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Effect of boron doping on optical properties of sol-gel based nanostructured zinc oxide films on glass

Sunirmal Jana^{a,*}, Angela Surca Vuk^b, Aparajita Mallick^a, Boris Orel^b, Prasanta Kumar Biswas^a

^a Sol–Gel Division, CSIR-Central Glass & Ceramic Research Institute, (Council of Scientific & Industrial Research, CSIR, India), 196 Raja S. C. Mullick Road, Kolkata 700032, India ^b National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

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ABSTRACT

Boron doped zinc oxide thin films (~80 nm) were deposited onto pure silica glass by sol-gel dip coating technique from the precursor sol/solution of 4.0 wt.% equivalent oxide content. The boron concentration was varied from 0 to 2 at.% w.r.t. Zn using crystalline boric acid. The nanostructured feature of the films was visualized by FESEM images and the largest cluster size of ZnO was found in 1 at.% boron doped film (B1ZO). The presence of mixed crystal phases with hexagonal as major phase was identified from XRD reflections of the films. Particle size, optical band gap, visible specular reflection, room temperature photoluminescence (PL) emissions (3.24–2.28 eV), infra-red (IR) and Raman active longitudinal optical (LO) phonon vibration were found to be dependent on dopant concentration. For the first time, we report the room temperature fine structured PL emissions as phonon replicas originated from the LO phonon (both IR and Raman active) in 1 at.% boron doped zinc oxide film.

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1. Introduction

Zinc oxide films have always attracted material researchers for [1–7] their novel optical, electrical and electronic properties and widespread applications. Optical properties of sol-gel based films depend on several factors [3,8–10] such as preparative method, precursor and substrate materials, annealing treatment, etc. Alternatively, the properties can be tailored by chemical doping in the precursor sol/solution especially with the elements of group IIIA (e.g. B, Al, Ga) [11–14]. Among the group IIIA elements, boron doping could be most effective [12] for tailoring the properties because the element has lowest cationic radius, highest electronegativity and Lewis acid strength along with the highest Z/r^2 (Z, empirical ionic radius and r, charge number of the atomic core) value. In this regard, it is sometimes observed that the starting material [12,15] of dopant can also be a predominant factor. As for example, no distinct deviation was observed in the optical band gap [12] of zinc oxide thin films derived from the precursors containing up to 1.4 at.% of boron if boron tri-i-propoxide be used as a starting material. On the other hand, use of trimethyl borate, even in a very low concentration of boron (0.2 at.%) showed the prominent effect [15] in optical band gap property. The reason for the effect is not yet clear.

Among the optical properties, the presence of longitudinal optical (LO) phonon vibrations in pure and doped ZnO is one of the important characteristics of exciton formation in nanoclusters. The vibrations are generally observed as the phonon replicas [2,4] in low temperature photoluminescence (PL) emissions. In general, the Raman spectral study [1,5–7,16,17] are mostly used to characterize the LO phonon vibrations of ZnO.

This report focuses on the effect of boron concentration upon the optical properties of sol-gel based boron doped nanostructured zinc oxide thin films using crystalline boric acid as a starting material of boron. In this work, for the first time, we are reporting the room temperature fine structured PL emissions as phonon replicas originated from both IR and Raman active LO phonon in 1 at.% boron doped zinc oxide film by Near Grazing Incidence Angle (NGIA) IR, Raman and photoluminescence studies.

2. Experimental

2.1. Preparation of precursor sols/solutions and thin films

All the precursor sols/solutions (4.0 wt.% equivalent oxides) were prepared by varying boron dopant concentrations from 0 to 2 at.% w.r.t. Zn. Zinc acetate dihydrate (GR, 99.5%; Sarabhai M. Chemicals, India) and crystalline boric acid (99.8%, Fluka) were used as the sources of ZnO and B, respectively while triethanolamine (TEA, 97%, E. Merck, India) was used as precursor sol/ solution stabilizer. Iso-propanol (99%, E. Merck, India) and doubly distilled water mixture (\geq 2.3 times higher than water by weight)

^{*} Corresponding author. Tel.: +91 33 2473 3476x3405; fax: +91 33 2473 0957. *E-mail address*: sjana@cgcri.res.in (S. Jana).

