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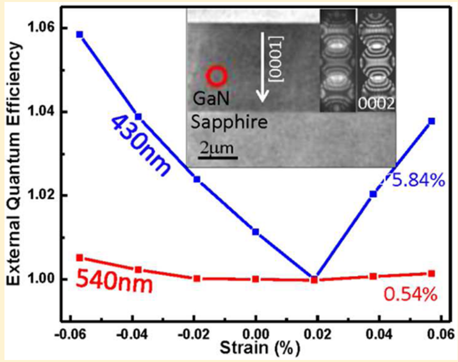
Piezo-Phototronic Effect on Electroluminescence Properties of *p*-Type GaN Thin Films

Youfan Hu,[†,§] Yan Zhang,[†,§] Long Lin,[†] Yong Ding,[†] Guang Zhu,[†] and Zhong Lin Wang*[,†,‡]

[†]School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, United States
[‡]Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China

ABSTRACT: We present that the electroluminescence (EL) properties of Mg-doped *p*-type GaN thin films can be tuned by the piezo-phototronic effect via adjusting the minority carrier injection efficiency at the metal−semiconductor (M−S) interface by strain induced polarization charges. The device is a metal−semiconductor−metal structure of indium tin oxide (ITO)−GaN−ITO. Under different straining conditions, the changing trend of the transport properties of GaN films can be divided into two types, corresponding to the different *c*-axis orientations of the films. An extreme value was observed for the integral EL intensity under certain applied strain due to the adjusted minority carrier injection efficiency by piezoelectric charges introduced at the M−S interface. The external quantum efficiency of the blue EL at 430 nm was changed by 5.84% under different straining conditions, which is 1 order of magnitude larger than the change of the green peak at 540 nm. The results indicate that the piezo-phototronic effect has a larger impact on the shallow acceptor states related EL process than on the one related to the deep acceptor states in *p*-type GaN films. This study has great significance on the practical applications of GaN in optoelectronic devices under a working environment where mechanical deformation is unavoidable such as for flexible/printable light emitting diodes.



KEYWORDS: *GaN film, piezo-phototronic effect, electroluminescence*

Gallium nitride (GaN) is a promising material for optoelectronic and high power high-frequency electronic devices, which has an exciton binding energy of 26 meV, wide band gap of 3.39 eV, and high electron mobility. The electroluminescence (EL) properties of GaN have been extensively investigated for decades for various applications, including light-emitting diodes, laser diodes, flat-panel display devices, and so forth.[1−5] Recently, wurtzite-structured GaN nanowires, which have the unique semiconducting and piezoelectric properties as ZnO nanowires, have been demonstrated as a great candidate for energy harvesting by using nanogenerator technology.[6,7] In this case, the piezo-electric potential (piezopotential) created by dynamic straining in the nanowires drives a transient flow of current in the external load, converting mechanical energy into electricity. Also, the piezopotential can be used to control the carrier generation, transport, separation, and/or recombination at the metal−semiconductor (M−S) junction or *p*−*n* junction, which is called the piezo-phototronic effect.[8,9] Recent studies have shown its applications in improving the performance of optoelectronic devices based on ZnO nanowires, such as photocells,[10] solar cells,[11] and light-emitting diodes.[12] So far, there have been no reports about the piezo-phototronic effect on the properties of GaN thin films, which may result in great influence for this most popular III−V semiconductor used in optoelectronic devices.

In this paper, transparent ITO electrodes were fabricated on Mg-doped *p*-type GaN thin films to form a metal−semi-conductor−metal (M−S−M) structure. When a constant voltage was applied, under different straining status, the current passing through the GaN film was increased or decreased step by step depending on the orientation of the *c*-axis of the film. Such a result is due to the tuning of the Schottky barrier height at the M−S contacts by strain induced local piezoelectric charges. The intensity of the EL emission from the M−S interface under the electrode was also modulated by the piezoelectric charges around this area under strain via adjusting the minority carrier injection efficiency. An extreme value for the integral EL intensity was observed. The EL at 430 nm owing to the shallow acceptor states was more significantly affected by this piezo-phototronic effect than the emission at 540 nm which is related to the deep acceptor states. This study is significantly important for GaN thin film applications in optoelectronic devices.

