



## Raman spectroscopic analysis on Li, N and (Li,N) implanted ZnO

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### ABSTRACT

Doping lithium (Li) and/or nitrogen (N) in ZnO and activation of shallow acceptors thereby have drawn specific scientific interest for the last few years. A comprehensive study employing Raman spectroscopy is being reported here on N and Li implantation effects in ZnO. Strong presence of  $275\text{ cm}^{-1}$  Raman mode after N and (Li,N) implantation confirms its relation with doped nitrogen in ZnO. Weak presence of  $510\text{ cm}^{-1}$  mode in the high fluence implanted ZnO indicates its origin with interstitial defects. No extra Raman mode has been identified in Li implanted samples. Raman mode with anomalously large intensity is found at  $1562\text{ cm}^{-1}$  after (Li,N) co-implantation (highest fluence). Implantation causes huge increase of Raman modes  $\sim 540, 555$  and  $579\text{ cm}^{-1}$ , with the last two bearing clear co-relations with interstitial Zn and O vacancy, respectively. To identify shallow acceptors due to dopant-defect complex, low temperature photoluminescence (PL) has been monitored but only donor related excitonic features are visible in the near band edge (NBE) emission. However, indications in favour of deep acceptor states are noted, particularly when Li is present in the sample. The deep acceptor level may be at  $\sim 300\text{ meV}$  above the valence band consistent with previous results.

### 1. Introduction

In search of acceptor dopants in ZnO, perhaps the most attempted elements are Li and N [1–5]. Even after so many reports, the configuration of Li and N in ZnO is still a matter of debate [6,7]. Apart from the problem of site specific location of Li and N, it is quite well known that such elemental doping essentially changes the vacancies and interstitials environment and creating further complexity on understanding the actual effect of doping itself [8]. In fact, incorporating dopants using ion implantation technique generates large number of unwanted defect species, which in turn, provides further scope for tailoring stable defect-dopant complex. It has been reported that N implantation induced vacancy clusters in ZnO are very much stable, presence of N may be one of the reasons [9]. Several vacancy complexes in N doped ZnO have been proposed in recent past such as  $N_{\text{O}}-V_{\text{Zn}}$ ,  $I_{\text{Li}}-N_{\text{O}}-V_{\text{Zn}}$ ,  $N_{\text{O}}-V_{\text{Zn}}-H^+$ ,  $N_{\text{Zn}}-V_{\text{O}}$  etc. some of which can even lead to shallow acceptor states in ZnO [10–12]. Interestingly, formation of molecular  $N_2$  is also likely which at vacant O site is a donor and at vacant Zn site is

an acceptor [3,13]. On the other hand, in case of Li doping stable  $V_{\text{Zn}}$  are generated in ZnO [14,15]. In such case, generation of  $Li_{\text{Zn}}$  acceptors is desired, however, Li at interstitial site is a donor and compensates the contribution of  $Li_{\text{Zn}}$  as well as  $V_{\text{Zn}}$  acceptors [16,17]. Still there exist reports on Li related shallow and deep acceptors in ZnO [18]. In this report, we have focused on the Raman spectroscopic analysis as a significant characteristic tool regarding overall disorder as well as contribution of individual intrinsic defects. This analysis, most importantly helps in identifying the chemical signature of implanted foreign atoms. Here we investigate the effects of Li, N and (Li,N) co-implantation on granular ZnO material by Raman spectroscopic measurements. Besides, low temperature photoluminescence (PL) measurements have been employed to identify, if any, acceptor bound exciton (ABX) or donor acceptor pair (DAP) transitions. Earlier studies on Ga,N and Al,N co-doped ZnO samples have indicated [6,19] that the presence of  $I_{\text{Zn}}$  related donors hinder effective acceptor activation through N chemical states. In turn, doping Mg [20], P [21], Li [1] along with N can be effective for reducing  $I_{\text{Zn}}$  related donors. In fact, strong

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Electroluminescence (EL) emissions have been observed in Li and N dual doped ZnO around 415 nm and 500 nm at room temperature leading to successfully fabrication of light-emitting diodes (LEDs) [5].

