Influence of annealing time on the structural and electrical properties of CdO thin films coated by sol- gel spin coating method

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ABSTRACT

Transparent conducting Cadmium oxide (CdO) semiconducting thin films were deposited by sol – gel spin coating technique on glass substrates. The structural and electrical properties of the deposited films have been studied with a view to investigate the influence of the annealing time on the different physical properties of the films. The structural studies show that the films are polycrystalline in nature with preferred orientation along the (111) plane. The structural parameters such as crystallite size and strain are obtained from the full width at half maximum (FWHM) values of the diffraction peaks. It has been found that the annealing time has a significant influence on the structural properties of the CdO films. The resistivity of the material decreases and reaches a minimum value at 60 minute annealing time, and then increases for further increase in annealing time. A Polycrystalline CdO film with high conductivity was obtained at an annealing time of 60 minutes.

KEY WORDS: Sol- gel spin coating, thin films, Cadmium oxide, Annealing time, structural properties, optical properties.

1. INTRODUCTION

Thin films play important role specifically in the field of microelectronics, optical coating, integrated optics and super conductors etc. Transparent conducting oxide (TCO) thin films such as Zinc oxide, Tin oxide and Cadmium oxide (CdO), have been studied extensively because of their use in semiconductor optoelectronic devices. Among these TCO films, CdO finds lot of applications such as Phototransistors, Gas sensor, and Solar cells. CdO thin films are generally synthesized by techniques such as Spray pyrolysis, Chemical vapor deposition, Sputtering, and Spin coating. Of these methods, Spin coating method is advantageous because of its simple and low cost of apparatus and highly reproducible results. Hence the present work employs this technique. CdO films with annealing time variation 0-120 minutes have been already reported by Vigil (2001). The linear variation in crystallite size and band gap value with the change in annealing time was reported by Vigil (2001). But, in this work the structural and electrical properties was enhanced for a particular annealing time after which the properties reverse their respective trends, indicating that the particular annealing time is optimum for preparing the CdO thin films. The study on the change in Physical properties of films in accordance with annealing time is very limited. In the present work, CdO thin films were prepared using sol- gel spin coating technique at different annealing times and the influence of annealing time over the structural and electrical properties of the CdO films was studied.

2. EXPERIMENTAL DETAILS

Thin Film deposition: The precursor solution for preparing the CdO films was obtained by dissolving cadmium acetate of 0.25 M (4.997 gm) in 75 ml of ethanol and 1ml of lactic acid is added to it to obtain the clear solution. The solution was constantly stirred using a magnetic stirrer for 2 hours at 65°C. The obtained solution was kept in a beaker for gelation. After three days of gelation the sol – gel is used for coatings. The films were coated onto glass substrates (25 mm x 25 mm x 1.35 mm thickness). Prior to coating, the glass substrates were well cleaned with soap solution, chromic acid (at 60°C for 2 hours) and washed with distilled water in ultrasonic bath for 20 minutes. The coating has been carried out using a microcontroller based spin coating unit. Eight successive coatings were made on the same glass substrate with a spin rate of 3000 rpm and a spin time of 15 s for each coating. After every coating the film was dried at 100°C for 5 minutes to evaporate the excess solvent and to remove the organic residuals. After the final coating, the film was annealed in the muffle furnace at 400°C for 30 minutes to obtain CdO films. Similarly CdO films annealed for 60 minutes, 90 minutes and 120 minutes at 400°C were also prepared.

Characterization: The structural characterization of the films has been carried out using X – ray diffractometer (PA analytical – PW 340/60 X'pert PRO). The thickness of the prepared films was measured by Stylus profilometer SURFEST SJ – 301. The resistivity of the films was measured by the Four probe method.

3. RESULTS AND DISCUSSION

Structural studies: X-ray diffraction patterns of the CdO films coated for various annealing times are shown in Figure 1. From the Figure 1, it is confirmed that all the CdO thin films belong to polycrystalline structure. The crystalline property increases as the annealing time was increased. For the CdO films, the main diffraction peaks obtained are assigned to (111), (200) and (220) at 2θ angles of 33.46°, 38.73°, and 55.69° which are well matched with the standard bulk CdO pattern [JCPDS data card No. 75-0594]. The lattice parameter `a' for all the films found to be 4.6326 Å which well matched with the standard JCPDS data. The preferred orientation of the CdO film was determined by calculating the texture coefficient TC (h k l) for all the planes using the relation,

$$\mathrm{TC\ (h\ k\ l)} = \frac{I(h\ k\ l)/I_0(\mathrm{h\ k\ l})}{\frac{1}{N}\sum_N I(h\ k\ l)/I_0(\mathrm{h\ k\ l})}$$

Where TC (h k l) is the texture coefficient of the (h k l) plane, I the measured intensity, I_0 the standard intensity and N the reflections observed in the X-ray diffraction patterns. The TC values obtained for different planes for the various annealing times are shown in Figure 2. It is seen that the TC value for (111) plane is the maximum for all the films which confirm that the (1 1 1) plane is the most preferential orientation for all the films which was also reported by Jeyaprakash (2011). The structural parameters such as crystallite size, micro strain, were calculated and Tabulated in Table 1.The crystallite size of the films were calculated by using the Debye-Scherrer formula.

