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# LINEAR AND NON LINEAR OPTICAL PROPERTIES OF Al:CdO FILMS DEPOSITED BY SPRAY PYROLYSIS

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CdO thin films with various molarities of doping of Aluminium have been prepared by spray pyrolysis method. The deposited CdO:Al films were characterized by studying their linear and non linear optical properties. Optical study shows 30 to 90% transparency depending upon the aluminium content in the films. The calculated values of absorption coefficient are in the order of $10^6$ cm$^{-1}$. The value of direct band gap has been found to decrease from 2.4 to 2.15 eV and the value of indirect band gap also decrease from 2.3 to 1.92 eV with increase of Al doping concentration. The nonlinear optical absorption of Al-doped CdO films have been measured used the Z-scan technique at a wavelength 632.8 nm. The nonlinear optical absorption coefficient (β) for 0.0001M, 0.0002M and 0.0003 are 4.82 x$10^{-3}$m/W, 8.63 x$10^{-3}$m/W and 10.77x$10^{-3}$m/W respectively.

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*Keywords:* Thin film, Cadmium oxide, Linear and non-linear optical properties, Z-scan

## 1. Introduction

Cadmium Oxide (CdO) based Transparent Conducting Oxides (TCOs) have received more attention due to their large carrier mobility and good optical transparency in the visible region [1,2]. CdO is used in the solar cell applications because of its electrical conductivity and optical transparency in the visible region of the solar spectrum [3,4]. A literature survey reveals that several methods are employed on preparation and characterization of aluminium doped CdO thin films [5-9]. Spray pyrolysis technique is simple and less expensive. This technique is used for the preparation of a large number of semiconducting and insulating thin films [8-11]. The nonlinear optical absorption of Al-doped CdO films have been measured used the Z-scan technique at a wavelength 632.8 nm. The observations indicate that the optical nonlinearities depend strongly on the pulse duration of the excitation laser, although many reports declared that the observed nonlinear effect is an instantaneous optical nonlinearity in the nanosecond and pico second regimes. Apparently, it is imperative to gain an insight on the underlying physical mechanisms for the observed optical nonlinearities at different time scales. In this paper, the linear transmittance spectrum and Z-scan technique are used to characterize the linear and nonlinear optical properties of aluminium doped CdO thin films, respectively. This paper also deals with the preparation and characterization of Al doped CdO thin films with various concentrations and the effect of doping on the electrical and optical properties of CdO thin films.

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## 2. Experimental details

A simple homemade spray pyrolysis experimental set up was employed to prepare pure and Al doped CdO on the glass substrates at a temperature of 300°C. In the preparation of CdO thin films, aqua solution containing 0.1M cadmium acetate dissolved in a mixture of methanol and distilled water was used. To achieve Aluminium doping, aqueous solution of aluminium nitrate with various concentration (0.0001M to 0.0005M) was mixed with the precursor solution. The resultant solution was sprayed on the glass substrates at 300°C. For each concentration, many sets of films were prepared and their optical and non linear optical properties were found to be highly reproducible and stable. Film thickness of CdO:Al was determined by gravimetric weighing method [12]**.** The film thickness was determined to be ranged between 620 nm to 1210 nm for the solution molarity of 0.0001M, 0.0002M, 0.0003M, 0.0004M and 0.0005M. This was consequently verified by the cross sectional studies of the film using Scanning Electron Microscope. Here, the film is mounted vertically to measure the thickness directly [13]. Optical transmittance and band gap energy was measured by UV-VIS single beam spectrophotometer (ELICO-159). The experimental accuracy for absorbance is ±0.005 abs and of wavelength is ± 0.05 nm.

## 3. Results and discussion

### 3.1 Linear Optical Studies

Fig. 1(a) shows transmittance spectra recorded in the wavelength range of 300–1100 nm for doped and undoped cadmium oxide thin films. It shows that addition of aluminium to cadmium oxide improve the transmittance.

