PROCESS TEMPERATURE, STRUCTURAL PROPERTIES.*

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1. INTRODUCTION

Cadmium Oxide (CdO) is one of the transparent conducting oxides which is widely studied because of its technological applications. In the thin film form, it finds applications in gas sensor devices, photodiodes, transparent electrodes, phototransistors and solar cells [1]. Several techniques have been used to prepare CdO films such as spray pyrolysis [2], chemical bath deposition [3], chemical vapor deposition [4], sputtering [5], dip coating [6], spin coating [7, 8] and pulsed laser deposition [9].Among these, the sol-gel spin coating method is simple and economical which needs no sophisticated instrumentation and has been used in the present work. The present study aims at preparing CdO thin films using sol-gel spin coating technique at different process temperatures and to study the influence of the process temperatures on the structural, electrical, optical and morphological properties of these films.

2. EXPERIMENTAL METHODS

Cadmium oxide thin films (CdO) have been prepared by the sol-gel spin coating technique. The precursor solution for preparing the CdO films has been obtained by dissolving 0.025 mole cadmium acetate di hydrate in 100 ml ethanol and 2 ml of lactic acid has been added to the solution to avoid turbidity and to obtain a clear solution. The solution is refluxed at

65 °C for 2 hours. Now the sol is ready. It is kept in an open beaker for gelation. After 3 days of gelation the sol-gel is used for coating. The coatings have been carried out using an indigenously developed micro controller based spin coating unit. A spin rate of 3000 rpm and a spin time of 10 seconds have been used for coating the films. After each coating, films have been dried in an oven kept at 100°C for 3 min to evaporate the solvent and remove the organic residuals. Successive coatings have been made on the same substrate until 8 coating are obtained. The coated film has been heated in an air furnace kept at temperatures of 350 °C to obtain CdO films. Similarly CdO films have been prepared using process temperature of 400 °C, 450 °C and 500 °C. The Structural characterization of the films has been carried out using XPERTPRO X-ray diffractometer. The surface morphological studies have been made using JEOL 6360 Scanning Electron Microscope. The transition spectra of the films have been recorded using Perkin Elmer Lambda 35 UV-VIS spectrometer. The resistivity of the films has been measured by the four probe method.

3. RESULTS AND DISCUSSION

3.1 Structural studies

The X-ray diffraction (XRD) patterns of the (CdO) films prepared at different process temperatures of 350 °C, 400 °C, 450 °C and 500 °C are shown in fig. 1. The presence of several peaks in the XRD patterns reveals that all the films are polycrystalline in nature. For the CdO films, the main characteristic peaks are assigned to the (111), (200), (220), (311) and (222) orientations at 2θ angles of 33.05°, 38.35°, 55.36°, 65.96° and 69.24° which are well matched with the standard data for the CdO crystal with rock salt cubic structure.[JCPDS data card No.75-0594]. Further it can also be seen that the lattice parameter a for all the films works out to be 4.6931 A which also matches very well with the standard value of 4.6958 A [JCPDS data]. The relatively stronger intensity of the peak (111) indicates preferential orientation of the film and similar behavior has also been reported by other researchers [10, 11]. From the XRD patterns it can be seen that as the process temperature increases the peak intensities increase and it reaches a maximum at 450 °C, indicating an improvement in crystallinity up to 450 °C. The peak intensity falls after 450 °C. This decrease in peak intensity at 500 °C may be attributed to some sort of atomic disorder in the crystal lattice [12]. This shows that a process temperature of 450 °C is optimum for preparing CdO films by sol-gel spin coating method. Such trend that the peak intensity increases up to certain process temperature and then falls has been reported by several investigators who have studied CdO films grown by various techniques like activated reactive evaporation [10] and spray pyrolysis [11].

This trend may be attributed to the variation in the amount of oxygen intake and energy of ad atoms. The mobility of ad atoms and clusters on the surface of substrate is proportional to their energy, which increases with increasing substrate temperature [12].The Texture coefficient represents the texture of the particular plane [7] and is used to quantify the preferred orientation [13]. For a preferential orientation the Texture coefficient should be greater than one.

