ZnO Nanobelt/Nanowire Schottky Diodes Formed by Dielectrophoresis Alignment across Au Electrodes

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ABSTRACT

Rectifying diodes of single nanobelt/nanowire-based devices have been fabricated by aligning single ZnO nanobelts/nanowires across paired Au electrodes using dielectrophoresis. A current of 0.5 μA at 1.5 V forward bias has been received, and the diode can bear an applied voltage of up to 10 V. The ideality factor of the diode is ~3, and the on-to-off current ratio is as high as 2000. The detailed IV characteristics of the Schottky diodes have been investigated at low temperatures. The formation of the Schottky diodes is suggested due to the asymmetric contacts formed in the dielectrophoresis aligning process.

Zinc oxide is an important optical and optoelectronic material. Recently, utilizing its unique crystal structure and the three major fastest growth directions, various single-crystal/crystalline nanostructures of ZnO have been synthesized, such as nanobelts,1 nanorings,2 and nanohelices.3 From the abundance of the surface morphologies, ZnO offers the most diverse nanostructure of any material known today. With a large direct band gap of 3.37 eV, together with its piezoelectricity and pyroelectricity, ZnO is most attractive for applications as a field-effect transistor (FET)4 or sensor5 and in optical electronics.6 Extensive research on the electronic properties of various one-dimensional nanostructures has been performed.7-10

To apply ZnO nanostructures on various electronic devices, it is important for one to understand its transport properties and its interaction with metal contacts. In this letter, we investigated the contact of a single ZnO nanobelt with gold electrodes. After investigating the transport properties of over 60 single nanobelt-based circuits, we found a spontaneous formation of a Au/ZnO nanobelt Schottky diode in 80% of the samples when nanobelt sizes are well controlled. This effect is likely due to the nonsymmetric contacts at the two ends of the nanobelt.

The ZnO nanobelts to be used for fabricating the FET devices were synthesized through a solid—vapor process in a high-temperature horizontal furnace system.1 The Au electrode patterns were defined with photolithography on a SiO2 substrate. The electrodes consisted of two 3-μm-wide fingers pointed head to head at a distance of 4 μm. These two fingers are connected to two 500 × 500 μm2 contacting pads for probe contacts. The as-synthesized nanobelt samples were placed in ethanol and ultrasonicated for 15 min to disperse the bundles into individual nanobelts. A single nanobelt is “placed” across the prefabricated electrodes using the dielectrophoresis technique.11 After applying a droplet of the nanobelt suspension onto the electrodes, the electrodes were connected to a 5 V and 1 MHz AC signal, which was chosen for optimizing the alignment of a single nanobelt. This signal generated an alternating electrostatic force on the nanobelts in the solution. Under the electrical polarization force, the nanobelts were deposited on the electrodes. By precisely controlling the concentration of the nanobelt in the solution, a circuit with only a single nanobelt across the two electrodes has been made (inset of Figure 1).

The most striking feature is that the IV characteristics of the devices formed by this process displayed a rectifying behavior as shown in Figure 1. The inset is an SEM image of the electrodes. Data corresponded to different measure-
ments of the same devices at different time intervals after the device was made. The last measurement was performed 7 days after the device was exposed to air. It is consistent with the data obtained 2 h after the sample was made, showing that the rectifying behavior of the nanodevice is very stable.

Figure 2a is the detailed inversed current characteristic. At a 10 V reverse bias voltage, the reverse current was only 0.8 nA, corresponding to a current density of 10.5 A cm\(^{-2}\). The ideality of the diode can be determined from the forward bias characteristic, as shown in Figure 2b. The diode current is

\[ I = I_0 \left[ \exp \left( \frac{V - V_{th}}{n kT} \right) - 1 \right] \]  

where \( n \) is the ideality factor that is a quantity for describing the deviation of the diode from an ideal Schottky barrier, for which \( n = 1 \), \( I_0 \) is the saturation current, \( V_{th} \) is the threshold voltage, \( k \) is Bolzmann’s constant, and \( T \) is the absolute temperature. The ideality factor of the device is determined to be 2.87, larger than one. This higher value of \( n \) is probably due to a barrier at the ZnO–Au contact formed during the dielectrophoresis alignment.

The temperature dependence of the diode was measured (Figure 3). The current under the forward bias decreased with the lowering of the temperature. The resistivity of the nanobelt increased by a factor of 2 when the temperature decreased from 215 to 104 K, showing a typical semiconductor \( IV \) characteristic. When the temperature was below 50 K, the carrier transportation was depressed greatly. The device acted like an open circuit with a resistivity greater than \( 10^5 \Omega \cdot \text{cm} \).

