ADVANCED MATERIALS

Energy Harvesting Using Piezoelectric Nanowires–A Correspondence on "Energy Harvesting Using Nanowires?" by Alexe et al.

By *Zhong Lin Wang**

We have demonstrated an innovative approach to convert mechanical energy into electrical energy by piezoelectric zinc oxide nanowire (NW) arrays.[1,2] The mechanism of the nanogenerator (NG) relies on the coupling of piezoelectric and semiconducting dual properties of ZnO as well as the elegant rectifying function of the Schottky barrier formed between the metal tip and the NW.[3] Alexe et al.[4] have recently reported their assessment of the mechanism of the NG and they have raised the following three concerns.[5] First, the piezoelectric charges in the ZnO NW was suggested to be completely cancelled out by existing free charge carriers in a ZnO NW within a very short period of time, thus, a piezoelectric potential would not be observed. Second, the detected output voltage from a single NW in the order of ~10 mV was insufficient to drive the Schottky barrier formed between the Pt electrode and the ZnO NW, thus no rectifying effect would be expected. Lastly, an output voltage was observed by them using their equipment for Si NWs, which are non-piezoelectric, thus, it was suggested that the received output from a NG might not be a result of a piezoelectric effect.

This paper is set to fully analyze the questions raised and data presented by Alexe et al.[4] and give a full comment. Based on a series of systematic experiments that we have carried out over the past three years, my conclusions are as follows. Alexe et al.[4] overestimated the carrier density in the ZnO NW by up to two orders of magnitude. A UV-tuned conductivity experiment using a ZnO NW showed that the carrier density does affect the performance of the NG, but the conductivity of our as-synthesized NW is just right for one to observe the piezoelectric-potential-driven flow of external electrons.[6] The piezoelectric potential remains in the NW for an extensive period of time, which allows direct detection of a piezoelectric-induced effect.[7] The role played by the piezoelectric potential is to overcome the threshold voltage at the Pt–ZnO junction, while the observed output signal of ~10 mV is the difference in Fermi levels between the two electrodes connected to the Pt tip and the ZnO NW.[3] Finally, the observation of potential generation by Si NWs by Alexe et al.[4] is a result of system artifacts in their experiments. Their measurement system had a strong 25 Hz interference background from the environment, an output noise of ±10 mV, and a huge equivalent capacitance of ~320 pF. They used a bipolar amplifier with a bias current of −3.29 nA or even larger and an offset voltage of 32.5 mV to amplify the signal, which produced an RC (resistor–capacitor) discharge signal at a magnitude of ~800 mV and shadowed any true signal (−10 mV) one tried to measure. As a result, their output signal was independent of the type, the size, and aspect ratio of the NWs.

Consequently, they suggested without solid evidence that a piezoelectric effect was not responsible for the NG. More importantly, they mistakenly assumed that our measurement system was similar/identical to theirs, thus they used the artifacts (~800 mV peaks) received from their system to explain the results (~−10 mV) we have obtained using a highly sensitive measurement system (noise ~±0.5 mV, capacitance 1.2 pf, amplifier introduced voltage offset of 1 mV, and undetectable RC discharge effect (<1 mV)). Finally, Alexe et al.'s[4] model cannot explain 11 key experimental facts we have determined.

1. The Piezoelectric Potential in ZnO NWs and its Experimental Detection

When a ZnO NW is elastically deformed, a piezoelectric potential field is created in the NW. The piezoelectric potential is created by the polarization of ions in the crystal rather than the free-mobile charges. Since the charges associated with the ions are rigid and affixed to the atoms, they cannot freely move. Free carriers in the semiconductor NW may screen the piezoelectric charges, but they cannot completely deplete the charges. This is a distinct difference from the p–n junction in semiconductor physics. Therefore, the piezoelectric potential is still preserved, although a possible reduction in magnitude is possible owing to the finite conductivity of the NW.

The first question is how large is the piezoelectric potential? For a NW of 50 nm in diameter and 500 nm in length, the piezoelectric potential drop across the NW is ~0.6 V if the NW has no conductivity.[8] With consideration of the finite electric conductivity at a moderate carrier density of ~10^{16}–10^{17} cm^{-3},[9] which is determined by the synthesis conditions, the free carriers can screen the piezoelectric charge but they cannot totally cancel out the piezoelectric charges, which means that the magnitude of the piezoelectric potential is reduced by the charge carriers but it is still large enough to drive the flow of external electrons. Using a newly developed theory and considering the conductivity of ZnO, for a typical carrier density of 10^{16}–10^{17} cm^{-3}, the magnitude of the piezoelectric potential drop remains at ~0.3 V (Y. F. Gao, Z. L. Wang, unpublished). This is sufficient to operate a Schottky diode. Using a micrometer probe, the piezoelectric potential at

