IOP Conference Series: Materials Science and Engineering (ISSN 1757-8981, eISSN 1757-899X)

Citation Details

Citation for the version of the work held in 'OpenAIR@RGU':

SREEDHARAN, R. S., GANASAN, V., SUDARSANAKUMAR, C., PRABHU, R. and PILLAI, V. P. M., 2014. Highly transparent and luminescent nanostructured Eu203 doped ZnO films. Available from *OpenAIR@RGU*. [online]. Available from: http://openair.rgu.ac.uk

Citation for the publisher's version:

SREEDHARAN, R. S., GANASAN, V., SUDARSANAKUMAR, C., PRABHU, R. and PILLAI, V. P. M., 2014. Highly transparent and luminescent nanostructured Eu203 doped ZnO films. IOP Conference Series: Materials Science and Engineering, 64, 012027.

Highly transparent and luminescent nanostructured EU_2O_3 doped ZnO films

2014 IOP Conf. Ser.: Mater. Sci. Eng. 64 012027

(http://iopscience.iop.org/1757-899X/64/1/012027)

Highly transparent and luminescent nanostructured Eu_2O_3 doped ZnO films

R Sreeja Sreedharan[1], V Ganasan[2], C Sudarsanakumar[3], Radhakrishna Prabhu[4] and V P Mahadevan Pillai[1*]
[1]Department of Optoelectronics, University of Kerala, Kariavattom,
Thiruvananthapuram, Kerala 695581, India.
[2]UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore-452017,
Madhyapradesh, India.
[3]School of Pure and Applied Science, Mahatma Gandhi University, Kottayam, Kerala
686 560, India.
[4]School of Engineering, Robert Gordon University, Aberdeen, U.K
IOP Publishing, Dirac House, Temple Back, Bristol BS1 6BE, UK

[*]E-mail: vpmpillai9@gmail.com

Abstract. Zinc oxide is a wide, direct band gap II-VI oxide semiconductor. Pure and Eu-doped ZnO films are prepared by RF Magnetron sputtering at different doping concentrations (0.5, 1, 3 and 5 wt %). The films are annealed at 500 ^{0}C in air for two hours. The structural, morphological and optical properties of the films are characterized using XRD, micro-Raman, AFM, UV-Visible and photoluminescence spectroscopy. The thickness of the films is measured using stylus profilometer. XRD analysis shows that all the films are highly c-axis oriented exhibiting a single peak corresponding to (002) lattice reflection plane of hexagonal wurtzite crystal phase of ZnO. The micro-Raman spectra analysis reveals the presence of E_2 high mode in all the samples which is the intrinsic characteristic of hexagonal wurtzite structure of ZnO. The appearance of LO modes indicates the formation of defects such as oxygen vacancies in the films. AFM micrographs show uniform distribution of densely packed grains of size with well defined grain boundaries. All the films exhibit very high transmittance (above 80%) in the visible region with a sharp fundamental absorption edge around 380 nm corresponding to the intrinsic band edge of ZnO. All the films show PL emission in the UV and visible region.

1.Introduction

Zinc Oxide (ZnO) is a wide, direct band gap (E_g = 3.3 eV at room temperature) II-VI oxide semiconductor with a large excitonic binding energy of 60 meV at room temperature, making it suitable for exciton-related applications.[1-2] It is highly transparent in the visible region with a sharp cut-off around 380 nm. The band structure and optical properties of ZnO are similar to GaN, which is commonly used for the fabrication of photonic devices in the UV range. Owing to these characteristics, ZnO has attracted much attention for a variety of applications in the field of short wavelength optoelectronic devices such as blue and ultraviolet light emitters, laser diodes, phosphorescent display and photo detectors.[3] It is widely used as transparent conducting electrodes, window material, flat panel displays, gas sensors etc.[4] Several deposition techniques such as pulsed laser deposition (PLD)[5], molecular beam epitaxy (MBE)[6], spin coating[7], chemical vapor deposition

(CVD)[8], spray pyrolysis[9], sputtering[10] etc are employed for the preparation of high quality ZnO thin films. This paper reports the preparation of Eu-doped ZnO films by RF magnetron sputtering and their structural, morphological and optical characterisation using various techniques such as XRD, micro-Raman, AFM, UV-Visible and photoluminescence spectroscopy.

