Properties of Suspended ZnO Nanowire Field-Effect Transistor

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September, 2006

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Abstract – As a II-VI compound semiconductor with a wide and direct band gap of 3.37 eV, ZnO nanowires have attracted intensive research effort due to their unique properties and potential application as transistors, light-emitting diodes, photodetectors, and chemical sensors. Studies of the electrical transport characteristics, as well as the optical properties and mechanical properties of individual ZnO nanowires have been reported recently. In this report, the characteristics of suspended nanowires are presented. Single-crystalline ZnO nanowires are synthesized by a vapor trapping chemical vapor deposition method. They are configured as field-effect transistors (FET) with a suspended ZnO nanowire channel. Contacts between the ZnO nanowire and metal electrodes are improved through annealing and metal deposition using a focused ion beam. The gas sensing characteristics are studied and compared to those of the nonsuspended structure. In addition, the surface potential distribution of the suspended nanowire is investigated using scanning probe microscopy to characterize the uniformity of the nanowire. Continued work is underway to reveal the intrinsic properties of suspended ZnO nanowires and to explore their device applications.

Key words – zinc-oxide (ZnO) nanowire, gas sensor, suspended nanowire, field-effect transistor (FET), nanotechnology, semiconductor device.

I. Introduction

In recent years, quasi-one-dimensional (Q1D) semiconducting nanostructures have received tremendous research interest for their potential applications in nanoscale electronic and optoelectronic devices such as transistors, light-emitting diodes, photodetectors, and chemical sensors. Q1D nanostructures include such things as nanowires (NWs), nanotubes, nanobelts, and nanoneedles. The small dimensions of these structures promise increases in device packing density, decreases in power consumption, and also increases in sensitivity in chemical sensing applications. As a II-VI compound semiconductor with a wide and direct band gap of 3.37 eV, zinc oxide (ZnO) has been shown to be a prime candidate for the electronic and optoelectronic applications described above. In particular, the synthesis (Chang et al., 2004), properties (Fan and Lu, “Zinc Oxide”), gas sensing characteristics (Fan et al., 2004), and electrical characteristics in field-effect transistor (FET) configuration (Fan and Lu “Electrical Properties”) of ZnO nanowires have been reported previously. Gas sensing with nanowires is normally achieved by monitoring the conductance change of the nanowire when exposed to a particular gas. Q1D structures have very small radiuses giving them larger a surface-to-volume ratio that is highly susceptible to altered electronic properties by means of chemisorption.

In this report the properties of ZnO nanowires in a suspended FET configuration are studied. The vapor trapping chemical vapor deposition method of nanowire synthesis employed is described in detail. Also, the method of gas sensing with the nanowire FET, and characterization by scanning surface potential microscopy (SSPM), are detailed. The results are compared to previous reported results of gas sensing (Fan and Lu, 2006) and surface potential distribution (Fan and Lu “Electrical Properties”) with a nonsuspended FET device. It is found that these ZnO NW suspended FET devices have a reduced sensitivity to nitrogen dioxide gas (NO_2) as compared to the nonsuspended devices. SSPM analysis reveals semi-erratic results possibly due to mechanical stresses from NW deflection due to electrostatic forces between the tip of the scanning probe microscope (SPM) and the NW. Continued work underway will further reveal the intrinsic properties of suspended ZnO nanowires and explore their device applications.

II. Nanowire Synthesis and Device Fabrication

There are many documented ways of synthesizing nanostructures by a catalytic growth process (Hu et al., 1999). The ZnO nanowire synthesis technique employed was based on the vapor trapping chemical vapor deposition (CVD) method reported previously (Chang et al., 2004), and will be described here. With this method, a common CVD process is supplemented with a vapor trapping technique that facilitates the control of the charge carrier concentration in the nanowire, thus allowing a high concentration of charge carriers. The synthesis is done by means of a vapor-liquid-solid (VLS) growth mechanism where a metal catalyst of gold is melted and supersaturated in the presence of zinc vapor, and subsequently oxygen gas is applied causing the nucleation of a single-crystalline ZnO nanowire. The CVD apparatus consists of a horizontal quartz tube placed in a furnace that serves as vapor chamber. A small quartz vial with an internal diameter of 10 mm and an opening diameter of 5 mm is placed in the quartz tube where a zinc vapor rich environment can be established; this is the vapor trapping mechanism.

