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Linear And Non-Linear Optical Properties Of Flourine Doped Cadmium Oxide Thin Films

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Abstract

Thin films of Fluorine (F) doped Cadmium oxide (CdO) with three different molarities were prepared by a chemical spray pyrolysis method on glass substrates. The prepared films were analyzed by X-ray diffraction. It shows that doping of CdO with F exhibits the film's [111] preferred orientation and it causes move towards higher angles. The films were analyzed with a UV-VIS-NIR spectroscopy, electrical measurements, and Z-scan measurements. The absorption coefficient was found that in the order of 10^6 cm^{-1}. The direct band gap energy decreased with increase of F doping and corresponding carrier concentrations increases from Hall measurement results. The resistivity of CdO films decreased with increase of F doping and the mobility is increased. The nonlinear optical absorption of F-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 $3.83x10^{-3}$m/W, $5.7x10^{-3}$m/W and $5.48x10^{-3}$m/W respectively.

Keywords: Thin film, CdO, xrd, Linear and non-linear optical properties, Z-scan,

1. Introduction

Transparent Conductive Oxides (TCO's) have high optical transmissions, wavelength and electrical conductivity. They also reflect near infrared and infrared wavelengths and are used in products ranging from energy efficient low emissive windows to photovoltaic [1,2]. TCO's range from simple binary compounds to exotic ternary and quaternary compounds. They are used in wide range of applications flat panel displays, touch screens, solar cells and liquid crystal devices. TCO thin films are used as the transparent electrical contacts in sensors and optical limiters.

Thin films of CdO and doped CdO have been prepared by various deposition techniques solgel [3], ion beam sputtering [4], magnetic sputtering [5], chemical vapour deposition [6] and spray pyrolysis [7]. Among these techniques spray pyrolysis technique is simple method to deposit thin films. In this paper, we have deposited Flourine doped CdO thin film onto a glass substrate by a spray pyrolysis technique, because it is more advantageous for its simplicity, cheapest, low cost and capability of large area deposition. Doping of CdO thin films with various elements like Tin by Yan et.al [8], Indium by Freemann et.al [9] and Flourine by Ghosh et.al. [10] have been done to increase in conductivity. For decreasing the resistivity of an n-type semiconducting material, the non-metal doping is more efficient than metal doping. Flourine has been used as a suitable dopent for other Transparent Conducting thin films. Flourine has seven electrons in the last orbit and oxygen has six, hence Flourine doping increases electrons in CdO and thereby increases n-type conductivity. In this paper, we report optical, structural and electrical properties of Flourine doped CdO with doping concentration was observed and also determination of third order nonlinear properties of CdO, which uses it interesting material for optical devices[11,12].

2. Experiments

2.1. Materials and methods

Cadmium oxide thin films doped with Fluorine were deposited on an optically flat well cleaned glass substrate by using a homemade double nozzle sprayer. The 50ml of the spray solution was prepared from aqueous 0.05M of Cadmium Acetate ($Cd(CH3COO)_2.2H_2O$) and 0.0001M of ammonium fluoride (NH_4F) dissolved in a mixture of methanol and deionized water (1:1). The chemicals used in this deposition were of analytical grade. The atomized chemical solution is sprayed on to the preheated substrate maintained at 230° C ± 2° C with the help of compressed air as carrier gas. The carrier gas flow rate was maintained at 3ml/min at a pressure of 12kg/cm^2. The distance between the spray nozzle and the substrate is 35cm. To avoid excessive cooling of the substrate, spraying was done with time gap of 30 seconds between successive spray. Details of this setup have been published elsewhere [13]. Films with different doping levels of Fluorine were also deposited by varying the Fluorine concentration 0.0001M, 0.0002M and 0.0003M precursor solution without changing the other process parameter. For each concentration the reproducibility of the films were verified by repeating the experiments several times. The deposited film was subsequently annealed in air at 300 °C for 1 hour. Film thickness of Fluorine doped Cadmium oxide was determined by gravimetric weighing method [14]. The film thickness was determined to be ranged between 550 nm to 850 nm for the solution molarity of 0.0001M to 0.0003M. 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 [15].

