Nitrogen doping in pulsed laser deposited ZnO thin films using dense plasma focus

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A R T I C L E   I N F O

Article history:
Received 4 May 2010
Received in revised form 14 September 2010
Accepted 14 September 2010
Available online 25 September 2010

Keywords:
Dense plasma focus
Amorphization
Nitrogen doping

A B S T R A C T

Pulsed laser deposition synthesized ZnO thin films, grown at 400 °C substrate temperature in different oxygen gas pressures, were irradiated with 6 shots of pulsed nitrogen ions obtained from 2.94 kJ dense plasma focus to achieve the nitrogen doping in ZnO. Structural, compositional and optical properties of as-deposited and nitrogen ion irradiated ZnO thin films were investigated to confirm the successful doping of nitrogen in irradiated samples. Spectral changes have been seen in the nitrogen irradiated ZnO thin film samples from the low temperature PL measurements. Free electron to acceptor emissions can be observed from the irradiated samples, which hints towards the successful nitrogen doping in films. Compositional analysis by X-ray photoelectron spectroscopy and corresponding shifts in binding energy core peaks of oxygen and nitrogen confirmed the successful use of plasma focus device as a novel source for nitrogen ion doping in ZnO thin films.

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1. Introduction

The increasing demand for short wavelength, high power solid-state emitters and detectors has inspired research on wide bandgap semiconductors. ZnO is a wide direct bandgap II–VI semiconductor having an energy gap of 3.37 eV at room temperature. Growth of ZnO thin films are key considerations for the next-generation of microelectronic, optical and magnetic devices. zinc oxide thin films have been grown by several plasma based or plasma assisted techniques such as magnetron sputtering [1,2], electron cyclotron resonance (ECR) plasma assisted molecular beam epitaxy (MBE) [3] plasma enhanced chemical vapor deposition (PECVD) [4], expanding thermal plasma [5], filtered vacuum arc deposition [6], pulsed laser deposition (PLD) [7,8], etc. Among them, PLD is very useful to grow high quality thin films. PLD is one of the better techniques to grow oxide films as well as to maintain the stoichiometry of the target into the film structure. Most of the ZnO thin films deposited using these plasma based methods are n-type [6,7], however for its application in semiconductor industry it is necessary to control the concentration and type of the carriers. Several n-type (donor) dopants for ZnO have been discovered but to find suitable p-type (acceptor) dopants is rather difficult. In reality, the recognition of p-type ZnO is very challenging due to its asymmetric doping limitations such as self-compensation, deep acceptor level and low solubility of the acceptor dopants [9]. Theoretically, studies done by Kobayashi et al. [10] showed nitrogen as an optimal doping candidate for getting p-type ZnO. Nitrogen is a suitable dopant for producing a shallow acceptor level in ZnO. By considering these theoretical estimations [10], some techniques were employed to obtain p-type ZnO through nitrogen (N) doping [11,12]. In the present paper, we report the nitrogen doping in PLD grown ZnO thin films using the dense plasma focus device.

... Dense Plasma focus (DPF) is mainly an ingenious source of neutrons, X-rays, energetic ions and relativistic electrons [13]. DPF utilizes the self-generated magnetic field to compress the plasma to very high densities (∼ 1025–26 m−3) and temperatures (∼ 1–2 keV) [14]. It is a potential candidate for the generation of highly energetic high flux (25 keV to 8 MeV) ions, relativistic electrons, X-rays and neutrons [14]. Being a source of such a wide range of phenomena, the device has found applications in other areas too [15]. Highly energetic ions from the plasma focus have been used for processing of various thin films [16–21] irradiated at different distances from the top of the anode. The plasma focus device has also been used for implantation of nitrogen [22] and carbon [23] ions into different metallic substrates, and for lowering down phase transitions of magnetic thin films by exposing them with H+ ions [24]. To control the doping level in any system a control over the ion flux and ion energies are required. In plasma focus device, the flux and energies of the doping ions can be tuned by variation of different operation and design parameters of the plasma focus facility such as (i) the stored energy in the capacitor bank, (ii) the pinched...
plasma volume by changing the anode dimensions, (iii) number of ion exposure shots, and (iv) more simply, as the ions are emitted in a conical geometry with the ion flux having an angular dependence, their flux and energies can be controlled by changing the exposure distance or the irradiation angle or the combination of both.

