Abstract

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Title of the thesis: Ion implantation in nanostructured ZnO: A study on defect evolution

The thesis entitled "Ion implantation in nanostructured ZnO: A study on defect evolution" deals with the defect evolution and interactions with the implanted ions in the ZnO nanorods (NRs) and nanoparticle thin films with the detail characterizations of structural, electrical and optical properties. ZnO is a multifunctional wide bandgap (~3.37 eV) II−VI semiconductor that has distinctive properties, such as large excitonic binding energy of ~60 meV, high optical emission efficiency, visible light transparency, ultraviolet (UV) sensitivity, nontoxicity, and good compatibility, which make ZnO to be used in various low-cost technological applications such as transparent conducting electrode, photoelectrochemical water splitting, UV light-emitting diodes, photodetectors, solar cells, gas sensors, and so on. Moreover, as compared to conventional devices, nanodevices based on one dimensional (1D) NRs of ZnO have advantageous properties like ultrahigh speed as well as frequency, large integration density, and low power consumption other than the size factor. However, the fact is that the electrical and optical properties and therefore the applications of ZnO are vastly driven by its inherent vacancies, interstitials, and anti-sites of Zn and O related defects. From this point of view, study on ZnO nanostructured thin films is of great interest to the researchers because these usually exhibit diverse material properties as compared to the corresponding bulk crystal owing to the modified defect states, lattice imperfection, structural disorder, high surface area, exotic polar topology, and so on. To produce highly performing devices, the key factor is the processing of better-quality materials. Doping is one of the well-known processing steps in the semiconductor industry for the fabrication of various optoelectronic devices. Though the impurity incorporation into ZnO nanostructured thin films has been already achieved successfully using doping during growth and doping by diffusion, a controllable and reproducible doping is still difficult for 1D NRs. In such cases, the post-growth doping via ion implantation method can be a solution for successful doping in ZnO NRs. However, in the process of ion implantation, the interaction between the host lattice and the energetic ions produces point defects inside the target material due to the collisions by the energetic ions. Minute concentrations of defects and impurities can hugely alter the mechanical, electrical, and optical properties of ZnO. The implantation induced defect states in ZnO crystal act as recombination or trapping centres and thus affect the relaxation process of the photoexcited carriers. In addition to it, the implanted induced complex defects control the charge carrier profiles and modifies the conductivity of ZnO. ZnO always exhibits n-type conductivity which can further be enhanced by doping with n-type dopants. But the formation of reproducible and stable p-type ZnO still remains a major challenge due to low or limited solubility and high activation energies of the acceptor dopants and the presence of huge compensating defects. Therefore, the effort to overcome the difficulty of achieving controllable and reproducible p-type ZnO is still one of the needs for the successful fabrication of p-n homojunction based nanodevices.

With the above-said motivation, the work embodied in this thesis has focused mainly on two aspects:

(i) Studies on the role of defects on the room temperature (RT) photoluminescence (PL) and electrical properties the defects identification mechanism in ZnO nanoparticle thin films as well as in ZnO NRs implanted with donor dopant (Al ion).

(ii) Studies on the evolution of the acceptor defects and their compensation with the donor defects in ZnO NRs implanted with various acceptor dopants (N, Li ions) under various ion fluences and post-implantation annealing ambiences.

The entire thesis consists of total nine chapters. The chapter wise contents are given below:

The chapter 1 provides a brief general introduction on ZnO and ion implantation followed by the objectives and organization of the thesis work. In the chapter 2, a critical assessment of the recent ion implantation efforts in ZnO mainly focusing on the status, opportunities, and challenges in the modification of the optical and electrical properties followed by their applications in optoelectronic devices have been presented. The chapter 3 consists two sections: (i) Details of the growth techniques for ZnO nanoparticle thin films by sol-gel and 1D ZnO NRs by aqueous chemical growth techniques have mainly been elaborated firstly. (ii) Secondly, the characterization techniques used for this thesis work have been illustrated in details. The formation of various structural defects and the modifications of the optical and electrical properties in sol-gel grown ZnO thin films implanted with various fluences (1×10^{13} to 6×10^{15} ions/cm^2) of 100 keV

