LABORATORY DIRECTED RESEARCH & DEVELOPMENT

SAND2015-8086R
LDRD PROJECT NUMBER: 185054
LDRD PROJECT TITLE: Photoelectrochemical Etching of GaN Quantum Wires
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ABSTRACT: (250 word limit)

For this Exploratory Express LDRD we investigated the use photoelectrochemical etching to demonstrate GaN quantum wires with a diameter of less than 10 nm. Although GaN nanowires with much larger sizes (200 nm – 2 microns) have been demonstrated by a number of techniques, quantum wires are much more difficult to realize due to the very small dimensions (< 10 nm). Previous demonstrations of semiconductor quantum wires have relied on colloidal methods resulting in large size distributions or complicated regrowth on the edge of a cleaved wafer. Here we propose to use photoelectrochemical etching to realize GaN quantum wires. Previously we have been able to show that this technique can be used to make InGaN quantum dots and we propose to use similar methods to realize GaN quantum wires. To our knowledge, GaN quantum wires have never been demonstrated due to growth and fabrication difficulties. Photoelectrochemical etching has also never been used to demonstrate quantum wires in any material system. If our quantum wire fabrication method is successful, it will open up a new research area centered around GaN quantum wires and related applications. Quantum wires can be used as an efficient nanoscale conduit for the transport of charge and energy and will find applications in nanoelectronics, energy harvesting (solar), nanoscale light emitters, and chem/bio sensors.

INTRODUCTION:

We have recently demonstrated that InGaN quantum dots (QDs) can be fabricated using laser -based photoelectrochemical (PEC) etching of InGaN quantum wells or InGaN epilayers. This process, which we call quantum size control, works because the PEC etch terminates when an InGaN nanostructure reaches a particular size the quantum size regime. Here we are using the quantum nature of the InGaN nanostructure to enable a QD fabrication process. We have also previously shown that this process can be used to make different sized QDs where the size of the QD depends on the wavelength used to do the PEC etching. This process has the potential to make QDs with very uniform size distributions which would be very beneficial for many light emitting devices such as quantum dot laser diodes. This process also has the potential for deterministically placing a QD at an exact location in a photonic structure such as at the anti-node of an optical cavity. The process of quantum size control will be described in much greater detail below. For this work we will focus on GaN nanostructures, but the basic process is expected to be applicable to any semiconducting material that can be PEC etched.

For this small research project we proposed to extend the concept of quantum size control from 0D quantum dots to 1D quantum wires (QWRs). QWRs are desired for applications in nanoelectronics, energy harvesting (solar), nanoscale light emitters, and chem/bio sensors.

However, quantum wires with diameters less than 10 nm are very difficult to fabricate in a controlled manner. Here we propose to start with nanowires with larger diameters (500 nm to 2 μm) and use PEC etching to reduce the diameter of the wire until it reaches the quantum size regime. At this point, the energy levels will become quantized and the transition energy will increase which will act to terminate PEC etching.

We will grow GaN via metalorganic chemical vapor deposition and etch nanowire posts using a top-down fabrication process. Since this process has been described in detail in many previous reports, here we will give only a brief description. Planar GaN films are patterned using self-assembly of nanoscale polystyrene spheres. These spheres are used as an etch mask for reactive ion etching of the GaN to make nanowires. This top-down nanowire fabrication process was developed as a part of a previous program. These top-down nanowires will then be etched using PEC etching.

If this concept and fabrication method can be extended to QWRs and the same properties hold, we would have a novel method for fabricating QWRs where the resulting diameter of the wire can be selected by the proper choice of the PEC etch wavelength. Deterministic placement of a PEC etched GaN QWRs may also be important for light emitting applications. In addition, it may be possible to controllable reduce the size of semiconductor nanostructures to sizes not accessible using standard photolithographic approaches. This may be useful, for example, for sensors based on quantum wires. This report details the work done to date towards fabrication of GaN quantum wires using PEC etching.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD:

The work on this project consisted of several steps. The first step was the fabrication of top-down nanowires using a process previously developed. Whenever possible we used previously fabricated nanowire samples in order to reduce the financial burden on this small LDRD project. We used top-down nanowires samples both with and without the KOH etch for reducing side-wall damage as described in more detail below. Top-down fabrication of GaN nanowires is a reasonably well-established process at Sandia and no further description of this process will be given here. The second step is to perform PEC etching under various conditions to hopefully fabricate QWRs. The third step is to characterize the resulting samples via scanning electron microscopy (SEM) and photoluminescence. Although we initially considered have one or two transmission electron microscope images made for our samples, this was never done due mostly to the limited budget.

