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Visible luminescence from highly textured Tb^{3+} doped RF sputtered zinc oxide films

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ABSTRACT

Highly transparent, luminescent, c-axis oriented Tb^{3+} doped ZnO films are prepared by RF magnetron sputtering technique. The structural, morphological, optical and luminescence properties of these films are investigated as a function of Tb^{3+} doping concentration by X-ray diffraction (XRD), micro-Raman spectroscopy, atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), spectroscopic ellipsometry, UV-Visible spectroscopy and photoluminescence spectroscopy. The as-deposited films are found to be highly crystalline with wurtzite hexagonal phase of ZnO. The characteristic features of hexagonal wurtzite structure of ZnO, particularly the appearance of non-polar E_2 modes are easily identified from the Raman spectra of the films. The surface morphology of the films revealed by FESEM and AFM images present a dense distribution of grains. The elemental analysis carried out using energy dispersive X-ray (EDX) spectra confirms the incorporation of Tb^{3+} ions in the ZnO lattice. The films are highly transparent in the visible region. Using ellipsometric analysis, the variation of refractive index, dielectric constant and thickness of the films are studied as a function of Tb^{3+} doping concentration. The photoluminescence spectra of the Tb^{3+} doped ZnO films recorded using an excitation radiation of wavelength 325 nm from a He-Cd laser exhibit visible luminescence ~430, 490, 516 and 542 nm. The origin of visible emissions ~490 and 542 nm in the doped films can be attributed to $5D_4 \rightarrow 7F_6$ and $5D_4 \rightarrow 7F_5$ transition of Tb^{3+} ion respectively. The intensity of the emission at 542 nm is found to be decreasing at higher doping concentration due to concentration quenching effect. The blue emission in the films can be attributed to the electron transition from shallow donor level formed by interstitial Zn atoms to the top of the valence band. The origin of the visible emission ~516 nm is attributed to antisite oxygen defects in ZnO.

1. Introduction

The large exciton binding energy (60 meV) of zinc oxide (ZnO) leads to strong near band edge (NBE) excitonic emission at room temperature and even at high temperatures because its binding energy is much greater than the thermal energy at room temperature ($K_BT = 25$ meV) [1]. Hence, lasing action based on exciton recombination can be expected from ZnO nanostructures [2]. ZnO is a good substrate material for the fabrication of light emitting diodes and laser diodes due to its isomorphic structure and lattice matching in thin film form with GaN, which is commonly used for these applications [3]. Room temperature UV lasing from ZnO films have been demonstrated by many researchers [4,5]. ZnO possess some unique properties such as wide direct band gap nature, high transparency in the visible region, thermal and chemical stability, large piezoelectric coefficient, non-toxicity, low cost etc. ZnO can be doped with a wide variety of materials to tune its optical, electrical and luminescence properties making it suitable for technological applications such as transparent conducting electrodes in solar cells, flat panel displays, chemical sensors etc. [6,7].

The optical emission behavior of ZnO is the most important property for its luminescence applications. ZnO usually show two luminescent emissions; a narrow peak in the UV region due to near band edge (NBE) emission and a broad visible emission originating from the intrinsic defects in ZnO [8]. Even though many investigations are done so far, the exact mechanism of visible emission in ZnO is not clearly understood [9]. The optical properties of rare earth doped semiconductors are expected to be

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modified remarkably [10]. In rare earth ions, the luminescence is caused by 4f intrashell transitions. The 4f shell in rare earth ions is shielded by outer electron shells, which gives rise to a series of discreet energy levels [11]. Hence Tb^{3+} ion can exhibit typical PL spectra under UV excitation with its fluorescence wavelength extending from UV to IR range when incorporated in to a suitable host material [12,13]. The emission from Tb^{3+} ion is a series of lines mainly centered ~489, 548, 588 and 620 nm corresponding to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions respectively [12]. Among these transitions, the emission ~548 nm is the most intense one [11]. Hence Tb^{3+} ions are potential candidate to obtain green emission due to their intense $^5D_4 \rightarrow {}^7F_5$ transition. The intense line spectra are the typical feature of isolated ions. But the emissions become broader as the rare earth ion interact with the host lattice. Rare earth ion may stabilize intrinsic defect sites, which could also give rise to broad visible emission in ZnO [14]. White light emission can be obtained from rare earth doped ZnO which originates from the intrinsic defects as well as the rare earth emissions from the ZnO matrix [15].

The reports on visible luminescence from Tb^{3+} doped ZnO films are scanty. Fang et al., prepared ZnO:Tb films at a substrate temperature of 250 °C and observed that Tb doping stimulate the grain growth of ZnO films, the PL properties are not investigated [16]. Ziani et al. [15] and Teng et al. [17] investigated the effect of post-annealing treatment on the structural and optical properties of Tb doped ZnO films prepared by RF sputtering. Both of them observed an improvement in growth orientation along (002) direction with increase in annealing temperature up to a certain limit. Falcony et al. [18] deposited Tb doped ZnO films at substrate temperature varied from 270–400 °C using spray pyrolysis. Wu et al. [19] reported the synthesis of Tb doped ZnO films by Ion-beam sputtering. Some works dealing with the synthesis of Tb doped ZnO nanoparticles by wet chemical route [20], sol-gel technique [21] and Tb doped nanocrystals by colloidal synthesis [22] and Tb implantation in ZnO [14] are also available in literature.

