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Strong piezoelectricity in individual GaN nanowires

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Abstract

GaN nanowires are promising building blocks for future nanoelectronics, optoelectronic devices, and nanogenerators. Here, we report on strong piezoelectricity in individual single-crystal GaN nanowires revealed by direct measurement of the piezoelectric constant using piezoresponse force microscopy. Our experimental results show that individual *c*-axis GaN nanowires, with a characteristic dimension as small as 65 nm, show a shear piezoelectric constant of $d_{15} \sim 10$ pm/V, which is several times that measured in bulk. The revealed strong piezoelectricity could open promising opportunities for application of GaN nanowires in nanowire-based sensors and generators for self-powered nanodevices.

Semiconductor nanowires have been proposed as building blocks for nanoscale electronic, optoelectronic devices, and nanogenerators for self-powered nanodevices.[1,2] Recent demonstrations of energy harvesting from individual piezoelectric nanowires[2,3] added another important dimension to the possible application of these nanostructures in future devices. The proposed nanogenerators for energy harvesting, in either nanowire[3] or nanoribbon form,[4] rely on the piezoelectric and semiconducting properties of these nanostructures. Piezoelectric materials convert mechanical deformation directly into electrical charges, which can be harvested and used for driving small-power nanodevices. Furthermore, nanostructures such as nanowires, due to their excellent mechanical properties arising from a low defect density, can undergo large deformation,[5,6] producing larger electric charges, rendering them attractive for energy applications.

Here, GaN nanowires are studied because of their technological potential, including their wide band gap, high thermal conductivity, temperature stability, and piezoelectricity.[7] Nanodevices based on GaN such as light emitting diodes (LEDs),[8] blue emitting lasers,[9] nanowire-based field-effect transistors,[7] and many more have been developed. Piezoelectricity in GaN nanowires has been demonstrated through voltage (charge) generation under applied mechanical deformation, and it is shown that the output voltage is higher than in ZnO nanowires.[10] Also using an improved atomic force microscopy (AFM) cross-sectional method, voltage generation as high as 150 mV for GaN nanowires was recently reported.[11] However, there has been no report on direct quantification of the piezoelectric constants in *individual* GaN nanowires. Given that application of these nanowires in future energy devices would require a knowledge of their piezoelectric constants, it is highly relevant to quantify them. Herein, we report on the first quantification of the shear piezoelectricity in individual *c*-axis single-crystal GaN nanowires, using piezoresponse force microscopy (PFM).

PFM is a method based on AFM for probing converse piezoelectric effects at the nanoscale.[12,13] It has been extensively used for probing piezoelectric and ferroelectric properties with nanometer spatial resolution. Specifically, PFM has been used to investigate piezoelectricity in ZnO nanobelts,[14] PZT nanowires,[15] $BaTiO_3$ nanowires,[16,17] individual collagen fibrils,[18] and thin films of III-nitride materials.[19]

In addition to experimental studies, recent quantum mechanical calculations based on density functional theory have revealed a giant piezoelectric size effect for ZnO and GaN nanowires ranging from 0.6 to 2.4 nm in diameter, with GaN showing a more enhanced size-dependence.[20] Surface reconstruction and associated volume change, together with change in local polarization, was proposed as the mechanism of the observed size effect.[20] These previous results underscore the need to perform experimental studies on individual nanowires in order to quantify their piezoelectric response.

Experimental method

Experiments were performed using an XE-120 Park AFM (Park Systems, Santa Clara, CA, USA) with a custom-designed PFM setup. Humidity was kept below ~15% by enclosing the setup in a humidity chamber regulated by nitrogen gas flow. Nanowires were dispersed on a gold-coated Si substrate (acting as the bottom electrode). An external lock-in amplifier (Stanford Research 830, Sunnyvale, CA, USA), a function generator (Stanford Research 5520, Sunnyvale, CA, USA), and a signal access module were used in the setup. Conductive

