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Shallow acceptor state in ZnO realized by ion irradiation and annealing route

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ABSTRACT

Activation of shallow acceptor state has been observed in ion irradiated and subsequently air annealed polycrystalline ZnO material. Low temperature photoluminescence (PL) spectrum of the sample exhibits clear signature of acceptor bound exciton (ABX) emission at 3.360 eV. The other two samples, pristine and ion irradiated (without annealing), however, do not show acceptor related PL emission in the nearby energy region. Electron transition from shallow donor (most probable site is interstitial zinc for undoped ZnO) to such newly formed shallow acceptor state creates new donor-acceptor pair (DAP) luminescence peak ~ 3.229 eV. ABX and DAP peak energy positions confirm that the acceptor is N related. The acceptor exciton binding energy has been estimated to be 180 ± 15 meV which is in conformity with earlier reports. The activation of shallow acceptors without any source of atomic nitrogen can only be possible through diffusion of molecular nitrogen inside the sample during annealing. The N_2 molecules get trapped at bulk defect sites incorporated by ion irradiation and subsequent annealing. X-ray diffraction (XRD) and Raman spectroscopic (RS) investigation have been employed to probe the changing defective nature of the ZnO samples. Irradiation induced increased disorder has been detected (both by XRD and RS) which is partially removed/modified by annealing at 300 °C. Simultaneous activation of molecular nitrogen acceptor in purposefully defective ZnO is the key finding of this work. Results presented here provide a simple but controlled way of producing shallow acceptor state in ZnO. If optimized through suitable choice of ion, its energy and fluence as well as the annealing temperature, this methodology can trigger further scope to fabricate devices using ZnO epitaxial thin films or nanowires.

1. Introduction

Nitrogen being the prime suspect of inducing p-type conductivity in traditionally n-type ZnO, large effort has been put forward to dope ZnO by N using various techniques [1–15]. Obviously, N doping replacing an O atom is easier as the ionic radius of N atom is closest to that of O atoms compared to other group V elements. Back in 1988, Gutowski et al. experimentally [16] pointed out the presence of shallow acceptor complexes in ZnO. Further, fabrication of p-type ZnO has been reported by Look et al. [2], Zeuner et al. [3] and Tsukazaki et al. [4]. A brief summary of other studies can be found in ref. 1. However, optimization of defects, chemical nature of the incorporated N atoms and reproducibility of such results have remained as major source of concern till date [17]. Theoretical calculation [9] followed by its experimental [10] confirmation have revealed that N in an O vacancy site (N_O) is indeed an acceptor but its energy level (~1.3 eV above the valence band maximum (VBM)) does not allow sufficient number of holes to be activated at room temperature (corresponding thermal energy ~ 25 meV). So the shallow N related acceptor as reported by several research groups are most probably not N_O. It has also been pointed out that in ZnO, Zn rich configuration cannot be made p type by N doping only [5,9]. On the other hand, it is natural that abundant Zn vacancies (V_{Zn}) are not helpful to achieve the hole induced conductivity as V_{Zn} being a deep acceptor in ZnO [18]. So the focus has been shifted towards the generation of defect complexes involving N and V_{Zn} with energy

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levels sufficiently close (within few hundred meVs) to the VBM. It has been reported [1] that V_{Zn}—N_O—H^+ type stable acceptors with hole binding energy ~ 130 meV in requisite concentration can be formed in ZnO. Recent first-principles calculations [17] also emphasize the presence of H to stabilize V_{Zn}—N_O related shallow acceptors. However, the formation of such complexes in ZnO is rather tricky and there exists an alternative possibility of forming V_O—N_{Zn} (O vacancy-N at Zn site) pair defects which are donors in ZnO [19]. In another track, acceptor doping in ZnO using N_2 or NH_3 molecules have also been explored [20] and recently in a more convincing way [21,22]. However, debates and search for new avenues of purposefully controlled N doping are continuing till date [23]. In this article, we have provided clear cut evidence of evolution of shallow acceptor state in ZnO through ion irradiation and annealing route. It has been understood that the most probable nature of this shallow acceptor is molecular nitrogen at V_{Zn} and/or Zn-O di-vacancy (V_{Zn}-V_O) sites.

2. Experimental outline

Commercial polycrystalline ZnO powder (99.99%, Sigma-Aldrich, Germany) have been pelletized and then annealed at 500 °C for 4 h and cooled slowly (30 °C/30 min). The pellets have been pre-annealed before irradiation to make the sample free from any residual organic materials or adsorbed species like H_2O or H_2 if any [24]. The pre-annealed pellet has been irradiated with 96 MeV O ions with fluence 2.3×10^{13} ions/cm^2 at Inter university accelerator centre (IUAC), New Delhi, India. Choice of such fluence ensures, but not much, special overlapping of collision cascades of the projectiles, taking each of their lateral straggling ~200 Å (estimated using SRIM software [25]). The irradiated sample has been divided into two parts. One of them has been annealed at 300 °C for 4 h followed by furnace cooling. These samples are hereafter referred as: ZnO-U (unirradiated), ZnO-I (irradiated) and ZnO-IA (irradiated and annealed). X-ray diffraction (XRD) patterns have been recorded using powder x-ray diffractometer (model: X'Pert Powder, PANalytical) using Cu K_α (1.54 Å) radiation. The diffraction pattern of all the samples have been refined by Rietveld analyses [26] using the MAUD software [27]. According to Warren's treatment of fault probability analysis [28] three kinds of planar defects, namely intrinsic (α') and extrinsic (α'') deformation, and twin (β) fault probabilities have been used as refinable parameters. Photoluminescence (PL) spectra in the range (10–300 K) have been recorded using 325 nm He-Cd laser as excitation source (output power 45 mW) and a TRIAX 320 monochromator fitted with cooled Hamamatsu R928 photomultiplier detector. Taking the absorption coefficient (α_{abs}) of ZnO to be 1.6×10^5 cm^{-1} at 325 nm [29], the characteristic penetration depth ($1/\alpha_{abs}$) of the 325 nm laser excitation can be estimated ~ 60 nm. So, the observed PL emission spectra will contain information about the region up to few tens of nanometer from the upper surface of the sample. The Raman measurements were performed using a micro Raman set-up consisting of a spectrometer (Lab RAM HR Jovin Yvon) and a Peltier cold CCD detector. A He-Ne laser with wavelength of 633 nm was used as an excitation light source. Sheet resistance have been measured by usual two probe method (with deposited gold contacts) using Keithley K2000 multimeter and K2400 current sources.

