NANO LETTERS

2008
Vol. 8, No. 11
3973-3977

Piezoelectric-Potential-Controlled Polarity-Reversible Schottky Diodes and Switches of ZnO Wires

Jun Zhou,[†,‡] Peng Fei,[†,§] Yudong Gu,[†,§] Wenjie Mai,[†] Yifan Gao,[†] Rusen Yang,[†] Gang Bao,[‡] and Zhong Lin Wang*[,†]

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, Department of Biomedical Engineering, Georgia Institute of Technology and Emory University, Atlanta, Georgia 30332, and Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, 100084 Beijing, China

Received August 14, 2008

ABSTRACT

Using a two-end bonded ZnO piezoelectric-fine-wire (PFW) (nanowire, microwire) on a flexible polymer substrate, the strain-induced change in *I*−*V* transport characteristic from symmetric to diode-type has been observed. This phenomenon is attributed to the asymmetric change in Schottky-barrier heights at both source and drain electrodes as caused by the strain-induced piezoelectric potential-drop along the PFW, which have been quantified using the thermionic emission−diffusion theory. A new piezotronic switch device with an "on" and "off" ratio of ∼120 has been demonstrated. This work demonstrates a novel approach for fabricating diodes and switches that rely on a strain governed piezoelectric-semiconductor coupling process.

Binary switching is the principle of many electronic devices for applications such as data storage and logic circuits. Up to now most of the nanoscale switches are operated by an electrostatic force between a suspended carbon nanotube (CNTs)/nanowire and its counter electrode to switch between "on" and "off" depending on mechanical contact.[1−3] As the size of the devices reaching nanoscale, a small gap of ∼10 nm is required to be maintained between the CNTs/nanowire and the electrode for electro-mechanical switching. In such a case, the van der Waals interaction between the CNT and the electrode may be strong enough to bind the two together so that the device cannot perform the "off" function as required. Furthermore, the random thermal vibration at the tip of CNT may also become sufficiently large at conventional operating temperatures, which can strongly increase the device instability.[4] As a result, the reliability, lifetime and manufacturability of these devices are challenged.

The Schottky barrier diode, a metal-semiconductor (MS) rectifying junction that generally exhibits switching effect, may overcome the drawbacks. ZnO, a material that exhibits semiconductor and piezoelectric properties, is likely a candidate for fabricating diode-based switching devices. Recently, various novel devices have been fabricated using ZnO nanowires/nanobelts by utilizing its coupled piezoelectric and semiconducting properties (piezotronic effect), such as nanogenerators,[5,6] piezoelectric field effect transistors and chemical sensors,[7,8] piezoelectric diodes,[9] triggers,[10] transducer and actuator,[11] and flexible piezotronic strain sensors.[12]

In this letter, we report a new type flexible piezotronic switch device that is built using a single ZnO piezoelectric fine wire (PFW) (nanowire, microwire). Its operation mechanism relies on the piezoelectric potential induced asymmetric change in Schottky-barrier height (SBH) at the source and drain electrodes. The change of SBH is caused by the combined effects from strain-induced band structure change and piezoelectric potential. The device demonstrated here presents a new electromechanical switch built based on piezotronic effect.[13]

For this study, the device was fabricated by bonding an ultralong ZnO PFW laterally on a polystyrene (PS) substrate, which has a thickness much larger than the diameter of the PFW, as schematically shown in the upper-inset of Figure 1a. The detail device fabrication process was introduced elsewhere.[12] Briefly, single ZnO PFW (typical diameter of several micrometers and length of several hundred micrometers to several millimeters), which was synthesized by a high temperature physical vapor deposition process,[14] was placed on PS substrate (typical length of ∼3 cm, width of ∼5 mm

* To whom correspondence should be addressed. E-mail: zlwang@gatech.edu.
[†] Georgia Institute of Technology.
[‡] Georgia Institute of Technology and Emory University.
[§] Peking University.