Since PEC etching is very important for the work performed on this project, PEC etching will be scribed here in further detail. PEC etching is a wet etch process where the etch proceeds only if light is absorbed in a semiconductor above the band gap. Figure 1 shows a schematic of our setup which is used for PEC etching. Since this is an electrochemical process, an electrical contact must be made to the underlying n-type GaN. This is done by using a diamond scribe to make a scratch on the surface to expose the underlying n-type GaN. A small piece of high purity metallic indium is then pressing into the scratch to create the electrical contact. The sample is then annealed above the melting point of indium (156 °C) to complete the contact. A simple alligator clip is used to both clamp the sample in place and make electrical contact to the indium. The circuit is completed by completing an electrical connection to a platinum counter electrode.

Etch current is monitored using a Keithley 2400 source measurement unit. A narrow linewidth fiber-coupled laser is used for sample illumination during PEC etching. Although many different lasers could be used, for this work, we used the second harmonic of a tunable Ti:sapphire laser operating in the wavelength range from 350 nm to 380 nm.

As shown schematically in Fig. 1, for PEC etching to proceed, the sample is immersed in an electrolyte solution most commonly potassium hydroxide (KOH). However, for this work we used 0.2M H_2SO_4 which was the electrolyte used for all of the InGaN QD work. Recent data indicates that at least for InGaN, the use of H_2SO_4 is important in preventing oxide formation during the etch process. For GaN PEC etching and specifically for GaN nanowire PEC etching, it is not known if H_2SO_4 is required or if, perhaps, KOH would be as good or better. This is a subject for future investigation.

Etching proceeds when the electrochemical circuit is closed and a photon is absorbed. When a photon is absorbed, an electron-hole pair is created. The electrochemical bias causes the hole to travel to the surface to perform etching and the electron travels to the Pt counter electrode. If no photon is absorbed, then no etching occurs. In this sense, PEC etching is band gap selective. For example, we can choose a PEC etch wavelength of 410 nm which will be absorbed in 15% InGaN, but no absorption will occur in GaN. The band gap selective nature of the PEC etch is critical in making the quantum size controlled fabrication work. As an InGaN nanostructure is PEC etched, the size gets smaller. As the nanostructure size reaches the quantum size regime, the energy levels become quantized and the transition energies go up. At some point, depending on the PEC etch wavelength, the quantum structure will stop absorbing and PEC etching will terminate. A second important key to making this process work is the narrow linewidth nature of the illumination source. It is possible to perform PEC etching with a broad band lamp source such as a Xe arc lamp. However, the broadband nature of this type of source means that etching will not terminate at a specific size.

We have shown that this process of quantum size control works for fabricating InGaN QDs. We performed the same type of PEC etching on top-down GaN nanowires. The results of this work will be presented in the next section.

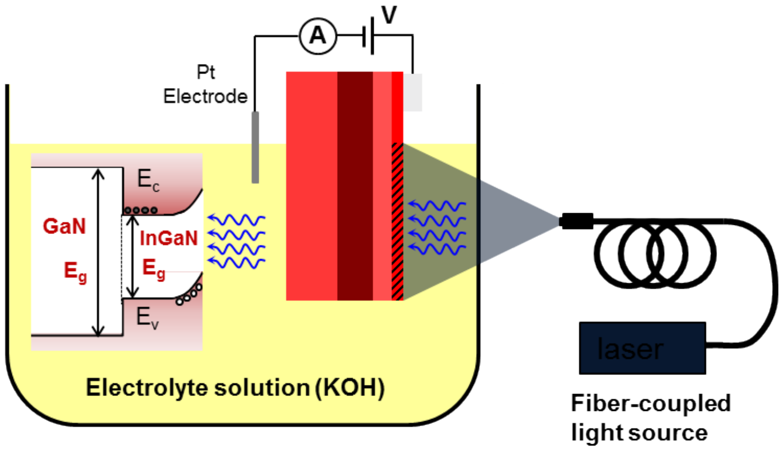

Fig. 1. Schematic diagram showing the experimental set-up for PEC etching. Note that our light source is a fiber-coupled, narrow-linewidth laser.

