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2012 Nanotechnology 23 365203

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Nanotechnology 23 (2012) 365203 (10pp)

# Microstructure evolution and development of annealed Ni/Au contacts to GaN nanowires\*

# Andrew M Herrero, Paul T Blanchard, Aric Sanders, Matt D Brubaker, Norman A Sanford, Alexana Roshko and Kris A Bertness

Quantum Electronics and Photonics Division, National Institute of Standards and Technology, Boulder, CO, USA

E-mail: bertness@boulder.nist.gov

Received 30 April 2012, in final form 2 May 2012 Published 21 August 2012 Online at stacks.iop.org/Nano/23/365203

#### Abstract

The development of Ni/Au contacts to Mg-doped GaN nanowires (NWs) is examined. Unlike Ni/Au contacts to planar GaN, current–voltage (I-V) measurements of Mg-doped nanowire devices frequently exhibit a strong degradation after annealing in  $N_2/O_2$ . This degradation originates from the poor wetting behavior of Ni and Au on SiO<sub>2</sub> and the excessive void formation that occurs at the metal/NW and metal/oxide interfaces. The void formation can cause cracking and delamination of the metal film as well as reduce the contact area at the metal/NW interface, which increases the resistance. The morphology and composition of the annealed Ni/Au contacts on SiO<sub>2</sub> and the p-GaN films were investigated by scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS) and x-ray diffraction (XRD) measurements. Adhesion experiments were performed in order to determine the degree of adhesion of the Ni/Au films to the SiO2 as well as observe and analyze the morphology of the film's underside by SEM. Device degradation from annealing was prevented through the use of a specific adhesion layer of Ti/Al/Ni deposited prior to the nanowire dispersal and Ni/Au deposition. I-V measurements of NW devices fabricated using this adhesion layer showed a decrease in resistance after annealing, whereas all others showed an increase in resistance. Transmission electron microscopy (TEM) on a cross-section of a NW with Ni/Au contacts and a Ti/Al/Ni adhesion layer showed a lack of void formation at the contact/NW interface. Results of the XRD and TEM analysis of the NW contact structure using a Ti/Al/Ni adhesion layer suggests Al alloying of the Ni/Au contact increases the adhesion and stability of the metal film as well as prevents excessive void formation at the contact/NW interface.

(Some figures may appear in colour only in the online journal)

## 1. Introduction

GaN nanowires (NWs) are promising for a number of technical applications, including high-performance LEDs [1–3] and lasers [4, 5] as well as numerous other electronic device applications [6, 7]. Despite the significant increase in research on GaN nanowires that has occurred in the past decade, only a handful of articles have been published on p-GaN nanowires, of which, very little electrical characterization of isolated nanowires has been presented. When comparing the deposition and annealing of Ni/Au contacts on p-GaN films versus p-GaN nanowires, some significant challenges become apparent for p-GaN NWs. The standard Ohmic contact scheme for p-GaN films uses very thin layers (5–40 nm) of Ni and Au annealed at 400–600 °C in an oxidizing environment [8–15]. For NWs, a much thicker contact (>100 nm) is required in order to get a continuous metal film from the substrate and over the NW. The large increase in the thickness of these layers affects their behavior upon annealing. The most common procedure for characterizing

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the electrical properties of any NW material is to randomly disperse them onto an insulating substrate followed by photolithography of the contact pattern and the metal contact deposition. The insulating substrate most commonly used is a SiO<sub>2</sub> film on a Si wafer. We show that, upon annealing, the poor adhesion of the thicker Ni and Au to SiO<sub>2</sub> can cause severe cracking or delamination of the Ni/Au film from the substrate and that large voids form at the contact/NW interface. The poor adhesion and void formation frequently degrade the contact performance after annealing. To address both of these issues, the use of an adhesion layer with a specific composition is required. The addition of a Ti/Al/Ni layer is shown to improve adhesion and to reduce voids formation upon annealing.