10.1021/nl802497e CCC: $40.75
Published on Web 09/30/2008

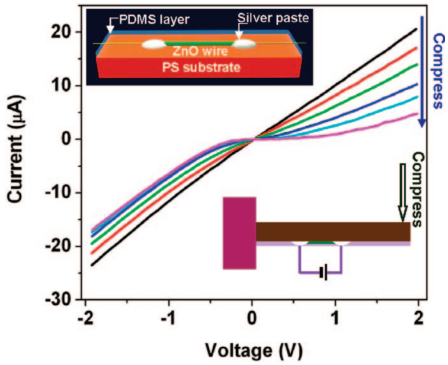

Figure 1. Typical $I-V$ characteristics of the device under different compressive strains (Device no. 1). Black line is the $I-V$ curve without strain. The direction of the blue arrowhead indicates the increase of applied compressive strain. Upper inset shows the schematic of a single ZnO PFW-based device. Lower inset shows the schematic of the electromechanical measurement system.

and thickness of 1 mm) by using a probe station under optical microscopy. Then silver paste was applied at both ends of the ZnO PFW to fix its two ends tightly on the substrate; silver paste was also used as the source and drain electrodes. After the silver paste was dried, a thin layer of polydimethylsiloxane (PDMS) was used to package the device. Finally, a flexible, optically transparent, waterproof and well-packaged device was prepared (see Supporting Information, Figure S1).

The study of electromechanical properties of the device was carried out in atmosphere at room temperature. The lower inset in Figure 1 shows the measurement setup. One end of the device was affixed on a sample holder with another end free to be bent. A three-dimensional mechanical manipulation stage with displacement resolution of 1 μm was used to bend the free end of the device to produce a compressive strain. Meanwhile the $I-V$ characteristics of the device during deformation were measured by a computer-controlled measurement system. As discussed in ref 12 with consideration of the extremely small diameter of the PFW in comparison to the thickness of the PS substrate, and the length of the substrate is much larger than the length of the PFW; a bending of the PS substrate produces solely a tensile or compressive strain in the PFW depending on its bending direction.

Before the electromechanical measurements, we first tested the original $I-V$ characteristic of the device. We found various $I-V$ characteristics for over two hundreds of devices that were prepared under similar conditions, and most of them have nonlinear behavior. Previously, we focused on the devices which originally exhibit rectifying $I-V$ behavior, and flexible piezotronic strain sensors based on those devices have been demonstrated.[12] In this study, we focus only on the devices that have symmetric or nearly symmetric $I-V$ behavior. Typical $I-V$ characteristics under various compressive strains (Device no. 1) are shown in Figure 1. When the compressive strain was increased, the currents both under positive bias and negative bias were suppressed. Finally a downward diodelike $I-V$ behavior is received. Some devices exhibited upward diodelike $I-V$ behavior under compression

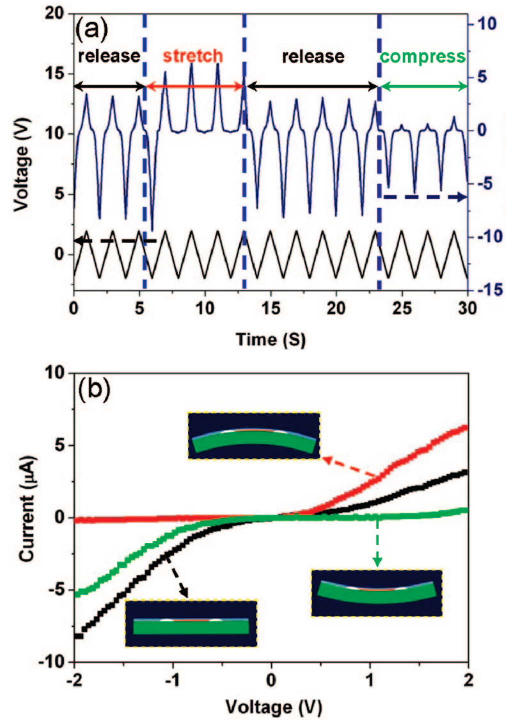

Figure 2. (a) Current response under repeated compressing-releasing-stretching-releasing straining process (Device no. 2). The blue line and black line are current response and applied sweeping bias voltage over time, respectively, from which the $I-V$ characteristic as a function of time was captured. (b) $I-V$ characteristics under different strain: released (black), compressive strain (green), and tensile strain (red). The inset schematically shows the device under various straining conditions.

strain. Statistic study showed that the ratio of the devices, which exhibited downward and upward diodelike $I-V$ behavior under compressive strain, is nearly 1:1 (see Supporting Information, Figure S2).

