Voltage Generation from Individual BaTiO₃ Nanowires under Periodic Tensile Mechanical Load

Zhaoyu Wang, Jie Hu, Abhijit P. Suryavanshi, Kyungsuk Yum, and Min-Feng Yu*

Department of Mechanical Science and Engineering, University of Illinois at Urbana–Champaign, 1206 West Green Street, Urbana, Illinois 61801

ABSTRACT

Direct tensile mechanical loading of an individual single-crystal BaTiO₃ nanowire was realized to reveal the direct piezoelectric effect in the nanowire. Periodic voltage generation from the nanowire was produced by a periodically varying tensile mechanical strain applied with a precision mechanical testing stage. The measured voltage generation from the nanowire was found to be directly proportional to the applied strain rate and was successfully modeled through the consideration of an equivalent circuit for a piezoelectric nanowire under low-frequency operation. The study, besides demonstrating a controlled experimental method for the study of direct piezoelectric effect in nanostructures, implies also the use of such perovskite piezoelectric nanowires for efficient energy-harvesting applications.

Energy-harvesting devices have been long pursued with the purpose of powering sensor networks and mobile devices without a battery.[1–2] Piezoelectric crystals, which can generate electrical charges when mechanically deformed, are among the most promising material candidates for developing energy-harvesting devices.[2,3] Piezoelectric energy-harvesting devices have been envisioned for applications in residential sensors,[3] foot-powered radio "tag",[4,5] vibration absorbers,[6] and PicoRadio.[7] As the dimension of various functional devices is reduced down to microscale and even nanoscale, the need for nanoscale piezoelectric energy-harvesting devices is accordingly getting greater in order to effectively power various nanosystems.[8] Recently, direct electricity generation from single piezoelectric nanowires, such as ZnO[8–10] and GaN[11] nanowires, has been successfully demonstrated. In such studies, the mechanical deformation was induced by deflection of the cantilevered nanowires with a probe tip or ultrasonic wave, and the resulted electric response was sensed through the probe tip. Considering the relatively low charge constant (piezoelectric constant) of ZnO (∼12 pC/N)[12] and GaN (∼3 pC/N),[13] it is desirable to use nanowires made of perovskite piezoelectric materials with high charge constant such as BaTiO₃ and lead zirconate titanate (PZT) for energy harvesting. The longitudinal d_{33} charge constant for single-crystal BaTiO₃ and ceramic PZT can reach 85 pC/N[14] and 268 pC/N,[15] respectively. It is also desirable to adopt a more controlled approach to apply the mechanical load so that the charge generation and the direct

piezoelectric effect in such piezoelectric nanowires can be studied in more detail.

In this letter, we report the study of charge generation from a suspended and doubly clamped single-crystal BaTiO₃ nanowire under periodic tensile mechanical load. The periodic tensile load was provided by a miniaturized piezoelectric flexure stage with nanometer displacement resolution. The time and strain rate-dependent charge response from the nanowire was measured with a high-sensitivity fast-response charge amplifier.

The BaTiO₃ nanowires used in the experiment were synthesized by a salt-assisted high-temperature solid-state chemical reaction.[16] Such BaTiO₃ nanowires have previously been shown to be ferroelectric and have a single ferroelectric domain formation polarized along the length direction.[17,18] For the charge-sensing measurement, a nanowire was picked and placed with nanomanipulation onto a piezoelectric flexure stage based tensile loading platform specifically designed for mechanical testing of nanowire. The loading platform consists of two coplanar bases separated by a ∼3 μm gap. The nanowire was placed across the gap and fixed at the two ends via localized electron beam induced deposition of Pt inside a scanning electron microscope (SEM), as shown in the inset of Figure 1. One of the bases is fixed, the other is mobile and driven by a single-axis piezoelectric flexure stage with a displacement resolution better than 1 nm. As schematically shown in Figure 1, during the experiment, periodic tensile load in the form of strain was applied onto the nanowire by the periodic displacement generated from the flexure stage. A high-sensitivity charge
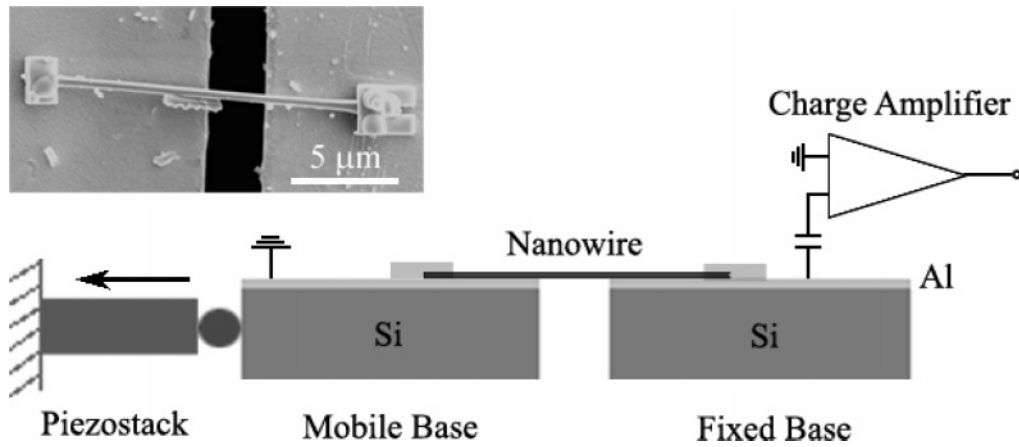