## 2. Experimental procedure

The GaN nanowires were grown by catalyst-free molecular beam epitaxy (MBE) on Si(111) substrates. The details of the nanowire growth conditions were presented elsewhere [16]. To prepare NWs for dispersal, small pieces of the as-grown substrate are put in isopropanol and sonicated in order to remove the NWs from the substrate. The NW solution is then dispersed onto a SiO<sub>2</sub>/Si wafer. Once the isopropanol has evaporated, the SiO<sub>2</sub>/Si wafer is gently dipped in successive baths of acetone and isopropanol to remove unwanted impurities, followed by a rinse in deionized water and blown dry in N<sub>2</sub>. Standard photolithographic techniques were used to create the contact pattern. The patterned wafer is given a 5-10 min UV ozone treatment followed by a 1 min HCl:H<sub>2</sub>O (1:10) dip prior to loading it into the electron-beam evaporator for metal deposition. The thickness of the Ni films was held constant at 50 nm, while the thickness of the Au layer was varied from 50 nm to 150 nm. Unless stated otherwise, all Ni/Au films used in this study were annealed under UHP  $N_2/O_2$  (3:1) at 550 °C for 10 min. In the adhesion experiments, carbon tape was used to peel off the Ni/Au films from the SiO<sub>2</sub> substrate for NW device samples that were already tested and imaged. The carbon tape with the peeled film was then mounted and imaged in the SEM. Imaging of the NWs was done using a field-emission scanning electron microscopy (FESEM). A different SEM was used for the EDS measurements. XRD measurements were performed using a materials research triple-axis diffractometer. TEM cross-sections were prepared using a focused ion beam (FIB) tool, and images were taken with a conventional 200 kV TEM with a LaB6 filament. The resistance was extracted from I-Vmeasurements taken with a semiconductor characterization probe station. I-V measurements were performed on single homogeneous NWs from the same growth run. The I-Vmeasurements are representative of those taken for at least 10 NWs for each different device structure. The contact resistivity of the p-GaN films was determined by means of the circular transmission line method (CTLM).

### 3. Results

Our experiments show that the poor adhesion of Ni and Au to  $SiO_2$  can cause severe cracking or delamination of the Ni/Au



**Figure 1.** Effects of poor adhesion of Ni/Au on SiO<sub>2</sub>: (a) micro-cracks in Ni/Au (50/100 nm) (b) Large cracks in Ni/Au (50/150 nm) causing the NW to pop off. (c) Large-scale delamination of Ni/Au (50/50 nm) film from a SiO<sub>2</sub> surface.

film from the substrate when annealed in  $N_2/O_2$ , as shown in figure 1. Very often, micro-cracks, such as the ones shown in figure 1(a), will form in the Ni/Au film but will go unnoticed due to their small size and the roughened morphology of the Ni/Au surface. Larger cracks, such as the ones in figure 1(b), can have a much more direct effect on the NWs. Stress from the Ni/Au film has caused the NW to break free from the metal and pop off. In severe cases, there is large-scale delamination of the Ni/Au film from the SiO<sub>2</sub> surface. An example of this is shown in figure 1(c). Sometimes this delamination can be observed by the naked eye.



**Figure 2.** (a) SEM image of the Ni/Au contact pad edge after annealing. (b) SEM image of the underside of the Ni/Au film shown in (a) after removal with carbon tape. (c) Magnified view of the underside of the annealed Ni/Au film. (d) EDS of the annealed Ni/Au film underside. (e) Illustration of the cross-section of Ni/Au on SiO<sub>2</sub> after annealing.

Adhesion experiments were performed that removed the Ni/Au films from the SiO<sub>2</sub> substrate in order to image the underside morphology. In figure 2(a), the top surface of a Ni/Au contact on SiO<sub>2</sub> after annealing is shown. Figure 2(b) shows the underside of the same area of that particular Ni/Au film after removal with carbon tape. The dark spots on the surface of the Ni/Au in (a) coincide with the dark features on the underside of the film seen in (b). The dark spots seen in (a) are normally observed on the surface of an annealed Ni/Au film deposited on p-GaN or SiO<sub>2</sub>. They are typically identified as a region of NiO surrounded by the lighter Au matrix [17]. In figure 2(c), the magnified view of the Ni/Au underside shows the critical features of the Ni/Au morphology. Under closer inspection, it is apparent that the dark features observed on the surface correspond to holes in the underlying Au-rich

