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RAPID COMMUNICATION

Piezoelectric gated ZnO nanowire diode studied by in situ TEM probing

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Abstract
The piezoelectricity of ZnO nanowires has shown rising interests during the last few years and fields such as piezotronics and piezophotonics are emerging with a number of applications and devices. One such device is the piezoelectric gated ZnO nanowire diode, where the *p-n* junction is replaced by a dynamically created potential barrier created simply by bending the otherwise homogeneously doped nanowire. To further study this type of diode we used in situ transmission electron microscope (TEM) probing, where one electrode was fixed at the end of a ZnO nanowire and another moveable electrode was used both for bending and contacting the wire. Thereby we were able to further characterise this diode and found that the diode characteristics depended on whether the contact was made to the stretched (*p*-type) surface or to the compressed (*n*-type) surface of the wire. When the neutral line of the wire contacted, between the stretched and the compressed side, the *I-V* characteristics were independent on the current direction. The performance of the diodes upon different bending intensity showed a rectifying ratio up to the high value of 60:1. The diode ideality factor was found to be about 5. Moreover, the reverse breakdown voltages of the diode were measured and a local but permanent damage to the diode action was found when the voltage went over the reverse breakdown voltage.

Introduction

The piezoelectricity of nanomaterials have a number of piezotronic [1-3] applications including nanogenerators [4,5], resonators [6], and field-effect transistors [7], as well as piezo-phototronic [3,8] applications such as LED and solar

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cell [9]. A fundamental building block in nanoelectronics is the diode, and the piezotronic variant is the piezoelectric-gated diode [10,11]. where the standard *p*-*n* junction is replaced by a dynamically formed barrier simply by bending a homogeneous piezoelectric nanowire. The potential barrier induced by bending the piezoelectric nanowire is caused by the charge difference between the stretched and compressed surface [10]. In general, a potential is generated when a piezoelectric material is deformed by an external force. A mechanical force acting on piezoelectric materials changes the equilibrium crystal structure, for example, an external force on a ZnO nanowire change the charge-centre of cations in the ZnO crystal [1]. In a similar way as in ZnO, other wurtzite nanomaterials, like GaN and CdS, are piezoelectric, due to the polarisation of ions in the crystal with non-central symmetry [2].

The piezoelectric-gated diode is not only of importance as a fundamental building block in nanoelectronics but also enable novel types of devices such as mechanically gated RAM memories [10] or photodetectors [12]. The piezoelectric-gated diode is also of importance since *n*-type conductivity is common in ZnO nanowires even without doping, while *p*-type doping remains hard to accomplish [13-15].

To study piezoelectric-gated diodes, in situ electron microscopy probing has been used, allowing experiments on single nanowires. Zhong Lin Wang's group used a combination of a scanning electron microscope (SEM) and a multiprobe Ti/Au/W tip and the other end was bent by a moveable tip, demonstrating the piezoelectric-gated diode [10].

In the suggested mechanism for the piezoelectric-gated diode, one should expect a different behaviour of the electron transport depending on whether the contact is made to the stretched side of the nanowire or onto the compressed one. There should also be a point between these regions where there is no such diode effect. However, these kinds of experiment has not been addressed in the earlier [10,11] studies, and should be of importance to firmly establish this piezotronic mechanism. Furthermore, some of the parameters of the piezoelectric-gated diode, such as the reverse breakdown bias and ideality factor, remain to be studied.

Here, we addressed the above issues using in situ transmission electron microscope (TEM) probing [16-18]. Piezoelectric-gated ZnO nanowire diodes were made by first gluing the nanowires on a gold tip using silver epoxy, and then contacting another gold tip to a selected single nanowire for electrical probing and mechanical bending. By choosing specifically shaped tips, we managed to contact all sides of the nanowires, both the stretched and the compressed surface, as well as the zero energy barrier phase between these two surfaces (Figure 1). In this way we got clear evidence for the piezoelectric-gated diode model described above, with reversed diode curves depending on whether the stretched or compressed surface was contacted, as well as no diode behaviour when the contact was applied between these surfaces. In addition, by using rather thin nanowires and high bending angles we got an order higher rectifying ratio (60:1) than earlier reported. Moreover, the diodes reverse breakdown bias and the diode ideality factor were measured adding further details to these piezoelectric-gated diodes.

