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EFFECT ON OPTICAL AND LUMINESCENCE PROPERTIES OF PVA ASSISTED CD DOPED ZNO THIN FILMS

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ABSTRACT- Pure and Cd doped ZnO thin films were prepared by solgel method and coated on glass substrate using spin coating method. Structural studies were carried out by XRD and FTIR techniques. The elemental composition to confirm the doping of transition metals is studied by EDX analysis. The optical effects such as absorptions, transmittance and excitation of luminescence have been studied by UV-Vis DR Spectroscopy and PL spectroscopy. Further the bandgap investigations of thin films have been studied using the transmittance analysis. The doped thin film has the Moss-Burstein shift and show blue shift with high bandgap.

Keywords – [ZnO, solgel,Moss-Burstein shift,bandgap, Cadmium Oxide]

1. INTRODUCTION

Zinc Oxide (ZnO) is an incredible material for numerous applications. It, II-VI group semiconductor material,has wide band gap (~3.37eV at room temperature). The native doping of the semiconductor due to oxygen vacancies or zinc interstitial is n-type. This semiconductor has several favorable properties, including good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence. Electronegativity should be high [Cd is (χ-1.7)] with compare to pristine ZnO [Zn is (χ-1.6)], can have bandgap should be reduced, because of well-known bonded to the nearest valance electrons of impurities, whereas main features of enhances the bandgap could be dependent to the atomic radii [Zn ion's is (135pm) and Cd ion's is (155pm)] of dopant [1, 2]. The structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions stacked along the c-axis. ZnO crystallizes in a hexagonal wurtzite structure (a = b = 3.25 Å, c = 5.20 Å). For material science applications, zinc oxide should have a high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties[2].Recent reports on the transition metal doped zinc oxide thinfilms are useful in optoelectronic applications [3].The structural and physical properties of pure and Cd doped ZnO thin

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films prepared by sol-gel technique using various inorganic and organic precursors at different deposition conditions have been reported here.

1.1 EXPERIMENTAL PROCEDURE

One molar Zinc acetate dihytrate (Zn $(CH_3COO)_2.2H_2O$) was dissolved in a mixture of ethanol [10ml] and Diethanolamine (DEA) [0.2ml] and the molar ratio has maintained at 1: 0.02 Mol% with respect to zinc acetate and DEA [4]. Polyvinyl alcohol (PVA) [0.5g], the conducting polymer, is dissolved in water [10ml] at room temperature and added to the starting solution and used as a coating agent. The resultant solution was stirred at 60°C for 2 h to yield a clear and homogeneous solution. A transparent glass substrateis used for deposition process and heated upto 150^{o}C for 1 hour for stabilizing the film. Similar procedure is followed to dope the CdO (0.02 mol %) with ZnO and Cd doped ZnO film is prepared.

2. RESULTS AND DISCUSSION

2.1 STRUCTURAL ANALYSIS

The X-Ray diffraction patterns of pure and Cd doped ZnO thin films were given in Figure 2. The prominent peak was obtained at (101) which exhibited it's one of the conformations; typically hexagonal wurtzite structure.Also ZnO is preferentially oriented along the c-axis and good agreement to the JCPDS card files (ZnO-361451) and (Zn-653573). The other peaks observed at (002) and (102) has slight changes compared to the standard values due to Cd doping [4, 5]. Also, it is found that the doped ions concentration resulted into slight decrease in the intensity with increase the FWHM of the (101) peak. The XRD spectra indicated that the films were of polycrystalline in nature. The crystalline size for pure and Cd doped ZnO thinfilms have same crystalline size and is ~31.02 nm. The narrow peaks indicate the good quality of ZnO thinfilms.