Figure 2a shows a current response under a repeated stretching-releasing-compressing-releasing straining cycle over a period of time for Device no. 2.[15] The blue line and black line are current response and sweeping bias over time, respectively. The corresponding $I-V$ behaviors under each straining condition are shown in Figure 2b. When the device was under tensile straining, upward diodelike $I-V$ behaviors was observed (red line); downward diodelike $I-V$ behavior (green line) was observed when the device was under compressive straining. The $I-V$ curve (black line in Figure 2b) fully recovered when the strain was relieved. Our extensive study indicates that the $I-V$ behavior is introduced by strain rather than poor or unstable contact.

Transformation of symmetric or nearly symmetric $I-V$ behavior to rectifying $I-V$ behavior under strain is a novel phenomenon which was first reported by He et al.[9] When they used an Au/Ti-coated tungsten probe to bend a one-end fixed ZnO nanowire, the linear $I-V$ characteristic of the ZnO nanowire was changed to a rectifying behavior with a rectifying ratio of 8.7:1. They proposed that electrical transport of the ZnO nanowire was governed by a potential energy barrier induced by the strain-induced piezoelectric potential. When the ZnO nanowire was bent, the outer

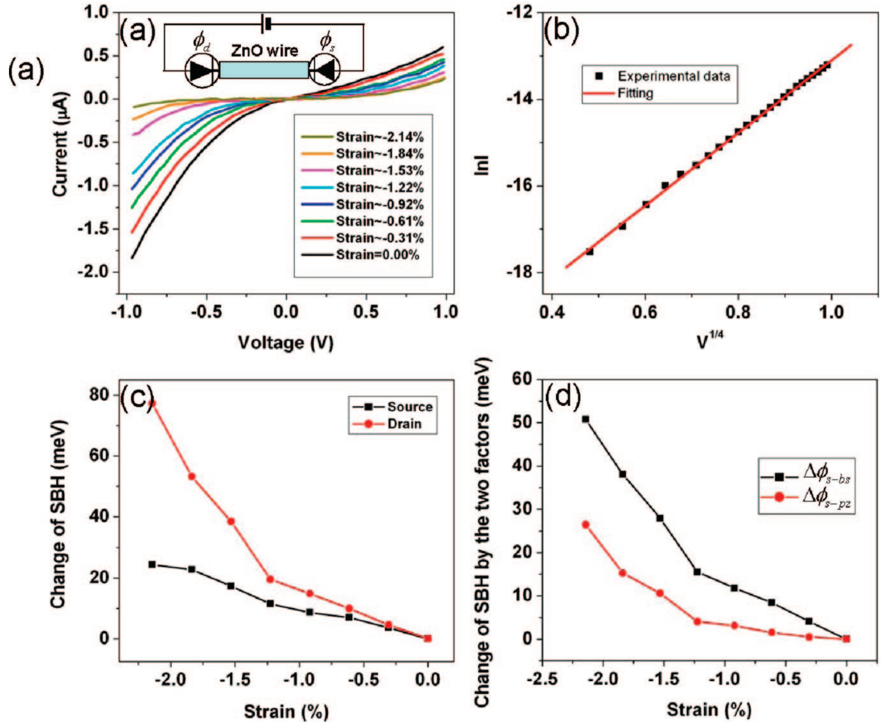

Figure 3. (a) $I-V$ characteristics of the device under different compressive strains (Device no. 3). The decreased current indicates an increase in SBH. Inset is the proposed sandwich model of the device, that is, two back-to-back Schottky diodes connected to a ZnO wire. (b) Plot of ln I as a function $V^{1/4}$, by using the data provided by the black line in panel a. The red lines are theoretically fitting according to eq 1. (c) The derived change in SBH as a function of stain using the thermionic emission−diffusion model. Black curve and red curve are the SBH change for source contact and drain contact at a drain-source bias of $V = 1$ and -1 V, respectively. (d) The derived changes in SBH as contributed by band structure effect (black curve) and piezoelectric effect (red curve), respectively.

surface is stretched and has positive piezoelectric potential and the inner surface is compressed and has negative piezoelectric potential; thus a piezoelectric potential drop was produced across the diameter of the ZnO nanowire.[9] The probe was in contact with the tensile surface of the nanowire. In our case, the ZnO PFW is fixed tightly at its two ends on the PS substrate, and both the outer and inner surfaces of the ZnO PFW are solely under tensile or compressive strain depending on the bending direction of the PS substrate, thus, the piezoelectric potential is along the axial direction of the PFW rather than across its diameter.

