

On the origin of blue-green luminescence in spray pyrolysed ZnO thin films

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Abstract Origin of the well-known blue-green emission of spray pyrolysed ZnO thin films has been discussed on the basis of variation of the properties due to different treatment of the samples such as ion beam irradiation and doping. 120 MeV Au ions and 80 MeV Ni ions were used for ion beam irradiation while indium was used for doping studies. It was assumed that, Au ions might have produced huge amount of defects while the defects might be less in Ni irradiated films due to the difference in energy and mass number. Photoluminescence studies of pristine sample showed only one emission at 517 nm at room temperature while the irradiated films showed a decrease in intensity of this emission. Indium doping also reduced the intensity of this emission. But additional emissions were also observed in these films. Based on the observations, we proposed that the blue-green emission was due to the transition from conduction band to the level due to oxygen antisite (O_{Zn}).

Introduction

Zinc oxide (ZnO) is an attractive semiconductor material in optoelectronic applications because of its ultra violet emission and large excitonic binding energy (60 meV) which is much higher than that of ZnSe (20 meV) and GaN (21 meV) [1]. Its application

includes antireflection coatings, transparent electrodes in solar cells, gas sensors and light emitting devices [2]. Also it can be prepared at lower temperature than that of ZnSe and GaN. The luminescence of ZnO films typically consists of near band edge emission and a deep level (blue-green) emission. Owing to these properties, ZnO can be used to make devices for UV or blue emission. Therefore, there are serious efforts to understand the mechanism of these emissions. Researchers have considered that the UV emission could be due to the excitonic transition. But still, controversy exists in explaining the origin of blue-green emission [3].

In this paper, we report on the PL studies of doped and ion beam irradiated ZnO thin films prepared using chemical spray pyrolysed (CSP) technique and we focus only on the emission at 517 nm, which is the controversial blue-green emission of the films. We monitored the change of this emission after different treatment and tried to correlate this with the mechanism we proposed. These results are presented in this paper.

Experimental details

ZnO thin films were prepared over glass substrates, using Chemical Spray Pyrolysis (CSP) technique. Details of the preparation conditions were given elsewhere [4]. Thickness of the film, measured using Stylus profiler (Dektak 6M), was 540 nm and sample area was selected to be $1 \times 1 \text{ cm}^2$ for the further studies.

These films were subjected to ion irradiation with different ion fluences of 120 MeV Au and 80 MeV Ni

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ion beams. Samples were named as ZnO_F1Au (irradiated with Au ions of fluence 1×10^{12} ions/cm²), ZnO_F2Au (irradiated with a fluence of 3×10^{12} ions/cm²), etc. and Ni irradiated samples are named as ZnO_F1Ni (Fluence is 5×10^{11} ions/cm²), ZnO_F2Ni (fluence is 1×10^{12} ions/cm²), etc. Ion beam was focused to a spot of 1 mm diameter and then scanned over 1×1 cm² area using a magnetic scanner so as to get high space homogeneity. Energy of ion beams was selected such that the impact of irradiation was highest. Moreover, the range of these ions was few microns so that no ions were implanted in the film leaving only defects due to the irradiation.

Indium was doped in another set of similar samples. Indium chloride was used as precursor for indium along with the zinc acetate in the precursor solution. Other deposition conditions were kept unchanged. Two different doping concentrations (0.5 and 1 at%) were used for indium and these samples were named as ZnO_0.5In and ZnO_1In for 0.5 and 1 at% doping, respectively. Table 1 summarizes the details of ZnO samples, used in the present study. All these films were characterized with different techniques, but only the results of Photoluminescence (PL) studies will be discussed here, with emphasis on the blue-green emission. Structural analysis was done using X-ray diffraction (XRD) with a Rigaku (D.Max.C) X-ray diffractometer, having CuK_α ($\lambda = 1.5405$ Å) radiation and Ni filter operated at 30 kV and 20 mA. Photoluminescence studies were performed by exciting with 325-nm line from Kimmon He–Cd laser and Michelle 900 spectrograph was used to record the spectrum.