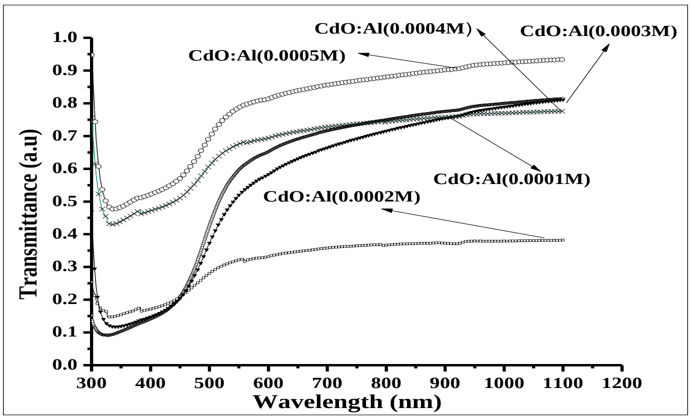

*Fig. 1 (a) Transmittance spectra of Al doped CdO films*

The undoped CdO film shows a transmittance of 60% and the transmittance increases up to 90% due to increase of aluminum doping.

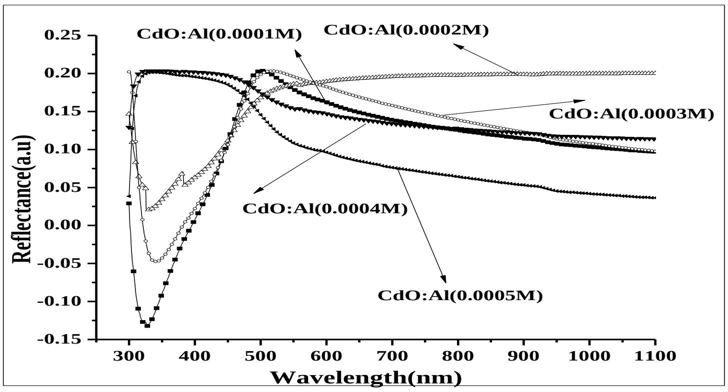

*Fig. 1 (b) Reflectance spectra of Al doped CdO films*

Figure 1(b) shows that the reflectance values of films in the visible region change with aluminium dopant.

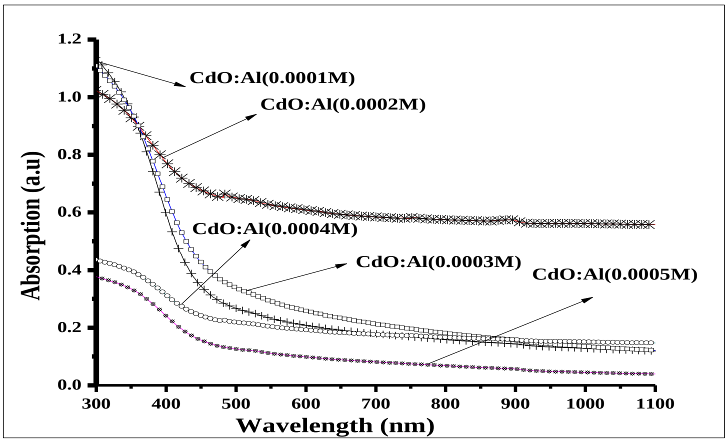

*Fig. 2a. Absorbance spectra of Al doped CdO films*

Figure (2a) shows that the absorbance decreases due to the increasing of aluminium doping concentration. The optical absorption edge of the films was determined by the optical absorption, which provides explaining features concerning the band structure of the film.