Gold nanoparticles having a diameter of 30 nm are dispersed on the surface of a small silicon Si) chip used as the substrate for the nanowire growth. This substrate is placed in the bottle neck of the horizontal vial as shown in Fig. 1. Zinc powder (99.9wt%) is placed in the end of the vial and serves as the source of the zinc vapor. The system is pumped down to about 10 mtorr and then purged three times with argon (Ar) gas flowing at 100 sccm to establish a pressure of 1 atm. The system is rapidly heated in the furnace to 700 °C, by which point the gold particles have melted and the now vaporized zinc has supersaturated the gold. Once the temperature has stabilized for 15 minutes, 100 sccm of 0.2% oxygen gas is flowed into the system for 30 minutes. When the oxygen comes in contact with the supersaturated Au-Zn alloy the ZnO crystal begins to nucleate creating the nanowire. By this method a zinc-rich, oxygen dilute atmosphere with a gradient of zinc-to-oxygen concentration is created in the vial. This environment facilitates the formation of native defects, such as zinc interstitials and oxygen vacancies, in the wire that contribute conduction electrons and give the NW its n-type semiconducting properties. Finally, the nanowires grown on the silicon substrate are viewed with a scanning electron microscope (SEM) as shown in Fig. 2(a) to verify the quality is good. If the zinc vapor concentration is too high or too low the nanowire quality may be low Fig. 2(b). Ideally, good quality nanowires will be high in density, have radiuses of 60–100 nm, and be a few microns in length.

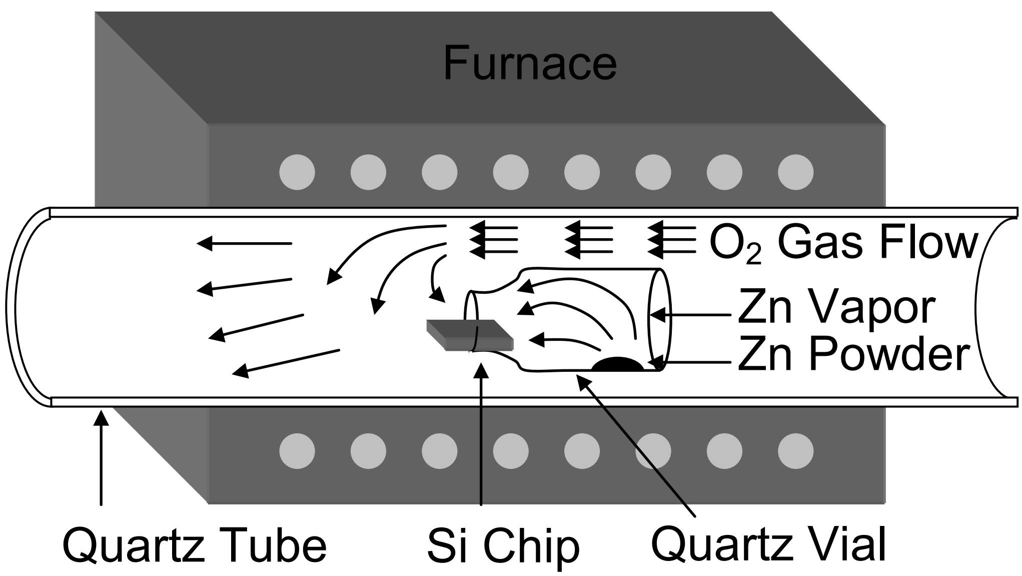


Fig. 1. Diagram of CVD process. The horizontal quartz tube is in the furnace, and holds the small quartz vial. The Si chip on which the NWs grow is in the opening of the vial. The vial serves to trap the zinc vapor during synthesis.