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were used as the dispersion medium of precursor sol/solution. Initially, requisite amount of zinc acetate and boric acid was dissolved in water at ~60 °C. Then iso-propanol and TEA mixture was added slowly to the aliquot in cold condition. The dipping technique with a lifting speed, 4 cm/min was used to coat (Dip Master 200, Chemat Technology Inc., USA) on the pre-cleaned pure silica glass (Suprasil grade, Heraus, Germany, dimensions: 20 mm × 15 mm × 0.25 mm) substrate. Adherence of freshly prepared precursors on glass surface was poor while ~72 h ageing produced good adherence to the substrate. The as-coated samples were baked in an air oven at 500 ± 5 °C for 60 min. The films were designated as B0ZO, B0.5ZO, B1ZO and B2ZO derived from the precursor sols/solutions having the dopant concentrations, 0.0, 0.5, 1.0 and 2.0 at.%, respectively.

2.2. Characterization of films

Gaertner make autogain Ellipsometer (L116B, 70° angle of incidence, He–Ne laser beam wavelength: 632.8 nm) was used to measure thickness and refractive index (RI) of the films. Variation of RI with dopant concentration was observed and the lowest RI (1.69) was found in B1ZO film. FESEM (ZEISS, SUPRATM 35VP) was used to characterize the surface morphology of films and cluster size of ZnO was calculated from the FESEM images. Crystallinity of the films was checked by XRD (Philips PW-1730, Ni-filtered CuK_α radiation). Shimadzu make UV-vis-NIR spectrophotometer (model UV3101PC) and Perkin-Elmer (LS55) spectrofluorimeter were employed to measure the optical (absorption and photoluminescence) properties of the films at room temperature. FTIR spectra

were measured using Thermo-Nicolet (model 5700, wavenumber accuracy: 4 cm^{-1}), USA from 4000 to 400 cm⁻¹ wavenumber region. Near Grazing Incidence Angle (NGIA) reflection-absorption (RA) IR spectra were recorded using Bruker spectrometer (model IFS 66/S). The NGIA IR spectra were obtained with the help of a Monolayer Grazing Angle Specular Reflectance Accessory (Specac) equipped with a standard polarizer for obtaining p-polarized infrared light. For this measurement, the films were deposited on fluorine doped tin oxide (FTO) glass (Pilkington) by sol-gel dip coating process from the aged (72 h) precursors maintaining the same curing conditions as done on silica glass substrate and the background was corrected from the FTO glass substrate. Room temperature substrate corrected Raman spectral study (micro-Raman, Renishaw inVia Raman microscope) was done using argonion laser with an incident wavelength of 514 nm as the excitation source.

3. Results and discussion

FESEM images (Fig. 1) reveal the nanostructured surface feature of the films. A uniform and dense microstructure was observed in B1ZO film. The average cluster size of ZnO calculated from the FESEM images of 1 at.% doped (B1ZO) film was 41 \pm 4 nm whereas in 0.5 at.% (B0.5ZO) and 2 at.% (B2ZO) boron doped films, the average clustered sizes were 30 \pm 4 and 22 \pm 2 nm, respectively. However, the average cluster size (21 \pm 2 nm) of undoped ZnO was almost equivalent to that of 2 at.% boron doped film. Hence, 1 at.% doped film (B1ZO) generated the largest size of ZnO cluster.



Fig. 1. FESEM images of pure and doped ZnO thin films on pure silica glass: (a) B0ZO, (b) B0.5ZO, (c) B1ZO and (d) B2ZO.



Fig. 2. XRD reflections of pure and 0, 1.0, 2.0 at.% B-doped ZnO thin films on pure silica glass. Inset shows the XRD reflections of 0.5 at.% B-doped ZnO thin films on pure silica glass.

The XRD reflections (Fig. 2) of the films confirmed the presence of mixed crystal phases of ZnO with hexagonal as major phase [16] along with a minor new phase, similar to that reported by Guo et al. [18]. From the XRD reflections, it is clear that the crystallinity is better in B1ZO film. The crystallite size was also calculated from the $h(1 \ 0 \ 0)$ plane reflection using Scherer's equation [19] and the average crystallite sizes were 15 ± 2 nm, 22 ± 2 nm, 25 ± 2 nm and

 19 ± 1 nm of B0ZO, B0.5ZO, B1ZO and B2ZO films, respectively. Hence, the trend of change of particle size was same as calculated from FESEM images.

ZnO is a direct transition semiconductor and its absorption coefficient (α) and optical band gap energy (E_g) are interrelated [13,19–22]. The band gap energy of the films was calculated from Eq. (1). The ($\alpha h\nu$)² versus $h\nu$ (energy) is plotted. The plots are parabolic in nature and the number of inflexions reveals the number of transitions. At inflexion, the tangential extrapolation to *X*-axis (energy) gives the band gap energy (E_g).

$$\alpha h \nu = A (h \nu - E_{\sigma})^{1/2} \tag{1}$$

where *A* is a constant.