RESULTS:

PEC etching was performed for top-down GaN nanowire samples which were described previously. We have investigated PEC etching of GaN nanowire samples with and without a KOH wet etch. During the fabrication process for GaN nanowires, a KOH wet etch is often used as the final step to remove sidewall damage. Figure 2 shows a SEM image for GaN nanowire samples before PEC etching with and without KOH etching. Note that the morphology of the GaN nanowires with and without the KOH wet etch is considerably different. Without the KOH wet etch, the nanowires typically have a somewhat rounded sidewall due to the ICP etch. After the KOH wet etch, the GaN nanowires have a very sharp, steep sidewall which has been cleaned up by the KOH wet etch. Furthermore, photoluminescence for the sample without the KOH etch has a considerable amount of yellow band luminescence at 550 nm. However, after the KOH wet etch, the yellow band emission at 550 nm is considerably reduced. This is because the high energy ions from the reactive ion etch cause sidewall damage which results in defect emission at 550 nm. The KOH wet etch removes the sidewall damage.

The first samples we PEC etched were samples without the KOH wet etch as shown in Fig. 2(a). We first tried etching samples using a PEC etch wavelength of 378 nm. This is a regime where there is very little absorption in GaN. Although there was a measureable etch current, very little etching occurred. In order to speed up the etch process we changed the PEC etch wavelength to 370 nm. At this wavelength the PEC etch current was approximately 10 times higher and etching proceeded much more rapidly. Figure 3 shows the resulting nanowire samples after etching for over two hours. The PEC etch preferentially etches away the core of the nanowire leaving behind the outer shell which has etch damage. Although the etch current does not decrease to zero as expected for the quantum size control process, the continued etch current indicates that the PEC etch continues, but it is likely that the GaN layer below the nanowires continues to etch although the nanowires no longer etch. Apparently the regions with ion damage from the reactive ion etching do not readily etch using PEC etching. The damaged region likely has enhanced non-radiative carrier recombination which suppresses PEC etching. Thus, after considerable effort at PEC etching, it appears that GaN nanowires without a KOH etch will not yield GaN quantum wires.

Next we investigated GaN nanowire samples which had the KOH wet etch. We etched the sample using a PEC etch wavelength of 370 nm. The sample was etched for 45 minutes and then subsequently etched for an additional 40 minutes for a total of 85 minutes. The SEM images look approximately the same after 45 minutes or 85 minutes of etching. Figure 4 shows the resulting structure after PEC etching for 85 min using a PEC etch wavelength of 370 nm. The PEC etching appears to stop at a wire diameter of approximately 30 nm. For this SEM image the average wire diameter is 31.0 nm with a standard deviation of 5.3 nm. Again, the PEC etch current does not decrease to zero after extended etching times. This is likely due to the lower GaN planar layer continuing to etch after etching of the nanowires stops. We originally assumed that the PEC etching stopped at a diameter of 31 nm due to the PEC etch wavelength of 370 nm.