[*] Prof. Z. L. Wang
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245 (USA)
E-mail: zhong.wang@mse.gatech.edu

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the tensile and compressive side surfaces of a ZnO wire has been directly measured experimentally.[7] The demonstrated piezoelectric diode and piezoelectric strain sensors directly prove the existence of the piezoelectric potential in ZnO.[10,11]

Furthermore, 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 characteristics from symmetric to diode-type has been observed.[12] 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. Our studies provide solid evidence about the existence of a 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 all of the charge. The existence of the piezoelectric potential not only supports the mechanism proposed for NGs, but can also be used to fabricate a new type of piezoelectric diode and switch.

The second question is how long will the piezoelectric potential last? We designed an experiment to measure the life-time of the piezoelectric potential. Using a long ZnO wire that was bonded at the two ends to metal contacts, we continuously monitored the current transported through the wire at a fixed applied external voltage once it was bent,[7] which means that the wire was under a constant strain. We noticed that, after the wire was bent and held stationary, a trend was seen in the recovery curve of the conductance in the current–time (I–T) curve. Since the piezoelectric potential can effectively modify the height of the Schottky barrier at the contacts,[10] the change in conductance directly reflects the change in barrier height. Therefore, the conductance of the device is tuned by the piezoelectric potential, which, in reverse, proves the existence of the piezoelectric effect and its life time.

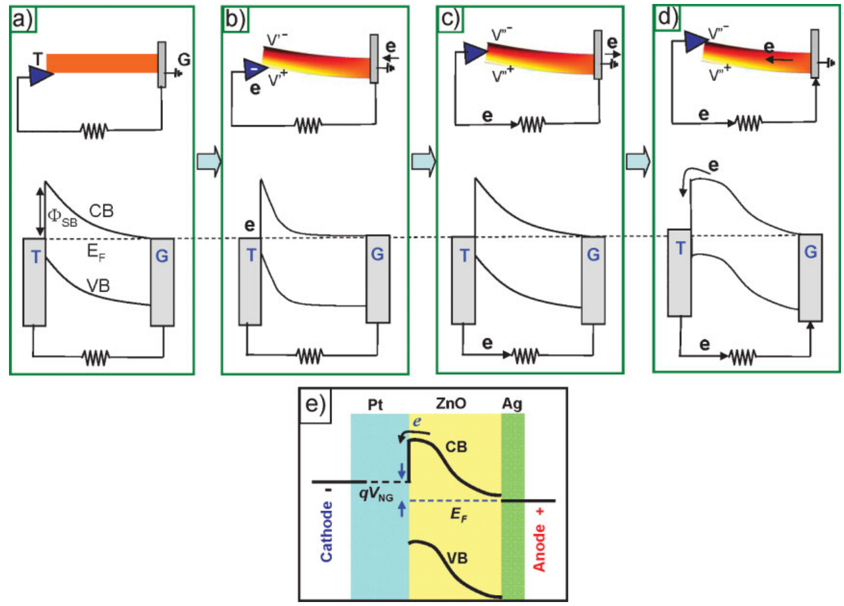

Figure 1. Band diagram for understanding the charge outputting and flowing processes in the nanogenerator. a) Schematic and energy diagram of a NW with one end grounded (G) and the other end to be pushed by a conductive AFM tip (T). A Schottky barrier is at the tip/NW interface. b) Once being slowly deflected, the asymmetric piezoelectric potential in the NW changes the profile of the conduction band (CB). The local positive piezoelectric potential at the contact area results in a slow-flow of electrons from ground through the load to the tip. The electrons will be accumulated in the tip. c) When the tip scans across the NW and reaches its middle point, a drop in the local potential to zero results in a back flow of the accumulated electrons through the load into ground. d) Once the tip reaches the compressive surface, a local negative piezoelectric potential raises the profile of the conduction band. If the piezoelectric potential is large enough, electrons in the n-type ZnO NW can flow to the tip. This circular motion of the electrons in the circuit is the output current. e) Energy band diagram for the NG, presenting the output voltage and the role played by the piezoelectric potential.

