Cation substitution induced blue-shift of optical band gap in nanocrystalline $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films deposited by sol–gel dip coating technique

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Abstract. Transparent nanocrystalline $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ ($0 \leq x \leq 0.20$) thin films were deposited on glass substrates by sol–gel dip coating method. The X-ray diffraction (XRD) pattern revealed the polycrystalline nature of the films with hexagonal wurtzite structure and confirmed the non-existence of the secondary phase corresponding to CaO indicating the monophasic nature of the deposited films. The crystallinity of the films deteriorated with higher dopant concentration due to the segregation or separation of dopant ions in grain boundaries. The lattice parameters and the unit cell volume increased to a higher Ca-dopant concentration. This was due to the successful incorporation of Ca^{2+} ions with larger ionic radius in the host zinc oxide (ZnO) lattice. The optical transmittance spectra of the samples showed transmittances above 60% in the visible spectral range and the absorption edge in the near ultra-violet region got blue-shifted with cation substitution. The estimated optical energy gaps confirmed the band gap widening with increase in Ca-dopant concentration. The calculated values increased from 3.30 eV for undoped ZnO to 3.73 eV for $\text{Zn}_{0.8}\text{Ca}_{0.2}\text{O}$ thin films giving 13.03% enhancement in the energy gap value due to the electronic perturbation caused by cation substitution as well as deterioration in crystallinity.

Keywords. Cation substitution; $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$; dip coating; blue-shift.

1. Introduction

Zinc oxide (ZnO), the present dominant candidate in the field of transparent conducting oxides, is an n-type semiconductor belonging to the II–VI semiconductor group. It has a wide direct optical band gap of energy 3.37 eV and a large excitation binding energy of 60 meV at room temperature making it suitable for blue and ultra-violet optical devices [1]. The intrinsic n-type nature of ZnO is mainly attributed to its native doping due to oxygen vacancies or zinc interstitials. Furthermore, the n-type conductivity of ZnO can be enhanced by doping with donor impurities like group III elements (B, Al, Ga, In). However, like many of the semiconductors, ZnO is not amenable to both types of doping and it is harder to develop p-type ZnO. This is mainly due to problems such as its self-compensating effect, deep acceptor levels and low solubility of acceptor dopants [2]. On the other hand, the optical band gap can be altered by making alloys or metalloids of ZnO.

For a semiconductor to be useful, particularly in the case of optoelectronic devices, band gap engineering is a crucial step. By alloying the starting semiconductor with another material of different band gap, the band gap energy of the resultant alloy can be fine tuned. Thus, ZnO can be alloyed with a variety of elements to engineer the band gap. For example,

by alloying with a wider band gap material like MgO ($E_g = 7.8$ eV), we will get an alloy of $\text{Zn}_{(1-x)}\text{Mg}_x\text{O}$ with larger optical gap [3]. Similarly, in order to decrease the band gap, cadmium can be mixed to ZnO [4]. In addition, we can extend this method with other earth–alkaline elements like Be and Ca and these will find applications in optoelectronic devices. However, there have been few reports on the properties of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films.

Numerous deposition strategies for the preparation of high-quality ZnO thin films such as atomic layer deposition [5], chemical vapour deposition [6], pulsed laser deposition [7], spray pyrolysis [8], sputtering [9], sol–gel technique [10,11] etc., have been reported in the literature. The sol–gel is a simple and less-expensive wet chemical technique used to obtain coatings at room temperature. The method is entirely based on hydrolysis and condensation reaction of organo-metallic compounds in alcoholic solution. The main benefits are excellent control of stoichiometry of precursor solution, ease of compositional modification, customizable microstructure, ease of introducing various functional groups, relatively low annealing temperature, feasibility of large area deposition, less-expensive equipment, etc. The three associated methods of producing the films are spin coating, dip coating and meniscus coating. Therefore, in the present work, we investigate the tailoring of optical band gap of ZnO thin

films by making an alloy with CaO having higher optical energy gap ($E_g = 7.0$ eV). Here, we adopted the sol-gel dip coating technique for the deposition of films on glass substrates.

