Post fabrication annealing effects on electrical and optical characteristics of n-ZnO nanorods/p-Si heterojunction diodes

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ABSTRACT

Annealing effects on optical and electrical properties of n-ZnO/p-Si heterojunction diodes are studied. ZnO nanorods are grown on p-Si substrate by aquous chemical growth technique. As grown samples were annealed at 400 and 600 ^{o}C in air, oxygen and nitrogen ambient. Structural, optical and electrical characteristics are studied by Scanning Electron Microscopy (*SEM*), Photoluminescence (*PL*), Current–Voltage *(I-V)* and Capacitance-Voltage *(C-V)* measurements. Well aligned hexagonal–shaped vertical nanorods are revealed in SEM. PL spectra indicated higher ultraviolet to visible emission ratio with a strong peak of near band edge emission (*NBE*) and weak broad deep-level emissions (*DLE*). For device fabrication Al/Pt non-alloyed ohmic contacts have been evaporated. *I-V* characteristics indicate that annealing in air and oxygen resulted in better rectifying behavior as well as decrease in reverse leakage current. An improvement in PL intensity has been shown by the samples annealed at 400 ^{o}C.

Keywords: heterojunction diodes, ZnO on Si, electrical properties, ZnO nanorods

1 INTRODUCTION

Being a semiconductor Zinc Oxide (ZnO) has attracted global interest in the research community due to its direct and wide bandgap (3.37 eV) and large exciton binding energy (60 meV). It is piezoelectric, which is a key property in building electromechanical coupled sensors and transducers. It exhibits near-ultraviolet emission which translates in bright light. Commercial possibilities are encouraging because electronic grade ZnO can be grown easily and cheaply on a variety of substrates using several different growth methods [1]. As grown ZnO is mostly resulted in n-type conduction, while obtaining p-type conductivity in ZnO is still a problem. That is why homojunction ZnO pn-diode is still an issue. That is why the hetero-junctions of ZnO nanorods have been realized with a variety of semiconductors like Si, GaN and SiC[2-7]. Among these, ZnO/Si hetero-junction is attractive since Si is a cost effective substrate compare to GaN and SiC, plus this heterojunction is flexible in fabrication.

For producing high quality devices, thermal treatment often plays an important role in improving material structural quality which results in improved electrical and optical properties. Restoration of crystal damage and electrical activation of dopants in various semiconductors are often achieved by thermal annealing. It effectively reduces strains and defects contained in ZnO nanorods due to low temperature growth.

Improvements in rectifying behaviour and ideality factor along with better optical properties are reported for ZnO nanostructures [8-13] after annealing in different conditions. In the present work we are reporting the annealing effects on electrical and optical properties of the nanorods of n-ZnO/p-Si heterojunction diodes. Post fabrication annealing of ZnO nanorods is done in air, oxygen and nitrogen ambient at 400 and 600 ^{o}C. The structural and electrical characteristics are studied by scanning electron microscopy (SEM), photoluminescence (PL), current –voltage *(I-V)* and capacitance - voltage *(C-V)* measurements.

2 EXPERIMENTAL DETAILS

Vertically aligned ZnO nanorods were grown on p-Si substrate by low temperature aqueous chemical growth (ACG) technique to form pn-heterojunction. Si substrate of (100) orientation and p-type doping of 10^{16} cm^{-3} and 1.38 Ω-cm conductivity have been used. First, the substrate was ultrasonically cleaned for 15 min with acetone, methanol and then rinsed in de-ionized water.

Initially a ZnO seed layer was produced by diluting zinc acetate dehydrate in methanol. Few droplet of the solution were spin coated on the p-type substrates. The coating step was repeated three times and then sample was heated to 250 ^{o}C in air for 20 min to yield layers of ZnO on the substrate. An equimolar concentration of hexamethylenetetramine (HMT) ($C_6H_{12}N_4$) and zinc nitrate ($Zn(NO_3)_2 6H_2O$) 0.022–0.075 mM is used. The substrate was placed in the