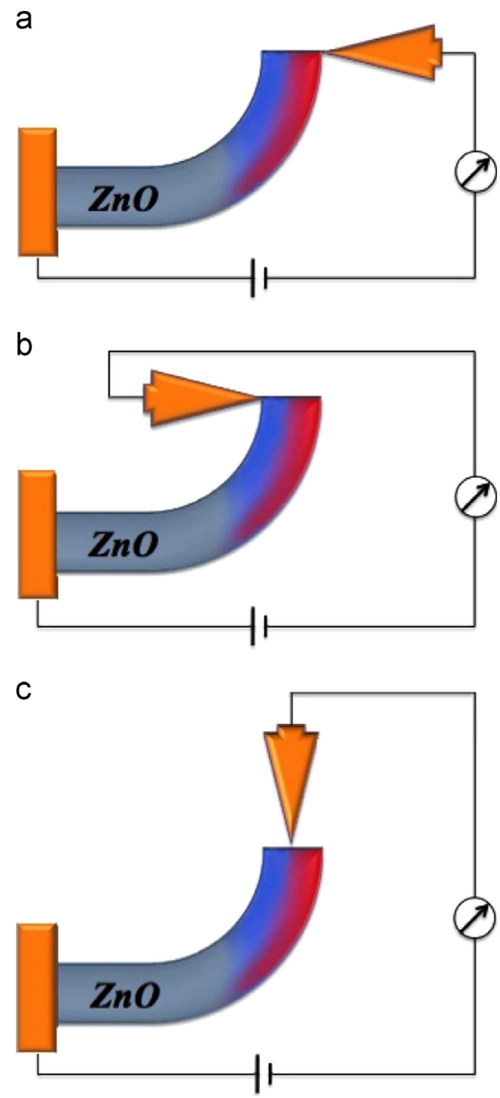

Figure 1 Schematic drawing of the contact between a gold electrode and a ZnO nanowire at the (a) stretched surface, (b) compressed surface, and (c) the interface between stretched and compressed surface.

Experimental

Synthesis of ZnO nanowires

$Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine were purchased from FLUKA, and used without further purification. The ZnO nanowires were synthesised using a wet chemical method [19]. Briefly, 0.5 g $Zn(NO_3)_2 \cdot 6H_2O$ and 0.5 g hexamethylenetetramine were mixed in 350 ml double distilled water with an aluminium foil at the bottom of the beaker as a substrate for nanowire growth. The mixture was heated at 80 °C for 4 h in an oven. The ZnO deposited aluminium foil was taken out after 4 h growth, and rinsed with 99.5% ethanol and double distilled water.

In situ TEM probing

To make sample for in situ TEM probing, a gold wire (diameter: 0.25 mm) was first dipped into silver epoxy to get some epoxy on the wire. Then, the epoxy covered gold wire was dried in air for 5 min. After that, we dipped the gold wire into the ZnO nanowires on the aluminium foil softly to get some nanowires attached to the epoxy. The sample was then kept in air for 30 min to let the epoxy dry completely. The gold wire was then fixed on an in situ TEM probe [16] (Nanofactory Instruments AB) to be contacted by another moveable gold wire attached to a piezo tube. The TEM used was a JEOL-2000FX microscope combined with digital camera that allowed for real time recording.

Results and discussion

Contacting different surfaces

As described by He et al. [10] the piezoelectric-gated ZnO nanowire diode is based on the charge difference between the stretched and compressed surface (Figure 1). In fact, one would expect three different *I-V* responses, depending on whether the electrical contact is made to the stretched surface, the compressed surface, or to the interface between the stretched and compressed phases. At both stretched (Figure 1a) and compressed (Figure 1b) surfaces, energy barriers are created when the ZnO nanowire is bent. While at the interface (Figure 1c) between the stretched and compressed phases, a zero energy barrier is expected, because the current can pass in both directions.