The Mg-doped *p*-type GaN films used in this work were grown on sapphire (0001) substrates by low-pressure metal organic chemical vapor deposition (MOCVD).[13] The samples were annealed for acceptor activation. The estimated concentration of Mg is around 3×10^{19} cm^{-3}, and the free

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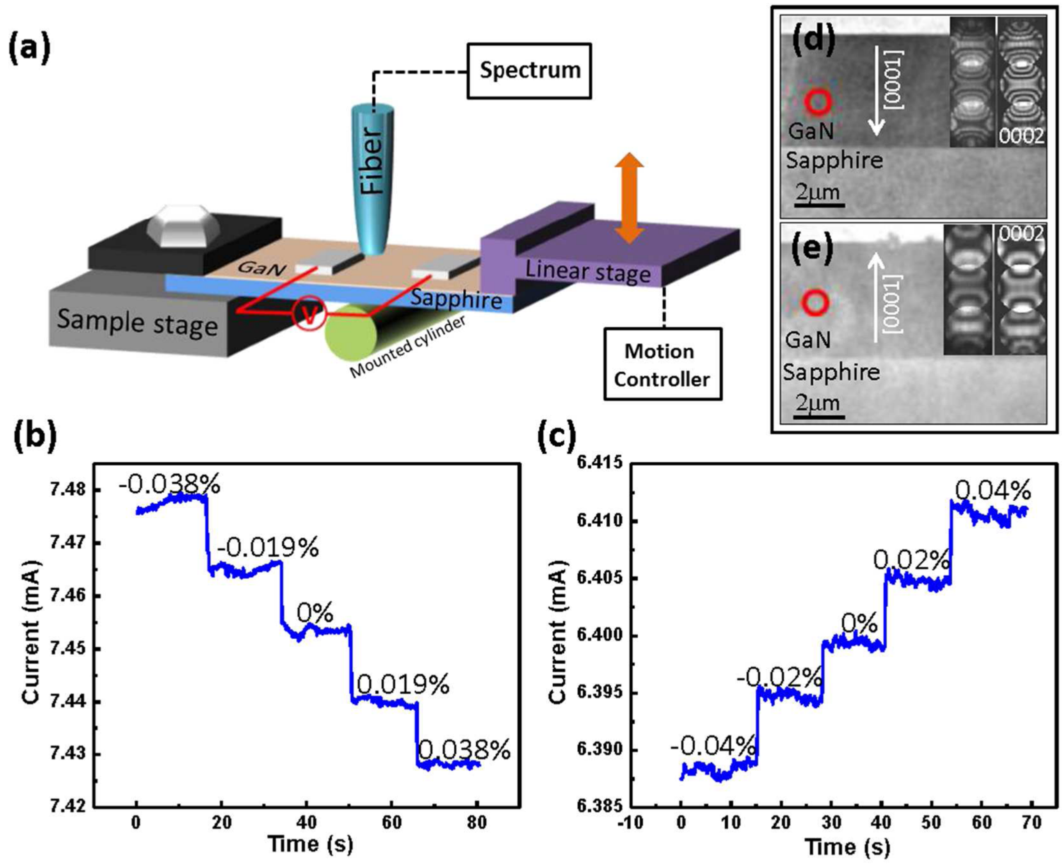

Figure 1. (a) Schematic diagram of the experiment setup. Under a constant applied voltage, the current passing through the GaN film was (b) decreased or (c) increased step-by-step as the applied strain was increased. Devices with the former behavior are assigned to the first group, while devices with the latter behavior are assigned to the second group. Parts (d) and (e) are the corresponding cross-sectional TEM results for the GaN film structures in the devices belonging to the first and second groups, respectively. The left-hand parts of the insets are the CBED patterns taken from the red circled areas. The right-hand parts are the corresponding simulated patterns.

