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XPS investigation of titanium contact formation to ZnO nanowires
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Abstract
Ti is often used to form an initial Ohmic interface between ZnO and Au due to its low work function, and the TiO₂/ZnO heterojunction is also of great importance for many practical applications of nanoparticles. Here, Ti has been controllably deposited onto hydrothermally grown ZnO nanowires and the formation of metal-semiconductor contact has been investigated using x-ray photoelectron spectroscopy (XPS), photoluminescence (PL) spectroscopy and scanning electron microscopy (SEM). XPS results showed that the Ti initially reacts with surface oxygen species to form TiO₂, and further deposition results in the formation of oxides with oxidation state numbers lower than four, and eventually metallic Ti on top of the TiO₂. The formation of TiC was also observed. XPS showed that the onset of metallic Ti coincided with a Zn 3p core level shift to lower binding energy, indicating upwards band bending and the formation of a rectifying contact. Annealing caused a near-complete conversion of the metallic Ti to TiO₂ and caused the Zn 3p to shift back to its original higher binding energy, resulting in downwards band bending and a more Ohmic contact. PL measurements showed that the optical properties of the nanowires are not affected by the contact formation.

Introduction
ZnO is a metal oxide semiconductor with a wide direct band gap of 3.37eV and a large exciton binding energy of 60 meV that has received much attention over the past 15 years [1, 2]. ZnO can form numerous nanostructures, including nanowires, that have many potential applications in microelectronics [3], mechanical energy harvesting [4], sensors [5], field emitters [6], ultra violet lasers [7], photovoltaics [8] and other optoelectronic devices [9]. All
these devices require the formation of metal/ZnO contacts, the nature of which has profound influence on device performance, with Ohmic contacts preferred for most applications [10, 11]. For nanowire array style devices, where the nanowires grow quasi-vertically from a substrate, one electrical contact can often be made using the seed layer from which the nanowires are grown [5, 12]. To form a similar contact to the free ends of the nanowires, one requires metal deposition using techniques such as sputtering or evaporation [13, 14]. Au is commonly used in contact fabrication as it does not oxidise in air; however, a Schottky contact forms when it is deposited on ZnO [15]. Therefore Ti is often used to form an initial Ohmic interface between the ZnO and Au due to its low work function [10, 16, 17]. A drawback of this approach is that Ti is extremely reactive and oxygen atoms out-diffuse from the ZnO into the Ti layer to form TiO$_2$ [18], which can cause a high contact resistance. Conversely, the formation of oxygen vacancies near the ZnO surface can increase carrier concentration and lower specific contact resistance [19]. The TiO$_2$/ZnO heterojunction is also of great importance for dye sensitised solar cells,[20, 21], photocatalysis[22-24], water-splitting and self-cleaning coatings [25]. It is therefore important to understand the formation of the Ti/ZnO contacts and the TiO$_2$/ZnO heterojunction in order to optimise device performances.

Here, we controllably deposit Ti onto hydrothermally grown ZnO nanowires and investigate the formation of the metal-semiconductor contact using x-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and scanning electron microscopy (SEM).
Experimental Methods

ZnO nanowires were synthesised hydrothermally on a Si substrate with a 30 nm ZnO seed layer using a 1:1 molar ratio solution of zinc nitrate and hexamethylenetetramine held at 90°C for 9 hours [26]. We tested two samples made using this procedure and it was found during the initial XPS analysis that one of the samples (hereafter referred to as Sample 2) had more surface oxygen species than the other (to be referred to as Sample 1). This discrepancy is likely due to storage time between synthesis and experiment and will be discussed further later in the paper. The nanowires were characterised with SEM (Hitachi S4800) and PL (Melles-Griot 325 nm He-Cd laser and Ocean Optics USB2000+ spectrometer) prior to loading into the XPS chamber (Thermo Scientific Escalab Mk 3, base pressure 10⁻¹⁰ mbar). The sample was scanned with XPS before and after each Ti deposition step. The Ti was deposited onto the nanowires using an in-situ e-beam evaporation source (Oxford Instruments EGN4) for increasing amounts of time. The thickness was determined from the deposition time by prior calibration of the source using a quartz crystal microbalance. The thickness of each deposition step is shown in Table 1. After the final deposition the sample was removed from vacuum, re-characterised with PL and SEM then annealed in a nitrogen atmosphere at 300°C for 3 minutes and allowed to cool naturally [27]. This annealing step is typical for the fabrication of Ohmic contacts between n-type ZnO and Ti [28-30]. Following the final annealing step, the sample was characterised once more by SEM and PL and then reloaded into the XPS and scanned a final time.

