



Intense, Broad and strongly coupled multiple Photoluminescence in Zirconium doped ZnO thin films

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Abstract

Zinc oxide (ZnO) and a series of Zirconium doped ZnO (ZZO) thin films are chemically spray coated on quartz substrate at 400°C. The films are further subjected to vacuum annealing at 400°C for three hours in an appropriate air (10^{-5} mbar) ambience. The X-ray diffraction analysis confirmed the structural purity and Zr addition in wurtzite ZnO matrix. Photoluminescence measurements were used to characterize the materials optically. Intense, broad and strongly coupled multiple photoluminescence were observed. These are indicative of relatively high concentration of defective oxygen and Zn vacancies in the film composition. Simultaneously, the strongly coupled ultraviolet near blue emissions authenticate that the Zr ions are capable of inducing modulated free excitonic (FX), donor acceptor pair (DAP) and longitudinal optical phonon emissions.

Keywords: Photoluminescence, Thin films, free excitons, XRD..

Introduction

Zinc oxide (ZnO) is the most acclaimed wide direct band gap semiconductor with countless applications including blue luminescent devices, low threshold room temperature UV lasers, solar cells, photo catalyst and near UV optoelectronic devices¹⁻³. N-type higher valent impurity in wurtzite ZnO at Zn^{2+} coordinates and pronounced oxygen deficiencies can lower the electrical resistivity and improve optical transmittance of ZnO thin films. Zinc oxide doped with zirconium; reviewed previously as stable transparent conducting materials (TCM) even at extreme conditions could be a promising candidate in optoelectronic devices, when tuned precisely⁴⁻⁵. Besides, rare-earth elements can provide better luminescent centres than the transition metal ions due to their 4f intrashell transitions which give rise to narrow and intense emission lines⁶. Zirconium is a known n-type impurity with a larger ionic radius (0.8\AA) than Zn^{2+} (0.74\AA), however, the ionic radii's are comfortably in the tolerance level for doping⁷. Hence, Zr^{4+} can occupy Zn^{2+} sites in crystal lattice. In ZnO, Zn interstitials induce a state with two electrons above the conduction band maximum (CBM) and these two electrons can be transferred to the conduction-band offering +2 charge state (Zn^{2+}) and thus intrinsically ZnO will always donate electrons to the conduction band by acting as a shallow donor⁸. Along with this, doping in ZnO films with Zr would results in donor electron population and likely to improves transparency in the visible range. This means that Zr doping can be used to alter the intrinsic properties of ZnO. Howbeit, the comprehensive discussions in terms of electronic structure, native point defects, impurities and their influence on certain color emissions are necessary to substantiate the role of such materials in certain devices like,

light-emitting and laser emitting diodes that operate in the blue and ultraviolet region of the spectrum⁹. This article presents the results on the intense and broad PL emission at room temperature on spray deposited Zr doped ZnO thin films. The structural and optical properties are measured, analysed and discussed in brief.

Materials and Methods

Six batches of Zr doped zinc oxide photo emitting transparent electrodes are prepared on quartz substrates using spray pyrolysis method, with Zr dopant concentrations of 0, 1,2,3,4 and 5 at%. Zinc acetate dihydrates dissolved in a mixture of methanol, water and acetic acid in a ratio 65:25:10 to prepare 0.2 molar solutions. Zr doping is achieved by adding zirconium acetyl acetate in calculated amount to this solution. The solution is ultrasonically stirred for two hours prior to deposition. Quartz plates cleaned ultrasonically and using nitric acid, chromic acid, hydrogen peroxide, acetic acid and water respectively are used as the substrate for deposition. The solution is sprayed on the substrate which is kept at a temperature of 400°C using Holmarc HO-TH 04 spray pyrolysis system. Same program under similar physical conditions are used for the spraying of every solution to assure uniformity of the film. Six samples with Zr atomic percentage varying from 0 to 5 are prepared and annealed for 3 hours at 400°C in air. Samples were further annealed at 400°C in high vacuum of 10^{-5} mbar. The structural properties of the samples are studied using XRD technique, Cu-K α -radiation, using Rigaku-Miniflex X-ray diffractometer, photoluminescence spectroscopy (Fluorolog III- Jobin Vyon, excited with 325nm laser) was employed to investigate the multicolour luminescence composed

in the wide visible region and the peak lines are deconvoluted to observe the corresponding transitions.