It has been reported that the SBH formed at the III−V semiconductor (GaAs,[16] GaN,[17] GaAlN[18])/metal interface can be modulated by strain due to the combination of strain-induced band structure change and piezoelectric polarization effect. The band structure effect may be attributed to strain-induced change in band gap. The effect of piezoelectric polarization on the SBH arises because the polarization produces charges at the metal-semiconductor interface,[16] which will shift the local Fermi level and modify the local conduction band profile. Thus, both of the band structure and piezoelectric polarization effects will affect the SBH and consequently the transport property of the devices, as elaborated in follows.

Figure 3a shows $I-V$ characteristics under various compressive strains for Device no. 3. The currents both under positive bias and negative bias are suppressed, and finally an upward diodelike $I-V$ behavior was observed under strain of $\sim -2.14\%$. The original $I-V$ curve (black line) shown in Figure 3a clearly demonstrates that there was Schottky barrier (SB) present at the contacts but with different barrier heights due to different interface properties.[19] Therefore, the structure of Device no. 3 can be considered as a single ZnO PFW sandwiched between two back-to-back SBs at the source and drain contacts with SBH of ϕ_s (in eV) and $\phi_d(\phi_d < \phi_s)$,[19,20] which is shown in inset of Figure 3a.

At a fixed bias voltage V, the voltage drop occurs mainly at the reversely biased Schottky barrier according to the measurement by in situ scanning surface potential microscopy.[21] In our case, when a positive bias voltage V is applied across the drain and source with the drain side positive, the voltage drop occurs mainly at the reversely biased Schottky barrier ϕ_s at the source side, and it is denoted by V_s; when a reversely biased voltage V is applied across the drain and source with the source side positive, the voltage drop occurs mainly at the reversely biased Schottky barrier ϕ_d at the drain side, and it is denoted by V_d. To simplify, we define that a positive voltage is applied at the drain side and assume that most of the potential drop occur at the reversely biased SB, $V_s \approx V$. With consideration that our measurements were made at room temperature and the ZnO PFW had a low doping/impurity level, the dominant transport property at the barrier is thermionic emission and diffusion, and the contribution made by tunneling is negligible. Thus, for a reversely biased SB under voltage V and at temperature T, the current through the reversely biased Schottky barrier ϕ_s is as follows based

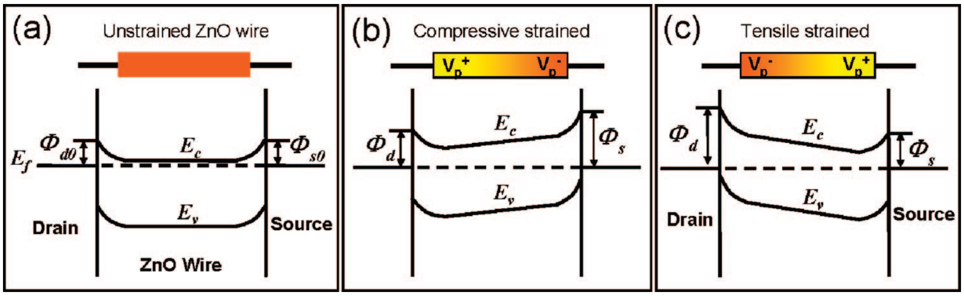

Figure 4. Schematic energy band diagrams illustrating the Schottky barriers at the source and drain contacts of a unstrained (a), compressive strained (b), and tensile strained (c) PFW, which illustrates the effect of switching the piezoelectric potential either by strain or by wire orientation on the local band structure and SBH.

on classic thermionic emission−diffusion theory (for $V \gg 3kT/q \sim 77$ mV)[22]

$$I = S_s A^{**} T^2 \exp\left(-\frac{\phi_s}{kT}\right) \exp\left(\frac{q\sqrt{q\xi/4\pi k_s}}{kT}\right) \quad (1)$$

$$\xi = \sqrt{\frac{2qN_D}{k_s}\left(V + V_{bi} - \frac{kT}{q}\right)} \quad (2)$$

where S_s is the area of the source Schottky barrier, A^{**} is the effective Richardson constant, q is the electron charge, k is Boltzmann constant, N_D is the donor impurity density, V_{bi} is the build-in potential at the barrier, and k_s is the permittivity of ZnO. To verify that eqs 1 and 2 can precisely describe the observed phenomenon, we plot ln I as a function of V and $V^{1/4}$ by using the data provided by the black line in Figure 3a. Figure 3b shows that the ln $I-V^{1/4}$ curve is very linear, which is consistent with eq 1. This not only indicates that the thermionic emission−diffusion model is the dominant process in our device, but this also shows that the theory can be applied to derive the SBH from experimental data, as described in follows.

