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Optical and Structural Properties of Doped and Undoped CdO Thin Films

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ABSTRACT

Optical and structural properties of pure CdO and Al:CdO thin films were presented in this work. The Cadmium Oxide (CdO) semiconducting films were deposited on a glass substrate by dip coating method using Cadmium Chloride as the precursor with ammonium hydroxide. The structural and optical properties of the films were observed. The crystalline structure was studied by X-ray diffraction (XRD) and found the presence of the CdO cubic phase. The variation of absorption with wavelength was studied. The absorption of the film was found to be increased with doping. The optical band gap of pure CdO is 3.8eV. The band gap energy for Al:CdO was observed to be 3.70eV with 3%Al doping and decreased to 3.66eV with 5% Al doping.

Keywords: Al doped Cadmium Oxide;Cadmium Oxide; Optical properties; Structural properties.

1. INTRODUCTION

Oxides of many metals such as tin, indium, zinc, cadmium and their alloys can be used as TCO's possessing transparent conducting property. Most of the transparent conducting metal oxides are anion deficient and hence are always n-type conductors. The transparent conducting metal oxides are also referred as oxide semiconductors. Role of metal oxide thin films are very important in the field of science and technology.

Cadmium Oxide properties such as large band gap, low electrical resistivity and high transmittance in the visible region make it useful for a plethora of applications such as photodiode, phototransistors, photovoltaic cells, gas sensors, transparent electrodes, liquid crystal displays, IR detectors and antireflection coatings.

Many methods have been used to synthesis CdO for various applications. Such methods include sputtering, SILAR method, spray pyrolysis, thermal deposition, metal organic vapor deposition, chemical bath deposition, etc.

Lalithambika *et al.* have prepared CdO thin films are deposited on glass plates using Chemical Bath method. Gokul et *al.* have prepared Cadmiumoxide (CdO) thin films by successive ionic layer adsorption and reaction (SILAR) method. Sivasankar *et al.* reported that Cadmium oxide (CdO) thin films were fabricated by spray pyrolysis technique. Eman Kareem *et al.*, have prepared CdO and Cu doped CdO thin film deposited on glass and Silicon substrate by pulsed laser deposition (PLD) method.

In this study, Cadmium Chloride is preferred due to its reasonable cost as a precursor. Using ammonia as the solvent, a transparent solution was prepared and CdO thin film was synthesized on a glass substrate by dip coating technique. Cadmium Chloride is chosen for its easy availability also. The present paper has two objectives :(i) to review the theoretical and experimental results of XRD analysis and (ii) to study the band gap energy of the deposited thin films for the corresponding absorbance spectra.

2. EXPERIMENT

In the present work, Cadmium oxide (CdO) thin films were prepared on glass substrates by sol-gel dip coating technique.

2.21 Cleaning Process

The cleanliness and nature of the substrate, the deposition conditions,post deposition heat treatment and passivation are vital process variables in thin film fabrication.

The cleaning of the substrate surface is an important process for the thin films formation. The glass substrates were cleaned with deionized water and detergent solution for 15 minutes. The substrates were soaked in chromic acid and washed with acetone.

In a conical flask, 0.1M of cadmium chloride ($CdCl_2$.2 ½.H_2O) was dissolved in 250ml of deionized water. The solution was continuously stirred by a magnetic stirrer for 1hour to get a clear homogeneous solution. Ammonium hydroxide ($NH_3.H_2O$) solution was added drop wise till the pH value is reached 12. The pure CdO solution was prepared. This solution was taken in small beakers and the glass substrates were dipped into beakers for 24 hours. These glass slides were dried in hot air oven. The slides were annealed to 500°C and used for the characterization technique.

$$CdCl_2 + NH_3H_2O \rightarrow [Cd(NH_3)_4]^{2+} + 2OH^- + Cl^-$$
$$2Cd^{2+} + 2OH^- \rightarrow CdO + H_2O$$

The same procedure is repeated to dope Aluminum to CdO. To the pure CdO precursor on the beaker was added anhydrous Aluminum Chloride ($AlCl_3$) at two different concentrations (3wt % and 5wt %). This solution was stirred using a magnetic stirrer for 2 hours and Ammonium hydroxide ($NH_3.H_2O$) solution was added drop wise till the pH value is reached 12. Al doped CdO (Al:CdO)was thus prepared. The glass substrates were dipped into the beaker for 24hours. Finally, the glass substrates were dried using hot air oven and annealed at 500 °C.

$$Al(H_2O)_{6Cl3} \rightarrow Al(OH)_3 + 3\,HCl + 3\,H_2O$$

On strong heating (~400°C), Aluminium Oxide is formed from the Aluminium Hydroxide via:

$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O$$

3. RESULTS & DISCUSSION

3.1 Structural Properties of CdO and Doped CdO Thin Films

3.1.1 X-Ray Diffraction of Pure CdO and Doped CdO Thin Films

For making uniform and well adherent films, the changes in the structure related properties with deposition at glass substrate and different concentration are studied.