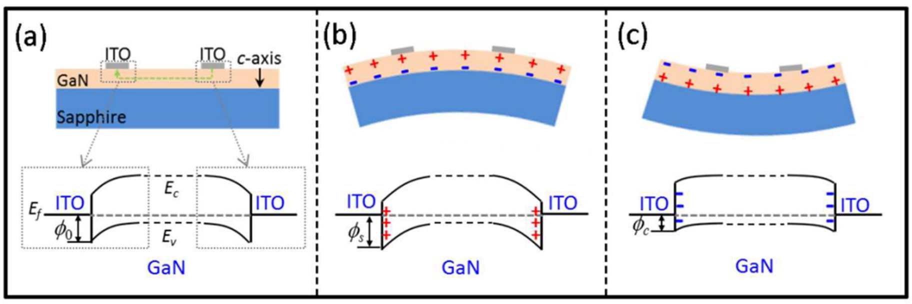

Figure 2. (a) Device construction and corresponding energy band diagram. Two Schottky barriers (ϕ_o) formed at the M–S contacts. Here we take the case of the *p*-type GaN film with *c*-axis pointing downward to the substrate as an example. (b) When the GaN film is stretched in parallel to the film plane, positive piezoelectric charges are introduced at the top surface of the GaN film, resulting in an increased Schottky barrier height (ϕ_s). (c) When GaN film is compressed in parallel to the film plane, negative piezoelectric charges are introduced at the top surface of the GaN film, resulting in an decreased Schottky barrier height (ϕ_c).

hole concentration is around 8×10^{17} cm^{-3}. ITO electrodes were deposited on the surface of the GaN film with a dimension of 2 mm × 2 mm. The distance between the two electrodes was around 1–2 mm. The experiment setup is shown in Figure 1a. One end of the substrate was fixed on a sample stage. A mounted cylinder was put underneath the substrate to support it with an adjusted position between the two electrodes. A three-dimensional (3D) DC-motor linear stage with a digital motion controller was used to push the free end of the substrate to introduce strain in the GaN film. The film can be stretched or compressed in parallel to the film plane by putting the substrate facing up or facing down. Electrical measurements were carried out by using a Keithley 4200 semiconductor characterization system. A fiber coupled with a grating spectrometer (Acton SP-2356 Imaging Spectrograph, Princeton Instruments) was put near the electrode area just above the mounted cylinder to collect the EL spectrum. This setup can ensure that the distance between the fiber and the GaN film is consistent when a strain is applied. The current passing through the GaN film and the corresponding EL

