Video Article

Analysis of Contact Interfaces for Single GaN Nanowire Devices

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Abstract

Single GaN nanowire (NW) devices fabricated on SiO_2 can exhibit a strong degradation after annealing due to the occurrence of void formation at the contact/SiO_2 interface. This void formation can cause cracking and delamination of the metal film, which can increase the resistance or lead to a complete failure of the NW device. In order to address issues associated with void formation, a technique was developed that removes Ni/Au contact metal films from the substrates to allow for the examination and characterization of the contact/substrate and contact/NW interfaces of single GaN NW devices. This procedure determines the degree of adhesion of the contact films to the substrate and NWs and allows for the characterization of the morphology and composition of the contact interface with the substrate and nanowires. This technique is also useful for assessing the amount of residual contamination that remains from the NW suspension and from photolithographic processes on the NW-SiO_2 surface prior to metal deposition. The detailed steps of this procedure are presented for the removal of annealed Ni/Au contacts to Mg-doped GaN NWs on a SiO_2 substrate.

Video Link

The video component of this article can be found at https://www.jove.com/video/50738/

Introduction

Single-NW devices are made by dispersing a NW suspension onto an insulating substrate and forming contact pads on the substrate via conventional photolithography and metal deposition, which results in randomly formed two-terminal devices. A thick SiO_2 film on a Si wafer is typically used as an insulating substrate[1,2]. For metals deposited on a SiO_2 surface, a common problem resulting from heat treatment is the occurrence of void formation at the metal/SiO_2 interface. In addition to cracking and delamination of the metal film, this void formation can negatively affect device performance from an increase in resistance caused by a reduction of the contact area. Ni/Au contacts oxidized in N_2/O_2 atmospheres are the predominant contact scheme applied to p-GaN[3-7]. During heat treatment in a N_2/O_2, the Ni diffuses to the surface to form NiO and the Au diffuses down to the substrate surface.

In this work, excessive void formation at the contact/NW and contact/SiO_2 interfaces was shown to occur during annealing of Ni/Au contacts to NWs on SiO_2[8]. The surface morphology of the annealed Ni/Au film, however, does not indicate the existence of voids or the degree to which void formation has occurred. To address this problem, we developed a technique for the removal of Ni/Au contacts and GaN NWs from SiO_2/Si substrates in order to analyze the interface of the contact with the substrate and NWs. This technique can be used for the removal of any contact structure that has poor adhesion to the substrate. The Ni/Au films with GaN NWs embedded in them are removed from the SiO_2 substrate with carbon tape. The carbon tape is adhered to a standard pin mount for characterization by use of scanning electron microscopy (SEM) along with several other tools. The detailed procedure for the fabrication of single GaN NW devices and analysis of their contact interface morphology are described.

Protocol

The GaN NWs used in these experiments were grown by catalyst-free molecular beam epitaxy (MBE) on Si(111) substrates[9]. The general procedure for preparing the NW suspension from the substrate with the as-grown NWs is illustrated in **Figure 1**.

1. Nanowire Suspension Preparation

1. Cleave a small (<5 mm x 5 mm) piece of the as-grown NWs on the substrate.
2. Fill a small capped vial with about 1 ml of isopropanol (IPA).
3. Place the cleaved piece into the vial, close the cap and sonicate for about 30 sec in order to remove the NWs from the substrate. Once prepared, the NW suspension remains viable for an extended period of time.

2. Substrate Preparation

The substrates used are heavily-doped (ρ ~0.001-0.005 Ω-cm) 3-inch Si wafers with 200 nm of thermally-grown SiO_2 on both sides.

1. If electrical contact to the silicon substrate is desired, etch off the oxide from the backside of the wafer using an RIE etcher with the following conditions, O_2 flow = 20 sccm, CHF_3 flow = 50 sccm, -240 V bias, 120 W for 20 min. This step also helps avoid charging of the specimen during electron microscopy.
2. After oxide etch, clean wafer by submersing it face down using a tripod holder into a 1,000 ml beaker with ~100 ml of acetone for 5 min.
3. Remove wafer from acetone and immediately rinse off both sides of the wafer using a squirt bottle of IPA over an empty 1,000 ml beaker, which will be used for solvent waste.
4. Repeat step 2 using IPA.
5. Repeat step 3 rinsing the wafer with deionized H_2O over the solvent waste beaker.
6. Repeat step 2 using deionized H_2O.
7. Blow wafer dry using compressed dry N_2.