Obaid *et al.* showed that the nanostructures CdO thin films exhibit a cubic rock salt (NaCl) type structure and confirmed it by XRD analysis. The XRD analysis observed by Gokul *et al.* revealed that the films were polycrystalline with cubic structure. Divyavijayanarayanan *et al.*, experimented the XRD analysis which revealed that the films were polycrystalline and the presence of tetragonal structure with (110), (101) and (200) orientations. M. Mozibur Rahman *et al.*, have. XRD patterns shows that it has polycrystalline nature with cubic crystal structure with (200) plane as preferential orientation. In his study, the grain size of undoped CdO film is 27.15 nm which increase for Al doped CdO thin film while it decreases with dual doping of Al and N. The optical band gap values were found to decrease from 2.58 eV to 2.52 eV for direct transitions.

Fig.1 shows the XRD of pure CdO films deposited at different concentration with same annealing temperature 500°C.

At the annealing temperature of 500°C, the peaks corresponding to pure CdO thin film phase started appearing. From the figures, it is observed that the films are cubic crystal structure with polycrystalline nature with preferred orientation along (200). Other XRD peaks obtained are at (111), (200), and (220).

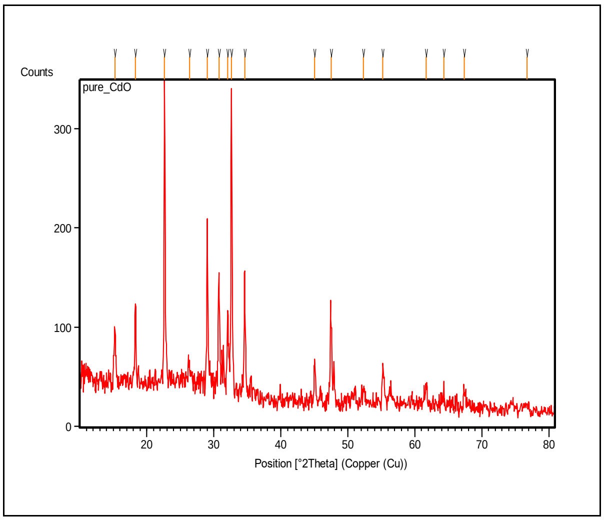

Fig. 1. Pure CdO

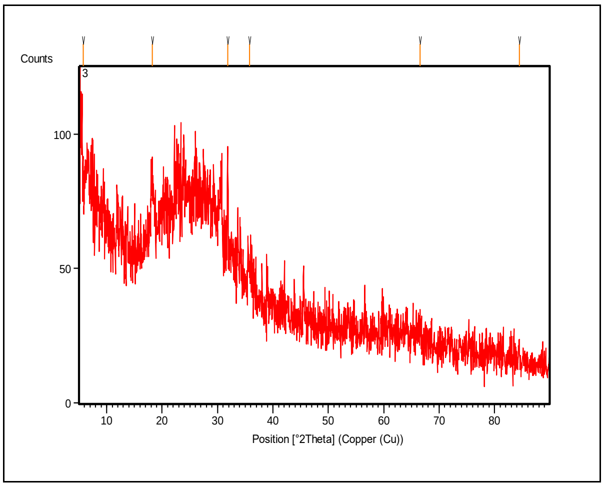

Fig. 2: Doping of 3% Al

Fig. 2, 3 explain the structural characterization of the Al doped thin films. It is an interesting result that the developed XRD peaks are found in the films heated even at a relatively same temperature of 500°C in the present study. Present result shows that the dip coating technique with different concentration is capable of providing cubic crystalline structure with polycrystalline nature for pure CdO and doped CdO thin film with same temperature 500°C.

The hkl and d values found the pure CdO and doped CdO film deposited at different concentration and the annealing temperature are 500°C for each deposited films agreeing well with the values found in JCPDS card.

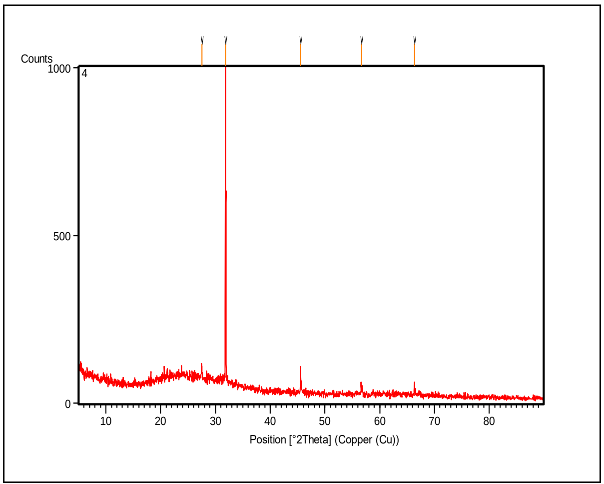

Fig. 3: Doping of 5% Al

3.1.2 Grain Size, Dislocation Density and Strain

The crystal structure properties are studied elaborately and the results are tabulated. The grain sizes is estimated using Scherrer's relation,

$$D = \frac{K\lambda}{(\beta \cos\theta)} \text{ m}$$

using the calculated grain size, the dislocation density can be calculated.