2. Experimental

In the present work, $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films were deposited on glass substrates by sol-gel dip coating method. Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and calcium acetate monohydrate [$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$] were used as the precursor and dopant, respectively, whereas 2-methoxy ethanol and monoethanolamine (MEA) were taken as the solvent and stabilizer, respectively. Throughout the experiment, the molarity of the precursor solution was kept fixed at 0.5 M. The precursor solution for undoped ZnO films was obtained by dissolving zinc acetate dihydrate in a mixture of 2-methoxyethanol and MEA. The molar ratio of MEA to zinc acetate was maintained at 1.0. To obtain calcium doping of 5, 10, 15 and 20%, appropriate quantities of zinc acetate dihydrate and calcium acetate monohydrate were dissolved in the mixture of 2-methoxyethanol and MEA. These solutions were stirred at 70°C for 1 h in a hot magnetic stirrer to yield a clear homogeneous solution and were then aged for 24 h at room temperature.

The aged solutions were then deposited on pre-cleaned glass substrates by sol-gel dip coating technique using Holmarc Dip Coating unit (HO-TH-01). Film deposition was carried out, in air, at room temperature with a controlled dipping and withdrawal speed of 50 mm min⁻¹. Every time the substrate was withdrawn from the solution, the film was allowed to dry and subjected to a pre-heat treatment at 200°C in a hydrothermal furnace. This procedure was repeated 5 times. As a final step, the film was post-heated at 450°C for 2 h in an electric furnace. Thus, we obtained five samples of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films with $x = 0.0, 0.05, 0.10, 0.15$ and 0.20 and were named as ZCO 0, ZCO 5, ZCO 10, ZCO 15 and ZCO 20, respectively.

The deposited films were then subjected to X-ray diffraction (XRD) studies for structural characterization using X-ray diffractometer (Bruker AXS D8 Advance) with CuK_α radiation ($\lambda = 1.5046$ Å) at 40 kV and 35 mA. The composition analysis of the samples was done by energy dispersive X-ray spectroscopy (EDX) on JEOL Model JSM-6390 scanning electron microscope attached with JEOL Model JED-2300, operated at 20 keV. The morphological studies were also performed on the same scanning electron microscope (SEM). The optical studies were carried out using Jasco V-650 UV-Vis Spectrophotometer in the wavelength range 300–900 nm. All these measurements were made at room temperature. Thickness of the deposited samples was determined by the gravimetric method using Shimadzu AY 220 Model Balance and the values are presented in table 2.

3. Results and discussion

3.1 Structural studies

The structural properties of the $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films were studied by analysing the XRD pattern shown in figure 1. All the patterns fitted well into the hexagonal wurtzite structure indicating only a single ZnO phase (JCPDS 36-1451) and it shows the polycrystalline nature of the films. As there is no sign of an additional phase of CaO, we can confirm that Ca^{2+} ions are successfully substituted in the Zn^{2+} lattice site. All the films are showing a preferred orientation along the (002) direction. However, the peaks shifted a little towards the lower 2θ values and broadened with increase in Ca-dopant concentration, which is shown in figure 2. The peak shift was related to the change in the chemical composition of ZnO with Ca^{2+} substitution, whereas the peak broadening could be because of the strain suffered by the lattice by impurity substitution. In addition, with increase in Ca concentration new peaks appeared in the diffraction pattern, which could be owing to the favouring of growth of films in newer directions as well. The mean crystallite size of the deposited films were calculated using the Scherrer formula [12] as shown in equation (1),

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where 0.9 is the value of the shape factor, λ ($=1.5406$ Å) the wavelength of the X-rays used, β the full-width at half maximum intensity in radians and θ the Bragg's angle. The lattice parameters for the hexagonal structure ($a = b$) can be determined from the following relation (equation (2)) [13]

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left[\frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2} \quad (2)$$

The unit cell volume can be determined using the expression given in equation (3) [13]

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (3)$$

All these parameters for the prepared samples are listed in table 1 as a function of Ca-dopant concentration. All the films were nanocrystalline and the crystallite size deteriorated with an increase in dopant concentration. This could be due to the defects or disorders introduced by the dopant in the ZnO structure by segregating into the non-crystalline region in the grain boundary [14]. In addition, the formation of stress induced by the difference in ionic radius between Zn^{2+} (60 pm) and Ca^{2+} (100 pm) can be considered as the reason for the aggravation in ZnO crystallinity [15].

The lattice parameters and unit cell volume monotonously increased with increase in Ca-dopant concentration. The larger ionic radius of Ca^{2+} ion compared to Zn^{2+} ion and the stress induced in the film due to increased doping might be the reasons for the observed variations. Thus, with increase in

Figure 1. XRD pattern of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films with $x =$ (b) 0.0, (c) 0.05, (d) 0.10, (e) 0.15 and (f) 0.2, respectively, along with (a) reference ZnO (JCPDS 36-1451).