Results and discussion

X-ray diffraction studies showed that the films were preferentially oriented along the (002) plane and with

Table 1 Details of ion fluence of Au and Ni ions and doping percentage of indium

Sample name	Ions/dopants	Ion fluence/doping percentage
ZnO_F1Au	Au	1×10^{12} ions/cm ²
ZnO_F2Au	Au	3×10^{12}
ZnO_F3Au	Au	1×10^{13}
ZnO_F4Au	Au	3×10^{13}
ZnO_F1Ni	Ni	5×10^{11}
ZnO_F2Ni	Ni	1×10^{12}
ZnO_F3Ni	Ni	3×10^{12}
ZnO_F4Ni	Ni	1×10^{13}
ZnO_F5Ni	Ni	3×10^{13}
ZnO_0.5In	In	0.5 at%
ZnO_1In	In	1 at%

the increase in the fluence of Au ions, intensity of this peak considerably decreased (Fig. 1). A monotonic decrease in electrical resistivity was also observed in the irradiated film, with the increase in ion fluence.

PL measurements were recorded at room temperature. Pristine sample showed a broad characteristic peak at 517 nm, which was corresponding to the well-known blue-green emission (Fig. 2). Au ion irradiated ZnO films also showed the emission at 517 nm and a continuous decrease in intensity of this emission was observed with the increase in the ion fluence (Fig. 3). No emission was obtained from ZnO_F3Au. The exact mechanism responsible for the blue-green emission in ZnO has not been completely understood. It was suggested that this peak was associated with copper impurities at a substitutional positions [5], oxygen vacancies, and porosity of the films [6]. Another suggestion was that the blue-green emission in these materials might be related to a transition within a self-activated center, formed by doubly ionized zinc vacancy (V_{Zn}^{2-}) and the ionized interstitial Zn_i or two nearest interstitials [7]. Very recently, Kang et al. [8] suggested that the green emission was related to singly ionized oxygen vacancies. Vanheusden et al. [9] proposed that the green emission might be due to the