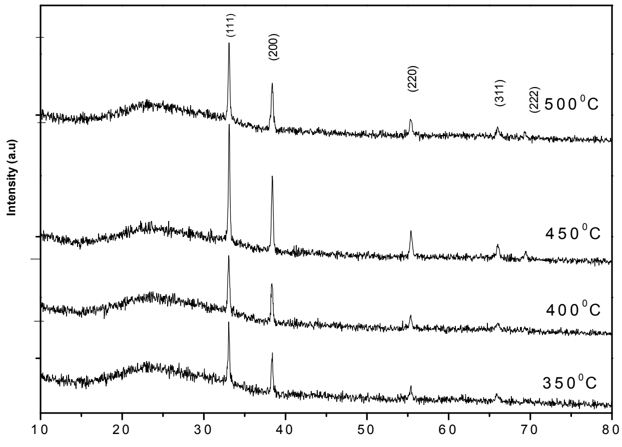

Fig. 1 *– The XRD patterns of the* CdO *films recorded at various temperatures*

The Texture Coefficient (*TC* (*hkl*)) for the various planes at different process temperature has been calculated using the relation [14].

$$TC(hkl) = \frac{I(hkl) / I_0(hkl)}{1 / N\sum_N I(hkl) / I_0(hkl)}, \qquad (1)$$

where $I(hkl)$ is the observed indensity of the (hkl) plane, $I_0(hkl)$ is the standard intensity of the (hkl) plane, taken from the JCPDS data and N is number of diffraction peaks. The results obtained for the films grown at 350 °C, 400 °C, 450 °C, and 500 °C are shown in fig. 2. From the fig it is seen that the TC is maximum for (111) plane for all the films deposited at different temperature. This shows that the (111) plane is the preferred orientation and that there is neither orientation change nor phase change with process temperature [15].

3.2 Electrical Studies

The fig. 3 gives the variation of resistivity of the CdO films prepared at the process temperatures of 350 °C, 400 °C, 450 °C, and 500 °C. The figure indicates that as the process temperature increases the resistivity falls and reaches a minimum value at 450 °C, and then increases for further increase of temperature. Thus 450 °C, is taken as the most suited temperature for preparing CdO films using the spin coating technique. The XRD study indicates that the crystallinity improves up to 450 °C. The SEM study shows that the particle size increases up to 450 °C. Thus, as the process temperature increases the crystallinity and size of the crystallites improve, tending to reduce the grain boundary scattering and increase the mean free path which in turn may improve the mobility and the film conductivity. However the number of oxygen vacancies may decrease with process temperature.

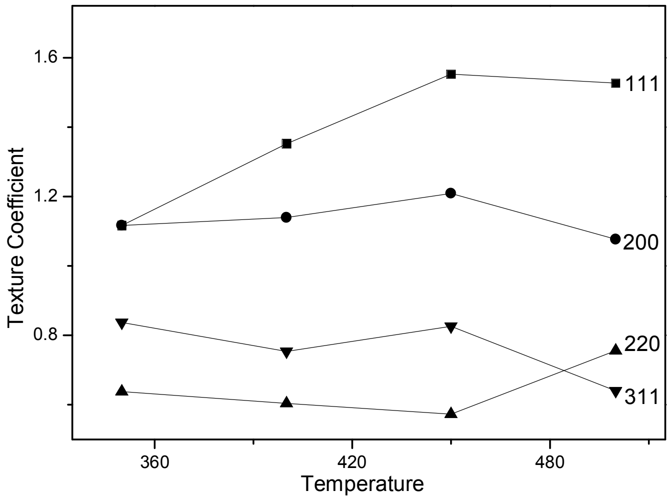

Fig. 2 – Variation of TC with process temperature

If the first factor which is an aiding factor dominates over the second factor, which is an impairing factor, the conductivity may increase (i.e. the resistivity may decrease). This is perhaps what happens up to 450 °C, at which stage the resistivity is minimum (2.552×10^{-3} Ωcm).

The XRD and SEM studies indicate that there is some disorder in the crystal lattice and there is decrease in particle size at an elevated process temperature of 500 °C, which may tend to increase the number of scattering centers and thus become an additional impairing factor, as a result of which the conductivity may decrease (i.e the resistivity may increase) at 500 °C. The minimum resistivity 2.55×10^{-3} Ωcm obtained from the present study is comparable with the value of 1.5×10^{-3} Ω cm reported by Ramakrishna Reddy et al. [10] for the CdO films grown by reactive evaporation method and it is one order of magnitude lower than the value of 2.01×10^{-3} Ωcm reported by Dakhel et al [16] for their Vacuum deposited CdO films and the value of 2×10^{-3} Ωcm reported by Carballeda et al for their CdO thin films obtained by the sol-gel method [17].

