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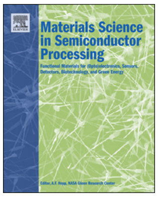

Blue-light luminescence enhancement and increased band gap from calcium-doped zinc oxide nanoparticle films

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ABSTRACT

Four-fold enhancement in emission in the blue region is observed for the first time from sol–gel deposited calcium doped zinc oxide ($Zn_{1-x}Ca_xO$) nanophosphor films having a hexagonal wurtzite structure. A 4.28% increase in the band gap has been obtained by introducing very small concentration (1.47 at%) of Ca dopant. A blue-shift of 55 meV in PL emission in UV region occurs with increase in dopant concentration. Optical transmission, FTIR spectra and surface structure of the films have been studied. Dopant concentration in the films is determined by EDX.

1. Introduction

Inorganic semiconductor nanostructures are considered promising for future electronics, photonics, biosensors and nanodevices [1–5]. ZnO is a II–VI semiconductor with band gap of 3.37 eV and exciton binding energy of 60 meV at room temperature. Such direct wide band-gap semiconductors are of considerable interest for blue and UV light-emitting devices [6–9]. Thin films of ZnO also play an important role in solid-state display devices [10,11], solar cells [12,13], etc. Dopants may affect the optical, electrical, sensing and piezoelectric properties [14–25] of ZnO. Band gap engineering of nanocrystalline ZnO plays key role for nanodevices [2,26]. For smooth variation in band gap, the change in cations in ZnO by isoelectronic impurities is important. Substitution of Zn by Cd and Mg or Ca tunes the optical band gap of ZnO films towards lower and higher energies, respectively [5,14,15,17,20]. ZnO based films can be obtained by chemical vapor deposition, thermal evaporation, magnetron sputtering, pulsed laser deposition, spray pyrolysis, sol–gel, etc. A sol–gel method is simpler besides producing good quality homogenous films and can be used to prepare ZnO based nanophosphors [27,28].

The quality of phosphor material being important for the brightness of display devices [29] makes the study of photoluminescence (PL) properties of the phosphor imperative. Emission in blue region is important for fabrication of white LEDs. In an earlier report [14] on the effect of Ca doping in ZnO by the authors the film samples did not show luminescence under photoexcitation. Molarity of those precursor solutions was 0.1 M and dopant concentration varied between 5 and 15 at%. To the best of our knowledge there is no report on PL from calcium doped zinc oxide ($Zn_{1-x}Ca_xO$) films prepared by the sol–gel method. In view of the importance of the subject and manipulation of emission in visible region, present work has been carried out. PL is known to be a surface effect and in order to obtain it the film surface has been modified by increasing the molarity two-fold and lowering the dopant concentration as compared to that in Ref.[14]. Increased molarity is expected to lead to denser films with suitable surface structure. In this paper, PL spectra and band gap enhancement of nanocrystalline $Zn_{1-x}Ca_xO$ thin films

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prepared by the sol–gel spin coating method is presented. Band gap tuning obtained is larger than those reported earlier [5,14].

2. Experimental details

The precursor for undoped film was prepared by obtaining 0.2 M solution of zinc acetate dihydrate in ethanol and diethanolamine. The mixture was magnetically stirred at 60 °C for 30 min to get a homogeneous solution. To this solution, appropriate volumes of 0.2 M solution of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) in ethanol were added to obtain 1, 2 and 3 at% doping of Ca. Now onwards atomic% is abbreviated as at%. These solutions were again stirred for 30 min. Both undoped and doped solutions were aged for 5 days and then were spin coated on properly cleaned glass slides. Spinning speed was kept at 3000 rpm while the spinning time was 30 s. After each coating, the sample was heated from room temperature to 400 °C for 60 min, cooling back naturally. The process was repeated 15 times to obtain appreciable thickness. Finally all the films were annealed at 450 °C for 4 h. The four samples: undoped ZnO, ZnO:1 at% Ca, ZnO:2 at% Ca and ZnO:3 at% Ca for which $x=0$, 0.01, 0.02 and 0.03 were named as samples 1, 2, 3 and 4 respectively.

