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Controlled and permanent induced Fermi shifts and upwards band bending in ZnO nanorods by surface stripping with argon bombardment

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Abstract

Optimised ZnO nanorod characteristics are essential for novel devices to operate efficiently, especially shifting the n-type nature towards intrinsic or p-type. The effects of argon bombardment for varying amounts of time on the surface chemistry and Fermi level of ZnO nanorods have been studied using XPS. Bombardment at 5 keV removed surface contamination caused by amorphous carbon and OH^-, H_2O and C-O groups. The bombardment also causes the O1s, Zn2p and valence band to shift to lower binding energies, indicating a shift towards intrinsic behaviour. Bombardment time can be used to effect a shift up to 0.8 eV, and this shift remains after the nanorods were re-contaminated by exposure to ambient conditions for 28 days. These results indicate that argon bombardment can permanently shift the n-type nature of ZnO to intrinsic for use in novel devices.

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Introduction

ZnO is a transparent, piezoelectric, wide-band gap semiconductor[1,2] and its nanostructures have been used in field effect transistors, chemical and biological sensors, and solar cells [2–4]. ZnO is naturally an n-type semiconductor which presents difficulties when doping to p-type or even an intrinsic state, which therefore limits the efficiency of devices and potential applications using ZnO nanostructures.

Others have observed that chemical passivation of ZnO nanowires with PMMA, Al_2O_3, aryldiazonium salt or hydrogen plasma, as well as annealing, reduced defects at the surface that cause surface charge and shift the n-type behaviour to intrinsic[5–11]. Our previous work has used argon bombardment to strip the surface of ZnO nanorods and nanosheets, causing a shift from near-ohmic to rectifying contacts, and suggested a shift from n-type towards p-type caused a reduction in surface defects[12–14]. Recent work using X-ray Photoelectron Spectroscopy (XPS) has shown that etching with a monoatomic Ar^+ beam at 5 keV for 5 minutes causes a shift of 0.3 eV in the valence band, indicating upward band bending[15].

In our previous work [15] we studied the effects argon bombardment source and power. Here, we investigate the effects argon bombardment time on an array of ZnO nanorods to find the maximum Fermi shift and whether it is controllable and also whether the shift is permanent, using in-situ XPS.

Method

A ZnO nanorod array was synthesised hydrothermally on Si using the same procedure described previously [15]. The sample was then scored using a diamond scribe into six 3 × 3 mm sections. XPS spectra were collected using a Kratos Axis Supra XPS equipped with a Minibeam 6-gas Cluster Ion Source at a base pressure ~10^{-9} mbar on each of the marked areas before and after argon bombardment with 5 keV monoatomic Ar^+ beam for times varying between 1 and 20 minutes. All experiments were performed on a single silicon wafer substrate in electronic contact and no charge neutralisation was used. In a typical experiment, the Ar^+ beam was rasterized over a 2 x 2 mm area and one control area was left untreated. In all cases, the absence of a Si2p signal was confirmed before and after etching to rule out contributions from the underlying silicon wafer. UV Photoelectron Spectroscopy (UPS) spectra was also collected in the same instrument using the He(I) line. Before and after argon

treatment (here after referred to after^{0}), each area of the sample was characterised using a Hitachi S4800 SEM. The sample was then removed from vacuum and kept in ambient conditions for 28 days, followed by repeated XPS measurements to assess any long-term changes, here after referred to as after^{28}.

Results and Discussion

SEM images (Figure 1) of the as-grown nanowires show that they are of hexagonal form with diameters ranging from 40-300 nm. Our prior work has shown that argon bombardment causes surface stripping of ZnO nanorods and here 1 minute at 5 keV (Figure 1b) has caused visible damage to the tops of the nanostructures similar to what was previous observed[15]. Longer bombardment results in visible morphological changes such that the hexagonal form of the nanorods cannot be clearly observed as much of the surface has been removed (Figures 1 d-f). Figures 1 e-f show signs of charging, indicating a reduction in conductivity, and is consistent with previous work.