Results and Discussion

X ray diffraction pattern of the doped and undoped zinc oxide films are presented in Figure-1. The patterns are compared and found identical with ICDD card 36-1451, which is the zincite (ZnO) card. No significant variation either in peak positions, relative intensity or number of peaks is detected from the XRD pattern of vacuum annealed films. The ZnO film is highly textured in a c-axis orientation (002), conjointly, the set of Zr doped ZnO film also exhibits the same orientation (002) with in the wurtzite matrix. In wurtzite ZnO, Zn interstitial atoms occupy tetrahedral sites or the octahedral sites. At the tetrahedral site, the Zn has one Zn and one O as nearest-neighbor atoms with Zn–O bond length along the *c* axis¹⁰. At the octahedral site, the Zn has three Zn and three O atoms as nearest neighbors. It is expected that the Zn interstitial will be more stable at the octahedral site where the geometrical constraints are comparatively weak. The polycrystalline nature and wurtzite structure of the films are confirmed. Lack of any secondary phase in the XRD patterns shows that no zirconium oxide phase is formed with preferential growth along (002) direction. High level doping is found to decrease the crystalline quality of the films. This can be due to the occupation of interstitial sites by Zr^{4+} ions at higher levels of doping. The result can be summarized as follows: At lower levels of doping, the Zr^{4+} ions prefer replacing a Zn^{2+} ion in the crystal. But as the doping level increases the Zr^{4+} ions tend to occupy the interstitial position. This indeed means that higher level doping will degrade the crystalline quality of the films and will eventually lead to amorphourization of the ZnO film beyond certain level of doping¹². It emphasis that the impurities at a particular level likely to modify the defect band structure and electronic level of ZnO and this opens opportunity to control the characteristics, in particular, the deep level emission (DLE), near

band emission and other defect induced light emission in visible region¹³.

Figure-2, shows the room temperature PL spectra of thin films of ZnO and Zr doped ZnO. The photoluminescence of same species vacuum annealed at 400°C are shown in Figure-4. Sharp intense UV emission is observed in the case of all thin films in its as deposited state, apart from this, broad visible DL emission was also observed from the films composed with Zr interstitials. However, for the films subjected for oxygen reduction by vacuum annealing visible emission is found stronger, broader and red shifted. From figures, the broad PL emissions clearly indicating unresolved excitonic and DL features resulted from the unique energy transition of ZnO thin films. The UV region broad emissions are resolved to investigate the transition energies and fitted with Gaussian line-shape. The exciton emission bands in UV region are fitted for free exciton (FX), donor acceptor pairs (DAP) and longitudinal optical phonon (DAPLO). Several imperfections or defects in the band gap could lead to such broad luminescence; further, the influence of Zr interstitials give rise to more type of donor and that directly modify the energy level transitions as depicted in the PL spectra of Zr doped ZnO films (ZZO (1%), ZZO (2%), ZZO (3%) and ZZO (4%)), meanwhile, the undoped and ZZO (5%), the emissions are identical with a intense pronounced red-shift. The assignments for various energy transitions in terms of the doping percentage are indicated in figure.3. The other emissions (DAP and DAPLO) are random, however, these emissions indicate the presence of more than one type of donor in the films doped up to 4% of zirconium. Feeble blue emissions are also found in the PL spectra of ZZO (2%), ZZO (3%) and ZZO (5%). The unsystematic emissions of photon in the ZZO films can be ascribed to the lattice defects induced by Zr atoms, at higher concentration levels it agglomerate at the grain boundaries as it cannot occupy interstitials positions as neutral defects and results in defect induced emissions¹⁴.

