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Structural, Optical and Electrical Properties of Al Doped CdO Thin Films Deposited by Spray Pyrolysis Method

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Abstract
Cadmium Oxide (CdO) and Al doped CdO semiconducting films have been fabricated onto glass substrate at temperature (330 ± 20) °C by chemical spray pyrolysis (CSP) technique using as a source material of cadmium acetate and aluminum chloride. The XRD study confirms that CdO and Al doped CdO thin films are polycrystalline in nature and can be indexed with cubic structure with (200) preferred orientation having lattice parameter of 0.4678 nm. The optical study showed that the films are highly transparent, above 85% transmission for wavelengths ≥ 900nm and the value of direct band gap has been decreases with the increase of Al doping concentration in CdO thin films and reaches a minimum of 2.43eV when doping level is 2 wt.%. The electrical conductivity increases with the increasing of doping level of Al in CdO thin films. A minimum resistivity of $3.79\times10^{-4}\Omega$-cm with carrier concentration of $1.30\times10^{20}cm^{-3}$ is achieved when CdO film is doped with 2 wt.%. The measurement of thermoelectric power confirms that the thermal emf of CdO thin film increases with increasing temperature and the value is positive that indicates n type semiconducting nature of the film.

Keywords: *Thin films, Spray pyrolysis, CdO, XRD, Electrical properties*

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I. Introduction

Transparent conducting oxides (TCOs), an attracting type of semiconducting materials that are both optically transparent and electrical conductive, have potential application in optoelectronic devices such as solar cells, photovoltaic, flat panel displays, transparent electrodes, Ohmic contact to LEDs and heat reflectors [1-4]. Transparent conducting oxides, such as pure and doped indium oxide, cadmium oxide, zinc oxide and tin oxide have been broadly studied because of their utilization in optoelectronic devices technology [5-8]. In recent years CdO based TCOs are of great attraction due to their exceptional carrier mobility, simple crystal structure and nearly metallic conductivities [9]. CdO has high electrical conductivity and optical transmittance in the visible region of the solar spectrum. Due to these properties of CdO, it is one of the promising TCO from II to VI group of semiconductors [10]. Cadmium oxide (CdO) is an n-type semiconductor with nearly metallic conductivity with a band gap that varies from 2.2-2.8 eV and possesses low resistivity (10^{-2} to 10^{-4} Ω-cm) due to cadmium intensities with a rock-salt crystal structure (fcc) and the defect of oxygen vacancies [11-13]. Fabrication process of CdO films reported in the literature are mainly by dc magnetron reactive sputtering, metal organic chemical vapor deposition, vacuum evaporation, electrochemical deposition, pulse laser deposition, electron beam deposition, spray pyrolysis, sol-gel, RF magnetron sputtering [14-16]. Among these film growth methods, spray pyrolysis method is quite simple, low cost and easy to control growth parameter. The basic advantages of this method are that the capable of large area fabrication, can be carried out at low temperature and mostly no needed of vacuum system [17-20]. In this study we have prepared the CdO thin films using low cost spray pyrolysis method and study the effect of Al doping concentration on the structural, optical and electrical properties of CdO films.

II. Experimental Details

The CdO and Al doped CdO thin films were prepared by a simple home-made spray pyrolysis method on glass substrates. The glass substrates were ultrasonically cleaned in chromic acid and double distilled water before the film deposition. To prepare undoped CdO thin film, a 0.1M working solution was prepared by taking cadmium acetate ($(CH_3COO)_2Cd.2H_2O$) as source compound and deionized water as solvent. And to prepare Al doping, aqueous solution of aluminum chloride with various doping concentrations (1,2 wt.%) was mixed with the precursor solution. A small amount of acetic acid was added to increase the solubility of cadmium acetate and aluminum chloride solution. A resultant solution was sprayed on glass substrates at a temperature of 300°C.

The optimized deposition parameters such as solution flow rate (0.5 ml/min), nozzle to substrate distance (22cm), deposition time (5-10 min) and deposition temperature (573K ~ 623K). The pressure of the carrier gas (air) was kept constant at 2.2 BAR/min (32 psi/min). Several sets of CdO films were prepared for each concentration and structural, optical and electrical properties were found to be highly formative and static.