One of the biggest advantages of pulsed ion irradiation using a plasma focus device is that the significant doping can be achieved with ion pulse duration of the order of a few hundred ns which is much smaller compared to the significantly longer duration continuous ion implantation sources \[25,26\]. So the ion irradiation using plasma focus device can significantly reduce the total exposure duration as compared to that of continuous ion sources. Our group has successfully applied this pulsed ion irradiation for nanosstructuring of FePt thin films with substantial reduction in phase transition temperature \[27\] and also for nitridation of zirconium \[28\].

In this paper, we present the use of dense plasma focus as pulsed plasma driver for energetic nitrogen ions irradiation of ZnO thin films grown by pulsed laser deposition (PLD) technique. The use of pulsed energetic ions of few hundreds of nanoseconds from plasma focus device provides a fast and effective way of doping of nitrogen ions with significant changes in the physical properties of PLD synthesized ZnO thin film.

2. Experiments

ZnO thin films were grown on sapphire (001) substrates by PLD in different O\(_2\) ambient gas pressures at substrate temperature of 400 °C. High purity oxygen was used as the reactive gas and was applied at filling gas pressures of: 0.1, 0.4, 0.8, and 1 mbar. A pressed ceramic ZnO target disk (99.99% purity, 2.5 mm thick and 24 mm in diameter) fabricated by compressing ZnO powder was used as a target in the PLD system for thin film synthesis. In order to grow ZnO films, the Nd:YAG pulsed laser (Lotis TII, 8 ns, 532 nm) was used as an energy source. In order to get a uniform film thickness, the target was rotated during the deposition. The laser repetition rate, laser energy per pulse, and incident angle between target surface and laser beam were kept at 10 Hz, 75 mJ and 45°, respectively. At these parameters the laser energy density on the target was estimated to be 47 J/cm\(^2\). The target-substrate distance was set at 50 mm. The substrates, before being mounted inside the PLD chamber, were cleaned in acetone, alcohol, distilled water separately and dried. Before deposition, the vacuum chamber was pumped down to 7 × 10\(^{-5}\) mbar. Deposition time was about 20 min (12,000 laser pulses) and the typical thickness of thin film was about 60 nm. After the successful growth of thin films, the samples were irradiated with nitrogen ions using DPF machine. DPF is a simple pulsed plasma ion source in which electrical energy of a capacitor bank, upon discharge, is converted into plasma energy resulting in the formation of short lived, but hot and dense plasma \[10\]. We used a single-capacitor (30 μF) based UNU/ICTP (United Nation University/International Centre for Theoretical Physics) plasma focus device charged to 14 kV, with storage energy of 2.94 kJ. The working gas used in the DPF is nitrogen, and the gas pressure was kept at 1 mbar. It may be noted that depositions in PLD chamber were done at significantly higher oxygen ambient gas pressures of 0.1, 0.4, 0.8 and 1 mbar. The nitrogen ion doping was done in plasma focus device which operates well, i.e. with efficient pinching resulting in best possible ion energies and flux, at about 1 mbar. This device was also pumped down to the base pressure of about 5 × 10\(^{-5}\) mbar. The various sub-systems of the device are shown in Fig. 1. The PLD deposited ZnO thin film samples, as shown in Fig. 1, were affixed to the substrate holder placed along the anode axis at a fixed distance of 8 cm from the top of the copper anode. An aperture assembly

Fig. 1. Schematic of UNU/ICTP dense plasma focus device.
is employed, between the anode top and the thin film sample, to stop the plasma shock wave and to eliminate the possibility of contamination of the films by copper impurity coming from electron bombardment of copper anode rim. Each of the ZnO thin film samples was exposed to 6 shots of nitrogen ions.