2.Experiment

Europium oxide doped ZnO films are deposited on cleaned quartz substrate at room temperature (300 K) using RF (13.56 MHz) magnetron sputtering technique. Commercially available ZnO powder (Aldrich - purity 99.99%) is mixed with europium oxide powder (Aldrich - purity 99.99%) at different doping concentrations viz.,0, 0.5, 1, 3 and 5 wt % and the pressed pellets are used as the target for sputtering. The sputter chamber is initially evacuated to a pressure of 5×10^{6} mbar. Then argon is admitted into the chamber and argon pressure is maintained at 0.02 mbar. The target is powered through a magnetron power supply (Advanced Energy, MDX 500).The sputtering is carried out under constant RF power of 150 watts for 30 minutes on quartz substrate kept at a distance of 5 cm from the target. The as-deposited films are annealed in air at 500 ^{0} C for two hours. The films thus prepared with different Eu_2O_3 doping concentrations viz.,0, 0.5, 1, 3 and 5 wt % are designated as E0, E0.5, E1, E3 and E5 respectively

The crystalline quality and crystallographic orientation of the films are investigated using X-ray diffraction analysis (Brucker D8 Advance X-ray diffractometer) using Cu Kα1 radiation of wavelength 1.5406 A^{o} in the 2Θ range 20-70^{o}. The phonon vibrational modes of the films are recorded using micro-Raman spectrometer (Labram HR-800) with 514 nm argon ion laser as an excitation source at a spectral resolution of 1cm^{-1}. The surface morphology of the samples is investigated using AFM (Digital Instruments Nanoscope III) analysis. The transmittance, reflectance and absorption spectra of the films in the spectral range 200-900 nm.are measured using JASCO v-550, UV-visible double beam spectrometer. The thicknesses of the samples are measured using Dektak stylus profilometer. Photoluminescence spectra of the samples are recorded using Horiba Jobin Yvon Fluralog III modular spectro flourometer.

3 Results and Discussion

3.1. XRD Analysis

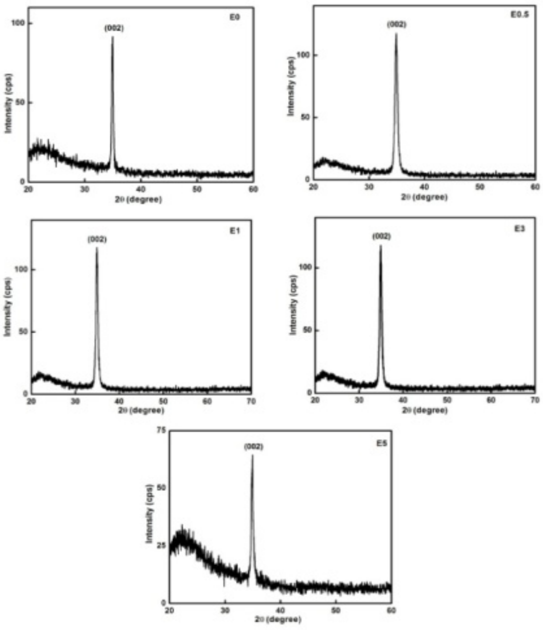

Figure 1: X-ray diffraction patterns of Eu_2O_3 doped ZnO films for different Eu_2O_3 doping concentrations

The X-ray diffraction analysis shows that all the films present a single sharp intense peak corresponding to (002) lattice reflection plane of hexagonal wurtzite structure of ZnO (JCPDS card No-75-0576)[11]presenting a single crystalline like structure with c-axis orientation due to lowest surface free energy of (002) lattice reflection plane.[12-]There is a slight enhancement in intensity of (002) peak with moderate Eu_2O_3 doping concentrations (up to 3 wt%). But in 5wt% Eu_2O_3 doped film, there is a reduction in intensity of (002) peak. The FWHM of the Eu_2O_3 doped films are found to be greater than that of undoped film. The stress introduced due to the mismatch of ionic radii of Zn (Zn^{2+} = 0.74Aº) and Eu (Eu^{3+} = 1.07Aº) can be the reason for enhanced FWHM of the (002) peak in Eu_2O_3 doped ZnO films compared to the undoped ZnO film.[13-14]

The c-values of all the films are found to be greater than the JCPDS value indicating that the crystallites are in a state of tensile stress. The increase in the out of plane c lattice constant indicates the expansion of the lattice due to the substitution of Eu^{3+} at Zn^{2+} sites. The introduction of dopant and lattice mismatch between film and substrate introduces strain in the film which can affect the structure and properties of the film to some extent. The positive value of stress indicates that the crystallites are in a state of tensile stress and is found to be decreasing from 5.54 - 4.93GPa with Eu doping. The average size of the crystallites in the films are estimated using the following Debye-Scherrer' formula and is found to be in the range 16-27 nm showing the nanostructured nature of the films.