Contacting the stretched surface is already studied [10] while the other two contacts are harder to realise. However, using in situ TEM probing, we managed to get all the three places contacted as shown in Figure 2. The contact to the interface between the differently charged regions was made by placing a sharp tip to middle of the cross section of a ZnO nanowire (Figure 2a). The contact on the stretched surface (Figure 2b) was done by contacting and pushing a gold tip on one side of the nanowire. The compressed side is less straightforward to contact, however with a specific shape of the gold tip it is possible (Figure 2c).

Figure 2a shows a TEM image of the contact of gold tip to the centre of the end of the nanowire, when the ZnO nanowire was bended. Current-voltage (*I-V*) measurements (curve a in Figure 2d) show a linear relationship with no diode behaviour at this neutral point between the stretched

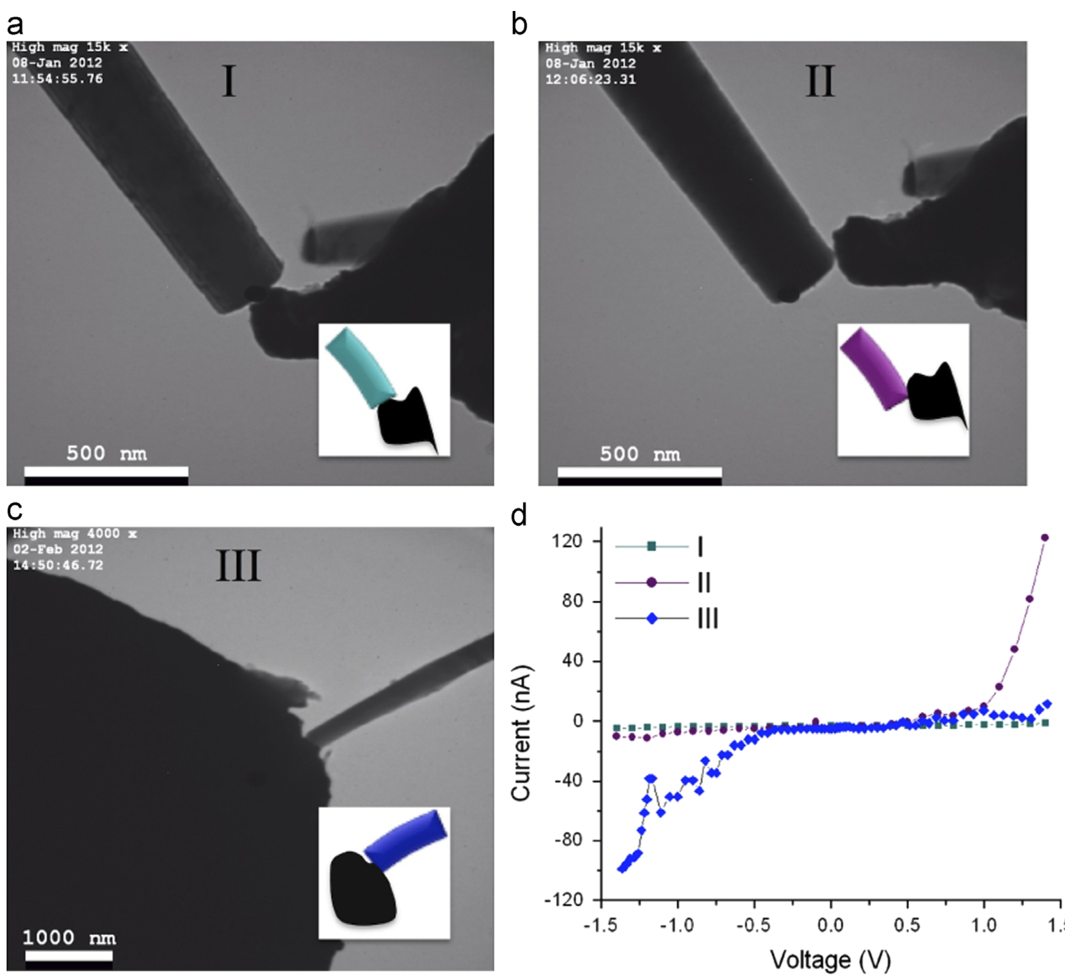

Figure 2 TEM and *I-V* measurements of the contacts between gold tips and different surfaces of bended ZnO nanowires. (a), (b), and (c) show TEM images of the different contact between the gold tips and ZnO nanowires. d, *I-V* measurement corresponding to contact cases in (a-c).