The crystallographic structure of the films was studied by X-ray diffraction (XRD), using a D2 PHASER (BRUKER) X-ray diffractometer with C_uK_a (λ=1.5418 Å) radiation with voltage 30 kV and tube current 10 mA, for 2θ values in the range of 10° to 70°. The optical transmittance spectrum was recorded by using a double beam UV-vis-NIR spectrometer (SHIMADZU, UV-1601PC) in the wavelength of 300 nm to 1100 nm at room temperature. Electrical properties were steered out using Hall effect measurements setup in van der Pauw's configuration [21]. In this work the gap between the pole pieces was 2 cm. Magnetic field of the order of 9.465 KG was used for the Hall voltage measurement. And the thermoelectric power was measured using Seebeck effect where the temperature of the sample was varied by varying voltage of a small heater from 300 K to 520 K.

III. Result and Discussion

The XRD pattern of CdO and Al doped CdO thin films are shown in Fig. 1. The characteristic peaks were identified by comparing with the JCPDS Card No. 75-0592 [22] and the characteristics planes are identified as (1 1 1), (2 0 0), (2 2 0), (3 1 1) for CdO and Al doped CdO films, which confirms that the undoped CdO and Al doped CdO thin films are polycrystalline in nature and can be indexed with cubic structure. The highest intensity peaks of CdO and Al doped CdO films were found in (1 1 1) and (2 0 0) planes. Therefore, preferred orientation of crystal growth is found in these crystallographic planes. Slight lateral shift in peak position is seen due to the dopant of Al in CdO.

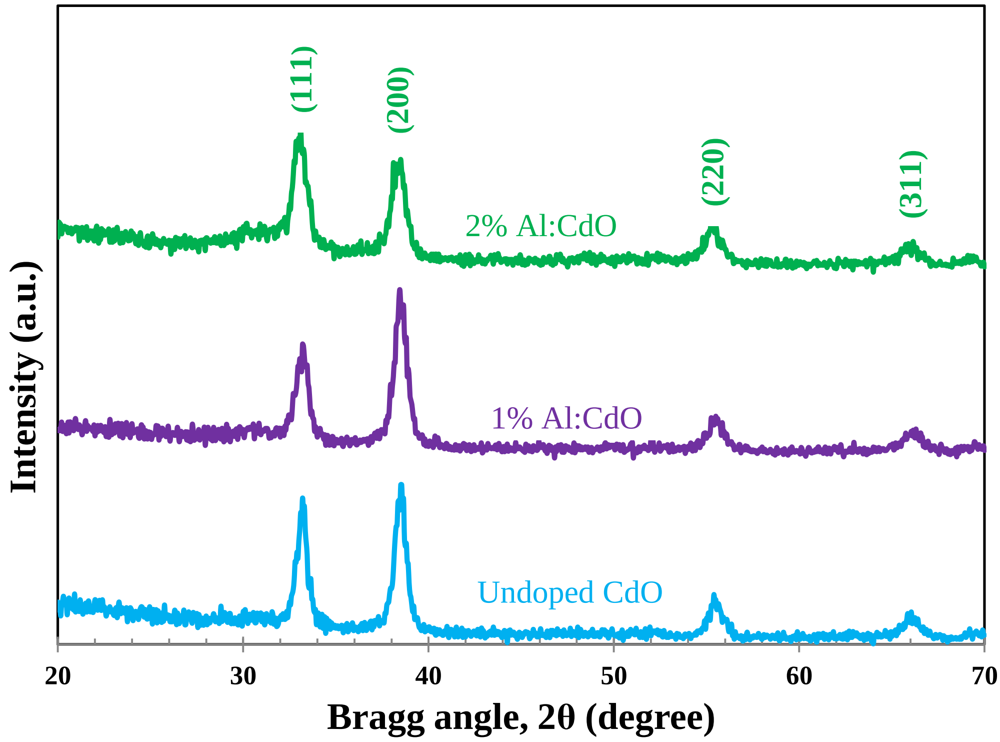

Fig. 1: Variation of X-ray diffraction patterns with intensity for CdO and Al doped CdO films

The direction of peak shift for 2% Al doping in CdO is found right to left while for 1% Al doping CdO peak shift is not significant to undoped CdO films. Due to the replacement of Cd^{2+} ions by Al^{3+} in CdO lattice this may be happened. The average lattice constant of the undoped CdO was found as a = 0.4685 nm as shown in table 1 which is consistent to the reported value a = 0.4694 nm [23]. The determined lattice constant is little bit smaller than reported value due to the lattice contraction [24] or to the presence of oxygen vacancies. The size of the grown crystallites was estimated by using the Debye-Scherrer's formula [25],

$$\xi = \frac{K\lambda}{\beta cos\theta} \quad \text{...} \quad (1)$$

Where, k is a constant whose value is very close to unity (0.94). ξ is the crystallite size, λ is the wavelength of the X-ray used, θ is the diffraction angle and β is the full width at half maxima (FWHM) measured in radians. The smallest crystallite size average to 13.82 nm was found for undoped CdO thin film which makes this nanoparticle suitable for application of gas sensors.

