

Site-Specific Fabrication of Nanoscale Heterostructures: Local Chemical Modification of GaN Nanowires Using Electrochemical Dip-Pen Nanolithography

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Abstract: This article describes a new method for site-specific, atomic force microscope (AFM) fabrication of nanowire heterostructures using electrochemical dip-pen nanolithography (E-DPN). We have demonstrated that E-DPN is ideally suited for the in situ modification of nanoscale electronic devices; the AFM tip and the nanowire device can be used as electrodes and the reactants for the modification can be introduced by coating them onto the AFM tip. Specifically, we have created GaN nanowire heterostructures by a local electrochemical reaction between the nanowire and a tip-applied KOH "ink" to produce gallium nitride/gallium oxide heterostructures. By controlling the ambient humidity, reaction voltage, and reaction time, good control over the modification geometry is obtained. Furthermore, after selective chemical etching of gallium oxide, unique diameter-modulated nanowire structures can be produced. Finally, we have demonstrated the unique device fabrication capabilities of this technique by performing in situ modification of GaN nanowire devices and characterizing the device electronic transport properties. These results demonstrate that small modifications of nanowire devices can lead to large changes in the nanowire electron transport properties.

Solid-state heterostructures are an integral part of the modern electronic and electrooptic device landscape. They are responsible for a variety of important electronic properties, including p–n junction current rectification and electroluminescence, avalanche breakdown in superlattice structures, and quantum-well emission in some types of laser diodes. As the miniaturization of electronic devices continues toward the nanometer regime, it is very important to find new ways to produce nanoscale analogues of metal–metal, metal–semiconductor, or semiconductor–semiconductor heterostructures. Several groups have reported the synthesis of nanowire heterostructures using a variety of methods and materials, including direct growth methods,^{1–11} template-directed synthesis,^{12–14} controlled postsyn-

thetic patterning and processing,^{15–19} or region-specific doping of carbon nanotubes.^{20–24} Many of these nanoscale heterostructures have been shown to possess a variety of interesting and technologically relevant properties, including rectification,^{16,18} luminescence,^{10,17,19} and negative differential conductance.²⁰ The recent success in synthesizing these types of materials and the demonstration that they possess important electronic properties suggest that nanowire heterostructures will play a significant role in future nanoelectronic devices.

In this report, we present a new method for site-specific, atomic force microscope (AFM) fabrication of nanowire heterostructures using electrochemical dip-pen nanolithography (E-DPN).^{25,26} E-DPN and other AFM lithography techniques

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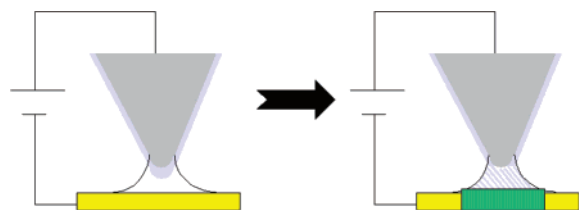


Figure 1. Schematic of the E-DPN modification of GaN nanowires. The AFM tip is first coated with KOH “ink” (blue) and engaged with the nanowire (yellow). During modification of the nanowire, KOH diffuses from the tip to the nanowire surface and electrochemically reacts with the nanowire to produce a gallium oxide heterostructure (green).

can be used to modify surfaces in a rational manner by simply repositioning the tip and chemically altering the surface using lithography. The AFM tip position can be controlled to nanometer and sub-nanometer accuracy, which makes AFM lithography ideally suited for the rational modification of nanomaterials where precise tip positioning is critical. In addition to E-DPN, many other AFM lithography techniques, including dip-pen nanolithography²⁷ or surface anodization,^{28–31} could be used to modify nanowires. We have chosen E-DPN for this proof-of-concept study because it is ideally suited for the in situ modification of nanoscale electronic devices; the AFM tip and the nanowire device can be used as electrodes and the reactants for the modification can be introduced by coating them onto the AFM tip. Specifically, we have created GaN nanowire heterostructures by a local electrochemical reaction between an n-type GaN nanowire and a tip-applied KOH “ink” to produce gallium nitride/gallium oxide heterostructures. By controlling the ambient humidity, reaction voltage, and reaction time, good control over the modification geometry is obtained. Furthermore, after selective chemical etching of gallium oxide, unique diameter-modulated nanowire structures can be produced. Finally, we have demonstrated the unique device fabrication capabilities of this technique by performing in situ modification of GaN nanowire devices and characterizing the device electronic transport properties. These results demonstrate that small modifications of nanowire devices can lead to large changes in the nanowire electronic transport properties.