Au/Cr-coated Si cantilevers (Mikromasch San Jose, CA, USA) with a nominal spring constant of $k = 0.15$ N/m were used for the measurements. For PFM measurement, an AC voltage A_0 sin (ωt) was applied between the conductive probe and the grounded bottom electrode. The lateral sensitivity of the AFM cantilever was calibrated using optical-grade, Y-cut, single-crystal $LiNbO_3$ with a well-defined piezoelectric constant,[21] as described in the supporting information. PFM measures the electric-field-induced displacement (x_i) of a piezoelectric sample, based on the converse piezoelectric effect ($x_i = d_{ik}E_k$), where d_{ik} is the piezoelectric tensor and E_k is the applied electric field. More specifically in the lateral PFM mode, the in-plane (shear) deformation of the sample surface, induced due to the piezoelectric effect, is measured through the torsional twist of the AFM cantilever. A high-sensitivity lock-in amplifier facilitates measurements of the small deformation often in picometer range. The GaN nanowires were grown by molecular-beam epitaxy in a catalyst-free process.[22] The nanowires are *c*-axis with polar axis of the hexagonal wurtzite structure of the nanowire along the [0001] direction, and the facets are $\{1\bar{1}00\}$ planes. Their single crystal structure was confirmed by transmission electron microscopy diffraction patterns.

Results and discussion

Figure 1(a) shows an AFM topography image of a nanowire with a height of $H = 64$ nm. Due to the tip–sample convolution effect, arising from the finite radius size of the tip, the nanowire dimensions look wider in in-plane dimensions. This effect is even more pronounced for the conductive AFM cantilevers used in this study, where a metal coating of ~40 nm dulls the tip radius to ~50 nm. The height H reported for the tested nanowire is based on the AFM out-of-plane measurement, which is quite accurate. Figure 1(b) shows an SEM image of an ~25 μm long nanowire with a uniform thickness along its entire length. Hexagonal cross-section of the nanowires is apparent in the inset in Fig. 1(b).

The randomly dispersed nanowires on the gold-coated substrate were imaged to identify a nanowire with uniform geometry. For quantitative measurement, it is critical to perform the measurements on a nanowire resting on one of the facets and with another facet parallel to the plane of the cantilever, as shown in the AFM line profile given in Fig. 1(a). In this manner, the maximum shear response is transferred to the cantilever. For a nanowire sitting on one of the vertices, the response may not fully transfer to the measuring system. Furthermore, for lateral PFM, it is critical to place the *c*-axis of the nanowire (in this case, the long axis) perpendicular to the long axis of the AFM cantilever.[23] For a nanowire oriented at an angle of θ with respect to the long axis of the cantilever, only a fraction of the induced response proportional to sin (θ) would be transferred to the AFM cantilever. Therefore, the nanowire was physically oriented at $\theta = 90°$ with respect to the cantilever axis by rotating the substrate, as shown in Fig. 2(a). For PFM measurement, the AFM tip was placed in the middle of the top facet of the nanowire. An AC voltage with a frequency of 10 kHz, identified from a frequency sweep to be away from the contact resonance, was applied (see Supporting information).

Figures 2(b) and 2(c) show the AFM topography and deflection image of the nanowire. Figures 2(d) and 2(e) show the simultaneously acquired piezoresponse amplitude and phase images obtained under 10 V_{pp} and a scanning speed of 0.25 Hz. As shown in a larger magnification in Fig. 2(f) of the area marked in Fig. 2(d), only the top facet of the nanowire exhibits a strong piezoelectric signal due to its proper orientation with the AFM tip. The lateral facets, identified mainly from the deflection image, show minimal to no piezoresponse. Furthermore, the piezoresponse amplitude signal is fairly uniform over the length of the nanowire (2 μm).

To obtain a quantitative measure of the piezoelectric constants in the nanowire, point measurements were performed with the AFM tip kept stationary on the nanowire. The AC voltage was swept from zero to 10 V_{pp}, and the lateral displacement of the AFM cantilever was monitored. Measurements were performed at four different locations along the long axis of the nanowire. The results in Fig. 3 show that the obtained