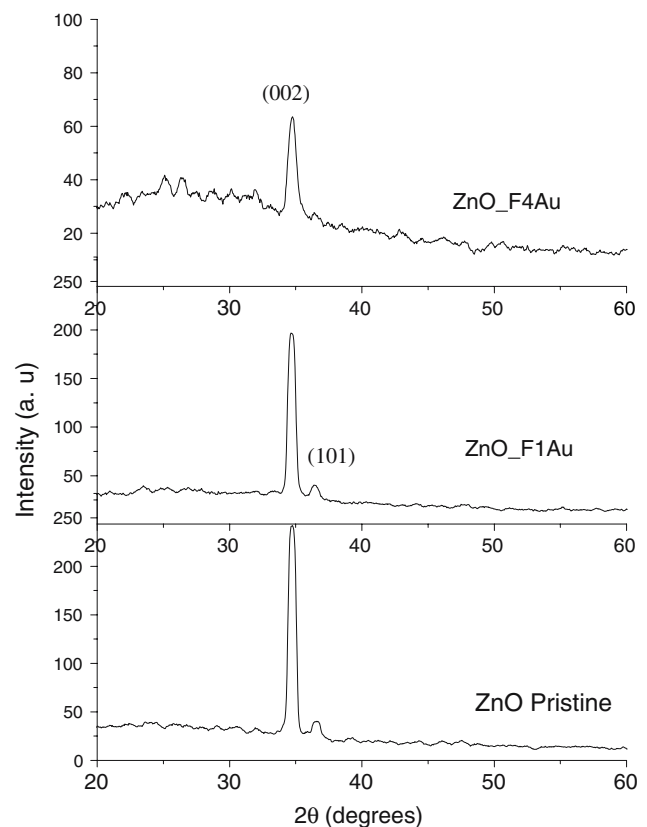


Fig. 1 XRD pattern of pristine and Au irradiated ZnO thin films

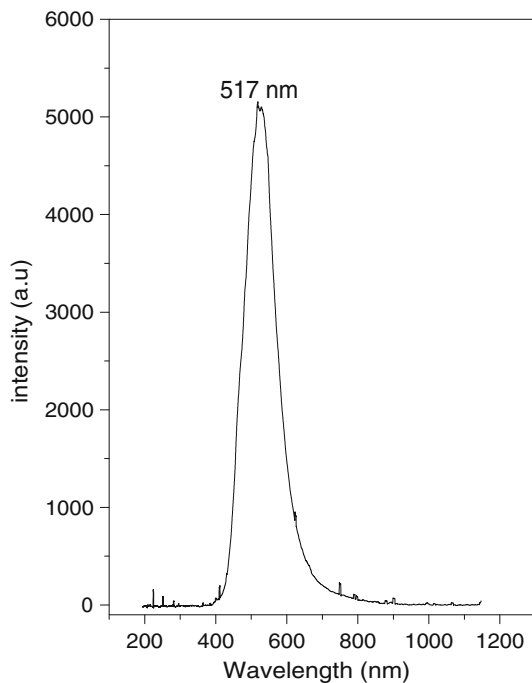


Fig. 2 PL spectrum of Pristine sample

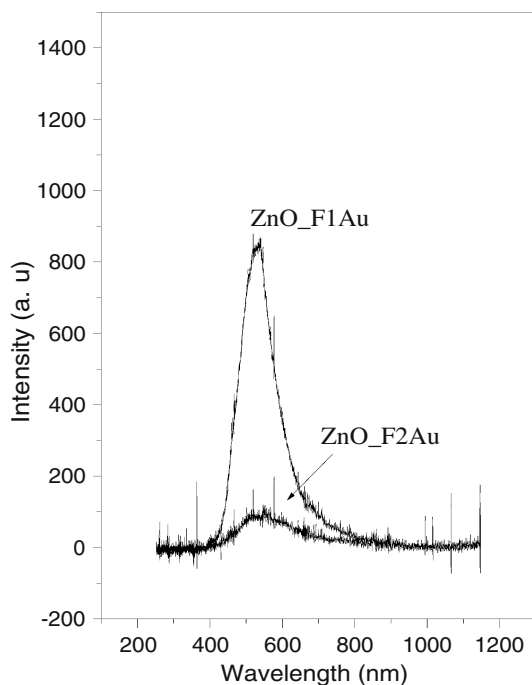


Fig. 3 PL spectra of irradiated films at two different fluences

transition from deep donor levels of oxygen vacancies to the valence band. Egelhaaf et al. [10] reported that the emission was due to the transition between oxygen vacancy (donor) and zinc vacancy (acceptor). Yet another suggestion was that, this emission resulted from the transition between zinc interstitials and zinc

vacancy [11]. It was also reported that origin of green emission was due to the electronic transition from the bottom of the conduction band to the antisite defect O_{Zn} level [12]. Hur et al. [13] also assigned the origin of this emission as due to the antisite oxygen. One of the possible explanations of the observed spectral features of the blue green luminescence for the doped ZnO spray pyrolysed films might be caused by an existence of large number of the trapping levels effectively interacting with phonon sub-systems [14]. Different arguments/suggestions put forward by different authors on the origin of blue-green emission are given in Table 2.

In the case of our undoped ZnO samples, no intentional or unintentional incorporation of copper was done. Also from X-ray photoelectron spectroscopy (XPS) and energy dispersive analysis of X-ray (EDAX) measurements, we could not make out the presence of any trace of copper in the film. Thus the green emission perhaps might not be related to the Cu impurity. Moreover, the decrease in intensity of this emission with increase in ion fluence could not be correlated with the Cu impurity, even if it was present. Hypothesis on porosity was also discarded since the SEM micrograph of ZnO films used in the present study was dense and free of porous (Fig. 4).