Table-1. Crystallite size of Al doped CdO films with different concentrations

Concentration of Al (wt.%)	Lattice parameter, *a* (nm)	Crystallite size (nm)	
		(111)	(200)
0	0.4685	17.97	13.05
1	0.4682	13.94	11.79
2	0.4695	12.32	10.12

The transmittance spectra for CdO and Al doped CdO films in the wavelength range (400- 1100) nm are shown in Fig. 2. These spectra shows that the transmittance of the CdO and Al doped CdO films is very low and remain constant up to 450 nm then it increases rapidly at near band wavelength region (450,550) nm, but at higher wavelength region it seems to attain saturation slowly up to measured range of 1100 nm. The ability of a material to absorb light is measured by its absorption coefficient. The absorption coefficient (α) can be determined using the well-known relation [26],

$$T = exp. (-\alpha t) \quad \text{..........} \quad (2)$$

Where, α is the absorption coefficient, T is the transmittance and *t* is the thickness of the film. The variation of the absorption coefficient of CdO and Al doped CdO thin films deposited on glass is shown in Fig. 3. From this figure it is observed that the absorption coefficient, α increase with increase of Al doping level in CdO shown in figure. The absorption coefficients for all films are in the order of 10^4 cm^{-1} at higher energy region.

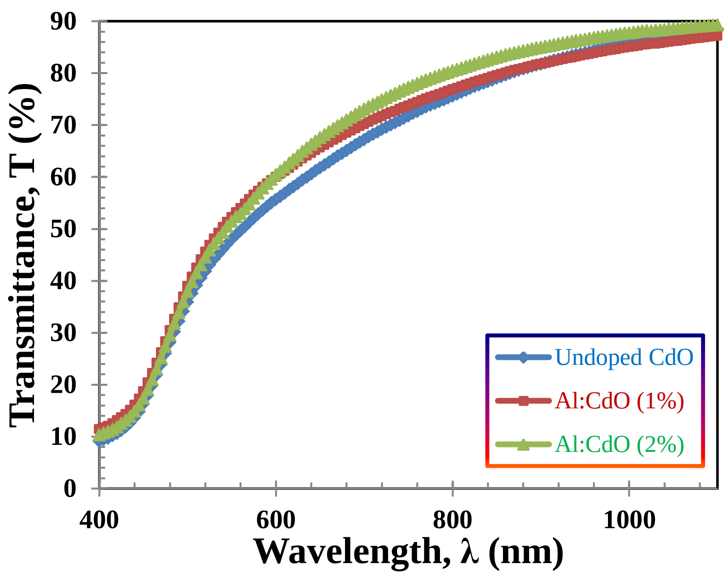

Fig. 2: Variation of optical transmittance with wavelength for CdO and Al doped CdO films.

The optical band gap could be estimated from the optical absorption spectra by using Tauc's relation [27],

$$\alpha h\nu = A(h\nu - E_g)^m \quad \text{..........} \quad (3)$$

Where, A is energy independent constant, *hν* is the photon energy and E_g is the optical band gap of the semiconductor and m is index related to the density of states for the energy band. The variation of $(\alpha h\nu)^2$ (direct allowed transition) with *hν* for the CdO and Al doped CdO films deposited on glass shown in. Fig. 4. The intercept of the energy axis provided the values of E_g which decreased from 2.48 eV to 2.43 eV with the increase of Al doping levels as shown in figure. It is seen that the band gap energy, E_g of undoped CdO films is 2.48 eV which is higher than the band gap (2.43 eV) of 2% Al doped CdO. A similar behavior has been investigated by Ramamurthi et al. [28].