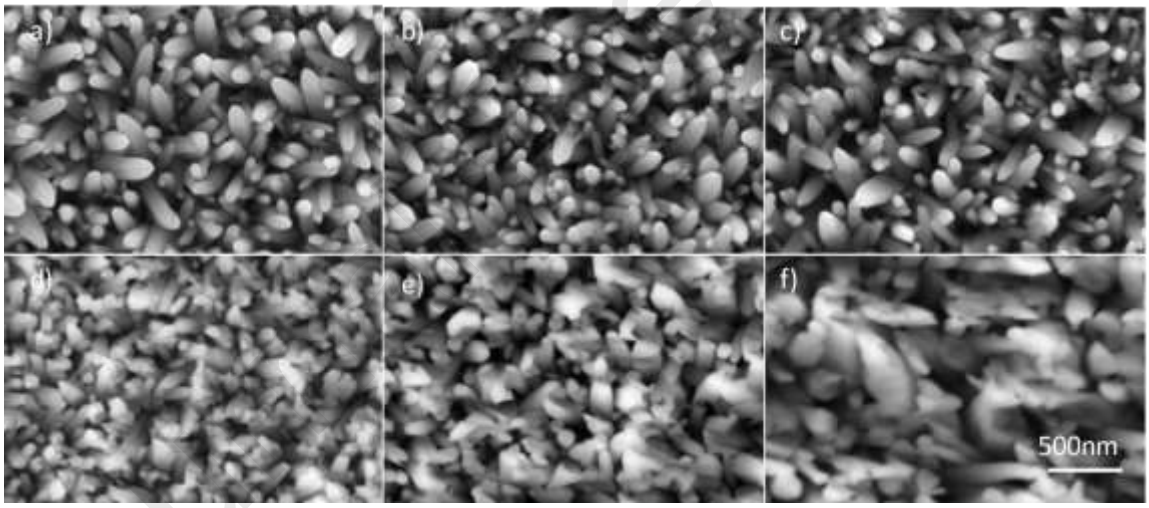

Figure 1. SEM images of ZnO nanowires a) as grown and after argon bombardment at 5 keV for b) 1 minute, c) 2 minutes, d) 5 minutes, e) 10 minutes and f) 20 minutes. (what size is the scale bar?) (add notations to the images)

Argon bombardment is often used to remove surface contamination[16] and previous work suggests that it can surface strip ZnO nanostructures, changing the electronic structure by reducing the n-type donors and causing a shift from ohmic to Schottky contacts[13]. Here, XPS scans have been recorded before and after each argon treatment including a survey scan (supplemental information, Figure S1), and detailed scans of the Zn2p, O1s, C1s and the valence band edge using UPS. The percentage composition is shown in Table S1 in the

supplemental information. The survey scans show no observable deviation with all chemical elements remaining after bombardment and no argon incorporated after bombardment.