Table 1 shows a summary of the \( IV \) characteristics of all of the devices we have made using ZnO nanobelts. The data show a high reproducibility of the diodes. Devices fabricated on two different substrates, SiO\(_2\) and Si\(_3\)N\(_4\), were tested. The data showed that there was no obvious difference in the \( IV \) characteristics of the devices; so, the influence of the substrate on the rectifying behavior of the devices is eliminated. By controlling the size of the nanobelts carefully at around 200 nm in width, most of the fabricated devices displayed the rectifying behavior. For nanobelts with widths greater than 500 nm, the devices showed an infinity resistance under both forward and inverse bias, which is probably due to the poor contacts on both electrodes. Because of the nonflatness of the gold electrodes, the wider nanobelts may not have a stronger contact with the substrate, possibly resulting in large contact resistance. The smaller one could
have a good contact possibly due to stronger van der Waals interaction. Thus, the size of the nanobelt played an important role in determining the contact property of the diode; the smaller nanobelt has a better contact with the electrodes. For the nanobelts of $\sim$200 nm in width, the forward current was as high as 0.5 $\mu$A at 1.5 V forward bias, corresponding to a resistivity of $8.7 \times 10^{-2}$ $\Omega$·cm; the reverse current was around 0.2 nA. The on-to-off current ratio is as high as 2000.

The rectifying behavior of ZnO nanowires was reported previously by Harnack et al. Their studies were for chemically synthesized ZnO nanorods that typically have lower crystallinity and higher density of defects. Their study focused on the electrical behavior of multiple nanowires dispersed randomly on interdigitated electrodes. By characterizing the IV characteristics of a single ZnO nanobelt/nanowire produced by a solid–vapor process at high temperature, our study has shown the following unique results. The current flowing through the diode is $\sim$0.5 $\mu$A at 1.5 V forward bias, which is about 100 times larger than that reported by Harnack et al. The ideality factor for our devices is $\sim$3, which is much smaller than the value of 25 reported in ref 14, indicating a much better performance of our devices.

As proposed by Harnack et al., the factor that produces this rectifying behavior could be the alternating zinc and oxygen layers parallel to the basal plane; they produce a dipole moment that leads to a potential gradient and then introduce the asymmetry of current flow along the c axis. This assumption is given based on the noncentral symmetric and layered distribution of cations and anions in the wurtzite structure, and more importantly, the contact is assumed at the top and bottom (0001) surfaces (for nanowires). This is apparently not the case in our experiment because the contacts are at the same side-surface of the nanowire lying on the gold electrodes (see Figure 4a) and the cation- or anion-terminated surface has no effect unless the contacts are at the top and bottom ends of the nanowire.

The diode effect could be a result of the asymmetrical contacts between the ZnO nanobelts and the Au electrodes. To identify the origin of the rectifying behavior for our case, we deposited Pt using a focused ion beam (FIB) microscope at the contacts between the nanobelt and Au electrodes, as shown schematically in Figure 4a. Careful operation was taken to avoid any ion contamination on the nanobelts so that the change in the IV characteristic is determined solely by the change in contact properties. The devices showed a linear IV curve after the Pt deposition (Figure 4b), indicating the disappearance of the rectifying effect. For a total of over 20 devices deposited with Pt, the current flowing through the nanobelts was increased greatly, 5–20 times. This means that the contact resistance was reduced significantly and the diode effect disappeared after Pt deposition at the contacts. An alternative explanation is that the Pt deposition results in symmetric contacts at both sides. This experiment also disproves the assumption about the role played by crystal polarity in forming the diode as discussed above.

The linear IV of the nanodevice after Pt deposition proved that the rectifying behavior came from the contact between the ZnO nanobelt and the Au electrodes. The ZnO–Au contact is usually a Schottky contact. From this point of view, an as-fabricated device is composed of two inversely

<table>
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<th>sample</th>
<th>number of devices with rectifying behavior</th>
<th>number of devices with infinity resistance</th>
<th>number of devices with linear IV</th>
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<tr>
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<td></td>
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<tr>
<td>$\sim$200-nm-wide belts</td>
<td>7</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>(Si$_3$N$_4$ substrate)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>total no. of devices</td>
<td>36</td>
<td>26</td>
<td>2</td>
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Figure 4. (a) Schematic view of the electrode structure after Pt deposition using an FIB. (b) Linear IV characteristics of the device after Pt deposition. The inset is the SEM image of the device after Pt deposition at the two ends.
In conclusion, rectifying diodes of single nanobelts/nanowires have been fabricated by aligning the as-synthesized ZnO nanobelts/nanowires onto paired Au electrodes using dielectrophoresis alignment. The detailed $IV$ characteristics of the Schottky diodes have been investigated. The ideality factor of the diode is $\sim 3$. The on-to-off current ratio is as high as 2000. The spontaneous formation of the Au/ZnO nanobelt diodes depends strongly on the sizes of the nanobelts. For the nanobelts with smaller sizes ($\sim 200$ nm), the Schottky diodes are preferentially formed. The formation of the Schottky diodes is suggested due to the asymmetric contacts formed in the dielectrophoresis aligning process. Our data show that the single nanobelt/nanowire-based diodes can be practically applicable for various applications.

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