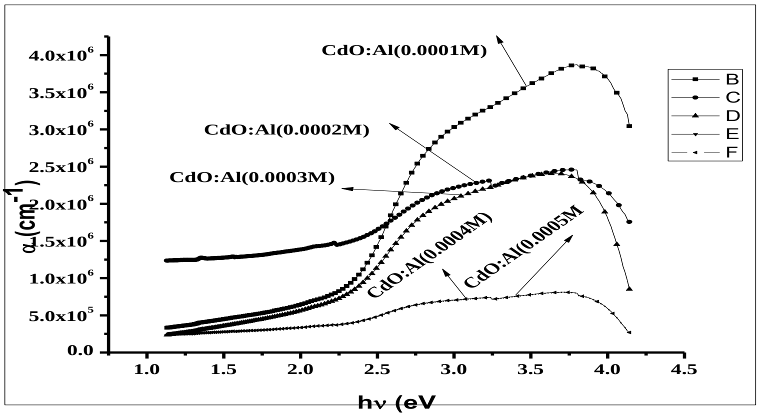

*Fig. 2b. Absorption co-efficient of Al doped CdO films*

The ability of material to absorb light is measured by its absorption coefficient. The absorption co-efficient ($\alpha$) is calculated using Lambert's law [14]. The calculated values of absorption coefficient are in the order of $10^6$ cm$^{-1}$. The optical absorption was analyzed by the following equation [15].

$$(\alpha h\nu) = A\,(h\nu - E_g)^n \qquad (1)$$

Where A is a constant, hν is the photon energy, Eg is the optical band gap and exponent n depends on the transition. n = 1/2, 2, 3/2 and 3 corresponding to allowed direct and allowed indirect, forbidden direct and forbidden indirect respectively. Taking n= ½ direct optical band gap values were calculated $(\alpha h\nu)^2$ versus (hν) plot by extrapolating the linear portion of the graph to (hν) axis. The intercept on the (hν) axis determines the direct band gap.

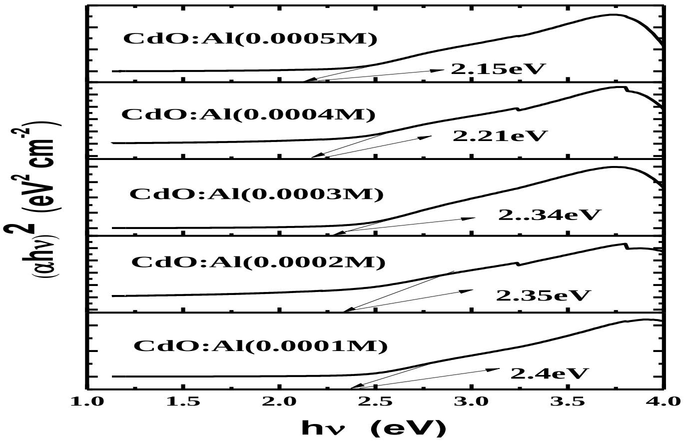

*Fig. 3a. Plot of $(\alpha h\nu)^2$ versus hν of Al doped CdO films*

The fundamental absorption, which corresponds to electron excitation from valance band to conduction band, can be used to determine the nature and value of band gap. The high α value ($>10^4$) confirms the existence of direct band gap [16]. The value of direct band gap has been found to decrease from 2.4 to 2.15 eV fig. 4a and the value of indirect band gap also found to decrease from 2.3 to 1.92 eV fig. 4b with increase of Al doping concentration. There are some other factors responsible for shrinkage of the band gap [17,18] is electron dopant interaction and electron-electron Coulomb and exchange interaction within the conduction band [19,6]. The decrease of optical band gap for CdO films with different Al contents are consistent with previous report of Al doped CdO films prepared by sol-gel [20] and rf sputtering [6] methods.