3. Results and discussion

The maximum penetration depth of 96 MeV O ion beam in ZnO is about 59 μm as estimated by SRIM [25] simulation software. In this calculation, the density of polycrystalline ZnO has been taken as 4.5 gm/cm^3 and the displacement threshold energies of Zn and O atoms are 34 eV and 44 eV respectively [30]. Along the path of the ion inside target material, it loses energy by both inelastic and elastic collisions known as electronic energy loss (S_e) and nuclear energy loss (S_n) respectively. The knockout of target atoms from their lattice positions takes place due to S_n only. S_e induces excitation and ionization of target electrons and thereby causing defect re-organization to some extent. Fig. 1 shows the variations of S_e and S_n with penetration depth calculated using SRIM. Within the first 100 nm from the surface, from where most of the PL signal comes, the values of S_e and S_n are 117.1 eV/Å and 0.068 eV/Å respectively. So, S_e is about 1730 times larger than that of S_n, which is quite different to the situation for low or medium energy ion irradiation on ZnO [31]. SRIM calculation also indicates that one 96 MeV O ion creates ~2400 vacancies (V_{Zn}: V_O ~ 2:1), most of them are populated at the last 5 μm of the range of the projectile. It is well known that dynamic recovery of irradiation generated defects is very high in ZnO [32] and particularly in systems with nano-scale dimensions [33]. Considering 99% of the V_{Zn}s get recovered immediately after generation and V_Os are more or less stable [32], one can estimate roughly one V_{Zn} and fifty V_Os in 10^7 atoms within the subsurface 100 nm region of ZnO-I sample. Annealing at 300 °C should induce at least four fold modifications in the ZnO-I sample, recovery of almost all the unstable interstitial defects, recovery of a fraction (unknown) of V_{Zn}s [34,35], migration and agglomeration of defects in the form of V_{Zn} clusters and/or V_{Zn}-V_O (altogether clustering of 2–4 vacancies) [34] and starting of generation of V_Os [36,37].

Low temperature PL spectra (10–300 K) have been recorded of all the three samples. Fig. 2 (upper panel) shows 10 K near band edge (NBE) PL spectra of the three ZnO samples. The donor bound exciton (DBX) emission has been found at the same position (3.365 eV) for all the three samples which indicates that same donors are present in all three samples. Based on previous literature, the DBX has been assigned as interstitial zinc (I_{Zn}) related emission [31,38]. Besides DBX, another intense but broad peak has been noticed around 3.313 eV in all 10 K PL spectra. This peak contributes up to room temperature (RT) PL spectrum as is seen in

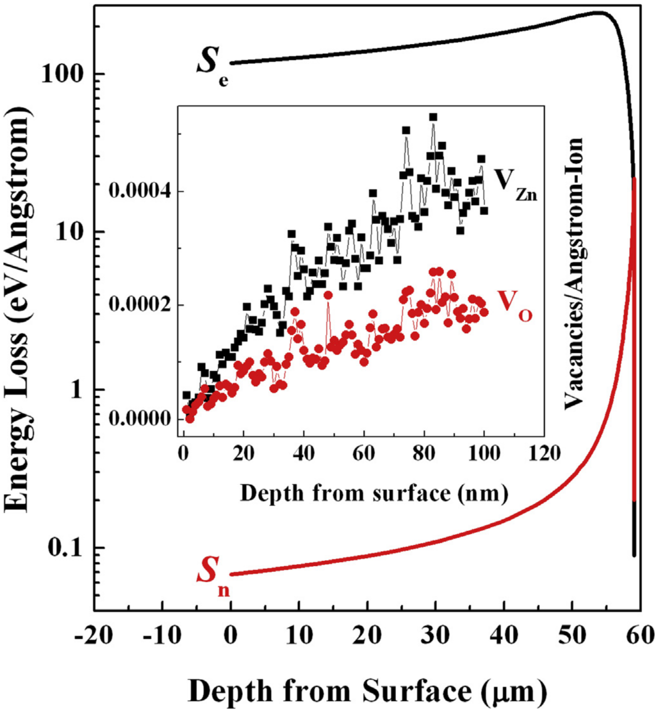

Fig. 1. Estimated S_e, S_n and vacancy concentration (in the inset) for 96 MeV O ions on ZnO target using SRIM software.