3.2. Micro-Raman analysis

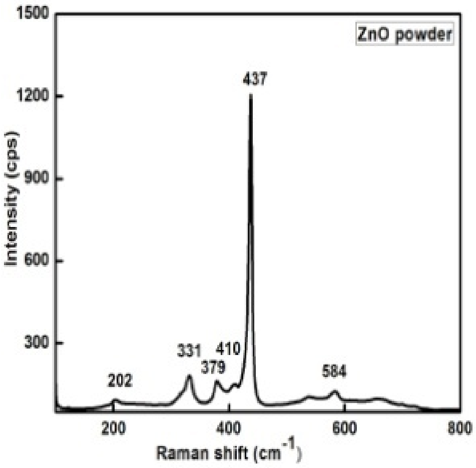

Figure 2: Micro Raman spectra of ZnO powder

Figure 2 shows the micro-Raman spectrum of bulk ZnO powder. The Raman spectrum of ZnO powder presents a very intense band at 437 cm^{-1} corresponding to E_2 high mode which is the intrinsic characteristic of hexagonal wurtzite structure of ZnO. This mode is related to the vibration of oxygen atoms and is considered as the Raman fingerprint of ZnO.[15-17] The Raman spectrum also shows medium intense band at 331 cm^{-1} and weak bands at 202, 379, 410 and 584 cm^{-1}. The band at 584 cm^{-1} can be due to E_1 (LO) mode which is associated with the formation of various crystal defects such as oxygen vacancy, zinc interstitials or other defect states.[18] The bands at 331 cm^{-1} and 379 cm^{-1}can be due to A_1 (TO) mode and E_1 (TO) mode respectively. The micro-Raman spectra of undoped ZnO and Eu_2O_3 doped ZnO films (figure not included) present an intense Raman band around 437 cm^{-1} which supports the presence of wurtzite ZnO phase in the films. The presence of E_1 (LO) mode at 581 cm^{-1} with appreciable intensity in all the films is an indication of the presence of various crystal defects such as oxygen vacancy, zinc interstitials or other defect states in them. Compared to the Raman spectrum of ZnO powder (bulk), the Raman spectra of films present a broad spectral feature. Here the ZnO is deposited on amorphous quartz substrate and the films can have residual stress. The broad nature of Raman spectra of the films can be due to this residual stress. The measured thickness of the films is in the range 83-94 nm and hence the spectral contribution from the substrate can also be expected in the Raman spectra of the films. The medium intense band around 488 cm^{-1} can be due to the vibration from the quartz substrate. Compared to the Raman spectra of other films, the Raman spectrum of 5% Eu_2O_3 doped film presents broader spectral feature. This can be attributed to the decline in crystallinity due to the higher doping concentration in this film as observed in the XRD analysis. Also the medium intense band observed in the Raman spectrum of E5 can be due to intrinsic host lattice defects such as oxygen vacancies and zinc interstitials.[19]

3.3.AFM analysis

The AFM (3D) images of undoped and Eu_2O_3 doped ZnO films are shown in Figure 3. AFM image of undoped ZnO film presents uniform distribution of densely packed grains of almost same size (around 45 nm) with well defined grain boundaries. The surface morphology of the Eu_2O_3 doped films presents the distribution of grains of varying sizes throughout the film. The films with Eu_2O_3 doping concentration 0.5 and 1 wt% show higher values of rms surface roughness compared to that of the other films. The variation of the grain size with Eu_2O_3 doping concentration obtained from the AFM analysis keeps the same trend as obtained from XRD analysis.

