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Cite as: AIP Advances 10, 055014 (2020); https://doi.org/10.1063/5.0008112
Submitted: 18 March 2020 . Accepted: 21 April 2020 . Published Online: 11 May 2020

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ABSTRACT
The non-centrosymmetric crystal structures of polar-semiconductors comprising GaN, InN, AlN, and ZnO intrigued the scientific community in investigating their potential for a strain-induced nano-energy generation. The coupled semiconducting and piezoelectric properties produce a piezo-potential that modulates the charge transport across their heterostructure interfaces. By using conductive-atomic force microscopy, we investigate the mechanism that gives rise to the piezotronic effect in AlGaN nanowires (NWs) grown on a molybdenum (Mo) substrate. By applying external bias and force on the NWs/Mo structure using a Pt–Ir probe, the charge transport across the two adjoining Schottky junctions is modulated due to the change in the apparent Schottky barrier heights (SBHs) that result from the strain-induced piezo-potential. We measured an increase in the SBH of 98.12 meV with respect to the background force, which corresponds to an SBH variation \( \partial \phi / \partial F \) of 6.24 meV/nN for the semiconductor/Ti/Mo interface. The SBH modulation, which is responsible for the piezotronic effect, is further studied by measuring the temperature-dependent I–V curves from room temperature to 398 K. The insights gained from the unique structure of AlGaN NWs/Mo shed light on the electronic properties of the metal-semiconductor interfaces, as well as on the potential application of AlGaN NW piezoelectric nanomaterials in optoelectronics, sensors, and energy generation applications.

BACKGROUND
Piezoelectric nanomaterials have attracted significant attention in the emerging field of piezotronics, as the piezotronic effect combines the piezoelectricity and semiconducting properties. These materials have found large applications as nanosensors, nanogenerators, and piezotronic transistors.1–3 So far, the most commonly used template has been made of ZnO nanowires (NWs)4,5 with a wurtzite structure, which give rise to a piezo-potential enabling the formation of an electric field dipole moment as a response to an applied force. Metal-semiconductor (MS) structures, i.e., Schottky barrier diodes, comprise the building blocks of such devices. In fact, when the depletion region is strained, there is a polarization change that results in a change in surface charges, thereby causing a modification in the barrier height. Such a property allows current modulation and, hence, the control of electronics using mechanical stimuli.1 Among wurtzite structured nanomaterials, group III-nitride NWs have attracted the attention for light-emitting applications, such as LEDs and laser diodes in the green-yellow gap.7 However, they have also been occasionally used in piezotronic devices,2,8,9 and insightful reviews on the subject were presented recently.10,11 GaN NW arrays have been used as nanogenerators where doping concentration studies have been performed to optimize the output voltage.12 Pressure sensors have been demonstrated using InGaN/GaN nanopillars,
where the photoluminescence of a single pillar can be modulated by applying strain and was envisioned for large-area devices.\textsuperscript{1,2} c-plane and m-plane GaN NW piezotronic transistors have also been compared and they show a high sensitivity in the vertical and transverse force, respectively, thereby confirming the piezotronic effect.\textsuperscript{3}

As mentioned, Schottky diodes are very important for the characterization of these devices, and the analysis of their current-voltage characteristics gives detailed information about the barrier formation that is responsible for the piezotronic effect. Recently, we have studied the piezotronic as well as the piezophototronic effect in n-InGaN NWs, where an increased strain resulted in photocathod carrier screening by the piezofield, thus leading to a reduced strain-induced Schottky barrier height (SBH).\textsuperscript{4,5} However, to the best of our knowledge, there are no piezotronic studies on wide bandgap AlGaN NW Schottky diodes.

In this Letter, we report the experimental results on the piezotronic properties of AlGaN NWs grown on a bulk metal substrate. To understand the barrier height and the role it plays in the Schottky diode piezotronic device, the current-voltage (I–V) measurements were performed by conductive-atomic force microscopy (c-AFM). An SBH modulation of 98.12 meV with respect to the background force was obtained, which corresponds to a \( \frac{\partial \phi}{\partial F} = 6.24 \text{ meV/nN} \). Moreover, the temperature-dependent study resulted in an SBH increment of 2.6 meV/K, demonstrating a dual force-temperature modulation capability of the AlGaN NW Schottky diodes.

The observation of the piezotronic effect in AlGaN NWs on the bulk metal enables the applicability of such nanostructures for the barrier height and carrier transport modulation in the presence of the strain. The discovery likewise opens a new route for the practical device implementation of ensemble wurtzite-structured NWs on metal platforms.

