Structural, Linear and Nonlinear Optical Properties of Zn@CdO Nanostructured Thin Films: A Quantitative Comparison With Dft

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Structural, linear and nonlinear optical properties of Zn@CdO nanostructured thin films: A quantitative comparison with DFT

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Abstract

This paper presents experimental and density functional theory (DFT) investigations of Zn doping role in the Zn@CdO ternary system. Zn doped CdO nanostructures with different Zn concentrations were successfully casted on glass substrates by sol-gel spin coating method. Cubic Zn@CdO structured ternary alloyed nanostructures thin films with 0.0%, 1.0%, 2.0% and 3.0% wt. Zn concentrations were obtained. An enhancement in the lateral growth of CdO cauliflower-like nanostructures was observed after Zn addition which leads to a 2D growth of nanostructured films with improved continuity. The effect of Zn doping on the linear optical parameters such as the optical band gap, the absorption index and the refractive index were also investigated. A remarkable blue shift in the band edge was observed as Zn is incorporated into the CdO matrix. In addition, the third order nonlinear optical parameters $\chi^{(3)}$ and n_2 were calculated and found to be about 2.89×10^{-12} - 4.33×10^{-14} esu and 2.89×10^{-12} - 4.33×10^{-14} esu; respectively. A density functional theory (DFT) based Wien2k package was utilized to theoretically investigate the lattice parameters, the electronic structure, the absorption index and the refractive index of the Zn@CdO ternary nanoalloys. The role of Zn doping on the aforesaid properties was theoretically investigated for 3.125%, 6.25%, 12.5% and 25% Zn doping concentrations

and was compared with the experimentally determined parameters. The combined theoretical and experimental investigations presented herein along with the detailed discussion of the obtained findings would provide a deep understanding of the optoelectronic behavior of the Zn doped CdO nanostructured films as well as their suitability for devices applications.

Key words: *Zn-CdO nanostructured films; morphology; structural properties; optical properties; DFT investigation*

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1. Introduction

Metal oxide based 2-D semiconducting nanostructures have demonstrated a high potential for many applications in the field of optoelectronics and gas sensing devices. CdO is one of the prominent II-VI group metal oxide semiconductor with a cubic structure and a direct band gap of about 2.20 eV. It also shows a narrow indirect band gap in the energy region below 1eV [1]. Moreover, CdO has an excellent conductivity and suitable transmission in the uv-vis region. It exhibits n-type conductivity with native oxygen vacancies (V_o) and Cd interstitials (Cd_i) which provide an easy way to alter the electronic structure of CdO by various metallic elements doping. This alteration in the electronic structure of CdO helps in the exploitation of CdO possible uses in various devices applications such as solar cells, detectors, transistors and sensors [2-10]. In addition, CdO exhibits significant third order nonlinear optical properties which are very useful for optical limiting and laser controlled devices applications [11-12]. To enhance the linear, the third order nonlinear optical and the electrical properties of the CdO films, the incorporation of a suitable external impurity into the CdO matrix is essential. Recently, CdO films have been fabricated with various doping elements such as Al, Ag,

Zn, Gd, Mn and Pr [13-17]. On the other hand, the facile and cost effective fabrications of the CdO films via sol-gel spin coating, chemical bath deposition and spray pyrolysis methods have attracted immense interests due to the low production cost in addition to the possible unique physical properties of the grown nanostructures [18-20]. In the current work, a sol-gel spin coating technique was employed to develop the Zn@CdO nanostructured thin films with different Zn doping concentrations. In the light of aforesaid significance of CdO, the investigation of the experimentally developed nanostructured films properties and their electronic behavior is very essential. Moreover, the comparison of the obtained experimental results with those acquired from density functional theory (DFT) studies would provide a better understanding of this material system and help to achieve a better controlling of the band gap variation in the CdO based nanostructures. The good control of the CdO band gap and the related optical and electronic properties would surely strengthen further the candidature of the CdO films for the above mentioned as well as future novel applications. Theoretical investigations of CdO have been reported by various researchers using DFT studies. S. A. Khan et al have investigated electronic structure variation of bulk CdO when transformed into nanosheet [21]. M. Durandurdu has investigated the CdO electronic structure properties via DFT theory and has reported on their suitability for electronic device applications [22]. R. Miloua et. al. have studied $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ alloys using wien2k via DFT approach. They have found in their study a clear phase separation with Zn doping [23]. However, structural, electronic and optical properties investigations of Zn@CdO alloys via Becke-Johnson(mBJ), with local gradient generalized approximation (GGA) found very rare in literature.