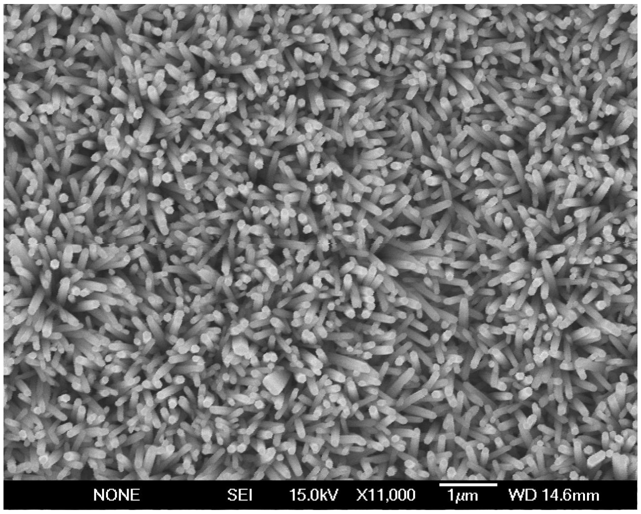

Fig. 1 SEM image of as-grown ZnO nanorods

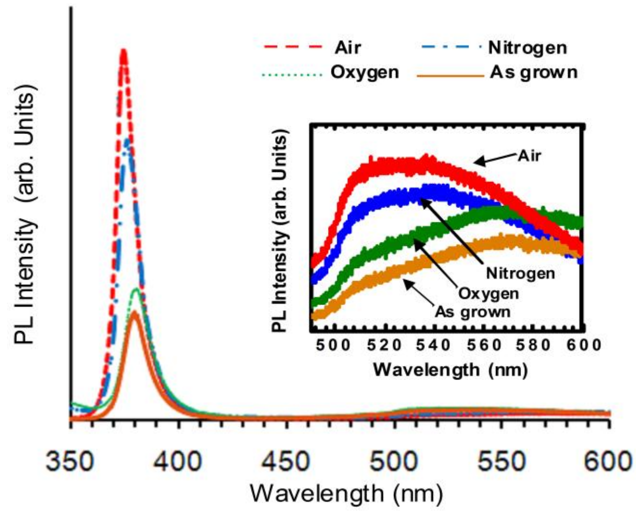

Fig. 2 PL spectra of as-grown and 400 ^{o}C annealed ZnO nanorods

solution and heated at 96 °C for 4 hours. This is well known technique for the growth of nanorods, developed by Greene et al. [14]. For this study, all the seven samples are treated independently. Six samples were annealed at 400 and 600 ^{o}C each in Air, Nitrogen and Oxygen. The seventh as grown sample was kept as reference. Prior to ohmic contacts evaporation an insulating PPMA layer was deposited between the nanorods. Then oxygen plasma cleaning was performed to remove excess PPMA from the top of the nanorods. About 150 nm thick ohmic contact of Aluminum (Al) have been evaporated in vacuum chamber on p-Si substrate. Al/Pt non-alloyed circular contacts were then evaporated to form ohmic contacts to n-ZnO. The diameter of the top contact was 0.58 mm with specific contact resistance of 1.2 x 10^{-5} Ω-cm^{-2} [2]. The nanorods were characterized by scanning electron microscope (SEM). Room temperature photoluminescence (PL) measurement have been performed using laser lines of wavelength 270 nm or 350 nm from an Ar+ laser as the excitation sources. Current-voltage *(I-V)* and capacitance-voltage *(C-V)* measurements have been done using Keithley SCS-4200.

3 RESULTS AND DISCUSSION

The morphology and the size distribution of the as grown nanorods have been studied by SEM. Hexagonal –shaped vertical nanorods with a mean diameter of 160-200 nm and approximate height of 1.2 μm are revealed as shown in Fig.1. Although the nanorods were not perfectly aligned on the substrate, they showed a tendency to grow perpendicular to the surface and distributed almost uniformly. PL emission spectra of the as grown and annealed ZnO nanorods are shown in Fig.2. Two emission peaks have been observed in all the cases. The observations revealed that the annealing ambient influences the light emission characteristics of ZnO nanorods. UV emission is enhanced after annealing the as-grown ZnO nanorods in air, oxygen and nitrogen ambient at 400 ^{o}C.