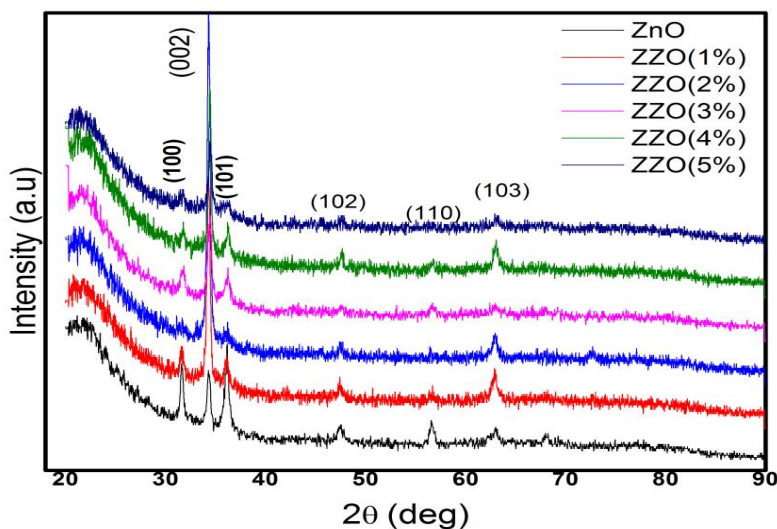


Figure-1
XRD pattern of undoped/Zr doped ZnO Films.

