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Single and multiphoton absorption induced photoluminescence in pulsed laser deposited $Zn_{1-x}Al_xO(0 \leq x \leq 0.10)$ thin films

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ABSTRACT

In the present paper, single and multiphoton absorption induced photoluminescence in pulsed laser deposited $Zn_{1-x}Al_xO$ ($0 \leq x \leq 0.10$) thin films, is reported. All the films were observed to be preferentially c-axis oriented in the 002 plane as indicated by the X-ray diffraction. A clear emergence of the dominating E_2(high) peak in the Raman spectra further confirmed the formation of Wurtzite phase. Single photon induced photoluminescence spectra of all the samples exhibited strong near band edge emission. Multiphoton absorption (MPA) induced photoluminescence (PL) in the thin films was experimentally observed by exciting with a cw He:Ne laser beam operating at a wavelength of 632.8 nm. A blue shift in the UV-PL spectra was observed in the films till $x = 0.05$ and beyond that it retraced to red-shift. The Intensity of the PL emission was found to be increased in the ZnO film with Al content up-to $x = 0.05$ due to the improvement in crystalline structure and it decreased with further increase in Al content. Logarithmic plot of the MPA PL intensity and excitation intensity displayed a slope, m, in the range of $1 < m < 2$ confirming two photon absorption induced PL emission in these films.

1. Introduction

Luminescence property of oxide based semiconductor materials has been in applications in variety of optoelectronic devices particularly towards the short wavelength regime [1]. Such applications require direct band gap material having large band gap energy for the emission in UV spectral range. Among various oxides, Zinc oxide (ZnO) is a promising material which can be used in optoelectronics, piezoelectronics, gas sensing, biomedical, nonlinear optical devices, optical waveguides etc. [2–4]. It possesses wide and direct band gap ($E_g \sim 3.37$ eV) having large exciton binding energy of ~ 60 meV at room temperature. The high excitonic binding energy of ZnO provides the stability of the excitons at room temperature which serves as an excellent source of radiation towards UV/blue light. It produces strong luminescence covering the UV–visible spectral region due to the near band edge emission and intrinsic as well as extrinsic point defects. The intrinsic point defects depend on the fabrication condition and contribute to the luminescence significantly. Extrinsic point defects such as interstitial and donor/acceptor bound excitons depend on the impurity concentration and the type of impurity associated with it. Zinc rich as well as oxygen rich environments are the two deciding factors determining the luminescence emission in blue-green region or orange-red region. The fabrication ease of the ZnO onto variety of substrates due to chemical stability also supports it as a multi-functional material. It is non-toxic, found abundant in the nature and is very cost effective. The wurtzite hexagonal structure of the ZnO is non-centro symmetric and is fore seen as a good candidate for harmonic generation as well as multiphoton absorption induced photoluminescence [5–8]. The conversion efficiency of the multi-photon absorption induced photoluminescence (MPA-PL) solely depends upon the electronic structure and the shape of the nanostructured formed. The MPA PL in the various nanostructured ZnO thin films have been reported under pulsed laser irradiation [6–10]. However there is hardly any report on the MPA-PL by using cw laser as a pump. The efficiency of MPA PL of ZnO can be improved by suitably infusing it with some impurities in small fraction eg. Aluminum. A variety of fabrication techniques are employed for the fabrication of the Al doped ZnO thin films viz; sol gel, sputtering, chemical vapor deposition and spray pyrolysis etc. [11–14]. The Al doped ZnO film can easily be fabricated via pulsed laser deposition (PLD) technique also. The PLD technique provides the flexibility over the growth conditions [15,16]. The emission of the highly energetic ionized species in the laser produced plasma from the target allows the fabrication of thin film at relatively low substrate temperature in this technique. Another important feature of the PLD technique is the nearly stoichiometric transfer of the target material towards the substrate.

In the present paper, $Zn_{1-x}Al_xO$ ($0 \leq x \leq 0.10$) thin films are fabricated via PLD technique. The structural information of the samples is carried out using XRD and Raman spectroscopy. The single photon PL

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spectra are recorded as a function of x. The multi-photon absorption induced photoluminescence spectra are recorded by exciting the samples with a cw laser and an attempt is made to correlate the influence of the Al concentration onto the PL emission.

2. Experimental details

The $Zn_{1-x}Al_xO$ ($0 \le x \le 0.10$) thin films were deposited via pulsed laser deposition (PLD) technique. The PLD targets were prepared using solid state synthesis route. Pure ZnO (99.9%) and Al_2O_3 (MERCK) powders in appropriate proportions were mixed homogeneously and crushed into a fine powder using pestle and mortar. The fine powder was pressurized to a pressure of 3 t using a KBr pressure machine to form a pellet of ~ 13 mm diameter. Pellets were sintered at 1150 °C for 6 h in an electric furnace in order to get hard dens to be used as a target for PLD of AZO thin films. The fused silica substrate (1×1) cm^2 was properly cleaned with acetone and mounted on the substrate holder equipped with a programmable heater for controlling the deposition temperature. The substrate and target distance was maintained to ~ 3 cm in the present experiment. The PLD chamber was initially evacuated to a base pressure of ~ 2.5×10^{-5} mbar using a turbo molecular pump backed up by the rotary pump and then pressurized with oxygen gas at a pressure of 1.0×10^{-1} mbar [17]. A high power laser beam from 2nd harmonic of a Q-switched Nd:YAG laser (Model No. Quanta Ray INDI-HG) having 10 ns pulse duration and 10 Hz repetition rate, was focused onto the target for ablation. The laser fluence at the target surface was maintained at ~ 10 J/cm^2. All the films were deposited at a substrate temperature of 500 °C and for 30 min duration. The thickness of the film was found in the range of 476–550 nm as estimated using Swanepoel envelope method from their respective UV–visible spectra [17,18]. All the films were subjected to X-Rays Diffractometer (Rigaku, TTRAX III 18 kW) operating at a wavelength of 1.5407 Å of Cu-Kα line for obtaining the information about their phase and orientation. The vibrational modes of the films were recorded using Laser Micro Raman spectrometer (Model No. LabRam HR 800) operating at a wavelength of 488 nm. Single photon absorption induced photoluminescence spectra of the films were recorded at room temperature using Flouromax spectrometer (Edinberg Instruments, Model No. FS920) equipped with Xenon lamp. Multi photon absorption induced photoluminescence (MPA PL) experiment using cw He:Ne laser as pump was performed at room temperature (RT) using the experimental setup, illustrated in Fig. 1.