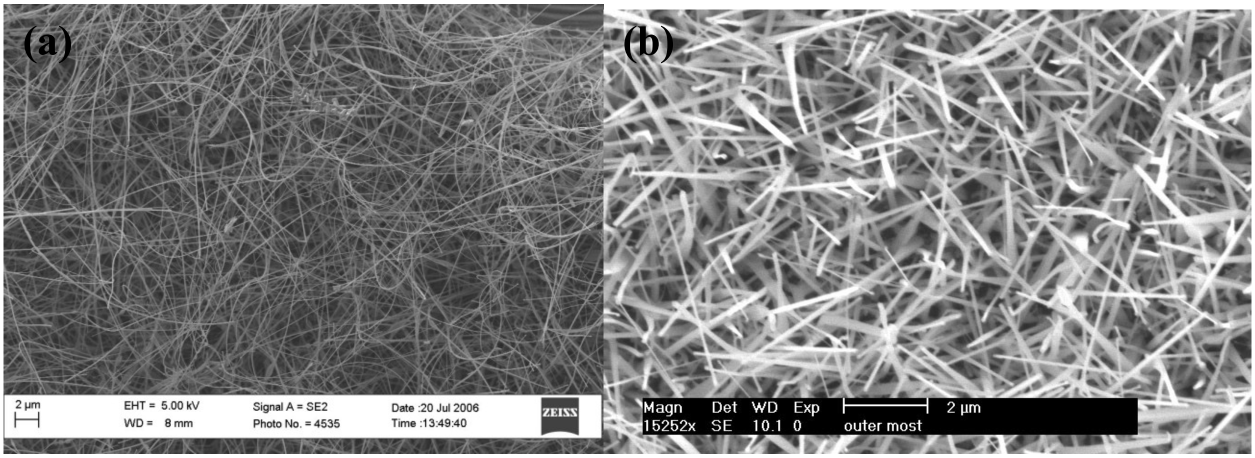


Fig. 2. (a) SEM image of high quality nanowires with an average radius of about 80 nm. (b) SEM image of poor quality nanowires.

The suspended FET device fabrication proceeds in similar fashion to that reported previously for the nonsuspended case (Fan et al., 2004). The substrate containing the nanowire bundles is then sonicated in isopropyl alcohol (IPA) to release the individual nanowires. The IPA solution is dropped onto a previously prepared array of metal contacts on a p-type Si substrate. The chip is prepared by the usual lithographic techniques. A bi-layer of titanium (20 nm) and gold (60 nm) is evaporated onto the Si in an array pattern of electrodes. The distance between neighboring electrodes of 4–5 μm provides contacts for a nanowire FET. Much of the oxide layer on the Si substrate is then etched away creating a trench between adjacent electrodes with a depth of about 500 nm. Once the nanowires are deposited on the chip, it is viewed under a high-powered optical microscope so that FET devices can be found. Fig. 3 shows an SEM image of a suspended nanowire FET device. When a device is found, it is tested for good electrical contact. As gold has a work function of 5.31 eV and the ZnO nanowire has a work function of 3.37 eV, there is a mismatch in work function at the interface and a contact Schottky barrier is usually observed. The Schottky contact has the rectifying characteristic observed in diode behavior, and contrasts with an Ohmic contact which has a linear characteristic. Previous report have also shown that the electron concentration and electron mobility of the nanowire can be estimated assuming a Q1D structure (Martel et al., 1998). For the nonsuspended FET structure investigated by Fan, the “electron concentration is on the order of 10^7 cm^{-1}, corresponding to a volume concentration of ~ 10^{19} cm^{-3}, and the electron mobility is on average 40 $cm^2/V \cdot s$” (2006).