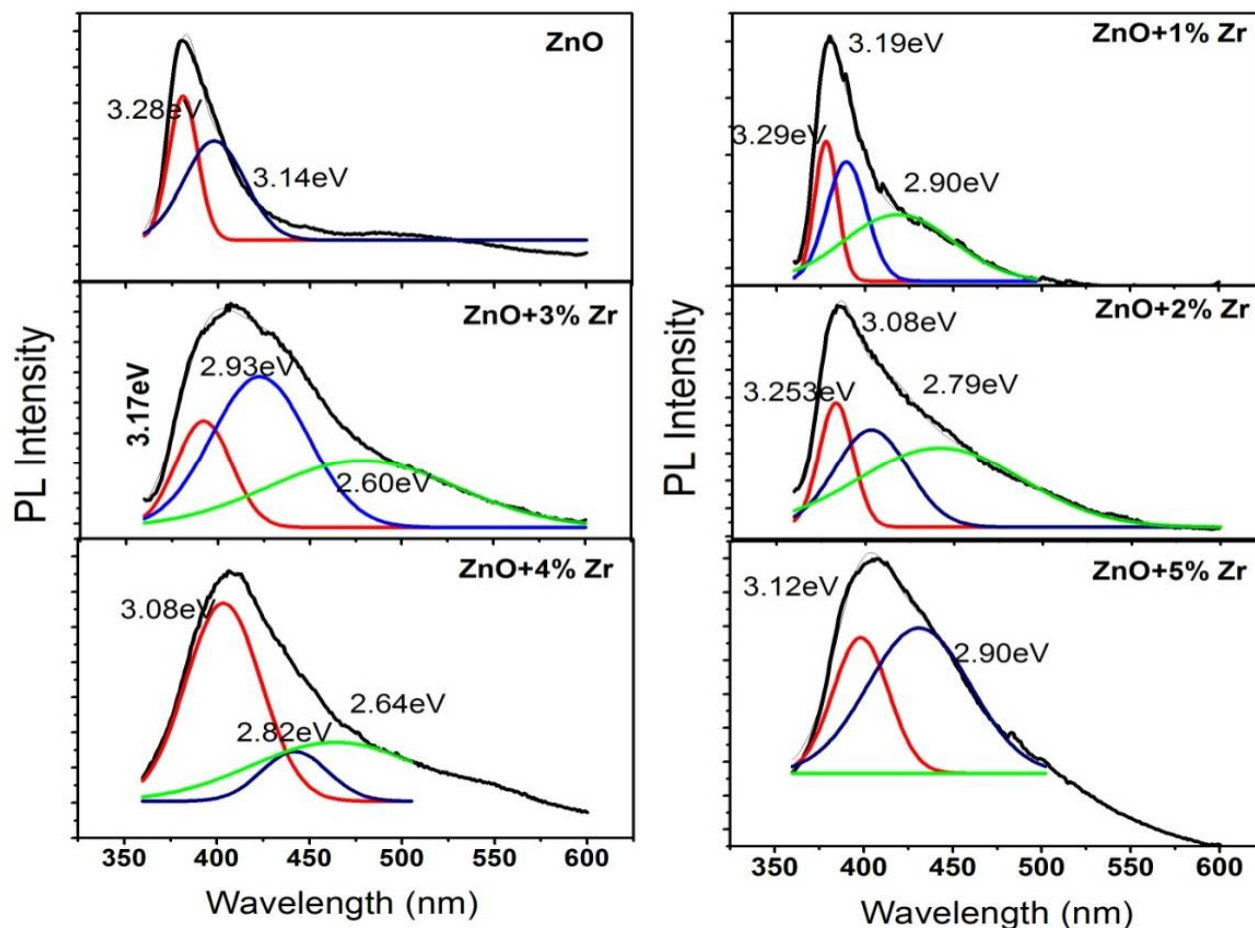


Figure-2

Photoluminescence spectra of undoped and Zr doped ZnO thin films in the as deposited state. The asymmetric shoulders are deconvoluted using Gaussian line-shape; corresponding emissions are indicated in terms of photon energy

A strong coupling between the FX and longitudinal optical phonon is frequently related to the bending effect on exciton-phonon interactions and this effect is strongly observed in both unannealed and vacuum annealed films. In Figure-3, vacuum annealing on the films contributed additional peaks in the PL spectra. The prominent broader emissions in PL spectra are resolved for multi colour emissions using Gaussian line shape, the centres of fitted curve correspond to blue and green colour discharges besides the intense collective (FX, DAP and DAPLO) emission (Figure-5). Figure 5 in comparison with the Figure-3, the photon emission assignment suggests meagre variation in crucial free exciton emission as well as the induced green emissions. The deep level emissions, especially, blue and green emissions are recognized as recombination centres in which a delocalized electrons occupied very near to the conduction band recombine with a deeply trapped hole in the singly ionized oxygen vacancy¹⁵⁻¹⁶. Conventionally, these are defect transition levels and are likely to be the shallow donors producing conduction in ZnO thin films. Precisely, the blue emissions (figure 3 and 5) are electronic transitions of ZnO by proving zinc vacancy instead of the zinc interstitial. Hence, the

phenomenon of color luminescence is directly related to Zn vacancies and O- defects; so these peaks are absent in non-vacuum annealed samples. When the samples are vacuum annealed more oxygen on the film surface escapes and density of oxygen vacancy levels increases and resulted in broad color luminescence. However, the strong emission coupling and multiple UV luminescences are greatly related to amount of dopant concentration. The Zr provides free electrons either to the conduction band minimum (CBM) or valance band maximum (VBM). As a result of this, in first case, these extra carriers induces the electron Fermi level to shift in the upward direction and the fundamental gap energy increases (ZZO(1%) , however, in second case, the electrons occupied on the top of VBM shift the Fermi energy into a lower value⁶. Under UV illumination number of electron hole pairs is generated. These extra carriers induces the electron Fermi level to shift towards conduction band also the hole Fermi level to shift towards valance band forming new quasi Fermi levels. These pairs resulted in the other donor acceptor pair, longitudinal optical phonon emissions and induced blue emissions at higher dopant concentrations.