X-ray diffraction (XRD) patterns for as-deposited and irradiated thin films were measured by a Siemens D5005 X-ray diffractometer with Cu Kα radiation. The electronic states of elements in the film samples were estimated by X-ray photoelectron spectroscopy (XPS) with Kratos Axis-Ultra spectrometer equipped with a focused monochromatic Al Kα X-ray beam. The photoluminescence (PL) measurements were done by using a 325 He–Cd laser line to estimate different emissions of as-deposited and nitrogen ions irradiated ZnO thin films at room and low temperature.

3. Results and discussion

The XRD patterns of ZnO thin films grown on heated sapphire substrates at oxygen gas ambient pressures of 0.1, 0.4, 0.8 and 1 mbar in PLD chamber are shown in Fig. 2. For all the samples, (002) and (004) reflections of ZnO wurtzite structure were observed which indicate that ZnO thin films formed under various oxygen pressure are highly c-axis oriented. In order to analyze the differences in the structure of thin film samples at different pressures, (002) reflections of various ZnO films were analysed. The (002) diffraction peaks appeared at $2\theta = 34.66^\circ$, $34.66^\circ$, $34.66^\circ$ and $34.51^\circ$ for thin films grown in oxygen pressure of 0.1, 0.4, 0.8 and 1 mbar, respectively. It is noted that the $2\theta$ value corresponding to (002) reflections in thin film samples increases with respect to the $2\theta$ value ($34.42^\circ$) in bulk ZnO. In addition to ZnO reflections, the (0006) diffraction peak at about $42^\circ$ corresponding to sapphire substrate is also observed on some of the samples. The strongest sapphire peak is observed on sample grown at 0.8 mbar whereas the sample grown at 1 mbar does not show any diffraction peak of sapphire; the reason for this variation is not clear to us.

After irradiation of 6 shots of nitrogen ions, shown in Fig. 3, no remarkable change in the structure of the ZnO films has been observed. Full width half maximum (FWHM) and corresponding average crystallite size with respect to (002) peak of ZnO thin films before and after nitrogen ions irradiation are tabulated in Table 1.

It may be interesting to note from Fig. 3 that sapphire substrate diffraction peak at about $42^\circ$ has completely disappeared from three of the ions irradiated samples; these samples had either weak or no diffraction peak of sapphire substrate. The high intensity sapphire substrate peak of 0.8 mbar as-deposited sample (refer Fig. 2) has also reduced significantly after nitrogen ion irradiation (refer Fig. 3). This indicates the amorphization of the top layer of sapphire substrate upon nitrogen ions irradiation. The following paragraph presents the plausible explanation for the amorphization of the top layer of the sapphire substrate near substrate–film interface.

Table 1

<table>
<thead>
<tr>
<th>Thin films before irradiation</th>
<th>Thin films after nitrogen irradiation</th>
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<tbody>
<tr>
<td>O₂ pressure</td>
<td>FWHM for (002) peak (degrees)</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
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<tr>
<td>0.1 mbar</td>
<td>0.78</td>
</tr>
<tr>
<td>0.4 mbar</td>
<td>0.68</td>
</tr>
<tr>
<td>0.8 mbar</td>
<td>0.55</td>
</tr>
<tr>
<td>1 mbar</td>
<td>0.66</td>
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</tbody>
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Fig. 2. XRD of thin films deposited in different O₂ pressures.

Fig. 3. XRD of thin films deposited in different O₂ pressures after nitrogen ion irradiation using DPF.
In dense plasma focus, the energy range of the emitted ions is from 25 keV to 8 MeV \[14\]. The estimations using SRIM code\(^\circledR\) showed that nitrogen ions with energy \(>32\) keV will penetrate through the 60 nm thick ZnO thin films. Hence, while low energy nitrogen ions \(<32\) keV) are stopped in the ZnO thin films, the nitrogen ions with energy \(>32\) keV can traverse through the ZnO thin film and be absorbed in the top layer of the sapphire substrate to cause substantial transient heating of the substrate and also defects in the

**Fig. 4.** (a) Room temperature PL spectra of the as-deposited thin films grown at different O\(_2\) pressures. (b) Room temperature PL spectra of thin films deposited in different O\(_2\) pressures after 6 shots of nitrogen ions irradiation using DPF.