Two E_g values were obtained (Fig. 3(i)–(iii)) as two inflexions were obtained for each film; one E_g was at 3.31 eV (~375 nm) for all films which would correspond to the bulk E_g [15] of zinc oxide and another E_g were found at 4.13 eV (~300 nm), 3.74 eV (~332 nm) (figure not shown here), 3.65 eV (~340 nm) and 3.80 eV (~326 nm) for B0ZO, B0.5ZO, B1ZO and B2ZO films, respectively. This was due to [22] the size effect of nanostructured ZnO semiconductor.

Single surface visible specular reflection (R) spectra (Fig. 3(iv)) of the films show that %R decreased with doping and it was lowest in 1 at.% doped film (B1ZO). We have also found that B1ZO possessed the lowest refractive index (1.69) which confirms with its visible reflection spectrum. This indicated the presence of relatively large amount of oxygen vacancy [22] in the film network. However, the low RI is contrary to the uniform and dense microstructure (Fig. 1(c)) of the film.

The FTIR spectra of the films are shown in Fig. 4(a). In B1ZO film, four distinct vibrations appeared at 407 cm⁻¹, 434 cm⁻¹, 472 cm⁻¹



Fig. 3. Plots of $(\alpha h v)^2$ versus hv for direct band gap determinations of (i) B0ZO, (ii) B1ZO and (iii) B2ZO films on pure silica glass. Single surface visible specular reflection spectra (iv) of pure and doped ZnO thin films on pure silica glass.



Fig. 4. Substrate corrected FTIR (a) and Near Grazing Incidence Angle (NGIA) IR spectra (b) of pure and doped ZnO thin films.

and 515 cm^{-1} . The peak appeared at 472 cm^{-1} may be assigned as the stretching vibration of Zn-O [23]. The presence of wurtzite crystal structure (hexagonal) was also evident from the appearance of FTIR peaks at 407, 434 and 515 cm^{-1} (related to oxygen vacancy) [5,23,24]. The IR active longitudinal optical (LO) phonon vibration could be present in the film but it was not identified distinctly in the FTIR spectra. Hence, the NGIA IR spectral measurement were done to reveal the LO phonon vibration. A strong vibration band at 573 cm⁻¹ (Fig. 4(b)) was observed in undoped (BOZO) film while in B0.5ZO, B1ZO and B2ZO films, it was 566, 570 and 572 cm⁻¹, respectively. The vibrations of hexagonal ZnO as found in FTIR spectra (Fig. 4(a)) were possibly overlapped within the broad intensity vibration of NGIA IR spectra. The observed vibrational peak energy matched with the LO phonon energy of nanostructured ZnO films and designated as E₁(LO) component [4]. The LO phonons at the Γ -point of hexagonal wurtzite ZnO crystal belong to the following irreducible representation (Eq. (2)) [16],

$$\Gamma = A_1 + 2B_1 + E_1 + 2E_2 \tag{2}$$

In Eq. (2), the A₁ and E₁ modes [5,16] are both IR and Raman active which split into LO and transverse optical (TO) components but the E_2 mode is only Raman active. The B₁ mode is forbidden. As Raman spectral study is very much useful to know the phonon modes [5–7,17] of ZnO, the study was performed on the undoped and doped



Fig. 5. Raman spectra (substrate corrected) of pure and doped ZnO films.

ZnO films. The Raman spectra (corrected from substrate) of the films are shown in Fig. 5. A strong intensity peak at \sim 436 cm⁻¹ along with a medium intensity peak at $\sim 408 \text{ cm}^{-1}$ (most prominent in case of B1ZO film) observed for all the films. The appearance of strong peak at \sim 436 cm⁻¹ confirmed the presence of wurtzite ZnO crystal and assigned as E_2 (high) mode [5–7] whereas the peak at \sim 408 cm⁻¹ corresponded to E₁(TO) component [5] of ZnO in the thin film form. A weak vibration appeared at \sim 380 cm⁻¹ which is most prominent in B1ZO film indicating the presence of $A_1(TO)$ component [6]. A prominent peak was found at 581 cm⁻¹ in undoped ZnO film which shifted towards lower energy at 575, 570 and 566 cm⁻¹ in B2ZO, B0.5ZO and B1ZO films, respectively. This peak corresponded to $E_1(LO)$ component of ZnO. It is interesting to note that the trend of peak shifting is similar to that of NGIA IR peak shifting (Fig. 4). The $E_1(LO)$ component is generally associated [1] with lattice defects, such as oxygen vacancies in ZnO nanocrystals and it generates photoluminescence (PL) emissions. The peak shifting of $E_1(LO)$ towards lower energy in both IR and Raman spectral studies was due to increase of ZnO grain size [1] as evidenced from FESEM (Fig. 1(c)) and XRD (Fig. 2) studies. Two additional peaks at \sim 492 and 540 cm⁻¹ was also prominently observed in B1ZO films. The former might be associated with the "defect band" [25] and the later corresponded to A₁(LO) component [6] of ZnO.