The structural properties were analyzed by X-ray diffractometer (Rigaku Model RAD II A) with Cukα radiation (λ = 1.54056 Å) in the span of 10 - 100º. Surface morphology of the film was determined by using Scanning Electron Microscope (TESCAN –VEGA 3 SEM). Optical transmittance and band gap energy was measured by UV-VIS single beam spectrophotometer (ELICO-159). The electrical properties such as resistivity (ρ), carrier concentration (n) and Hall mobility (μ) were measured by a standard four-probe technique (ECOPIA HMS5000 Hall system) and silver contacts were used for all measurements. The third order optical nonlinearity χ(3) was measured by using z-scan technique [16]. A He-Ne laser at wavelength 632.8 nm was used in the experiment. The laser beam was focused to a waist of 45.15 µm with a convex lens of focal length 12cm to give the intensity at the focus of 3.12 kW/cm.

3. Results and discussion

3.2.1. X-ray diffraction studies

The X-ray diffraction spectra of three different thin films of Fluorine doped Cadmium oxide prepared at 230 ºC are shown in Fig.1. The peaks observed in all the diffractograms confirm the nanocrystalline nature of the CdO: F film. The XRD pattern of the films also reveals that the CdO: F film is polycrystalline and got a cubic crystal structure with preferential orientation along (111) plane. The absence of the additional peaks in the XRD results of Fluorine doped Cadmium oxide thin film samples indicates the formation of single phase CdO. No phase corresponding Fluorine compounds was detected in the XRD. The observed diffraction peaks at 2θ values of 32.95, 38.24, 55.25, 65.90 and 69.18º which are verified with the known patterns of standard X-Ray Diffraction data file (JCPDS file No: 65-2908**)** and can be indexed to (111), (200), (220), (311) and (222) reflections respectively. While comparing the X-Ray Diffraction (XRD) pattern it is found that with the increase of Fluorine molarity (0.0001M, 0.0002M and 0.003M) in 0.05M CdO, the position of the preferred orientation peak in XRD pattern, shift towards higher angle. The observed slight deviation in the respective values with standard data is probably due to change in the crystallinity of the films (i.e.) in this case it is due to the decrease in grain size with increase in molarity of the dopant in as deposited film which is subsequently verified with calculation using Scherer's equation [17,18].

$$D = \frac{0.9\lambda}{\beta_{hkl}\cos\theta_{hkl}}$$

Where, D is the crystallite size (nm), β_{hkl} is the FWHM of the observed peak (radians), λ is the wave length of the X-ray diffraction (=1.54056 Å) and θ is the Bragg angle of diffraction. The average crystallite size determined it was found that in the order of 50 nm for 0.0001M to 0.0003M of CdO:F films.

However, the peak position not only depends on the substitution of F in CdO for CdO: F films, also due to the other parameters such as spray conditions and temperature.

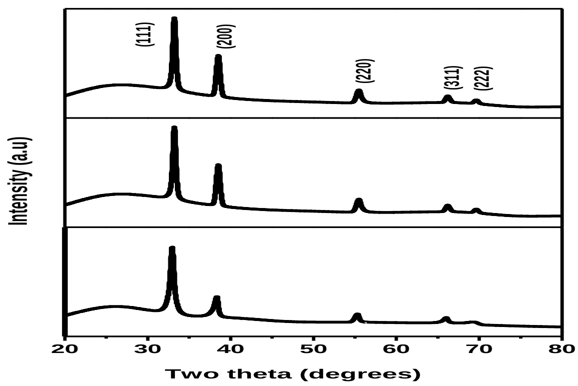

Fig.1.X-ray diffraction patterns of Fluorine doped CdO films: (a) 0.0001M (b) 0.0002M and (c) 0.0003M