3. Nanowire Dispersal

1. Cleave the clean wafer into 4 equal quarters. Each quarter will have 3 contact patterns deposited on it in the general areas shown in **Figures 2A** and **B**.
2. Sonicate the vial of NW suspension prior to dispensing in order to get a uniform NW concentration in the suspension.
3. Set the micropipette to the desired drop size (3-30 µl) and draw the NW suspension from the vial.
4. Take substrate piece (¼ wafer) that will be used for dispersal and ensure that it is level so that the NW suspension does not migrate away to the edges.
5. Dispense the NW suspension onto the (oxidized) front surface of the Si substrate in the general area where the contact pattern will be deposited. If desired, deposit additional drops of the NW suspension in the same area, after the solvent from the previous drop has completely evaporated.
6. Repeat step 3.4 for the other 2 areas where a contact pattern will be. Do not dispense the NW suspension from more than 1 growth run on a single substrate piece (¼ wafer) in order to avoid cross contamination. The dispersal of the NW suspension onto the substrate is illustrated in **Figures 2C** and **D**.
7. After the final drop of NW suspension has evaporated, place the sample face down in a tripod holder and gently dip in successive baths of acetone and isopropanol to remove unwanted impurities. Rinse in deionized H_2O, and blow dry in N_2. Do not use squirt bottles or sonicate the solvent during this cleaning process to avoid excess removal of NWs from the surface.

4. Photolithography of Contact Pattern

Use standard photolithographic techniques to create the contact pattern in a clean room with ambient conditions of ~20 °C and ~40% relative humidity. Mask aligner intensity (step 4.6), exposure time (step 4.8) and develop time (step 4.9) will be equipment-dependent and should be adjusted to produce maximum pattern definition with a lift-off-resist (LOR) undercut of about 0.5 µm.

1. Spin lift-off resist onto sample using a two step recipe of (1) 300 rpm for 10 sec (2) 2,000 rpm for 45 sec.
2. Place sample on a hot plate to bake for 5 min at 150-170 °C.
3. Remove sample and allow to cool for 30 sec and then spin on photoresist using a two step recipe of (1) 1,000 rpm for 3 sec (2) at 5,000 rpm for 45 sec.
4. Place sample on a hot plate to bake for 1 min at 115 °C.
5. Allow sample to cool for 1 min.
6. Calibrate mask aligner to a light intensity of ~1.90 mW/cm^2.
7. Load sample into mask aligner, with the proper mask for the contact pattern installed.
8. Bring sample into contact with mask and expose the sample for 24 sec.
9. Develop photoresist by swirling sample in a beaker of developer for 21 sec.
10. Rinse with deionized H_2O and blow dry with N_2.

5. Sample Pretreatment Prior to Metal Deposition

Prior to loading the samples into the electron-beam evaporator for metal deposition, give the patterned wafer a UV ozone treatment and a HCl:H_2O bath.

1. Load samples into UV Ozone generator for 10 min with an ultra-high-purity O_2 flow rate of 80 sccm.
2. After UV ozone treatment, place samples in a HCl:H_2O (1:10) solution for 1 min at room temperature.
3. Rinse samples with deionized H_2O and blow dry gently with N_2.

6. Electron-beam Evaporation of Contact Metals

1. Immediately after pretreatment, mount the samples to the platen using screws and clips and secure platen in the e-beam evaporator. Make sure that sufficient Ni and Au are available for deposition.
2. Pump down chamber until the pressure is below 1.3×10^{-3} Pa (1 µTorr) (may require to pump overnight).
3. Set high voltage to 10 kV and begin rotation of samples at 5 rpm. Make sure shutter is closed.
4. Select the Ni crucible and enter parameters for Ni into the crystal rate monitor. Deposit 50 nm (500 #) of Ni at a deposition rate of ~0.1 nm/s.

