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Enhancement in Visible Emission by the Doping of Ce in ZnO Thin Films

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Transparent Ce doped ZnO nanocrystalline thin films with crystallite size less than 46 nm are prepared by sol-gel spin coating method. Band gap increases monotonically from 3.24 to 3.30 eV with increasing doping of cerium up to 2 at. % which leads to band gap widening of 60 meV. UV emission disappears in doped samples and blue emission with continuously increasing intensity is obtained. FESEM shows that the surface consists of microclusters scattered throughout the surface making a network of clusters and voids, and EDX confirms the presence of cerium in the doped samples.

Keywords: Ce doped ZnO, Band gap, Enhanced visible emission.

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1. INTRODUCTION

ZnO is a II-VI semiconductor with wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature which is higher than GaN (24 meV) and ZnS (39 meV). It has various promising applications in the field of optoelectronic devices (like light-emitting diodes, laser diodes), photovoltaics, photocatalysis, and flat panel displays [1-7]. Substitution of a zinc ion by rare earth (RE) group ions generally produces additional electrons and improves the structure, morphology, optical, electrical, thermal, and magnetic properties. Cerium (Ce) is a center of attraction because of partially filled 4*f* shell located in the forbidden gap of ZnO and it influences the photoluminescence (PL) properties of RE-doped ZnO. RE metal ions act as electron trapping agents can trap photoinduced electrons thereby modifying the photoconductivity and photocatalytic activity [2, 3]. There are various methods for depositing ZnO thin films such as pulsed laser deposition, metal organic chemical vapor deposition, spin coating, spray pyrolysis etc. [1]. The sol-gel spin coating method is simpler yet produces good quality films. It allows homogenous mixing of the chemicals at atomic level, thus reducing the possibility of undetectable impurity phases [8]. In the present work, ZnO and Ce doped ZnO thin films have been successfully prepared by sol-gel spin coating. The effect of Ce dopant on optical band gap and photoluminescence are presented.

2. EXPERIMENTAL

2.1 Sample Preparation

For preparation of undoped and Ce doped ZnO films, Zinc acetate dihydrate and Cerium (III) chloride are the starting chemicals. The undoped, 1 and 2 at. % doped precursor solutions of 0.1 M are prepared in ethanol. Monoethanolamine is used to control the viscosity of precursor solution, which has been stirred magnetically at 60 °C for 30 min to get homogeneous solution. All the precursor solutions are aged for 15 days and then spin coated on separate glass slides. Each film consists of 10 layers leading to considerable thickness, each spun at 3000 rpm for 30 s [9]. After each coating, the sample is heated from room temperature to 400 °C for 30 min and finally all the films are annealed at 450 °C for 4 h. The prepared samples are named as a, b and c which are deposited using 0, 1 and 2 at. % Ce doped precursor solutions, respectively.

2.2 Characterization

The crystal phase and crystallinity of the samples is investigated by using X-Ray diffractometer (Model-Rigaku Ultima IV) using CuKα radiation (λ = 1.540598 Å), with a tube voltage of 40 kV and a tube current of 40 mA for 2θ values ranging from 20 to 70°. PL and transmittance spectra have been recorded using fluorescence spectrometer (Model-LS-55, Perkin Elmer) and UV-Vis spectrophotometer (Model-V670, Jasco), respectively. FESEM and EDX (Model-ZEISS) is used for surface morphology and elemental analysis, respectively. All the measurements have been performed at room temperature.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

X-ray diffraction patterns show that all the films are polycrystalline in nature with hexagonal wurtzite structure showing orientations along (100), (002) and (101) planes (Fig. 1). The peak along (002) plane occurs at 2θ = 34.27°, 34.37° and 34.49° for samples a, b and c, respectively. The orientation parameters vary from 0.220 to 0.512 indicating random orientation. Films are highly oriented along the plane (101) in the films. The crystallite size t_{DS} is calculated by the Debye-Scherrer (DS) formula [10] and lies between 32 to 46 nm along preferred planes (100), (002) and (101). The lattice constants *c* of undoped and Ce doped ZnO are calculated

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using the expression reported in Ref. [9] and lattice constants c are found to decrease with increase in doping. The diffraction peak shifts to higher value of 2θ, resulting in a decrease in lattice constant c with respect to doping of Ce. Decrement of c lattice constant may be due to large ionic radius of cerium as compared to zinc. The bond length decreases from 1.989 to 1.974 Å as Ce varies from 0 to 2 at. %. Dislocation density in the film varies randomly from $5.21 \cdot 10^{14}$ to $11.01 \cdot 10^{14}$ lines/m^2 for the undoped and doped samples.