The current study reports the investigation of pure and 1, 2 and 3 wt.% Zn doped CdO nanostructured thin films fabricated on glass substrates with a cauliflower morphology via a sol-gel spin coating method. The structural, linear optical and nonlinear optical properties of the films were estimated and discussed in correlation with the Zn doping concentrations. In addition, the reported experimental results are combined with detailed theoretical investigations of the structural and electronic structure of the Zn doped CdO films which were carried out using Wien2k code within framework of DFT. The combined experimental and theoretical investigations in the present work provides comprehensive information on the Zn@CdO nanostructured thin films and would be very useful for the next generation CdO 2D-nanostructures based optoelectronic devices.

2. Experimental and theoretical details

2.1 Experimental details and characterization techniques

Zn@CdO thin films with cauliflower morphology were developed successfully via facile and cost effective sol-gel spin coating method with 1, 2 and 3 wt.% Zn doping concentrations. Highly pure cadmium acetate and zinc sulfate heptahydrate (from Sigma Aldrich Company) were used as cadmium and zinc sources. To synthesize Zn@CdO sols for film casting, 0.75 M solution of cadmium acetate (1.99 gm) in 10 ml 2-methoxyethanol solvent was prepared separately in four beakers and stirred at 40 °C for 1 hr. After that, zinc sulphate heptahydrate was added to the prepared solution at different weight percentages 0, 1, 2 and 3 wt.% corresponding mass is 0 mg, 19.99 mg, 39.98 mg, 59.97 mg and with vigorous stirring for 1 hr at same temperature. Monoethanolamine was also added slowly to enhance the homogeneity and the stability of the solution. Then,

the as prepared solutions were used to fabricate uniform nanostructured thin films on pre-cleaned glass substrates via spin coating at 1500 rpm for 30 s. After the coating, the prepared films were placed on a hot plate at 140 °C for 3 min and the same process was repeated 10 times. The prepared films were then left, after completing all the deposition steps, on a hot plate at 150 °C for 10 min to remove any residual solvents from the samples. Finally, the samples were annealed in air in a furnace at 450 °C for 90 minutes.

The structural information of the grown films was obtained using Shimadzu X-ray diffractometer (X-600, Japan) with Cu-K α radiation in the angular range $\sim 10^\circ$ - 80° . The surface morphological studies of the films were investigated by scanning electron microscope (FEI Quanta 250). The transmittance, absorbance and reflectance spectra of the films in the range 190-2500 nm were recorded using a UV-Vis-Nir spectrophotometer (LAMBDA 1050+ PerkinElmer).

2.2 Theoretical details

The theoretical investigation of the structural, electronic and optical properties was conducted by density functional theory (DFT) implemented in WIEN2k code [24-25]. This approach yields reliable results for structural, electronic and optical properties of various solids as shown in several works. The study was performed with the full potential linearized augmented plane wave (FLAPW) method which has been shown to have a remarkable accuracy to study the electronic structure and the optical properties of the crystalline materials [26]. The gradient generalized approximation (GGA) combined with the modified Becke-Johnson exchange potential (mBJ) was used to investigate the optoelectronic properties of CdO binary and ZnCdO alloys. The parameter $R_{MT} \cdot K_{MAX}$ is chosen as 8. Here R_{MT} denotes the atomic sphere radius and K_{MAX} is the max modulus for

the reciprocal lattice vectors. The spherical harmonics overlapping muffin-tin (MT) spheres are expanded up to $l_{\max} = 10$. The muffin-tin radii R_{MT} are chosen to have the following values 2.6, 2.2 and 1.8 Bohr for Cd, Zn and O respectively. To turn the structural optimization and the optoelectronic properties we construct four configurations supercell $2 \times 2 \times 2$, $2 \times 2 \times 1$, $2 \times 1 \times 1$, and $1 \times 1 \times 1$ containing 64, 32, 16, and 8 atoms respectively in which Zn atom substitutes Cd in $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ ternary alloys.

