

Influence of doping on optical properties of ZnO nanofilms

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Spectrophotometric analysis for optical properties of spray deposited undoped ZnO nanofilms and doped with Al, Cd and Co films have been made on glass substrate. The investigations revealed that doping Al (5 mol%) in ZnO (0.5 M) causes shifting of absorption edges in the transmittance to the lower wavelength. While doping Co (5 mol%) results the absorption edges in the transmittance spectra to the higher wavelength and lies around 447 nm. However, doping Cd (5 mol %) shows shift in absorption edge in very narrow range. Moreover, a change in refractive index of the film doped with Al, Cd, and Co is in accordance with the changes in band gap value in visible region. Furthermore, the variation in the ratio of free charge carrier to effective mass (N/m^*) and plasma frequency (ω_p) are found to increase with Al and Cd doping and decrease with Co doping in ZnO lattice. The oscillation energy E_o , dispersion energy E_d , and other optical constants such as average oscillation wavelength λ_o , oscillator strength S_o , and lattice energy E_l have been determined using Wemple and Di-Domenico relation. With these results, intrinsic and extrinsic ZnO nanofilm have many applications in solar cell windows, LED with high quantum efficiency, thin film transistor and other optoelectronic devices. Decrease in bandwidth with Co and increase in bandwidth with Al are suitable for active and confining layer of heterostructure. Increase in lattice energy with Al, Cd, and Co doping increases the chemical stability and bond strength.

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1. Introduction

ZnO is a direct and wide band gap (3.4 eV) semiconductor. It can be deposited at lower growth temperatures than GaN which leads to the possibility of transparent junctions on cheap substrates such as glass, with the potential to realize low-cost UV lasers or light-emitting diodes for high-density data storage systems, solid-state lighting, secure communications, and biodetection. ZnO has several advantages over GaN for applications including the commercial availability of bulk single crystals and a larger exciton binding energy (~60 meV compared with ~25 meV for GaN) [1, 2]. The latter property should translate to even brighter light emission than obtained with GaN photonics. These can be used in fabricating a variety of devices including phosphor for color displays [3] and electrode material in LED and photovoltaic cells [4], gas sensors [5] and varistors [6].

Moreover, synthesis and characterization of ZnO nanofilm with several dopant ions like Mn, Al, Mg, Li, Cd, Co, etc. have already been researched. However, most of them presented structure, magnetic, and electrical properties in detail and very few have focused on optical properties, especially for Cd and Co. Furthermore, the presented optical results of doping Al inside ZnO matrix are found to have controversy in tailoring band gap and changes in optical constants. Some of them asserted that Al causes increasing band gap. However, the expressed results [7, 8] are found to decrease in optical gap and other

relevant optical constants of AZO nanofilms. But we disagree with latter one. So, the present study has been focused on elaborating optical properties of Al, Cd, and Co doped ZnO nanofilms which is quite essential for fluorescence material that ZnO have this properties for several photonic device applications

2. Experimental

A 0.5M aqueous solution of zinc acetate in ethanol was prepared as the precursor of the nanofilm. For doping, 5 mol% salt solutions of aluminum, cadmium and cobalt acetate have been mixed separately in precursor for aluminum ion doping. Few drops of acetic acid was added in the final solutions to get complete dissociation of zinc acetate and then stirred with magnetic stirrer at 60 °C for 10 minutes to obtain clear homogeneous solution. The homogeneous solution was kept in ultrasonicator for 10 minutes just before the deposition. Spray pyrolysis technique was applied on heated (380 °C) glass substrate to achieve nanofilms. The flow rate of the solution throughout the experiment was maintained at 5 ml per minute, keeping the spray nozzle 20 cm away from the substrate. The prepared films were dried at 500 °C for 1 minute just after the deposition so as to evaporate the solvent and to increase the smoothness of the film surface and then characterized with UV-VIS-NIR spectrophotometer.

3. Results and discussion

3.1 Film thickness and Band gap energy

Thin film of Al, Cd and Co doped as well as undoped ZnO samples were characterized by UV-VIS-NIR spectrophotometer. This instrument is capable to produce transmittance spectra in 300 to 1100 nm of wavelength range in 1 nm interval as shown in Fig. 1. The whole spectra have been employed to estimate the absorption coefficient ‘ α ’ using Lambert law as expressed in Eq.(1):

$$\alpha = -\frac{\ln T}{d} \quad (1)$$

Where, T is transmittance and d, the thickness of the film. The thickness values were determined by minimization among experimental transmittance value obtained from spectrophotometer (T_{exp}) and calculated transmittance value (T_{cal}) from Swanepoel equation [9]. This process is repeated for arbitrary values of thickness until we obtained the point of minima (Fig. 2) which gives the exact film thickness. The process is elaborated elsewhere [10].