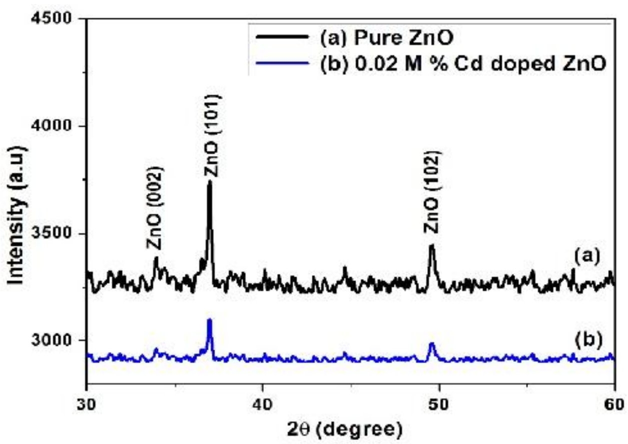

Figure 1 - XRD pattern of the samples

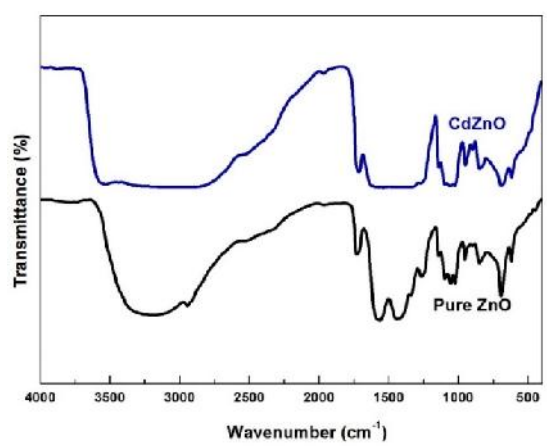

Figure 2 - FT-IR Spectra of the samples

2.2. FT-IR ANALYSIS

FTIR spectra of pure ZnO and Cd doped ZnO thin films are shown in Fig-2**.** The spectra of pure and Cd doped ZnO thinfilms are recorded at room temperature and the peaks are attributed to various vibrationassignments[5]. The absorption band observed at 620, 625cm^{-1} is attributed to the ZnO stretching vibrations. The absorption band observed at 687cm^{-1} can attributed to the Cd-O stretching vibrations. Broad peaks at 3000 and 3100cm^{-1} are attributed to C-H of ethanol stretching (m) vibrations. The small amount of dopant of Cd has shown new vibrations compare to the pure ZnO thinfilms,

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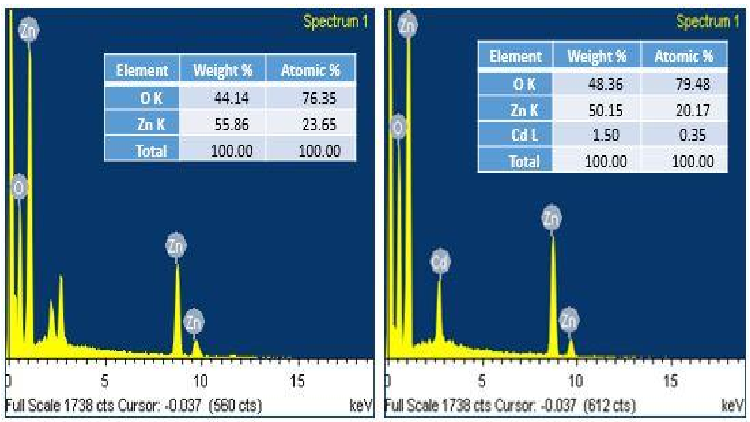
becauseof Cd has a high covalent radius and Vander-walls radius (Å).

2.3 ENERGY- DISPERSIVE X-RAY SPECTROSCOPY (EDX)

This EDX spectrum showing the doping of the metals and attributed to the ionic radii of Cd^{2+}ions and Zn^{2+}ions. Doping of Cdions retains the atomic % is 0.35, which is modified the original pure ZnO spectrum[5, 6]. Thereby the EDX spectrum indicates that the Cd^{2+} ionsare successfully substituted in Zn^{2+} thinfilms in the lattice point of ZnO during the crystallization.



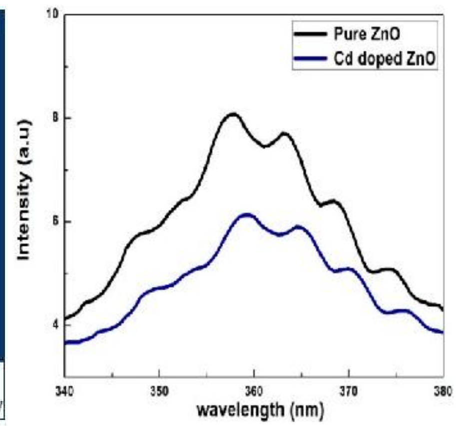


Figure 4 - EDX Spectra of the samples Fig.5. Photoluminescence spectra of the samples

2.5. OPTICAL ANALYSIS

2.5.1. PHOTOLUMINESCENCE SPECTROSCOPY

Fig.5.showing some emission peaks as observed in photoluminescence spectrum. A strong peak centered at 357 nm, near the band edge due to free exciton emission is observed in photoluminescence spectrum of pure ZnO. From photoluminescence analysis, it is observed that pure ZnO exhibit violet colour. Similarly, Cd doped ZnO is also exhibiting the violet colour in the luminescence spectrum at 359 nm with high intensity peak [6, 7]. Hence, the doping of Cd ions make blue shift and improve the luminescence properties of ZnO. Strong UV with valuable visible emission of PL enlarges the sensitivity of the nanostructures. Enhanced bandgap, superior textural properties and accomplished electron−hole separation features are responsible for enhanced fine luminescence activities[8]. Hence, the Cd doped ZnO with high bandgap will be more useful in sensible materials for optical applications.