layer and not necessarily to a difference in composition of the topmost layer. EDS measurements of the film underside, shown in figure 2(d), were done in order to determine the composition of the different features of the underside morphology. The EDS scans corroborate that the dark features are gaps in the Au-rich matrix layer, which exposes the top NiO layer and appear darker due to a change in contrast from the lack of material directly underneath. The most significant observation made after imaging the Ni/Au underside was the extensive voiding that had occurred in the Au layer adjacent to the SiO<sub>2</sub>. From the SEM and EDS of the underside of the annealed Ni/Au film, the general structure of the Ni/Au film on SiO<sub>2</sub> after annealing can be described with the illustration shown in figure 2(e). The illustration shows that mostly all of the Ni has diffused to the surface and formed NiO. The



**Figure 3.** SEM images of the underside of Ni/Au films deposited onto NWs dispersed onto  $SiO_2/Si$  substrates after being removed with carbon tape. (a) NW within the as-deposited Ni/Au film. (b) NW within the Ni/Au film after annealing. (c) Area where NW had been within the annealed Ni/Au film before dislodging. (d) A similar area to (c) before being subjected to aqua regia. (e) Same location in (d) after etching with aqua regia. (f) Illustrations of Ni/Au contact structure on a NW dispersed on SiO<sub>2</sub> before and after annealing in N<sub>2</sub>/O<sub>2</sub> ambient.

underlying layer is a gold-rich network with large voided regions. In addition to the poor adhesion of Au to  $SiO_2$ , the voided regions reduce the amount of metal/SiO<sub>2</sub> interface area, which further promotes cracking and delamination of the Ni/Au film.

The degree of voiding that had occurred at the Au/SiO<sub>2</sub> interface was unexpected and warranted further investigation due to the potential negative impact on making contacts to the NWs. An SEM image of a NW embedded in the as-deposited Ni/Au film that was removed with carbon tape is shown in figure 3(a). From the image, it is apparent that the Ni/Au/SiO<sub>2</sub> interface is extremely smooth before the contact anneal. Despite the smooth interface, the adhesion of the Ni/Au film to the SiO<sub>2</sub> surface was very poor. The red arrows in the picture point to the small gaps on either side of the NW. This is due to shadowing during the metal deposition. In figure 3(b), a similar NW embedded in a Ni/Au film after annealing is shown. The red arrows in the picture point to the new material that has filled in the gap around the NW. Figure 3(c) shows the underside of a Ni/Au film where a NW had been before it became dislodged when peeling the Ni/Au film off of the substrate. Within the trench where the NW had been, it can be seen that the Au layer did not uniformly contact the NW. Thus the voided regions that were created over the SiO<sub>2</sub> substrate are also produced in the specific area that is in contact with the NW. In order to help determine the composition of the underside morphology directly around the NW, etching experiments were performed that used aqua regia (HNO<sub>3</sub>:HCl:H<sub>2</sub>O = 1:3:1) to selectively etch the Au over the Ni. Figure 3(d) shows a similar spot to (c) where a NW had been before etching with aqua regia. The red arrows in figure 3(d) point to the areas of Au-rich material. In figure 3(e), the same area in (d) is shown after a few seconds of etching with aqua regia. Most of the Au-rich material was

etched away, leaving only the top NiO layer and the material that grew during annealing. This suggests that the newly formed material was NiO. The red arrows in figure 3(e) point to the areas that are NiO. The uniform etch of the Au-rich material shows that very little Ni-Au alloying has occurred and that most of the Ni has formed NiO on the surface, which was to be expected based on the literature [8-15]. Based on the results of the adhesion and etching experiments, we propose a model for the microstructure of the annealed Ni/Au contacts to GaN nanowires dispersed on SiO<sub>2</sub> as well as the mechanism that leads to device degradation. As illustrated in figure 3(f), upon annealing, most of the Ni has diffused through the Au to the surface to react with oxygen and form NiO, leaving voided areas at the metal/SiO<sub>2</sub> interface that make the film susceptible to cracking and delamination. The voided regions formed at the metal/NW interface decrease the NW contact area, resulting in an increase in resistance and possibly non-Ohmic behavior.