5. Once Ni source has sufficiently cooled down (~15 min), switch to Au crucible, change the parameters to those for Au, and deposit 100 nm (1,000 #) of Au at a deposition rate of ~0.1 nm/sec.
6. Once Au crucible has cooled down (~10 min), vent chamber and unload sample platen. If unsure of metal thickness, use a profilometer to determine the Ni/Au thickness.

7. Contact Metal Lift-off

1. Remove samples from platen and place in a photoresist stripper bath at room temperature for a few hours to lift off the metal deposited on the photoresist. If desired, elevate the bath temperature to around 50-60 °C to accelerate lift-off.
2. If the metal does not come off completely, use a squirt bottle of Remover PG to forcefully remove the remaining undesired metal from the surface. Do not sonicate the sample because this can cause the nanowires to break free from the metal.
3. Rinse off the Remover PG from sample with IPA into a solvent waste beaker and place sample into a beaker of clean IPA.
4. Repeat step 7.3 using deionized H_2O and then blow the sample dry using N_2.

8. Contact Anneal

Test devices before the contact anneal in order to compare these with annealed devices. Perform the contact anneal of the Ni/Au films using a rapid thermal annealer (RTA) with ultra-high-purity N_2/O_2 (3:1) as the process gas.

1. Wait at least 24 hr after removal of contact metal before annealing samples, to ensure the metal contacts have reached equilibrium after deposition.
2. Purge the RTA by running the N_2/O_2 at a temperature of 650 °C for 5 min without any samples.
3. Load samples and adjust flow rate of N_2/O_2 to 1.4 SLPM.
4. Anneal samples at 550 °C for 10 min. The temperature ramp rate was ~500 °C/min.

9. Ni/Au Film Removal

Since removal of the Ni/Au film is a destructive process, devices are typically imaged and tested before this step. The procedure for the Ni/Au film removal is illustrated in **Figure 3**.

1. Wait at least 24 hr after contact anneal before removing the Ni/Au film.
2. Cleave a piece of the sample from the area of interest. Make sure size of sample is large enough in order to grab the edges with tweezers without touching the area of interest.
3. Secure a SEM pin stub mount in a holder such that the mount can be easily moved or taken out.
4. Place a piece of conductive carbon tape flat onto the mount surface. The piece of carbon tape should be larger than the area of the film that is to be removed. A conductive carbon tab that is the precise size of the mount surface works very well for this application. Apply the carbon tape or tab to the mount surface slowly and carefully to ensure that the surface is as smooth as possible.
5. Before removing the backing of the tape, using a finger, press hard on the tape so that it is firmly adhering to the mount surface. This is very important so that the tape does not come off with the sample.
6. Take a cleaved sample piece and gently lay the area of interest directly onto the carbon tape along the edge of the mount such that the area of the sample that was used for handling with tweezers is hanging off the edge (**Figure 3A**). Once sample has been placed onto tape, do not remove it for repositioning in order to avoid destroying the Ni/Au film.
7. Press firmly down onto the back of the sample using forceps (**Figure 3B**). Take care not to press too hard on the sample around the mount edges because this can cause the sample to break.
8. To remove the substrate, take a clean razor blade or scalpel and gently nudge it in between the substrate and the tape along the edges of the sample (**Figure 3C**). Carefully repeat this process, nudging the razor blade a little further each time until the substrate can easily be peeled off by grabbing it with tweezers. Using too much force can break the sample. To keep the tape from coming off with substrate, place a pair of forceps or a probe onto the area of the tape that is adjacent to the substrate when prying the substrate off (**Figure 3C**). The annealed Ni/Au film should remain adhered to the tape (**Figure 3D**). On average, this step will take about 1 min to complete.
9. Image the newly removed Ni/Au film using SEM as soon as possible so as to observe the newly exposed interface of the film before it becomes contaminated.