A commonly observed yellow-green emission centered at 575 nm is shown in as-grown ZnO nanorods. Generally for as-grown nanorods the chemical components are non stoichiometric and usually consist of excess oxygen vacancies. As a result lattice defects are contained. These defects can act as non radiative centers therefore weak UV light emission is observed. Weak deep level emission might be due to the absorption of excess oxygen atoms during the growth process and resulting in less oxygen vacancies.

After annealing in oxygen the NBE emission is enhanced and DLE emission is quenched. It shows that during annealing in oxygen rich ambient oxygen diffuses in the lattice and fills the vacancies [13] as a result oxygen vacancies are effectively reduced.

ZnO nanorods annealed in nitrogen show better UV peak than as grown and oxygen annealed samples. Infact majority of oxygen vacancies related defects are generated by the evaporation of oxygen, and annealing in nitrogen probably supresses the reevaporation of oxygen and reduces the non-radiative related defects. Secondly due to smaller ionic radius than oxygen, nitrogen atoms might be easily trapped in ZnO nanorods and reduce intrinsic defects. This reduces the surface defects and UV peak intensity is enhanced. Comparatively higher DLE (green emisssion) centered from 510-540 nm for N_2 and air annealed samples might also be due to reduced surface defects. The

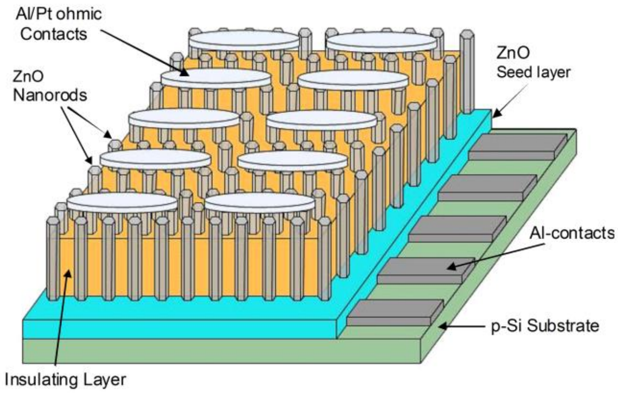

Fig. 3 Schematic n-ZnO/p-Si heterojunction

annealing atmosphere showed slight influence on the deep level defects except that some ions are possibly adsorbed on the surface of ZnO nanorods.

The schematic diagram of the diodes in cross-section is shown in Fig.3. A comparison of I-V characteristics of as-grown and annealed heterojunction diodes indicates that after annealing the properties of diodes are improved. The reverse leakage current is decreased while forward current is slightly increased. Current–voltage characteristics show a typical non linear and rectifying behavior as shown in Fig. 4. Annealing in air and oxygen resulted a decrease in reverse current through the hetero-barrier repairing leakage which may be present due to the inhomogenieties at the interface.

After annealing at 400 ^oC reverese current of as-grown diode decreased from 1.68 x 10^{-4} A to 1.39 x 10^{-4} , 4.89 x 10^{-5} and 1.53 x 10^{-5} amps for nitrogen, oxygen and air annealed samples respectively at -10V. The same trend is observed by Shu-Yi Liu *et al.* [11] after annealing in air.

Air and oxygen annealed diodes exhibited more stable rectification characteristics with high ratio of I_F/I_R. The rectification factor 46.3 of as-grown diode at ±4V is raised to 1890 and 271 after annealing at 400 ^oC in air and oxygen. No significant improvements were observed in I-V behavior of diodes annealed in N_2 at 400 and 600 ^oC. It seems that leakage current paths are generated after annealing in N_2, which make tunelling current more probable and increase the reverese current after annealing at 600 ^oC. The ideality factors for all the heterojunction diodes are in the range of 3 to 8. Higher values of ideality factors may be related to the presence of defects in the ZnO nanorods. Usually I-V characteristics of ZnO/Si heterojunctions are controlled by the interface properties and presence of oxide layer results in high ideality factors [15, 16, 17].