2. Understanding the Relationship between the Output Voltage of the NG and the Piezoelectric Potential

The band structure model for a NG was used to illustrate the relationship between the piezoelectric potential and the output voltage of the NG. The atomic force microscopy (AFM) tip (T) has a Schottky contact (barrier height Φ_{SB}) with the NW, while the NW has an Ohmic contact with the grounded side (G) (Fig. 1a). When the tip slowly pushes the NW, a positive piezoelectric potential V^+ is created at its tensile surface. As the tip continues to push the NW, electrons slowly flow from the grounded electrode through the external load to reach the tip, but the electrons cannot cross the tip/NW interface because of the presence of a reversely biased Schottky barrier at the contact for n-type semiconductors (Fig. 1b). In such a case, the accumulated free charges at the tip may affect the piezoelectric potential distribution in the NW owing to the screening effect of the charge carriers. The piezoelectric potential is generated because of the rigid and nonmobile ionic charges in the NW, it cannot be completely depleted by the free carriers. The local newly established potential V'^+ lowers the conduction band (CB) slightly.

When the tip scans in contact mode across the NW and reaches the middle point of the NW (see Fig. 1c), the local piezoelectric potential is zero. In such a case, with a sudden drop in local potential, the originally accumulated electrons in the tip back flow through the load to the ground. This is a process faster than the charge accumulation process presented in Figure 1b. An alternative case that gives the same result is that the tip temporarily lifts off from the NW, which also leads to the back flow of the accumulated electrons to the ground.

When the tip reaches the compressive side of the NW (Fig. 1d), the local potential drops to V'^- (negative), which results in a significant increase of the conduction band near the tip. If the increase in local potential energy is large enough, as determined by the degree of NW bending, the piezoelectric potential drives the flow of electrons in the external circuit, thus producing a current if the charge flow rate is appreciably large. This process is a lot faster than the charge accumulation process, thus, the created transient potential at the external load is large enough to be detected beyond noise level.

The presence of a Schottky at the tip–NW interface is mandatory for a NG, which acts like a 'gate' for separating and slowly accumulating the charges and then rapidly releasing the charges.[6] The lack of a 'gate' at an Ohmic contact results in no charge separation at the tip/NW interface, and no preservation of the piezoelectric potential in the NW, thus, no detectable signal will be received. This has been verified experimentally using a Pt tip and an Al–In tip.[6] A Pt tip that has a Schottky contact with ZnO gives an output voltage, while an Al–In tip with an Ohmic contact with ZnO produces no output voltage.

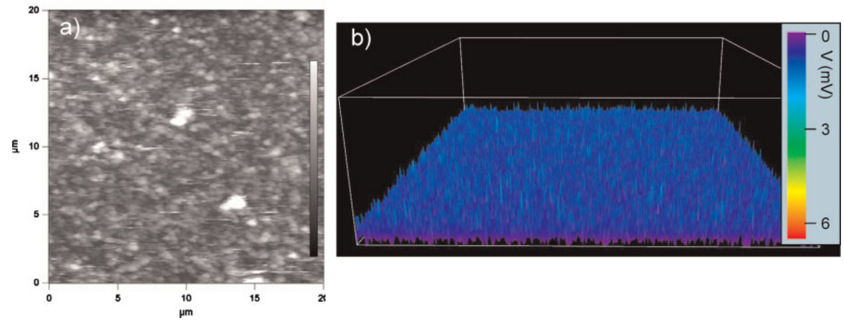

Figure 2. a) AFM image acquired from an array of semiconductive Si nanowires, which shows the tips of the nanowires. b) The corresponding piezoelectric potential output image across the sample measured by the AFM tip in contact mode. Within the experimental noise range, the Si nanowires produced no electricity. Transport measurement of the nanowire did show that they conducted electricity. The experimental set up and conditions were the same as in [1].

The next question is how large the output voltage is? This question can be answered by the energy band diagram shown in Figure 1e for the NG. *The role played by the piezoelectric potential is to drive the electrons from the ZnO NW to overcome the threshold energy at the metal–ZnO interface into the Pt electrode, but it does not directly determine the magnitude of the output voltage*. As more electrons are being 'pumped' into the Pt electrode, the local Fermi surface is transiently increased. *Therefore, the output voltage is the difference between the Fermi energies for Pt and the bottom electrode*. This is the origin of the ~10 mV we observed. The piezoelectric potential that overcomes the Schottky barrier is much larger than the measured voltage.

