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Citation for final published version:

Lord, Alex M., Maffei, Thierry G., Allen, Martin W., Morgan, David John, Davies, Philip Rosser, Jones, Daniel R., Evans, Jonathan E., Smith, Nathan A. and Wilks, Steve P. 2014. Surface state modulation through wet chemical treatment as a route to controlling the electrical properties of ZnO nanowire arrays investigated with XPS. *Applied Surface Science* 320, pp. 664-669. 10.1016/j.apsusc.2014.09.078

Publishers page: <http://dx.doi.org/10.1016/j.apsusc.2014.09.078>

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Surface state modulation through wet chemical treatment as a route to controlling the electrical properties of ZnO nanowire arrays investigated with XPS

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Abstract

ZnO is a wide bandgap semiconductor that has many potential applications including solar cell electrodes, transparent thin film transistors and gas/biological sensors. Since the surfaces of ZnO materials have no amorphous or oxidized layers, they are very environmentally sensitive, making control of their semiconductor properties challenging. In particular, the electronic properties of ZnO nanostructures are dominated by surface effects while surface conduction layers have been observed in thin films and bulk crystals. Therefore, the ability to use the ZnO materials in a controlled way depends on the development of simple techniques to modulate their surface electronic properties. Here, we use monochromatic x-ray photoelectron spectroscopy (XPS) to investigate the use of different wet chemical treatments

(EtOH, H₂O₂) to control the electronic properties of ZnO nanowires by modulating the surface depletion region. The valence band and core level XPS spectra are used to explore the relationship between the surface chemistry of the nanowires and the surface band bending.

Keywords: ZnO; nanowires; surface depletion; electrical properties; surface chemistry; XPS.

1. Introduction

ZnO has become a prominent semiconductor since the evolution of Nanotechnology due to the multiplicity of structures that can be grown. However, at the nanoscale the surface dominates over bulk properties, which is particularly true for metal oxides having no passivating, amorphous or oxide surface layer. For this reason, ZnO nanostructures are highly applicable in sensor devices due to the sensitivity of the surface to the surrounding environment. This fact facilitates modulation of the properties of a ZnO nanostructure simply by exposing the surface to different agents such as gases, vapours or liquids, for example, oxygen, water or ethanol (EtOH), respectively. Surface chemistry has been shown to be no less important for controlling the properties of electrical contacts to ZnO such as Schottky barriers to bulk crystals [1] and Ohmic contacts to nanowires.[2] The most widely applied effect of surface modulation is on the electrical transport properties, particularly through the action of the surface potential barrier and n-type carrier concentration.[3] It is possible to classify surface modulating agents into two categories: those that increase the surface depletion region (depleting) and those that decrease it (accumulating). Typically, it is thought oxygen ions adsorbed to the ZnO surface act as acceptors, increasing the depletion region, while water and OH groups act as donors.[4–6] To gain control over this effect it is possible to use a chemical such as EtOH which is known to react with adsorbed O₂ on the ZnO surface to release trapped charge and also donate electrons through the formation of hydroxyls, so reducing the surface depletion layer.

ZnO in its natural state after exposure to air has a surface state density balanced by acceptors and donors that create the surface band bending. For lower doped ZnO ($\leq 10^{17} \text{ cm}^{-3}$) typical of bulk crystals this leads to a surface accumulated layer (downward band bending) and a surface conduction mechanism.[7–9] For ZnO nanostructures that have by far a much greater carrier concentration ($\sim 10^{18} \text{ cm}^{-3}$), such as nanowires, this leads to a surface depletion region

(upward band bending) which has been measured by Souidi *et al.* using Kelvin probe force microscopy to be ~ 0.2 eV.[10]

In a previous article we used 4 probe electrical measurements to show that the resistivity of individual ZnO nanowires increases as their diameter decreases. [11] We interpreted this result in terms of the surface depletion region caused by chemisorbed species, effectively constraining electron transport to the bulk. This effect then essentially becomes more important as the nanowire diameter decreases, and significantly alters the resistivity below 120nm diameter. We supported this interpretation by measuring nanowires previously treated with EtOH, which showed a lower resistivity than untreated nanowires and almost no dependence on diameter. This latter result also confirmed the donor-like nature of EtOH.