Figure 2. Variation (002) peak position with Ca^{2+} concentration.

dopant concentration the lattice parameters are getting modified, which is an evidence for the successful incorporation of Ca^{2+} ion in the host ZnO structure. The variation in lattice constant with respect to that of the bulk ZnO implies that the films are under stress. In general, stress in thin films arises either from crystallite deficiency, defects, impurities, etc., or from growth parameters. In addition, there will be extrinsic stress, which can be generated during pressing, sintering, annealing, etc. The thermal stress in thin films deposited on substrates results from the difference in the coefficients of thermal expansion of film and substrate. The stress in thin films can be calculated based on the biaxial strain model [16]. The strain in c -axis, i.e., perpendicular to the film surface is given in equation (4),

$$\varepsilon = \frac{c_{\text{film}} - c_{\text{bulk}}}{c_{\text{bulk}}}, \quad (4)$$

where c_{film} and c_{bulk} ($=5.2069 \text{ \AA}$) are the lattice constants (c) of the prepared thin films and bulk (powder) ZnO, respectively. The stress parallel to the film surface was calculated using the formula as given in equation (5) [16]

$$\sigma_{\text{film}} = \left(2C_{13} - \frac{C_{33}(C_{11} + C_{12})}{C_{13}} \right) \varepsilon, \quad (5)$$

where C_{ij} are the elastic stiffness constants whose values are given by $C_{11} = 209.7 \text{ GPa}$, $C_{12} = 121.1 \text{ GPa}$, $C_{13} = 105.1 \text{ GPa}$ and $C_{33} = 210.9 \text{ GPa}$. This gives the following simplified relation for stress in equation (6) as

$$\sigma_{\text{film}} = -453.6\varepsilon \text{ GPa} \quad (6)$$

The out-plane strain and in-plane stress calculated for the (002) peak are summarized in table 1. The undoped sample has got lower c -value (compression) compared to bulk ZnO (JCPDS 36-1451), suggesting the film was under tensile stress. However, on Ca^{2+} substitution, the films experience compressive stress resulting from longer c -values.

3.2 Morphological and compositional studies

Figure 3 shows the SEM micrographs of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films. The SEM studies reveal that the grains are well connected and are uniformly distributed in all the five samples and all are nanostructured as well. The EDX spectra of the samples are shown in figure 4. The EDX spectra analysis confirmed the presence of calcium in Ca^{2+} substituted films in addition to Zn and O. In addition, the films are devoid of other impurities. Thus the observed band gap widening could be from the electronic perturbation caused by the substitution of Ca^{2+} .

3.3 Optical studies

Figure 5 shows the transmittance spectra of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films with $x = 0.0, 0.05, 0.10, 0.15$ and 0.20 recorded in the wavelength range 300–900 nm. All the films exhibited good transmittance, greater than 60% in the visible spectral region with oscillatory character in the wavelength range of 400–900 nm due to interference effects and sharp fundamental absorption edge in the near ultra-violet region. The crystal defects and disorders created by doping could cause increased scattering of photons and thus lead to a decrease of transmittance at higher doping levels as can be seen from the transmittance spectra in figure 5. In addition, with increase

Table 1. Variation of mean crystallite size (D), lattice parameters (a and c), unit cell volume (V), strain (ε) and stress (σ) with Ca-dopant concentration.

Sample	D (nm)	a (nm)	c (nm)	V ($\times 10^{-30} \text{ m}^3$)	ε ($\times 10^{-3}$)	σ_{film} (GPa)
ZCO 0	21.00	3.2419	5.2010	47.34	-1.07	485.35
ZCO 5	18.48	3.2459	5.2098	47.53	0.61	-276.69
ZCO10	14.51	3.2472	5.2187	47.65	2.32	-1052.35
ZCO 15	12.77	3.2476	5.2305	47.77	4.59	-2082.02
ZCO 20	11.69	3.2497	5.2483	47.99	8.01	-3633.33

in Ca-dopant concentration the absorption edge got blue-shifted indicating band gap widening. Similar results were also reported with Mg dopant [17–20].

The thickness (t) and refractive index (n) of the deposited films were calculated using the wavy transmittance spectra by

Swanepoel method [21]. According to Swanepoel, the refractive index of the film is given in equation (7),

$$n = \left[N_1 + (N_1^2 - n_s^2)^{1/2} \right]^{1/2} \quad (7)$$

Figure 3. SEM images of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films with $x =$ (a) 0.0, (b) 0.05, (c) 0.10, (d) 0.15 and (e) 0.20.