**EXPERIMENTAL**

**Material growth and device fabrication**

The AlGaN NWs were grown on a 1 × 1 cm\(^2\) polycrystalline Mo substrate under nitrogen-rich conditions using a Veeco GEN 930 plasma-assisted molecular beam epitaxy (PA-MBE) system. The commercial Mo substrate was first cleaned with acetone and iso-propanol and blow-dried with nitrogen. Subsequently, the substrate was coated with a 500-nm-thick layer of titanium by e-beam evaporation. Next, the coated substrate was introduced into the MBE loadlock where the temperature was maintained at 200 °C and was then transferred into a buffer chamber for further outgassing at 600 °C in order to remove any moisture and organic residues from the surface. Following the pre-growth outgassing procedure, the coated substrate was loaded into the growth chamber where it was irradiated with a nitrogen plasma for the conversion of Ti into TiN. Such a template has shown a reduction in the potential barrier at the n-GaN/Ti-Mo interface, thus creating a more ohmic-like contact with the substrate and enabling carrier transport control.\textsuperscript{7} During nitridation and growth, the nitrogen flow rate was kept at 1.055 SCCM with a plasma power of 400 W. A standard two-step method was utilized to grow high-quality NWs and to simultaneously control their density. The GaN seeds were first initiated at a substrate temperature of 485 °C for 10 min to reduce the desorption of adatoms and increase the probability of nucleation. The MBE cell was maintained at 830 °C for 2 h with a Ga and an Al beam equivalent pressure (BEP) of 4.25 × 10\(^{-8}\) Torr and 0.75 × 10\(^{-8}\) Torr, respectively, producing an alloy with a composition of Al\(_{0.14}\)Ga\(_{0.86}\)N. The composition of the alloy was corroborated by the photoluminescence response of the NWs (not shown). To control the doping of the NWs, the silicon effusion cell temperature was set at 1100 °C.

**Morphology characterization and I–V measurement setup**

Prior to the measurement, the sample was treated with a 10% KOH solution in order to remove the surface oxide layer and reduce the contact resistance.\textsuperscript{1,2} A 5-nm-Ni/5-nm-Au film was deposited on the surface to increase the conductivity. The deposition was performed using an angled e-beam evaporation technique, thus preventing the formation of a continuous film and ensuring that the NWs still stand segregated.

The surface topography and current map were obtained using an atomic force microscope (Agilent 5500 SPM). The probes utilized throughout the investigation were antimony-doped silicon probes with a conductive Pt–Ir coating from Bruker (CONTV-PT). As reported by the manufacturer, the probes have a nominal, minimum, and maximum spring constants of 0.2 N/m, 0.1 N/m, and 0.4 N/m, respectively. To experimentally substantiate such values, the Pico View’s Thermal K tool was employed to determine the force constant. In such a tool, the free oscillations of the AFM probe cantilever are recorded over a range of frequencies and the best fit curve is found, and the area under the curve is integrated to output the force constant. An average of 10 scans was obtained for each of the randomly selected six used probes. The average experimental spring constant was 0.34 N/m with a standard deviation of 0.042 N/m, which falls within the range of the manufacturer reported values. In addition to force constant determination, the deflection sensitivity was also extracted as the inverse of the slope of the force curve measured with the AFM probe in contact with a rigid silicon substrate for the calibration of the applied force. To vary the force applied by the AFM probe on the NWs, the set-point for the vertical deflection of the cantilever was adjusted. The force applied to the nanowires was computed as

\[
F = k \times DS \times SP,
\]

where \( k \) is the spring constant, \( DS \) is the deflection sensitivity, and \( SP \) is the vertical deflection set-point. For the piezotronic effect experiment, the obtained current map and the corresponding topography image were used to identify the contact of an individual NW with the AFM tip. The I–V curves were obtained at different applied forces by varying the set-point parameter.

The temperature-dependent I–V curves of the NW array were measured using the c-AFM setup equipped with a heating sample stage and a temperature controller (LakeShore 325 Temperature Controller).

**RESULTS AND DISCUSSION**

Figure 1(a) shows the surface topography of the AlGaN NWs on a 10 × 10 \( \mu \text{m}^2 \) area obtained by AFM in tapping mode. Figure 1(b)
is a 3D rendering of the scanned area in Fig. 1(a). Figure 1(c) shows a current map of a surrounding area obtained in contact-mode AFM at a bias of 5.3 V with respect to the grounded Pt–Ir coated AFM tip. The red spots in the current map confirm the high current injection of multiple NWs, while the blue region indicates the suppression of current leakage between the NWs. The prevalence of conducting NWs is attributed to the nanoscale current injection enhancement due to the thin Au–Ni metallic sheet deposited on the top surface, ensuing the KOH treatment. The effectiveness of the KOH treatment was intensively studied previously.\cite{14}

Figure 1(d) shows a top view of the scanning electron microscope (SEM) image taken after the Ni–Au deposition. Both the SEM image and the tapping mode height map indicate that the NWs are uniformly distributed on the Mo substrate without suffering from any critical coalescence, hence allowing the reliable measurement of individual NW in the array, as confirmed by the localization of conduction in the current map. Size uniformity and diameter estimation can also be obtained from the SEM image. The average diameter of the NWs was estimated to be around 72 nm by Hough transform analysis, while the expected height was approximated around 200 nm from the MBE growth time of the NWs.