Figure 1. Schematic showing the experimental setup for the piezoelectric charge detection from an individual BaTiO$_3$ nanowire. Inset shows the SEM image of the suspended nanowire under test.
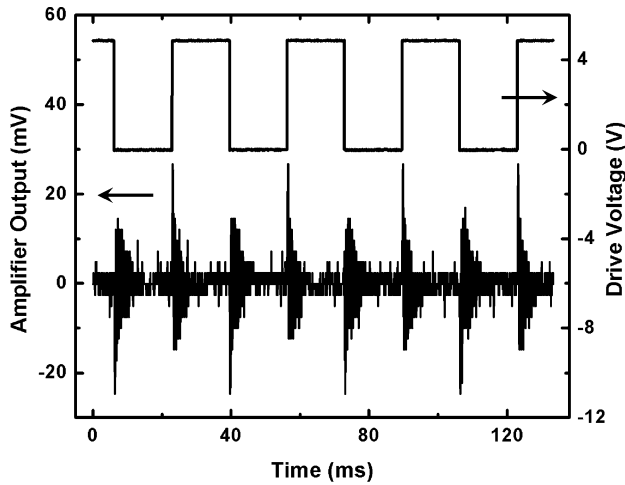

Figure 2. Acquired output signal from the charge amplifier for a BaTiO$_3$ nanowire under a periodic tensile load. A square wave voltage signal was applied onto a piezostack in the flexure mechanical stage to deform the nanowire.

amplifier (A250F, Amptek, Inc.) was used to detect and measure the electric charge response. The output signal from the charge amplifier was acquired with a computerized data acquisition system. The measurement was carried out in high vacuum ($\sim10^{-6}$ τ).

Figure 2 shows a typical piezoelectric voltage response from the nanowire measured from the charge amplifier when a square wave signal (5 V drive amplitude, 30 Hz) is applied to drive the piezostack actuator in the flexure stage. The nanowire was seen to respond to the sudden change of the applied mechanical strain, thus the strain rate occurred at the fast rise and fall of the square wave signal. A sudden increase followed by a decay of the voltage signal was seen in both occurrences. The signal output is zero when the expected strain rate applied onto the nanowire is zero. Square wave driving signals with different amplitude were used in the experiment and produced similar voltage responses.

Such a voltage response from a nanowire under a periodic tensile strain load can be understood through the modeling of an equivalent circuit by taking into account the piezoelectric response of the nanowire, the kinematics of the
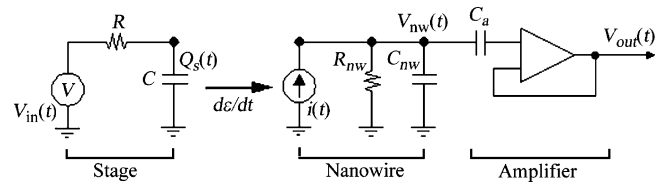

Figure 3. Overall equivalent circuit for the mechanical loading and charge sensing of piezoelectric nanowire.

piezoelectric flexure stage, and the dynamics of the involved sensing circuit, as shown in Figure 3.