Furthermore, the lattice parameters and the electronic properties are investigated with a specific number of k points in the irreducible Brillouin zone (IBZ) [27]. Here the values of k is equal to 63 for $x = \frac{1}{32}$, 87 for $x = \frac{1}{16}$, 108 for $x = \frac{1}{8}$, and 125 for $x = \frac{1}{4}$.

Finally, all the structural calculation of $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ ternary alloys, and CdO binary were performed in rock salt structure.

3.0 Results and discussion

3.1 Structural investigations

The effect of Zn doping on the structural properties of CdO nanostructured thin films was investigated by XRD patterns which are presented in Fig.1. All the prepared films with the different compositions show a characteristics diffraction peak at 2θ angle ~ 33.08 along (111) plane which is in a good agreement with the reported data of the cubic CdO structure (JCPDS # 05-0640) [28-29]. An interesting effect of Zn doping on the structural properties of the doped films can also be noticed from Fig.1, which is the degradations of the films crystallinity as Zn element is added into the CdO matrix. Debye Scherer's empirical relation ($D_{\text{avg}} = \frac{0.9\lambda}{\beta \cos \theta}$) was used to obtain the crystallite sizes of the films

which were found to be in range 12-23 nm [30]. The lattice parameter (a), the volume of

the unit cell (V), the dislocation density (δ_{ave}) and the strain (ε_{ave}) were calculated using

the relations: $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$, $\delta_{avg} = \frac{1}{D^2}$, $\varepsilon_{ave} = \frac{\beta \cot \theta}{4}$ [31-34]. The obtained

structural parameters of the films are presented in Table 1.

Table1: structural parameters of Zn@CdO nanostructured films.

Samples (Ag@CdO)	d_{111}	$a=b=c$ (Å)	V (Å) ³	D_{ave} (nm)	δ_{ave} (nm ⁻²) $\times 10^{-2}$	ε_{ave} $\times 10^{-2}$
JCPDS # 05-0640	2.7120	4.6953	103.5100	----	----	----
0.0 wt. %	2.7242	4.7183	105.040	12.68	0.6219	0.4312
1.0 wt. %	2.7137	4.7001	103.829	15.68	0.4067	0.3269
2.0 wt. %	2.6833	4.6474	100.376	17.23	0.3368	0.4777
3.0 wt. %	2.7072	4.6889	103.087	23.42	0.1823	0.7825

3.2 Morphological Studies

The surface morphologies of the films with the different compositions are shown in Fig. 2(a-d). It can be observed clearly from Fig. 3(a) that the pure CdO film contains cauliflower-like nanostructures. As Zn is incorporated into the CdO cauliflower nanostructures, the morphology of the films remarkably changes. It can be concluded that the increase in Zn concentrations leads to the merging of the cauliflower nanostructure and a well coverage of the substrates with a CdO film of a sea waves-like morphology. This suggests that the presence of the Zn enhances the 2D growth of the CdO based film. The growth in the case of the pure CdO samples takes place in both lateral and vertical directions at the same rate. However, it looks that in the case of the doped samples the lateral growth becomes dominant which promotes the 2D growth and hence results in the formation of a film instead of individual nanostructures. These observations can be also linked to the obtained structural parameters namely the variation in the strain values upon Zn doping. The overall increase in the strain values can be explained by the enhancement of the 2D growth in the samples after Zn addition.