3. Analysis of the Experimental System Used by Alexe et al.

The experimental set up developed by Alexe et al.[4] may *not* be eligible for measuring small electrical signals. First, their system has a huge noise level. The periodic background fluctuations and noise at ~25 Hz (with an amplitude of 5 mV) are present in the voltage output images of Alexe et al.[4] (see their Fig. 3g, Fig. S3d, Fig. S4b, and Fig. S8). The interference pattern rotates in orientation by changing the scanning direction (see Alexe et al., Fig. S8). This systematic periodic noise background clearly indicates the interference from the environment to their measurement system. From Figure 3g of Alexe et al., the noise level is very conservatively estimated to be ±10 mV,[13] which is the high end of the signal we detected for the piezoelectric output voltage of −10 mV. With a noise higher than the signal, no signal will be detected! The noise level in Alexe et al.'s system is close to 20 times that in our system (±0.5 mV) (see Fig. 2C in [1]). Our system was well isolated and there was no interference background in the electrical output (see Fig. 4B in [1]). In Figure 3c and 3d of Alexe et al.,[4] an enhanced electrical signal output is seen at the bottom edge of the scanning region, which suggests that artifacts are being introduced. By examining the feature shapes in Figure 1c and 1d of Alexe et al.,[4] the irregular shape of the contrast pattern indicates instantaneous system errors introduced in their measurements.

The set up of Alexe et al.[4] had a huge capacitance. Using the discharge curve presented in Figure S3b of Alexe et al., the discharge time constant τ is ~32 ms,[14] which is 50 times larger than ours (0.6 ms); the system capacitance C_p can be estimated for a load of 100 MΩ (from the caption of Fig. 3 of Alexe et al.[4]) to be ~320 pF, which is over 260 times larger than that of our measurement system (1.2 pF). This means that the charge storing capacity from the input bias of the op-amp in their system is extraordinary large (see Fig. 4 in Alexe et al.[4]). The release of the charges (at 800 mV from Fig. 3e,f of Alexe et al.[4]) will shadow any signal that one is intended to observe in the −10 mV range.

The op-amp used by Alexe et al. produced a large bias current and voltage. From their calibrations for different op-amps listed in Figure S3 and Table S1 in Alexe et al.,[4] for the discharge peaks of ~800 mV in magnitude, the op-amp used to generate the data in Figure 3e and 3f is likely to be the model OP 27 or LT1360 (see the caption of Fig. S4 of Alexe et al.), with the corresponding input bias current i_b to be −3.29 or −14.5 nA. The voltage to be charged to the capacitor C_p in Figure 2 of Alexe would be –32.5 mV for an OP 27 op-amp (for 100 MΩ load, see Fig. S2 of Alexe et al.[4]) and −1.44 V for LT1360. This is much much larger than the output produced by a ZnO NW (−10 mV). The shape of the electrical signal displayed in Figure S3b shows a curve that is a typical RC discharge curve. The discharge of the capacitor C_p at a voltage of 32.5 mV for OP27, for example, will override any weak signal that is produced by the NW. The performance of LT1360 would be even worse. Therefore, their measurement system totally shadowed and swallowed up any electrical signal produced by a tiny NW. In such a case, for any sample (disregarding metals, semiconductors, piezoelectrics or non-piezoelectrics) for which there is a variation in contact resistance across the surface with the tip, the measurement system would produce 'identical' electrical peaks of ~800 mV as those shown in Figure 1c of Alexe et al.[4] which is produced by the discharge of C_p. This is why their measured electrical signals from either ZnO or Si NW were identical, regardless of their size and aspect ratio, as claimed by Alexe et al. This is the reason why they found that "the signal amplitude depends rather on the read-out circuit than on the sample under investigation'', clearly admitting the artifacts of their system. When the tip is not in contact with the sample surface, the input bias current i_b (presumably -2.39 nA) charge of the measurement system is characterized by the capacitor C_p. Once the tip is in contact with the sample, an RC discharge occurs across the NW/substrate. Therefore, the measured signal is nothing but an instantaneous RC discharge potential across the NW with an instantaneous contact resistance. The only role played by the nanowire is to serve as a 'switch', as claimed by Alexe et al.[4] This is why the measured data in Figure 1c and 1d of Alexe et al.[4] are fairly random in shape and do not show good correspondence to the locations and shapes of the NWs.

Unfortunately, Alexe et al. assumed that our system had had the same level and same type of artifacts as theirs, thus they used the RC discharge artifacts obtained in their system to explain the signal received in our measurement system. In contrast, in our experiments, the input bias current was kept so small that the offset voltage created on the load was <1 mV and the noise level was kept at ±0.5 mV. This allows us to detect the –10 mV output from a ZnO NW. The capacitance of the system that included the NW was as low as 1.2 pF, so that the RC discharge was minimized to a level within 1 mV (see Fig. 4B in [1]). Therefore, Alexe et al.'s model (see their Fig. 4)[4] is only applicable to explain the artifacts produced in their measurement system, and *not* applicable for explaining our data. It is very inappropriate to draw a conclusion for our data based on the artifacts received from their completely incomparable system.