$$D = K\lambda/\beta\cos\theta$$

Where K is constant, β is full width at half maximum of the peak and θ is the diffraction angle. The crystallite size value increases with increase in annealing time from 30 minutes to 60 minutes and it decreases for further increase in annealing time to 90 and 120 minutes. Micro strain in the film restricts the growth of grains. From the Table 2, it can be found that the micro strain decreases from 30 minutues to 60 minutes of annealing time and then the strain gets increased on 90 minutes of annealing time which decreases the grain size. Ghosh (2004), observed the similar results for the ZnO films grown by sol-gel process. Because of increase in crystallite size the voids were expelled and the films become denser, resulting in the increase in intensity of the observed diffraction peaks. Crystalline nature also increases up to 60 minutes of annealing time and then fall. This is clear from the peak intensity which is shown in Figure 1.The decrease in peak intensity after 60 minutes of annealing time may be due to some sort of atomic disorder in the crystal lattice.

The micro strain in the films develops due to non-uniform compressive (or) tensile strain developed in the film. The micro strain was determined using the relation,

$$\varepsilon = (\beta\cos\theta) / 4$$

It was observed that the micro strain is lower for the film with annealing time of 60 minutes, than other films. It indicates that film with annealing time of 60 minute has a higher degree of crystallization.

Electrical studies: Due to good electrical conducting property of CdO thin film, it is used in optoelectronic devices technology. The variation of resistivity and crystallite size with annealing time is shown in the Figure 3.

From the Figure it is observed that as the annealing time increases the resistivity decreases and reaches minimum value at 60 minute of annealing time and then increases for further increase in annealing time. From the XRD study, it was noticed that the film has better crystallinity at annealing time of 60 minutes. Thus, as the annealing time increases from 30 minutes to 60 minutes, the crystallinity improves, which reduces scattering at the grain boundaries which in turn increases the mean free path. The increase of mean free path may be the cause for improvement in the electrical conductivity of the CdO thin film.

The XRD studies indicate that there is some disorder in the crystal lattice and there is decrease in crystallite size above the annealing time of 60 minutes. Decrease in crystallite size above the annealing time of 60 minute may increase the number of scattering centers and thus the electrical conductivity may decrease (i.e., resistivity increases). Thus the annealing time of 60 minutes may be taken as optimum for preparing sol-gel spin coated CdO films for optoelectronic device fabrication. The resistivity value is obtained for the optimum condition is 2.16 x 10^{-4} Ωm which is having good agreement with the CdO films deposited by solution growth method. The electrical conductivity of CdO thin film may be improved by adding various alkali metal ions as dopants.

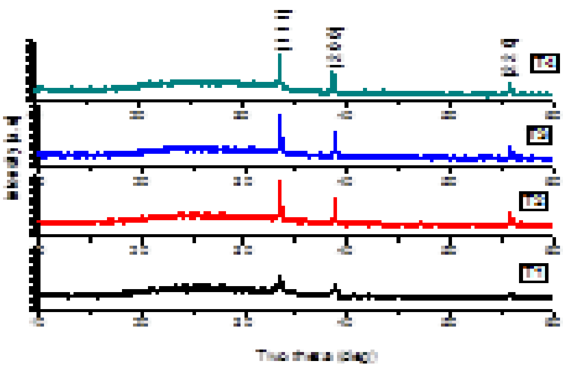

Figure.1.XRD patterns of CdO thin films for various annealing time in minutes.
T1 – 30 minutes, T2- 60 minutes, T3 – 90 minutes, T4 – 120 minutes.

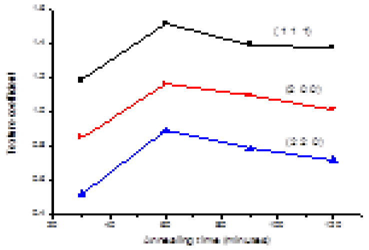

Figure.2.Variation in TC with Annealing time

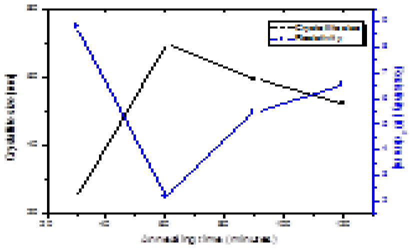

Figure.3.Variation of resistivity and crystallite size with annealing time

Table.1. Crystallite size and micro-strain for different annealing time

Annealing time (minutes)	Crystallite size (nm)	Micro-strain (10^{-3})
30	24.60	1.412
60	69.55	0.498
90	59.60	0.582
120	52.15	0.665

4. CONCLUSION

CdO thin films were successfully deposited by spin coating technique with different annealing times. The annealing time has a significant influence on the structural and electrical properties and the annealing time of 60 minutes has been found to yield films of best possible characteristics. The films exhibit a preferential orientation along the (111) diffraction plane and belongs to the polycrystalline nature. At the optimized annealing time of 60 minutes, CdO film of resistivity of 2.16 x 10 $^{-4}$ Ωm has been obtained.

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