The E-DPN process is schematically demonstrated in Figure 1. To perform the experiment, a KOH “ink” solution is applied to a highly doped silicon tapping mode AFM tip (Mikromasch, NSC-15) by dipping the tip in a 0.35 M KOH aqueous solution. The tip is then mounted on a ThermoMicroscopes Autoprobe CP AFM for imaging and lithography. The tip is then engaged into feedback and located on a CVD-grown, n-type GaN nanowire at a reduced feedback setpoint. A negative bias voltage is applied between the tip and the surface to facilitate an electrochemical reaction between the GaN nanowire and the KOH ink. This reaction forms a gallium oxide heterostructure on the nanowire.

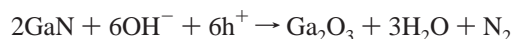
After modification, the resulting heterostructure can be characterized by AFM imaging at the original setpoint. This

AFM-based modification and characterization scheme is well suited for structure–function studies of nanowire superlattice structures; the transport properties of the wire can be measured, and then it can be modified, imaged, and measured again, enabling direct comparisons between nanowire structures before and after modification and the determination of the relationship between nanowire morphology and electronic properties.

Figure 2a shows a nanowire after E-DPN modification. Gallium oxide has a larger molecular volume than GaN, so the newly formed heterostructures appear as “bumps” along the nanowire. Due to AFM tip convolution effects arising from the cone-shaped tips and the relatively large diameter (about 100 nm) of these nanowires, the observed width using AFM imaging is much larger than the actual diameter. To assess the size of each nanowire, we measure its height on the surface. This procedure should give an accurate estimation of the nanowire diameter. During modification, the GaN is transformed to gallium oxide; to assess how much of the subsurface GaN has been reacted, the gallium oxide can be removed by selective etching in 1 M hydrochloric acid. The reduction in nanowire height is easily observed and is directly related to the amount of gallium oxide formed during the electrochemical reaction. Figure 2b shows a representative GaN heterostructure after oxide removal. Before any modification, the diameter of this nanowire was 102 nm; after local modification and etching, the diameter of the modified area is 79 nm. The E-DPN modification locally changed approximately 54% of the GaN volume to gallium oxide in the example shown in the figure.

In addition to the demonstrated local chemical modification, we believe that E-DPN is the only method to produce nanowire heterostructures with size modulation (Figure 2b). Other methods of producing superlattice structures rely on modulating the growth conditions to produce regions with heterogeneous chemical composition. However, due to the vapor–liquid–solid^{4,5} or epitaxial growth¹⁰ mechanisms that are employed, the diameter of the whole nanowire is relatively constant. Here we demonstrate the ability to produce novel nanowire structures by modulating the nanowire size, rather than its chemical composition. As will be discussed below, this size modulation can lead to interesting electronic properties.

The electrochemical reaction between GaN and KOH has been demonstrated elsewhere in bulk experiments.³² This chemical reaction is used for etching of GaN in basic solution, and the mechanism is listed here:



We believe that a similar oxidative process is occurring during E-DPN modification of GaN nanowires, where KOH delivered from the AFM tip reacts with the nanowire. We have confirmed the importance of the KOH ink by performing control experiments with tips with no ink and tips with a control ink (discussed below). These results indicate that KOH ink plays an integral role in GaN modification. Electric-field induced generation of reactive oxygen species from condensed water or oxygen, as occurs for silicon anodization, is not sufficient for significant GaN modification; KOH ink must be present for significant GaN to gallium oxide transformation. We have also noted that it is

