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Deep level defect correlated emission and Si diffusion in ZnO:Tb^{3+} thin films prepared by pulsed laser deposition

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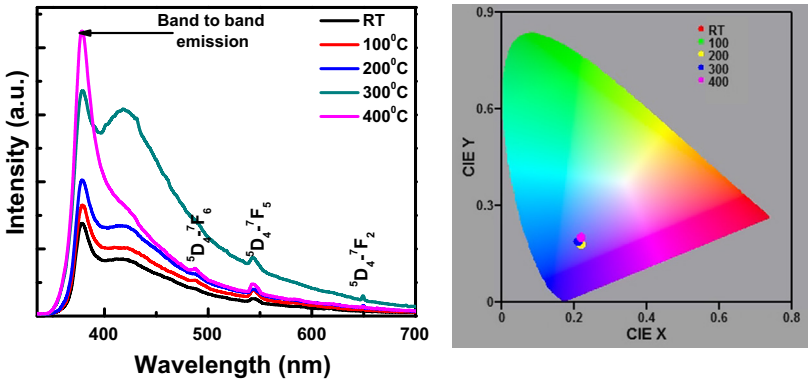
GRAPHICAL ABSTRACT



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ABSTRACT

Terbium (Tb^{3+}) doped zinc oxide (ZnO) or (ZnO:Tb^{3+}) thin films were grown on silicon substrates by the pulsed laser deposition technique at different growth temperatures that were varied from room temperature (RT) to 400 °C. The effects of substrate temperature on the structural and optical properties of the ZnO:Tb^{3+} films were investigated by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and RT photoluminescence spectroscopy. The band to band and deep level defect emissions were observed for all substrate temperatures. The silicon that has diffused from the substrate has occupied the position of the Zn vacancies in the ZnO:Tb^{3+} thin films at the higher substrate temperatures (400 °C). A blue emission was observed for all the ZnO:Tb^{3+} thin films deposited at the different substrate temperatures.

1. Introduction

Nowadays, the use of semiconducting materials in the form of thin films is very common in both the basic as well as applied research. Zinc oxide (ZnO) is a technologically useful material due to its wide band gap of 3.37 eV. Furthermore, ZnO has other advantages such as high chemical and physical stability, thermal stability in hydrogen plasma atmosphere, large exciton binding energy of 60 meV, ease of preparation and high electrical conductivity, usability in solar cells [1], ultraviolet (UV) lasers [2], light emitting diodes [3], and UV detectors [4]. ZnO thin films have been prepared using several deposition techniques such as chemical

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vapor deposition [5], atom beam sputtering [6], pulse laser deposition (PLD) [7] and sol–gel [8]. Compared with other thin film deposition techniques, PLD has many advantages such as; the composition of the films grown by PLD is quite close to that of the target, the surface of the films is very smooth; good quality films can be deposited at room temperature due to the high kinetic energies of atoms and ionized species in the laser-produced plasma. Especially ideal for films with complex stoichiometry in which the films consist of the same stoichiometry after deposition [9]. So that PLD is more preferred to the fabrication process of the optoelectronic devices [10].

The composition of films grown by PLD is quite close to that of the target, even for a multi component target. Pulsed laser deposited films may be crystallized at deposition temperatures lower than those of other physical vapor deposition techniques due to the high kinetic energies of the ionized and ejected species in the laser plumes [11]. However, the problem of efficient doping and controlling the properties of the films has remained to be solved as another technological issue. The substrate temperature of the film is one of the most important parameters in the film deposition process. It can enormously affect the crystallinity of the film, which can change the structural, optical and electrical properties of the film [12]. However, only a few studies of PLD deposition at different substrate temperature conditions were reported [13,14] but the role of substrate temperature on the defect related emission is still not very clear. Considerable interest is still growing on the investigating of the role of substrate temperature on the ZnO thin film because of their great potential for optical applications. Rare earth (RE) doped ZnO systems have been attracting much interest for possible applications in high power lasers, visible emitting phosphors in displays and other optoelectronic devices [15]. It has been found that the optical properties of RE^{3+} doped ZnO depend on the dopant concentration, host structure and fabrication process. It is well known that the substrate temperature not only improves the crystal quality of thin films but also leads to the reaction between the film and the dopant as well as the substrate [16]. There are two main factors leading to the stable and sharp luminescence in RE elements: one is that the 4f orbital of the RE^{3+} ions is shielded by the outer 6s, 5p and 5d orbitals, which weakens its coupling with the surrounding ligands; the other is that the f–f transitions are parity forbidden, thus resulting in small absorption cross sections [17], but the initial efforts of incorporating RE ions into Si and other narrow band gap semiconductors suffered severe limitations due to the solubility constraints and the thermal quenching [18,19]. Tb^{3+} is one of the RE's that is a suitable choice for doping in a host matrix because it has a relatively large absorption region and a bright green emission. The photoluminescence properties of Tb^{3+} ions in the different host material have been extensively reported [20,21]. Tb^{3+} doped green phosphors are used in three band fluorescent lamps [22], projection television tubes [23], and X-ray intensifying screens [24]. Tb^{3+} has shown a relatively simple energy level structure, low energy states 7FJ (J = 0–6) and excited states $^5D_3/^5D_4$ leading to emission in the visible region [20]. In our previous work, the optimization and characterization of Tb doped ZnO (ZnO:Tb^{3+}) nanophosphors using different characterization tools was reported [19]. The optimum doping concentration of Tb in ZnO was observed to be 5 mol% with near white light emission. The reported optimized nano-powder was used for the preparation of the target of the ZnO:Tb^{3+} thin films using PLD.

