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Forming reproducible non-lithographic nanocontacts to nanomaterials

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Abstract

The application of electrical nanoprobes to measure and characterise nanomaterials has become widely spread. However, the formation of quality electrical contacts using metallic probes on nanostructures has not been directly assessed. We investigate here the contact electrical behaviour of non-lithographically formed contacts to ZnO nanowires and develop a method to reproducibly form contacts. The contacting method NWs relies on an electrical feedback to determine the point of contact, ensuring minimal compressive strain at the contact. This developed method is compared with the standard tip deflection contacting technique and shows a significant improvement to reproducibility. The effect of excessive compressive strain at the contact was investigated, with a change from rectifying to ohmic I-V behaviour observed as compressive strain at the contact is increased, leading to irreversible changes to the electrical properties of the NW. The potential effect of current annealing the nanowire and contacts was considered and shown not to be a major contributing factor to the change in I-V behaviour. This work provides an ideal method for forming reproducible non-lithographic nanocontacts to a multitude of nanomaterials.

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Introduction

A considerable amount of work has been performed on the electrical characterization of nanomaterials such as nanowires. This is typically achieved by using lithographic techniques to pattern contacts onto the nanostructures which are subsequently electrically characterized [1–4]. Although the lithography method provides electrical measurements of the nanostructure, the intrinsic properties are often suppressed due to the passivation of the nanomaterials as a result of the photoresist and chemical treatments [5,6]. This becomes more prominent when trying to measure the effects a surface treatment has on the nanomaterials' electrical properties as the resulting behaviour can often be attributed to the surface passivation resulting from the resist application and not the desired surface treatment[7].

Therefore, more recently the development of electrical nanoprobes have allowed intrinsic measurements of nanomaterials by removing the requirement of any lithographic processes [8–12]. These nanoprobes consist of multiple etched metal probes which can be manually positioned onto nanomaterials using high resolution SEM and as such can form nanocontacts onto various nanomaterials. This offers a significant advantage in electrical characterization of nanomaterials, allowing contacts to be formed and repositioned on several regions of a single nanostructure as the SEM navigation provides high precision xy manoeuvrability of the probes. However, there is still a limiting factor when identifying the z position and the point at which non-tunnelling electrical contact is made between the probe and sample. Consequently, the point of non-tunnelling electrical contact is usually defined by a deflection of the probe under SEM observation. Often at this point there can be significant compressive strain at the contact area in addition to the uncontrollable probe deflection leading to changes to contact size. It is well understood that compressive strain to semi-conducting materials leads to changes in the band structure [13]. Therefore, current-voltage (I-V) curves measured using a tip deflection approach method cannot achieve intrinsic characterisation of the material. Furthermore, having an uncontrollable contact area can lead to large variations between measurements. Zhang *et al.* have shown that I-V curves on nanowires are very sensitive to changes in the contact [14].

Here, the effect of compressive strain on I-V measurements is presented using ZnO nanowires (NW) as an example nanomaterial. Electrical contacts to ZnO NWs often exhibit Schottky behaviour [15,16], attributable to a surface free of an amorphous dielectric layer and an extensive defect chemistry [17–20], making it an ideal test material. This work replies upon having a reproducible point of reference at which no compressive strain at the contact exists, with a solution achieved utilizing a side contact, zero strain condition. This in turn allows an electrical feedback to be used to distinguish the point of non-tunnelling electrical contact whilst forming a top contact and as such minimizes compressive strain. This reproducible point of initial contact is used as a reference point to consider the effect of compressive strain on contact I-V behaviour. Furthermore, consideration of permanent changes to the nanowires conductive properties resulting from excessive compressive strain is considered. The compressive strain is first increased and then decreased, whilst monitoring the effect in the contact I-V behaviour and demonstrates irreversible changes to the NW conductive properties.

Methods and Materials:

NW growth and substrate transfer

CVD catalytic NWs were grown on α-Al2O3 substrates with a 6nm sputter deposited Au layer in a typical horizontal tube furnace setup [21,22]. Implementing ZnO and graphite mesh as source material, NW growth occurred at ~900°C, under flow of 49sccm of Ar and 1 sccm of O2 for a growth period of 120 minutes. During growth, the chamber pressure was maintained at 30mbar. To minimize the application of any processing steps onto the ZnO NWs, following growth the vertical arrays were transferred onto Si substrates with a 100 nm SiO2 insulating layer, using direct frictional force. This removes any requirement for solvents and as such retained the NW intrinsic behaviour.