**Fig. 5.** Low temperature PL spectra of as-deposited and nitrogen ions irradiated (6 DPF shots) ZnO thin films grown at 0.8 mbar ambient pressure of O\(_2\).
substrate material leading to reduction in its crystallinity (amorphization), as observed in XRD results. The similar amorphization of Si substrate using energetic ions of plasma focus has been reported by Sadiq et al. [29].

The room temperature PL spectra of ZnO films prepared under different oxygen pressures were measured for as-deposited and ion irradiated samples and are shown in Fig. 4a and b. By comparing these PL spectra, it can be found that for all samples there exists a strong near-band edge (NBE) emission peak within the UV range. The NBE peak is quite broad for the films before and after irradiation. The room temperature PL spectra of the as-deposited samples grown at different O₂ pressures and nitrogen ions irradiated samples show almost similar emissions. But the nitrogen ions irradiation from the DPF affects the temperature dependent PL of the ZnO thin films.

Low temperature PL spectra for ZnO thin films grown in 0.8 mbar O₂ gas pressure, before and after nitrogen ions irradiation from DPF, are shown in Fig. 5. The as-deposited films at low temperature shows donor bound exciton (D²X) emissions observed around 3.36 eV often observed in ZnO. After nitrogen irradiation of thin films, a clearly distinct PL emission peak starts appearing at 3.3 eV with the decrease in temperature (at about 120 K) as shown in Fig. 5. The emission at 3.30 eV is similar to emissions often observed in p-type doped ZnO. This emission is usually caused by acceptor-related transitions such as free electron to neutral acceptor (FA) and donor–acceptor-pair (DAP) [30–32]. Xue et al. observed a similar emission peak at 3.30 eV in N doped ZnO and attributed it to a DAP emission [33]. The DAP transition is a process by which some of the electrons on the neutral donors combine radiatively with holes on the neutral acceptors. It is well known the defect binding energy falls in the range of 5–50 meV for donor and 20–200 meV for acceptor depending on the material parameters [34]. At high temperatures when the thermal energy is comparable to the donor binding energy, it is easier for electrons to ionize. Thus the DAP transition is replaced by free electron to acceptor (FA) emission and a blue shift can be observed. However, in our case, we did not see the blue shift in the PL spectrum of the samples after nitrogen irradiation, and only red shift has been observed. Thus we can conclude that the peak at 3.30 eV appears due to FA emissions. The acceptor binding energy can be estimated based on the temperature dependence of the FA emission using the following equation, 

\[
E_{\text{FA}}(T) = E_{\text{FA}}(0) - k\frac{T}{T + \beta},
\]

where \(E_{\text{FA}}(0)\) is the bandgap energy and \(E_{\text{FA}}\) is the acceptor binding energy, respectively. The temperature dependence of the bandgap energy of ZnO can be described by Varshini equation [35,36], 

\[
E_{\text{g}}(T) = E_{\text{g}}(0) - \alpha T^2 / (T + \beta),
\]

where \(\alpha = 8.2 \times 10^{-4} \text{eV K}^{-1}\), \(\beta = 700 \text{K}\) and \(E_{\text{g}}(0) = 3.44 \text{eV}\) [32,37]. Using these values, the acceptor energy \(E_{\text{FA}}\) is estimated to be 140 meV which is comparable to the estimated values in the range of 120–200 meV. In order to confirm the activation of FA transition at low temperature; the PL measurements were also done for ZnO thin films deposited in 0.4 mbar ambient O₂ gas pressure. Fig. 6 shows low temperature (10 K) PL spectra of the ZnO thin film samples grown at 0.4 and 0.8 mbar ambient O₂ gas pressure, before and after nitrogen ions exposure. Hence, the appearance of the peak at 3.30 eV for nitrogen ions irradiated samples at low temperature is attributed to the activation of FA transitions. The observation of PL emission peak at 3.3 eV for the nitrogen ions irradiated ZnO thin film grown at 0.4 and 0.8 mbar ambient O₂ gas pressure indicate the samples are doped with nitrogen because FA emission peak is the symbol of the successful nitrogen doping. Accepter level of nitrogen can only activate when nitrogen doped properly in the ZnO.