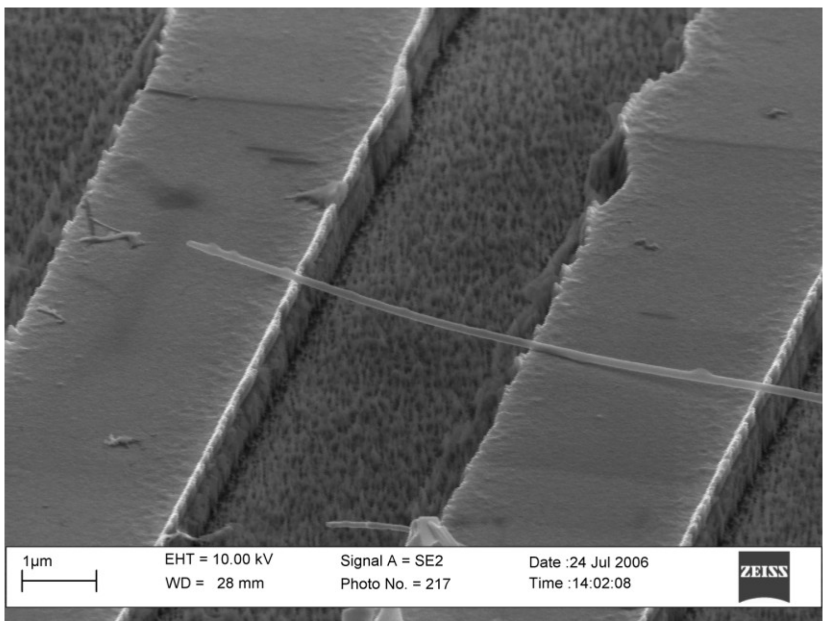
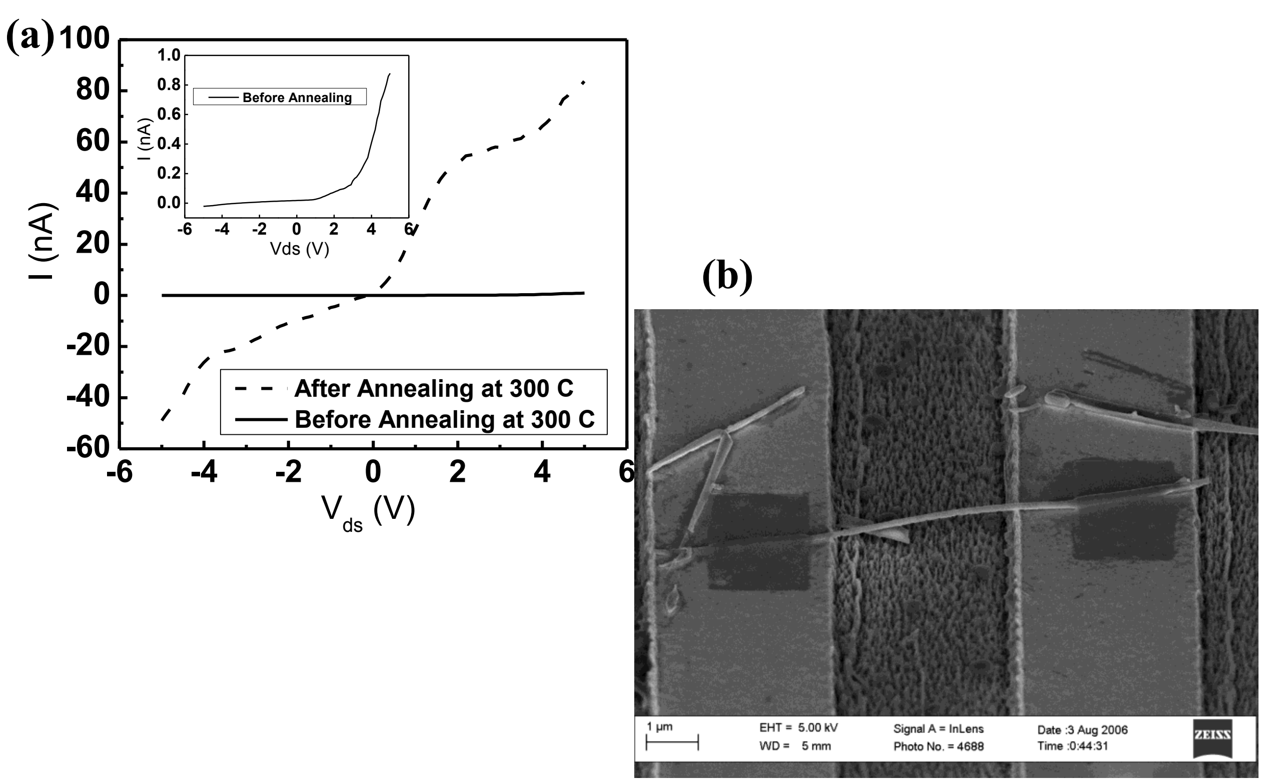