By assuming S, A^{**}, T, and N_D are to be known, ϕ_s can, in principle, be derived from the ln $I-V$ plot.[12] Subsequently, the strain-induced change in SBH can be determine by[12,17,18]

$$\ln[I(\varepsilon_{zz})/I(0)] \sim \Delta A^{**}/A^{**} - \Delta\phi_s/kT \quad (3)$$

where $I(\varepsilon_{zz})$ and $I(0)$ are the current measured through the PFW at a fixed bias V_a with and without being strained, respectively. Since the stress dependence of A^{**} arises only from the stress dependence of the effective mass, the first term is much smaller than the second term and is thus neglected in the following discussion.[17,18,23] The change of SBH $\Delta\phi_s$ with strain for bias of 1.0 V is plotted in Figure 3c (black curve). Similarly, under a bias of −1.0 V, the change of SBH $\Delta\phi_d$ with strain is calculated and the data are plotted in Figure 3c (red curve).[24] The result shows that both the SBH at the source and drain contacts were increased with increased compressive strain.

The SBH change for the Ag/ZnO/Ag device structure under strain is a combined effect from both strain induced band structure change and piezoelectric polarization.[12] The contributions from band structure effect to SBH change in source and drain contacts are denoted as $\Delta\phi_{s-bs}$ and $\Delta\phi_{d-bs}$, respectively. As discussed above, the axial strain in the ZnO PFW is uniform along its entire length, thus we can assume $\Delta\phi_{s-bs} = \Delta\phi_{d-bs}$ if the two contacts are identical. The contribution of piezoelectric effect to SBH can be described as follows.

As discussed above, the axial strain in the ZnO PFW is uniform along its entire length in our device. Under straining, the cations and anions in ZnO polarize along the straining direction, forming a piezoelectric charge induced polarization. It is important to point out that these piezoelectric ionic charges cannot freely move. They can be screened by the external electrons but cannot be completely depleted.[16] This means that the effect of piezoelectric charges still preserved, although at a reduced level, even ZnO has a moderate conductivity. The effect of piezoelectric polarization to the SBH can be qualitatively described as follows. For a constant strain of ε_z along the length of the PFW, an axial polarization P_z is then created inside the wire and along the wire direction, $P_z = \varepsilon_z e_{33}$, where e_{33} is the piezoelectric tensor.[16,25,26] A potential drop of approximately $V_p^+ - V_p^- = |\varepsilon_z| L e_{33}$ is created along the length of the wire, where L is the length of the wire. Therefore, the modulations to the SBH at the source and drain sides are of the same magnitude but opposite sign ($V_p^+ = -V_p^-$), which are denoted by $\Delta\phi_{s-pz}$ and $\Delta\phi_{d-pz}$ ($= -\Delta\phi_{s-pz}$). Thus the total strain-induced change in SBH at the source and drain contacts are

$$\text{Source:} \quad \Delta\phi_s = \Delta\phi_{s-bs} + \Delta\phi_{s-pz} \quad (4)$$

$$\text{Drain:} \quad \Delta\phi_d = \Delta\phi_{s-bs} - \Delta\phi_{s-pz} \quad (5)$$

which yield $\Delta\phi_{s-bs} = (\Delta\phi_s + \Delta\phi_d)/2$ and $\Delta\phi_{s-pz} = (\Delta\phi_s - \Delta\phi_d)/2$. The $\Delta\phi_{s-bs}$ and $\Delta\phi_{s-pz}$ as a function of strain are plotted in Figure 3d, in which both show linear relationship under smaller strain and nonlinear behavior under larger strain. It has been reported that under small strain, both the band gap change[27,28] and piezoelectric polarization[26] have an approximately linear relationship with strain. The nonlinear effect under high strain needs to be analyzed using more sophisticated theory.