However, no detailed direct measurement of the surface band bending has been conducted for nanostructures exposed to chemical agents that are known to modulate the surface and electrical properties.[5,12] This is particularly important as surface donors are thought to have a significant impact on the formation of electrical contacts formed on planar ZnO which often require reactive plasma etching to remove OH groups and reduce oxygen vacancies near the surface to produce quality Schottky contacts.[1,13] Another method of reducing oxygen vacancies at the surface is to expose the material to an oxidising agent such as H₂O₂ which has been shown to have the opposite effect to EtOH and increase the resistivity of nanowires[2,12] and improve Schottky contacts on bulk ZnO.[14,15] However, although a study by Maffei *et al.* investigated the effect of H₂O on the surface of nanowires [4], there has been no direct comparison of the surface modulating effect of chemical treatments on ZnO nanowires which we achieve here with the application of monochromatic X-ray photoelectron spectroscopy (XPS) to directly measure the valence band offset and chemical components. The measurements show EtOH treatment does indeed reduce the surface barrier while H₂O₂ increases it, confirming our previous model [11] which shows surface states have an increasing influence on the resistivity of high-quality ZnO nanowires as their diameter decreases. Interestingly, the surface treatment is reversible showing one chemical can counteract the other and return the surface potential barrier close to its as-grown original state.

2. Experimental methods

2.1 ZnO Nanowire Growth

The ZnO nanowires were grown by a high temperature vapour phase method using the carbothermal reduction of ZnO and vapour solid nucleation on a crystalline substrate. Before the growth experiment, a GaN substrate was cleaned with solvents and rinsed thoroughly with DI water and dried.[16,17] The substrate was placed in a tube furnace and NW growth was performed with the following experimental parameters – furnace temperature 1050 °C, substrate temperature 600-650 °C, pressure 1.6 *mbar*, gas flow 100 *sccm* Ar and 10 *sccm* O₂, growth time 60 *mins*. To achieve a high purity Zn vapour the source materials were ZnO (Alfa Aesar 99.99%) and carbon (sigma Aldrich 99.99%) 325 mesh.

2.2 X-ray photo-electron spectroscopy (XPS)

The samples were analysed using a Kratos Axis Ultra-DLD photoelectron spectrometer, utilising monochromatic Al K α radiation, operating at 144 W (12 mA x 12 kV) with an effective energy resolution ~400 *meV*, with a take-off angle of 90°. Charge compensation was achieved utilising the Kratos magnetic lens system. Survey spectra were collected at a pass energy of 160 *eV*, from -5 *eV* to 1200 *eV*, while high resolution spectra were collected between 520 *eV* and 540 *eV* (O 1s), from 1012 *eV* to 1030 *eV* (Zn 2p 3/2), from 276 *eV* to 300 *eV* (C 1s) and valence band (VB) spectra were collected over the range -5 *eV* to 20 *eV*. For each scan a pass energy of 40 *eV* was used.

3. Results and discussion

High quality ZnO nanowires were grown by a vapour phase method producing nanowires with intrinsic n-type properties and a surface depletion region that remains in ultra-high vacuum (UHV) conditions.[3,10,11] Following growth time the substrate was inspected with scanning electron microscopy (SEM) as shown in Fig. 1(a) and (b). The nanowires were well aligned, of high quality as we have previously shown, [11] and growing along [0001] with diameter ranging from 50 to 100nm and an average length of 7 μm . The nanowire array was divided into 4 equal parts and underwent one of the following treatments: no treatment other than air exposure (as-grown), exposure to liquid ethanol (EtOH), 10 *sec* dip in 5% H₂O₂ (5% H₂O₂), and finally, the last section underwent the H₂O₂ treatment and then the EtOH treatment (5% H₂O₂ + EtOH). The EtOH treatment was simply performed by pipetting 200 proof ethanol (EtOH) onto a section of the nanowire array and allowing to dry. The 5% H₂O₂

treatment was performed by dipping the array section for 10 *sec* in 5% H₂O₂ diluted in DI water before rinsing thoroughly with DI water and drying.