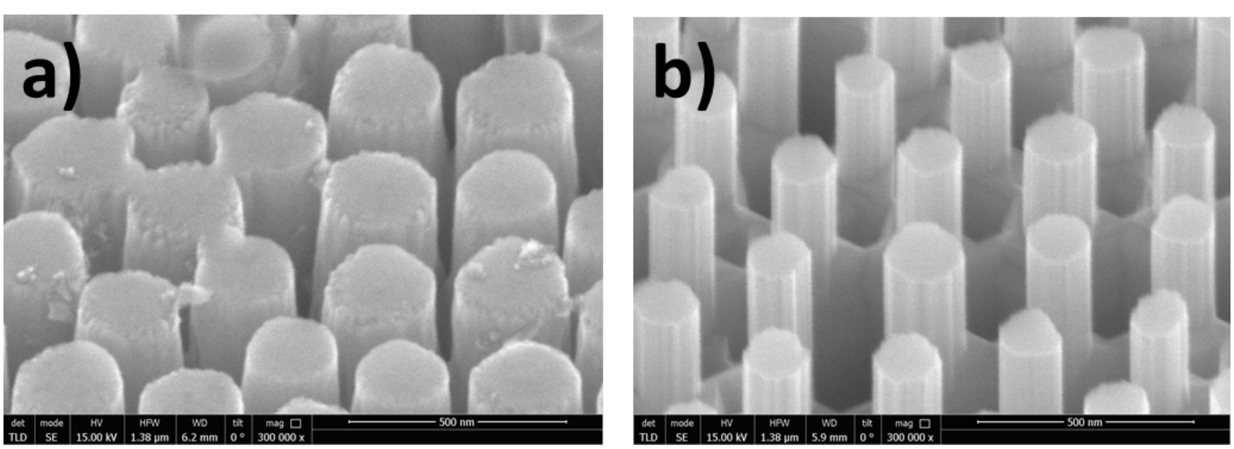

Fig. 2. Scanning electron microscope (SEM) images of top down GaN nanowires (a) with no KOH wet and (b) with a KOH wet etch. Note the straight sidewalls for the sample after the KOH wet etch.

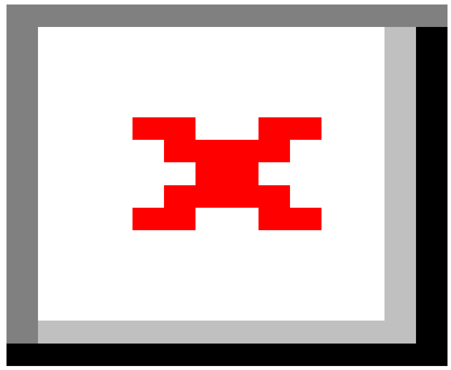

Fig. 3. Scanning electron microscope (SEM) image of a KOH-etched top-down GaN nanowire which was etched using a PEC etch wavelength of 370 nm. Note that the resulting nanowire diameter is approximately 30 nm.

Our next step was to PEC etch a second KOH-etched GaN nanowire sample, but to use a shorter wavelength for the PEC etch with the hope of fabricating a nanowire with a smaller diameter in the quantum size regime. Figure 4 shows a SEM image of a sample etched using a PEC etch wavelength of 355 nm. This sample also shows that the PEC etch stops when the nanowires reach a diameter of approximately 30 nm. The SEM image in Fig. 4 shows an average diameter of 32.3 nm with a standard deviation of 4.9 nm. Thus, the diameter for a 370 nm PEC etch is the same as the diameter for a 355 nm PEC etch within experimental error. For the experiments to date, etching using a shorter wavelength does not produce nanowires with a smaller diameter. The PEC etching appears to stop at a diameter near 30 nm regardless of PEC etch wavelength which is different than what is observed for InGaN QDs. Further study will be required to understand these results.

DISCUSSION:

Our results to date show that for PEC etching of nanowires, the resulting diameter is on the order of 30 nm regardless of the PEC etch wavelength. This indicates that the mechanism at play for PEC etching of InGaN QDs is different than that for GaN nanowire PEC etching. One theory we developed as a part of this work is that the etch diameter is determined by the transport of carriers through the nanowire as the nanowire reached the quantum size regime. Etching is dependent on the transport of holes to the surface and electrons to the platinum counter electrode.