Nanoprobe measurements

Electrical measurements on individual NWs were performed in ultra-high vacuum (UHV) conditions ($<2\times10^{-10}$ mbar) in an Omicron LT nanoprobe at room temperature. The system consisted of four individually controlled probes which were guided using a Gemini SEM column. Probing tips were constructed from dc etched tungsten wire which was direct current annealed to >2200K in UHV, ensuring the removal of all of the oxide [23]. I-V sweeps were conducted using a Keithley 2626B source measure unit alongside a Keithley 7174A low current matrix card fitted into a Keithley 708B switching matrix used for probe selection.

Results:

Forming initial contact to NWs

To investigate the effect of the compressive strain on I-V measurements of NWs, a method of distinguishing the point of non-tunnelling electrical contact must be implemented. Typically, this would be achieved looking for a deflection of the probe in the SEM image. However, this is purely qualitative and not reproducible. To improve on this method and provide a quantitative description for the point of contact, the probes were initially approached onto the sides of a flat-lying NW and not onto the uppermost surface illustrated in Figure 1. Approaching onto the side of the NW prevents any compressive strain to the NW as it is free to move laterally across the surface.

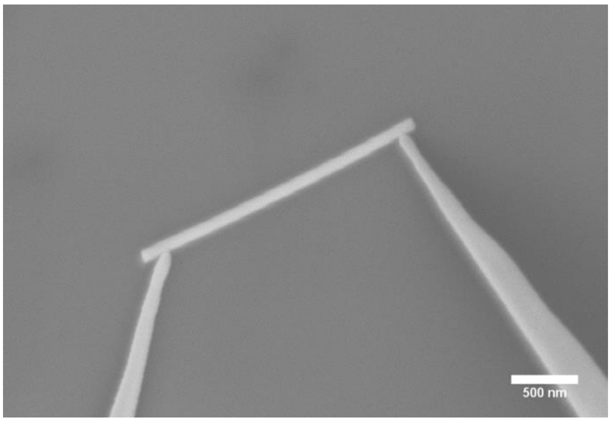

Figure 1: SEM image showing the probes approached onto the side of a ZnO NW

The first physical contact between probes and NW was formed when the NW was seen to deflect laterally in the SEM image. Subsequently, one of the probes is removed and positioned above the NW, this is denoted as the ‘hi’ probe - the high potential terminal. Using an iterative process, the probe is slowly approached to the surface in 1 nm steps whilst performing an I-V sweep after each nanometre step. The initial point of non-tunnelling electrical contact is given when the I-V sweep changes from the instrumental noise level (~pA) to a typical contact sweep (nA-µA), usually with several orders of magnitude greater current. The typical change in current observed when the probe is in and out of contact is presented in Figure 2 and occurs in a single 1 nm z-piezo step. The same method was used to approach the second probe to the top of the NW.

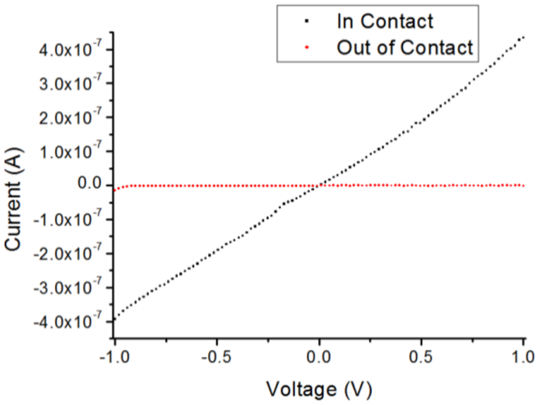

Figure 2: I-V sweeps demonstrating point of initial contact.