According to TRIM calculations, Au ions could produce more than 3,000 vacancies per ion in the ZnO films and earlier calculation showed that the probability of forming oxygen vacancies was more than that of zinc vacancies [15]. Hence if this emission was due to the oxygen vacancies, one could expect an increase in the emission with the increase in the fluence of Au ions. But here intensity was decreasing with increase in ion fluence and hence we propose that oxygen vacancies were not responsible to the blue-green emission at 517 nm.

Table 2 Some of the earlier reports on the possible mechanisms of blue-green emission in ZnO

1st Author	Mechanism	Year of Publication
Garces [5]	Cu impurity	2001
Stdenikin [6]	Oxygen vacancy/porosity	1998
Minami [7]	Transition with in a vacancy–interstitials complex	1981
Kang [8]	Singly ionized oxygen vacancy	2004
Vanheusden [9]	Oxygen vacancy	1996
Egelhaaf [10]	Donor (V_O)—acceptor (V_{Zn})	1996
Xu [11]	Donor (Zn_i)—acceptor (V_{Zn})	2003
Lin [12]	Oxygen antisite	2001
Heo [3]	Donor—deep acceptor	2005
Hur [13]	Oxygen antisite	2003
Kityk [14]	Existence of trapping levels	2002

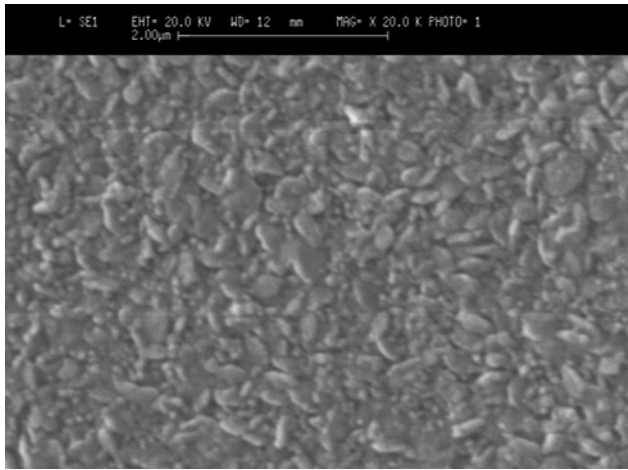


Fig. 4 SEM micrograph of pristine ZnO thin film

Using full-potential linear muffin-tin orbital method, the energy levels of intrinsic defects were calculated earlier [16]. It was shown that the energy interval from the bottom of conduction band to the O_{Zn} level is 2.38 eV, which was in good agreement with the energy of green emission of PL observed in our experiment (2.40 eV). From XPS analysis, we found that the concentration of oxygen decreased on ion irradiation. The decrease in resistivity of ZnO might be due to this reduction in oxygen concentration in the film, since the zinc interstitials and oxygen vacancies were responsible for the conductivity of ZnO films. Hence it was assumed that, due to the irradiation, oxygen was diffused from the film, causing the depletion of the level due to antisite oxygen also. Considering all these facts, we suggest that the characteristic blue-green emission in ZnO film may be due to the antisite oxygen in our samples. As the ion fluence increased, we observed a decrease in the intensity of the PL spectra and this might be due to the fact that as the ion fluence increases, this level due to the antisite oxygen was getting depleted from the sample.

ZnO films were also irradiated using Ni ions and PL spectra were also recorded (Fig. 5). From the figure it was clear that, with the increase in the ion fluence, the emission intensity corresponding to the blue-green emission decreased and the intensity of new emission at 590 nm increased, which was probably due to oxygen vacancies [17]. This result showed that, with the increase of ion fluence, more and more oxygen vacancies were created. Here also, due to the irradiation, the level due to antisite oxygen might be getting depleted from the film. This also proved the role of antisite oxygen in the blue-green emission.