<table>
<thead>
<tr>
<th>Thickness deposited (nm)</th>
<th>0.2</th>
<th>0.2</th>
<th>0.4</th>
<th>0.8</th>
<th>1.6</th>
<th>3.2</th>
<th>6.4</th>
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<tr>
<td>Total thickness (nm)</td>
<td>0.2</td>
<td>0.4</td>
<td>0.8</td>
<td>1.6</td>
<td>3.2</td>
<td>6.4</td>
<td>12.8</td>
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Table 1: sequence of Ti deposition steps and total thickness deposited.
Results and Discussion

Figure 1 shows top down SEM images of the nanowires before and after 12.8 nm Ti deposition and after annealing. The as-grown nanowires exhibited the typical ZnO hexagonal cross-section, with an average diameter of 48.1 ± 1.2 nm and an average length of 1.70 ± 0.10 μm. After Ti deposition the nanowire surface became rougher, with the hexagonal facets no longer distinguishable and the mean diameter increasing to 63.3± 1.5 nm. Annealing resulted in an apparent “smoothing” of the surface with the hexagonal facets becoming visible under SEM and a reduction in diameter to 50.7± 1.4 nm, suggesting the titanium had diffused into the ZnO nanowires. Ti evaporation can be ruled out because of the very low vapour pressure of Ti at 300°C and the Ti 2p core level intensity, discussed later in the text.

Figure 1: SEM images of ZnO nanowires a) before Ti deposition, b) after Ti deposition (12.8 nm) and c) after annealing (Sample 2).

XPS scans were recorded following each stage of the Ti deposition procedure, including a survey spectrum and detailed spectra of the Zn 2p, Zn 3p, O 1s, C 1s, and Ti 2p core levels. Figure 2 depicts the changes of the survey scans and Ti 2p core level for Sample 2 with increasing Ti coverage and following the anneal. The same features and trends were observed for Sample 1. After the first Ti deposition of 0.2 nm, the spectrum consists of a peak centred at 458.5 eV which is attributed to the Ti 2p3/2 level for TiO2 (Ti4+) [31], suggesting that the
titanium reacted with the surface oxygen of the nanowires, possibly sourced from OH\textsuperscript{-} groups.

Figure 2: a) Evolution of the survey scans before Ti deposition, after 12.8 nm of Ti deposition and after the final annealing step. b) Evolution of the Ti 2p core level in Sample 2 with increasing Ti thickness and after the final annealing step. The spectrum from the annealed step is offset vertically for clarity.
As the thickness of Ti increased, more features appeared on the lower binding energy side of the TiO$_2$ peak. These features are attributed to lower oxidation states of Ti (Ti$^{3+}$, Ti$^{2+}$, Ti$^+$) and TiC, as well as TiCO [32]. The lowest energy feature, centred 4.8 eV lower than TiO$_2$ peak and clearly visible at 6.4 and 12.8 nm coverage, is likely to correspond to metallic Ti [31]. The corresponding metallic Ti 2p$_{1/2}$ peak is also visible at 6 eV higher binding energy, in agreement with data within the literature [31]. These features indicate that the majority of deposited titanium was no longer reacting with surface oxygen at this stage of the deposition, and thus remains in a metallic state. Exposing the sample to air and annealing in nitrogen at 300$^\circ$C caused the peaks corresponding to metallic Ti to decrease and the TiO$_2$ peak to dominate.