To consider the reproducibility of this approach method, using a nanowire with 88 nm diameter, one of the probes is taken out of contact and then placed back into contact five times, with I-V sweeps performed after each approach as shown in Figure 3a. This process yielded a maximum standard deviation of 35.6 nA, equating to differences in current of 9.6% at +1V and 8.3% at -1V. The resistivity of the nanowire was calculated using the minimum and maximum gradient of the I-V curves leading to a resistivity value of 0.058 ± 0.019 Ωcm. For comparison, the standard SEM guided probe deflection method of approaching onto NWs was performed on a second NW, diameter of 70 nm, with the resulting I-V curves exhibited in Figure 3b. There is an obvious large deviation in current between approaches, leading to a maximum standard deviation 342 nA, which equates to a change of 258% and 74% at ±1 V respectively. The resistivity values using this approach method are calculated in forward bias at +1 V due to the rectifying I-V behaviour. The resistivity was calculated to be 0.074 ± 0.41 Ωcm. The resistivity measurements from both tip approach methods fall within the statistical variance of previous studies [8]. However, by implementing the electrical feedback technique to establish contact instead of the tip deflection method, significantly less variation in I-V behaviour is observed. When comparing the approach methods across multiple ZnO NWs, it is more beneficial to consider changes in current after each approach as a percentage, instead of absolute current value. This is because the resistivity across multiple ZnO NWs has previously been shown to change by orders of magnitude[8].

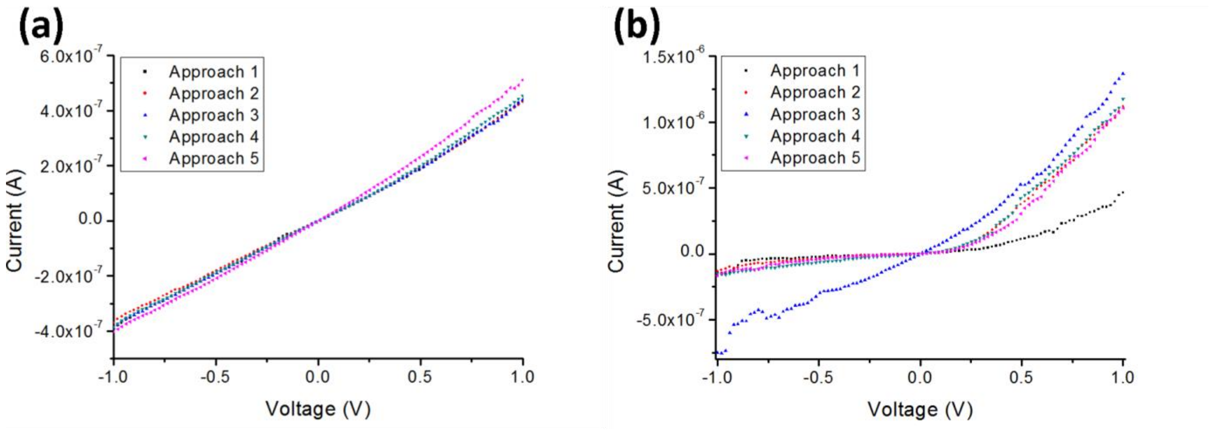

Figure 3: Reproducibility of I-V sweeps when approaching using (a) I-V sweep feedback and (b) only SEM.

These measurements have demonstrated an effective and reproducible method for contacting NWs with vastly reduced variation in current when compared to previous methods. The improved method can be implemented across multiple nanowires, ensuring that all measurements are taken with respect to the initial point of contact and removing the influence of both user error and contact compressive strain from the measurements, ensuring true characterisation of the intrinsic properties. The approach method was described for a 2-probe measurement as this is the most sensitive configuration to variations in the contact barrier; however, the process can be applied for any number of probes depending on the type of measurement being performed.

Effect of pressure on the contact

The electrical response to increasing the compressive strain at the nanowire contact has been assessed. Using the optimised contacting method described above and defining the initial point of contact as Z = 0 nm, the z piezo of the 'hi' probe i.e. the probe which injects electrons into the NW, was approached in increments of 1 nm, effectively increasing the compressive strain at the contact after each increment; the second probe was already in ohmic contact with the NW. After each increment, an I-V curve was taken and is displayed in a 3d surface plot in Figure 4.