and compressed surfaces. This linear behaviour was also observed on the same contact before bending, indicating an ohmic contact [20] (See supporting information, Figure S1).

Figure 2b and c shows TEM images of the contact at the stretched and compressed surfaces. Curve b and c in Figure 2d show the *I-V* measurements corresponding to Figure 2b and c, showing different responses for positive or negative bias. The results shows direct evidence that the diode is due to the piezo-potential of the bended ZnO nanowire, and not a Schottky diode. A Schottky diode would show the same *I-V* response independent on the contact places, making it highly plausible that it was the piezo-potential generated charge difference at the stretched and compressed surface that was causing the different responses.

Diode characterisation

To investigate the diode behaviour under different degrees of bending we performed a series of measurements on a 4.5 μm long ZnO nanowire (Figure 3a). The distance stated in the figure is the actual moved distance of the gold tip. The forward current increased with increasing bending intensity (Figure 3b). The backward current also increases slightly (from 15 nA to 30 nA in the range shown in Figure 3b) while in an ideal case it should have decreased due to a higher piezo induced barrier (Figure 3c). The reason for this increase of the backward current is a larger contact area because of the elasticity of the gold tip, resulting in a lower contact resistance. The rectifying ratio is independent of any such change in contact resistance and was at ±2 V increased from 4:1 at 200 nm bending to 60:1 at 600 nm bending (Figure 3d). Real time monitoring of the current on the ZnO nanowire upon different bending distance and bias was shown in supporting information (Figure S2). Another parameter for this type of diode is the piezo induced barrier height could be determined from *I-V* measurements [10]. The method used in Ref. [10], however, require that the contact resistance is constant and independent on the applied bending force, which is not the case here, and we do not address this parameter here.

Reverse breakdown voltage

Another parameter is the reverse breakdown voltage of the ZnO nanowire diode. This parameter is of importance in