Representative Results

An example of SEM analysis on annealed Ni/Au films removed from the SiO_2 substrate using carbon tape is shown in **Figure 4**. The surface of a Ni/Au contact prior to removal is shown in **Figure 4A**. The underside of the same area of that particular Ni/Au film after removal is shown in **Figure 4B**. Comparison of the surface and underside morphology can help determine if there is a relationship between the two. For example, when the two images are compared, it can be seen that the dark spots in (a) coincide with the dark features in (b). At higher magnifications, critical features of the Ni/Au underside morphology can be discerned. Along with the use of energy dispersive spectroscopy (EDS), in order to determine the composition of the different features of the underside morphology, the general structure of the Ni/Au film on SiO_2 after annealing can be ascertained. A removed Ni/Au film that was properly prepared is shown at a lower magnification in **Figure 4C**. The void formation is uniform across the film and no cracking or breaking of the film has occurred. **Figure 4D** is an example of a removed Ni/Au film that was poorly prepared. This sample had received no cleaning pretreatment prior to the metal deposition, and the residual contamination produced nonuniform void distribution and large macrovoids that resemble blisters. Upon removal of the film, the tape had come off some from the mount and wrinkled, causing the film to break apart.

One important application of this technique is analyzing the contact/NW interface morphology. **Figure 5** shows SEM images of the underside of annealed Ni/Au films that had been deposited onto NWs dispersed onto SiO_2/Si substrates. The NWs, which are embedded in the Ni/Au films,

also come off with films upon removal with the carbon tape. At larger magnifications, like the image shown in **Figure 5A**, the distribution of voids relative to the NWs can be observed. At higher magnifications, such as the images in **Figures 5B** and **C**, the contact/NW microstructure can be more thoroughly studied. It is not uncommon for NWs to become dislodged from the Ni/Au film upon peeling it off of the substrate, as shown in **Figures 5A** and **C**. This allows for the examination of the contact/NW interface that would otherwise be obscured if the NW had remained in place.

A more quantitative analysis can be performed through the use of imaging software. The example shown in **Figure 6** is based on the correlation of residual contamination from processing with void formation at the interface of the Ni/Au with the SiO_2[10]. The presence of this residual contamination can cause a significant increase in the number of voids observed at the contact/substrate interface. By quantifying the degree of void formation at the contact/substrate interface, the effectiveness of different cleaning methods can be evaluated. These experiments focused on the effectiveness of the various cleaning methods prior to deposition of the Ni/Au onto the SiO_2 for the removal of the residual contamination. The area of the voided regions was determined using imaging software. Using SEM images, multiple 100 μm^2 areas were analyzed for each sample and the average void area (as a percentage of the total area) for each of the different preparation and cleaning methods was determined. The data is plotted in **Figure 6G** with the standard deviation of the data set represented by error bars.

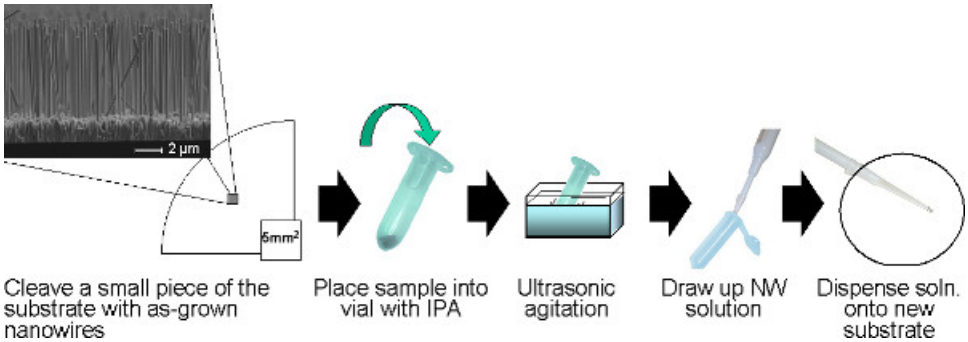

Figure 1. General procedure for NW suspension preparation and dispersal. Click here to view larger image.