To address the issues of void formation and poor adhesion of the Ni/Au contacts deposited on SiO2, the use of an adhesion layer was investigated. The adhesion layer would need to be deposited on the SiO<sub>2</sub> prior to the NW dispersal and be patterned exactly like Ni/Au contacts. Figure 4 shows how the surface roughening of the Ni/Au on the SiO<sub>2</sub> and adhesion layers directly affects the Ni/Au areas that are in direct contact with the NW. Figure 4(a) shows the morphology of the Ni/Au layers deposited on a randomly dispersed NW on SiO<sub>2</sub> prior to annealing. The Ni/Au layers have a fine grain size and conform to the shape of the NW such that the outline of the NW and its faceted sides are clearly seen. In figure 4(b), the same contact after being annealed is very rough, and the outline of the NW is no longer well defined. The surface has a ridge-like morphology with significantly larger grains, which is typical of NiO at these temperatures [18]. The



**Figure 4.** SEM images of similar NWs with the same Ni/Au thicknesses deposited on different substrates. (a) As-deposited Ni/Au contact for a NW device on a SiO<sub>2</sub> substrate. (b) Same NW as in (a) after  $N_2/O_2$  annealing. Ni/Au contact on NWs deposited on (c) Ti/Ni and (d) Ti/Al/Ni adhesion layers after annealing under the same conditions as in (b).

adhesion layers studied were all Ti-based. Ti is normally used as an adhesion layer for Au and other metals when they are deposited on SiO2. All annealed Ni/Au films that were deposited on any Ti-based adhesion layer could not be removed with carbon tape and exhibited excellent adhesion to the adhesion layer and substrate. The use of a Ti-based adhesion layer resolved the delamination issue for the contact scheme in this study. One concern for p-type GaN NWs is that Ti may react with GaN, forming TiN at the GaN surface, which creates N vacancies that are n-type defects [19, 20]. In order to avoid any possible reactions of Ti with the GaN NW surface, a layer of Ni was deposited over the Ti. Figure 4(c) shows the Ni/Au morphology on a Ti/Ni (10/50 nm) adhesion layer after annealing. Although the NiO grain size is not as large as that shown in figure 4(b), there is a significant amount of large-scale roughening of the metal film, which may be due to void formation. Despite this surface roughening, the Ni/Au film had excellent adhesion to the Ti/Ni adhesion layer. Another contact scheme that was investigated for use as an adhesion layer was Ti/Al/Ni (10/100/50 nm). The top Ni layer was still needed in order to prevent excessive oxidation of the Al prior to the Ni/Au deposition and to avoid any unwanted reactions between the Al and the GaN NW. The image in figure 4(d) shows that the roughening of the Ni/Au after being annealed on a Ti/Al/Ni adhesion layer is minimal, and the grain size, which is difficult to discern in the image, remained small. The Ni/Au directly on the NW has roughened some, so that the outline of the NW is not as well defined, but it remains particularly smooth and conforms well to the NW. The morphology of the as-deposited Ni/Au layers on both adhesion layers is the same as that shown in figure 4(a). From figures 4(b)-(d), it can clearly be seen that even though the same Ni/Au contacts were deposited on similar NWs and annealed under the same conditions, their resulting morphology is quite different. This demonstrates that the behavior of the Ni/Au film directly in contact with the NW strongly depends on its behavior at the underlying substrate.