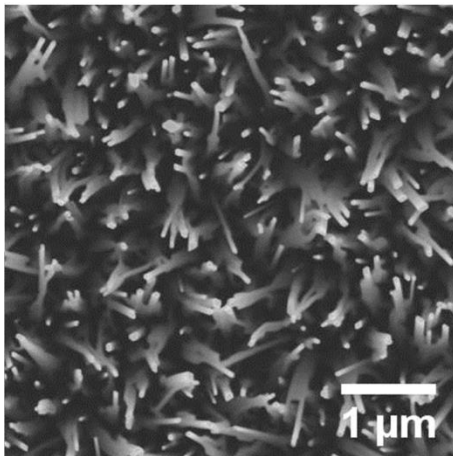
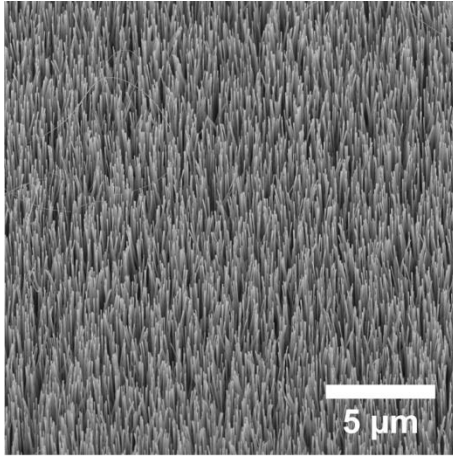


Fig. 1. (a) SEM image of the sample used for the analysis shown at 30° tilt and in (b) the top-down perspective showing the good alignment with nanowires of 50-100 nm diameter and length $\sim 7 \mu\text{m}$.

3.1 Valence Band Offset

The valence band offset (VBO) can be directly measured by collecting the photoelectrons emitted at energies from the Fermi level E_F to the valence band (VB) maximum E_V and beyond. The point at which the valence band emission onset occurs can be used to measure the VBO from the Fermi level and, with a well-defined bandgap the surface band bending can then be calculated in the following manner. A linear fit is extrapolated from the lower binding energy edge of the VB spectrum to a line fitted to the instrument background which provides the exact onset of the VB emission $\zeta = E_V - E_F$ as shown in Fig. 2(a) and (b). [9,18] The position

of the Fermi level E_F was calculated using the nanowire free carrier concentration [3,11] of $n=1 \times 10^{18} \text{ cm}^{-3}$ using $\xi = (kT/q) \ln(N_C/n)$ relative to the conduction band (CB) minimum which gives $\xi=0.03 \text{ eV}$, where the CB effective density of states [9] for ZnO is $N_C=2.94 \times 10^{18} \text{ cm}^{-3}$. Therefore, the surface potential barrier V_{BB} can be calculated from measured ζ as $V_{BB}=E_g-\xi-\zeta$, where $E_g=3.37 \text{ eV}$ [19] is the bandgap of ZnO. Positive values of V_{BB} correspond to upward band bending (and consequently surface electron depletion) while negative values indicate downward band bending (and electron accumulation).