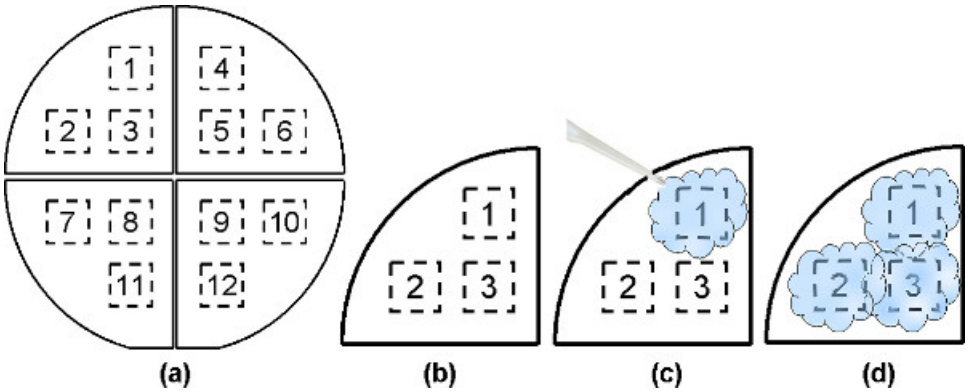

Figure 2. Procedure for dispersal of NW suspension. Click here to view larger image.

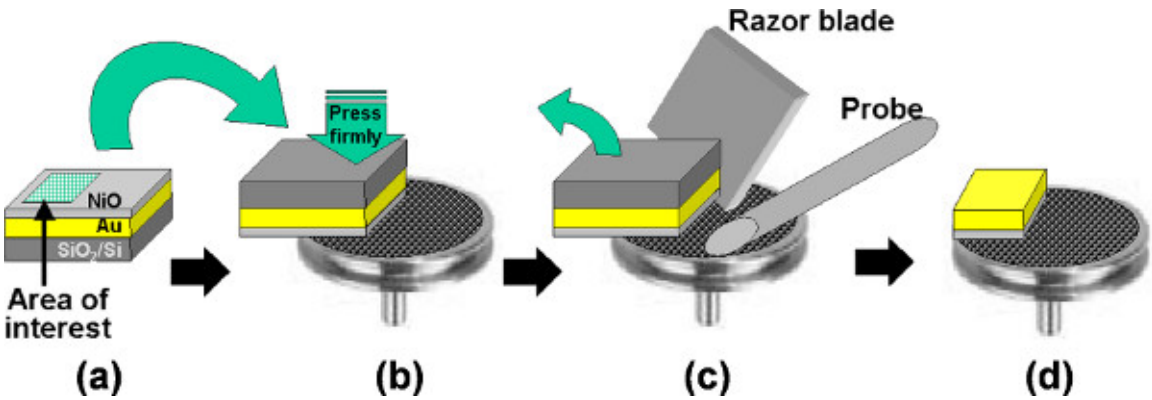

Figure 3. Procedure for removal of annealed Ni/Au film from SiO_2/Si substrate. (**a**) Step 9.6, Sample is gently laid onto the mount with carbon tape. (**b**) Step 9.7, Force is applied to the back of sample. (**c**) Step 9.8, Removal of substrate from carbon tape using a razor blade. (**d**) Step 9.8, Annealed Ni/Au film remains adhered to the tape. Click here to view larger image.