Hall effect measurement on the film prepared at the optimized process temperature of 450 °C, indicate that the carrier concentration and mobility work out to be 1.269×10^{19} cm^{-3} and 129 cm^{2}V^{-1}s^{-1} respectively. The mobility value obtained is comparable to the highest values reported in the literature [18]. Such a high mobility value may be attributable to the low carrier concentration and low grain boundary scattering (which is due to large grain size).

3.3 Optical studies

The transmittance spectra of spin coated CdO thin films prepared at the process temperatures of 350 °C, 400 °C, 450 °C and 500 °C are displayed in Fig. 4.

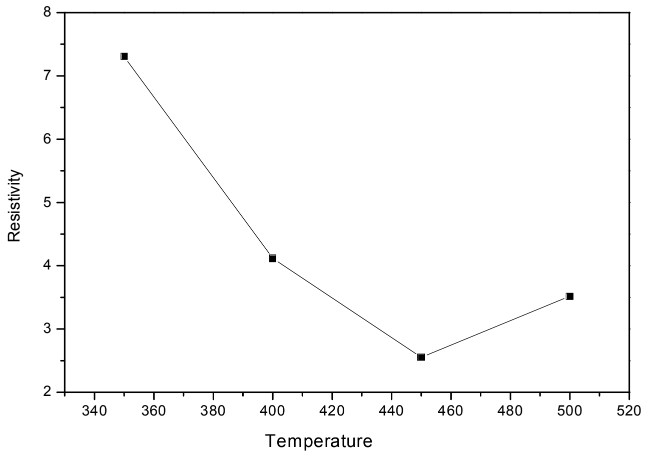

Fig. 3 *– Variation of Resistivity of CdO films with different process temperatures*

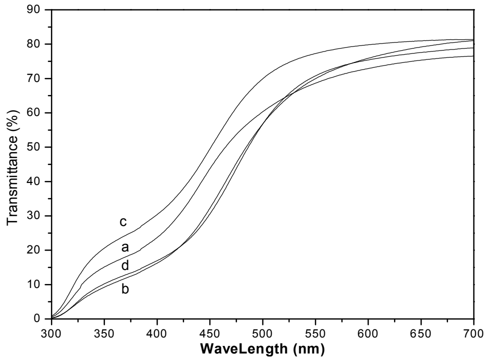

Fig. 4 *– Transmittance spectra of* CdO *films* (8 *coatings*) *prepared at different process temperatues* (*a*) 350 *°C,* (*b*) 400 *°C,* (*c*) 450 *°C and* (*d*) 500 *°C*

The optical transmission in the visible region of the CdO films increase with the process temperature and attain a maximum values at 450 °C and then falls for further increase in temperature. Hence 450 °C may be considered as the optimum temperature and at this stage the transmittance is 80 % at 600 nm.The increase in visible transmittance of the film with temperature up to 450 °C may be attributable to the improvement in the crystallinity of the crystallites and improvement in the structural and surface homogeneity of the films. The reduction in the transmittance after 450 °C may be due to some sort of disorder in the crystal lattice which is evidenced from the XRD and SEM results. The same conclusion has been arrived at by Joseph prince et al. [19] for their sprayed In_2O_3 films and savarimuthu et al. [12] for their spin coated In_2O_3 films.

The Plot of $(\alpha h\nu)^2$ with photon energy $h\nu$, has been used to evaluate the energy band gap of the CdO films. The typical plot for the film prepared at 450 °C is given in the Fig. 5. The band gap values have been found to vary from 2.28 to 2.45 eV. The energy band gap has been found to shift towards