Ni irradiated films were showing more or less same crystallinity quality as that of the pristine (Fig. 6). But

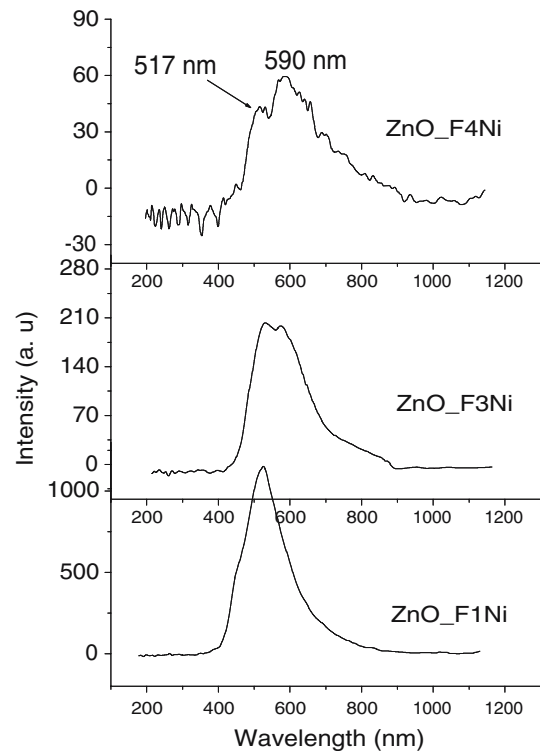


Fig. 5 PL spectra of Ni irradiated films

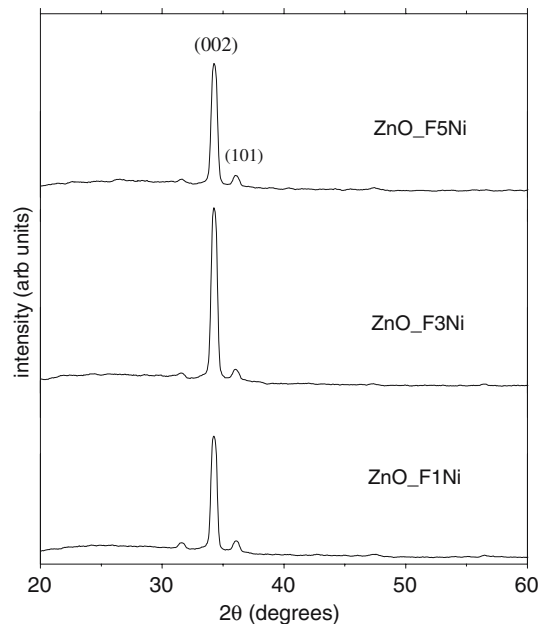


Fig. 6 XRD pattern of Ni irradiated ZnO films

for the Au irradiated films, both crystallinity/grain size and intensity of blue-green emission decreased with increase in the ion fluence. Hence we could not find a direct relation between the crystallinity and emission intensity, since such a relation was not observed in the

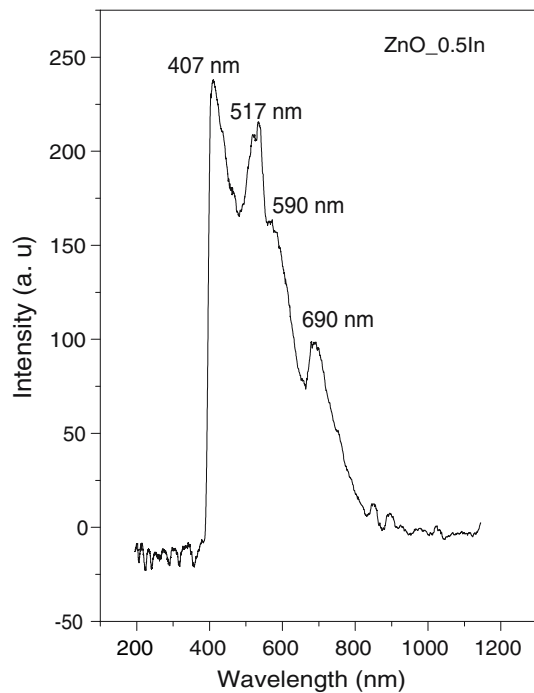


Fig. 7 PL spectrum of indium doped film

case of Ni irradiated films. Even though the emission due to oxygen vacancy (590 nm) was expected to be present in the Au irradiated film, this emission was absent in these samples, probably due to heavy damage created by Au ion.