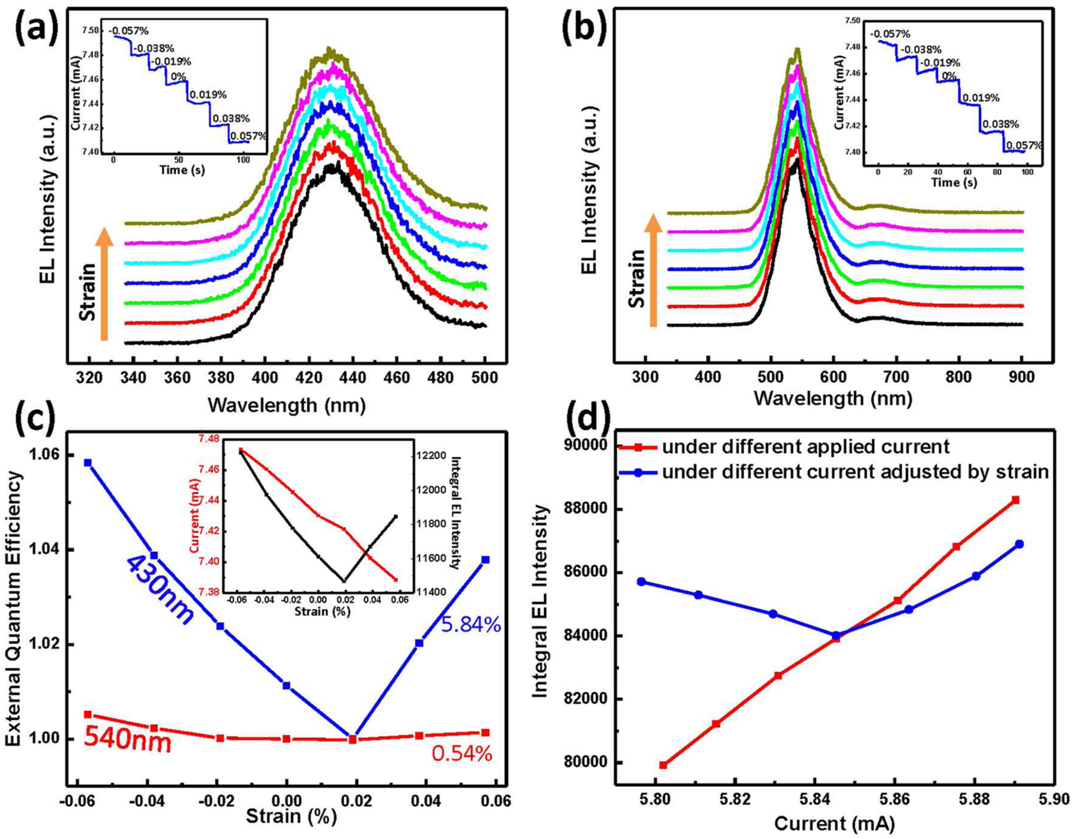

Figure 3. Recorded EL spectra at (a) 430 nm and (b) 540 nm when different strain was applied to the GaN film under a constant applied voltage. The vertical axes are shifted for clarity. The insets are the corresponding measured current response. (c) External quantum efficiency of the EL emission at 430 and 540 nm when different strain was applied. The insert is the change of current and integral EL intensity under different strain conditions corresponding to the data in (a). (d) The change of integral EL intensity due to the current change introduced by two different approaches.

spectrum was recorded simultaneously under different straining conditions.

The experiment results show that, when a constant voltage was applied between the two ITO electrodes, the measured current passing through the GaN film was changed step-by-step under different straining conditions. A linear relationship between the measured current and the applied strain was obtained for all devices, but it can be divided into two groups with opposite trends. For the first group, as shown in Figure 1b, the current was decreased as the strain was increased. While for the second group, as indicated in Figure 1c, the current was increased as the strain was increased. To correlate the measured data with the crystallographic polar directions of the films, transmission electron microscopy (TEM) investigations were carried out using a Hitachi HF2000 operated at 200 kV. Cross-sectional samples were prepared for the thin films so that the GaN films and the sapphire substrates can be simultaneously captured. By using the convergent beam electron diffraction (CBED) technique, which is unique in determining the polar direction of the thin film in reference to the simulated CBED patterns, the results show that the two different behaviors as presented in Figure 1b and c correspond to GaN films with opposite *c*-axis orientations in reference to the sapphire substrates, as shown in Figure 1d and e, respectively. The structures of both films are single crystals with a thickness around 4 μm. The interface between the GaN film and the sapphire is clear. The only difference is that, for the first group, the *c*-axis of the GaN film points downward to the substrate, while it points upward from the substrate for the second group.

We take the case of the first group as an example to explain that how the orientation of the *c*-axis plays a key role on the experimentally observed current dependence on the strain applied to the film. As shown in Figure 2a, the two ITO electrodes and the GaN film form an M−S−M structure. Due to the difference in work functions between ITO and GaN, Schottky barriers (ϕ_o) formed at the two M−S contacts. When a voltage is applied between the two electrodes, the path of the current going through the device is schematically indicated by the green dashed line in Figure 2a (or going through in the opposite direction depending on the polarity of the applied voltage). When the substrate is curved bent so that the film is under tensile strain in parallel to the film plane (Figure 2b), net piezoelectric charges are generated at the top and bottom surfaces of the GaN film. According to the orientation of the *c*-axis in this case, positive piezoelectric charges present at the top surface of the GaN film, which is the area of two ITO-GaN contacts, as shown in Figure 2b. As a result, the Schottky barrier heights increase at both contacts (ϕ_s, where $\phi_s > \phi_o$; note, GaN is *p*-type). So, under a constant applied voltage, the measured current passing through the GaN film would be reduced. Alternatively, when the substrate is curved bent so that the film is under compressive strain in parallel to the film plane (Figure 2c), negative piezoelectric charges are generated at the top surface of the GaN film, and the Schottky barrier heights at the two contacts are reduced (ϕ_c, where $\phi_c < \phi_o$). Thus, the measured current would be increased.

While for the devices in the second group with the *c*-axis orientation of the GaN film points upward from the substrate, when the film is under tensile strain in parallel to the film plane, negative piezoelectric charges are generated at the top surface of the GaN film. Thus, the Schottky barrier heights at the two contacts are reduced simultaneously, and the measured current passing through the GaN film increases with the increase of strain. This is the result observed experimentally in Figure 1c. By the same token, the experimental data in the case when the film is under compressive strain in parallel to the film plane can be explained as well.