3.3 Uv-Vis-Nir spectroscopic investigations

Fig. 3(a-c) represents the absorbance, transmittance and reflectance spectra of the Zn@CdO nanostructured thin films in Uv-vis-NIR region. The optical parameters of the prepared films such as the optical band gap, the absorption index (k) and the refractive index (n) were estimated from these spectra. Fig. 3(a) shows the absorption edge at 520 nm which is related to the band to band transition of the CdO material. However, exceptional behavior of the absorbance of the pure CdO films was recorded, may be due to the cauliflower morphology of the films, and is entirely different in comparison with the Zn doped CdO films. Unlike the doped films, the pure ones show a strong absorbance at 1400 nm. Fig. 3(b) shows a significant improvement in the transmittance of the films in the visible to the NIR region upon incorporation of Zn into the CdO films. Fig. 3(c) shows the reflectance spectra of the pure and Zn doped CdO thin films. The reflectance of the films in region 250-500 nm is very low as observed and increases in region 500-2500 nm.

The optical band gaps of the films were calculated using Tauc relation $(\alpha h\nu) = A(h\nu - E_g)^m$, where α , ν , h , E_g , m and A stand for absorption coefficient, photon frequency, Planck constant, optical band gap, transition type and transition constant [35]. The optical band gap values of the films were extracted from the plots in Fig. 4(a), and were found in to be in the order of 2.07 eV, 2.39 eV, 2.60 eV and 2.47 eV for pure, 1 wt.% Zn, 2 wt.% Zn and 3 wt.% Zn; respectively. The optical band gap of the films increases with the increase in Zn doping concentrations. Similar values of the optical band gap of sol-gel synthesized CdO films have been reported earlier [36-37].

The relation $k = \frac{\alpha\lambda}{4\pi}$, was used to estimate the extinction coefficient where α denotes the absorption coefficients and λ denotes the wavelength [38]. Fig. 4(b) illustrates the absorption index of the pure and Zn doped CdO nanostructured films. The values of k were obtained in the range of 0.01-0.21. Fresnel relation $n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2}$ was used to determine the refractive index of the pure and Zn doped CdO nanostructured films in the spectral range 190-2500 nm [39]. The refractive index values n of the films was found to be in the range of 1.05-2.36. A significant effect of Zn doping on the refractive index of the films can be noticed from Fig. 4(c), as Zn atoms replaces Cd atoms in the CdO matrix, the refractive indexes of films are remarkably enhanced in the region 500-2500 nm. These results indicate that these films can be good contenders for optoelectronic applications.

The real (ϵ_1) and imaginary (ϵ_2) parts of the optical dielectric constant of a material reflect the electronic transition finger prints of that material as a function of the photon energy. The relations, $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$ was used to determine the real and the imaginary parts of the optical dielectric constant [40-42]. Fig. 5(a) shows the real part of the dielectric constant where the values of ϵ_1 were recorded in range of 1.22-5.5. Zn doped films reveal a noticeable enhancement in ϵ_1 in the energy range 0.5-2.0 eV. The imaginary part ϵ_2 is shown in Fig. 5(b). The values of ϵ_2 were found to be in the range of 0.04-0.53. It can be seen that ϵ_2 decreases in the photon energy range 0.75-2.75 eV as Zn doping concentrations increase. The reduction in the value of ϵ_2 with the increase in the Zn doping concentrations indicates the minimization of defects in the Zn@CdO films.

3.4 Nonlinear optical properties of the Zn@CdO nanostructured film

The third order nonlinearity plays a significant role in the advancement of the next generation photonics devices. The third order nonlinearity occurs in materials when an intense ray of light passes through the materials. For example, the nonlinear refractive index n_2 varies with the change in the light intensity. When films are exposed to an intense light, electronic polarization causes a nonlinear optical behavior of the material with the electric field. This nonlinear electronic polarization P_{NL} is expressed by the following relation [43]:

$$P_{NL} = \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \quad (1)$$

Where $\chi^{(2)}$ and $\chi^{(3)}$ stand for the second and third order nonlinear optical susceptibilities, respectively. A general relation of the refractive index as a function of the wavelength can be expressed as: $n(\lambda) = n_o(\lambda) + n_2(E^2)$ where (E^2) stand for the mean square electric field. In this equation the linear refractive index $n_o(\lambda) \gg n_2(\lambda)$ and by considering this approximation in refractive index equation, it becomes $n(\lambda) = n_o(\lambda)$. The linear optical susceptibility $\chi^{(1)}$ of a medium is related to the refractive index via the relation