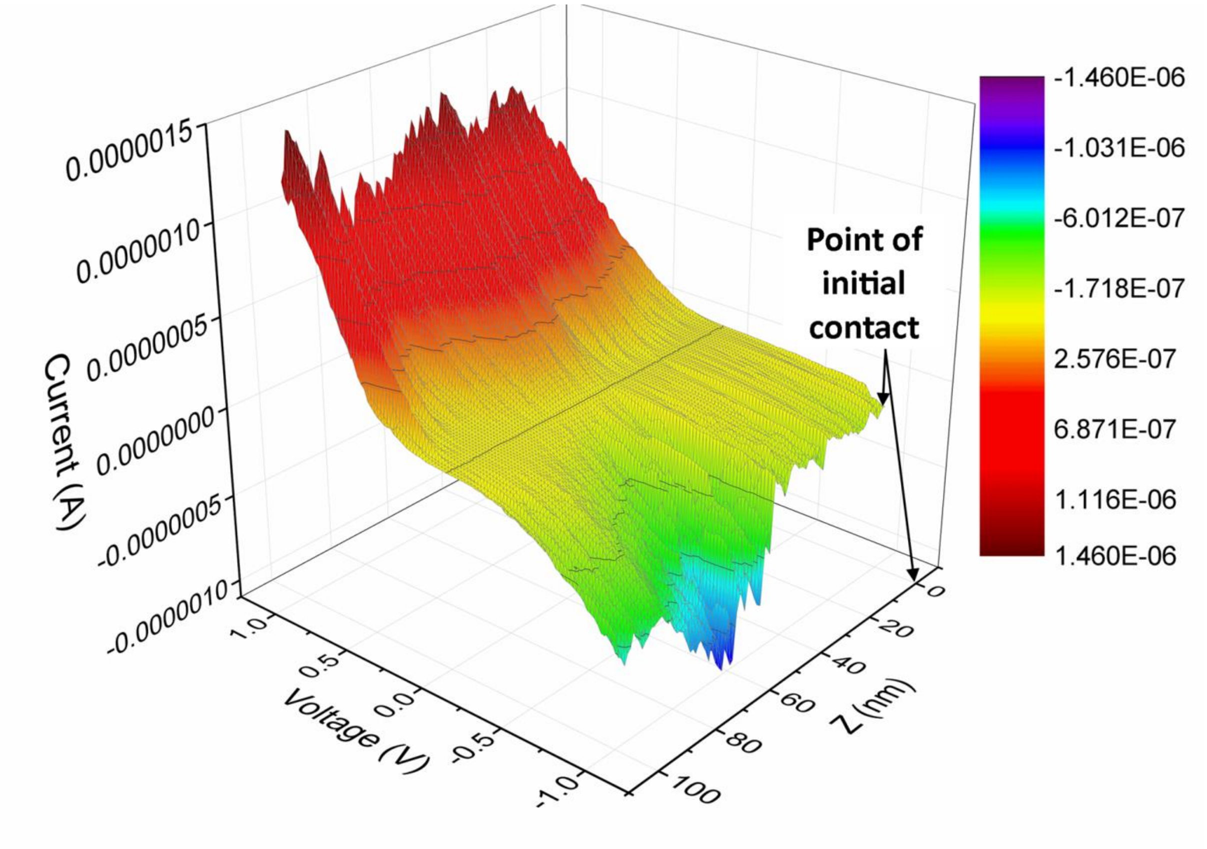

Figure 4: 3D surface plot of I-V sweeps as a function of probe z-position.

At the point of initial contact, with minimal compressive strain, the I-V curve demonstrates a strongly rectifying behaviour. As z is increased to ~40 nm past initial contact, the I-V continues to show rectifying behaviour, whilst exhibiting increased current in forward bias. Changes in electrical measurements with increasing compressive strain have been observed on macroscopic materials [24,25], but to the authors knowledge, this is the first time a similar nanoscale effect has been reported.