Al ions have been assessed extensively in the chapter 4. For the highest fluence (6×10^{15} ions/cm^2), the sheet resistance is found to be 156 Ω/sq with an average visible transmission of 82%. The high figure of merit value of the Al implanted ZnO films are of prospective as a transparent conducting electrode. Detailed investigation of the implantation mechanism reveals that zinc vacancy (V_{Zn}) defects are formed in large number due to implantation, which on healing produces further higher conductivity in the films. A comprehensive study on the effect of Al ion implantation on RT PL properties of vertically-aligned ZnO NRs implanted with 100 keV Al ions by varying the fluences from 1×10^{13} to 1×10^{16} ions/cm^2 followed by an annealing process at 450 °C in an inert ambient has been presented in the chapter 5. As compared to pristine, an unprecedented enhancement (1.4 times) in the ratio of the intensities of the near band edge, I_{NBE} (UV) to the defect level, I_{DL} (visible) emissions has been observed for the ZnO NRs implanted with of Al ions of 5×10^{13} ions/cm^2. The ratio I_{NBE}/I_{DL} decreases beyond 5×10^{13} ions/cm^2 with an increase in Al ion fluence. Detailed analyses of the recombination mechanism show that the excitons bound to neutral Al donors are responsible for highly enhanced PL emissions in lower fluence Al implanted ZnO NRs. On the other hand, the implantation induced defects acting as non-radiative recombination centres are responsible for the reduced PL emissions in higher fluence Al implanted ZnO NRs. In the chapter 6, the interplay of point defects in ZnO NRs implanted with 50 keV N ions having fluences from 1×10^{14} to 1×10^{16} ions/cm^2 followed by a thermal annealing at 450 °C separately in Ar, O_2, and excess Zn ambiences has been discussed. The detailed analyses validate the incorporation of N at O sublattice forming isolated N_O acceptor and N_O-V_{Zn} acceptor complex in the implanted NRs and N implantation-induced structural disorders increase with an increase in the N ion fluence. The study on the influence of post-implantation annealing reveals that annealing in Ar and O_2 ambiences causes only N_O state, while annealing in excess Zn ambient induces an additional shallow donor $(N_2)_O$ by substituting N_2 at O site. Thus, the post-implantation annealing in O_2 and Ar ambiences play a key role to stabilize the N dopants in ZnO. The evolution of various point defects in 100 keV Li ion implanted ZnO NRs with varying the fluences from 1×10^{14} to 7×10^{15} ions/cm^2 has been discussed with the experimental and theoretical simulation results in the chapter 7. The experimental results indicate that the Li^{1+} ions are incorporated at Zn^{2+} sites forming Li_{Zn} acceptor in the implanted NRs and the structural disorders increase drastically with an increase in the Li fluence. Both the formation of acceptors and implantation-induced defects make the Li implanted NRs electrically highly resistive. The yellow-orange PL emission of the as-grown ZnO NRs has been evolved into a green emission in the implanted NRs. The simulation results explain the quantitative energy loss, the distributions of the implanted Li ions and the point defects along the target ZnO NRs. The consistency between the experimental and theoretical simulations validates our analyses on the formation and evolution of various point defects in highly resistive Li implanted ZnO NRs. The formation and evolution of various point defects in 1D ZnO NRs co-implanted with 100 keV N and Li ions as a function of various co-implantation fluences resulting in the changes in structural, and optical properties have been presented in the chapter 8. Detailed analyses show that the implantation-induced structural disorder increases with an increase in the implantation fluence and both the N_O and Li_{Zn} acceptors are produced in co-implanted NRs. The N_O may form Li_i–N_O complex with the Li interstitials (Li_i) and thus the concentration of Li_i and the possibility of the generation of $(N_2)_O$ donors are reduced. As a matter of fact, there still exits Li_{Zn} acceptors which may contribute to creating p-type ZnO NRs in case of N-Li co-implanted ZnO NRs. Due to co-implantation implantation, the formation of V_{Zn} is indicated by the appearance of a green PL emission.

A list of up-to-date references relevant to the topic has been included at the end of each chapter.

Finally, in the chapter 9, a summary of the important results emerging from this thesis work has been presented followed by a future outlook of the work.

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