ZnO films with different Tb^{3+} doping concentrations are fabricated at room temperature using RF magnetron sputtering technique. The structural, morphological, optical and luminescent properties of the as-deposited films are studied extensively using techniques like, XRD, micro-Raman spectroscopy, atomic force microscopy, scanning electron microscopy, EDS analysis, spectroscopic ellipsometry, UV-visible spectroscopy and photoluminescence spectroscopy.

2. Experimental

Pure and Tb^{3+} doped ZnO films were fabricated on cleaned quartz substrates using RF magnetron sputtering technique. Commercially available ZnO power (Aldrich 99.99%) was mixed well with Tb_2O_3 powder (Aldrich 99.99%) with desired Tb doping concentrations (0, 0.5, 1, 2, 3 and 5 wt%) and the mixer was thoroughly ground using agate mortar and pestle. The pressed powder of the mixer was used as the target for film preparation. The deposition was carried out at room temperature inside a vacuum chamber evacuated initially to a base pressure of 3×10^{-6} mbar using a diffusion pump and a rotary pump. Argon gas was then admitted in to the chamber and argon pressure was maintained at 0.02 mbar. An RF power of 150 W operating at 13.56 MHz (Advanced Energy, MDX 500) was used for the deposition of the films. The films were fabricated on cleaned quartz substrates kept at a distance of 5 cm from the target surface and the deposition was done for duration of 45 min. The as-prepared films with Tb^{3+} doping concentrations 0, 0.5, 1, 2, 3 and 5 wt% are designated as T0, T0.5, T1, T2, T3 and T5 respectively.

The structural properties and crystallographic orientation of the films were characterized by X-ray diffraction technique (Brucker AXS D8 Advance X-ray diffractometer) using Cu $K\alpha_1$ radiation of wavelength 1.5406 Å. The X-ray diffractograms were recorded in the Bragg-Brentano $\theta-2\theta$ configuration with 0.0203° angular step size in the 2θ range 10–70°. The vibrational spectra of the films were recorded using micro-Raman spectrometer (Labram-HR 800) with a spectral resolution of 1 cm^{-1} using an excitation radiation of wavelength 514.5 nm from an argon ion laser. The surface morphology of the films was characterized using atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). AFM (Brucker – Dimension edge with scan Asyst having nanodrive) measurements were carried out using Si tip on nitride lever having force constant 0.4 N/m. The AFM data were analyzed using Nanoscope software. FESEM measurements were carried out using Nano SEM-450 (FEI-Nova Model No. 1027647) equipped with XFlash detector 6/10 (Bruker). The elemental analysis of the films was carried out using energy dispersive X-ray spectrometer (EDS) (Quantax 200). The thickness and optical constants of the films were estimated using spectroscopic ellipsometry (Horiba Jobin Yvon MM 16). The thickness of the films was also measured using lateral FESEM measurements. The transmittance spectra of the films were recorded in the spectral range 200–900 nm using UV-visible double beam spectrometer (JASCO V-550). The photoluminescence spectra were recorded by Flourolog III modular spectroflourometer (Horiba Jobin Yvon) equipped with a photomultiplier tube (Hamamatsu R928-28) using an excitation wavelength of 325 nm from a He-Cd laser (Kimmon Koha).

3. Results and discussions

3.1. Structural properties

Fig. 1 shows the micro-Raman spectra of the undoped and Tb^{3+} doped ZnO films. ZnO with wurtzite structure belong to space group C_{6v}^4 with two formula units per primitive cell, all the atoms occupying the C_{3v} site. Group theoretical analysis based on Fately et al. [23] yields the following nine optical modes at the centre of the Brillouin zone,

$$\Gamma_{opt} = A_1(IR, R) + 2B_1 + E_1(IR, R) + 2E_2(R) \quad (1)$$

Of these, the B_1 modes are silent modes and other modes are Raman active [24]. The Raman spectra of the undoped and Tb^{3+} doped films present almost similar patterns indicating that the structure of ZnO is not altered much due to Tb^{3+} doping. The characteristic features of hexagonal wurtzite structure of ZnO, particularly the appearance of non-polar E_2 modes can easily be identified from the Raman spectra of the films. Since the light penetration depth of 514.5 nm laser is greater than the thickness of the films, the contribution from quartz substrate is also observed in the Raman spectra of all the films ~490 cm^{-1}. The broad nature of the Raman bands in films may be attributed to the effect of substrate contribution, structural disorder, residual stress, defects in the films etc.

All the films present E_2 (Low), 2 E_2 (Low), E2 (High), E_1 (LO) and E_2 (High)-E_2 (Low) modes. The low and high frequency E_2 modes are associated with the vibration of Zn sub-lattice and oxygen atoms respectively [25]. The appearance of intense and sharp E_2(High) mode in the undoped as well as Tb^{3+} doped ZnO films around 437 cm^{-1} (Table 1) indicates the preservation of wurtzite hexagonal structure with good crystalline nature. The intensity of this band is higher in T2 film. In the Raman spectra of all the films, the E_2 (Low) mode is observed around 100 cm^{-1} with high