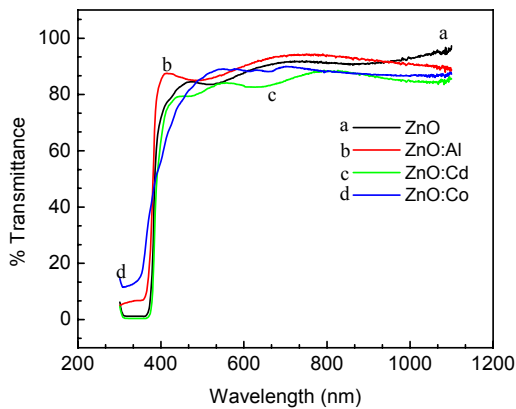


Fig. 1. Distribution of % transmittance vs. wavelength for varying doping element.

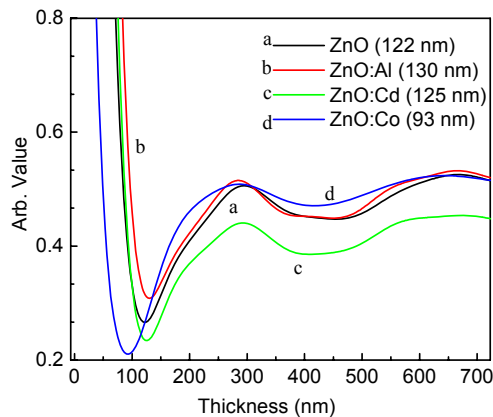


Fig. 2. $\Delta T (T_{exp}-T_{cal})$ vs. thickness (nm) for varying

doping element.

Tauc model [11] and Davis and Mott model [12] in the high absorption region described by Eq.(2), has been used to determine the optical band gap.

$$\alpha h\nu = D (h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

Where $h\nu$ is the photon energy, E_g is the optical band gap and D is a constant. The value of E_g was obtained by extrapolating the linear portion to the photon energy axis on the plot of $(\alpha h\nu)^2$ vs. $h\nu$ as explained elsewhere [1]. Doping Al inside the ZnO caused gap enlargement showing blue shift, this occurs due to the lowest state of the conduction band that are blocked; which is believed to be Burstein-Moss effect [13]. While doping Cd and Co causes narrowing the optical gap showing red shift. A narrowing caused by the correlated motion of charged carriers and the scattering against ionized impurities, counteracts the widening of the gap.

3.2. Complex refractive index and interrelated constants

Complex refractive index is the most desirable optical constants of photonic materials for the fabrication of quantum photonic devices. So, the complex refractive index as a function of wavelength for different doping atoms viz. Al, Cd, Co and undoped ZnO nanofilm has been estimated by Kramer’s Kronig relation [14]. The estimated value of complex refractive indices – real value (n) and imaginary value (k) are shown in Fig. 3 and Fig. 4 respectively.

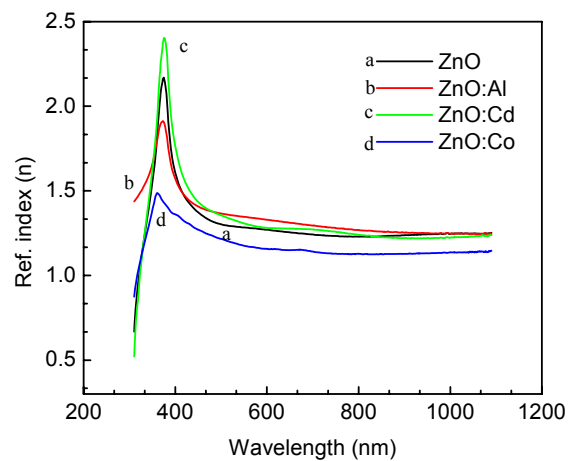


Fig. 3. Distribution of Ref. index (n) vs. wavelength (λ) for varying doping element.

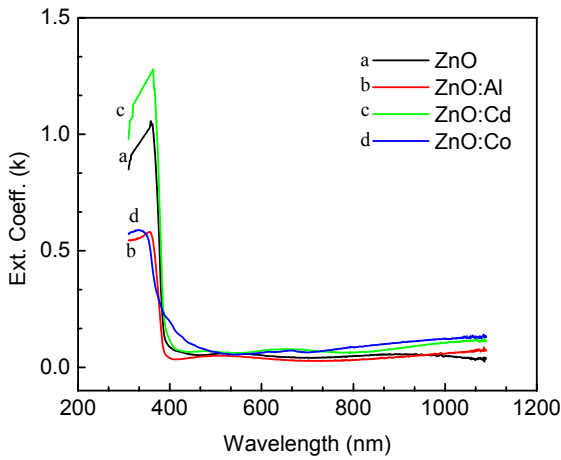


Fig. 4. Distribution of Extinction coefficient (k) vs. wavelength (λ) for varying doping element.