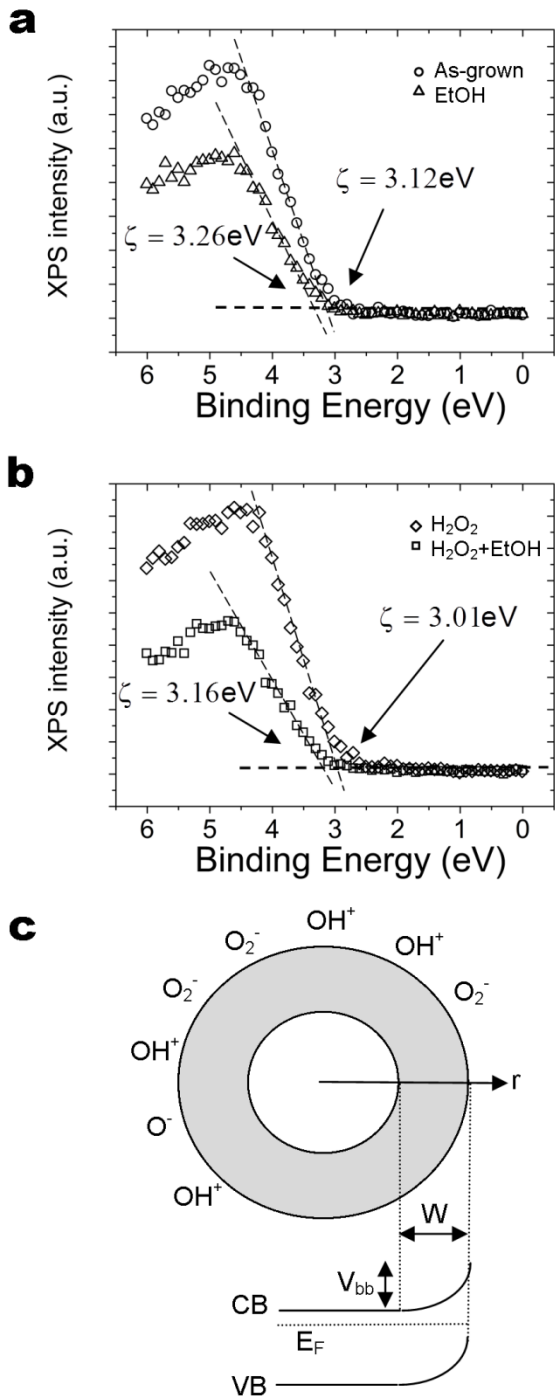


Fig. 2. (a) The valence band spectrum measured from the as-grown and EtOH treated ZnO nanowire samples showing the linear fit extrapolated from the valence band edge to the instrument background providing a measure of ζ ; similarly, (b) showing the valence band spectrum for the H_2O_2 and $\text{H}_2\text{O}_2+\text{EtOH}$ samples. (c) a schematic diagram showing a cross-sectional approximation of a ZnO nanowire and the band bending created by adsorbed ions, OH groups and H_2O .

For nanowires below 120 nm diameter the width of the surface depletion region that occurs on (01 $\bar{1}$ 0) side facets impacts on the conductivity of the nanowire.[11,20] Therefore, it is useful in the context of this study to estimate the depletion width W (shown in Fig. 2(c)) from the surface potential barrier V_{bb} and carrier concentration n using the standard depletion approximation $W = \sqrt{\frac{2\epsilon_{sr}\epsilon_0 V_{bb}}{qn}}$. [21] The band bending induced by the surface treatments are summarised in Table 1 along with the calculated depletion widths.

| Treatment | ζ (eV) | $\Delta\zeta$ (eV) | V_{bb} (eV) | W (nm) |
|-----------------------------------------|---------------------|--------------------|---------------|----------|
| As-grown | 3.12 (± 0.04) | - | 0.22 | 14.50 |
| EtOH | 3.26 (± 0.03) | -0.14 | 0.08 | 8.63 |
| 5% H ₂ O ₂ | 3.01 (± 0.04) | 0.11 | 0.33 | 17.85 |
| 5% H ₂ O ₂ + EtOH | 3.16 (± 0.03) | -0.04 | 0.18 | 13.13 |

Table 1. The analysis of the valence band spectra yielded the values shown in the table. ζ is the energy difference between the valence band maximum and E_F , $\Delta\zeta$ the change in ζ after surface treatment and V_{bb} the surface potential barrier which creates a depletion region of width W .

For the as-grown nanowires the measured value of $V_{bb}=0.22$ eV agrees well with Kelvin probe force microscopy measurements performed by Soudi *et al.* on individual ZnO nanowires which yielded $V_{bb}=0.2$ eV. [10] Interestingly, the measurements of Soudi *et al.* were performed in air indicating exposure to UHV does not change the surface potential barrier of the nanowires. This can be explained by the presence of tightly bound species such as oxygen and hydroxyls along with adsorbed water that can only be removed by heating [4,9] and remain on the surface in UHV at room temperature. However, exposing the nanowires to EtOH dramatically reduced the surface potential barrier to a value of $V_{bb}=0.08$ eV. This result supports our previous electrical measurements on EtOH exposed nanowires which have a resistivity that is relatively independent of diameter, unlike as-grown nanowires for which the resistivity increases as their diameter is reduced. The diminished effect of the surface on the nanowire electrical properties after EtOH exposure is explained by a reduction in the width of the surface depletion region which is much wider ($W=14.5$ nm) for untreated as-grown nanowires. A wider surface depletion region on the (01 $\bar{1}$ 0) side facets of the