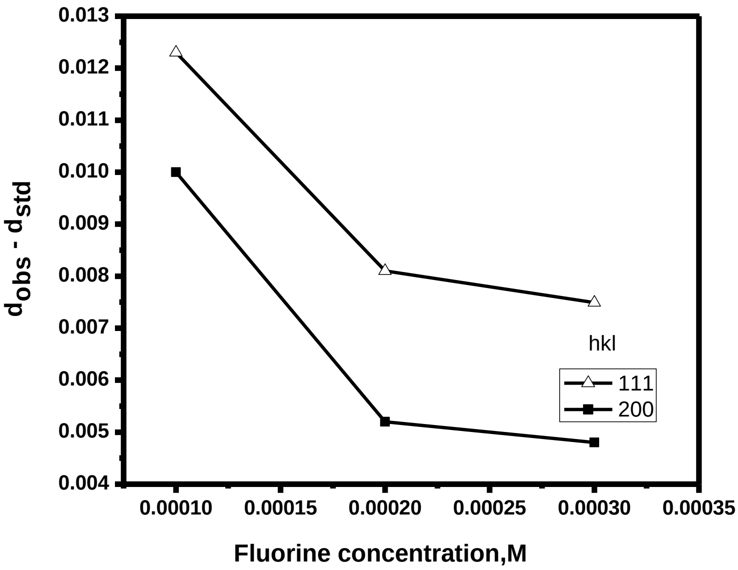

Fig.2. Variation of d_{obs} - d_{std} with Fluorine concentration

As in Fig.2, the difference between observed and standard d values as a function of fluorine concentrations are plotted for the planes (111) and (200). The difference d values of standard and observed for the plane (200) plane are smaller than the (111) plane. The smaller values may be due to the oxygen vacancies in the lattice. And also it may be noted that fluorine concentration increases d values of both planes decreases. It may be attributed to the smaller grain size in higher solution concentration of both planes. Similar results can be carried out in previous literature [19,20].

3.2. Optical Studies

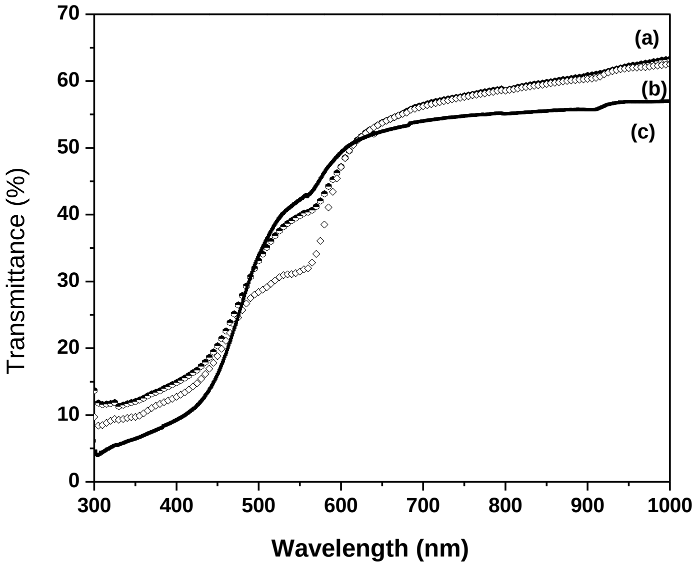

Fig.3. Optical transmission spectra of Fluorine doped CdO films: (a) 0.0001M (b) 0.0002M and (c) 0.0003M

Fig.3. shows that the optical transmission spectra of Fluorine doped CdO films. The plot shows a sharp rise in transmittance near the band edge attributed to the good crystallinity of the film [21]. Transmittance spectra of as deposited films show a narrow range of variation with the increase in dopant molarity. It is felt that the doping of Ammonium fluoride in CdO may lead to increase in the metallic nature of the films, which results in light absorption. The solution concentration of Ammonium fluoride increases, there is increase in transparency of the film 60% at 650 nm of given wavelength.