Electrical characterization of Mg-doped GaN NWs has proved challenging due to the NW dimensions and the difficulty in achieving a high hole concentration. The low hole concentration produces a large depletion layer on the surface, and due to the small diameter of the NW, a significant amount of the NW volume will be depleted of carriers. I-Vmeasurements of Mg-doped GaN NWs show that they are particularly resistive and produce non-Ohmic curves both before and after annealing. This has made it difficult to do a quantitative analysis of the electrical properties of Mg-doped GaN NW devices. Therefore, well-characterized n-type GaN nanowires were processed and tested alongside of the Mg-doped GaN nanowires in order to assist in evaluating the effect of the different adhesion layers. Both Mg-doped and n-GaN NW devices fabricated using Ni/Au contacts on SiO<sub>2</sub> showed an increase in resistance after annealing. Both also showed an increase in resistance when using a Ni/Au contact on a Ti/Ni adhesion layer after annealing. As seen in figure 4(c), the large-scale roughening of the Ni/Au film on a Ti/Ni adhesion layer, which is suspected of being caused by excessive void formation, appears to have a detrimental effect on the NW contact properties. In contrast, NW devices fabricated using a Ni/Au film on a Ti/Al/Ni adhesion layer showed significantly decreased resistance after annealing. The decrease in resistance for both n- and p-type GaN NWs suggests that the mechanism responsible is mechanical rather than chemical or electrical. Figure 5(a) illustrates the contact geometry for a NW using a Ti/Al/Ni adhesion layer. The NiO layer shown at the interface between the Ni/Au and the adhesion layer is assumed to have formed due to exposure to air during processing. Figure 5(b) shows typical I-V curves for n-type GaN NWs both before and after the contact anneal, for contacts with and without an adhesion layer. Before the contact anneal, the majority of the I-V curves for the as-deposited Ni/Au contacts with and without an adhesion layer are very similar, being highly resistive and displaying an asymmetry.

Due to their high resistivity, the specific effect of the addition of Al to the Ni/Au contacts on the Mg-doped GaN NWs is unclear, making it difficult to separate the NW resistance from the contact resistance. In order to help determine what effects Al may have on the contacts to Mg-doped NWs, a specific metal scheme of Ni/Au with a layer of Al was deposited onto p-GaN films. Because it is not possible to exactly replicate the contact geometry used for a NW sandwiched between two metal layers, the aim of this experiment was to examine the electrical properties of annealed Ni/Au with Al with respect to making contact to p-GaN material. Figure 6(a) shows the metal scheme that made up the test structure. The I-V curves of the Ni/Au and Ni/Au:Al contacts on the p-GaN films before and after annealing in N<sub>2</sub>/O<sub>2</sub> are shown in figure 6(b). The



**Figure 5.** (a) Illustration of Ni/Au contact structure on a NW dispersed on SiO<sub>2</sub> using an adhesion layer. (b) Typical I-V measurements for n-type GaN NWs before contact annealing and after contact annealing with and without an adhesion layer.



Figure 6. (a)Test structure made to investigate the effect of Al on Ni/Au contacts. (b) I-V measurements of the Ni/Au and Ni/Au:Al contacts before and after annealing in N<sub>2</sub>/O<sub>2</sub>.

as-deposited *I–V* curve for the Ni/Au and Ni/Au:Al contacts was approximately the same, and thus is represented by one curve in figure 6 for the sake of simplicity. As shown in figure 6(b), there is a significant decrease in the resistance for both contacts after annealing, but the decrease in resistance for the Ni/Au:Al contact is not as large as that for the contact without Al. The effective contact resistivity was determined for both contacts using the linear portion of their curves and was calculated to be 6.8 and  $4.1 \times 10^{-2} \Omega$  cm<sup>2</sup> for the Ni/Au contacts, with and without Al. The smaller decrease in resistance for the Ni/Au:Al contact could possibly be explained using the XRD results presented in section 4.

In order to determine the change in the Ni/Au structure and composition after annealing, XRD measurements were made on the same Ni/Au film deposited on three different substrates. For each sample,  $\omega$ -rocking curves of the Au(111) were taken before annealing and after annealing two successive times. Each anneal was performed at standard conditions, including time. In figure 7, the scans for each are compared in order to determine the change in crystallinity of the Au film due to annealing. As can be seen in figures 7(a) and (b), the Ni/Au film on both the p-GaN and SiO<sub>2</sub> substrates shows an increase in the Au(111) peak intensity after annealing, which indicates an increase in the size of the Au(111) grains and agglomeration of the Au during the anneal. Due to the relative change in the intensity, it is also evident that the degree of Au agglomeration is much greater on the SiO<sub>2</sub> substrate compared to the p-GaN film. This is most likely due to the difference in the as-deposited condition of the Ni/Au on the SiO<sub>2</sub> versus the p-GaN. The amorphous nature of the SiO<sub>2</sub> and the low-temperature and low-energy deposition via e-beam evaporation caused the growth of a very polycrystalline and poorly textured Ni/Au film. This is apparent in the much lower peak intensity of the as-deposited Au(111) peak on SiO<sub>2</sub> versus the p-GaN film. Since the Ni/Au film on SiO<sub>2</sub> started with a much less textured structure, the effect on the peak intensity of the agglomeration and grain growth of the Au from annealing is much more significant. The same mechanisms that cause void formation in Ni/Au films on p-GaN are enhanced when Ni/Au is deposited on SiO<sub>2</sub>, due to the particularly poor wetting behavior of Ni and Au on SiO<sub>2</sub>.