$$\chi^{(1)} = \frac{(n^2 - 1)}{4\pi} \quad [44].$$

Miller's generalized rule also gives the opportunity to roughly

estimate the third order nonlinear optical susceptibility $\chi^{(3)}$ of a medium through the relation $\chi^{(3)} = A (\chi^{(1)})^4$, where A is a constant ($\sim 1.7 \times 10^{-10}$ esu) and has the same value for all materials. The nonlinear refractive index n_2 of the films were calculated using the

$$n^{(2)} = \frac{12\pi\chi^{(3)}}{n_o} \quad [45].$$

The

calculated $\chi^{(1)}$, $\chi^{(3)}$ and n_2 of the Zn@CdO nanostructured thin films are shown in Fig. 6(a-c). Fig. 6(a) shows a significant enhancement in the first order linear optical susceptibility of the films with increasing Zn doping concentrations. The values of $\chi^{(1)}$

were found to be in the range 0.016-0.36. Moreover, the values of $\chi^{(3)}$ were estimated to be in the range of 2.89×10^{-12} - 4.33×10^{-14} esu for all the films with the different compositions which reveals a remarkable improvement in the $\chi^{(3)}$ values as compare to the earlier reported work on Zn doped CdO system [11]. The nonlinear refractive index n_2 of the films was found in to be in the range 2.89×10^{-12} - 4.33×10^{-14} esu. The third order nonlinear parameters values suggest that the Zn@CdO films have good nonlinear optical properties and can be potential candidates for next generation photonic devices.

3.5 DFT investigations of Zn@CdO alloys

The structural parameters of the Zn@CdO alloys were estimated for the optimized structure with different compositions by the minimization of energy versus the cell volume. The cubic rock salt crystal structures of $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ with 3.125% and 6.25 % Zn doped supercell are shown in Fig.7 (a-b). Fig.8 also illustrates the plot of the total energy versus the cell volume for 3.125% Zn doped CdO alloys. The lattice parameters of the pure CdO were found to be in range 4.788-4.7044 Å. However, the lattice parameter of the sample doped with 12.5% Zn was found to be about 5.231 Å which reveals a significant increase in lattice parameter after doping. Moreover, the calculated lattice parameters were found to be slightly larger than those experimentally obtained. The lattice parameters of the nanostructured alloyed films also decrease with increasing Zn doping concentrations in both sides of the current investigations which indicates a good agreement between the experimental and theoretical findings regarding the behavior of the lattice constants of CdO films with Zn doping. R. Miloua et. al. have investigated the structural properties of Zn@CdO alloyed films with LDA approximation and have found similar behavior of the lattice parameters with the increase in Zn concentrations.

However, they have reported lesser lattice parameters value than the present work [23].

Fig. 9 shows the comparative behavior of the lattice parameters experimental and theoretical values as a function of Zn doping concentrations.

The electronic structure variation with the Zn doping in the cubic CdO alloys was investigated through the total density of states (TDOS) within the energy interval from E_F , -8.0 and 8.0 eV and is presented in Fig.10 (a-b). As can be seen from Fig. 10(a), the top of the valence band from -2.0 to 1.0 eV is mainly arises due to the contribution of the O-p state and reveals minor contribution of the Cd-d state. Furthermore, the conduction band from 2.0-6.0 eV arises due to the overlapping of the O-p, the O-s and the Cd-p states and the core bands are mainly consisting of the O-p and the Cd-d state. The peaks of core bands are centered at 6-7 eV [46]. Fig.10 (b) shows the 3.125% Zn doped CdO system TDOS. With the incorporation of Zn into the CdO matrix, the role of Zn-4s can be observed clearly. A significant shifting in the bottom of conduction band occurs and hence an increase in the band gap of the CdO after Zn doping is observed. A comparable effect on TDOS can be seen clearly after Zn incorporation from TDOS plots of both systems, a new bunch of TDOS arises at -4.72 eV, which is mainly due to the Zn-d state.