Here we use a schematic energy band diagrams to illustrate how piezoelectric polarization affects the Schottky barriers at the source and drain contacts. Figure 4a shows an unstrained device with the c-axis of ZnO pointing toward the source. When the device is under compressed strain, the drain has a higher piezoelectric potential (see Figures 4b), resulting in higher SBH at source side. Alternatively, by changing the compressive straining to tensile straining simply by changing the bending direction of the PS substrate, the piezoelectric potential-drop in the PFW reverses, as shown

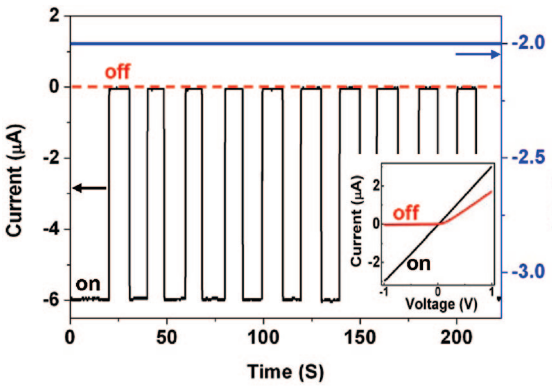

Figure 5. Current response of Device no. 4 to periodic releasing-bending process under a fixed bias of −2 V, showing an "on"−"off" ratio of ∼120. Inset is $I-V$ characterization of Device no. 4 without (black curve) and with stain (red curve).

in Figure 4c, leading to a higher SBH at the drain side. If the modulation to SBH by bond structure change is significantly smaller than that due to piezoelectric potential, the reversal in strain results in the reversal in rectifying polarity of the device, which is just what we observed experimentally in Figure 2b.

Furthermore, the profile of the piezoelectric potential depends not only on the sign of the strain (compressive ($\varepsilon_z < 0$); tensile ($\varepsilon_z > 0$)), but also the *c*-axis orientation of the PFW. A simple change in wire orientation can result in a reverse in the piezoelectric potential profile and thus the observed diode polarity. In our fabrication, the *c*-axis of the PFW is random. This is why the ratio of the devices that exhibit downward and upward diodelike $I-V$ behavior under compressive strain is nearly 1:1 (see Supporting Information, Figure S2).

Our device can act as an effective electromechanical switch. Inset in Figure 5 shows the $I-V$ characterization of Device no. 4 without (black curve) and with (red curve) stain. When the device is free of strain, it shows a symmetric $I-V$ behavior; when the device is under strain, it shows a rectifying $I-V$ behavior. The change is highly reversible. At a fixed bias of −2 V, the current across the device is ∼6 μA (defined as "on" state) and ∼0.05 μA (defined as "off" state) when the device is free of strain and under strain, respectively. By periodically bending and releasing the device under a fixed bias of −2 V, an electromechanical switch with on−off ratio as high as ∼120 has been demonstrated (Figure 5).

In summary, using the strain-induced change in transport property of ZnO wire, we have demonstrated a piezoelectric diode based switches with an on-to-off ratio of ∼120. The wire was laterally bonded and fully packaged, and the design can be easily extended for nanowires, which are expected to have superhigh sensitivity. Our studies provide solid evidence about the existence of piezoelectric potential in the ZnO wire although it has a moderate conductivity. This means that the free carriers can partially screen the piezoelectric potential/charges, but they cannot completely neutralize the charge. The existence of the piezoelectric potential not only supports the mechanism proposed for nanogenerators[5] and piezotronics,[13] but also can be used to fabricate a new type of piezoelectric diodes and switches, which are highly sensitive, cost-effective, versatile and fully packaged for a wide range of applications.

Acknowledgment. This research was supported by DARPA, BES DOE, NSF, and Emory-Georgia Tech CCNE funded by NIH. P.F. and Y.D.G. thank the partial fellowship support by the China Scholarship Council (CSC) (No. 20073020).