Figure 4. EDX spectra of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films with $x =$ (a) 0.0, (b) 0.05, (c) 0.10, (d) 0.15 and (e) 0.20.

Figure 5. Transmittance spectra of $Zn_{(1-x)}Ca_xO$ thin films.

where

$$N_1 = \frac{n_s^2 + 1}{2} + \frac{2n_s}{T_m} \quad (8)$$

for transparent region and

$$N_1 = \frac{n_s^2 + 1}{2} + 2n_s \frac{T_M - T_m}{T_M T_m} \quad (9)$$

for weak and medium absorbing regions. Here n_s is the refractive index of the substrate and T_M and T_m are the transmission maximum and the corresponding minimum at a certain wavelength λ . The film thickness was calculated using the relation in equation (10),

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}, \quad (10)$$

where n_1 and n_2 are the refractive indices at two adjacent maxima (minima) and λ_1 and λ_2 are the corresponding wavelengths. All the calculated values are presented in table 2. Optical band gaps (E_g) of the deposited $Zn_{(1-x)}Ca_xO$ thin films were calculated using the Tauc relation in equation (11) [22]

$$\alpha = \frac{B}{h\nu} (h\nu - E_g)^n, \quad (11)$$

where $h\nu$ is the photon energy, B the slope of the Tauc edge called the band tailing parameter and n is a constant equal to 1/2 for direct gap materials and 2 for indirect transitions.

Table 2. Variation of film thickness (t), energy gap (E_g) and bowing parameter (δ) as a function of dopant concentration.

Sample	t (μm)		E_g (eV)	δ (eV)
	Gravimetric method	Swanepoel method		
ZCO 0	0.767	0.713	3.30	—
ZCO 5	0.670	0.654	3.45	0.73
ZCO 10	0.744	0.786	3.48	2.11
ZCO 15	0.717	0.761	3.65	1.61
ZCO 20	0.791	0.743	3.73	1.94

Figure 6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of $Zn_{(1-x)}Ca_xO$ thin films for band gap energy (E_g) determination. The inset graph shows the observed blue-shift in energy gap with increase in Ca concentration.

The $(\alpha h\nu)^2$ vs. $(h\nu)$ plots for the films are presented in figure 6. From the linearity of the plots near the absorption edge, it was confirmed that all the films possessed direct optical gap and were obtained as the intercepts on the energy axis by extrapolating the linear portion of the graph. The obtained band gap energies are listed in table 2, which shows that the energy gap value increases monotonously with Ca-dopant concentration. The electronic perturbation due to cation substitution and deterioration in crystallinity could be considered as the origin of band gap broadening.

As a first-order approximation, the band gap energy of a ternary alloy such as $Zn_{(1-x)}Ca_xO$ can be written in terms of the composition weighted average of ZnO and CaO band gaps as $E_{gZn_{(1-x)}Ca_xO}(x) = (1-x)E_{gZnO} + xE_{gCaO}$, where x is the Ca composition. A more realistic description includes a nonlinear term given by $E_{gZn_{(1-x)}Ca_xO}(x) = (1-x)E_{gZnO} + xE_{gCaO} - \delta x(1-x)$ known as the Vegard's law, where δ

is known as the band gap bowing parameter. The calculated values of band gap bowing parameter are presented in table 2. The variation of band gap with dopant concentration is shown in the inset of figure 6. The linear fit to the obtained data is given in equation (12)

$$E_g(x) = 3.304 + 2.140x \quad (12)$$

Thus by forming a solid solution of ZnO with a wider gap insulator CaO, we are able to tune the band gap of $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ films from 3.30 to 3.73 eV giving 13.03% enhancement in the energy gap value. A similar result was reported by Misra *et al* [23] for $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films prepared by the spin coating method. They reported 12.72% enhancement of optical band gap with 15% Ca substitution. Mahdhi *et al* [24] reported the effect of sputtering power on the electrical and optical properties of Ca-doped ZnO thin films sputtered from nanopowders compacted target. They obtained a maximum energy gap of 3.49 eV with 100 W. Therefore, these band gap extended $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ thin films can be used for window and contact layers in thin film solar cells, where a better band edge alignment is needed.