The band structures of the Zn@CdO alloys with 3.125%, 6.25%, 12.5% and 25% Zn doping concentrations are illustrated in Fig.11 (a-e). The calculated values of the band gap for the 3.125%, 6.25%, 12.5% and 25% Zn doped samples were obtained as 1.47 eV, 1.69, 1.69, 1.03 and 1.83 eV; respectively. Interesting changes can be seen from Fig.11 (a-e), where the pure CdO sample shows an indirect nature of the band gap while the Zn@CdO samples reveal a direct nature of the band gap. Additionally, these theoretical findings agree well with the experimentally obtained results regarding the band gap

nature from Fig. 4(a). Tauc plot for the pure CdO films shows a band gap of 2.07 eV along with a 0.85 eV indirect transition. The calculated band gap of the films increases by about 25% as a function of Zn concentrations. The increase in the band gap is due to the upward shifting of the bottom of the conduction band along the Γ point as observed from Fig. 11(b-c) for the CdO samples doped with 3.125% and 6.25% Zn. However, the sample doped with 12.5% Zn concentration demonstrates a different band gap behavior. At this concentration, 12.5% Zn, the band gap value significantly increases and then decreases with further increase in Zn concentration. Such variation in the band gap might be due to the phase transition of the CdO structure from cubic to hexagonal. Further investigations especially on the experimental side, at high doping concentrations, is currently ongoing in order to determine the reason of such observed behavior of the band gap and will be reported in the near future.

The optical properties of the Zn@CdO ternary alloys with various Zn concentrations were obtained using the complex function of the optical dielectric constant $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the optical dielectric constant $\varepsilon_2(\omega)$ is described via the direct transition [47-50]:

$$\varepsilon_2(\omega) = \frac{4\pi e^2}{m^2 \omega^2} \sum_{ij} \int \langle k_i | p | k_j \rangle^2 f(k_i) (1 - f(k_j)) \delta(E_{k_i} - E_{k_j} - \hbar\omega) d^3k \dots\dots\dots(2)$$

Here p is symbolized for the dipole matrix. The conduction and valence band wave functions of i^{th} and j^{th} eigenvalues are symbolized $|k_i\rangle$, $|k_j\rangle$ for the crystal momentum k .

The real part of the optical dielectric constant $\varepsilon_1(\omega)$ was deduced from Kramers-Kronig relations [51]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega \dots\dots\dots(3)$$

The real and imaginary parts of the optical dielectric constant are the sources of the optical parameters of materials. Here, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are used to calculate the extinction coefficient (k), the refractive index (n) and the absorption coefficient (α). Fig.12 (a-b) presents the calculated real and imaginary parts of the optical dielectric constant in the range of 1-10 eV. Fig. 12(a) shows peaks at 2-3 eV range which are related to the interband transition of the Zn@CdO ternary alloys. An interesting change can be observed with the Zn incorporation in the CdO system that is a clear blue shift with increasing Zn doping concentrations. However, the 12.5% Zn doped CdO sample shows anomalous behavior which supports the previous observation regarding the occurrence of some phase changes in structure of CdO at this Zn concentration. The static dielectric constant $\epsilon_1(\omega=0)$ values of the samples were found to be in the range 3.2-3.4 and slightly decreases with the increase in Zn doping concentrations. Moreover, the 12.5% Zn doped sample shows an enhancement in the static dielectric constant in comparison to other samples. Fig.12 (b) shows that the band edge of the films is around 2.2-2.5 eV which is very close to the experimentally obtained values of band gap. The DFT investigation of the films reveals a blue shift in band edge as Zn doping concentrations increase in CdO system indicating a shift of the bottom of the conduction band to the higher energy levels. A similar behavior of the Zn@CdO alloyed systems was confirmed through the experimental investigation of the electronic structure. Fig. 13(a) depicts the calculated absorption index (k) of the Zn@CdO alloys with the different Zn doping concentrations. The plots of the calculated absorption index show that the band edge is in the similar range as estimated from the Uv-visible-nir spectroscopy. In the higher energy region from 3-10 eV, the absorption index increases. The calculated values of k were found in to

be in the range of 0.01-1.0. A significant blue shift was also observed in band edge as found experimentally. The calculated refractive index n of the Zn@CdO alloys is depicted in Fig.13 (b) in the range of 0-10 eV. The refractive index of the alloys increases with the increase in the photon energy up to 3 eV and then decreases at higher energy values. The values of n at $\omega=0$ were found to be in the range of 1.75-2.2. In addition, the refractive index of the alloys slightly decreases in the energy range 0-2 eV with the incorporation of Zn in the CdO system.