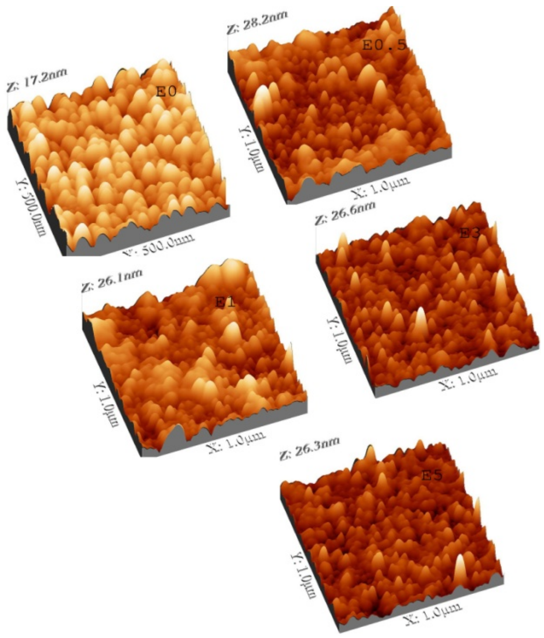

Figure 3. AFM (3D) pictures of ZnO films with different Eu_2O_3 doping concentrations

3.4.Optical properties

Figure 4 shows the transmittance spectra of undoped and Eu_2O_3 doped ZnO films recorded in the wavelength range 200 – 900 nm. Average transmittance of the films in the wavelength range 400 – 900 nm are calculated and found that all films show very high transmittance above 85%. For all the films the transmittance exhibits a sharp reduction at around 380 nm corresponding to the fundamental absorption of ZnO. The sharp absorption onset in the UV- region and high transmittance in the visible region indicates the good crystalline and optical quality and direct band gap nature of the films. The oscillations observed in the transmission and reflection spectra (figure not given) of the films can be due to the interference of light arising from the difference in refractive indices of the film and the substrate. This interference of multiple reflections arising from the film and substrate surface shows the thickness uniformity of the films. These oscillations in the spectra indicate that smooth films are formed on quartz substrate as evident from the AFM analysis.[20-21] This reduces the scattering loss at the surface. [22]

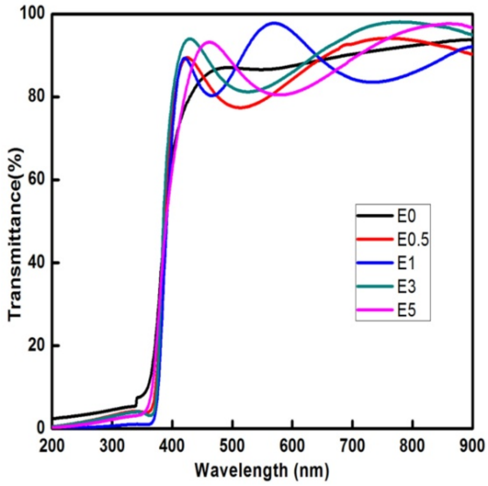

Figure 4: Optical transmittance spectra of undoped and Eu_2O_3 doped ZnO films

The optical band gap of the films are calculated using the Tauc plots. Undoped film shows a band gap of 3.24 eV and Eu_2O_3 doped films show higher values of band gap energy. There are several reasons for the shift of band gap in the films such as improvement or reduction in crystallinity, modification in barrier height due to the change in crystallite dimension, quantum size effect, change in the density of impurities, tensile or compressive strain in the films etc.[23] It can be expected that the contribution from Eu^{3+}ions on substitutional sites of Zn^{2+}ions and Eu-interstitial atoms determine the widening of the band gap caused by increase in carrier concentration. Typically the blue shift of the absorption edge of the Eu_2O_3 doped ZnO films is associated with an increase in the carrier concentration blocking the lowest states in the conduction band, the well known Burstein-Moss effect.[24]

3.5.Photoluminescence Spectra

The PL spectra of undoped and Eu_2O_3 doped ZnO films recorded using excitation wavelength of 325nm. The undoped film shows PL emission in the UV and visible regions. The intense UV emission in ZnO film arises from the near band edge emission due to the free excitonic emission of ZnO. The weak visible emission at 450, 540 and 570 nm can be due to the defects such as oxygen vacancy, Zn interstitials, antisite oxygen etc in the films.[25-26]In the doped films the intensity of the UV emission decreases and the emissions in the visible region enhances its intensity. The film with 5wt% Eu_2O_3 doping concentration show highest visible PL intensity. Europium doping in the ZnO lattice introduces defects in the lattice such as oxygen vacancies, zinc interstitials etc. The Raman spectrum of 5 wt% Eu_2O_3 doped ZnO film presents defect related vibrational mode at 288 cm^{-1}. The enhanced PL intensity in the visible region observed in Eu_2O_3 doped films can be due to the enhanced defects introduced in the ZnO lattice by Eu_2O_3 doping.

