Superlattices and Microstructures 53 (2013) 164–172

Contents lists available at SciVerse ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Structural, electrical, and optical characteristics of lithium-implanted ZnO thin films

S. Nagar [a], S.K. Gupta [b], S. Chakrabarti [a,*]

[a] Centre of Excellence in Nanoelectronics, Department of Electrical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India
[b] Bhabha Atomic Research Center, Mumbai 400 085, India

ARTICLE INFO

Article history:
Received 9 July 2012
Received in revised form 12 October 2012
Accepted 17 October 2012
Available online 2 November 2012

Keywords:
Zinc oxide
Pulsed laser deposition
X-ray diffraction
Scanning electron microscopy
Hall measurements
Photoluminescence

ABSTRACT

Lithium ions were implanted at low energies (40 and 50 keV) and at a dosage of 5×10^{13} ions/cm^2 over ⟨002⟩ ZnO thin films that had been deposited by pulsed laser deposition. The implanted samples were subsequently treated by rapid thermal annealing at 750 °C. Scanning electron microscopy images revealed improved grain formation for the implanted samples. However, a presence of microvoids was also observed in these samples; the amount of microvoids tended to increase on high-temperature annealing. Dominant donor-bound-exciton peaks is observed in all the samples along with some defect related to the exciton bound peaks although with a lesser intensity compared to as-deposited sample.

1. Introduction

ZnO has been extensively studied as a potent photonic material because of its wide bandgap (3.437 at 2 K) and large exciton binding energy (60 meV) [1]. These properties make it an interesting candidate for fabricating optoelectronic devices that function in the ultraviolet region such as laser diodes, light-emitting diodes, invisible field effect transistors, and phosphorescent displays [2–6]. However, because of the presence of defects like zinc interstitials and oxygen vacancies, ZnO intrinsically grows as an *n*-type material [7,8]; thus, production of reliable *p*-type ZnO films is a major obstacle in fabricating ZnO-based devices. The self-compensating nature of dopants, their low solubility in ZnO, and their lack of stability pose further obstacles in the production of *p*-type ZnO films [9–11]. Many researchers have reported the production of *p*-type ZnO using group I (Ag and Li) and group V (N,

* Corresponding author. Tel.: +91 22 2576 7421; fax: +91 22 2572 3707.
E-mail address: subho@ee.iitb.ac.in (S. Chakrabarti).

0749-6036/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.spmi.2012.10.008

P, As, and Sb) elements and using co-doping of group III–V elements (Al–N and In–N) [12–20]. However, most of these techniques involve a nonlocalized doping mechanism. Selective doping, which could be possible through the use of an ion implantation technique, is recommended for fabrication of devices. In addition, selective doping provides lateral selectivity, a suitable doping area and fluence control. Although many researchers have tried *p*-type doping using ion implantation, few have succeeded [3,21,22]. Furthermore, lithium-implanted or lithium doped studies have been performed by many people, but most have done optical or electrical study and a detailed study in the structural, electrical and optical studies is limited [23–27]. Thus, in this work, we intend to do a detailed study on the structural, electrical, and optical properties of lithium implantation on ZnO films at different energies.

2. Experimental

A 500-nm thick ZnO film was deposited over ⟨001⟩ sapphire substrates using pulsed laser deposition at 400 °C. Prior to deposition, the substrates were degreased in tri-chloroethylene, acetone, and isopropyl alcohol for 2 min each. The ablation of the 99.999% pure ZnO target (diameter, 25 mm) was achieved by using a KrF excimer laser (248 nm; 6 ns pulse). A pre-ablation vacuum of 3×10^{-5} m Torr was maintained in a high-vacuum chamber preceding the deposition, during which an oxygen environment of 75 m Torr was sustained. A target-to-substrate distance of 5 cm and an energy density of 1.8 J/cm^2 were maintained during the 40 min of deposition. Thus, sample A1 was obtained.

Subsequently, Li ion implantation was performed at room temperature with low energies of 40 and 50 keV and constant dosage of 5×10^{13} ions/cm^2 to obtain samples B1 and C1 respectively.

The experiment was undertaken at the Low Electron Accelerator Facility, Bhabha Atomic Research Center, Mumbai, India. The projected range of 165 and 207 nm was estimated based on TRIM calculations. Samples A1, B1, and C1 were subjected to rapid thermal annealing (AS ONE 150, Annealsys) at 750 °C, in an Ar environment for 30 s to yield samples A2, B2, and C2, respectively.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed to study the structural characteristics of the implanted films using PANalytical and Raith 150 Two systems.

A Van der Pauw Hall measurement system (HMS 5000, Ecopia) was used to determine the electrical behavior of the obtained films. Temperature-dependent photoluminescence (PL) spectra were obtained to study the films' optical characteristics. A He–Cd laser with a wavelength of 325 nm was used as an excitation source for the PL measurements while a silicon detector array was used for recording the spectrum.

3. Results and discussion

3.1. Structural properties

Fig. 1 depicts the XRD patterns from the obtained samples. Presence of a ⟨002⟩ peak in all of the samples confirmed the growth of highly *c*-axis-oriented films. The markedly diminished peak intensity for samples B1 and C1 implied deterioration of film crystallinity and increased defects owing to the inclusion of Li ions; however, the lower peak intensity was regained on subsequent annealing (samples B2 and C2). This was verified by reviewing the full width at half maximum (FWHM) values of the samples (Table 1); samples B2 and C2 showed lower FWHM values, thus confirming the reduced defects and greater crystallinity following annealing. Moreover, it is also observed that samples, A2, B2 and C2 are shifted towards a higher 2θ value as compared to samples A1, B1 and C1. The relaxation of strain on annealing the samples causes such a shift in the peak position.

Surface morphology of the obtained samples was assessed from SEM images (Fig. 2). Better grain formation was observed in samples A2, B1, and C1 (Fig. 2b, c and e, respectively), as compared to the as-deposited samples (Fig. 2a). While annealing the as-deposited sample at 750 °C results in the formation of better grains, a possible cause for the better grain formation in the non-annealed B1 and C1 might be related to the generation of heat in those samples during implantation. Formation