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Structural and optical properties of Nd^{3+} doped zinc oxide thin films deposited by spray pyrolysis

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ABSTRACT

Un-doped and Neodymium (Nd)-doped zinc oxide (ZnO) thin films were deposited on glass substrates by spray pyrolysis experimental setup at 400 °C. The doping concentration of Nd is varied between 0.05 at.% and 0.25 at.%, in the spray solution. XRD studies confirmed the hexagonal wurtzite crystal structure of the deposited films irrespective of the variation in the Nd doping concentration. The SEM microstructures reveal that the average diameter of the Nd ring on the ZnO surface is ranging between 1.87 μm and 11.45 μm depending on the Nd doping concentration. EDS analysis confirmed the presence of Nd in the doped samples. Further, it is understood that Nd/Zn ratio in the deposited films is varied between 0.05 at.% and 0.25 at.%. The optical band gap is found to be ranging between 3.20 eV and 3.22 eV for the variation in Nd/Zn ratio from 0.05 at.% to 0.25 at.%. The PL of films is more intensive in UV region. Concentration of oxygen vacancy related defects and excitation wavelength in ZnO film were observed by PL studies. The green emission has been interpreted as the transition between singly charged oxygen vacancy and a photoexcited hole from PL studies.

1. Introduction

Rare-earth (RE) doped semiconductors have attracted several research groups because they constitute materials for opto-electronic devices such as light-emitting diodes (LED). A considerable interest has been shown recently to utilise the RE chelates as the emissive materials in such devices [1]. De-excitation of RE ions produce narrow, well-defined emission lines over the entire visible region of electromagnetic spectrum and extending into the infrared (IR) as well. The sharp emission lines obtained from the relaxation of RE ions are desirable in the visible region for the full colour displays with well-defined red, green, or blue components. In the IR region, the focus changes to telecommunications as wavelengths corresponding to intra-4f transitions of erbium (1.5 μm), Nd (1.3 μm) and ytterbium ions (0.98 μm) are widely used for fibre optic based systems. Nd is one of the most widely used RE elements for high power laser applications and Nd doped lasers have recently been utilised in inertia confined fusion experiments [2]. Diluted magnetic semiconductors (DMS) systems, formed by substituting a fraction of host semiconductor cations with magnetic ions, are preferred for spintronics applications [3]. ZnO is a well-known wide band gap semiconductor material, which has been applied in various applications such as UV LEDs, cold field emitters, solar cell electrodes and chemical sensors [4]. ZnO with unique optical, electrical, ferromagnetic, and morphological properties were obtained by doping RE elements. In recent years, RE doped ZnO polycrystalline materials have gained great attention in both fundamental studies and applications [2,5]. ZnO is a proven candidate as host material for the visible and IR emission of various RE ions. On the other hand, RE ions are effective luminescence centres due to their narrow and intense emission lines originating from intra-4f shell transitions [6]. RE^{3+} doped ZnO are also expected to

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be one of the promising materials for emissions in the near infra red (NIR) spectral region, particularly in connection with optical fibre telecommunication. Deeply insight into optical properties of Nd^{3+} doped ZnO, Particularly, the host to Nd^{3+} energy transfer, is of great importance to material applications such as optoelectronic devices [7]. Nd (a lanthanide) doped ZnO leads to a band gap narrowing although the dopant is in +3 state. Douayar et al. has reported that according to Zheng et al., Nd 4f electrons introduce new states close to conduction band of ZnO. A newer LUMO is therefore formed which leads to a reduction of the band gap [8,9]. The decrease in band gap value may be due to the result of improvement in the crystal quality. Spray pyrolysis is an effective solution-process method for the deposition of various metal oxide thin films, and so, it has been chosen to deposit undoped and Nd-doped ZnO thin films in the present work.

2. Experimental details

The precursor solution was sprayed onto pre-heated substrates using a glass spray-nozzle with a filtered-compressed (40 lb/cm^2) air as carrier gas [10]. The sprayed aerosol containing fine-mist of solution decomposes to yield the desired chemical compound (ZnO in the present study) on reaching the surface of pre-heated substrates by getting deposited as thin film. ZnO thin films were deposited onto ultrasonically cleaned microscopic glass substrates. A precursor solution, containing zinc acetate dissolved in deionised water, was used as a starting solution. A few drops of acetic acid were added to this aqueous solution to prevent the formation of hydroxides [10]. For each Nd-doping concentration, required amount of neodymium acetate hydrate was dissolved in deionised water and mixed with the starting solution. The nozzle-substrate distance was maintained as 30 cm and the solution flow rate was kept constant at 1.1 ml/min. The pyrolytic process occurs when the aerosol is close enough to the substrate, and consecutively highly adherent ZnO films are deposited. Prior to deposition, the substrates were pre-heated to 400 °C for 30 min. The solution was sprayed several times in a discrete manner (in order to allow the decomposition of previously sprayed solution) with a spray time of 30 s.