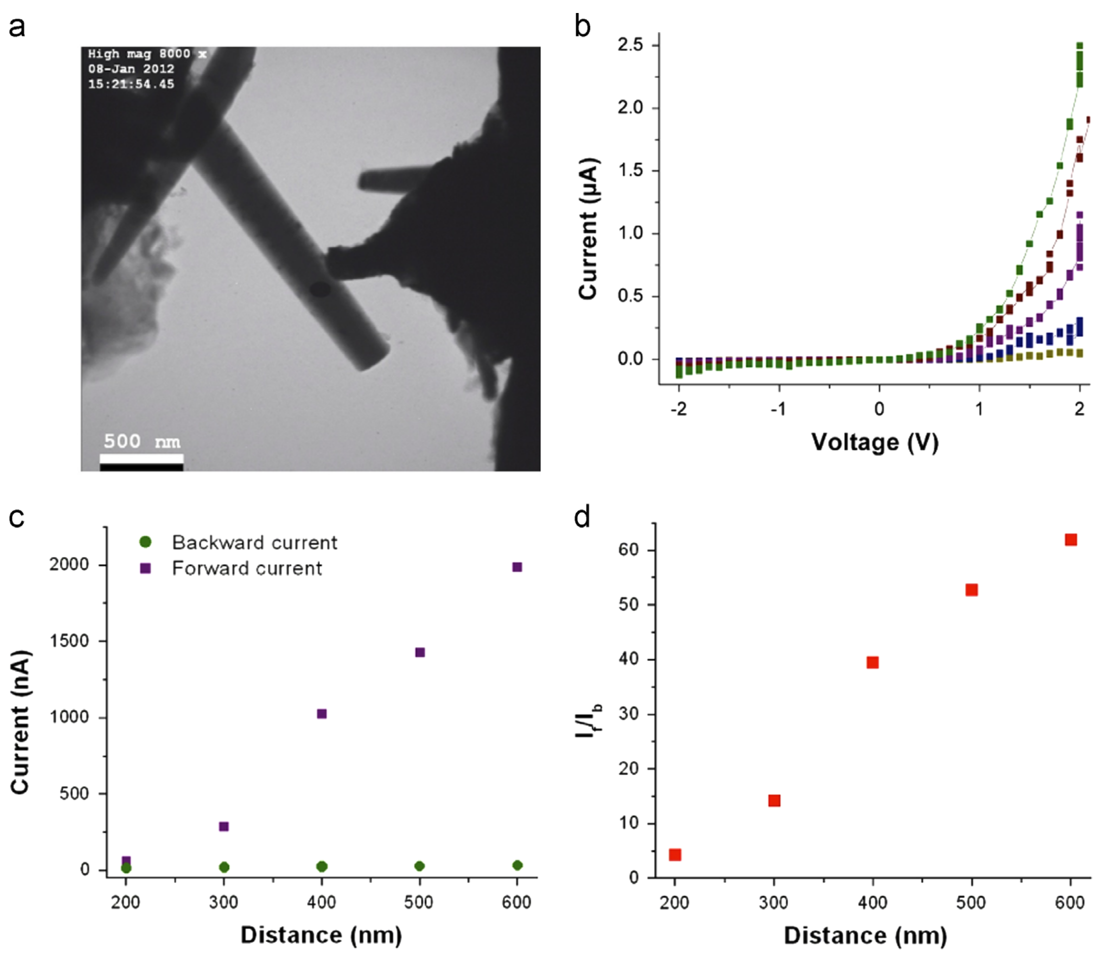

Figure 3 Piezoelectric-gated ZnO diode under different bending action. (a) TEM image of the contact position of a gold tip on ZnO nanowire (the 4.5 μm ZnO long nanowire is only partly visible in the image). (b) *I-V* measurements on the ZnO nanowire diode under different bending distance (200–600 nm in 100 nm steps). (c) Forward and backward current under bending showing the decrease in contact resistance as well as the increasing degree of the diode effect. (d) The rectifying ratio of forward and backward current under different bending distance showing the increase in the piezoelectric gated diode effect.

certain applications, for example, a radio frequency identification (RFID) tag requires sufficiently large reverse breakdown voltage and small turn on voltage [21]. Figure 4 shows the breakdown voltage of a ZnO nanowires, one of the nanowire (length: 3 μm, diameter: 60 nm) had a reverse breakdown voltage of −11 V (Figure 4a), while another nanowire (length: 5 μm, diameter: 400 nm) had a reverse breakdown voltage of −7 V (Figure 4b). When the reverse breakdown voltage was exceeded the diode was destroyed, as seen in the more or less linear *I*-*V* curves in Figure 4. Subsequent *I*-*V* curves did not show any diode behaviour. However, if a novel contact to the nanowire was made by moving the tip to another area of the nanowire, the diode curves reappeared. This indicates that only a local damage of the ZnO nanowire structure resulted when exceeding the breakdown voltage. The reason for the breakdown could be due to several mechanisms including Joule heating. The current density is very high at the breakdown voltage, particularly at the contact region, and it is known that the temperature could rise above 1000 K due to such Joule heating [22]. Up to the decomposition temperature of nanowires [22], or to evaporation of silver [23] or gold [17,23], or to a temperature where carbon nanostructures are growing [17].