One of the main pieces of experimental evidence that Alexe et al. presented is that they observed a voltage output at the level of ~800 mV using Si NWs. We have used our system to measure the power generation from an array of semiconductive Si NWs, we did not receive any appreciable output signal (see Fig. 2). In addition, the samples used by Alexe et al.[4] (see their Fig. 3b and Fig. S5) do not look like nanowires at all, but rather nanoparticles. The aspect ratio is about 0.6–2.

For the same wurtzite-structured family of materials as ZnO, we have observed power generation from CdS NWs[15,16] GaN NWs,[17,18] but not TiN or AlN NWs owing to poor conductivity.[16]

It is also worth noting that the voltage measured by Alexe et al.[4] is always *positive* in reference to the grounded NW sample, because the input bias current flowed from the op-amp through the load R_L into ground. The signal sign is the opposite to ours, which further proves that what they measured is a different type of signal from ours.

The model by Alexe et al.[4] in their Figure 4 cannot explain the following *11 key experimental facts* observed consistently and reproducibly in our series of works:

i) The electrical output signal had a very sharp and regular shape that was always *negative* in reference to the grounded bottom ends of the NWs. (Note that the signal was inverted for convenience of the 3D display in [1]). In contrast, the signals received by Alexe et al. were always *positive*. This is a very different character.
ii) No output was received when the tip first touched the NW and pushed the NW, but the electrical output was observed only when the tip was almost leaving the NW at the second half of the contact.[1]
iii) The electrical output occurred exclusively when the tip touched the compressive side of the NW instead of the tensile side, which was first in contact with the tip (see the Supporting Information of [2]).
iv) No electrical output was received beyond a noise level of ~±0.5 mV when the AFM was in tapping mode (Fig. 4 in [1]).
v) No electrical output was received when the samples were aligned non-piezoelectric tungsten oxide NWs[1,19] or Si NW (see Fig. 2), which are semiconductors with moderate conductivity.[20,21]
vi) No electrical output was received when the sample was aligned carbon nanotubes, which are known to be (semi) conductive but non-piezoelectric.
vii) No electrical output was received when the sample was a metal plate with a rough surface.[1] The contact between the tip and the rough metal surface varied during scanning, which should lead to a change in contact resistance.
viii) The electrical output signal depends sensitively on the size of the NWs (~ –10 mV output for NWs with a diameter of 40 nm and lengths of ~500 nm;[1] and – 40 to –50 mV for NWs with diameter 300 nm and lengths of 2 μm[22]).
ix) The voltage and current outputs received for the direct-current NG driven by ultrasonic wave without using AFM.[23,24]
x) The voltage/current output of the NGs obeys the linear superposition, which means that the output currents add up if two NGs are in parallel, and the output voltages add up if two NGs are connected in series.[3,25,26]
xi) The voltage/current output of the NG switches in polarity by switching its connection to the electrical measurement system.[23,24]

In summary, in contrast to the claim of Alexe et al.,[4] we have experimental data that show the existence and observation of a piezoelectric potential in ZnO NWs although they have a moderate conductivity. The free electrons can screen the piezoelectric charge, but they cannot completely cancel the piezoelectric charge. The ~10 mV output voltage from the NW nanogenerator is the difference in Fermi levels between the tip and the ground electrode rather than the piezoelectric potential; the role played by the piezoelectric potential (~0.3 V) is to drive the flow of electrons across the Pt–ZnO contact, which forms a circular charge flow through the external circuit. Alexe et al.'s experiments were based on an AFM measurement system that is dominated by large system artifacts (800 mV) and a noise (±10 mV) comparable or even higher than the piezoelectric signals from a tiny NW (−4 to −10 mV). The only evidence presented by Alexe et al. was that they received some discharge peaks from Si nanowires that were 'identical' to that from ZnO. Since Si is not piezoelectric, they concluded that the signal from the ZnO nanowires might not be due to a piezoelectric effect. But they missed that their measurement system was incomparable to our system in noise level, sensitivity, and system RC response. We have obtained 11 key experimental facts that cannot be explained using their model, but can be explained by our model. The NG is based on a piezoelectric effect, and it is a result of coupled piezoelectric and semiconducting dual properties of ZnO with the presence of a Schottky barrier between the metal tip and the NW.[3,27]

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Note added in Proof: Two additional papers have been published recently that prove the existence of piezoelectric potential in ZnO [28,29]. In collaboration with a group in Taiwan, our most recent energy generation using p-type ZnO nanowires has produced positive output voltage, while n-type ZnO nanowire produces negative output potential, which is another solid evidence supporting the mechanism for nanogenerators proposed in[1].

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