4 Conclusion

Highly c-axis oriented Eu_2O_3 doped ZnO films with good structural and optical quality are prepared using RF magnetron sputtering technique. The X-ray diffraction analysis shows that all the films present a hexagonal wurtzite structure of ZnO. The presence of an intense Raman band around 437 cm^{-1} corresponding to E_2 high mode in the micro-Raman spectra of undoped ZnO and Eu_2O_3 doped ZnO films supports the presence of wurtzite ZnO phase in the films. AFM images present a smooth surface morphology for all the films. Average transmittance of the films in the wavelength range 400 – 900 nm are calculated and found that all films show very high transmittance above 85%. The blue shift in the band gap energy observed in the Eu_2O_3 doped ZnO films due to Burstein-Moss effect. The enhanced PL intensity in the visible region observed in Eu_2O_3 doped films can be due to the enhanced defects introduced in the ZnO lattice by Eu_2O_3 doping.

5 . References

[1] Klingshirn 1975 Phys. Status Solidi B **71**547.

[2] Shan F K, Liu G X, Lee W J, Shin B C 2007 J. Appl. Phys **101** 053106.

[3] Lu J G, Fujita S, Kawaharamura T, Nishinaka H and Kamada Y 2008 Phys. Stat. Sol.(c) **5** 3088 .

[4] Sun X W, Kwok H S, 1999 J. Appl. Phys **86** 408**.**

[5] Tsoutsouva M G, Panagopoulos C N, Papadimitriou D, Fasakic I and Kompitsas M 2011 Materials Science and Engineering B **176** 480

[6] Heo Y W, Ip K, Pearton S J, Norton D P and Budai J D 2006 Applied Surface Science **252** 7442

[7] Smirnov M, Baban C and Rusu G I 2010 Applied Surface Science **256** 2405.

[8] Tan S T, Chen B J, Sun X W, Fan W J, Kwok H S, Zhang X H and Chua S J 2005 J.Appl. Phys.**98** 013505.

[9] Lehraki N, Aida M S, Abed S, Attaf N, Attaf A and Poulain M 2002 Curr. Appl. Phys. **12** 1283.

[10] Suvorova N A, Usov I O, Stan L, DePaula R F, Dattelbaum A M, Jia Q X and Suvorova A A 2008 Appl. Phys. Letters **92** 141911.

[11] Culity B D 1978 *Elements of X-Ray Diffraction* (Addison-Weseley) p.102.

[12] Deng H, Ressel J J, Lamb R N and Jiang B 2004 Thin solid Films **458** 43.

[13] Fujimura N, Nishihara T, Goto S, Xu J, Ito T 1993 J. Cryst. Growth **130** 269.

[14] Zhang Y Z, Liu Y P, Wu L H, Xie E Q and Chen J T 2009 J. Phys. D: Appl. Phys. 42085106.

[15] Ilican S, Caglar Y and Caglar M 2008 J Optoelectronics and Advanced Materials **10** 2578.

[16] Vinodkumar R, Navas I, Chalana S R, Gopchandran K G, Ganesan V, Reji Philip, Sudheer S K and Mahadevan Pillai V P 2010 Applied Surface Science **257** 708.

[17] Sharma S K and Exarhos G J 1997 Solid State Phenom. **55** 32.

[18] Soni B H, Deshpande M P, Bhatt S V, Chaki S H and Sathe V 2013 J.Appl.Spectros. **79 901**

[19] Scepanovic M, Srećkovic T, Vojisavljevic K and Ristic MM 2006 Sci. of Sint. **38** 169.

[20] Swanepoel R 1983 J. Phys E. Sci. Instrum.**16** 12.

[21] Moshfegh A Z, Azimirad R, Akhavan O 2005 Thin Solid Films **484** 124.

[22] Rambu A P, Sirbu D, Sandu A V, Prodanand G and Nica V 2013 Bull. Mater. Sci.**36** 231.

[23] Suchea M, Christoulakis S, Kartharakis M, Vidakis N and Koudoumas E 2009 Thin Solid Films **517** 4303

[24] Burstein E 1954 Phys. Rev. **93** 632.

[25] Chen Y, Bagnall D M, Koh H J, Park K T, Hiraga K, Zhu ZQ and Yao T 1998 J. Appl. Phys. 84 3912.

[26] Vinodkumar R, Navas I, Porsezian K, Ganesan V, Unnikrishnan N V and Mahadevan Pillai V P2014 Spectrochimica Acta Part A: **118** 724