2.5.2 UV- VIS DIFFUSE REFLECTANCE SPECTROSCOPY – BANDGAP ANALYSIS

The transmission spectrum of pure and Cd doped ZnO thinfilms are shown in fig.6. The transmittance increases more than 90% in the visible region for both materials. It is observed that the cutoff wavelength is shifted to ultra violet region when the dopant is added. The Zn-O-Cd phases in the thin films decreases the transmittance of the film grown by doping[9]. The absorption peaks havethe cutoff wavelengths of 225 and 211 nm for pure and Cd doped ZnO thinfilms respectively. This cutoff are in ultra-violet region and there is no sign for absorbing of visible light by ethanol and Zn^{2+} ions.

The optical bandgaps of pure and doped zinc oxide are estimated from the [Fig.7] plots of $(\alpha h\upsilon)^2$ (a.u) verses photon energy (eV). The band gap estimated for pure zinc oxide is 3.34 eV which is comparable with the literature value [10]. Many researchers tuned the bandgap by doping upto 0.02M % of Cd ions in their methods and showed enhanced bandgap at large level. This increasing in the energy band gap is known as the Moss-Burstein shift [10]. The present work also showing the same effect.

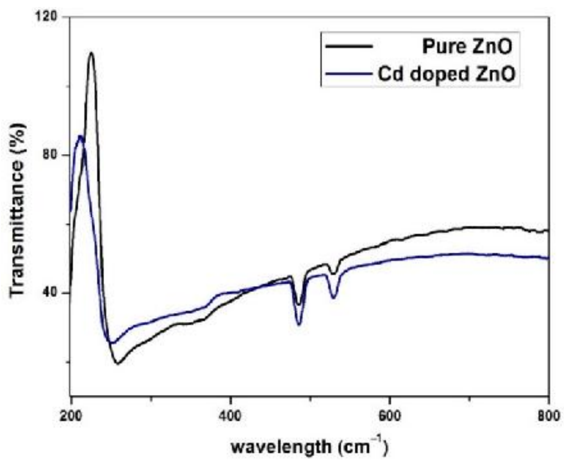


Figure.5- Optical transmission spectra

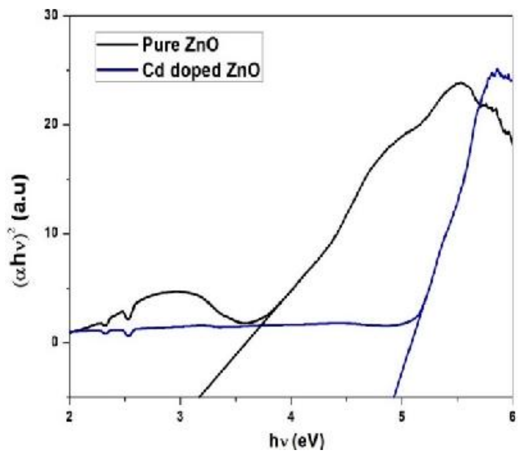


Figure.6. Bandgap evaluation of the samples

4. SUMMARY AND CONCLUSIONS

Preparation of polycrystalline nature of Cd doped ZnO thin films were achieved by solgel with spin coatingmethod and its optical characterizations have been reported. The crystalline size is same for pure and Cd-ZnO thinfilms and is ~31.02nm. The narrow peaks indicate the good quality of ZnO thinfilms. The FTIR absorption confirms the Zn-O bond with good interactions of Cd ions.EDX spectrumexplore the growth process of ZnO films and indicating that the Zn^{2+} ionsis successfully substituted (0.35%) by Cd^{2+}in the lattice of ZnO.The absorption peaks have the cutoff wavelengths of 225 and 211 nm for pure and Cd doped ZnO thinfilms respectively and exhibit the Moss-Burstein shift. The bandgapis 3.18eV for pure ZnO, but Cd doped ZnO thin film has high bandgap value of 4.91eV which will be useful for optoelectronic device fabrications.PL spectra confirm the altered band structure of ZnO thinfilms by Cd dopants and show the blue shift in luminescence. Based on the wide bandgap and high crystalline nature of this high transparent material, it is a potential candidate in optoelectronic and sensors fields.

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