Structural characterization was performed using a Bruker D8 Advance X-ray diffractometer with CuKα radiation ($\lambda=1.541841$ Å) for 2θ values ranging from 26 to 65° and the step size was 0.05°. The FTIR transmission spectra were obtained using a Bruker Alpha FTIR spectrometer. Supra 40 VP from Zeiss FESEM and EDX was used to obtain surface morphology of the films and the amount of calcium dopant in them. Surface topology had been investigated using PicoSPM II AFM from Molecular Imaging. The optical transmission spectra were recorded using a UV–vis–NIR spectrophotometer (JASCO, Model-V670) in wavelength range 300–900 nm for normal incidence and 0.25 nm step size. PL spectra had been recorded for every 0.5 nm using fluorescence spectrometer (Model- LS-55, Perkin-Elmer). The excitation wavelengths were obtained from a 20 kW Xe discharge lamp. All the measurements had been performed at room temperature.

3. Results and discussion

3.1. XRD and FTIR

The X-ray diffraction (XRD) pattern for all the samples is shown in Fig. 1. The peaks correspond to the hexagonal wurtzite structure of ZnO showing preferred orientations along (100), (002) and (101) planes [5,14,20,23,27,30]. No other diffraction peak except that for ZnO is detected, indicating that the doping of Ca does not alter the wurtzite structure of $Zn_{1-x}Ca_xO$ films. In earlier reports where Ca doped ZnO films were prepared by sol–gel spin coating [14] and PLD [5] no impurity phase was found for doping up to 15 and 22.4 at% respectively. Cao et al. [5] have demonstrated that wurtzite structure of ZnO remains intact with Ca doping up to 22.4 at% and a new phase corresponding to CaO occurs when dopant increases to 27.8 at%. CaO phase is also reported in Ca doped ZnO nanoparticles obtained by a precipitation method and subsequent annealing at 650 °C for 4 h in air atmosphere [17]. In the present work the orientation parameter $\gamma_{(hkl)}=I_{(hkl)}/(I_{(100)}+I_{(002)}+I_{(101)})$ [27,31,32] corresponding to different planes varies from 0.291 to 0.416 indicating random orientation; see Table 1. The peak along the c-axis occurs at $2\theta=34.25^{\circ}$, $34.05^{\circ 0}$, 34.50° and 34.65° for samples 1, 2, 3 and 4 respectively. The diffraction peak shifts to lower value of 2θ for sample 2, resulting in an increase in c-lattice constant; see Table 1. Such an increment can be attributed to increase in interstitial Zn/Ca. For higher concentration of Ca, angle of diffraction again increases and the lattice constant decreases since Ca get substituted at Zn sites instead of increasing the metallic ions in interstitials. Bond length [33] is calculated to be 1.980, 2.004, 1.988 and 1.981 Å. Maximum error in the determination of the lattice constants, bond length and crystallite size is ±0.015 Å, ±0.009 Å and ±1 nm respectively.

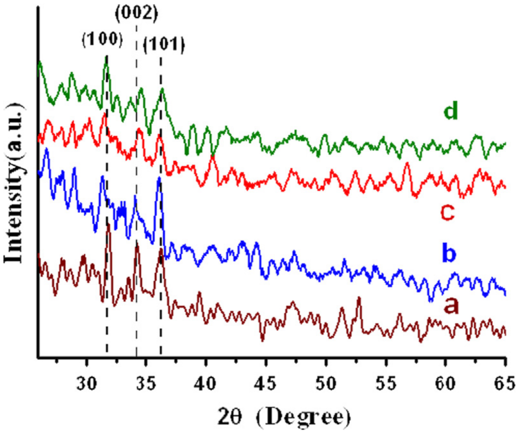

Fig. 1. XRD spectra for $Zn_{1-x}Ca_xO$ thin films. Curves a, b, c, and d correspond to samples 1 2, 3 and 4 respectively.

Table 1
Orientation parameter, lattice constant and bond length determined from XRD data for $Zn_{1-x}Ca_xO$ films.

Samples	**Orientation parameter (γ)**			**Lattice constant**		***c/a***	**Anion–cation bond length** (Å)
	(100)	**(002)**	**(101)**	***a*** (Å)	***c*** (Å)		
1	0.378	0.319	0.302	3.246	5.239	1.613	1.980
2	0.309	0.317	0.373	3.296	5.269	1.598	2.004
3	0.386	0.321	0.292	3.276	5.202	1.587	1.988
4	0.416	0.292	0.291	3.266	5.180	1.586	1.981

The lower bound of the crystallite size in the sample is estimated using the Debye–Scherrer (DS) formula as follows [14,34]:

$$t_{DS}=\frac{k\lambda}{\beta \cos \theta} \tag{1}$$

where t_{DS} is the particle diameter, and k is the Scherrer constant taken equal to one. β is full width at half-maximum (FWHM) of X-ray diffraction peaks in radians.