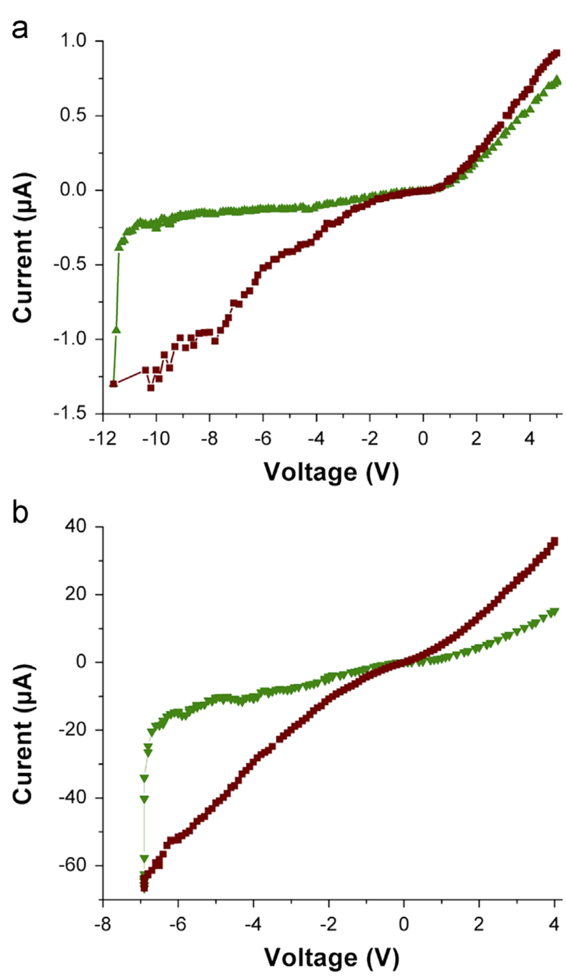

Figure 4 Reverse breakdown voltage of piezoelectric-gated ZnO nanowire diode. (a) Measurements on a 3 μm long, 60 nm diameter nanowire. (b) Measurements on a 5 μm long, 400 nm diameter nanowire. Data points marked by triangles shows the current towards the breakdown voltage, while the data points after breakdown are marked by rectangular symbols.

Diode ideality factor

The diode ideality factor, n, which is a measure of the deviation from the Shockley ideal diode equation, were extracted by obtaining the slope of log I vs. V of the forward voltage characteristic in the low voltage region from the measured *I*-*V* data shown in Figure 4a and b, measured before breakdown [24]. The ideality factors were determined to be $n=3.8$ for measurements on the 3 μm long nanowire diode shown in Figure 4a and $n=5$ for the 5 μm as shown in Figure 4b. The ideality factors for ZnO micro/nanowire piezotronic Schottky diodes is 3.7 when unbent and increases to 25.6 with increasing load, which has been attributed to increasing electron trapping in the electronic bound states [25]. For a diamond/ZnO *p*-*n* junction diode, the ideality factor can be over 6 [26]. Generally for diodes, when the ideal diffusion current dominates $n=1$ and when recombination current dominates $n=2$ and if both are comparable n is between 1 and 2. A higher ideality factor than 2 indicates defects in the interface that gives rise to increased recombination current [27,28]. The series resistance, R_S, were extracted from a I/gd vs I plot, as described in [29], where $gd=dI/dV$ *is* the diode conductance. It was found that the series resistance, R_S, for the 3 μm diode $R_S=5.8\ \mathrm{M\Omega}$ and for the 5 μm diode $R_S=250\ \mathrm{k\Omega}$.

Conclusion

In conclusion, we investigated the piezoelectric-gated ZnO nanowire diode using in situ TEM probing, where we achieved the contacts to the stretched (*p*-) surface, compressed (*n*-) surface, and the phase between these two. The *I*-*V* diode curves showed a forward respectively backward behaviour depending whether the stretched or the compressed surface was contacted, while no diode behaviour was detected when the phase between these two was contacted. These findings confirm that the diode is actually gated by the piezoelectric effect. The diode effect increased by increasing bending and a rectifying ratio of 60:1 was found at a bias of 2 V. Moreover, a reverse breakdown voltage of about 10 V was measured and the diode ideality factor was determined to about 5. Our results show direct evidences of piezoelectric-gated ZnO nanowire diode, which would be of importance for the fields of piezotronics and piezophotonics.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2013.10.002.

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