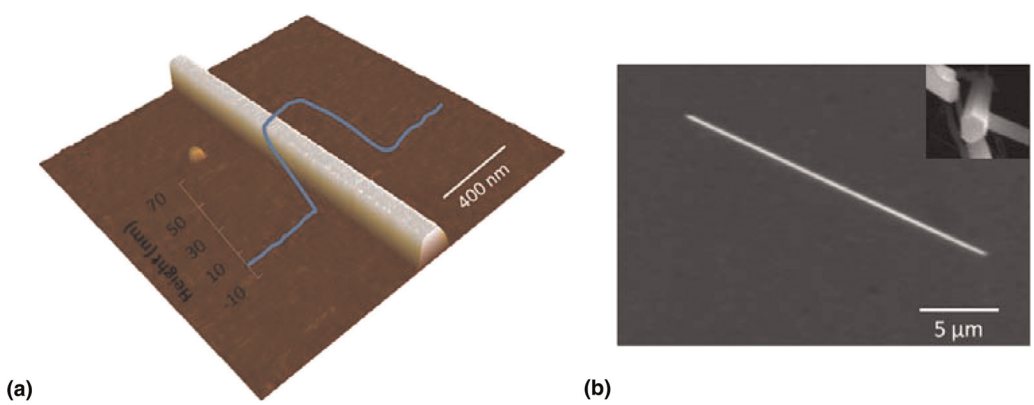

Figure 1. (a) Atomic force microscope topography image of a 64 nm GaN nanowire with the line profile overlaid on the image, (b) SEM images of an ~25 μm long individual GaN nanowire on a Au-coated Si surface. Inset in (b) showing the hexagonal structure of the nanowire cross-sections.

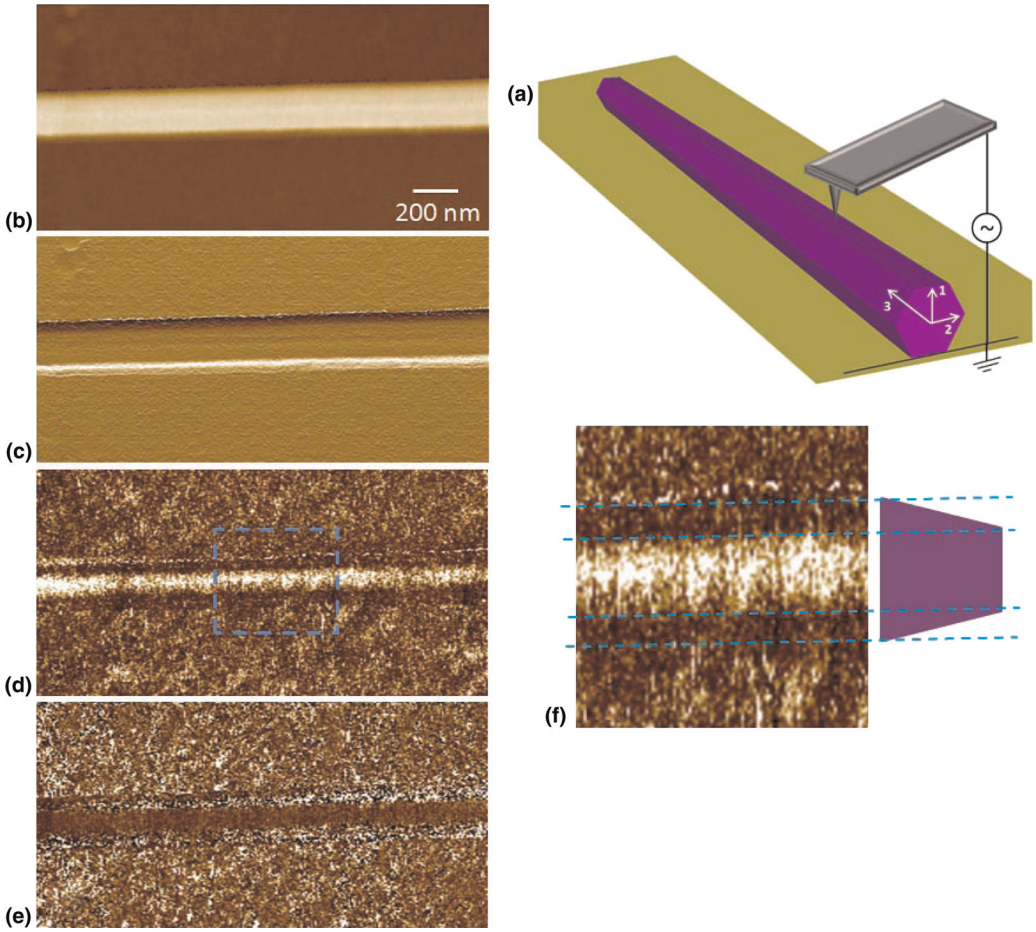

Figure 2. (a) Schematics of the PFM setup and alignment of the nanowire with respect to the AFM cantilever. Coordinate system used in defining the direction of electric field, strain components, and piezo electric coefficients. (b) AFM topography image and (c) deflection image of an $H = 64$ nm nanowire, along with (d) PFM piezoresponse amplitude image and (e) phase image. (f) A higher magnification image of the area marked in (d): It is clear from the image that the top facet of the nanowire shows strong piezoresponse due to its alignment with the AFM probe, while the side facets show weak to no response. In this configuration, $2\varepsilon_{13} = d_{15}E_1$, where ε_{13} is the shear strain measured from lateral torsion of the AFM cantilever.