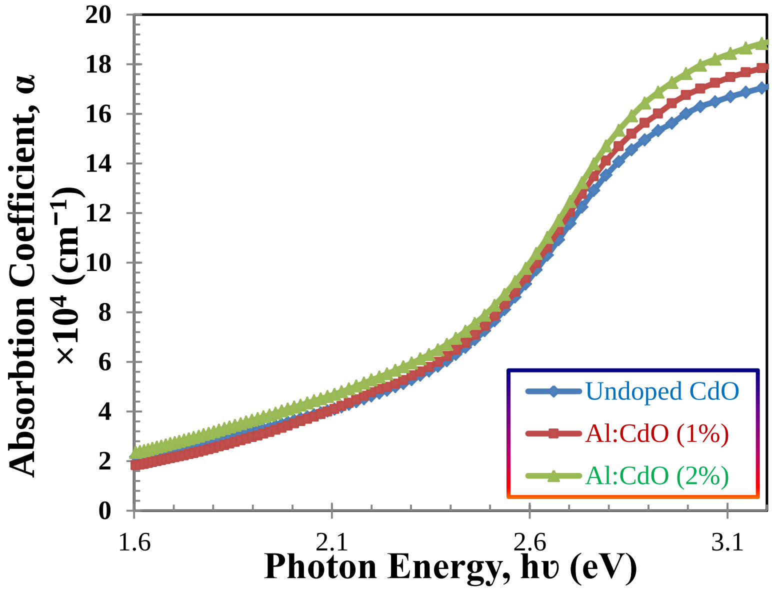

Fig. 3: Variation of absorption coefficient with photon energy for undoped CdO and Al doped CdO thin films.

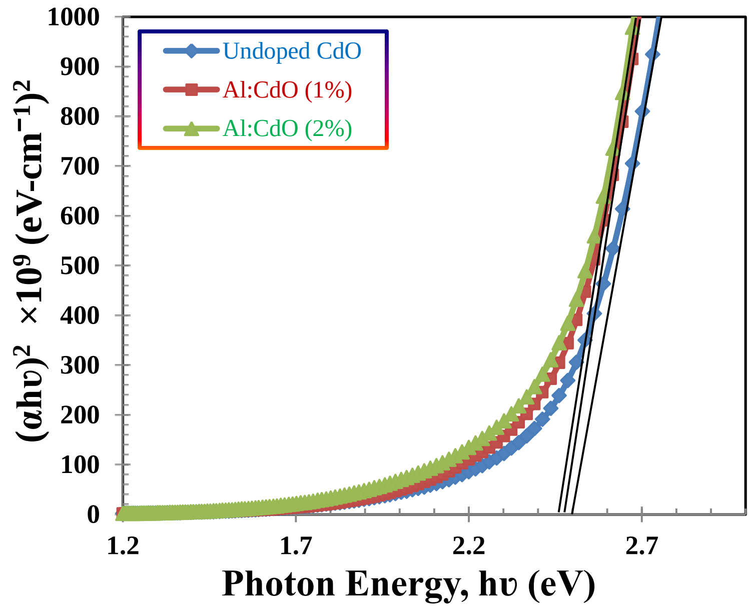

Fig. 4: Variation of $(\alpha h\nu)^2$ with Photon energy for CdO and Al doped CdO thin films.

The size of the band gap of these films grown by spray methods may be suitable for the applications in photodiodes, transparent electrodes, liquid crystal displays, phototransistors, photovoltaic, IR detectors, information storage and anti-reflection coatings [29].

The electrical resistivity of undoped CdO and Al doped CdO thin films were measured as a function of temperature using Vander Pauw's method of four probe arrangements in air ambient. It is seen that the resistivity of the undoped CdO and Al doped CdO films decrease lightly with the increase of temperature which confirmed the semiconducting behavior of CdO. We also found that 1% and 2% Al doped CdO films exhibit lower sheet resistance than undoped CdO thin film. From the Arrhenius plot of $ln\sigma$ vs $10^3/T$ for CdO films, the activation energy was negative at high temperature which indicates that the transition is free band due to the conducting behavior of the films as shown in Fig. 5. Table-2 shows the carrier concentration and mobility of the CdO films with respect to doping level of Al at room temperature. Hall measurement confirms that the majority charge carrier is electron and all the CdO films exhibits n-type conductivity.

