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The Effects of Vacuum Annealing on the Conduction Characteristics of ZnO Nanorods

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Abstract

Optimised ZnO nanorods characteristics are essential for novel devices to operate efficiently. The effects of vacuum annealing on the electrical transport properties and defect chemistry of ZnO nanorods have been studied. Annealing to 500 °C removed surface contamination causing reduced resistance while annealing to 600 °C created acceptor defects, changing the contact type from ohmic to rectifying. At 700 °C donor defects reduced leading to increased resistance while annealing to 800 °C caused a reduction in all defects and decreased resistance. This suggests that contact resistance is the major contributor to the system's resistance rather than the inherent material resistance alone. The results indicate that contact type can be controlled by manipulating the defect chemistry via controlled annealing.

1. Introduction

ZnO is a wide band gap semiconductor that can form nanowires, nanosheets and nanorods that are used in devices such as gas, chemical and bio sensors, optoelectronic, and solar cells. However, optimising the electronic conduction characteristics is desirable for device efficiency. [1-5]. Low dose argon bombardment can remove surface contamination leading to reduced contact resistance while higher doses result in surface stripping, reduced defects and increased resistance [6,7]. Annealing ZnO nanostructures also changes the defect chemistry which suggests that annealing can control defects and allow for tailored electrical

conduction [8-12]. Previous work on polycrystalline nanosheets showed annealing also caused grain sintering and affected conductivity [8].

Annealing is often used in device fabrication and in the case of gas sensors heating is used in operation. Therefore, understanding the effects of annealing on ZnO nanostructures is important for device optimisation. Here, ZnO nanorods/microrods have been direct-current annealed in ultra-high vacuum (UHV) and characterised using scanning electron microscopy (SEM), photoluminescence (PL) and nanoscale 2-point probe (2pp) to investigate the changes of defect chemistry on electronic conduction.

2. Method

ZnO nanorods/microrods were synthesized hydrothermally at 90°C for nine hours in a solution of zinc nitrate and hexamethylenetetramine (Sigma Aldrich) [13] and mechanically transferred to the Si/SiO_2 wafer and characterised. After direct-current annealing at increasing increments of 25 °C for 1 hour, samples were investigated using SEM. At every 100 C increments samples were studied with PL and 2pp.

Three room temperature PL spectra were acquired from different sample areas, normalised and averaged. Nanoscale 2pp measurements were performed using tungsten tips on at least three nanorods/microrods and at multiple locations on each nanorod with five repeat measurements.