Under different straining conditions, the EL spectra were recorded from the electrode area that was under forward bias, for example, with the GaN film having a higher potential than the ITO. Two dominant peaks were observed. One is located at 430 nm, which is related to the emission between the conduction band or shallow donors to the Mg shallow acceptors,[14−16] as shown in Figure 3a. The other one is located at 540 nm, where deep Mg acceptors are involved in the emission process,[17−19] as shown in Figure 3b. The insets of these figures are corresponding current changes under different applied strain with a constant applied voltage. We can see that the current decreased as the applied strain increased, which indicates that the *c*-axis of the GaN film pointed downward to the sapphire substrate in this case, as we have discussed in the previous section. For both wavelength emissions, no shift in emission energy was observed when strain was applied or when the current passing through the GaN film was changed. The measured current has a linear relationship with the applied strain, but the integral EL intensity has a "V" shape, as shown in the inset of Figure 3c. When the applied strain was increased, first, the integral EL intensity was decreased as the measured current was decreased. But then, it reached a minimum and then went up while the current kept decreasing when strain was further increased. We can define the external quantum efficiency as the ratio of the integral EL intensity to the measured current and normalize it using the minimum value for comparison purposes, which is plotted in Figure 3c. In addition to the observed minimum, another very interesting thing is that the external quantum efficiency of the blue EL emission at 430 nm was changed by 5.84% under different applied strain, while for the emission at 540 nm, it was only changed by 0.54%, which is 1 order of magnitude smaller. It seems that the shallow acceptor states related emission process is more sensitive to the M−S interface environment than the deep acceptor states related one. The mechanism of this phenomenon is still under investigation.

As we know, the intensity of the current passing through the GaN film plays a very important role on the EL emission intensity, but it is not the only determining factor. To elaborate this, we compared the integral EL intensity change due to the change in current introduced by using two different approaches, as shown in Figure 3d. For the first approach, different current was applied directly to the device. A linear relationship was observed between the integral EL intensity and the applied current. For the second approach, the applied voltage was fixed. Then, by introducing different strain in the GaN film, the transport current can be tuned. In this case, a minimal value was observed for the integral EL intensity. When comparing these two cases, it is very interesting that, even under the same current conditions, the integral EL intensity is obviously different for the two approaches. It means that, when strain is present in the film, there should be some factors that can change the ratio between the currents that contribute to the emission and nonemission processes. The strain induced piezoelectric charges at the ITO/GaN interface are suggested to be the dominant one.

As shown in Figure 4a, a Schottky barrier is formed at the ITO/GaN interface. To stimulate EL emission, the Schottky

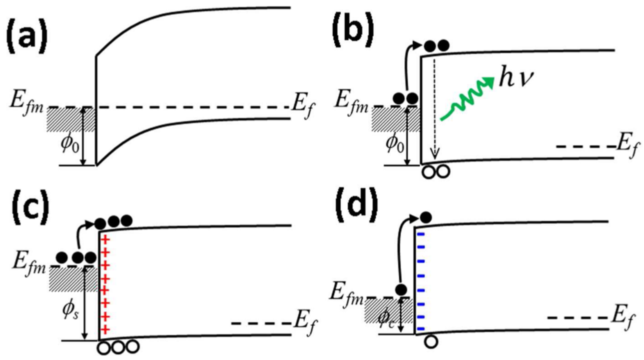

Figure 4. Proposed working mechanism: (a) A Schottky barrier is formed at the ITO/GaN interface. (b) Under forward bias, electrons as the minority carriers inject from ITO to GaN and recombine with holes in GaN accompanied with radiative emission. (c) When the GaN film is stretched in parallel to the film plane, positive piezoelectric charges are created at the interface. The injection efficiency of electrons from ITO to GaN and thus the emission efficiency are promoted. (d) When the GaN film is compressed in parallel to the film plane, negative piezoelectric charges present at the interface. The injection efficiency of electrons from ITO to GaN and, thus, the emission efficiency are suppressed.