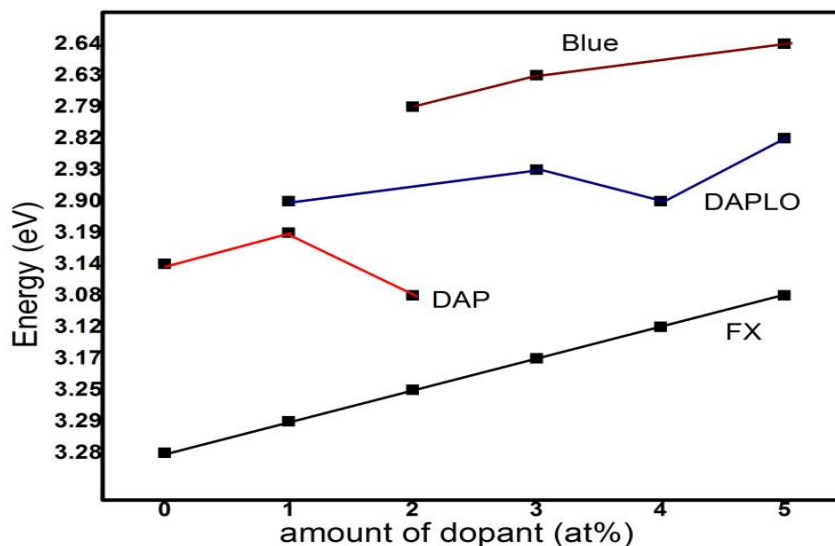


Figure-3

the transition energies obtained from fitted components of free exciton, (FX), donor acceptor pairs (DAP), LO phonon at donor acceptor pair (DAPLO) and colour emission in Zr doped Zinc oxide films