The comparison of I-V characteristics of as-grown and annealed diodes indicates that the properties are improved after annealing. This is most likely due to improvement in the crystalline quality of ZnO nanorods [18]. Better

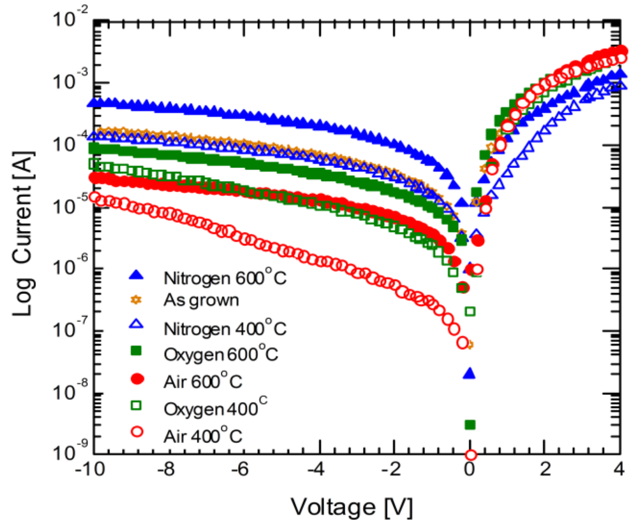

Fig.4 I-V characteristics after annealing at 400 and 600 ^oC in air, oxygen and nitrogen.

electrical properties are observed for diodes from 400 °C annealed ZnO nanorods.

Capacitance-Voltage technique is useful for the study of built in potential of pn-junctions. In our devices ZnO is lightly doped than Si substrate. Therefore our diodes can be considered as one sided step heterojunction. Capacitance – voltage (C-V) measurements have been performed at frequencies from 10K to 1MHz. Figure 5 shows the measured $1/C^2$–V characteristics of n-ZnO/p-Si heterojunction annealed at 600 ^oC in oxygen. The C–V characteristic reveals almost a linear relationship in $1/C^2$ vs. voltage plot. Built in potential (V_{bi}) can be obtained from the intercept point of the linear curve and voltage axis. The voltage intercepts of the extrapolated straight lines with the

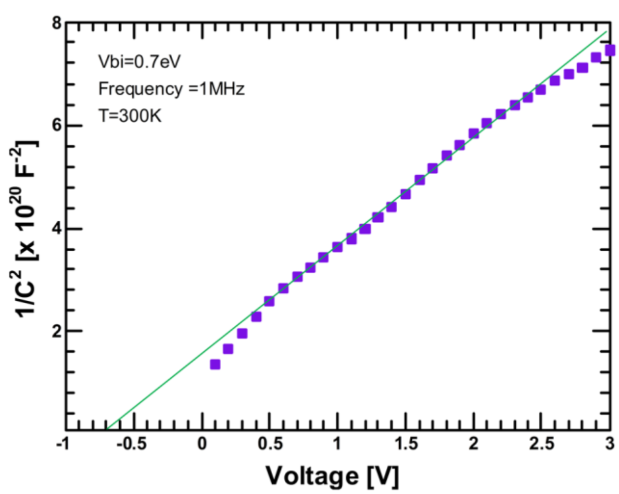

Fig. 5 $1/C^2$ versus reverse voltage plot obtained at 1MHz for n-ZnO/p-Si heterojunction diode annealed at 600^oC in oxygen.

voltage axis are 0.65V and 0.7V corresponding to the diodes annealed at 600 ^{o}C in nitrogen and oxygen.

4 CONCLUSION

ZnO nanorods have been synthesized by hydrothermal growth method. The PL spectra exhitbit higher ultraviolet (*UV*) to visible emission ratio with a strong peak of near band edge emission (*NBE*) centered from 375-380 nm and very weak broad deep-level emissions (*DLE*) centered from 510-580 nm. Annealing in air and O_2 at 400 ^{o}C resulted in decrease in leakage current and increase in rectification ratio and over all good optical quality is observed.

This work demonstrates that improved optical and electrical properties can be obtained by post fabrication annealiong of ZnO nanorods. The present work helped us to understand the effects of annealing on photoluminiscence, rectifying behaviour and ideality factor of n-ZnO/p-Si heterojunction diodes.

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