Basics of Raman spectroscopy and its application in ZnO are well documented [22,23]. Still, debates continue regarding nitrogen related Raman modes in ZnO [2,6,24,25]. Particularly, it is very much difficult to identify the origin of a specific Raman mode when substitution or ion implantation related defects are simultaneously present in the system. In case of Li, till date it has been conjectured that presence of Li does not generate any Raman mode in ZnO although theoretical calculations in its favour exist [17]. It has been shown by Lu et al., that Li concentration below 1% is effective to reduce Li related donors in ZnO [4]. In this study, atomic concentrations of implanted Li and N have been kept much below 1% to avoid unwanted dopant interstitials.

## 2. Experimental outline

Commercially available high purity ZnO polycrystalline powder (99.99% pure, Sigma-Aldrich, Germany) has been pelletized and thereafter annealed at 500 °C for four hours. Removal of unwanted organic samples or any H<sub>2</sub> or H<sub>2</sub>O molecules was the main objective of pre-implantation annealing. After annealing, 50 keV Li-ion and 50 keV N-ion have been implanted on those samples successively with fluence 10<sup>15</sup>, 5 × 10<sup>15</sup> and 10<sup>16</sup> ions/cm<sup>2</sup> each, at Inter University Accelerator Centre (IUAC), New Delhi, India. Samples have been labeled as ZnO: Li (L), ZnO: Li (M), ZnO: Li (H) - implanted by only Li-ions, ZnO: N (L), ZnO: N (M), ZnO: N (H) - implanted by only N-ions and ZnO: Li,N(L), ZnO: Li,N(M), ZnO: Li,N(H) - co-implanted by both N and Li ions with fluence 10<sup>15</sup>, 5 × 10<sup>15</sup> and 10<sup>16</sup> ions/cm<sup>2</sup> respectively. Pristine ZnO sample is labeled as ZnO: U.

Raman scattering (RS) measurement has been done by Lab RAM HR Jovin Yvon Raman set-up equipped with Peltier cold CCD detector. Argon-ion laser with wavelength of 488 nm has been used as excitation in Raman measurement. Temperature dependent PL properties of all samples have been studied using 325 nm laser source with output power 45 mW and a TRIAX 320 monochromator was fitted with a cooled Hamamatsu R928 photomultiplier detector.

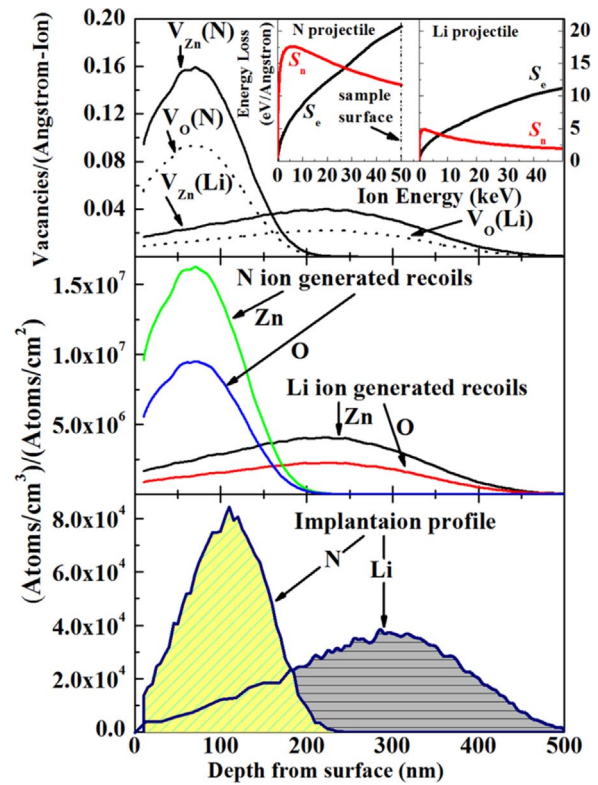
## 3. Result and discussion

Using SRIM (The Stopping and Range of Ions in Matter) software [26] an estimation of generated defect species for Li and N implantation has been carried out. The density of ZnO samples is taken as 4 g/cm<sup>3</sup> and the displacement threshold energies for Zn and O atom in the ZnO lattice is taken as 34 eV and 44 eV respectively. A brief sketch of results obtained here has been provided in Table 1 and Fig. 1. It can be seen that implanted N atoms are more localized in the subsurface regions compared to that of Li atoms. Also to note, recoiled Zn atoms are also steeply concentrated (Fig. 1 middle panel) in the same region in case of N implantation induced effect. Although ~ 99% of the generated V<sub>Zn</sub> and I<sub>Zn</sub>s get dynamically recovered [27] just after their formation, still higher fraction (unknown) of I<sub>Zn</sub>s should be found near the subsurface