response is linear and reproducible. The slope of the obtained response represents the shear piezoelectric constant of the nanowire, as $d_{15} = 2\varepsilon_{13}/E_1$.[18] From the lateral sensitivity calibration, the obtained shear piezoelectric constant of the nanowire was $d_{15} = 10 \pm 0.7$ pm/V.

To confirm that the obtained response is indeed the result of the in-plane shear response ε_{13}, the nanowire was physically rotated by 90°, parallel to the long axis of the cantilever. As expected, the measured response in this orientation was negligible. Lateral PFM is largely unaffected by the electrostatic signal, since the electrostatic signal is symmetric with respect to the torsional degree of freedom of the cantilever.[18] We confirm this by measuring the 2ω signal—which is the second-order electromechanical response proportional to electrostatic and electrostrictive effects—from the lock-in amplifier, where ω is the frequency of the applied electric field. We also performed vertical PFM measurement on the *c*-axis GaN nanowires (see Supporting information). As expected, the top facet of the nanowire did not show any measurable vertical PFM signal.

To our knowledge, this is the first report on the direct measurement of piezoelectric constant of individual GaN nanowires. Previously, only voltage generation close to −20 mV,[10] and using an improved method up to 150 mV,[11] was shown by direct bending of GaN nanowires, but no direct measurement of piezoelectric constants was reported. On the other hand, the shear piezoelectric constant of bulk GaN from direct first-principles density functional calculations was reported to be $d_{15} \sim 1.8$–3.3 pm/V.[24] Experimentally, the shear piezoelectric constant, measured using a laser-based interferometer for a single-crystal GaN film, resulted in $d_{15} \sim 3.1$ pm/V.[25] The value obtained for a single GaN nanowire in this study is three times the bulk value, which is promising for nanoscale devices, especially for energy harvesting in nanogenerators, as previously pointed out by Agrawal and Espinosa.[20]

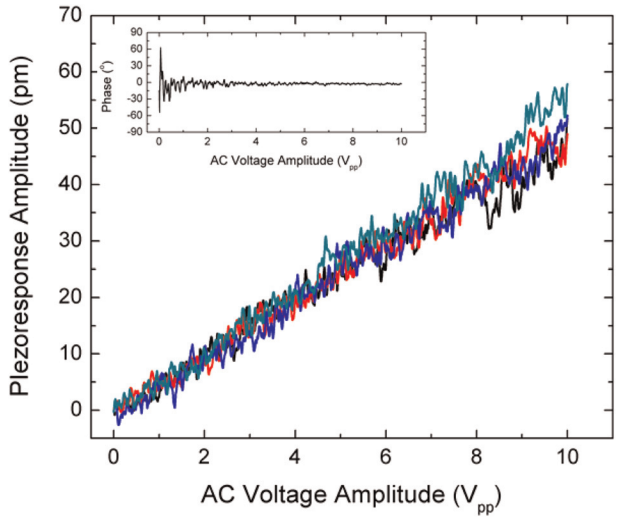

Figure 3. Lateral piezoresponse amplitude versus applied AC voltage peak-to-peak amplitude; four responses measured on different points on the same nanowire are overlaid showing the reproducibility of the measurement. The average slope of the response is $d_{15} \sim 10$ pm/V, which is three times the bulk value. The inset shows the phase signal versus applied AC voltage, which is very stable, an indication of fixed polarization in the nanowire.

Conclusion

In summary, we report on the strong shear piezoelectricity in individual single-crystal GaN nanowires quantified using the lateral PFM technique. A value of $d_{15} \sim 10$ pm/V, more than three times the bulk value, was obtained for a single nanowire with a diameter of $H = 64$ nm. This strong piezoelectricity could have implications for the design of nanosensors and energy-harvesting systems based on GaN nanowires.

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Supplementary materials

For supplementary material for this article, please visit http://dx.doi.org/10.1557/mrc.2011.14

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