To confirm the presence of nitrogen in irradiated samples, we did XPS scanning for all the ZnO thin film samples before and after irradiation with nitrogen ions from DPF. All binding energies are referenced to the C 1s peak at 285 eV [38]. For N ions irradiated samples, we observed a broad core peak of N 1s centred at around 396.4 eV for 0.4 mbar and 396.3 eV for 0.8 mbar O₂ ambient gas pressure grown films as shown in Figs. 7 and 8, respectively, Ma et al. [39] reported a binding energy (BE) of 396.2 eV for N₀–Zn bonds in ZnO:N by rf reactive magnetron sputtering. “N₀” is the nitrogen substitution on the oxygen sublattice in ZnO structure. Cong et al. [40] reported a binding energy of N 1s located at 396.35 eV in ZnO:(Al, N) and 399.97 eV in ZnO:N. While Joseph et al. [41] reported 397.84 eV for N₀–Zn bonds in (N, Ga) codoped ZnO films and 406.5 eV in N mono-doped ZnO. The binding energy assignment for the N₀–Zn bond still seems very controversial. Perkins et al. [42] recently compared data from the sputter-produced and MOCVD grown ZnO:N thin films with XPS data taken on in situ N implanted Zn metal foil, N implanted ZnO films, N implanted single crystal ZnO and have undertaken a systematic and reliable study on the identification of nitrogen chemical states in ZnO. They observed peaks at 404.9 and 396.6 eV for the N-implanted Zn foil, 404.5 and 396.5 eV for the ZnO:N film and around 404.9, 396.6 and 399 eV for the nitrogen implanted single crystal ZnO. The binding energy peak near 396.5 eV corresponds to nitrogen substitution on the oxygen sublattice (N₀), the desired location for p-type doping. N 1s peak is visible for all the nitrogen ion irradiated samples supporting the PL results [43].

![Fig. 6. Comparison of the low temperature (10K) PL spectra of the ZnO thin film samples grown at 0.4 and 0.8 mbar ambient O₂ gas pressure, before and after nitrogen ions exposure.](image-url)

![Fig. 7. XPS data of N 1s core peak for the thin films sample grown at 0.4 mbar O₂ ambient pressure after nitrogen ions irradiation.](image-url)
values at 529.2, 529.7 and 530.8 eV. While the de-convoluted peak for O 1s after N irradiation gives increased BE values at 530.1, 531.4 and 533.2 eV. The binding energy of the O 1s spectrum at 531.4 eV is associated with O2 ions in the oxygen-deficient regions within the matrix of ZnO [44,45]. The change in the binding energy of the O 1s indicates the nitrogen substitution into oxygen sites. This indicates that part of nitrogen ions have occupied at the oxygen vacancies (sites). Based on above-mentioned results, it can be inferred that the amount of concentration of antisite N_o would increase after irradiation.

4. Conclusion

In the present work, systematic study has been performed to demonstrate the successful doping of nitrogen in PLD synthesized ZnO thin films using pulsed energetic nitrogen ions DPF device. Structural analysis showed certain degree of amorphization of the substrate surface, just below the ZnO layer, by energetic nitrogen ions as evidenced by the decrease in peak intensity of the sapphire substrate. The room temperature PL spectra of ZnO films prepared under different oxygen pressures exhibits near-band edge (NBE) emission peak within the UV range. But the PL results at low temperature showed extra emissions which can only be developed due to nitrogen doping in the ZnO structure, specifically the appearance of emission peak at 3.30 eV for nitrogen irradiated samples at low temperature which is attributed due to the activation of FA transitions. XPS analysis shows the nitrogen presence and the change in oxygen binding energy confirmed the occupancy of oxygen vacancy by nitrogen ions.

Acknowledgments

The authors are grateful to the National Institute of Education/Nanyang Technological University, Singapore, for providing the AcRF grant RI 7/08/RSR. One of us, S. Karamat, would like to thank NIE/NTU for providing the research scholarship.

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