A piezoelectric element under mechanical load can be traditionally modeled as a current source in parallel with a capacitor,[2,3] as shown in Figure 3. R_{nw} represents the total resistance of the nanowire and any other parallel resistive sources, and C_{nw} represents the total capacitance, including the capacitance of the nanowire and any parasitic capacitance. The current source is then described according to

$$i = d\frac{\partial F}{\partial t} = dAE\frac{\partial \epsilon}{\partial t} \tag{1}$$

where i is the current, d is the charge constant, and E is the Young's modulus of the piezoelectric element, F is the applied load, A is the load area, and ϵ is the resulted strain. The current response from a piezoelectric element is thus proportional to the applied strain rate.

The kinematics of the single-axis piezoelectric flexure stage determines the actual strain rate applied onto the nanowire and can be modeled by mainly considering the response characteristics of the piezostack actuator in the stage. The response characteristics of a piezostack actuator driven by a periodic voltage signal for low-frequency operation is simply described by a serial RC equivalent circuit (as shown in Figure 3), with R_s being the resistance representing the dielectric loss and C_s being the capacitance associated with the piezostack actuator: $V_{in} = (dQ_s/dt)R_s + Q_s/C_s$, where V_{in} is the applied voltage and Q_s is the distributed charge on the piezostack actuator. Q_s determines the induced strain ϵ_s according to $Q_s = d_sA_sE_s\epsilon_s$, here the subscript s denotes the piezostack actuator. In the experiment,

a square wave signal with an amplitude of V_0 and a frequency of 30 Hz is applied to drive the piezoelectric flexure stage. The resulted displacement Δl of the nanowire is determined by the response of the piezostack actuator, and can be expressed as, in the rising phase of the square wave:

$$\Delta l(t) = \beta D_s V_0 [1 - \exp(-t/\tau_s)] \qquad (2)$$

and in the falling phase:

$$\Delta l(t) = \beta D_s V_0 \exp(-t/\tau_s) \qquad (3)$$

where $\tau_s = R_s C_s$, D_s is the piezoresponse factor of the specific piezostack used in the stage, $D_s = 60$ nm/V, and β is a conversion factor. $\beta = 0.35$ based on the calibration of the flexure stage. This displacement (so the applied strain) induces a current according to eq 1:

$$i(t) = \beta(D_s/S_{nw})(V_0/\tau_s) \exp(-t/\tau_s) \qquad (4)$$

where $S_{nw} = L_{nw}/(d_{nw} A_{nw} E_{nw})$, and L_{nw} is the length of the nanowire.

The voltage V_{nw} produced from the nanowire can then be obtained by solving the differentiation equation: $i(t) = V_{nw}/R_{nw} + C_{nw} dV_{nw}/dt$, according to the equivalent circuit in Figure 3. The result is:

$$V_{nw}(t) = \kappa V_0 [\exp(-t/\tau_{nw}) - \exp(-t/\tau_s)] \qquad (5)$$

where $\kappa = \beta(D_s/S_{nw})(1/C_{nw})(\tau_{nw}/(\tau_{nw} - \tau_s))$. The voltage response from the piezoelectric nanowire has a form of exponential decay after the initial sudden rise, with the decay time constant determined by both the flexure stage and the nanowire. The measured voltage output from the amplifier is then:

$$V_{out}(t) = g C_a V_{nw}(t) \exp(-t/\tau_a) \qquad (6)$$

where g is the gain factor and τ_a is the output time constant of the charge amplifier. They are specified to be 4 V/pC and 0.25 ms, respectively, according to the data sheet.