The phonon replicas (Fig. 5(A)) of the films have also been well understood from the PL spectral study at room temperature. The PL spectrum of B1ZO film showed fine structured emissions with relatively high intensity (inset (b), Fig. 6(A)) in the visible region and a broad tail extended towards the ultraviolet (UV) region when the film was excited at 340 nm (inset (c), Fig. 6(A), photoluminescence excitation (PLE) spectrum of B1ZO film, fixing the emission peak at 426 nm). The fine structured PL emissions appeared prominently at 401, 406.5, 426, 436.5, 447.5, 459, 471 (shoulder), 485, 498 (shoulder), 512, 530 and 544 nm in B1ZO film. The peak intensity of the other films was very low. We have plotted (inset (b), Fig. 6(A)) the intensity of PL peak at 426 nm with dopant concentration to compare the change of PL intensity among the doped and undoped films. Although, part of the spectrum below 400 nm is not well resolved but its second derivative spectrum (inset (a), Fig. 6(A)) shows three distinct emissions at 382.5, 391 and 397 nm. The origins of the fine structured PL visible emissions are already reported by several authors [1–6,14,26–32] and these have been assigned mostly due to various types of oxygen



Fig. 6. (A) Characteristics of room temperature photoluminescence (PL) emissions of pure and doped ZnO thin films on silica glass. Insets: (a) 2nd derivative PL spectrum of B1ZO film, (b) change of PL intensity of 426 nm emission peak with dopant concentration of the films and (c) photoluminescence excitation (PLE) spectrum of B1ZO film fixing PL emission at 426 nm. (B) Excitation dependent PL spectra of 1 at.% boron doped ZnO thin film (B1ZO) on pure silica glass show the emissions of free and bound excitons.

vacancies, oxygen interstial, free holes, etc. The PL emissions below the 391 nm are fully dependent on excitation energy [22] which is evident from the excitation dependent PL spectra (Fig. 6(B)) of the B1ZO film. Hence, on the basis of excitation dependent PL emissions, we may divide the observed emission peaks into two main groups that appeared in the 3.24-2.28 eV. The emission peaks appeared up to 391 nm could be considered due to near band edge (NBE) exciton transitions of wide band gap ZnO [26,27] while the emission peaks appeared above 391 nm attributed to bound exciton recombination [22] which trapped in the potential well of the defect centres such as oxygen vacancy of nanostructured ZnO film. The emission peaks appeared at 382.5 nm and 391 nm were considered as the phonon replicas generated from both IR and Raman active LO phonon of the film because the presence of LO phonon vibration was confirmed by NGIA IR and Raman spectral studies (Fig. 4(b)). On the other hand, the fine structure PL emissions observed above 391 nm in the visible region could also be considered as phonon replicas [2] as these were considered as bound excitons [22]. The emission peak appeared at 397 nm may be considered as zero-phonon transition for the visible region. It is already reported [2,4] that the phonon replicas of ZnO was observed in PL study at very low temperature (10 K). This was for the first time, we have observed the phonon replicas in PL emissions at room temperature of sol-gel based boron doped nanostructured ZnO thin film. The large amount of defect concentration in the B1ZO film might be the reason for generating fine PL emissions as [3] larger the grain size, smaller is the nonradiative relaxation rates.

4. Conclusions

Boron doped nanostructured ZnO thin films of mixed crystal phases with hexagonal as major phase were prepared by sol-gel technique using crystalline boric acid as the source of boron. The presence of both IR and Raman active longitudinal optical (LO) phonon vibration was observed by NGIA IR and Raman spectral studies. Boron doping controls the LO phonon energy, refractive index (RI), band gap and grain size of ZnO in nanostructured ZnO thin films. The variation of RI due to boron doping has been observed in the specular reflectance. For the first time, we observed the room temperature fine structured PL emissions in the UV-vis regions (3.24–2.28 eV) as phonon replicas originated from the LO phonon (both IR and Raman active) in 1 at.% boron doped film.

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