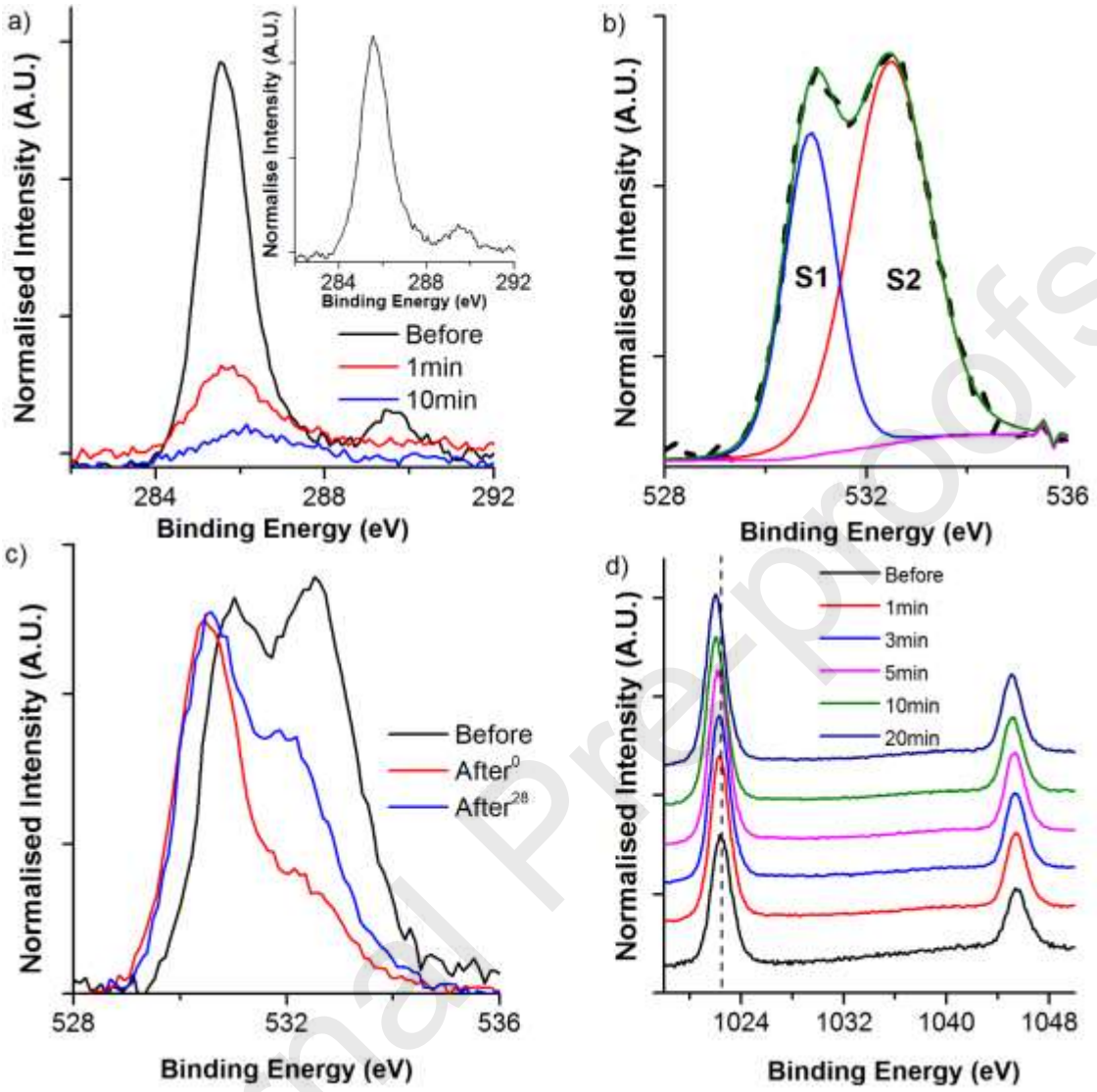

Figure 2. XPS scans of ZnO nanowires. a) normalised C1s peak scans before and after^{0} 1 and 10 minutes of Argon bombardment with inset showing carbon 1s peak after^{28} 10 minute sample b) O1s peak with fitted components c) normalised O1s peak before, after^{0} 10 minute of Argon bombardments and after^{28} 10 minutes sample and d) normalised Zn2p peak before and after^{0} argon bombardment and off set be 0.2 with dashed line indicating original position of the Zn2p$_{3/2}$ peak.

Figure 2a shows the C1s peak, where the intensities have been normalised for each scan for better comparison. The inset shows the after^{28} C1s peak of the area subject to 10 minutes bombardment which, due to the sample being removed from the XPS and potential for height changes that can affect measurements, is not directly compared to those in the main figure. Previously, we attributed the improved contact consistency to the removal of adventitious

carbon by argon bombardment [12,13,15]. Here, after 1 minute of argon bombardment the carbon is reduced by 70% of its original value, and areas subject to treatment for longer times reduced by an average of 84 ±2 %. It can also be seen the C1s peak becomes less defined and the component at ~290 eV is removed. The after^{28} C1s peak has regained its definition and its component at ~290 eV suggesting re-contamination by adventitious carbon.

Before treatment, the O1s peak (Figure 2b) consisted of 2 peaks centred at 530.8 eV which is attributed to metal oxide and marked as S1, and at 532.6 eV which is attributed to surface states and contamination such OH^-, H_2O and C-O groups and marked as S2 [9,17–21]. Before argon bombardment, the average percentage contribution of the S1 peak O1s peak was 63 ±3 % while after^0 it reduced to 29 ±4 % for all treated areas. With after^{28}, the contamination component had increased to 54 ±4 % indicating recontamination with OH^-, H_2O and C-O groups. Figure 2c also shows the O1s peak shifts to a lower binding energy after bombardment, indicating a shift from n-type behaviour towards intrinsic and this shift is not altered after 28 days in ambient conditions. The Zn 2p peak (Figure 2d) also shows that the position of the peak shifts to a lower binding energy after argon bombardment, and that the shift is dependent on the bombardment duration.