The voltage output from the amplifier is simulated with a commercial Spice program and compared with the measured response for an applied square wave signal of 5 V in amplitude and 30 Hz in frequency, as shown in Figure 4. For the simulation, the following parameters were used: $D_s = 60$ nm/V according to the specifications of the commercial piezostack, $\beta = 0.35$ according to our calibration, $\tau_s = 0.05$ ms according to the estimated response time of the piezostack, $E_{nw} = 70$ GPa according to the bulk properties of BaTiO$_3$ single crystal, $d_{nw} = 45$ pC/N according to the measurement described below, $R_{nw} = 100$ MΩ (In the measurement, a resistor of 100 MΩ was connected in parallel with the BaTiO$_3$ nanowire. The BaTiO$_3$ nanowire is practically an insulator based on our IV measurement.), and $C_{nw} = 5$ pF according to the curve fitting. The studied BaTiO$_3$
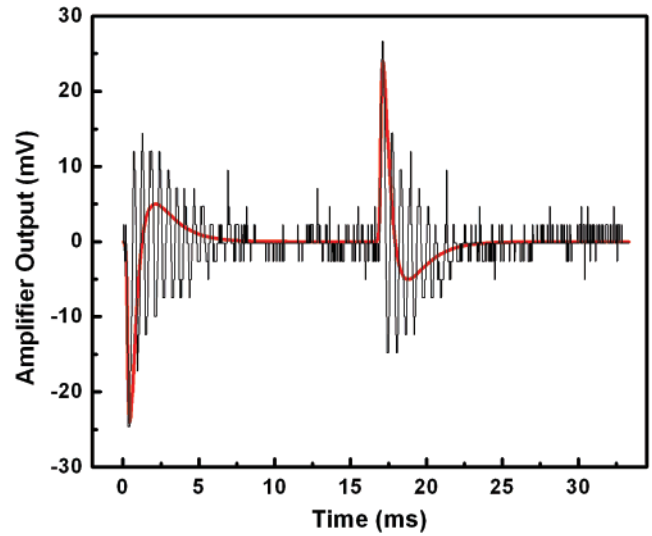
Figure 4. Plots show the measured response (black) from the charge amplifier and the modeled response (red) for the nanowire under periodic square wave tensile load.
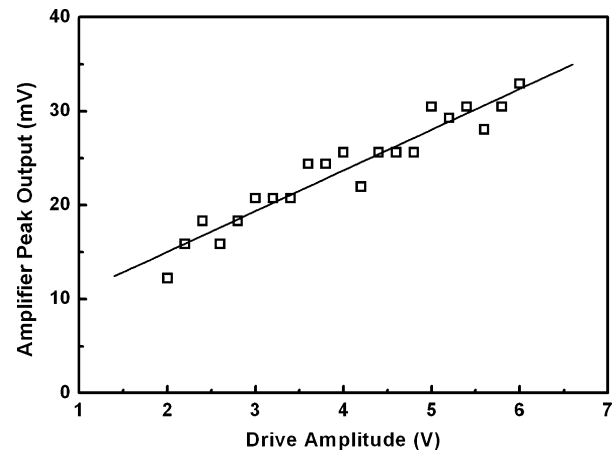
Figure 5. Plot of the amplifier peak output vs the square wave amplitude. The solid line shows the linear data fit.

nanowire has a diameter of ∼280 nm and a length of ∼15 μm. The simulated response reproduces the essential features in the measured voltage response and shows a sharp rise corresponding to the sudden application of strain on the nanowire and a relatively slow decay to zero voltage output corresponding to the charge dissipation process when the applied strain rate is zero.

The amplitude dependent voltage response from the BaTiO$_3$ nanowire was also measured. Figure 5 shows the plot of output peak voltage versus square wave amplitude. A linear trend is seen. This linear dependence is expected from eqs 5 and 6, which gives a peak response voltage in the form of:

$$V_{out}^{peak} = g C_a \Gamma \kappa V_0 \propto V_0 \qquad (7)$$

where Γ is a unitless constant from the combination of the related time constants and is 0.47 from our calculation. The measured linear dependence thus allows us to conveniently calculate the charge constant (piezoelectric coefficient) of

the BaTiO$_3$ nanowire, as κ in eq 7 is directly related to this charge constant according to our previous definition. The calculated charge constant for the BaTiO$_3$ nanowire from this measurement is $\sim$45 pC/N.