With a further increase to z > 40 nm, an increase to current in reverse bias of approximately 900 nA is exhibited. This can be attributed to both an increase in compressive strain and also an increase in contact size [26]; however, it could suggest a structural alteration at the probe/NW interface . Additionally, surface contaminants readily bind at the ZnO surface. Such contaminants include doubly and singly ionized surface oxygen which are considered electron acceptors[17,27,28]. As a result, a depletion layer forms at the surface of the NW causing a reduction in the effective conductive channel [8,29,30]. As the probes are contacting the NW surface they effectively have to measure through this depletion layer, which could be the cause of the initially observed Schottky behaviour. Approaching the probes >40 nm could puncture through the NW surface, effectively bypassing the depletion layer; therefore, with minimal surface depletion an ohmic contact is formed. This is highly significant when intrinsic characterization of the NWs is desired. This discussion leads to the debate of whether the intrinsic properties are those of the as grown NWs, with the surface contaminants, or if the intrinsic properties are to be measured with the surface contamination removed via methods such as sample annealing inside UHV. Having formed contacts which demonstrate ohmic behaviour, when the probe was approached more than 60 nm towards the sample from the point of initial contact, a return to rectifying behaviour was observed. As a piezoelectric material, the significant compressive strain induced at the contact of the ZnO NW could result in an increased Schottky barrier height [30].

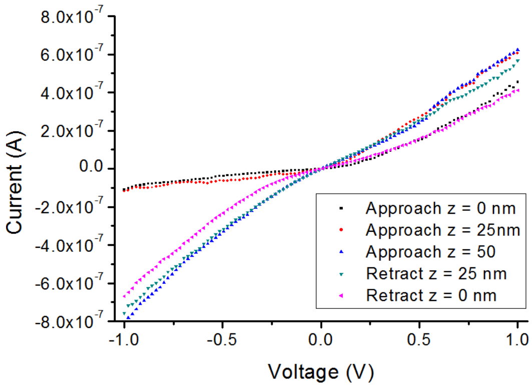

Figure 5: I-V sweeps performed during probe approach and retraction in 25 nm steps.

In the case here, we assessed whether the removal of surface species or annealing of the contact/nanowire had a significant impact on the contact properties by performing large steps in the Z approach, thus reducing the number of I-V measurement that would cause self-heating. Measurements were repeated on a NW with a diameter of 76 nm using 25 nm steps between I-V measurements to minimize the number of sweeps performed and as such reduce the potential effect of NW annealing. Figure 5 demonstrates the effect of compressive strain on I-V characteristics after approaching and retracting one probe, in 25 nm increments. At the point of initial contact the I-V curve exhibits strong rectifying behaviour. This is still apparent following 25 nm approach into further contact with the sample, with a slight increase in current in forward bias. An additional approach of 25 nm (to a total approach of 50nm from initial contact) results in almost ohmic behaviour with a significant increase of current in reverse bias. This corresponds to similar behaviour observed in Figure 4 suggesting that current annealing of the NWs is not the major factor in altering the I-V characteristics. Retracting the probe 25 nm still presents an I-V curve similar to that measured at 50 nm from the point of initial contact, therefore suggesting that the increased compressive strain at the contact has permanently changed the I-V characteristics of the NW. A further retraction back to the point of initial contact results in a reduction in current in forward bias equalling that measured during the approach. In reverse bias there is also a slight decrease in current; however, it is still significantly higher than at the point of initial contact. This is an important point which we investigated in more detail on a wire of diameter 68 nm.

Permanent changes induced by compressive strain at the contact

The significant effect of compressive strain at the contact on I-V measurements of NWs has been demonstrated. It is important to consider if subjecting the NW to increased compressive strain causes a permanent change to the conductive properties, or if the I-V returns to the initial state as the probe is withdrawn. To measure this, a similar approach to above is performed, first forming initial contact to a NW as described. Following this, the ‘hi’ probe is stepped into the NW in 1 nm increments with the manual control of the z piezo, taking I-V sweeps after each step. The I-V sweeps were monitored until an obvious increase of ohmic behaviour is observed. The probe was then withdrawn in 1 nm increments performing I-V sweeps after each step. Surface plots of the approach and withdraw can be observed in Figure 6. It is clear that during the probe approach in Figure 6a, there is a clear Schottky behaviour at the point of initial contact (z = 0 nm). Furthermore, as the probe is stepped into the NW instabilities in the I-V measurements are observed, which are more significant in reverse bias. After further steps are performed and the effective compressive strain is increased the I-V curves become more uniform and exhibits ohmic behaviour. Dissimilar to the NW measured in Figure 4, this ohmic behaviour begins after just 23 nm past the point of initial contact, instead of the 60 nm of the previous measurement. This is probably due to fluctuation in surface contaminants between NWs, resulting in changes depletion width and NW diameter with the NW measured in Figure 4 having a diameter of 124 nm compared with 68 nm of the NW measured in Figure 6.