**Figure 7.**  $\omega$ -rocking curve of Au(111) peak for Ni/Au (50/150 nm) films deposited on (a) p-GaN, (b) SiO<sub>2</sub>, (c) Ti/Al/Ni/SiO<sub>2</sub> before and after annealing twice. (d)  $\omega/2\theta$  scan of Au(111) for Ni/Au (50/150 nm) film on Ti/Al/Ni before and after annealing twice.

The Ni/Au film deposited on the Ti/Al/Ni adhesion layer shows the opposite behavior after annealing. The significant decrease of the Au(111) peak intensity after annealing indicates that either the Au film became more randomly oriented or that it formed a new phase through alloying. Figure 7(d) shows the  $\omega/2\theta$  of Au(111) for a Ni/Au film deposited on Ti/Al/Ni after two successive anneals. The color coding for the scans and peak labels are the same as in figures 7(a)–(c). The increase in the number of peaks after each anneal is indicative of the formation of new phases from the heat treatment. Phase diagrams predict the formation of several different intermetallic compounds for Au–Al and Ni–Al interactions in the temperature range used for the contact anneal. The new peaks correspond to Au–Al and Ni–Al alloys, as labeled in figure 7(d).

Because the contact/NW interface cannot be directly observed by removing of the metal layer with carbon tape, a TEM cross-section was made of a typical n-GaN NW with Ni/Au (50/100 nm) contacts and a Ti/Al/Ni adhesion layer. The NW chosen had decreased its resistance by half after annealing. In order to observe the condition of the contact/NW interface around the whole of the NW, different regions of the same NW were thinned. Figure 8 shows the longitudinal TEM cross-sections made from the different regions. Figure 8(c) illustrates the contact/NW/adhesion layer structure after annealing and the approximate location on the NW from where the cross-sections were made. Due to the tilt of the NW lamellae during thinning, the outlines of the cross-sections in figure 8(c) are slightly tilted in order to illustrate the actual area that they were taken from. Figure 8(a)

is a cross-section made directly from the center of the NW and shows the contact/NW interface of the top facet of the NW. Identification of the different layers is based on the extensive TEM analysis of similar structures reported in the literature [9–15]. The typical microstructure of annealed Ni/Au contacts on GaN is shown, where layer reversal has occurred by Ni diffusing to the surface to form NiO and the Au diffusing down to the GaN surface. It can be seen that no void formation occurs at the top interface between the Au and the NW and that Au layer is made of large grains with no evidence of alloying occurring. The adhesion layer under the NW appears to be made up of multiple phases, which were seen in the XRD scan. In the image shown in figure 8(a), the adhesion layer has started to become detached from the NW, which occurred upon removal of the cross-section from the substrate during sample preparation. The formation of a distinct layer can be seen at this interface, which is most likely a Ni-Al-O oxide due to the similarity in grain size and structure to those of NiO and the large affinity for Ni and Al to react with oxygen. Figure 8(b) shows the cross-section made along the side of the NW. This section was prepared by carefully thinning only the NW side until the cross-section became electron transparent. Due to the thinness of the cross-section, some external damage that can be seen in the image was not removed, out of concern for possibly destroying the delicate sample. By using this approach, the contact/NW interface along the side of the NW becomes observable, showing the lack of any void formation. Figures 8(d) and (e) are close-ups of the contact/NW and NW/adhesion layer interfaces, respectively, of the cross-section shown in figure 8(a).



**Figure 8.** (a), (b) Bright-field TEM cross-sections of annealed Ni/Au/NW/adhesion layer/SiO<sub>2</sub> contact structure. (c) Illustration of the approximate location where the cross-section was made for (a) and (b). (d) Close-up of contact/NW interface shown in (a). (e) Close-up of NW/adhesion layer interface shown in (a).