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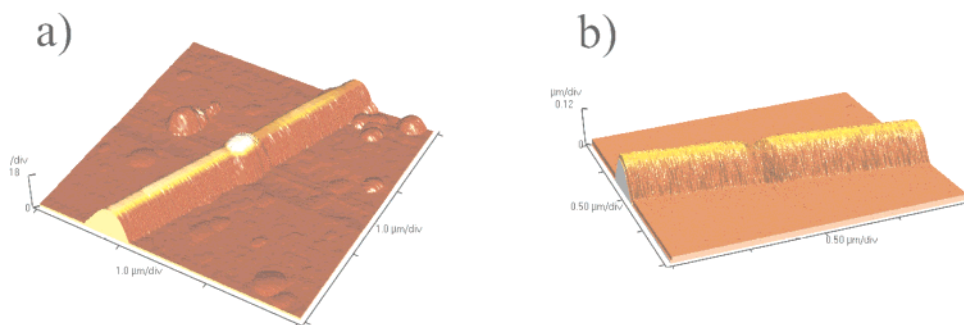


Figure 2. Representative AFM surface images of a GaN/gallium oxide heterostructure (a) before and (b) after selective etching in 1 M HCl. The modification in (a) was performed at 40% humidity, 10 V surface-tip bias voltage, 30 s dwell time. The modification in (b) was performed at 50% humidity, 10 V surface-tip bias, 10 s dwell time. The image in (a) is $3 \mu\text{m} \times 3 \mu\text{m}$ image and the image in (b) is a $2 \mu\text{m} \times 2 \mu\text{m}$ image.

possible to oxidize the GaN nanowire to a depth of tens and even hundreds of nanometers simply by increasing the modification time; in fact, we can modify and etch nearly the entire nanowire. Because these areas are not in direct contact with the AFM tip, reactive oxygen species must be transported through the gallium oxide layer to the unreacted GaN region by diffusion or electric field induced migration. This observation also suggests the importance of hydroxide ion mobility.

Due to the extremely localized nature of the modifications and serial nature of fabrication, it would be difficult to locate the modified areas using microscopy techniques such as TEM to explicitly confirm that the structure of the modified areas because sample preparation would require the random deposition of nanowires on a sample holder. Therefore, we have not attempted to use these types of techniques to characterize the local modifications. However, the observation that the modified areas dissolve in acidic solution (Figure 2) agrees with previous reports of acidic etching of gallium oxide,³² suggesting that the modified areas are also gallium oxide.

The conversion of GaN to gallium oxide requires the oxidation of the semiconductor, so the surface is always positively biased with respect to the tip. As mentioned above, E-DPN was performed under reduced feedback setpoint, which accomplished two things: it increased the electric field at the surface by decreasing the average tip–surface separation and it facilitated the diffusion of KOH from the AFM tip. Other researchers have noted that in tapping mode dip-pen nanolithography is more efficient when the tip driving force is increased significantly because it creates more intimate tip–surface contact.³³ Our approach of reducing the tapping amplitude during modification rather than increasing the driving forces should accomplish the same purpose.

As demonstrated in Figure 3, significantly more modification of the nanowire was observed as the bias voltage was increased, indicating that the modification is an electric-field dependent process. The reaction mechanism for the E-DPN modification of GaN nanowires may appear similar to AFM anodization of silicon or other semiconductors, where the high electric field at a biased AFM tip facilitates the electrochemical oxidation of the surface and the transport of reactive oxygen species through the surface oxide layer.^{28–31} However, we have found the unique ability of E-DPN to carry “ink” to specific locations is an important factor for this type of modification. In fact, simple anodization of the GaN nanowire does not produce large oxide

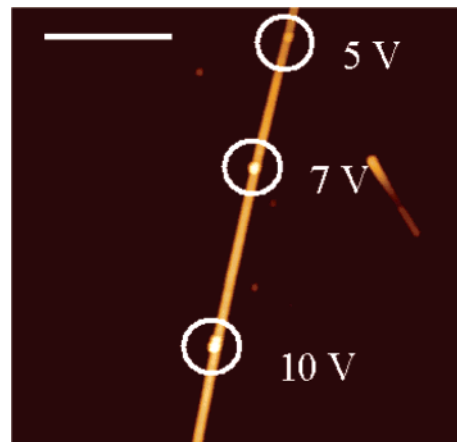


Figure 3. AFM image demonstrating the voltage dependence of GaN nanowire modification. This nanowire was modified in three different areas using three different voltages, as indicated above. The modification size increases with increasing applied bias voltage. These modifications were performed at 50% humidity, 10 s dwell time. Scale bar: $3 \mu\text{m}$.