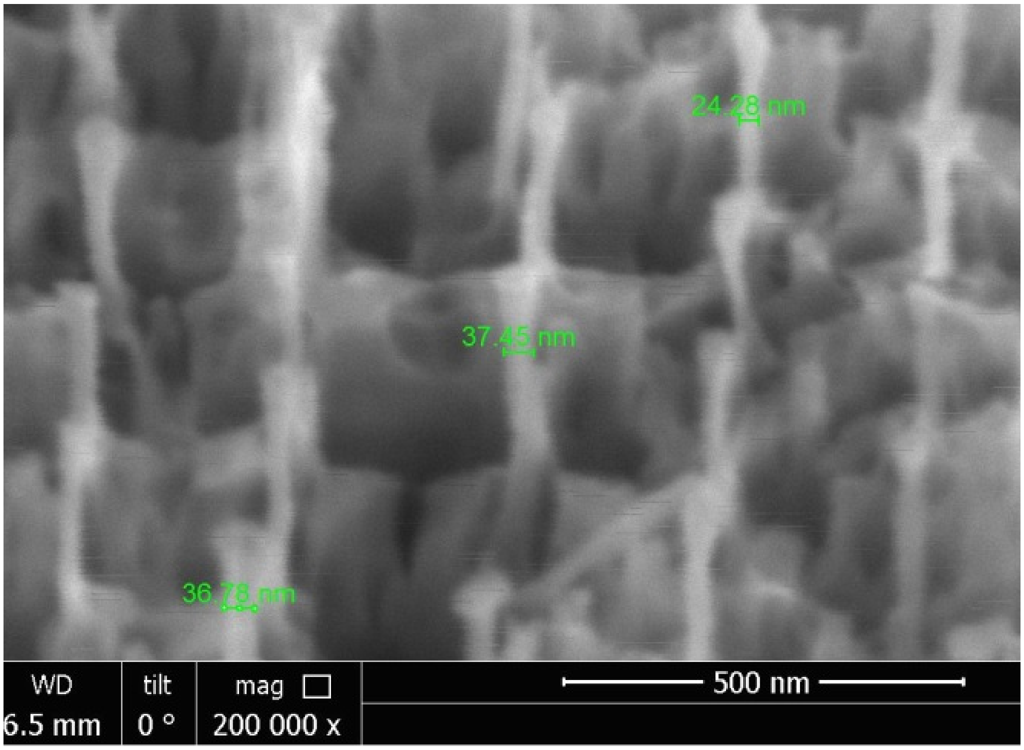

Fig. 4. Scanning electron microscope (SEM) image of a KOH-etched top-down GaN nanowire which was etched using a PEC etch wavelength of 355 nm. Note that the resulting nanowire diameter is on the order 30 nm.

During PEC etching, when the nanowire diameter is reduced to 30 nm, it is possible that the transport of electrons to the counter electrode is inhibited, which may be the reason that the wire diameter is not dependent on the PEC etch wavelength. This is just one hypothesis that will require more testing to validate. There may be other reasons that quantum size control did not work for GaN nanowires in these initial studies. With further work, we may find PEC etch conditions (or better GaN nanowires) where quantum size control will be effective at producing quantum wires.

One of the indicators of reaching the quantum size regime is a blue shift of the luminescence. This has been observed for InGaN QDs where the emission wavelength shifts from QW emission at 510 nm to emission at 410 nm after QD formation. The same blue shift of the luminescence is expected for GaN QWRs, but based on calculations, the wavelength shift is expected to be smaller. Therefore, our plan was to measure the photoluminescence (PL) spectrum for a sample before and after PEC etching. Figure 5 shows the PL spectrum on a log scale for samples before and after PEC etching. Three PL spectra are shown in the image. The green curve shows the PL spectrum for a sample before PEC etching and with no KOH wet etch. This PL spectrum shows the normal 365 nm band edge peak as well as a large yellow band peak at 550 nm. The red curve shows the PL spectrum for a GaN nanowire sample without the KOH etch which has been PEC etched using a PEC etch wavelength of 370 nm. This spectrum shows

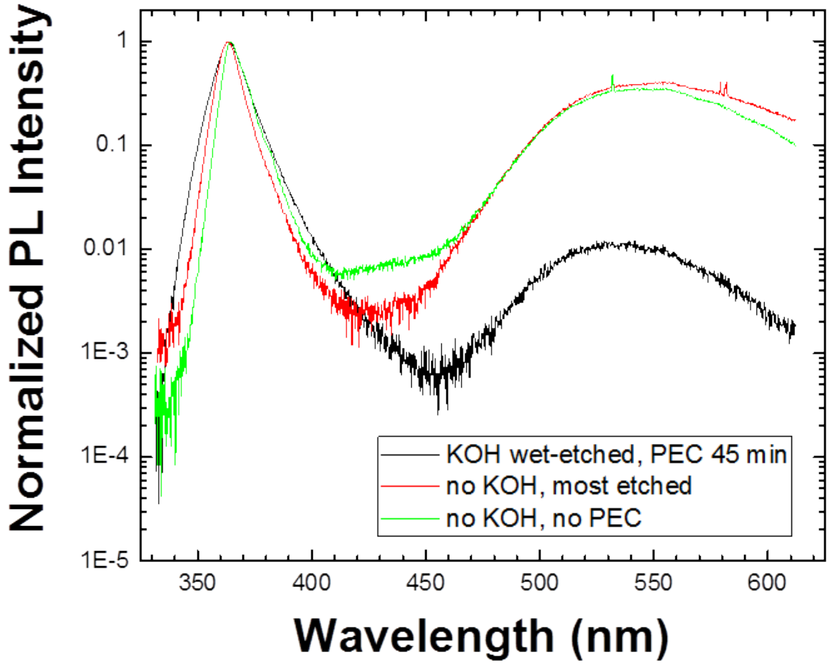

Fig. 5. Photoluminescence data plotted on a log scale for samples before and after PEC etching. There is no significant change in the PL data before and after PEC etching.