Fig. 3. SEM image of suspended nanowire FET device.

In order to improve the contact between the ZnO nanowire and the Au electrode, one of two methods were employed. The first method of improving the contact is by the process of annealing. The device is placed in a furnace and heated to 300–700 °C for 30 minutes or more. When heated, the crystal structure of the nanowire and metal at the interface is altered for better alignment and a better contact is achieved. Fig. 4(a) shows the electron transport properties of a suspended NW FET before and after annealing. As revealed in the inset of Fig. 4(a), the current shows an increase of almost 2 orders of magnitude due to the improved contact. The second method used was metal deposition with a focused ion beam (FIB). The ion beam was used to deposit pads of platinum (Pt), which has work function of 5.68 eV, on top of the ends of the nanowire where there is contact with the electrode. Fig. 4(b) is an SEM image of the suspended nanowire FET with Pt deposited on the contact points. Fig 4(c) shows the improved transport properties of a suspended NW FET device after FIB metal deposition, revealing an increase of about 3 orders of magnitude. One observance of note is that in the metal deposition with the FIB, sometimes the Schottky contact characteristic was lost and an Ohmic contact was observed. This change in contact characteristic could be attributed to the focused ion beam which uses gallium (Ga) ions, whose work function is 4.20 eV. The more closely matched work function of the Ga would favor a more Ohmic contact.



(c)

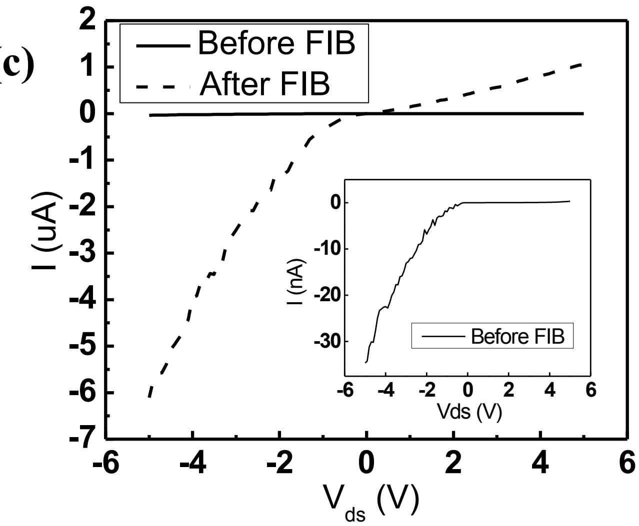


Fig. 4. (a) Electron transport properties of NW FET before and after annealing at 700 °C. Inset: Transfer characteristic of FET before annealing. (b) SEM image of suspended nanowire after FIB metal deposition on electrode contacts. (c) Electron transport properties of NW FET before and after platinum deposition with FIB. Inset: Transfer characteristic of FET before platinum deposition with FIB.