## 4. Discussion

Void formation has been seen for Ni/Au contacts annealed on p-GaN films [9–13]. A major cause of the void formation for Ni/Au contacts on p-GaN and SiO<sub>2</sub> is most likely due to the Kirkendall effect, which occurs when two solids diffuse into each other at different rates. The diffusion of Ni to the surface is much faster than the diffusion of Au down towards the SiO<sub>2</sub>. The faster diffusion rate of Ni produces an overall net flow of matter towards the surface. Since diffusion occurs via a vacancy mechanism, there will be an equally large net flow of vacancies in the opposite direction. The vacancies condense to form pores, which produce voided regions at the Au/SiO<sub>2</sub> and Au/NW interfaces, as were seen in figures 2 and 3. Another contributing factor is the agglomeration of the thick Au layer apparent in the  $\omega$ -rocking curves of the Au(111) on both p-GaN and SiO<sub>2</sub> films. The recrystallization and grain growth of Au occurs in order to minimize the total free energy of the system by reducing the total number of grain boundaries. As the Au starts to cluster, so do the voided regions, resulting in large areas that are not in contact with the SiO<sub>2</sub> and NW surface. Due to the poor wetting of Ni and Au to  $SiO_2$ , growth of the voided regions is exacerbated by the Au agglomeration, which can lead to large-scale cracking and delamination of the Ni/Au film from the SiO<sub>2</sub>. Since little to no Ni-Au alloying has occurred, which was evident from the etching experiments, there was no hindering of Au

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grain growth or NiO formation responsible for void formation. Thus, even though the Au is brought into contact with the p-GaN NW surface, the increased voided regions decrease the NW contact area resulting in an increase in resistance.

The use of a Ti-based adhesion layer for Ni/Au contacts on SiO<sub>2</sub> resolves the poor adhesion issue, most likely due to Ti reacting with the SiO<sub>2</sub> to form TiO<sub>2</sub>. Although the use of an adhesion layer prevents excessive cracking and delamination of the Ni/Au film from the substrate, it does not necessarily address the issue of void formation, as seen when a Ti/Ni adhesion layer is used. Alternatively, when a Ti/Al/Ni adhesion layer is used, there is a significant difference in the surface morphology and contact properties of the annealed Ni/Au films. The decrease in the resistance of both n- and p-type NW devices fabricated on SiO<sub>2</sub> with a Ti/Al/Ni adhesion layer compared to those without one, supports the hypothesis that a change in contact area is the source for device degradation from annealing in the absence of an adhesion layer. The role that Al plays on inhibiting the excessive agglomeration of the Au layer during the heat treatment is most likely due to the similarity of silver (Ag) and Au; both are noble metals with a low modulus of elasticity. Like Au, Ag also has a problem with agglomeration during heat treatment. It has been reported that the addition of Al to the Ag prevents its agglomeration when heated [21–23]. It was shown that even at very small amounts (few at.%) of Al completely prevent agglomeration of Ag films on SiO<sub>2</sub> [21]. Although the solubility of Ni and Au in Al is very limited, Al is quite soluble in both of them (up to 6–10 at.%) at low temperatures. In particular, the solubility of Al in Ni has been reported to be up to 10 at.% at room temperature [24]. This suggests that the dominant interaction between the metals during annealing was the one-way diffusion of Al into Ni and Au. The excess Ni and Au available to react with Al would lead to formation of Ni and Au-rich Al alloys, which is consistent with the peak identification shown in figure 7(d).