nanowires consumes a greater proportion of the conductive channel; for thinner nanowires an increase in the surface depletion region is to effect an increase in the resistivity, which is most noticeable when the diameter $<120\text{ nm}$. [11] The H_2O_2 treatment, although relatively dilute, has the opposite effect of EtOH increasing the surface potential barrier to a considerable height of $V_{bb}=0.33\text{ eV}$ producing a depletion width of $\sim 18\text{ nm}$. This substantial depletion width increases the influence of the surface on the nanowire conductivity with nanowires becoming increasingly less conductive as the width is reduced below 120 nm . [2] This measurement of V_{bb} is in good agreement with the upward band bending of $\sim 0.4\text{ eV}$ measured on H_2O_2 treated bulk ZnO. [15] The fact that we observe a smaller shift could be due to the lower carrier concentration of bulk ZnO compared to the nanowires measured here, and the milder H_2O_2 solution applied to the nanowires. However, as many device processing steps expose the nanowires to various chemicals it is important to control the final properties of the nanowires with the ability to reverse the effect of each treatment step. Our results show that treating NWs that have been exposed to H_2O_2 with EtOH has the effect of restoring the surface potential barrier to a similar position as the as-grown and untreated nanowires with only a small difference $\Delta\zeta=-0.04\text{ eV}$ in V_{bb} .

3.2 Elemental peaks

3.2.1 Binding Energy

Examining the core-level peaks of O 1s, Zn 2p/3 and C 1s we can infer some details of the surface chemistry that leads to the change in the potential barrier. Of most interest is the O 1s spectrum as this can reveal details of oxygen associated with hydroxyls, water, surface lattice oxygen and organic molecules. To examine the measured changes the O 1s peak was fitted with two Gaussian-Lorentzian components [12,22] which accurately matched the envelope to the raw data. The normalised peaks are shown in Fig. 3 and the associated data in Table 2. To simplify the discussion we can label the main O 1s peak associated with the ZnO lattice as O-Zn, while the surface oxygen which occurs as a shoulder in the O 1s peak and at greater binding energy as O-S. The FWHM of the O-Zn component for each sample was fixed at 1.13 eV which was obtained from the fitting of the as-grown sample O 1s data.