III. Gas Sensing Experiments and Results

ZnO nanowires have potential application as chemical gas sensors because of the property of chemisorption. Chemisorbed gas molecules on a metal-oxide surface have strong chemical bond that which will either withdraw or donate electrons to the metal-oxide (Henrich, 1996). The withdrawing or donating of electrons to the NW channel of the FET will bring about a change in the conductance of the device. Therefore, by observing the conductance of the NW FET, the presence of chemicals can be sensed. Previous experiments have shown that a nonsuspended ZnO NW FET shows decreased conductance when exposed to O_2, NO_2, and NH_3

(Fan and Lu, 2006). Additionally, higher concentrations of these chemical gases caused a further decrease in conductance. As the conductivity of the NW is affected by the surface adsorption of gas molecules, it is expected that a greater surface area-to-volume ratio will result in greater sensitivity. It has been shown that for NWs with smaller radiuses where the surface-to-volume ratio is larger, surface adsorption does indeed have a much greater affect on conductance (Fan at al., 2004). It would be expected also that a suspended NW FET structure would have more surface area than a comparable nonsuspended structure, and thus more sensitivity to surface adsorption, but this was not found to be the case.

Gas sensing experiments were carried out by placing the suspended NW FET device in a vacuum chamber at room temperature where various concentrations of gas could be applied. Electrical feedthroughs allowed the device to be attached to an analyzer where the sensing response could be observed. The chamber was initially purged of all contaminants by pumping it down to 10 mtorr, and then flowing 1000 sccm pure Ar at 1 atm for 15 minutes. The gas used for the experiment, NO_2, was then introduced, mixed with Ar, with mass flow controllers. In this way the concentration of NO_2 could be precisely regulated. The suspended NW FET device used had a NW channel radius of 80 nm. Fig. 5 shows the time domain conductance response in the nanowire when exposed to a concentration of 1000 ppm NO_2 gas. Fig. 6 shows the I–V curve of the suspended NW FET for different concentrations of NO_2 with zero gate voltage applied. The sensitivity of the device is defined as the relative conductance change after the NW is exposed to the target gas, i.e.,

$$\frac{\Delta G}{G_0} = \frac{|G_{gas} - G_0|}{G_0},$$

where G_0 is the conductance before exposure in the inert environment (pure Ar). At a concentration of 20 ppm NO_2, the suspended ZnO NW FET shows a sensitivity of approximately 11%. Previous experiments with a nonsuspended ZnO NW FET have shown a sensitivity greater than 90% to 20 ppm NO_2. The mechanism that makes the suspended structure less sensitive is not totally limpid. It is assumed that the SiO_2 surface, with which the NW makes contact in the nonsuspended structure, plays a role in the greater sensitivity. One possibility is the adherence of oxygen to the SiO_2 surface that contributes to the adsorption on the NW surface.

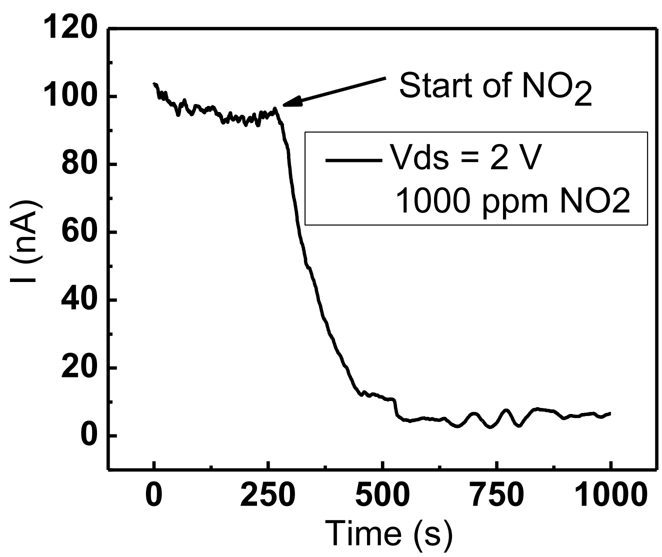


Fig. 5. Conductance of the suspended ZnO nanowire in the presence of a concentration of 1000 ppm NO_2, with a 2 V bias.