Figure 3 shows the progression of the O 1s peaks of Sample 1 and Sample 2 during Ti deposition. Prior to Ti deposition, the O 1s peak of both samples consisted of a main component centred at 530.2 eV, which may be attributed to lattice oxygen, and a shoulder on the higher binding energy side caused by surface oxygen and commonly attributed to hydroxide ions [33-35]. Previous works have fitted this surface contribution with one or two components [33-35] and in this work, consistent with our previous publication [36], we fitted the surface contribution to the O 1s core level with two components: the component located 1.35 eV from the main lattice oxygen component and denoted S1 is attributed to hydroxide ions, while the second component, which is centred 2.3e V from the lattice oxygen component and shall be referred to as S2, is thought to correspond to water vapour. It should be noted that this interpretation is speculative as our previous result [36] suggested that the middle component could comprise of two different bonds with similar binding energy. Additionally, the surface components have also been attributed to oxygen bonded to carbon or oxygen vacancies and other sub-surface defects [37-39].
It is clear from Figure 3 that the contribution of the surface oxygen is significantly larger (99% of the lattice oxygen component, calculated using the areas of the oxygen lattice component and the surface oxygen components) for Sample 2 than in the case of Sample 1 (52% of the lattice component), indicating higher quantities of surface oxygen. The difference is probably due to the fact that Sample 2 was stored for 12 months prior to the experiment, whilst Sample 1 was scanned almost immediately after growth. Different humidity conditions during synthesis could also be a factor. Figure 3 shows that, for both samples, the surface oxygen components decreased in intensity relative to the main lattice oxygen component with Ti deposition up to 1.6 nm coverage (see inset), as the Ti reacts with the surface oxygen to form TiO$_2$ and TiO$_x$ (x<2) species. From the 3.2 nm deposition step onward, the surface oxygen component intensity does not decrease anymore, indicating that the surface oxygen has stopped reacting with the Ti. This also corresponds to the point where TiC and metallic Ti begin to appear on the Ti 2p core level (Figure 2).

The O 1s peak also broadened after the 6.4 nm and 12.8 nm Ti deposition steps, which is indicative of the formation of new species with a higher binding energy than the lattice oxygen of ZnO. These components may be attributed to TiO$_x$ (x<2) species as well as TiCO, suggesting that some of the deposited Ti may have begun to react with the lattice oxygen. The position of the O 1s peak shifted by 0.6 eV to lower binding energy after annealing, which likely corresponds to a chemical shift resulting from the oxidation of the metallic Ti to TiO$_2$. The broad shoulder on the high binding energy side is probably caused by the underlying ZnO and also surface oxygen species. This interpretation is supported by previous work such as Rtimi et al. [40], who reported that the O 1s core level binding energy for TiO is 1.4 eV greater than for TiO$_2$, and Kumar et al. [41], who identified a 1.8 eV gap between
the two chemical states. The TiO$_2$ that formed initially following the first few Ti depositions, which was clearly apparent in the Ti 2p spectra is not readily observed within the O 1s spectra, probably because it provides a much smaller contribution than the oxygen contained within the ZnO lattice.
Figure 3: The O 1s peak before Ti deposition, showing fits and background for a) Sample 1 and b) Sample 2. Evolution of the O 1s with increasing Ti thickness and following the final annealing step for c) Sample 1 and d) Sample 2. Insets show overlay
of the O 1s core level peak-shape with increasing Ti thickness up to 1.6 nm, showing the reduction in the surface oxygen components.

The evolution of the C 1s core level is plotted in Figure 4 for Sample 1. Initially the C 1s peak consisted of a main component centred at 284.4 eV, which may be attributed to C-C and C-H bonding resulting from ambient hydrocarbon contamination. After 3.2 nm Ti deposition, a second component centred at a binding energy 3 eV lower than the main component appeared, which likely corresponds to the formation of TiC [42, 43]. These results, together with the O1s results, suggest that the deposited Ti initially reacted with surface oxygen up to 1.6 nm thickness, whereas the formation of TiC occurred at Ti coverages greater than 1.6 nm. This suggests that Ti reacted preferentially with surface oxygen and only started to form TiC once the available surface oxygen had been consumed in the formation of TiO$_2$. This is in agreement with the evolution of the O1s core level peak shape of Figure 3 which shows that the decrease in surface oxygen stopped at Ti coverage greater than 1.6 nm. Following the anneal, the hydrocarbon contribution increased greatly due to exposure to ambient air but the TiC component remained, although with diminished intensity due to the enhanced surface contamination.
Figure 4: Evolution of the C 1s core level with increasing Ti thickness and following the final annealing step. The spectra are offset vertically for clarity.