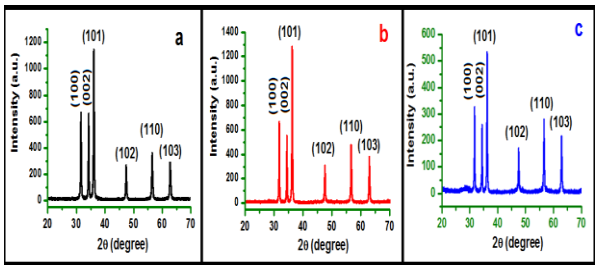

Fig. 1 – XRD patterns of samples a, b and c

3.2 EDX

The EDX patterns confirm the presence of Zn and O as the only elementary species in the undoped sample. The presence of Ce in the doped samples is also confirmed by EDX (Fig. 2). The concentration of Ce is found to be 0.70 and 1.45 at. % whereas the precursor solutions were prepared with 1 and 2 at. % Ce doping.

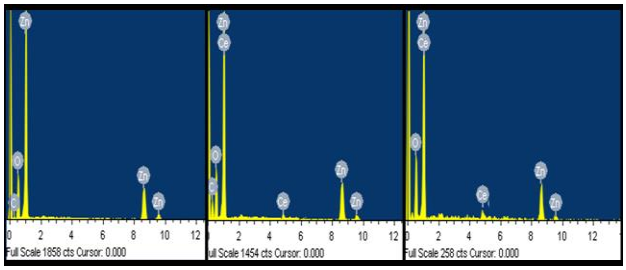

Fig. 2 – EDX spectra of samples a, b and c

3.3 FESEM

FESEM images of the all three samples are shown in Fig. 3. For undoped ZnO, i.e. sample a, the surface consists of microclusters scattered throughout the surface and making a network of clusters and voids. For sample b, these microclusters start to club together and they are completely clubbed for sample c. The porosity of films also increases with increase in dopant concentration.

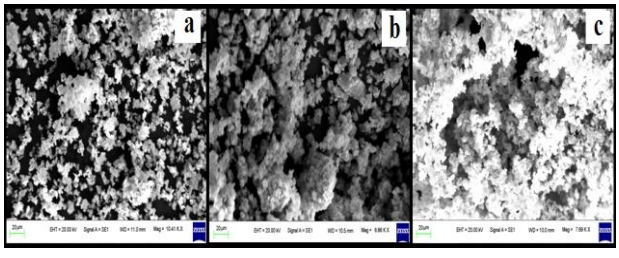

Fig. 3 – FESEM of samples a, b and c

3.4 Optical Transmission and Band Gap

The optical transmittance spectra (Fig. 4) is recorded using UV-Vis-NIR spectrophotometer in the range 300-900 nm. Undoped film is showing 75 to 86 % transmittance in visible and infrared region. There is a sharp cut-off in the transmittance curve near 379 nm which shifts towards lower wavelength with increase in dopant. The transmittance is more for sample b and less in sample c as compared to the undoped sample. Using the transmission data, Tauc's plot [9, 10] is drawn which gives the value of band gap as 3.24, 3.28 and 3.30 eV for undoped, 1 and 2 at. % Ce doped ZnO films respectively. Thus, the widening of 60 meV in optical band gap of ZnO is obtained. The narrowing of band gap in Ce doped ZnO nanoparticles (3.35 to 3.2 eV) is reported by Sharma et al. [7]. There, the reduction in band gap by Ce doping in ZnO happens due to the formation of Ce related, localized, density of states closer to the conduction band minima of ZnO [7].

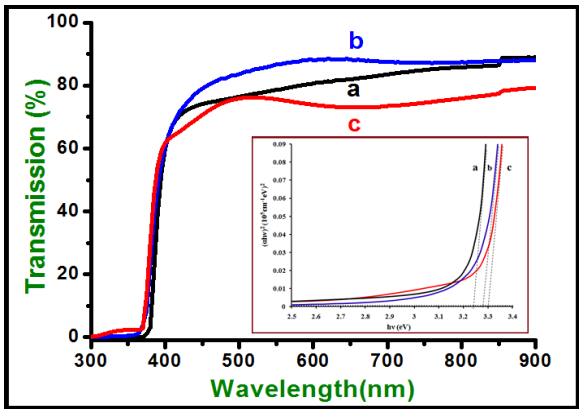

Fig. 4 – Transmission spectra of samples a, b and c. The insets show Tauc's plot, i.e. $(ahv)^2$ versus photon energy

3.5 Photoluminescence

PL spectra for all samples are recorded using excitation wavelength 325 nm. The undoped sample a shows UV emission peak at 389 nm with visible emission at 458 and 489 nm (Fig. 5). The intensity of UV emission is higher than the peaks occurring in visible region.