In this paper, the effect of substrate temperature on the structural and luminescence properties of ZnO:Tb^{3+} thin film is reported. The interaction between the substrate and film at higher substrate temperature is also discussed. Detailed growth mechanism of thin films synthesis with substrate temperature is proposed.

2. Experimental details

ZnO:Tb^{3+} thin films were deposited on polished silicon {Si (100)} wafers using a ZnO:Tb^{3+} target in a reactive PLD process. The optimization and synthesization of the ZnO:Tb^{3+} nanophosphors powder by the solution-combustion method has already been reported elsewhere [19]. These ZnO:Tb^{3+} powder was used for preparation of the target. The 266 nm Nd:YAG laser was used for the ablation. The Si substrate was cleaned ultrasonically using acetone, ethanol and deionized water after that it was dried by N_2 gas. The substrate temperature was varied from room temperature (RT) to 400 °C during deposition of the thin films in a vacuum chamber backfilled with oxygen gas. The laser energy and deposition time were fixed at 40 mJ and 25 min, respectively. The chamber was pumped down to a background pressure of 5×10^{-5} mbar and was then backfilled with O_2 to a partial pressure of 5×10^{-2} mbar.

The structural properties were analyzed with an X-ray diffractometer (XRD) (PAN analytical X'pert PRO). The surface morphology and roughness of the films were examined from images captured in the contact mode using a Shimadzu SPM-9600 atomic force microscope (AFM). The root mean square (RMS) roughnesses were estimated by analyzing the topographic scans of the films. The X-ray photoelectron spectroscopy (XPS) analysis was carried out with a PHI 5000 Versaprobe-Scanning XPS Microprobe before and after 30 s Ar^+ sputtering. Photoluminescence (PL) data were recorded using a 325 nm He–Cd laser with as excitation source. A PHI 700 Auger Nanoprobe was used for the depth profile analyses. A 25 keV, 10 nA electron beam was used. The Auger peak to peak heights (APPHs) were monitored while sputtering with 2 keV, 2 mA Ar^+ ions using a raster that scanned the Ar^+ ion beam over a 2×2 mm^2 area and the sputtering rate was 8.5 nm per minute. All characterizations have been done at room temperature.

3. Role of substrate temperature on the growth mechanism of the thin films

The most important part of any PLD process is the different physical processes involved between the laser and the material interaction. Firstly is the formation of the plasma plume containing high energetic species and secondly the subsequent transfer of the ablated material through the plasma plume onto the heated surface of the substrate and thirdly the final film growth [25–28]. All the elements in the target surface are rapidly heated up to their evaporation temperature at a sufficiently high energy density for a short pulse duration when the laser beam is focused onto the surface of the solid target. The materials are dissociated from the target and ablated with the same stoichiometry as the target. The instantaneous ablation rate is highly dependent on the fluencies of the laser beam incident on the target. The emitted materials move toward the substrate [25,26]. The uniformity of the deposited film is dependent on the laser spot size and the plasma temperature as well as the distance between the target and substrate. The ejected high energy species impinge onto the surface of the substrate and may induce various types of damage to the substrate. These energetic species sputter some of the surface atoms and a collision region is established between the incident flow and the sputtered atoms. After the formation of a thermalized region, the film growth is started, Fig. 1.

The region served as a source for the condensation of the particles. When the condensation rate is higher than the sputtering rate of the particles a thermal equilibrium condition can be reached and the film grows on the substrate surface at the expense of the direct flow of the ablation particles. The nucleation and growth of a thin film dependent on many factors such as the density, energy,