The total electric energy generated in the process can also be estimated based on the above analysis. The electric energy U generated from the nanowire per cycle is simply:

$$U = 2 \times \frac{1}{2} C_{nw} (V_{nw}^{peak})^2 \propto d_{nw}^2 \qquad (8)$$

For nanoscale energy-harvesting applications, nanowires with high piezoelectric constant is thus preferred. Specifically for the measured BaTiO$_3$ nanowire actuated with a square wave of 5 V in amplitude, the estimated electric energy output per cycle is $\sim$0.3 aJ. Under the same conditions, this output would already be more than 16 times that from a similar ZnO nanowire. However, the energy conversion efficiency is quite low in this nonoptimized circuit configuration due to dielectric losses and damping in the mechanical system. The elastic energy input per cycle is simply $\Delta E = 1/2 E_{nw} \epsilon_{nw}^2 \Omega$, where ϵ_{nw} is the maximum strain of the nanowire and Ω is the volume of the nanowire. ΔE is estimated to be $\sim$1.4 pJ for the measured nanowire actuated with a square wave of 5 V in amplitude, much larger than the electric energy output calculated above. Circuit analysis indicates that lowering the parasitic capacitance and increasing the parallel load resistance in the circuit can effectively increase the energy conversion efficiency. For example, by lowering the parasitic capacitance from 5 pf in the current circuit to 0.1 pf and increasing the load resistance to 1 GΩ, the energy conversion efficiency can increase more than 10 fold.

In conclusion, the controlled measurement of voltage generation from an individual perovskite BaTiO$_3$ nanowire was successfully carried out with the development of a precision tensile mechanical testing stage integrated with high-sensitivity charge-sensing electronics. The nanowire was found to behave as a perfect nanoscale piezoelectric element showing the direct piezoelectric effect that converts mechanical energy in the form of periodically applied mechanical load to electric energy. Further analyses and modeling found that the voltage response from the nanowire was directly proportional to the applied strain rate and thus to the amplitude of the applied square wave signal in the setup. The experimental development and the present study lay a solid ground for the systematic characterization of such piezoelectric nanowires and for their potential applications in nanoscale energy harvesting.

References

(1) Rahimi, M.; Shah, H.; Sukhatme, G. S.; Heideman, J.; Estrin, D. *Proceedings of the ICRA '03 IEEE International Conference on Robotics and Automation*, September 14−19, 2003; Vol. 1, pp 19−24.

(2) Ottman, K. G.; Hofmann, H. F.; Bhatt, A. C.; Lesieutre, G. A. *IEEE Trans. Power Electronics* **2002**, *17*, 669.

(3) Ayers, J. P.; Greve, D. W.; Oppenheim, I. J. *Smart Struct. Mater.* **2003**, *5057*, 364−375.

(4) Kymissis, J.; Kendall, C.; Paradiso, J.; Gerhenfeld, N. *Proceedings of the 2nd International Symposium on Wearable Computers*, Pittsburgh, PA, October 19−20, 1998; pp 132−139,

(5) Shenck, N.; Paradiso, J. A. *IEEE Micro* **2001**, *21*, 30.

(6) Davis, C.; Lesieutre, G. J. *Sound Vibr.* **2000**, *232*, 601.

(7) Rabaey, J. M.; Ammer, M. J.; da Silva, J. L., Jr.; Patel, D.; Roundy, S. *J. Comput.* **2000**, *33*, 42−48.

(8) Wang, Z. L.; Song, J. *Science* **2006**, *312*, 242.

(9) Song, J.; Zhou, J.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 1656.

(10) Wang X. D.; Song J. H.; Liu J.; Wang, Z. L. *Science* **2007**, *316*, 102.

(11) Su, W. S.; Chen, Y. F.; Hsiao, C. L.; Tu, L. W. *Appl. Phys. Lett.* **2007**, *90*, 063110.

(12) Karanth, D.; Fu, H. *Phys. Rev. B* **2005**, *72*, 064116.

(13) Fu, H.; Bellaiche, L. *Phys. Rev. Lett.* **2003**, *91*, 057601.

(14) Berlincourt, D.; Jaffe, H. *Phys. Rev.* **1958**, *111*, 143.

(15) Moulson, A. J.; Herbert, J. M. *Electroceramics: Materials, Properties, and Applications*; Chapman and Hall: New York, 1990; pp 293.

(16) Mao, Y.; Banerjee, S.; Wong, S. S. *J. Am. Chem. Soc.* **2003**, *125*, 15718.

(17) Wang, Z.; Hu, J.; Yu, M. -F. *Appl. Phys. Lett.* **2006**, *89*, 263119.

(18) Wang, Z.; Suryavanshi, A.; Yu, M.-F. *Appl. Phys. Lett.* **2006**, *89*, 082903.

NL070814E