4. Conclusions

Optically transparent nano-crystalline $\text{Zn}_{(1-x)}\text{Ca}_x\text{O}$ ($0 \leq x \leq 0.20$) thin films were deposited on glass substrates by sol-gel dip coating method. XRD pattern revealed the polycrystalline nature of the films with hexagonal wurtzite structure and showed no additional phase corresponding to CaO. However, the crystallinity of the films deteriorated with increase in Ca-dopant concentration due to the segregation of dopants at the grain boundaries and due to the stress induced by the difference in ionic radii of Zn^{2+} and Ca^{2+} . On the other hand, the lattice parameters and the unit cell volume got increased with doping because of the larger ionic radius of Ca^{2+} . This clearly suggested the successful incorporation of Ca^{2+} ions in the host ZnO structure. All the films exhibited transmittance above 60% in the visible region, but got decreased at higher doping levels because of the increased scattering of photons by crystal defects and disorders created by doping. In addition, these films exhibited blue-shift of optical band gap with increase in Ca substitution giving 13.03% enhancement in the energy gap value due to the electronic perturbation caused by cation substitution and degraded crystallinity. In conclusion, these extended band gap materials can be used in applications like window and contact layers for thin film solar cells where an upward shift of band gap edge is required.

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References

- [1] Mang A, Reimann K and Rübenacke St 1995 *Solid State Commun.* **94** 251
- [2] Park C H, Zhang S B and Wei S H 2002 *Phys. Rev. B* **66** 073202
- [3] Makino T, Segawa Y, Kawasaki M, Ohtomo A, Shiroki R, Tamura K *et al* 2001 *Appl. Phys. Lett.* **78** 1237
- [4] Ramakrishna Reddy K T, Prathap P, Revathi N, Reddy A S N and Miles R W 2009 *Thin Solid Films* **518** 1275
- [5] Lujala V, Skarp J, Tamenmaa T and Suntola T 1994 *Appl. Surf. Sci.* **82/83** 34
- [6] Polley T A, Carter W B and Poker D B 1999 *Thin Solid Films* **357** 132
- [7] Ardakani H K 1996 *Thin Solid Films* **287** 280
- [8] Griebner U, Kaendl R A, Elsaesser T and Seeber W 1998 *Appl. Phys. B* **67** 757
- [9] Han M-Y and Jou J-H 1995 *Thin Solid Films* **260** 58
- [10] Mizuta T, Ishibashi T, Minemoto T, Takakura H and Hamakawa Y 2006 *Thin Solid Films* **515** 2458
- [11] Kim Y-S, Tai W-P and Shu S-J 2005 *Thin Solid Films* **491** 153
- [12] Sahay P P, Tewari S, Nath R K, Jha S and Shamsuddin M 2008 *J. Mater. Sci.* **43** 4534
- [13] Suryanarayana C and Grant Norton M 1998 *X-ray diffraction—a practical approach* (New York and London: Plenum Press)
- [14] Ayadi L, Mir El, Djessas K and Alayo S 2008 *Mat. Sci. Eng. C* **28** 615
- [15] Jin-Hong Lee and Byung-Ok Park 2004 *Mat. Sci. Eng. B* **106** 243
- [16] Gupta V and Mansingh A 1996 *J. Appl. Phys.* **80** 1063
- [17] Ohtomo A, Kawasaki M, Koida T, Masubuchi K, Koinuma H, Sakurai Y *et al* 1998 *Appl. Phys. Lett.* **72** 2466
- [18] Matsubara K, Tampo H, Shibata H, Yamada A, Fons P, Iwata K *et al* 2004 *Appl. Phys. Lett.* **85** 1374
- [19] Suchand Sandeep C S, Reji Philip, Satheeshkumar R and Kumar V 2006 *Appl. Phys. Lett.* **89** 063102
- [20] Yow-Jon Lin, Ping-Hsun Wu, Chia-Lung Tsai, Chia-Jyi Liu, Zhi-Ru Lin, Hsing-Cheng Chang *et al* 2008 *J. Appl. Phys.* **103** 113709
- [21] Manificier J C, Gasiot J and Fillard J P 1976 *J. Phys. E* **9** 1002
- [22] Ohta Y, Haga Y and Abe Y 1997 *Jpn. J. Appl. Phys.* **36** L1040
- [23] Misra K P, Shukla R K, Srivastava A and Srivastava A 2009 *Appl. Phys. Lett.* **95** 031901
- [24] Mahdhi H, Ben Ayadi Z, Gauffier J L, Djessas K and Alaya S 2015 *Opt. Mater.* **45** 97