4.0 Conclusion

Zn@CdO alloyed nanostructured thin films were developed by sol-gel spin coating method on glass substrates. A quantitative comparison was made between experimental and DFT investigation of the role of Zn incorporation into the CdO system. From the XRD patterns, the crystallites sizes of films were estimated to be about 12-23 nm. The lattice parameters of the Zn@CdO alloys change significantly with the increase in Zn doping concentrations. 1 wt.% and 2 wt.% Zn doped samples show a reduction in the lattice parameters while sample doped with 3 wt.% Zn reveals an increase in the lattice parameter. However, the overall lattice parameters values decrease with the incorporation of Zn into the CdO system. The optical band gap values were obtained from the Tauc plots in the range ~ 2.07-2.60 eV, and were found to increase with increasing Zn doping concentration. The Zn@CdO cubic structures were optimized with 3.125%, 6.25%, 12.5% and 25% Zn concentration using mBJ-GGA incorporated in the Wien2k package based on DFT. The calculated structural and optical parameters such as the lattice parameters, the band gap, the absorption index, the refractive index, the band edge and their variation with Zn incorporation into the CdO system reveals good agreement with

the experimental findings. However, 12.5% Zn doped samples show anomalous behavior which might be due to the structural changes in the CdO system. All the obtained results for the samples with this doping concentration indicate a significant variation in the properties of these samples and support the occurrence of a phase change in the Zn@CdO systems. To explore such effect in details, further experimental investigations of CdO nanostructured films with high Zn doping concentrations are required.

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Figures

Figure 1

XRD patterns of Zn-CdO nanostructures thin films (a) Pure (b) 1 wt.% Zn (c) 2 wt.% Zn (d) 3 wt.% Zn.

Figure 2

SEM images of Zn-CdO nanostructure thin films (a) Pure (b) 1 wt.% Zn (c) 2 wt.% Zn (d) 3 wt.% Zn.

Figure 3

Uv-vis-nir spectra of Zn-CdO nanostructure thin films (a) Absorbance (b) Transmittance (c) Reflectance

Figure 4

Tauc's plots and optical parameters of Zn-CdO nanostructure thin films (a) $(\alpha h\nu)^2$ vs. $h\nu$ (b) Absorption index (k) (c) Refractive index (n).

Figure 5

Optical dielectric constant of Zn-CdO nanostructure thin films (a) Real part (ϵ_1) (b) Imaginary part (ϵ_2).

Figure 6

Third order nonlinear optical parameters of Zn-CdO nanostructures (a) $\chi^{(1)}$ (b) $\chi^{(3)}$ (c) n_2 .

Figure 7

Structure of Cd_{1-x}Zn_xO supercell; green, red and blue balls represent cadmium, oxygen and zinc atoms respectively (a) 3 % Zn (b) 6.25% Zn.

Figure 8

Variation of the total energy versus the volume for the $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ alloys for $x=3.125\%$.

Figure 9

Variation of the experimental and calculated lattice parameters 'a' of Z@CdO alloys with different Zn concentrations.

Figure 10

Total density of states of Cd_{1-x}Zn_xO with different Zn doping concentrations (a) Pure CdO (b) 3% Zn (Cd₃₂Zn₀₃₂).

Figure 11

Band structure of Cd_{1-x}Zn_xO with different Zn doping concentrations (a) Pure CdO (b) 3% Zn (c) 6% Zn (d) 12.5% Zn (e) 25% Zn.

Figure 12

Calculated real and imaginary part of optical dielectric constant of Cd_{1-x}Zn_xO with different Zn doping concentrations (a) Real part (b) Imaginary part.

Figure 13

Calculated real and imaginary part of optical dielectric constant of Cd_{1-x}Zn_xO with different Zn doping concentrations (a) Absorption index (k) (b) Refractive index (n).