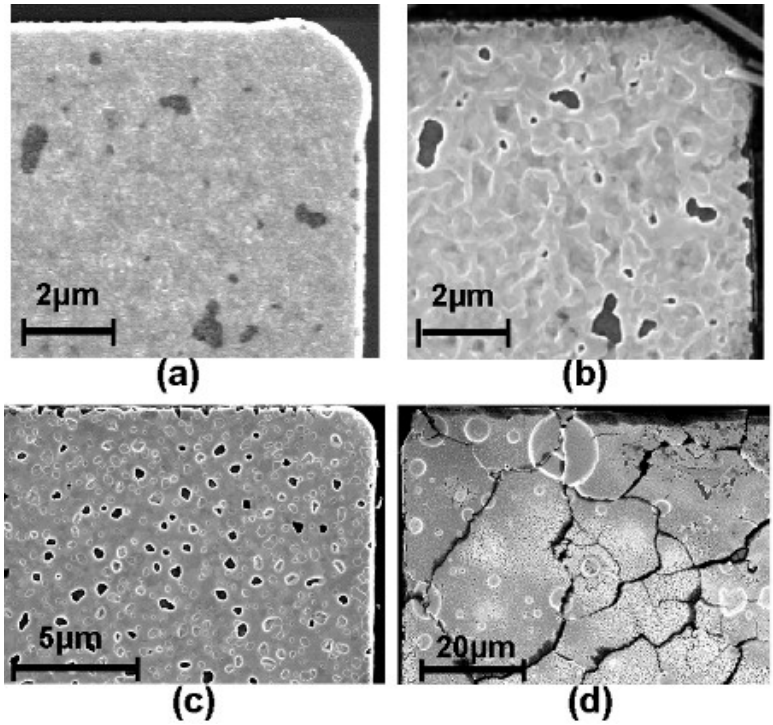

Figure 4. (a) SEM image of annealed Ni/Au contact. (**b**) SEM image of same Ni/Au film shown in (**a**) after being removed with carbon tape to reveal its underside. (**c**) Removed Ni/Au film that was properly prepared. (**d**) Removed Ni/Au film that was poorly prepared. (Images (**a**) and (**b**) taken from reference[8]). Click here to view larger image.

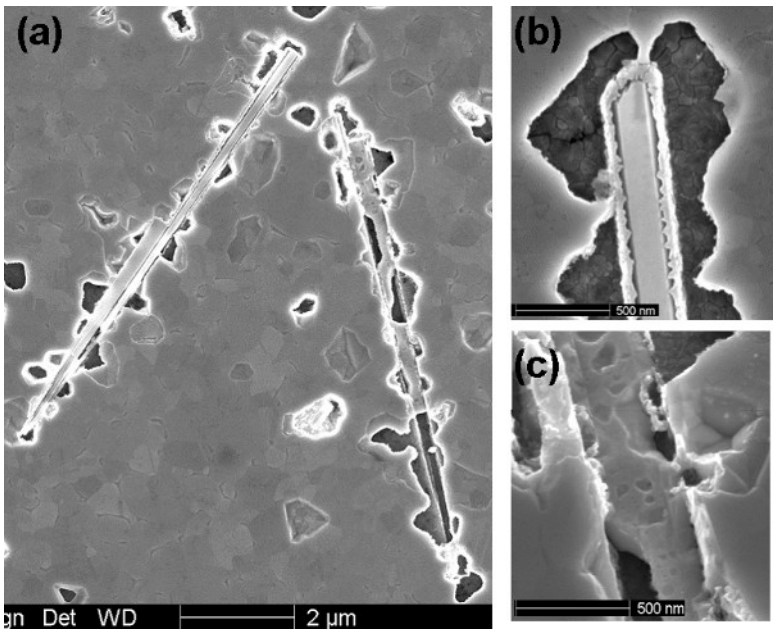

Figure 5. SEM images of the underside of annealed Ni/Au films that were deposited onto NWs that had been dispersed onto SiO_2/Si substrates and then removed with carbon tape. (**a**) Area showing a NW within the annealed Ni/Au film alongside where a NW had been before dislodging. (**b**) Close-up view of a NW within the annealed Ni/Au film. (**c**) Close-up of where a NW had been before dislodging. (Images (**b**) and (**c**) taken from reference[8]). Click here to view larger image.

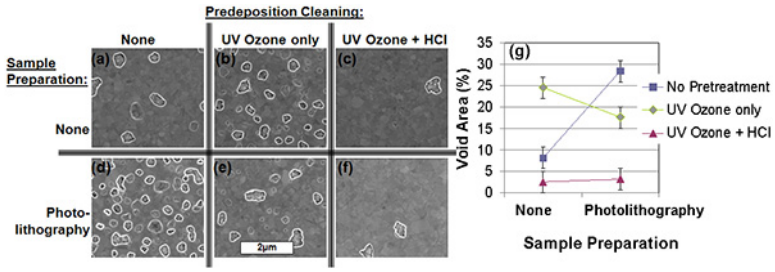

Figure 6. SEM images of the underside of annealed Ni/Au films deposited on SiO_2 surfaces that had received varying surface treatments. (**a**)-(**c**) Samples where the SiO_2 surface received no photolithographic processing prior to predeposition cleaning. (**d**)-(**f**) Samples where the SiO_2 surface received photolithographic processing prior to predeposition cleaning. (**g**) Values of the areas of the voided regions plotted for each sample shown in (**a**)-(**f**). (Images and plot taken from reference[10]). Click here to view larger image.