$$\text{Dislocation density } \delta = \frac{1}{D^2} \text{ lines/m}^2$$

$$\text{Micro strain } \varepsilon = \frac{\lambda}{\sin\theta} - \frac{\beta}{\tan\theta}$$

The calculated values of lattice parameters for pure CdO thin film are a=4.011nm and c=2.7413nm (approximately). The lattice parameters for 3wt% Al doped CdO film are a=4.032nm and c=6.3245nm. For the increased concentration of 5wt% Al, the values are a= 4.076nm and c=1.4035nm. These values are in very good agreement with the reported values of JCPDS card no.78-0653. The crystalline size (D) was calculated from the full width at half maximum (FWHM) β, of the prominent XRD peaks using the Scherer - Bragg's relation.

The variation of micro structural parameters like grain size, dislocation density, and strain number of crystallites with varying concentration deposition is listed in table 1. It shows that the average grain size of pure CdO reaches a maximum of 38.76 nm. When the pure CdO is doped with 3 wt% Al, the crystallite size becomes 28.148nm. This is increased to 45.624nm as the Al doped CdO film deposition increases from 3wt% to 5wt% at the annealing temperature 500°C. It is observed that the dislocation density and micro strain are found decreased for the concentration of 5wt% of Al.

3.2 Optical Properties of Cdo Thin Films

Eman Kareem *et al.*,inquired optical properties and noted that it is transparent in the visible region for CdO film, and it is increasing and shifted toward the visible region for Cu doped CdO film. Optical studies of Divyavijayanarayanan *et al.*, revealed the maximum transmittance of 90% and the optical band gap due to its direct transitions was varying from 3.95 to 4 eV. G. Sivasankar *et al.*, reported that the direct band gap energy of the CdO thin film was 2.39 eV calculated from UV-Vis absorption spectrum.

Optical properties of pure Cadmium Oxide (CdO) thin film and Al:CdO for different concentrations (Al:3wt% and 5wt%) were investigated by UV-Vis spectrophotometric technique.

The absorption spectra in the wavelength region of 200nm -1100nm for the pure CdO and doped CdO of different concentrations deposited on glass substrates at annealing temperature 500°C were studied. The absorbance spectrum of pure CdO and doped CdO thin films are shown in fig 4, 5. It is clear that as the doping concentration increases, the absorbance of the film is also increased.

In our result, the band gap energy for the pure CdO film was found to be 3.8eV. The band gap energy for Al:CdO the band gap energy is are 3.7eV (3wt% Al) and 3.6eV(5wt% of Al).The band gap energy value for the 3wt% Al:CdO was identified to decrease compared to the pure CdO material. For the 5wt% Al:CdO the band gap value was further decreased.

Table 1. The structural parameters of pure CdO and Al:CdO thin film

Film	$2\Theta_{deg}$	$FWHM_{RAD}$	Lattice strain	Dislocation density (δ) lines/$m^2 \times 10^{14}$	Micro strain(ε)	Average crystalline size(D)nm
CdO	15.2526 18.3321 22.6727 26.3868 29.0478	0.3444 0.1476 0.1968 0.5904 0.1476	0.0225 0.0080 0.0087 0.0223 0.0051	17.1319 03.1414 05.5651 49.9450 03.1105	9.0365 8.7565 6.8558 4.2314 5.5734	38.76
Al:CdO 3%	5.7385 18.2243 31.8419 66.5304 84.4461	0.5063 0.5196 0.1299 0.9092 0.2598	0.0882 0.0285 0.0041 0.0133 0.0029	37.18024 38.91642 2.401467 110.1068 8.524695	20.67552 6.48847 5.160884 1.422715 4.87948	28.148
Al:CdO 5%	27.4841 31.8421 45.5578 56.7029 66.3474	0.3897 0.1299 0.0974 0.2598 0.3897	0.0141 0.0041 0.0021 0.0045 0.0057	21.71463 2.401467 1.323002 9.205038 20.235832	1.50669 5.16084 3.738737 2.762732 2.219410	45.624

4. CONCLUSION

WO_3 nanoparticles were successfully synthesized by low cost wet chemical method with PVP. The obtained XRD showed that the monoclinic structure of WO_3. The dielectric constant, dielectric loss and AC conductivity were investigated. DC electrical conductivity was measured for all the prepared samples conductivity in the temperature range 303-403 K. The temperature dependence of electrical conductivity is decreases with increasing PVP content. The conductivity increases with increasing the temperature showing the semiconducting nature of the samples. From the Arrhenius plot, activation energies are calculated. The observed value of electrical and dielectric constant shows that the synthesized WO_3 is a good for high frequency device applications.

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