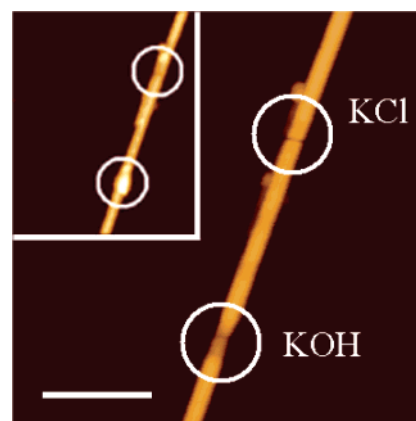


Figure 4. AFM image of a GaN nanowire modified with KOH ink and KCl ink in adjacent areas, after selective etching of gallium oxide with 1 M HCl. Inset: AFM image of the same area before selective etching. These modifications were performed at 10 V bias, 50% humidity, 10 s dwell time. Scale bar: $1 \mu\text{m}$.

features. Control experiments using KCl ink, which cannot participate in the oxidation reaction of the nanowire, confirm the critical role of the KOH for the process. Figure 4 shows a GaN nanowire modified in one location with KOH ink and in another location with KCl ink using the same AFM tip and under identical reaction conditions. Significantly less modification is observed in the KCl-treated area. It may appear to the reader that the nanowire has been completely etched; in fact, the depth

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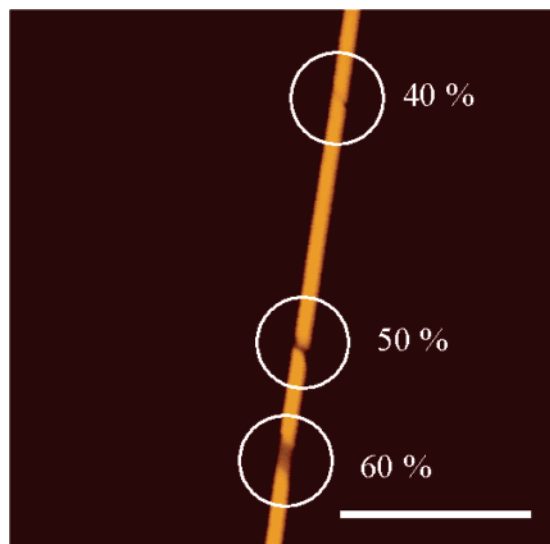


Figure 5. AFM image illustrating the humidity dependence of the E-DPN modification, taken after selective etching. This nanowire was modified in three areas at three different humidities as indicated above and selectively etched in 1 M HCl. The spatial dimensions of the modification increases as the humidity increases, indicating that the condensed meniscus between the tip and surface possibly facilitates KOH transport from the tip to the surface. Each modification was performed at 10 V surface-tip bias and 10 s. dwell time. Scale bar: 2 μm .

Table 1. Summary of the Topographic Measurements in the Figures. The Parentheses in the Height and Width Measurements for the Figure 4 Row Are for the Inset, before HCl Etching

images	nanowire diameter	modification height	modification width
Figure 3	95 nm	5 V 10 nm	440 nm
		7 V 20 nm	320 nm
		10 V 29 nm	200 nm
Figure 4	75 nm	KOH 11 nm (17 nm)	600 nm (600 nm)
		KCl 4 nm (12 nm)	160 nm (230 nm)
Figure 5	96 nm	40% 4 nm	600 nm
		50% 27 nm	360 nm
		60% 23 nm	130 nm
Figure 6	115 nm	32 nm	200 nm
		32 nm	200 nm

of the modifications is only 10 nm, while the diameter of the nanowire is 75 nm (Table 1). To highlight the changes in nanowire structures, we had adjusted the false-color scheme in our AFM images so that an extremely sharp contrast is achieved. Unfortunately, it also made it difficult to visually resolve the degree of modification from the background. The detailed information of the depth of modification is summarized in Table 1.