barrier was forward biased. In our experiments, normally the device is operated at a high voltage (larger than 20 V), so that a flat band condition is used here, as shown in Figure 4b. The current passing through the ITO/GaN interface is contributed from two parts: the flow of holes from GaN to ITO and the flow of electrons from ITO to GaN. For the EL emission process, we are more interested in the latter process, which is the injection of minority carriers into the *p*-type GaN. The injected minority carriers can then recombine with holes radiatively in the GaN, as shown in Figure 4b. Thus, the injection efficiency of minority carriers at the interface plays a very important role on the luminescence efficiency.[20] When the GaN film was under tensile strain in parallel to the film plane (applied strain > 0), positive piezoelectric charges showed up at the ITO/GaN interface, and the Schottky barrier height for holes was increased (ϕ_s), while the barrier for electron injection from ITO to GaN was decreased, as shown in Figure 4c. Also the positive piezoelectric charges at the interface in GaN will attract more electrons diffusing from the ITO side. Both of them will enhance the injection efficiency of minority carriers and, therefore, the luminescence efficiency. This is the reason for the observed phenomenon that, although the total current passing through the GaN film was reduced step-by-step, the obtained integral EL intensity started to increase under certain straining conditions, as the results shown in Figure 3c. Starting from this point, although the total current was reduced, the part of the current contributing to the EL emission process increased due to the enhanced injection efficiency of electrons at the ITO/GaN interface, which is the result of introduced positive piezoelectric charges around this area, or the piezo-phototronic effect. When the GaN film was compressed in parallel to the film plane (applied strain < 0), negative piezoelectric charges showed up at the ITO/GaN interface, as shown in Figure 4d. The barrier for electron injection at the interface was increased, and the negative piezoelectric charges in the GaN would also resist the injection of electrons. So, the injection efficiency of minority carriers and, therefore, the luminescence efficiency were decreased. This is why the integral EL intensity for the same device is lower when the GaN film was compressed than when it was in a nonstraining status even under the same current conditions, as the right part of the plot shown in Figure 3d. Our former theoretical simulations have predicted that the strain induced piezoelectric charges can adjust the minority carrier injection at the interface of a p−n junction.[21] Here, our experimental results demonstrated that this can also work on the Schottky barrier at the metal−semiconductor interface.

To further verify our proposed mechanism, we applied a constant current passing through the GaN film and checked the change of the integral EL intensity under different straining conditions. The results are shown in Figure 5. In such a situation, the change in EL intensity induced by current change is eliminated. The dominant factor here is the injection efficiency of the minority carriers. A linear relationship was obtained between integral EL efficiency and the applied strain. It means that, when the GaN film is stretched in parallel to the film plane, the positive piezoelectric charges at the interface of ITO/GaN will increase the contribution of the minority carrier injection in the total current and, thus, the luminescence efficiency. While when the GaN film is compressed in parallel to the film plane, the negative piezoelectric charges at the interface will reduce the current contributed by the minority carrier injection and, thus, the luminescence efficiency. This is consistent with our proposed mechanism. In this case, by eliminating the current change effect, the integral EL intensity was modulated by 2.11% for the emission at 430 nm and 0.21% for the emission at 540 nm due to the piezo-phototronic effect under different straining conditions. Because the current is constant here, it is equal to the changes of external quantum efficiency.

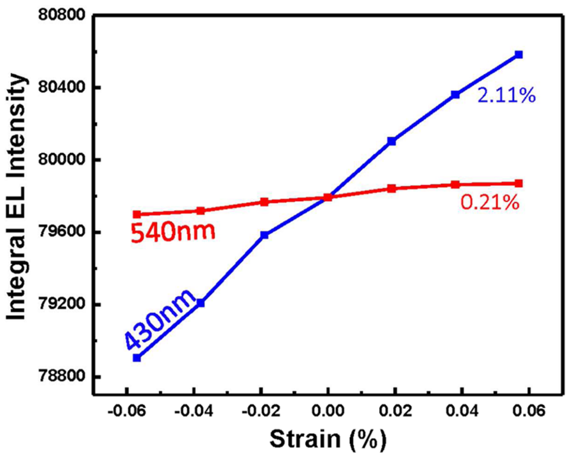

Figure 5. When a constant current was applied on the device, a linear relationship was obtained between the integral EL intensity and the applied strain in the device, consistent with our proposed working mechanism.

In conclusion, in this work, the piezo-phototronic effect was investigated on GaN thin films for the first time. By depositing transparent ITO electrodes on the film, a metal−semiconductor−metal structure was formed. When strain was applied to the GaN film, the induced piezoelectric charges at the ITO/GaN interface modified the Schottky barrier height, and two kinds of changing trends of the transport properties were obtained depending on the c-axis orientations of the GaN films. Also these piezoelectric charges changed the minority carrier injection efficiency at the M−S interface, which resulted in a modification of the EL emission intensity. The piezo-phototronic effect has a more pronounced effect on the EL emission process involving the shallow acceptor states than the one involving the deep acceptor states in the p-type GaN thin films. As a dominant material for the optoelectronic devices, this study provides a further understanding of GaN and may be significant for its future applications in flexible optoelectronics.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zlwang@gatech.edu.

Author Contributions

[§]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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