**Table 1**  
Table showing parameters estimated using SRIM software.

Energy and ion type	Projected Range (nm)	Atomic concentration of implanted ions (%)	V <sub>Zn</sub> Atomic concentration (%)	V <sub>O</sub> Atomic concentration (%)
Lithium (Li)	290	0.33 (0.085)*	3.85 (3.43)*	2.14 (1.86)*
Nitrogen (N)	111	0.65 (0.52)*	12.27 (21.99)*	7.41 (13.6)*

Calculations are done for fluence 10<sup>16</sup> ions/cm<sup>2</sup>.  
(\*Values within 60 nm from the surface are given inside brackets).



**Fig. 1.** (Upper panel) Generated Zn and O vacancy profiles for Li and N ion beams on ZnO target. Corresponding S<sub>e</sub> and S<sub>n</sub> values at different ion energies (up to 50 keV) has been shown in the inset. (Middle panel) Profile of Zn and O ion recoils due to energetic collisions with Li and N beams. (Lower panel) Profile of Li and N deposition in the target material.

region for N implantation compared to that for Li implantation. It is also indicated in Table 1 that N ions are more damaging for ZnO compared to Li ions of same energy.

The prominent Raman modes in wurtzite ZnO system E<sub>2</sub><sup>low</sup>, E<sub>2</sub><sup>high</sup> and E<sub>2</sub><sup>high</sup> – E<sub>2</sub><sup>low</sup> are at 100 cm<sup>-1</sup>, 439 cm<sup>-1</sup> and 333 cm<sup>-1</sup> [22,28]. The A<sub>1</sub> and E<sub>1</sub> modes are both polar and split into transverse (TO) and longitudinal (LO) phonon modes. A<sub>1</sub>(LO), E<sub>1</sub>(LO), A<sub>1</sub>(TO) and E<sub>1</sub>(TO) can be found respectively at 575, 591, 380, 412 cm<sup>-1</sup> [29]. It is generally understood that Raman signatures below 300 cm<sup>-1</sup> arises from the Zn sub-lattice vibrations and above are due to vibrations oxygen atoms [28]. Particularly, E<sub>2</sub><sup>high</sup>, A<sub>1</sub>(LO) and E<sub>1</sub>(LO) are very much sensitive on the O site disorder in ZnO lattice. Also there exists subtle effect on relative intensities of A<sub>1</sub>(TO) and E<sub>1</sub>(TO) [30] depending on O stoichiometry. Presently, the measured Raman spectra of pristine and implanted samples have been shown in Fig. 2(a)-(c). As observed in earlier studies, E<sub>2</sub><sup>high</sup> Raman mode degrades heavily after implantation and also its FWHM increases. Fig. 3 (upper panel) shows reduction of intensity of E<sub>2</sub><sup>high</sup> (439 cm<sup>-1</sup>) mode with Li, N and (Li,N) implantation fluence. Surprisingly, the proportion of decrease is more or less same for both the ions. This is interesting because SRIM analysis shows that N implantation can induce much higher damage (Fig. 1) compared to Li ions of similar energy. Therefore, it is possible only when some fraction of implanted N occupies vacant O sites and reducing the effect of V<sub>O</sub>s (because N<sub>O</sub> is more probable than Li<sub>O</sub> due to close ionic radius of N and O). Different trend of decrease is visible only when Li-N co-implantation is done. It has been found that Li has specific effect in stabilizing disorder in N implanted ZnO. However, the increase of FWHM of E<sub>2</sub><sup>high</sup> Raman mode is distinctively higher for N implantation (Fig. 3, lower panel). At the same time, implantation induced asymmetrical tailing of E<sub>2</sub><sup>low</sup> peak in the higher energy side is clearly seen (Fig. 2). Similar observations have been reported previously in ion irradiated [31,32] and in nano-grained [33] ZnO material. Evolution of a disorder

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