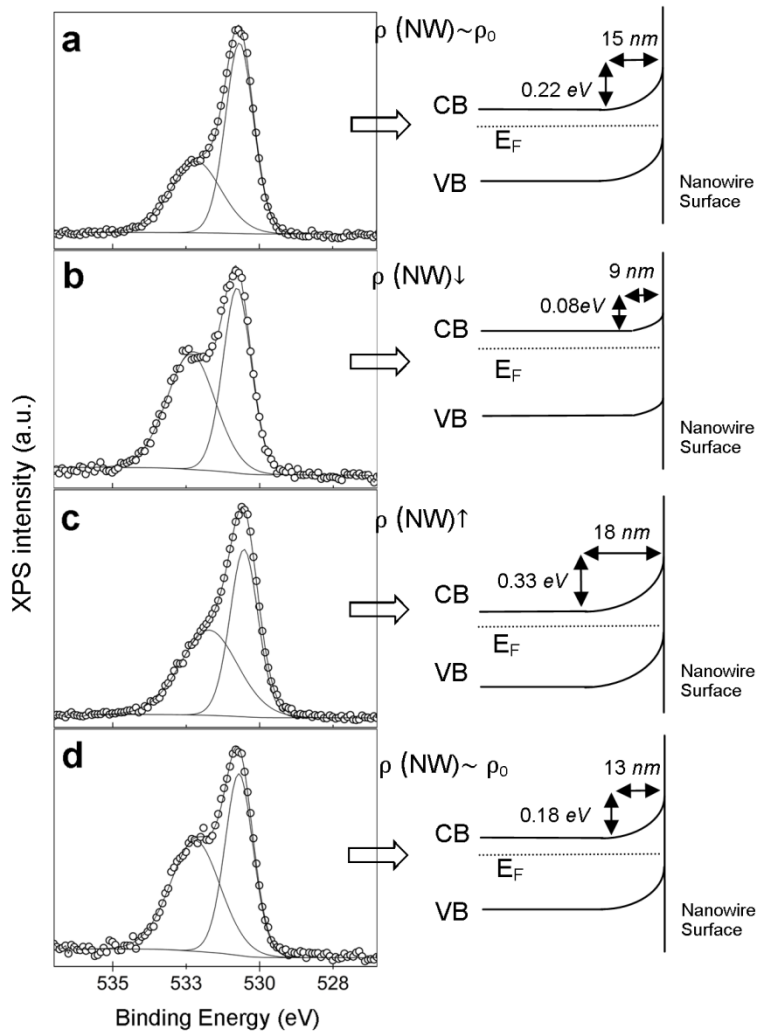


Fig. 3. Normalised XPS O1s spectra for each of the treatments (a) as-grown, (b) EtOH, (c) 5% H₂O₂ and (d) 5% H₂O₂ + EtOH. The raw data (dots) is fitted with an envelope approximated with 2 components, one being the O-Zn bonding, the other broader shoulder is associated with OH, oxygen ions, oxocarbons and H₂O. Also included are the schematic representations of the surface band bending that results from each treatment and the effect this has on the nanowire resistivity ρ .

| Treatment | As-grown | EtOH | 5% H ₂ O ₂ | 5% H ₂ O ₂ + EtOH |
|--------------------------|----------|--------|----------------------------------|-----------------------------------------|
| Peak O-Zn (eV) | 530.67 | 530.77 | 530.53 | 530.72 |
| Peak O-S (eV) | 532.14 | 532.33 | 531.73 | 532.26 |
| % O-S | 40.89 | 53.50 | 50.01 | 51.50 |
| O-S _{FWHM} (eV) | 2.07 | 2.02 | 2.26 | 1.98 |
| Δ O-Zn (eV) | - | -0.10 | 0.14 | -0.04 |
| (O-S)-(O-Zn) (eV) | 1.47 | 1.56 | 1.20 | 1.49 |

Table 2. Data showing the analysis of the O 1s peak for each chemical treatment. Δ O-Zn (eV) specifies the shift in the O-Zn peak relative to the as-grown sample, while (O-S)-(O-Zn) is the energy offset between the O-Zn peak and the high binding energy shoulder attributed to surface oxygen (O-S).

3.2.2 Intensities

For both EtOH (Fig. 3(b)) and the 5% H₂O₂ (Fig. 3(c)) treatments the proportion of the O-S component is similar, see Table 2. However, the shape (FWHM of 2 eV and 2.3 eV, respectively) and position relative to O-Zn (1.56 eV for EtOH compared to 1.20 eV for H₂O₂) are quite different (Table 2), indicating that the chemical bonds of the surface oxygen are different between the two treatments. This can be explained by the chemical interaction of EtOH which may introduce ethoxy groups to the surface, leading to an emission at a greater binding energy than for OH groups, and may increase hydroxyl formation by reaction with lattice oxygen on the nanowire surface. In comparison, H₂O₂ has the effect of reducing oxygen vacancies V_O or increasing Zn vacancies V_{Zn} in the ZnO lattice with oxygen radicals penetrating into the ZnO to form oxygen interstitials or antisite defects [23,24]. EtOH can induce surface metallicity [7] from binding of H to the lattice oxygen $O^{2-}+H \rightarrow OH^-+e^-$ and reduce surface band bending as the hydroxyls act as donors.[19] This is enhanced by the reaction of EtOH with adsorbed surface oxygen ions that act as acceptors (O^- , O_2^-).[13] While H₂O₂ can also lead to the formation of OH bonds, it has the additional effect of reducing the number of oxygen vacancies and/or increasing Zn vacancies which reduce the carrier concentration near the surface.[1,12,14,15,23]