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Kinaret, J. M.; Nord, T.; Viefers, S. *Appl. Phys. Lett.* **2003**, *82*, 1287.
(2) Cha, S. N.; Jang, J. E.; Choi, Y.; Amaratunga, G. A. J.; Kang, D. J.; Hasko, D. G.; Jung, J. E.; Kim, J. M. *Appl. Phys. Lett.* **2005**, *86*, 083105.
(3) Jang, W. W.; Lee, J. O.; Yoon, J. B.; Kim, M. S.; Lee, J. M.; Kim, S. M.; Cho, K. H.; Kim, D. W.; Park, D.; Lee, W. S. *Appl. Phys. Lett.* **2008**, *92*, 103110.
(4) Badzey, R. L.; Zolfagharkhani, G.; Gaidarzhy, A.; Mohanty, P. *Appl. Phys. Lett.* **2005**, *86*, 023106.
(5) Wang, Z. L.; Song, J. H. *Science* **2006**, *312*, 242.
(6) Wang, X. D.; Song, J. H.; Liu, J.; Wang, Z. L. *Science* **2007**, *316*, 102.
(7) Wang, X. D.; Zhou, J.; Song, J. H.; Liu, J.; Xu, N. S.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 2768.
(8) Lao, C. S.; Kuang, Q.; Wang, Z. L.; Park, C. M.; Deng, Y. *Appl. Phys. Lett.* **2007**, *90*, 262107.
(9) He, J. H.; Hsin, C. L.; Liu, J.; Chen, L. J.; Wang, Z. L. *Adv. Mater.* **2007**, *19*, 781.
(10) Zhou, J.; Fei, P.; Gao, Y. F.; Gu, Y. D.; Liu, J.; Bao, G.; Wang, Z. L. *Nano Lett.* . **2008**, *8*, 2725.
(11) Buchine, B. A.; Hughes, W. L.; Degertekin, F. L.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 1155.
(12) Zhou, J.; Gu, Y. D.; Fei, P.; Mai, W. J.; Gao, Y. F.; Yang, R. S.; Bao, G.; Wang, Z. L. *Nano Lett.* . **2008**, *8*, 3035.
(13) Wang, Z. L. *Adv. Mater.* **2007**, *19*, 889.
(14) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.
(15) To apply a consecutive release-stretch-release-compress strain condition to the device, the device was bent manually instead of by the 3D mechanical stage.
(16) Chung, K. W.; Wang, Z.; Costa, J. C.; Williamson, F.; Ruden, P. P.; Nathan, M. I. *Appl. Phys. Lett.* **1991**, *59*, 1191.
(17) Liu, Y.; Kauser, M. Z.; Nathan, M. I.; Ruden, P. P.; Dogam, S.; Morkoc, H.; Park, S. S.; Lee, Y. K. *Appl. Phys. Lett.* **2004**, *84*, 2112.
(18) Liu, Y.; Kauser, M. Z.; Ruden, P. P.; Hassan, Z.; Lee, Y. C.; Ng, S. S.; Yam, F. K. *Appl. Phys. Lett.* **2006**, *88*, 022109.
(19) Zhang, Z. Y.; Yao, K.; Liu, Y.; Jin, C. H.; Liang, X. L.; Chen, Q.; Peng, L. M. *Adv. Funct. Mater.* **2007**, *17*, 2478.
(20) Wu, X. S.; Sprinkle, M.; Li, X. B.; Ming, F.; Berger, C.; de Heer, W. A. *Phys, Rev, Lett.* **2008**, *101*, 026801.
(21) Fan, Z. Y.; Lu, J. G. *Appl. Phys. Lett.* **2005**, *86*, 032111.
(22) Sze, S. M. *Physics of semiconductor devices*; John Wiley & Sons: New York, 1981.
(23) Shan, W.; Ager, J. W., III; Yu, K. M.; Walukiewicz, W.; Haller, E. E.; Martin, M. C.; Mckinney, W. R.; Yang, W. *J. Appl. Phys.* **1999**, *85*, 8505.
(24) In the calculation presented above, we assumed that the applied voltage was totally consumed at the reversely biased Schottky barrier formed at the source electrode. In reality, V_s (V_d) < V, thus the calculated $\Delta\phi$ value may be slightly affected by the choice of V.
(25) Zhao, M. H.; Wang, Z. L.; Mao, S. X. *Nano Lett.* **2004**, *4*, 587.
(26) Nye, J. F. *Physical Properties of Crystal*; Oxford: London, 1955.
(27) Minot, E. D.; Ysish, Y.; Sazonova, V.; Park, J. Y.; Brink, M.; McEuen, P. L. *Phys. Rev. Lett.* **2003**, *90*, 156401.
(28) Cao, J.; Wang, Q.; Dai, H. J. *Phys. Rev. Lett.* **2003**, *90*, 157601.

NL802497E