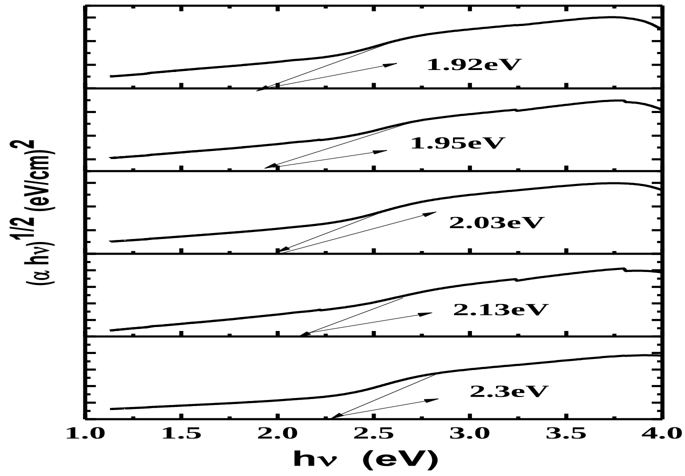

*Fig. 3b. Plot of $(\alpha h\nu)^2$ versus hν of Al doped CdO films*

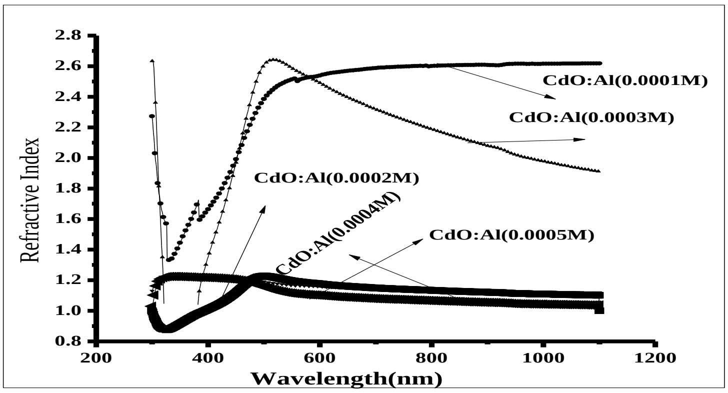

*Fig. 4. Variation of refractive index of Al doped CdO thin films*

Generally, the refractive index decreases with aluminium dopant due to the structural changes in the films. Probably the good packing density of undoped CdO film on the surface caused this sample to have the lowest transmittance and highest refractive index values. For the doped samples, there was a correlation between the film doping level and refractive index variations with RMS roughness values, high refractive index corresponded to high film roughness, high aluminium doping and lower grain size.

### 3.2. Physical mechanisms of optical nonlinearities in Al doped CdO thin films

Optical nonlinear response of the Al doped CdO thin film partly depends on the laser characteristics, in particular, on the laser pulse duration and on the excitation wavelength, and partly on the material itself. The optical nonlinearities usually fall in two main categories: the instantaneous and accumulative nonlinear effects. If the nonlinear response time is much less than the pulse duration, the nonlinearity can be regarded justifiably as responding instantaneously to optical pulses. On the contrary, the accumulative nonlinearities may occur in a time scale longer than the pulse duration. Besides, the instantaneous nonlinearity (for instance, two-photon absorption and optical Kerr effect) is independent of the laser pulse duration, whereas the accumulative nonlinearity depends strongly on the pulse duration. Examples of such accumulative nonlinearities include excited-state nonlinearity, thermal effect, and free-carrier nonlinearity. The simultaneous accumulative nonlinearities and inherent nonlinear effects lead to the huge difference of the measured nonlinear response on a wide range of time scales.

#### *3.2.1 Nonlinear refractive index*

The physical mechanisms of nonlinear refraction in the Al doped CdO thin films mainly involve thermal contribution, optical electrostriction, population redistribution, and electronic Kerr effect. The thermal heat leads to refractive index changes via the thermal-optic effect. The nonlinearity originating from thermal effect will give rise to the negative nonlinear refraction. In general, the thermal contribution has a very slow response time (nanosecond or longer). On the picosecond and femtosecond time scales, the thermal contribution to the change of the refractive index can be ignored for it is much smaller than the electronic contribution. Optical electrostriction is a phenomenon that the inhomogeneous optical field produces a force on the molecules or atoms comprising a system resulting in an increase of the refractive index locally. This effect has the characteristic response time of nanosecond order. When the electron occurs the real transition from the ground state of a system to a excited state by absorbing the single photon or two identical photons, electrons will occupy real excited states for a finite period of time. This process is called a population redistribution and mainly contributes the whole refractive nonlinearity of Al doped CdO films in the picosecond regime. The electronic Kerr effect arises from a distortion of the electron cloud about atom or molecule by the optical field. This process is very fast, with typical response time of tens of femtoseconds. The electronic Kerr is the main mechanism of the refractive non-linearity in the femtosecond time scale.