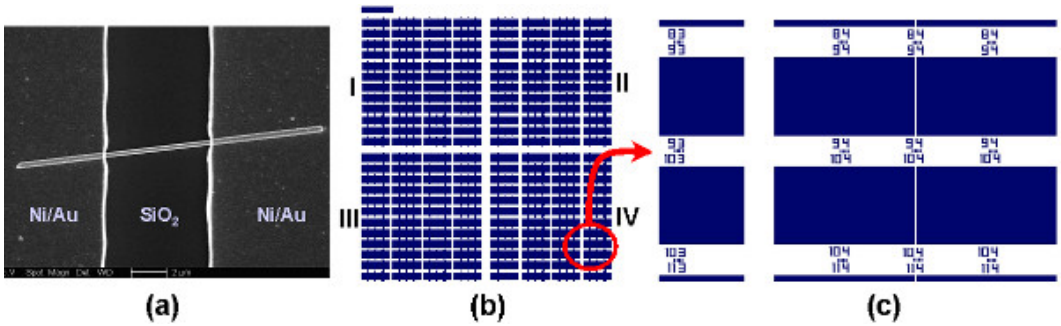

Figure 7. (a) SEM image of an individual NW device. (**b**) Complete contact pattern. (**c**) Close-up view of contact pattern. Click here to view larger image.

Discussion

The technique presented allows for analysis of the contact/substrate and contact/NW microstructure of single NW devices. The main advantages of this technique are its low cost and simplicity. It allows for qualitative and quantitative analysis of the contact interface on a large scale with the substrate as well as on a submicrometer scale with individual NWs. The use of carbon tape for the film removal and SEM pin stubs for sample mounting make it possible for analysis using characterization techniques that require clean low-pressure environments. In addition to using SEM for imaging the interface morphology, numerous other characterization techniques can be used, including EDS, x-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES) and atomic force microscopy (AFM).

One possible modification to the NW dispersal procedure would be to etch a pattern into the substrate prior to dispersal that shows the specific location of where each contact pattern will be in order for more exact placement of the NW suspension. This will require extra processing steps that increase the complexity of the process as well as the chance for residual contamination. Another issue for the NW dispersal process is the amount of NW suspension that is to be dispersed. The specific amount is dependent on the size of the contact pattern. For the 1 cm^2 sized contact pattern that was used in our experiments, a 30 μl sized drop was sufficient to cover the contact pattern area. It is recommended that not more than two applications of NW suspension be applied in a given area in order to avoid excess build-up from the solvent. If a more dense NW population is desired on the substrate, a smaller amount of solvent should be added to the NW suspension during preparation.

The parameters of the photolithography process are dependent on the specific photoresists and developer used, and therefore the contact pattern photolithography may require modification in order to achieve optimal pattern definition. The exact exposure and developing conditions will also vary as a function of the ambient conditions in the clean room. For application of the photoresist, it is recommended that the sample size not be smaller than a quarter wafer and that the contact patterns not be placed along the edge of the sample due to the edge effects on the photoresist. The contact pattern used in these experiments was for producing 2-terminal NW devices, an example of which is shown in **Figure 7A**. The contact pattern (1 cm^2) consisted of 4 arrays of 48 sets of 2 pads (250 μm x 500 μm) separated by a specific gap size, as shown in **Figures 7B** and **C**. Each array has a different gap size; array I is 3 μm, II is 4 μm, III is 5 μm, and IV is 6 μm. As shown in the Representative Results, Ni/Au film removal can also be accomplished without photoresist patterning of the Ni/Au film.

The simplicity of the Ni/Au film removal process makes it fairly straightforward but some steps may take some practice. In particular, steps 7 and 8 should be rehearsed using dummy samples in order to determine the correct amount of force to apply for the film to adhere to the tape without breaking the sample. In order to determine the void area using imaging software, the SEM images of the removed films must be of large uniform areas that are not excessively broken up like that shown in **Figure 4C**.

Disclosures

No conflicts of interest declared.

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