3. Results and Discussion

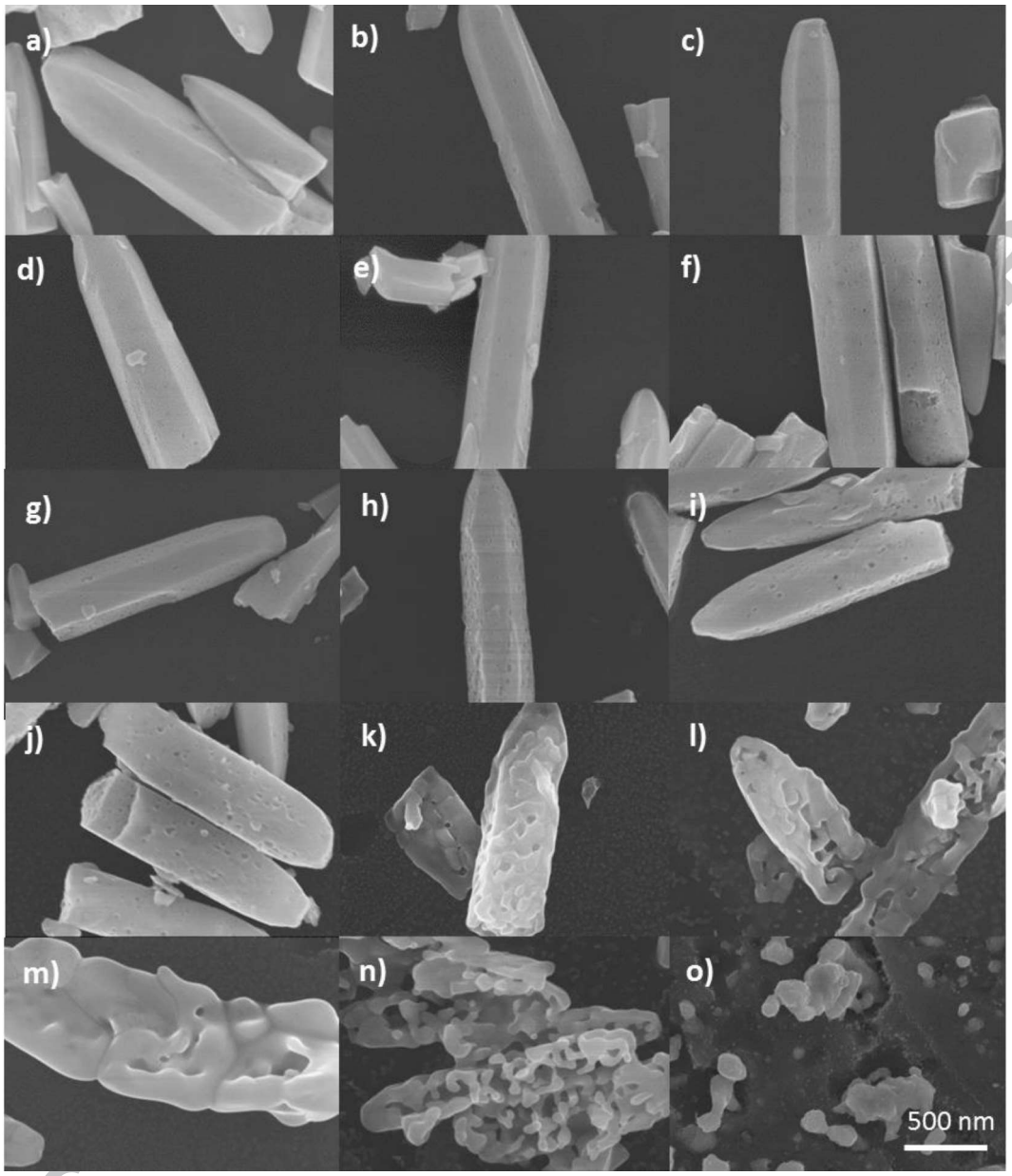

Figure 1: SEM images of ZnO nanorods a) before annealing, and after annealing at b) 600 °C, c) 625 °C, d) 650 °C, e) 675 °C, f) 700 °C, g) 725 °C, h) 750 °C, i) 775 °C, j) 800 °C, k) 825 °C, l) 850 °C, m) 875 °C, n) 900 °C and o) 925 °C.

The nanorods/microrods formed had a hexagonal wurtzite crystal structure comparable to that reported in the literature [3]. Annealing the nanorods up to 800 °C (Figure 1a-g) causes "pitting" similar to that observed by Richardson et al. who suggested the process is caused via the coalescence of zinc and oxygen vacancies that result from the incorporation, and subsequent removal, of a large concentration of hydroxide ions substituting for oxygen in the

ZnO lattice [14]. Annealing past 800 °C induced partial melting and decomposition causing globular structures.

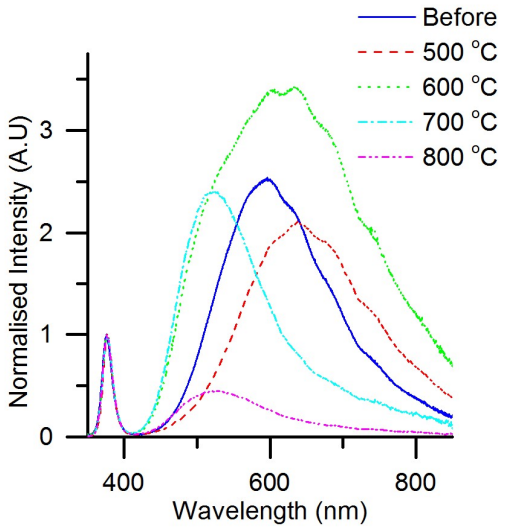

Figure 2: PL of ZnO before and after annealing.

PL spectra (Figure 2) have been normalised to the near band edge (NBE) peak. Before annealing the NBE peak is centred at 376 nm and a Deep Level Emission (DLE) peak, attributed to defects, is apparent at 595 nm. Annealing to 500 °C caused a shift in the DLE peak to 640 nm with significant shoulders at higher wavelengths centred at ~680 nm and ~765 nm. Annealing to 600 °C caused a relative increase in the DLE peak with a significant shoulder at 520 nm and increasing to 700 °C caused a reduction in the components of the DLE peak except that centred at ~520 nm. Final annealing to 800 °C caused a reduction in the DLE peak but no change in shape. Annealing did not alter the position of the NBE peak suggesting no change in crystallinity [15, 16].

There is debate over the origins of the DLE peak components and defects in ZnO concerning the role of zinc and oxygen vacancies, interstitials, hydrogen impurities and density of states confinement effects[17- 26]. Trends in the literature suggest components situated at ~595 nm and ~640 nm are caused by charged oxygen vacancies which are considered to be donor defects [17, 19, 20, 22, 27]. The components centred at ~520 nm, ~680 nm and ~765 nm have been attributed to oxygen anti-sites and neutral oxygen vacancies, both considered acceptor states [18, 22, 23, 28 ,29].

The pitting of the surface indicates a change in the defect chemistry and the PL shows increased oxygen vacancies and at temperatures higher than 600 °C, formation of oxygen anti-site defects. Our previous work suggests that defects in ZnO nanostructures are situated at the near-surface, therefore we attribute the reduction in defects after annealing at 800 °C to sublimation of the surface [6,7].