The use of Al in the adhesion layer brings up an issue of concern, which is similar to the issue mentioned earlier about using Ti. Due to the solubility of Al in Ni and Au and the alloy formation seen in the XRD, there is the potential for Al to have diffused to the GaN NW surface and react to form AlN. Al has been shown to react with GaN to form a thin AlN layer at temperatures near those used for annealing in this study [25, 26]. The formation of an AlN layer at the contact/NW interface would produce nitrogen vacancies that would increase the electron concentration at the NW interface. The increased electron concentration would be detrimental to p-GaN by compensating holes and bringing down the p-type carrier concentration. Also, since AlN has a larger bandgap than GaN, the AlN layer should lead to an increase in the barrier height. The formation of an interfacial AlN layer could possibly explain the smaller decrease in resistance for the Ni/Au contact with Al compared to the Ni/Au contact without any Al on p-GaN films seen in figure 6(b). For n-GaN material, the effect of the formation of an interfacial AIN layer is more ambiguous, due to the competing mechanisms of the increased electron concentration and the wider bandgap of AlN. From the TEM images of the n-GaN NW shown in figure 8, there is no evidence to suggest that Al has diffused to the contact/NW interface or that AlN has formed. In figure 8(d), there is no interfacial layer at the Au/NW interface and no indication of Au alloying. Also, the observation of what is most likely a Ni-Al-O layer forming between the NW and the adhesion layer, seen in figure 8(e), would inhibit the Al from diffusing to the NW surface, particularly during a high-temperature anneal in an oxidizing environment. Thus, the issue of Al potentially having a negative effect on the contact properties appears to not be applicable to the NW contact geometry used in this study.

Based on the previous work done with Al and Ag, the solubility analysis and the data presented here, the most probable mechanism for the decreased resistance from using a Ti/Al/Ni adhesion layer is due to the interaction of Al with the Ni and Au. Diffusion of Al into the Ni and Au leads to the formation of Au–Al and Ni–Al intermetallic compounds, which increases the bonding strength between the films. The intermetallic compounds hinder the rapid diffusion of Ni and Au, which suppresses the formation of NiO and the agglomeration and grain growth of Au, leading to a significant decrease in void formation. The increase in the large-scale stability of the metal films on SiO<sub>2</sub> after annealing prevents stress and strain from locally deforming the contact/NW structure. For the annealed Ni/Au that is in direct contact with the NW, no alloying with Al is evident, and it appears

that there has been some growth of the Au grains. Despite both of these occurrences, no void formation is evident. A possible explanation could be that alloying of the Ni with Al reduces the amount of Ni that diffuses through the Au to the surface to form NiO, thereby minimizing the void formation within the Au layer. An observation that supports this is that the NiO layer formed on top of the Au/NW interface is thinner than expected for the 50 nm of Ni deposited, especially considering that the volume of the Ni layer is supposed to increase by over 50% upon transforming into NiO [27]. Also, the Au grain boundaries are very narrow and show little NiO formation.

#### 5. Conclusion

The post-anneal degradation of the electrical properties of Ni/Au contacts to GaN NWs randomly dispersed on SiO<sub>2</sub> was examined and shown to originate from (a) the poor adhesion of Ni and Au on SiO<sub>2</sub>, and (b) their diffusion behavior, which results in interfacial void formation along with cracking and delamination of the Ni/Au film. By removing the Ni/Au film from the SiO<sub>2</sub> substrate with carbon tape, SEM and EDS were used to observe and determine the composition of the different features of the underside morphology. Although the desired layer reversal of the Ni and Au did occur, the excessive void formation at the metal/SiO2 and contact/NW interfaces is thought to have led to a decrease in the NW contact area, which produced an increase in resistance after annealing. Use of different Ti-based adhesion layers prior to the nanowire dispersal and Ni/Au deposition eliminated the delamination of the Ni/Au films after annealing, yet some degradation in the I-V response of the nanowires still occurred. XRD measurements of the Ni/Au layers before and after annealing on p-GaN films and SiO<sub>2</sub> with and without an adhesion layer showed that the phase formation and evolution of the crystallinity of the metal films are dependent on the substrate material. The key to preventing degradation during annealing was the use of an adhesion layer that included Al. The alloy formation of Al with Ni and Au seen in the XRD scans inhibits the mechanisms that are responsible for the void formation. The lack of void formation at the contact/NW interface after annealing when a Ti/Al/Ni adhesion layer is used was confirmed using TEM. The resulting increase in the contact area to the NW surface is believed to be responsible for the large decrease in resistance.

#### Acknowledgments

The authors thank Professor Fatemeh (Shadi) Shahedipour-Sandvik from the University of Albany for providing the p-GaN films used in this study and Ann Chiaramonti of NIST for capturing the TEM images shown.

#### Disclaimer

Any reference to specific vendors or products does not constitute an endorsement by the National Institute of Standards and Technology.

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