XRD patterns were obtained using the computer controlled PANanalytical Xpert PRO X-ray diffractometer (Cu*K*α with a wavelength of 1.5406 Å) in Bragg–Brentano geometry ($\theta/2\theta$ coupled). The surface microstructures were obtained from a NanoNova SEM from FEI, which also has provided the EDS data. The UV–vis spectroscopy measurements were performed with a Cary 100 Scan spectrometer from Varian. PL spectra were recorded using a He–Cd laser (325 nm) as light source. PL spectra of $Zn_{1-x}Nd_xO$ thin films were recorded at room temperature (RT).

3. Results and discussion

3.1. Structural properties

XRD patterns confirmed the absence of any secondary phases and large internal tensions with a shifting of diffracted peaks for the films doped with RE elements [3]. Matching of the obtained diffraction peaks with standard ZnO data [11] confirmed that the deposited films are polycrystalline with a hexagonal wurtzite crystalline structure. It is also evident that all the films exhibit preferential *c*-axis orientation due to the lowest surface free energy of the (0 0 2) plane. From the XRD patterns, it is observed that the (0 0 2) diffraction peak is shifted towards the higher diffraction-angle with the increasing Nd-doping level as shown in Fig. 1. The improvement in crystallinity has been evidenced by the reduction in FWHM of the (0 0 2) diffraction peak and it's shift towards

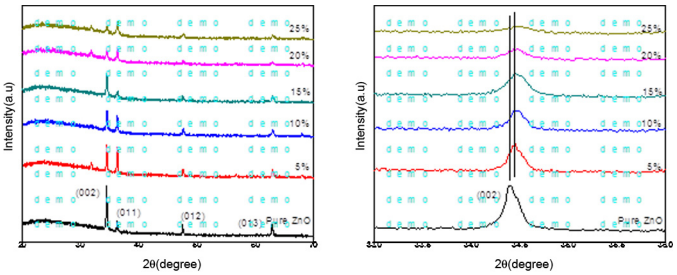

Fig. 1. XRD patterns from un-doped and Nd-doped ZnO films deposited by spray pyrolysis.

higher angle [12]. It is observed that the *c*-axis length (Undoped ZnO = 5.211 Å, 0.05 at.% Nd = 5.208 Å, 0.10 at.% Nd = 5.199 Å, 0.15 at.% Nd = 5.204 Å, 0.20 at.% = 5.195 Å, 0.25 at.% = 5.204 Å) decreases with the increasing Nd concentration. This could be attributed to Nd ions occupying the Zn sites that are in tetrahedrally coordinated in the wurtzite crystal structure [10]. No characteristic diffraction peaks from other impurities such as zinc acetate are observed.

The diffraction peaks of Nd-dopant were also not observed, which is presumably due it's small quantity, and/or the diffraction intensity of Nd dopant is weak and occulted by strong ZnO peaks [13]. The (0 0 2) peak widths reflect the average crystallite size, and of course, peak broadening is possible due to bulk defects such as stacking faults [14]. Peak broadening of X-ray profiles can be caused by a variety of factors such as crystallite size, non-uniform strain, stacking faults and instrumental defocussing [15]. The narrow FWHM of obtained diffraction peaks is probably revealing the absence of defects. However, the crystallite size estimated from the line width at FWHM of the (0 0 2) peak using Scherrer's relation [16] is decreased with the increasing Nd doping concentration. The estimated crystallite size is decreased from 32 nm to 25 nm for the increase in Nd doping concentration from 5 at.% to 0.25 at.%.

3.2. Microstructural properties

The surface of the deposited films was analysed by SEM and the obtained microstructures are shown comparatively in Fig. 2 as a function of Nd doping concentration. SEM microstructure of undoped ZnO shows that the surface is covered with crystallites that are homogeneously distributed with uniform size. The obtained microstructures are probably indicating the segregation of Nd above the ZnO surface. In the case of increasing Nd doping, the Nd ion is appearing on the ZnO surface with a bubble-like morphology that is spherical in shape. Similar result was observed

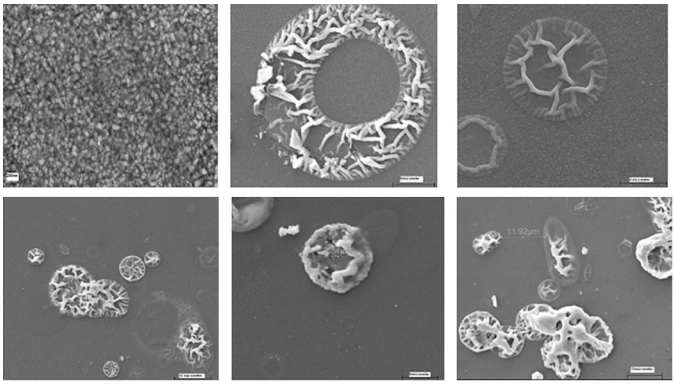

Fig. 2. SEM microstructures at different scan-lengths obtained from: ZnO (a), $Zn_{95}Nd_5O$ (b), $Zn_{90}Nd_{10}O$ (c), $Zn_{85}Nd_{15}O$ (d), $Zn_{80}Nd_{20}O$ (e), and $Zn_{75}Nd_{25}O$ (f) films-deposited by spray pyrolysis onto glass substrates.