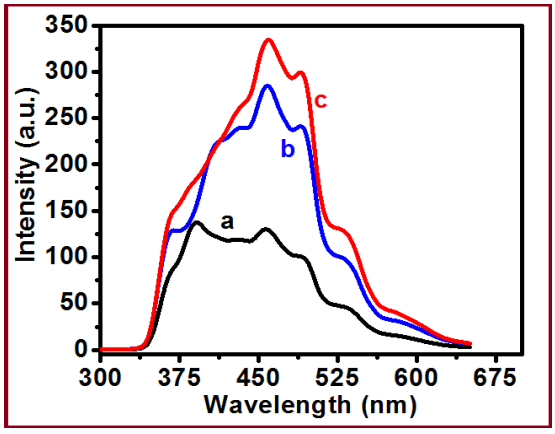

Fig. 5 – PL spectra of samples a, b and c

The UV emission is a near band-edge (NBE) emission which may be due to crystalline quality of the films and is attributed to free and bound exciton recombination, [11, 12]. NBE emission peak disappears in doped samples and intensity of visible emission is increased in doped samples. The intensity of visible emission at 458 nm is increased by 2.4 and 2.9 times for 1 and 2 at. % Ce doping. "The blue emission, centered on ~ 458 nm may be attributed to singly ionized V_{Zn}^{-} and the blue-green emission centered on ~ 489 nm is due to radiative transition of an electron from the shallow donor level of Zn_i to an acceptor level of neutral V_{Zn} is reported in Ref. [1]. Authors previously reported that luminescence in the visible region is usually attributed to intrinsic defects of ZnO which may get enhanced or diminished due to the presence of unintentional impurities or intentional dopants. Oxygen vacancy is accepted to be the most likely defect responsible for luminescence in the visible part of the spectrum [13].

4. CONCLUSIONS

Undoped and Ce doped nanocrystalline films having hexagonal wurtzite structure with crystallite size less than 46 nm are deposited using sol-gel spin coating method. Enhancement of 60 meV in the optical band gap in ZnO thin films is obtained by Ce doping. The band gap increases from 3.24 to 3.30 eV as Ce doping increases from 0 to 2 at. %. The intensity of blue emission is continuously increasing with doping. The intensity of visible emission at 458nm is increased by 2.9 times for 2 at. % Ce doping. FESEM shows that the surface consist of microclusters scattered throughout the surface and making a network of clusters and voids and EDX confirms the presence of cerium in the doped samples.

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REFERENCES

1. N. Kumar, A. Srivastava, *J. Alloy. Compd.* **706**, 438 (2017).
2. N. Wu, Q. Luo, X. Qiao, C-Q. Ma, *Mater. Res. Exp.* **2**, 125901 (2015).
3. B. Chouchene, T.B. Chaabane, L. Balan, E. Girot, K. Mozet, G. Medjahdi, R. Schneider, *Beilstein J. Nanotechnol.* **7**, 1338 (2016).
4. R. Kumar, A. Umar, G. Kumar, M.S. Akhtar, Y. Wang, S.H. Kim, *Ceram. Int.* **41**, 7773 (2015).
5. A. Srivastava, N. Kumar, S. Khare, *Opto-Electron. Rev.* **22**, 68 (2014).
6. N.C.S. Selvam, J.J. Vijaya, L.J. Kennedy, *J. Nanosci. Nanotechnol.* **14**, 2317(2014).
7. D.K. Sharma, K.K. Sharma, V. Kumar, A. Sharma, *J. Mater. Sci.: Mater. Electron.* **27**, 10330 (2016).
8. F.K. Shan, B.I. Kim, G.X. Liu, Z.F. Liu, J.Y. Sohn, W.J. Lee, B.C. Shin, Y.S. Yu, *J. Appl. Phys.* **95**, 4772 (2004).
9. A. Srivastava, N. Kumar, K.P. Misra, S. Khare, *Electron. Mater. Lett.* **10**, 703 (2014).
10. K.P. Misra, R.K. Shukla, A. Srivastava, A. Srivastava, *Appl. Phys. Lett.* **95**, 031901 (2009).
11. J-S. Bae, M-S. Won, J-H. Yoon, B-S. Lee, E.S. Pak, H-J. Seo, J-P. Kim, *J. Anal. Sci. Technol.* **2**, 6 (2011).
12. A. Fatima, S. Devadason, *J. Pure Appl. Ind. Phys.* **1**, 115 (2011).
13. N. Kumar, A. Srivastava, *J. Alloy. Compd.* **735**, 312 (2018).

Посилення видимого випромінювання легуванням Ce в тонких плівках ZnO

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Прозорі нанокристалічні тонкі плівки ZnO, леговані Ce, з розміром кристалітів менше 46 нм отримують методом золь-гелевого спін-покриття. Ширина забороненої зони монотонно збільшується з 3,24 до 3,30 еВ із збільшенням легування церієм до 2 ат. %, що призводить до збільшення ширини забороненої зони на 60 меВ. Ультрафіолетове випромінювання зникає в легованих зразках, і отримується синє випромінювання з постійно зростаючою інтенсивністю. FESEM показує, що поверхня складається з мікрокластерів, розсіяних по всій поверхні, які утворюють мережу кластерів і порожнеч, а EDX підтверджує наявність церію в легованих зразках.

Ключові слова: ZnO, легований Ce; Ширина забороненої зони; Посилене видиме випромінювання.