A cw He:Ne laser beam operating at 632.8 nm wavelength and of 32 mW power was steered using a mirror (M) and focused on the sample (S) by a cylindrical lens (L_1) of 25 cm focal length as shown in Fig. 1. The focal region at the surface of the sample was observed to be of the form of a rectangular strip of 2000×600 μm^2. The sample was oriented at ~ 45° to the incident beam and the PL signal was imaged through another convex lens (L_2) of 5 cm focal length on the entrance slit of monochromator and detected by a photomultiplier tube (PMT). The output of PMT signal was interfaced to the computer. The monochromator was scanned in the spectral range of 330–390 nm to record the multiphoton induced PL spectra. A neutral density filter (NDF) of various optical densities (OD) was introduced in the path of incident beam in order to study the dependence of PL signal on the pump intensity.

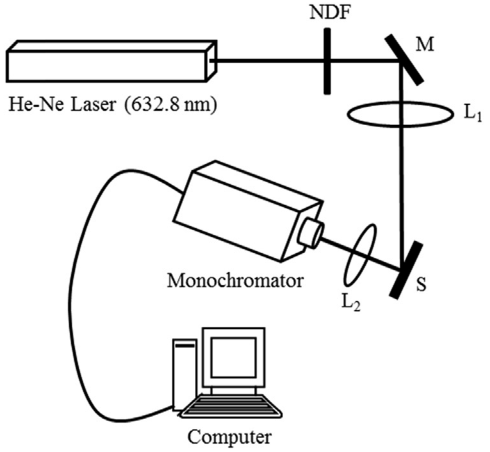

Fig. 1. Schematic diagram of MPA PL experimental setup.

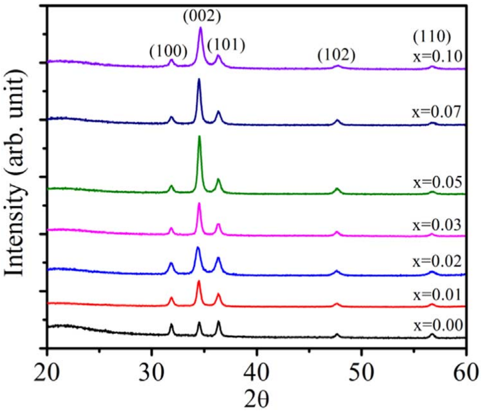

Fig. 2. XRD spectra of $Zn_{1-x}Al_xO (0 \le x \le 0.10)$ thin films.

3. Results and discussions

The XRD spectra of the ZnO thin films doped with different Al concentrations are shown in the Fig. 2.

The XRD spectra of the Al doped ZnO films clearly depict the preferred 002 plane orientation at 34.7°. The absence of any peak corresponding to Al_2O_3 in the films indicates the uniform substitution of the Al^{3+} ions at the Zn^{2+} sites. The 002 peak intensity increases initially with the Al concentration upto 5 wt% and then with further increase in its concentration, there is a slight reduction in the intensity of this peak but over all it is always larger compared to that of pure ZnO. This enhancement in 002 peak confirms the increase in the number of grains oriented in 002 direction and regular arrangement of the crystallites in the Al doped films [19]. The full width at half maxima (FWHM) of the Al doped film is observed to be low as compared to that of pure ZnO film also indicates improvement in crystallinity of the films. However, with the increase in the Al concentration ($x > 0.05$), the excess Al atoms occupy within the grain boundary and interstitial position resulting in the reduction of the 002 peak intensity [20,21]. The enhancement in 002 peak intensity in the Al doped ZnO thin film as compared to that of pure ZnO film is also reported in some of the recent publications [22–24]. The average crystallite size was estimated using the Debye-Scherrer equation [25] and was found to be in the range of 12–19 nm [17].

Fig. 3 shows the Raman spectra of $Zn_{1-x}Al_xO$ thin films.

Raman peak, E_2(high), at 438 cm^{-1} corresponds to the wurtzite hexagonal crystal lattice of ZnO. Additional peaks at 378 cm^{-1} and 578 cm^{-1} are corresponding to the E_1(TO) and A_1(LO) modes respectively [26]. A peak at 330 cm^{-1} which corresponds to A_1(TO), is due to the second order Raman process [27]. A weak Raman peak at 279.2 cm^{-1} is also observed in the films, which is associated with the Al_2O_3 in the films [28]. The similar peak was also shown by some research group in pure ZnO as well as doped ZnO which was assigned as anomalous inactive B_1 mode [29,30]. The dominating E_2 (high) mode in the Raman spectra is the clear indication of the growth of the films along the c-axis. The gradual diminution of the defect related peak, A_1(LO) in the $Zn_{1-x}Al_xO$ films with the increase in x up-to 0.05 suggests the improvement in the crystalline quality in the films. The increase in