Figure 5 shows Zn 3p normalised spectra for both samples. It is known that the Zn 3p core level binding energy (as well as the Zn 2p) is almost independent of the type of chemical bonds [44] and, as expected, we did not observe any significant change in the Zn 3p or 2p peak envelope with Ti deposition. The Zn core levels are therefore good indicators of band bending for semiconductors as they are affected negligibly by chemical shifts [45]. Figure 5 show that up to 1.6 nm Ti thickness, no Fermi shift was observed. This indicates that there was no electron transfer between the ZnO and TiO$_2$, as might be expected from the small difference in electron affinity between the two semiconductors [46]. A small, gradual shift to lower binding energy between the 1.6 nm and 12.8 nm thicknesses was observed for both
sample. The total shift was 0.4 eV for Sample 1, whilst a smaller shift of 0.15 eV was observed in the case of Sample 2. These shifts were also apparent on the O 1s core level until the 12.4 nm deposition, where the contribution of TiO$_x$ species distorted the peak envelope. The shifts indicate upwards band bending resulting in a more rectifying contact.

Annealing caused the Zn 3p peak of both samples to shift back to the binding energy measured for the pre-deposition surface. It is therefore evident that the annealing step counteracted the potential barrier at the interface between Ti and ZnO, thereby resulting in a more ohmic contact, despite the procedure leading to extensive oxidation of the Ti. The fact that Sample 2 exhibited a smaller shift in binding energy compared to Sample 1 is likely to be due to sample 2 possessing higher amounts of oxygen present at its surface. The oxygen species may act as either donors or acceptors depending on their exact nature: hydroxyl groups, for example, behave as donors [33], whilst oxygen ions are acceptors [47]. Both species therefore influence surface band bending and create surface states which may pin the Fermi level [48]. For this reason, it is likely that Sample 2 exhibited a higher density of surface states than Sample 1 prior to Ti deposition. As the Ti was deposited, it consumed some of the ZnO surface oxygen species to form TiO$_2$ but a significant amount remained: from zero to 1.6 nm coverage, the surface oxygen to lattice oxygen ratio for Sample 1 and Sample 2 decreased from 52% to 26% and from 99% to 42%, respectively.

The fact that not all the surface oxygen was consumed by the Ti hints at the presence of two types of surface oxygen, in good agreement with our previous work [47]. In this earlier paper, we studied the effect of UHV annealing on ZnO nanowires and found that whilst annealing at 300°C in UHV removed around half of the surface oxygen, additional annealing steps up to 600°C resulted in no further measurable change. For Ti thicknesses greater than 1.6 nm, the
amount of surface oxygen stopped decreasing and less oxidised Ti species began to form, as the deposited Ti stopped reacting with surface oxygen. Metallic Ti then became apparent at thicknesses above 3.2 nm. It is probable that transfer of electrons occurred from the ZnO to the metallic Ti, leading to upward band bending and the associated formation of a slightly rectifying contact. However, due to the likelihood that a higher concentration of surface states existed in Sample 2 than Sample, it is possible that the band bending resulting from the presence of metallic Ti was less pronounced in the case of Sample 2 as the Fermi level may have been partially pinned by the surface states. For both samples, however, the N₂ anneal negated the effect of the Ti by converting most of the metallic Ti to TiO₂.