To understand the effects of the defect changes on the conduction characteristic, nanoscale 2pp measurements were performed. Before annealing the mean normalized resistance, calculated by dividing the measured resistance at +0.05 V by the probe separation (shown in Figure 3(a) at 25 °C), was 1.30×10^{-12} Ωm^{-1}, and the normalised I-V curve shown in Figure 3(b) shows ohmic behaviour, which is comparable to previous results and [6].

Annealing to 500 °C reduced the normalised resistance to 7.77×10^{-10} Ωm^{-1} and the normalised IV curve remained ohmic and is consistent with surface contamination removal, allowing for improved contact formation [6, 7]. It is also possible that part of the reduction is a result of an increased number of donor states defects. The PL results indicate an increase in the number of acceptor states instead, so it is possible that these states may only be optically active rather than electrically active.

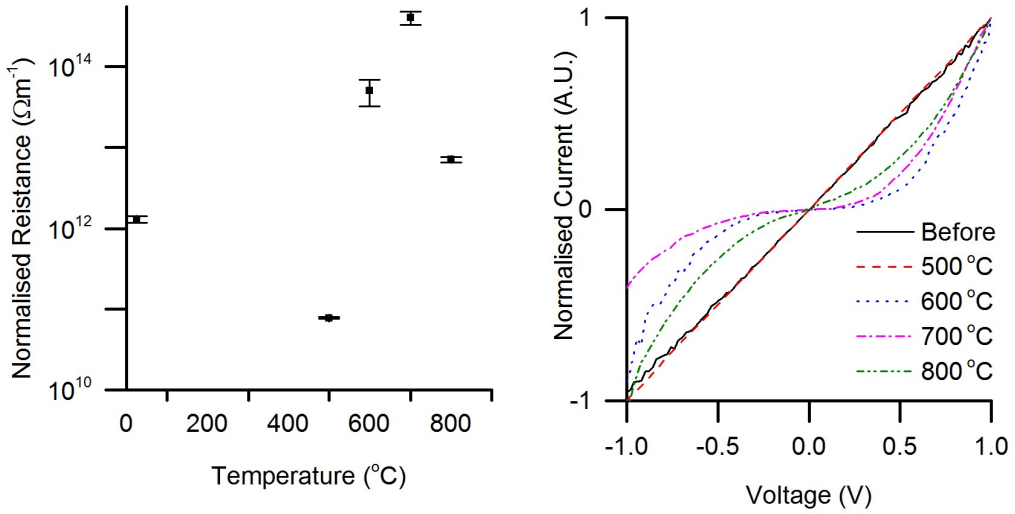

Figure 3 (a). Graph of normalized resistance against annealing temperature. Error bars show the standard deviation. (b) Normalised IV curves.

Annealing at 600 °C led to a rectifying contact with an increased resistance of 5.03×10^{-12} Ωm^{-1} with further annealing to 700 °C causing another resistance increase and an even more rectifying IV curve. We attribute this to acceptor state defect creation shown by the component centred at 520 nm in the PL spectra and in the case of the measurements taken after annealing at 700 °C, the reduction in other components of the PL spectra which are attributed to donor states. Increased acceptor states and decreased donor states resulted in increased band bending at the contact causing the, normalised IV curve to become rectifying. In the case of the measurements taken after annealing to 600 °C, the PL spectrum shows an increase in donor states, as well as an increase in acceptor states. However, ZnO is naturally n-type, therefore an increase in donor defects will have a minimal effect when compared to an increase in the number of acceptor defects [26].

Annealing to 800 °C resulted in a less band bending at the contact causing a less rectifying contact and decreased resistance, attributed to a reduction in acceptor defects when compared to annealing at 700 °C. The reduction in the defect also results in fewer carriers and our results suggest that the contact plays a greater role in the overall resistance of the system than the intrinsic resistance of ZnO.

4. Conclusion

ZnO nanorods/microrods have been synthesised the change in electrical transport properties measured and attributed as a function of annealing temperature in vacuum. Annealing at 500 °C caused a decrease in the measured resistance due to the removal of surface contamination. Compared to using argon bombardment for cleaning nanostructures prior to contact formation, annealing offers a more consistent and simpler process. Annealing to higher temperatures of 600 °C and 700 °C caused acceptor state defects creation resulting in a shift from ohmic to rectifying contacts and increased resistance. Further annealing to 800 °C caused a reduced DLE peak relative to the NBE peak indicating a reduction in both donor and acceptor state defects and a less rectifying contact with lower resistance.

The results show that annealing stages during device fabrication, and in the case of gas sensors during operation, can change the conduction characteristics of the nanorods. Controlling the defect chemistry can allow controlled contact formation to ZnO nanostructures with reductions in donor defects or introduction of acceptor states, changing the contact type from ohmic to rectifying, and therefore offering flexibility for different

device designs. It is possible to predict the contact type by using PL and analysing the DLE components. The results also show that the largest contributor to resistance of the system is contact resistance rather than the resistance of ZnO material.

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Defects can be controlled with vacuum annealing
Controlling the defect can control conduction characteristics
PL and be used to predict contact type