The real part describes the phase velocity whereas imaginary part determines the absorption in the material. It is observed that the changes in refractive index remain approximately constant at visible and NIR wavelength. This behavior can be attributed with the indication of optical stability. It is clear that doping Al and Cd in ZnO caused increase in refractive index within visible region while Co causes decrease in value. In contrary, the value of 'n' in UV region increases for all Al, Cd and Co doping atoms (Fig. 3). The low value of 'n' and high value of 'k' in UV region can be attributed to high absorption in this region, which is desirable when ZnO is used to fabricate UV related devices such as UV LED, UV sensors and UV protecting layers, etc.

Table 1. Band gap E_g , Lattice energy E_l , Oscillation energy E_o , Dispersion energy E_d , for undoped and Al, Cd, and Co doped ZnO thin films.

Sample	Doping element (5 Mol %)	E_g (meV)	E_l (eV)	E_o (eV)	E_d (eV)
ZnO	Undoped	3.225	60	6.240	2.992
ZnO:Al	Aluminum	3.270	115	5.416	2.857
ZnO:Cd	Cadmium	3.237	156	2.500	0.829
ZnO:Co	Cobalt	2.771	271	4.153	0.965

Moreover, using single term Sellmeier oscillator model [17], the estimated value of refractive index as a function of wavelength and can also be analyzed to find the static refractive index n_0 and average oscillator wavelength λ_0 and oscillator strength S_0 of the nanofilm.

$$\frac{n_0^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda} \right)^2 \quad (6)$$

In order to introduce optical dispersion property of deposited thin film, Wemple and Di-Domenico model [15] have been analyzed. The dispersion curve is obtained according to the relation as expressed in Eq.(3):

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - (hv)^2} \quad (3)$$

Where, E_0 and E_d are single oscillator constants. Plotting $(n^2 - 1)^{-1}$ against $(hv)^2$ and fitting a straight line allows to obtain E_0 and E_d from the slope and intercept values which are summarized in Table 1. It is found that the oscillator energies $E_0 \sim 2E_g$ for undoped ZnO film and $E_0 \sim 1.6E_g$ for Al and Cd doped and $E_0 \sim 0.8E_g$ for Co doped ZnO film. The decrease in value of E_d (more than two times) could be attributed to the decrease in average coordination number of atoms.

In the case of wavelengths much shorter than the phonon resonance, the lattice contribution is given by [16].

$$n^2 - 1 = \frac{E_0 E_d}{E_0^2 - E^2} - \frac{E_l^2}{E^2} \quad (4)$$

Where, E_l is the lattice energy. At longer wavelength where $E_0^2 \gg E^2$, Eq.(4) can be written as:

$$n^2 - 1 = \frac{E_d}{E_0} - \frac{E_l^2}{E^2} \quad (5)$$

A plot of $(n^2 - 1)$ vs. $1/E^2$ is nearly a straight line. The slope gives the value of E_l which are listed in Table 1 and depicted in Fig. 5. It is observed that doping Al, Cd and Co ion inside ZnO by sol-gel route results increase in lattice energy.

$$(n^2 - 1) = (n_0^2 - 1)^{-1} - (n_0^2 - 1)^{-1} \times \left(\frac{\lambda_0}{hc} \right)^2 \times (hv)^2 \quad (7)$$

According to relation derived in Eq.(7), the value of static refractive index n_0 and average oscillator wavelength λ_0 was determined from the slope and intercept value of plot of $(n^2 - 1)^{-1}$ against $(hv)^2$ and are given in Table 2. It is clear that change in n_0 (Fig. 5) is in correlation with the band gap. However, λ_0 increases with Al, Cd and Co ion doping in ZnO lattice.

Furthermore, Eq.(6) can also take the form:

$$(n^2 - 1) = \frac{S_0 \lambda_0^2}{\left(1 - \frac{\lambda_0^2}{\lambda^2}\right)}$$

Where, the average oscillator strength S_0 is defined as Eq.(8)

$$S_0 = \frac{(n_0^2 - 1)}{\lambda_0^2} \quad (8)$$

The determined values of S_0 are listed in Table 2 and shown in Fig. 5. It observed that the value of S_0 decreased with doping Al, Cd and Co inside the host matrix of ZnO.