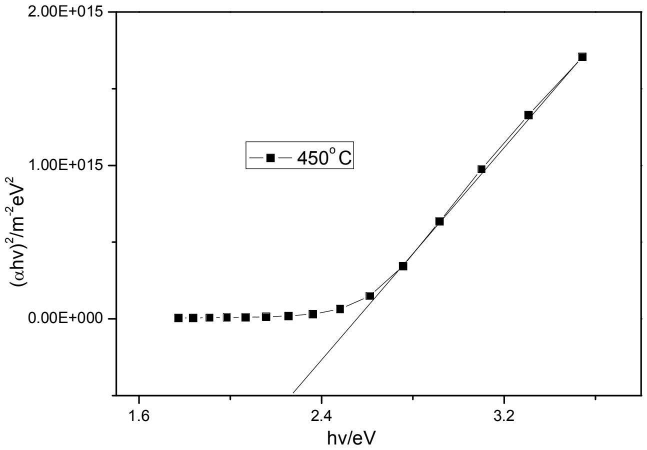

Fig. 5 – Band gap value of CdO *thin film prepared at* 450 *°C*

the lower energies with increasing process temperature and this may be attributed to the Burstein shift [20].The films formed at 350 °C, 400 °C, 450 °C, and 500 °C exhibit a sharp decrease in transmittance at lower wavelength indicating direct optical absorption in the films (Ramakrishna Reddy et al. [10]). The band gap of CdO film prepared at optimised temperature is 2.28 eV which is cmparable to the values (2.32 and 2.30 eV) reported by Gurumurugan et al. [13] for their sprayed CdO films and the CdO films prepared by solution growth technique].

3.4 Surface Morphological Studies

The scanning electron micrographs of spin coated CdO thin films prepared for the present study, at the process temperatures of 350 °C, 400 °C, 450 °C, and 500 °C, are presented in Fig. 6 a, b, c and d. These micrographs show that all the films are uniform and completely devoid of pin holes and cracks. This indicates that the films are well adherent with substrate. However, it can be seen that better uniform surface morphology is seen for the film prepared at the process temperature of 450 °C (Fig. 5c), then that obtained at lower and higher process temperatures (Fig 5.a, b and d). The average particle sizes as derived from the images are 74.79, 89.71, 99.08 and 76.18 nm for the films grown with process temperatures of 350 °C, 400 °C, 450 °C, and 500 °C indicating that the particle size increases with process temperature and attain a maximum value at 450 °C and then falls for further increase in process temperature. These clearly establish that a process temperature of 450 °C is optimum for preparing CdO thin films by the sol-gel spin coating technique.

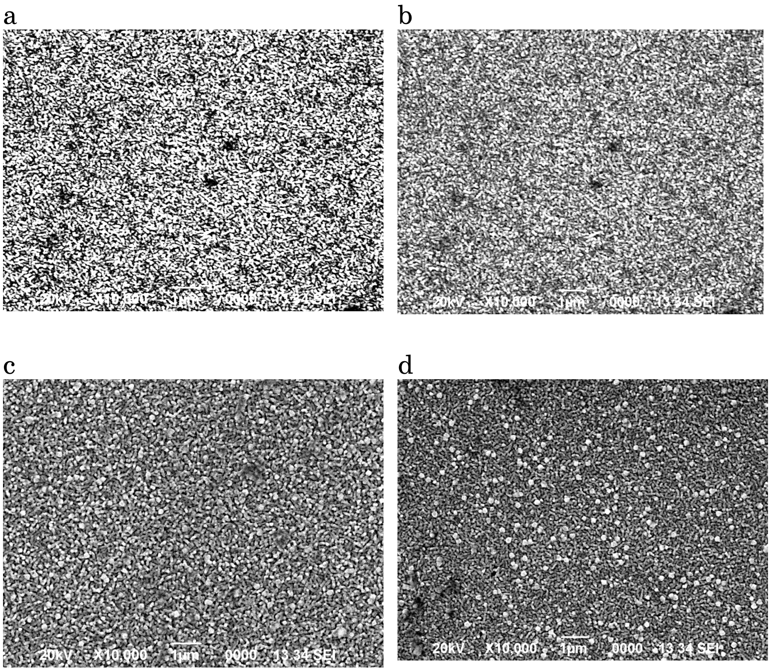

Fig. 6 – *The SEM micrograph of* CdO *thin films deposited at different temperature* 350 *°C,* (*b*) 400 *°C,* (*c*) 450 *°C, and* (*d*) 500 *°C*

4. CONCLUSION

The CdO films have been developed by sol gel spin coating technique by varying the process temperature. It has been found that the process temperature has a decisive influence on the electrical, optical, structural and surface morphological properties and a process temperature of 450 °C has been found to yield films of best possible characteristics. The XRD results showed that all the films are polycrystalline in nature and have preferential orientation along (111) direction with lattice parameter 4.6931 A. At the optimized temperature of 450 °C, CdO films with a resistivity of 2.55×10^{-3} Ωcm, carrier concentration of 1.261×10^{19} cm^{-3}, mobility of 129 cm^{2}V^{-1}s^{-1}, transmittance of 80 % at 600 nm and band gap value of 2.28 eV have been obtained.

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