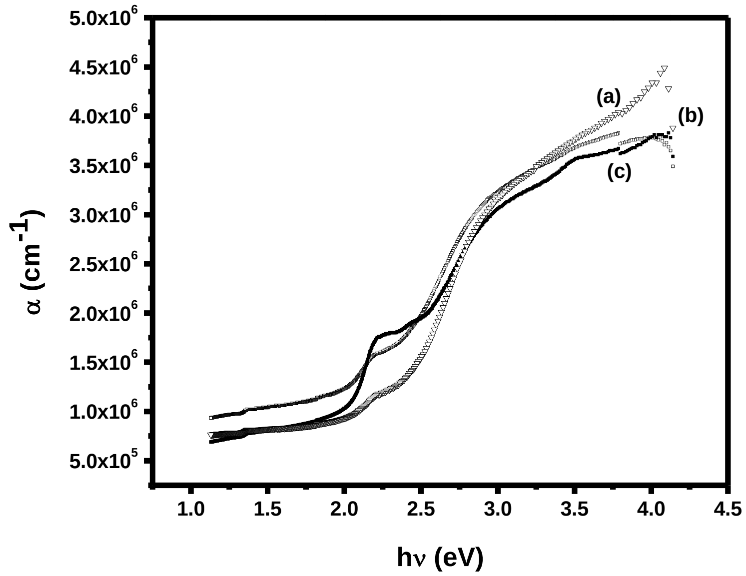

Fig.4. Absorption coefficient spectra of Fluorine doped CdO films: (a) 0.0001M (b) 0.0002M and (c) 0.0003M

The absorption co-efficient (α) is calculated using Lambert's law [22] and it is shown in Fig.4. The absorption co-efficient (α) is found to be in the order of 10^6cm-1. The high α value (>10^4) confirms the existence of direct band gap [23]. The typical plots of $(\alpha h\nu)^2$ versus hν for CdO:F thin films deposited on glass substrate is shown in Fig.5. It was observed that increase in concentration of the dopant in the precursor solution yields slight shrinkage in optical band gap (2.34eV-2.17eV). Generally, the optical band gap widening and shrinkage was attributed to Moss-Burstein shift [24,25] and the optical band gap widening is due to the optical band filling effect. The optical shrinkage is due to the electron-electron interaction at higher carrier concentration films surfaces particularly for larger thickness. Therefore, the film thickness is another cause added to the effect of surface roughness, which participates in the drastic change in the transmission for films prepared with lowest solution concentration.

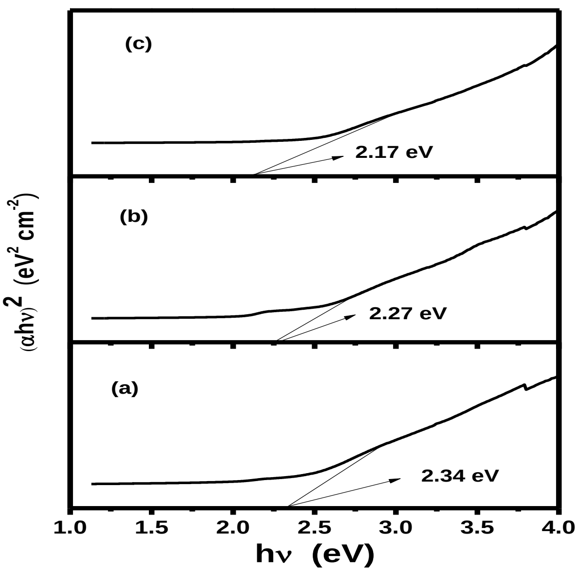

Fig.5. Band gap energy of Fluorine doped CdO films: (a) 0.0001M (b) 0.0002M and (c) 0.0003M