Figure 2(a) shows a schematic of the AlGaN NW ensemble probed with the Pt–Ir coated AFM tip where the applied force results in a piezo-potential that modulates the SBH as expanded upon in the following text. The AFM tip, n-AlGaN, and Mo substrate together form a metal–semiconductor–metal junction. The band diagram drawn using Anderson’s rule is depicted in Fig. 2(b). The top metal contact is a consolidation of the Pt–Ir coated tip and the thin deposited Ni–Au. The bottom contact is formed by the titanium coated Mo substrate. An aluminum tape and a silver paste were used to secure the sample to the AFM stage for the force-dependent measurements and temperature-dependent measurements, respectively.

Typical I–V curves at room temperature (RT = 295 K) for four different AlGaN NW Schottky diodes are shown in Fig. 2(c). The NWs were chosen from different locations on the sample in order to have a better statistical analysis. The I–V plot shown exhibits mostly the symmetric I–V curves, such that the apparent SBH values of the two metal junctions are close to each other. The junction at the positive sample bias shows more statistical variations than the one at the negative bias region does. The variations from one NW to another are found in recent works related to the AlGaN and InGaN NWs and have been attributed to the inhomogeneity of the NWs and the radial temperature gradient that affects the growth.\cite{14,16,17} The lag in the turn-on of the two junctions allowed the extraction of a separate diode parameter.

An example showing the extracted parameters from the fitting of the experimental data is shown in Fig. 2(d). The SBHs ($\phi_{n1}$ = 0.61 eV and $\phi_{n2}$ = 0.66 eV) for the top and bottom junctions were subsequently extracted from the slope of the curve by fitting the linear region of the natural logarithmic I–V curve. It is noted that these values deviate from the theory based on the electron affinity model depicted in Fig. 2(b), thus showing the apparent SBH. The tip background force as well as the residual epilayer strain most likely affected the barrier heights. In this regard, Pérez-García et al. reported that the deviation from the thermionic emission (TE) theory in the Pt/ZnO nanostructure was dependent on the MS interface condition. The results from the study by Pérez-García et al. showed
that only when the MS contact area between the tip and nanowire exceeded a threshold value, did the nanostructures start behaving as large-area devices exhibiting adherence to the TE theory.\(^\text{17}\)

The respective ideality factors \(n_1\) and \(n_2\) were extracted from the \(y\)-axis intercept of the same fitting curve. The series resistance was estimated from the derivative of the natural logarithmic I–V curves [Eq. (8)], but due to the relatively small magnitude, it was omitted in the following analyses.

In piezoelectric nano-systems, the SBH emanating at the end contacts of NWs controls the current transport across the metal-semiconductor junction, influencing both the performance and the efficiency of such systems.\(^\text{19}\) The barrier at the contact of piezoelectric NWs could spontaneously originate from the strain at the NW interface with other materials or due to applied forces straining the nano-system. The dynamic relationship between the modulated barrier height and current transport can be derived from the current-voltage relationship shown in Eqs. (2)–(6), according to the Schottky diode equation. The change in the SBH induced by the applied strain can then be expressed as derived in Eq. (6),

\[
I = I_0 e^{\frac{qV_{bias}}{nkT}} \left[ 1 - e^{\frac{qV_{bias}}{nkT}} \right],
\]