The importance of the KOH ink was further demonstrated by assessing the effect of ambient humidity on the modification morphology. As shown in Figure 5, larger areas are modified at higher ambient humidity. This is due to transport of the KOH ink away from the AFM tip through the condensed water meniscus at the tip–surface interface. As the ambient humidity increases, the spatial extent of the water meniscus also increases, which enables the KOH ink to diffuse further from the AFM tip before reacting with the nanowire. Essentially, the ambient humidity determines the size of the electrochemical “reaction zone” between the AFM tip and the nanowire. This type of humidity dependence and characteristic diffusion-based ink dynamics have been observed in other dip-pen nanolithography experiments.^{27,34,35} The observation of a distinct humidity effect on the modification morphology is further evidence of the integral role of KOH transport in heterostructure formation. By

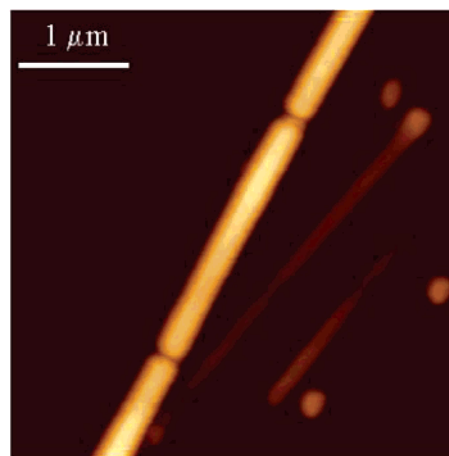


Figure 6. AFM image of a GaN nanodevice that was modified in situ using E-DPN. The first modification (on the right) was performed at 10 V, 40% humidity, 50 s dwell time. The second modification (on the left) was performed at 10 V, 40% humidity, 30 s dwell time.

controlling the voltage, modification time, and ambient humidity, the specific morphology of the heterostructure should be controllable.

To demonstrate the utility of this technique for device applications, we have performed in situ modification of GaN nanowire devices. Specifically, these devices were prepared by dispersal of CVD-grown GaN nanowires on Si wafers with 1000 nm thermal oxide. Electrodes were fabricated on the surface using standard photolithography of a 20 e pattern with 20 μm separation between electrodes, Cr/Au deposition and lift-off. Despite the fact that the nanowires had random arrangements on the surface, a few of the GaN nanowires were long enough and were oriented properly to bridge adjacent electrodes, resulting in the formation of a few devices per sample. Though this fabrication scheme has a very low yield of usable devices (<5 per wafer), we found that it was less time-consuming than using other electrode patterning techniques such as electron-beam lithography. Devices were identified using optical microscopy and scanning electron microscopy and characterized before modification using current vs voltage electronic transport measurements. After a suitable GaN nanodevice was identified, the device was first imaged with AFM and a small section of the nanowire was modified using E-DPN with KOH ink, as described above. Electronic transport measurements were performed before and after chemical etching to assess the impact of the modification on the device properties. Figure 6 shows an AFM image of a GaN nanowire. The image was taken after HCl etching to highlight the subsurface oxidation of GaN. This device was modified in two locations to produce a superlattice structure. The current vs voltage plots before and after local modification are shown in Figure 7a. Figure 7b is a magnification of the I – V curve of the nanodevice after modification (shown in Figure 7a) which demonstrates that the nanowire device was still conductive after modification, albeit significantly less so. As demonstrated in these figures, dramatic changes in the electronic transport properties were observed after chemical modification and etching. For this device, fabrication of a diameter-modulated GaN heterostructure resulted in a dramatic