3.3. Electrical Studies

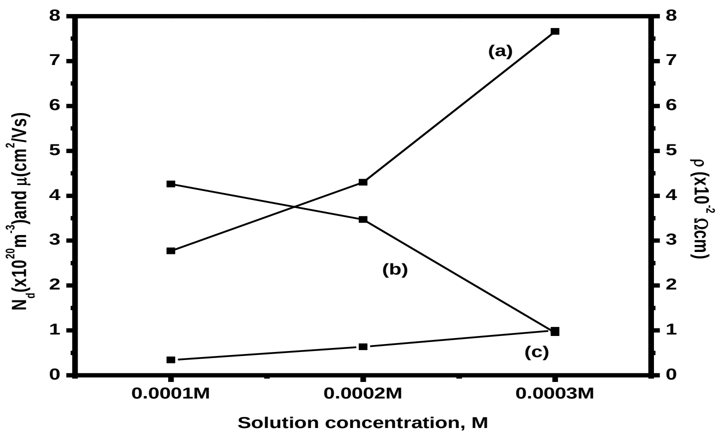

Fig.6. **Electrical parameters of CdO thin films (a) Hall mobility (μ) (b) Electrical resistivity (ρ) (c) Carrier concentration (N_d) with different solution concentration**

The changes in electrical parameters as a function of various solution concentration of CdO:F thin films are presented in Fig.6. It is noted that mobility increases with increase in solution concentration of F. Thus doping concentration has great influence on carrier mobility.

3.4. Non linear optical Studies

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

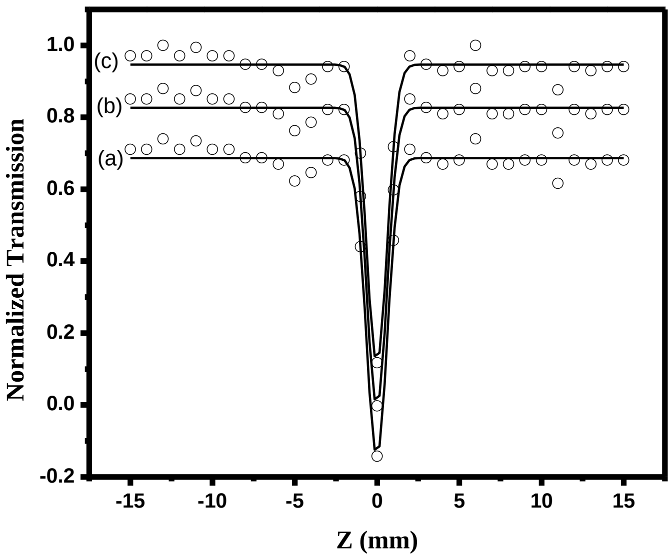

Fig. 7 Open aperture z-scan response; the dots represent the measurement data; the line corresponds to a fit of equation (2).

Figure (7) shows the Z-scan results of films correspond to the normalized transmittance T as a function of distance from the beam focus Z/Z_0. 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 [26] is

$$T_{open} = 1 - \frac{\Delta\emptyset}{1-x^2} \qquad \text{------------------------- (2)}$$

Where $x = \frac{z}{z_0}$, $z_0 = \frac{\pi\omega_0{}^2}{\lambda}$, ω_0 - is a beam waist, $\Delta\emptyset = \frac{\beta I_0 l}{2}$ and $l = \frac{[1-\exp(-\alpha_0' d]}{\alpha_0'}$ with α_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 (7) and gives the value of the nonlinear optical absorption coefficient β for 0.0001M, 0.0002M and 0.0003 are $3.83x10^{-3}$m/W, $5.7x10^{-3}$m/W and $5.48x10^{-3}$m/W respectively.

4. Conclusion

In summary, Fluorine (F) doped Cadmium Oxide (CdO) with three different molarities were fabricated by spray pyrolysis technique. Optical, electrical and morphological studies were observed. The non-linear optical absorption co-efficient of various molarities of Flourine doped Cadmium Oxide thin films were calculated by using z-scan tchinque.

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