the same high level of yellow band emission and no change to the band edge peak. Finally the black curve shows sample that has had the KOH wet etch and the 370 nm PEC etch. The only significant change is that the KOH wet etch reduces the yellow band emission. We would expect a slight shoulder at higher energy near 350 nm for a sample with a GaN quantum wire. However after performing PL on many PEC etched GaN nanowire samples, no blue-shifted emission peak was observed. Further work is required to understand PEC etching of GaN nanowire samples. With further analysis, a path to PEC etched GaN nanowires may eventually be realized, but to date we have fabricated samples with diameters of about 30 nm which we suspect is limited by the transport of electrons through the 30 nm GaN nanowire.

ANTICIPATED IMPACT:

Our goal for this project was to demonstrate GaN quantum wires with a diameter of less than 10 nm. Although we have not reached this goal, we have been able to reproducibly make nanowires with diameters of about 30 nm. It is very difficult to make nanowires with dimensions this small. Therefore we have already realized a method making nanowires with very small diameters which will be useful for future nanowire studies.

We have also learned that etch damage can impede the PEC etch process. This is due to the fact that regions with etch damage have very fast non-radiative recombination processes which take carriers away from the etch process. In fact, any recombination process whether radiative or non-radiative can take carriers away from the etch process. Even the etch process itself is really a non-radiative recombination process. However, what matters for PEC etching is the rate of recombination from PEC etching compared to other recombination processes. The fact that PEC etching doesn't occur for regions with etch damage tells us that the recombination processes in that region are very fast and take carriers away from the PEC etch process. We are working on developing a rate equation model to understand the carrier dynamics associated with PEC etching which will hopefully allow us to predict the etch behavior as we change the pump power, applied voltage and other parameters.

The fact that we did not demonstrate quantum wires with diameters of 10 nm or less does not mean that quantum size control will not work for quantum wires. The limited budget for this Exploratory Express LDRD constrained us to carefully select only a few different experiments. Based on the results obtained from this project, we would like to investigate several new directions. Based on our work with QDs, we used a reverse bias voltage of 0.9 volts. We know from experience that this bias voltage produces InGaN QDs with wavelength ranging from 400 to 500 nm. The results from this project suggest that the PEC etching may be in a transport limited regime and therefore it may be possible to change the PEC etch dynamics by changing the bias voltage used during the PEC etch. For example, the nanowire diameter may depend more strongly on the applied voltage during PEC etching than on the wavelength used for PEC etching. The bias voltage used during PEC etching is a parameter that was not investigated as a part of this study but looks very promising for future work. We would also like to investigate variation to the electrolyte solution and variations in the laser power.

Since we have already demonstrated quantum size control for InGaN QDs, we think the same process will work for GaN QWRs, but that we haven't found the right experimental conditions to realize QWRs with diameters of less than 10 nm. Furthermore, the PEC etch process is not understood in sufficient detail to guide our experimental studies. Further development work on both modeling and experiment will almost certainly yield GaN quantum wires as the process of quantum size control likely will extend beyond 0D quantum dots to other quantum nanostructures.

CONCLUSION:

We have investigated PEC etching of GaN nanowires with the goal of demonstrating GaN quantum wires with a diameter of less than 10 nm which would be an indication that our nanostructures have entered the quantum size regime. To date we have demonstrated GaN nanowires with a diameter of about 30 nm, which is already an interesting and useful accomplishment. This gives us a simple method of reproducibly fabricating nanowires with very small dimensions. For these initial studies the GaN nanowire diameter was about 30 nm both when etching at 370 nm and when etching at 355 nm. We would have expected wires with a smaller diameter when etching using a shorter PEC etch wavelength. Since the quantum size control process works for InGaN QDs, it is likely that we have not found the correct experimental parameters to realize PEC etched quantum wires. Specifically we think that the PEC etching is limited by transport through a narrow diameter GaN nanowire. The PEC etch dynamics and electron transport will likely change at higher bias voltages and we think this is a particularly promising area for further investigation. With further work we believe we will be able to show that quantum size controlled PEC etching is a viable method for fabricating quantum wires.

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