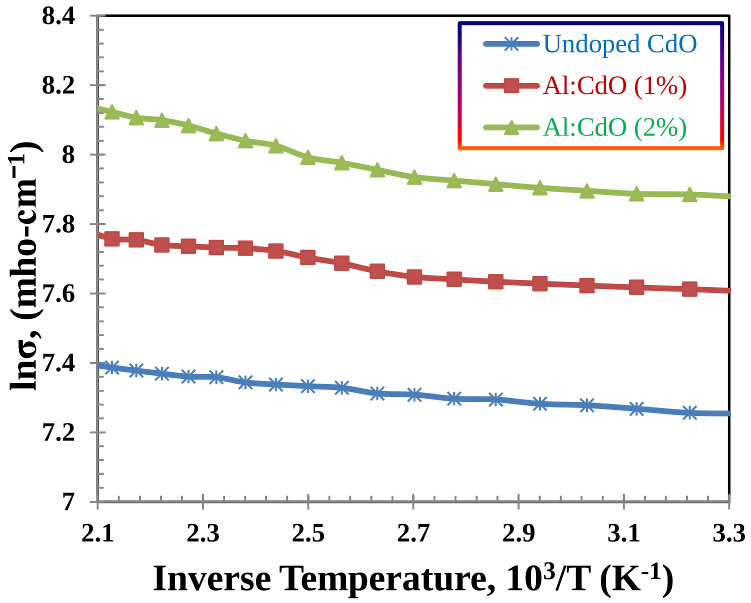

Fig. 5: Variation of *lnσ* with inverse temperature for CdO and Al doped CdO thin films.

A minimum resistivity of $3.79\times10^{-4}\Omega$-cm with carrier concentration of 1.30×10^{20}cm^{-3} is achieved when CdO film is doped with 2 wt.%. A similar behavior has been observed by Sachet and Maity et al. [30-32]. The Hall concentration of the CdO and Al doped CdO thin film is of the order of 10^{20} (cm^{-3}).

Table 2. Measurement of carrier concentration (n) and Hall mobility (μ_H)

Sample	Hall mobility, μ_H (cm²/V-sec)	Hall Concentration, n x10^{20} (cm^{-3})	Resistivity, ρ x10^{-4} (Ω-cm)	RT Conductivity, σ x10^3 (mho-cm^{-1})
Undoped CdO	90.07	0.98	7.07	1.41
Al:CdO (1%)	77.22	1.62	4.97	2.01
Al:CdO (2%)	126.77	1.30	3.79	2.64

Thermoelectric power measurements of the undoped CdO and Al doped CdO thin films were performed using Seebeck effect by taking copper wire as the reference metal as shown in Fig. 6.

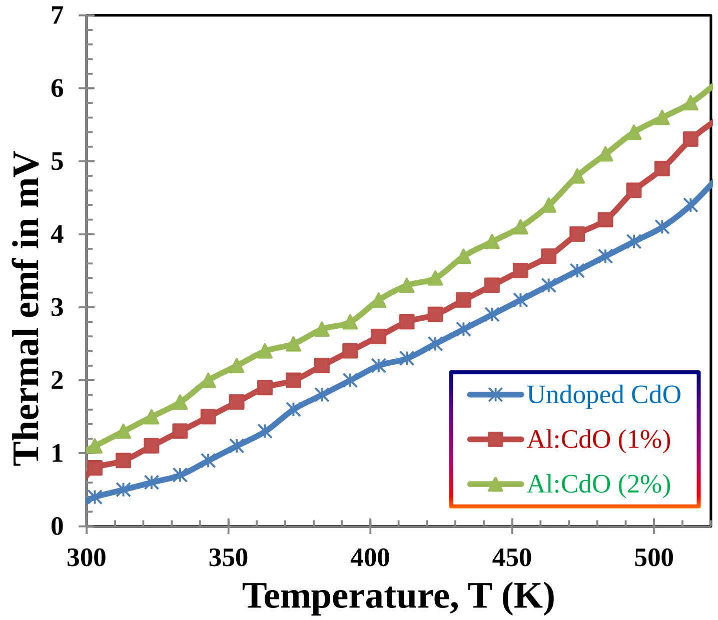

Fig. 6: Variation of thermal emf with temperature for CdO and Al doped CdO thin films.

It observed that the thermal emf is positive and increases with increasing temperature difference between hot and cold junction which indicates n-type nature of the CdO and Al doped CdO films with respect to the reference metal.

IV. Conclusion

The undoped CdO and Al doped cadmium oxide thin films have been prepared by homemade spray pyrolysis method on glass substrate. Various physical properties such as structural, optical, electrical, Hall effect and thermoelectric were investigated as a function of Al doping concentration. The structural study confirms that the fabricated films are polycrystalline in nature and can be indexed with cubic structure. The optical study showed that the films are highly transparent, above 85% transmission for wavelengths ≥ 900nm and the value of direct band gap has been decreases with the increase of Al doping concentration in CdO thin films and reaches a minimum of 2.43eV when doping level is 2 wt.%. A minimum resistivity of $3.79\times10^{-4}\Omega$-cm with carrier concentration of $1.30\times10^{20}cm^{-3}$ is achieved when CdO film is doped with 2 wt.%. The electrical conductivity increases with the increasing of doping level of Al in CdO thin films. The thermoelectric measurements confirm that both the CdO and Al doped CdO thin films under study are n-type in nature and majority carrier is electron.

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