FIG. 2. (a) An AlGaN Schottky diode c-AFM measurement setup and an equivalent circuit with the Pt–Ir coated tip at ground and bias applied to the substrate. (b) Energy band diagram at a sample bias of 0 V and 0 nN applied force (c) Room temperature I–V curves for four different NWs showing statistical variation. (d) I–V fitting and the extracted fitting parameters of NW No. 3. (e) Positive sample bias force-dependent I–V curves at RT. (f) Change in the SBH with the applied force.
The I–V measurements for multiple NWs at different temperatures were then acquired to further analyze the barrier height at the metal/AlGaN interfaces. From the I–V measurements, the diode 0 V bias current was extracted as the exponential of the y-intercept and was then utilized in computing the SBH and Richardson constant. A theoretical value of the Richardson constant of 2.62 A m$^{-2}$ K$^{-2}$ was computed using the effective masses of GaN (0.22 m$_{0}$) and AlN (0.35 m$_{0}$), based on the Al molar fraction deduced from the growth condition and PL measurements. The apparent SBH can be estimated from the extracted zero bias current according to Eq. (4), and the ideality factor can be estimated from the slope of the linear region of the logarithmic I–V curve. At RT, the AlGaN Schottky diode showed an apparent SBH of $\phi_{\text{B App}} = 0.51$ eV at the Pt–Ir junction and $\phi_{\text{B App}} = 0.52$ eV at the Ti/Mo junction. The value of $\phi_{\text{B App}}$ is comparable to the previously reported AlGaN/GaN planar Schottky diodes of 0.517 eV with a similar Al composition. Other works on $n$-GaN Schottky diode reported the SBH values between 0.59 eV and 1.03 eV adopting different metals. The temperature-dependence of $\phi_{\text{B App}}$ and $\phi_{\text{B App}}$ is depicted in Figs. 3(a) and 3(b). Both barriers show the same response to the variation in temperature, i.e., they have the same slope (as shown from the linear equation), but different starting points [Fig. 2(b)]. The apparent SBH at both junctions has an increment of 2.6 meV/K. This trend is readily reported for other NW diodes and indicates deviation from the TE theory and cannot be explained theoretically. Nonetheless, it commonly happens in real Schottky diodes, and it can be better explained by barrier height inhomogeneity. It is noted that a large barrier height variance has been previously attributed to the Fermi level pinning. In this regard, Tung et al. proposed a model that describes the inhomogeneous Schottky contact as a distribution of "patches" with different barrier heights within an ideal higher barrier. The current then preferentially flows through the lower barriers at low temperatures. As the temperature increases, the carriers gain enough energy to overcome the higher barrier. The Gaussian distribution of the inhomogeneous barrier heights has been widely accepted in the TE theory and reported by several groups. The temperature-dependence of the ideality factor values extracted from the measured current–voltage curves are shown in Figs. 3(c) and 3(d). Reduction in the ideality factor is observed for both of the back-to-back diodes. The values higher than one are not uncommon for GaN-based materials and are readily observed in nanostructures. Similar to the SBH, the ideality factors’ decrement with temperature show the same slope, thereby confirming that both junctions have the same response to the temperature change.

To quantify the piezotronic effect, the I–V curve under force is fitted with the linear equation $I = n I_{0} e^{\frac{\Delta \phi_{B}}{kT}}$, but different starting points [Fig. 2(b)]. This is a promising achievement, as previous work on GaN NWs reported an applied force in the range of 1–1.3 mN. With force applied on the NWs, the charge carrier transport could be altered by different mechanisms, including piezoresistive and piezotronic effects. The piezoresistive effect is due to the conductance change under strain, which is a uniform and symmetric effect existing in both piezoelectric and non-piezoelectric semiconductors. Due to the polarity of the piezo-induced charges, the piezotronic effect is asymmetric and exists only in piezoelectric materials. Previous studies have shown that in piezoelectric materials, the piezotronic effect is dominant, where the strain induces a change in charge transport characteristics. This provides an explanation of the dependence on the force of the measured change in the SBH.
The inclusion of the high-temperature (above 100 °C) data points (decreasing trend with an increase in the temperature) resulted in Richardson’s constant values that were a number of orders of magnitude lower than the theoretical value. Previous works reported a discrepancy between the theoretical value and the Richardson plot and this was attributed to the tunneling current due to the surface defects.\[^{25,27}\] Moreover, the presence of thin surface oxide in GaN NWs has been investigated and ascribed to be a tunneling path. However, more investigation is required to fully understand the transport mechanism involved in such nanostructures.

CONCLUSION

In conclusion, the AlGaN NWs Schottky diode SBH was controlled in terms of the piezotronic effect by applying an external force that results in a compressive-strain-induced piezo-potential. We achieved an SBH modulation of 98.12 meV with respect to a background force of 35.7 nN. The SBH slope was as high as 6.24 meV/nN, confirming the excellent performance of the AlGaN NWs piezotronic properties. The SBH modulation was also studied as a function of the temperature, and we attained an increment of 2.6 meV/K demonstrating the dual force–temperature modulation.
capability of the AlGaN NW Schottky diodes grown on the Mo substrate. Therefore, the two-way coupling of mechanical and electrical energy shows the effectiveness of piezotronics in such nanostructures to enable piezoelectricity for practical applications in energy collection and sensor devices.

AUTHOR’S CONTRIBUTIONS

L.A.-M., C.H., D.P., and M.T. contributed equally to this work.

ACKNOWLEDGMENTS

We acknowledge the financial support from the King Abdulaziz City for Science and Technology (KACST) under Grant No. KACST TIC R2-FP-008. This work was partially supported by the King Abdullah University of Science and Technology (KAUST) baseline Funding No. BAS/1/1614-01-01, MBE equipment Funding Nos. C/M-20000-12-001-77 and KCR/1/4055-01-01, the National Natural Science Foundation of China under Grant No. 61905236, the University of Science and Technology of China (USTC) under Grant No. KY2100000081, the USTC National Synchrotron Radiation Laboratory Grant No. KY2100000099.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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