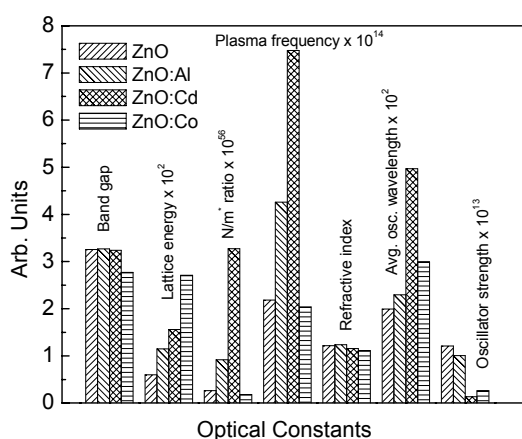


Fig. 5. Distribution of optical constants for varying doping element.

Furthermore, the values of n and k have been used to define the complex dielectric constant, labeled by Eq. (9) and Eq.(10).

Real part:

$$\epsilon_1 = n^2 - k^2 = \epsilon_\infty - \frac{e^2}{4\pi^2 c^2 \epsilon_0} \frac{N}{m^*} \lambda^2 \quad (9)$$

Imaginary part:

$$\epsilon_2 = 2nk = \frac{\epsilon_\infty \omega_p}{8\pi^3 c^2 \tau} \lambda^3 \quad (10)$$

Here, ϵ_0 is the free space dielectric constant, c is the velocity of light in free space, e is the electronic charge, τ , the optical relaxation time of film, ϵ_∞ is the high frequency dielectric constant, N/m^* , the ratio of free carrier concentration to the free carrier effective mass. ω_p is the plasma frequency for the valence electrons and is given by Eq.(11):

$$\omega_p = \sqrt{\frac{Ne^2}{m^* \epsilon_0 \epsilon_\infty}} \quad (11)$$

In this study, the real part of dielectric constant has been employed to estimate N/m^* ratio and imaginary part for ω_p . Plotting of ϵ_1 vs. λ^2 and fitting straight line at longer wavelength allows to obtain N/m^* from slope value and this was used to approximate ω_p . These obtained values for Al, Cd, Co doped and undoped nanofilms are summarized in Table 2 and shown in Fig. 5.

Table 2. N/m^* ratio, Plasma frequency ω_p , Refractive index n_0 , Avg. Osc. wavelength λ_0 , Oscillator strength S_0 , for undoped and Al, Cd, and Co doped ZnO thin films.

Sample	$N/m^* \times 10^{56}$ (m^3/kg)	$\omega_p \times 10^{14}$ (sec^{-1})	n_0	λ_0 (nm)	$S_0 \times 10^{13}$ (m^{-2})
ZnO	0.260	2.183	1.216	199.0	1.209
ZnO:Al	0.918	4.259	1.235	299.3	1.002
ZnO:Cd	3.273	7.477	1.154	496.8	0.134
ZnO:Co	0.179	2.038	1.110	299.1	0.259

Results revealed that the variation in both N/m^* and ω_p increases with mixing the salt solution containing Al and Cd ions in ZnO matrix while with mixing Cd ion by sol-gel route, the value decreased to lower value than undoped ZnO film. The discrepancy in N/m^* may be attributed to the change in carrier concentration that is consistent (assuming that m^* is constant in the first approximation). The increase in carrier concentration could be attributed to the substitution of Zn^{2+} by Al^{3+} ion.

4. Conclusions

The inclusion of Al, Cd, and Co doping in intrinsic ZnO material structure showed a significant variation in

estimated optical parameters. Investigations of ZnO:Al film confirmed that there is increase in optical constants such as E_g , E_i , N/m^* , ω_p , n_0 , and λ_0 , but decrease in S_0 . For ZnO:Cd film, the value of E_g and n_0 showed opposite in nature than ZnO:Al film and other constants behavior remained same. Similarly, for ZnO:Co film, the value of E_g , N/m^* , ω_p , n_0 showed conflicting behavior than ZnO:Al and rest of the parameters were similar in nature. This discrepancy in optical constants with Al, Cd and Co doping can be attributed to the variation in structural homogeneity and crystallinity. Therefore, further investigations are required and experiments in these directions are in progress. A large decrease in bandwidth of ZnO from 3.5 eV to 2.77 eV after Co doping made it

possible to excite the material in visible region and apply in photo-electrochemical devices. Moreover, decrease in bandwidth with Co and increase in bandwidth with Al are suitable for active and confining layer of heterostructure.

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