3.2.3 Shifts and widths

The difference in chemical reaction on the surface explains the shift in band bending and the differences in the O1s shoulder of each treatment. The O-S peak of the as-grown ZnO nanowires originates from a combination and balance of adsorbed surface oxygen ions, H₂O,

hydroxyls and adventitious carbon molecules all competing for adsorption sites. The emission associated with hydroxyl groups, or O^{2-} ions in oxygen deficient regions on the ZnO surface, is often considered to be at a BE of ~ 1 eV nearer to the O-Zn peak than adsorbed H_2O , O_2^- and oxocarbons which are generally considered to create a peak at up to ~ 3 eV greater BE than the O-Zn.[4,9,25,26] The measurements in the case here show the O-S peak for the H_2O_2 treatment is closer in BE to the O-Zn peak than EtOH treated nanowires. The observed difference in O-S BE is not large enough to allow fitting of 2 separate O-S peaks which could be clearly labelled as hydroxyls and adsorbed oxygen. This is because the peak separation of O-S to O-Zn (Table 2) for all samples is approximate to the separation of ~ 1.4 eV often attributed to hydroxyl bonds.[9,22] However, the other evidence such as the valence spectra, the electrical measurements and the detailed data of the O1s shoulder show there are some significant differences between the samples. To explain the observed change in O-S BE for the chemically treated samples we can look at the reaction of EtOH which has two pathways of binding with the ZnO surface. One mechanism is the complete molecule C_2H_5OH binding to the ZnO surface, and the other is the dissociative binding with the formation of a hydroxyl with a surface lattice O atom and ethoxy C_2H_5O binding to V_O or Zn^{2+} .[5,6] The resulting effect is for ethanol to act as a reducing agent and donate electrons at the surface. The presence of the C-O bond in ethoxy will likely have the effect of changing the O-S position to a different BE to that of hydroxyl bonds alone, possibly to a similar position BE ~ 532.5 eV that has been attributed to adventitious CO_2 adsorbed to the ZnO surface.[27] In contrast, oxidising treatments such as the H_2O_2 dip act to reduce oxygen point defects near the ZnO surface, which may increase the lattice oxygen O-Zn signal and the emission due to O^{2-}/O_2^{2-} which appears at the same BE as O-H bonds.[28] The wet H_2O_2 treatment must also have the effect of increasing water coverage, which is used as the solvent, resulting in a broader O-S peak but at lower BE ~ 531.7 eV. The oxidising effect of H_2O_2 provides the measured increase in surface band bending and consequent reduction in nanowire conductivity [11,12]. Combining H_2O_2 with the additional EtOH treatment provides a reduced number of point defects on the surface for chemisorption of ethoxy and hydroxyls resulting in the surface potential barrier being slightly lower than the as-grown nanowires but larger than EtOH treatment alone.[5]

| Treatment | As-grown | EtOH | 5% H ₂ O ₂ | 5% H ₂ O ₂ + EtOH |
|---------------------------|-------------|-----------------|----------------------------------|-----------------------------------------|
| Zn 2p/3 (Δ) (eV) | 1021.98 (-) | 1022.08 (-0.10) | 1021.92 (0.06) | 1021.97 (0.01) |
| C 1s (Δ) (eV) | 285.38 (-) | 285.44 (-0.06) | 285.18 (0.2) | 285.40 (-0.02) |
| C:Zn | 0.88 | 1.04 | 0.59 | 0.82 |
| Zn:(O-S+O-Zn) | 1.16 | 1.51 | 1.52 | 2.12 |

Table 3. The data from a single fitting component using a Gaussian-Lorentzian approximation for the Zn 2p/3 and C1s peaks for each treatment of the nanowires.