It has been suggested that reduction in the OH^- ions will result in a shift of the valence band and Fermi level to lower energy, resulting in upwards band bending and a shift from n-type to intrinsic ZnO [8–10]. Here, the valence band (VB) has been scanned using UPS and the band edge fitted with a step-down function and the x-axis intercept was found by applying two tangents (Figure 3a). Before argon bombardment, the average Fermi level value was 3.5 ±0.1 eV. With after^0, 10 minutes of argon bombardment has resulted in a shift to 2.8 ± 0.1eV. Figure 3b shows the Fermi level shift calculated from the VB scans of samples after^0 and after^{28} against bombardment time, which is non-linear and suggesting a maximum shift of ~0.8 eV. Also, being left in ambient conditions for 28 days does not cause the VB to shift back to high binding energy, indicating the shift is long-term and that recontamination with

OH^- does not shift the ZnO nanorods back towards n-type.

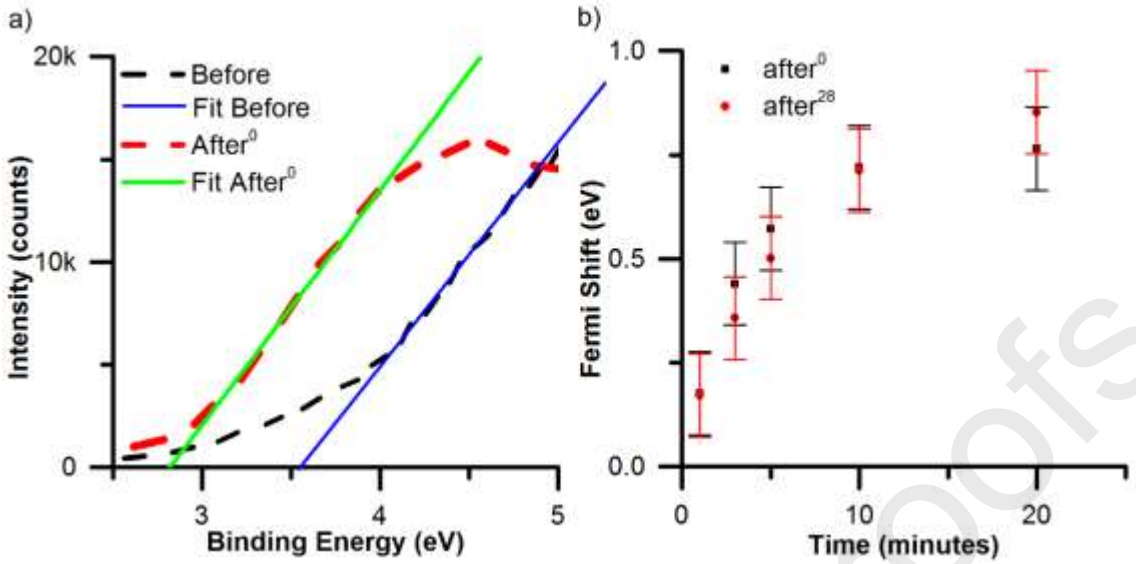

Figure 3. a) UPS valence band scans before and after^0 argon bombardment for 10 minutes. b) Evolution of Fermi shift against time for argon bombardment for after^0 and after^{28}.

Conclusion

ZnO nanorods have been synthesised hydrothermally and characterised before, immediately after, and 28 days after argon bombardment using with SEM and XPS. Our work here shows that the duration of argon bombardment can be used to control a permanent shift in the VB edge of up to 0.8 eV even after re-contamination, and therefore this can control the contact type and the electronic nature of the ZnO surface. The shift towards intrinsic also indicates that carrier concentration has reduced and Mott-Schottky measurements should be considered to assess the scale of the reduction. The work presented here, leads to the possibility of using argon bombardment surface stripping to controllably shift n-type ZnO to intrinsic, which will allow other processes to convert it to stable p-type ZnO which has so far been challenging [22]. By overcoming this previous challenge this method will positively impact devices applications and devices such as LEDs which require p-type ZnO [23].

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Argon bombardment duration can control the Fermi shift of ZnO nanowires and control the shift from n-type towards intrinsic/p-type.
The maximum Fermi shift caused by surface stripping with argon bombardment ~0.8 eV
Fermi shift and shift from n-type towards intrinsic remains after 28day in ambient condition and recontamination.

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