When retracting the probe in Figure 6b, I-V sweeps are performed at each step, demonstrating a much reduced variation than during the approach. Furthermore, the I-V measurements do not revert to a rectifying behaviour as shown at the initial point of contact. This would suggest that the contact, the NW or a combination of both have been irreversibly altered. As such, it raises the concern that non-lithographic measurements performed using only SEM for probe positioning could be bypassing the surface layer whilst causing a permanent change to the NW properties.

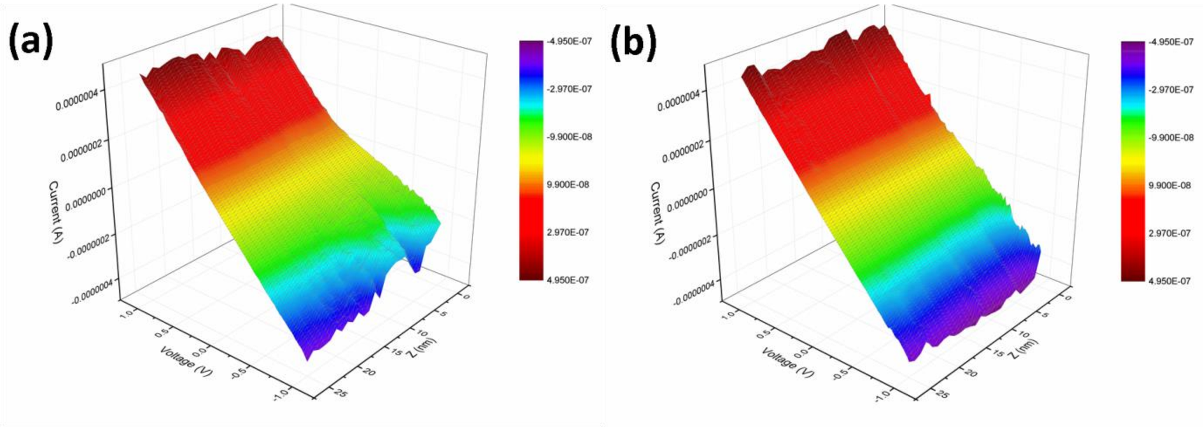

Figure 6: 3D I-V surface plots of (a) the probe approach and (b) the probe retraction.

Therefore, compressive strain at the contact directly influences I-V behaviour of the NW. In conclusion, the hysteresis behaviour of compressive strain to contact I-V measurements of NWs has been observed. It was demonstrated that excessive compressive strain at the point of contact results in significant irreversible changes to the I-V behaviour of the NW.

Conclusion

In conclusion, the I-V behaviour of non-lithographically formed contacts to ZnO NWs has been investigated, focussing on the effect of contact compressive strain. A method to produce reproducible contacts to the NWs is presented using an electrical feedback for determining the point of contact. This has been compared with previous methods for forming contacts and shows a significant improvement in reproducibility. The effects of deviations from the point of initial contact have been considered, achieved by increasing compressive strain at the NW contact. Increased compressive strain transforms the initially rectifying behaviour to ohmic. Further increments to compressive strain at the contact result in the ohmic behaviour reverting back to rectifying behaviour, due to a piezoelectric response of the ZnO NW. Furthermore, the hysteresis effect of I-V measurements has been performed, suggesting that excess compressive strain to the NW at the contact point can cause irreversible changes to the I-V behaviour of the NW. In addition the potential effect of current annealing during these measurements was considered and shown to not be a major contribution to the change in electrical behaviour.

This work provides an ideal method for forming reproducible non-lithographic nanocontacts to nanomaterials. Although the process is demonstrated for NWs, a similar approach can be made to any nanostructures. This method could be beneficial in the intrinsic electrical characterization of all of nanomaterials

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