PL studies on In doped ZnO thin films showed a drastic decrease in the intensity of the blue-green emission (Fig. 7). Again, additional three emissions (407, 590 and 670 nm) appeared in the doped film. The violet emission at 407 nm was probably due to the radiative defects related to the interface traps existing at the grain boundaries and the emission was due to the transition between this level and the valence band [18]. The emission at 690 nm was originated due to the transition from conduction band to the acceptor level, corresponding to oxygen interstitial [19]. When indium was doped in the film, it was assumed that, indium occupied in the zinc lattice site, reducing the probability of forming oxygen at zinc sites. Hence the density of oxygen antisites would be less in the film. This might be the reason for the decrease in intensity of the blue-green emission due to doping. Resistivity of the film decreased with the indium doping at low concentration, which proved the occupancy of indium at zinc site.

Hence according to the detailed analysis of the blue-green emission with different experiments, we were able to conclude that, the mechanism of blue-green emission was strongly associated with antisite oxygen. We suggest that the emission resulted from the transition from conduction band to the acceptor level corresponding to antisite oxygen.

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References

1. Sano M, Miyamoto K, Kato H, Yao T (2004) *J Appl Phys* 95:5527
2. Norton DP, Heo YM, Ivill MP, Ip K, Pearton SJ, Chisholm MF, Steiner T (2004) *Mater Today* 7(6):34
3. Heo YW, Norton DP, Pearton SJ (2005) *J Appl Phys* 98:73502
4. Ratheesh Kumar PM, Sudha Kartha C, Vijayakumar KP, Singh F, Avasthi DK, Abe T, Kashiwaba Y, Okram GS, Kumar M, Sarvesh Kumar M (2005) *J Appl Phys* 97:13509
5. Garces NY, Wang L, Bai L, Giles NC, Halliburton LE, Cantwell G (2001) *Appl Phys Lett* 81:2285
6. Studenikin SA, Golego N, Cocivera M (1998) *J Appl Phys* 84:2287
7. Minami T, Nanto H, Takata S (1981) *J Lumin* 24/25:63
8. Kang HS, Kang JS, Kim JW, Lee SY (2004) *J Appl Phys* 95:1246
9. Vanheusden K, Seager CH, Warren WL, Tallant DR, Voigt JA (1996) *Appl Phys Lett* 68:403
10. Egelhaaf H.-J., Oelkrug D (1996) *J Cryst Growth* 161:190
11. Xu PS, Sun YM, Shi CS, Xu GFQ, Pan HB (2003) *Nucl Instrum Meth Phys Res B* 199:286
12. Lin B, Fu Z, Jia Y (2001) *Appl Phys Lett* 79:943
13. Hur T-B, Jeon GS, Hwang Y-H, Kim H-K (2003) *J Appl Phys* 94:5787
14. Kityk IV, Ebothe J, Hichou AE, Addou M, Bougrine A, Sahraoui B (2002) *J Phys Condens Matter* 14:5407
15. Van Vechten JA (1975) *J Electrochem Soc* 122:419
16. Sun YM (2000) Ph.D. Thesis, University of Science and Technology of China, July 2000
17. Ortiz A, Falcony C, Hernandez AJ, Garcia M, Alonso JC (1997) *Thin Solid Films* 293:103
18. Jin BJ, Im S, Lee SY (2000) *Thin Solid Films* 366:107
19. Wang YG, Lau SP, Zhang XH, Lee HW, Hng HH, Tay BK (2003) *J Crystal Growth* 252:265