Figure 5: Evolution of the Zn 3p core level with increasing Ti thickness and following the final annealing step for sample 1 and 2. The spectra are offset vertically for clarity. The dotted line is a guide to the eye emphasising the small binding energy shifts.
Figure 6 shows the evolution of the normalised intensity of the measured core levels as a function of Ti thickness and following the post deposition anneal for Sample 2. The Ti 2p intensity decreased slightly after annealing whilst the intensity of both Zn core levels remained the same. These trends may be attributed to the diffusion of Ti into the ZnO nanowires, which also accounts for the decrease in diameter and the “smoothing” of the facets observed in the SEM image of Figure 1c. The O 1s intensity remained almost constant up to 1.6 nm thickness whilst the C 1s and Zn core levels decreased. This behaviour is consistent with the formation of TiO$_2$ at the surface of the nanowires observed in the Ti 2p spectra. At thicknesses above 1.6 nm, the C 1s intensity decreased less sharply than during the initial depositions, and this can be correlated to the onset of TiC formation at the surface, as evident from the C 1s spectra.

Figure 6. Normalised peak intensity of the O 1s, C 1s, Zn 3p and Ti 2p against Ti thickness and following the final annealing step. The intensities are normalised to their initial values (before Ti deposition)
Figure 7. Normalised PL spectra of ZnO nanowires before Ti deposition, after 12.8 nm of Ti deposition and after the final anneal. Error bars indicate the standard deviation across the sample.

In order to investigate the effects of the contact formation on the optical properties of the nanowires, PL spectra were recorded before Ti deposition, after Ti deposition and after the anneal. The PL spectra are shown in Figure 7 and are normalised to the near band edge (NBE) peak intensity, which always remained centred at a wavelength of 374.7 nm, to allow direct comparison between the three cases. The position and shape of the deep level emission peak also stayed constant, and the location of the peak maximum at a wavelength of 595 nm indicates that oxygen vacancies were the main contributors to the emission [18, 49]. Ti deposition and annealing in nitrogen at 300°C did not significantly alter the deep level band. This suggests that the deep level band was not affected by modification of the surface, unlike previously published results where surfactants were highly efficient in suppressing deep level emission [50]. Similarly, annealing in Ar at 700°C has been reported to completely suppress
the deep level emission [51]. Our results, however, show that the 300°C anneal in nitrogen had no effect on the optical properties of the nanowires. The optical properties were therefore preserved after contact formation, a result which could be beneficial for optoelectronic devices. Additionally, the PL results indicate that the Ti diffused into the lattice during the anneal, rather than lattice oxygen diffusing [but][01] and creating oxygen vacancies which would have altered the deep level emission. It is likely that the conversion of the metallic Ti to TiO₂ occurred as soon as the sample was removed from vacuum and exposed to air, rather than reaction with lattice oxygen during the anneal. This is in agreement with the SEM images and the XPS intensity data.

Conclusions

Following hydrothermal synthesis of ZnO nanowires, the stepped formation of a titanium contact and the effect of subsequently annealing in nitrogen at 300°C have been studied using XPS, SEM and PL. For thicknesses up to 0.8 nm, the Ti reacted with surface oxygen species to form TiO₂. Increased Ti deposition (from 1.6 nm thickness) resulted in the formation of Ti oxides with a lower oxidation state number, and eventually metallic Ti. It was also observed that the Ti reacted with surface carbon contamination forming TiC and possibly TiCO for Ti thicknesses of 3.2 nm or higher. Exposure to air and annealing the sample resulted in a conversion to TiO₂, with little metallic Ti or TiC present at the surface.

The appearance of metallic Ti, following Ti deposition of thickness greater than 3.2 nm, caused the binding energy of the Zn 3p signal to shift to lower values, indicating upwards band bending and the formation of a rectifying contact.[02] Moreover, annealing resulted in the diffusion of Ti into the ZnO nanostructure, yielding a surface consisting mostly of TiO₂. The formation of the Ti contact was investigated on two different samples, which produced
very similar behaviour, confirming the reproducibility of the results. The only discernible difference between the two samples concerned the magnitude of the band bending caused by the metallic Ti, which was attributed to the different amount of initial surface oxygen present on the two samples. Finally, PL results showed that the formation of the contact did not alter the optical properties of the nanowires, which is beneficial for the realisation of optoelectronics devices.

These results provide insights into the complex ZnO/Ti interface formation and have implications for ZnO nanowire device manufacture where Ti is intended as an ohmic contact and also for devices that make use of ZnO/TiO$_2$ heterojunctions.

**Competing interests**

The authors declare that they have no competing interests.

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