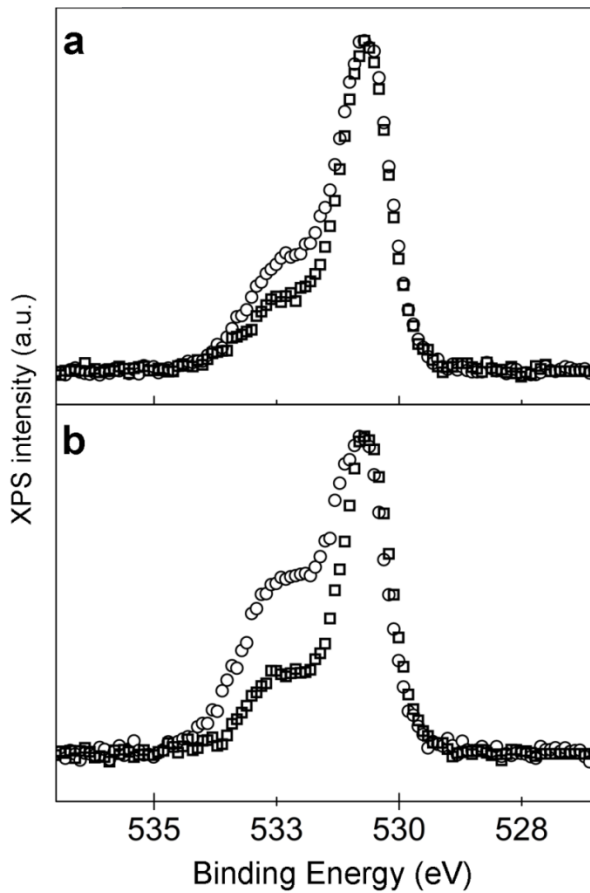


Fig. 4. Normalised XPS O1s spectra for each of the treatments (a) as-grown, and (b) EtOH, measured with a take-off angle normal to the sample surface (90°) (shown as open circles) and 60° (open squares).

3.2.4 Zn 2p/3 and C1s peaks

Fitting one Gaussian-Lorentzian component to the Zn 2p/3 and C1s peaks, Table 3 shows shifts in peak energy on a similar scale to those measured from the valence data confirming the EtOH treatment reduces the width of the surface insulating layer and H₂O₂ increases it.

Examining the ratio of Zn 2p/3 to the total O1s (Table 3) shows an increase in Zn after each treatment which may result from the reaction of the chemical agents with the ZnO surface and oxygenated adsorbed species such as H₂O, O₂ and CO₂ and replacing them with preferential binding to native oxygen of OH and/or carbon/organic molecules. A significant increase in the carbon C 1s peak, which is associated with the C-C bond and is at the centre of the ethanol/ethoxy molecule, is observed after EtOH treatment seemingly confirming the presence of ethoxy/EtOH on the ZnO surface. To further confirm this surface layer after EtOH treatment scans were acquired at 60° off normal emission, effectively increasing the escape depth of the photoelectrons for nanowires standing normal to the substrate. The O 1s peak reveals a large reduction (44%) in the O-S component for the EtOH sample compared to normal emission (Fig. 4(b)) indicating the O-S signal originates from a concentration of oxygen molecules on the nanowire surface. Whereas, the difference between the O-S shoulder for the two take-off angles is much less (29%) for the as-grown sample, (Fig. 4(a)). Finally, we note that H₂O₂ is a strong oxidiser that removes carbon and organic molecules often forming H₂O as a by-product as shown by the large decrease in the C1s signal (Table 3), confirming the ability of the chemical to react with contamination and clean the nanowire surface.

4. Conclusion

Monochromatic XPS was used to directly measure changes in the surface band bending of ZnO nanowires caused by wet chemical agents. The results are consistent with previous electrical transport measurements on ZnO nanowires and showed that ethanol treatment reduced the surface potential barrier to ~0.08 eV, while hydrogen peroxide increased it to ~0.33 eV, from an original potential barrier of 0.22 eV for the untreated nanowire surface. Wet chemical treatment of nanowires provides a relatively straightforward method for modulating their surface chemistry and electronic properties, and as such is an essential process for nanowire device fabrication. Use of this knowledge will allow processing steps to be tailored to ensure that nanowires have controlled and reproducible properties.

Acknowledgments

AL would like to thank Philip R. Davies at Cardiff Catalysis Institute for making this work possible.

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