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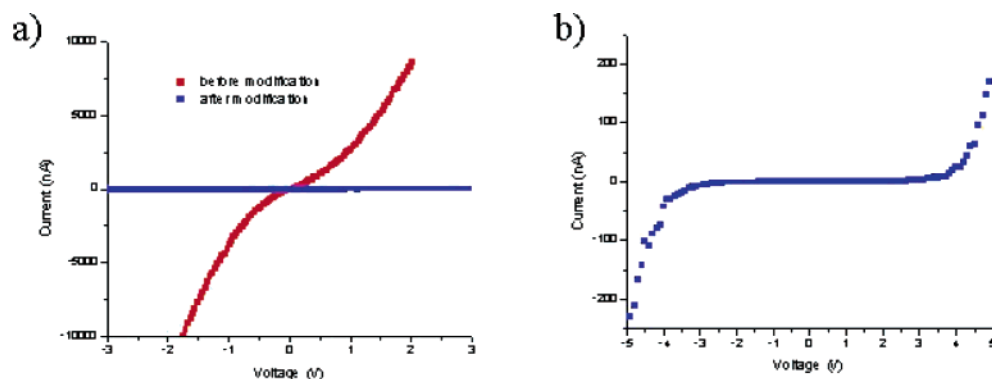


Figure 7. Source-drain current vs source-drain voltage (a) before and after modification for the device pictured in Figure 6. (b) Magnification of the after modification measurement.

decrease in the conductivity of the device and introduced a significant nonlinearity to the I – V curve. We believe that these observations are due to the introduction of a significant electron transport barrier into the nanowire structures.

Before the chemical etching, electronic transport behavior is more unpredictable. Typically, large reductions in current are observed, but sometimes current reduction is less obvious until after etching. This may be a result of the existence of conduction path within the oxide section which is then removed by the etching process. After removal of the gallium oxide layer, large current reduction is always observed. Interestingly, the reduction in current through etched devices may be much greater than what one would expect from a simple reduction in nanowire diameter. Though the observed height of the modified areas could depend on AFM tip convolution effects, we believe that the observed size of the modifications is an accurate depiction of their actual size. AFM tip convolution is most important for high aspect ratio structures, but the modifications do not have a particularly high aspect ratio, usually less than 0.15 (see Table 1). Furthermore, the AFM tip should be very sharp (<10 nm) and is much smaller than the length scale of lithography; any changes in height should be able to be resolved. Therefore, the changes in device conductivity are most likely due to some other phenomenon rather than diameter reduction, such as changes in the band structure or in the underlying crystal structure of the nanowire. We believe that the transport behavior of these devices strongly depends on the nature of the transport barriers, surface defect sites, GaN/gallium oxide band structure interactions, etc. We are currently studying these devices to determine the exact nature of the transport phenomena and to exploit these behaviors for the creation of devices with desirable electronic properties.

In conclusion, we have developed an AFM-lithography based methodology for fabrication of GaN/gallium oxide heterostructures and size-modulated GaN nanowire structures and devices. This technique uses E-DPN to electrochemically react prefabricated GaN nanowires via a reaction with tip-applied KOH “ink”. Furthermore, we have demonstrated that these unique heterostructures possess radically different electronic properties than the original GaN nanowires because the modification creates electronic transport barriers. Using this AFM-based methodology, it is easy to create many types of structures, including single-barrier and superlattice heterostructures, simply by moving the ink-coated AFM tip to desired locations and modifying the nanowire by applying an appropriate bias voltage for a desired length of time. In addition to the modification of GaN, this modification scheme should also be applicable for other semiconductor nanowires such as CdS or InP. This E-DPN modification scheme provides a convenient means to deliver chemicals to specific locations on an existing nanostructure to perform chemical and structural modification. We believe it will have broad applications in the creation of unique nanostructures/devices for the understanding of electronic transport in nanoscale junctions and size-modulated nanostructures.

Acknowledgment. This work is supported by Grant 49620-02-1-0188 from AFOSR. B.W.M. is a recipient of a Gates Millennium Scholarship. J.L. gratefully acknowledges the 2002 Young Professor Award from Dupont.

Supporting Information Available: Detailed experimental procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0317832