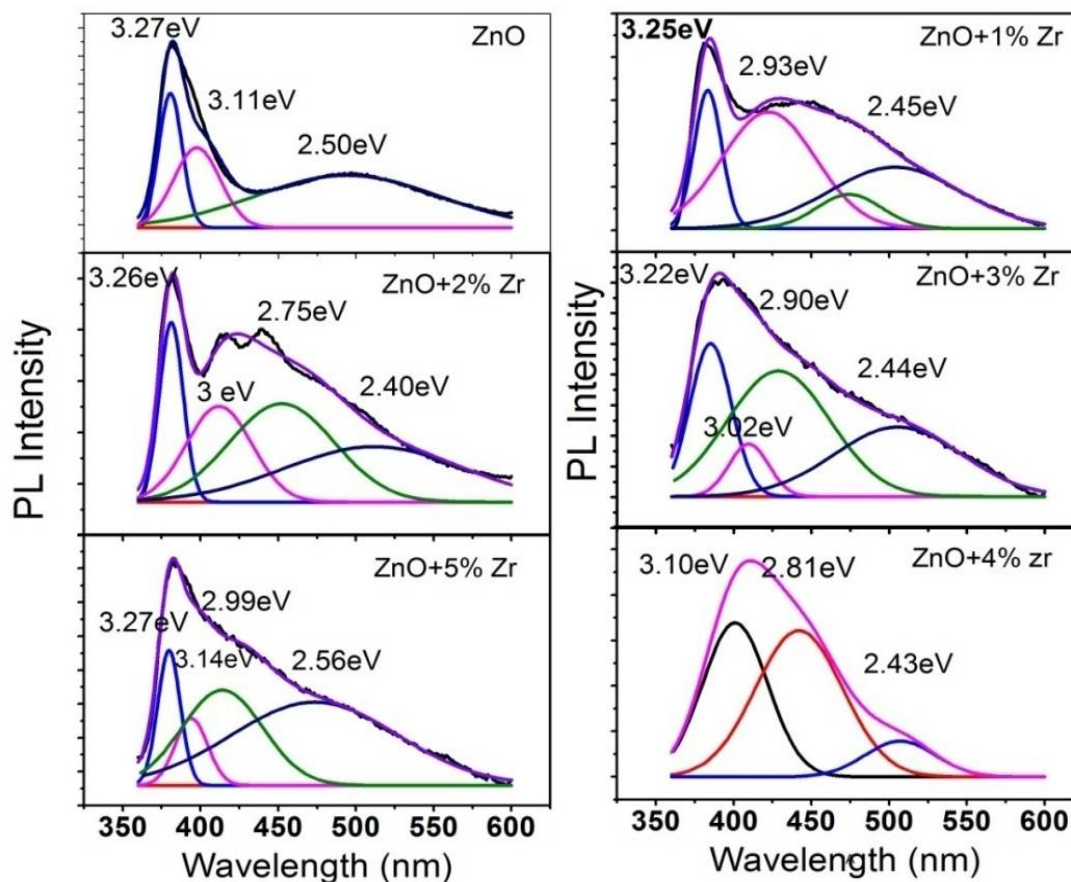


Figure-4

Photoluminescence spectra of vacuum annealed undoped and Zr doped ZnO thin films. The asymmetric shoulders are deconvoluted using Gaussian line-shape; corresponding emissions are indicated in terms of photon energy

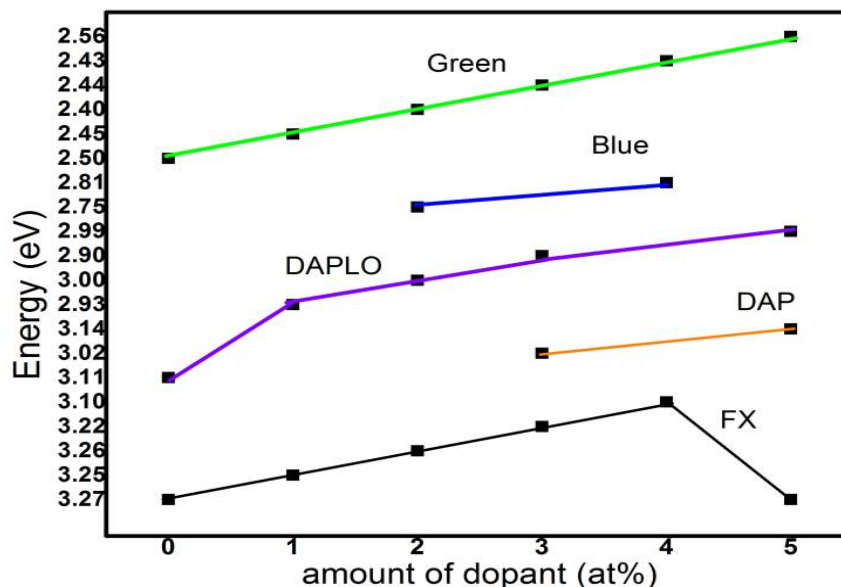


Figure-5

The transition energies obtained from fitted components of free exciton, (FX), donor acceptor pairs (DAP), LO phonon at donor acceptor pair (DAPLO) and colour emission in Vacuum annealed Zr doped Zinc oxide films

Conclusion

ZnO and Zr doped ZnO thin films were grown on quartz substrate at 450°C substrate by automated chemical spray pyrolysis technique. The doping concentration of the films set varied from 1at% to 5at%. The films are further subjected to high temperature annealing at 400°C in a vacuum of 10^{-5} mbar. The structural and optical properties of the films were studied. The structural proof investigated by XRD revealed the phase purity and polycrystalline nature of the films with preferred orientation of (0 0 2) plane and the crystalline quality of films found reduced as Zr doping increases. No detectable change in crystallinity is observed due to vacuum annealing. However, the luminescence bands in ZnO, Zr doped ZnO and vacuum annealed similar samples exhibited an interesting physical phenomenon; the Zr dopants can be used control the intensity and width of ultra-violet emissions and the vacuum annealing is contributed to broad deep level green emissions. These results have practical relevance considering perturbations in excitonic band and colour emissions. The results propose the possibility to modulate the intensity and width of photon emissions in ZnO.

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