### *3.2.2 Nonlinear absorption*

In general, nonlinear absorption in Al doped CdO thin films can be caused by two-photon absorption, three-photon absorption, or saturable absorption. When the excitation photon energy and the band gap of the film fulfill the multiphoton absorption requirement [(n-1) hν < E*g* < n*hν*] (here *n* is an integer. n=2 and 3 for two- and three-photon absorption, respectively), the material simultaneous absorbs ‘n’ identical photons and promotes an electron from the ground state of a system to a higher-lying state by virtual intermediate states. This process is referred to a one-step ‘n’ photon absorption and mainly contributes to the absorptive nonlinearity of most Al doped CdO films. When the excitation wavelength is close to the resonance absorption band, the transmittance of materials increases with increasing optical intensity. This is the well-known saturable absorption. Accordingly, the material has a negative nonlinear absorption coefficient.

### *3.2.3 Non linear absorption coefficient*

The non linear absorption coefficient β of Al doped CdO thin films were determined from Z-scan open aperture measurements.

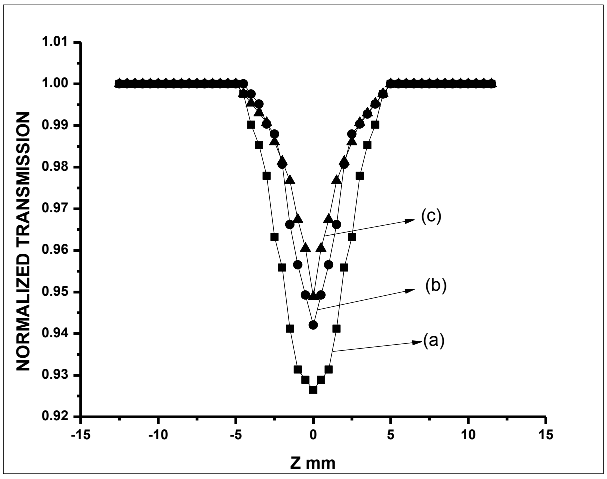

*Fig. 5 Open aperture z-scan response; the dots represent the measurement data; the line corresponds to a fit of equation (2). (a) 0.0001M (b) 0.0002M (c) 0.0003M*

Figure (5) shows the Z-scan results of films correspond to the normalized transmittance T as a function of distance from the beam focus Z/Z0. The transmission is symmetric with respect to the focus (z=0), where it has minimum transmission. For a Gaussian beam, the normalized transmittance for open z-scan [21] is

$$T_{open} = 1 - \frac{\Delta\emptyset}{1-x^2} \tag{2}$$

Where $x = \frac{z}{z_0}$, $z_0 = \frac{\pi{\omega_0}^2}{\lambda}$ , $\omega_0$ - is a beam waist, $\Delta\emptyset = \frac{\beta I_0 l}{2}$ and $l = \frac{[1-\exp(-\alpha_0' d]}{\alpha_0'}$ with $\alpha_0'$ is a linear absorption coefficient at 632.8nm, d is the sample thickness, l is the effective thickness of the sample, $I_0$ is the intensity of the laser beam at the focus and β is the non-linear absorption coefficient.

A fit of equation (2) to the experimental data is depicted in figure (5) and gives the value of the nonlinear optical absorption coefficient β for 0.0001M, 0.0002M and 0.0003 are 4.69 x$10^{-3}$m/W, 4.99 x$10^{-3}$m/W and 4.74x$10^{-3}$m/W respectively.

## 4. Conclusion

In summary, Aluminium (Al) doped Cadmium Oxide (CdO) with five different molarities were fabricated by spray pyrolysis technique. Optical and non linear optical studies were observed. The non-linear optical absorption co-efficient of various molarities of Al doped Cadmium Oxide thin films were calculated by using z-scan technique.

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