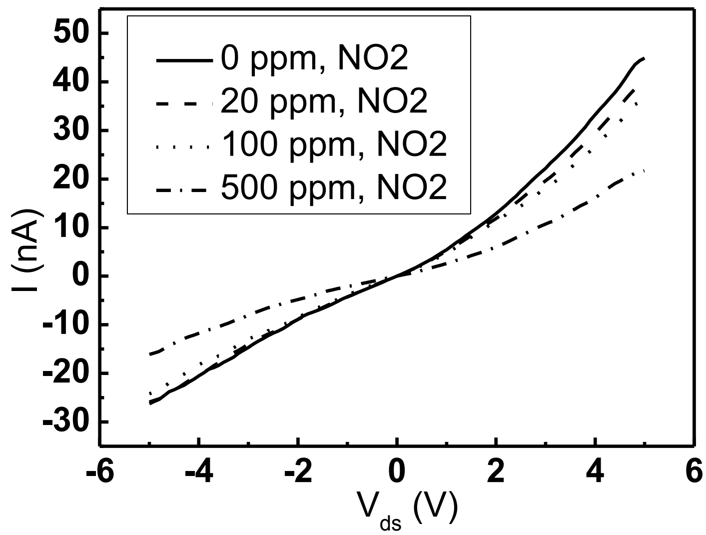


Fig. 6. I–V curve of suspended ZnO nanowire with varying concentrations of NO_2 when $V_g = 0$ V.

IV. Surface Potential Distribution Experiments and Results

The surface potential distribution of the suspended ZnO NW FET was performed by way of scanning surface potential microscopy (SSPM). SSPM is accomplished with a scanning probe microscope (SPM) (Digital Instruments Nanoscope IIIa) operating in tapping mode. As explained previously, SSPM is based on the principle in which the electrostatic force between a biased SPM and the sample can be characterized as

$$F = \frac{dC}{dz} V_{ac} (V_{tip} - V_{sample}),$$

where F is the electrostatic force, *dC/dz* is the derivative of the tip-sample capacitance with respect to their separation, V_{ac} is the magnitude of the ac signal applied to the tip to drive its vibration near the resonant frequency, and $V_{tip} - V_{sample}$ gives the dc potential difference between the tip and the sample (Fan and Lu “Electrical Properties”). This means that when the electrostatic potential difference between the tip and the sample is large, there is a large force, and when the potential difference is small, there is a smaller force. As the potential difference between the tip and the sample becomes smaller, the force between them is reduced.

Once the sample is loaded into the SPM, the NW FET is biased with a drain-source potential of 2 V. At this bias with no tip interaction, the FET exhibited a current of 1 nA. Fig. 7(a) is an SEM image of a suspended ZnO NW FET with Pt deposits on the end electrodes. Fig. 7(b) and 7(c) show the topographic image and the surface potential image, respectively, of the same device under the 2 V bias. Additionally, the Fig. 7(d) shows the section analysis of the potential image along the nanowire. Here the potential profile is apparent from drain to source. The section analysis reveals the general trend from high potential at the drain B, to low potential at the source A. Along the nanowire channel the expected linear change in potential observed by Fan for a nonsuspended device, is not observed. The semi-erratic variation in potential along the NW channel could be due to a number of factors including flexing of the NW or even NW contact with the underlying oxide surface due to the electrostatic force between the SPM tip and nanowire. Changes in the NW conductivity due to mechanical stresses may be apparent. Further analysis of the results concerning NW uniformity is difficult due to this erratic behavior.

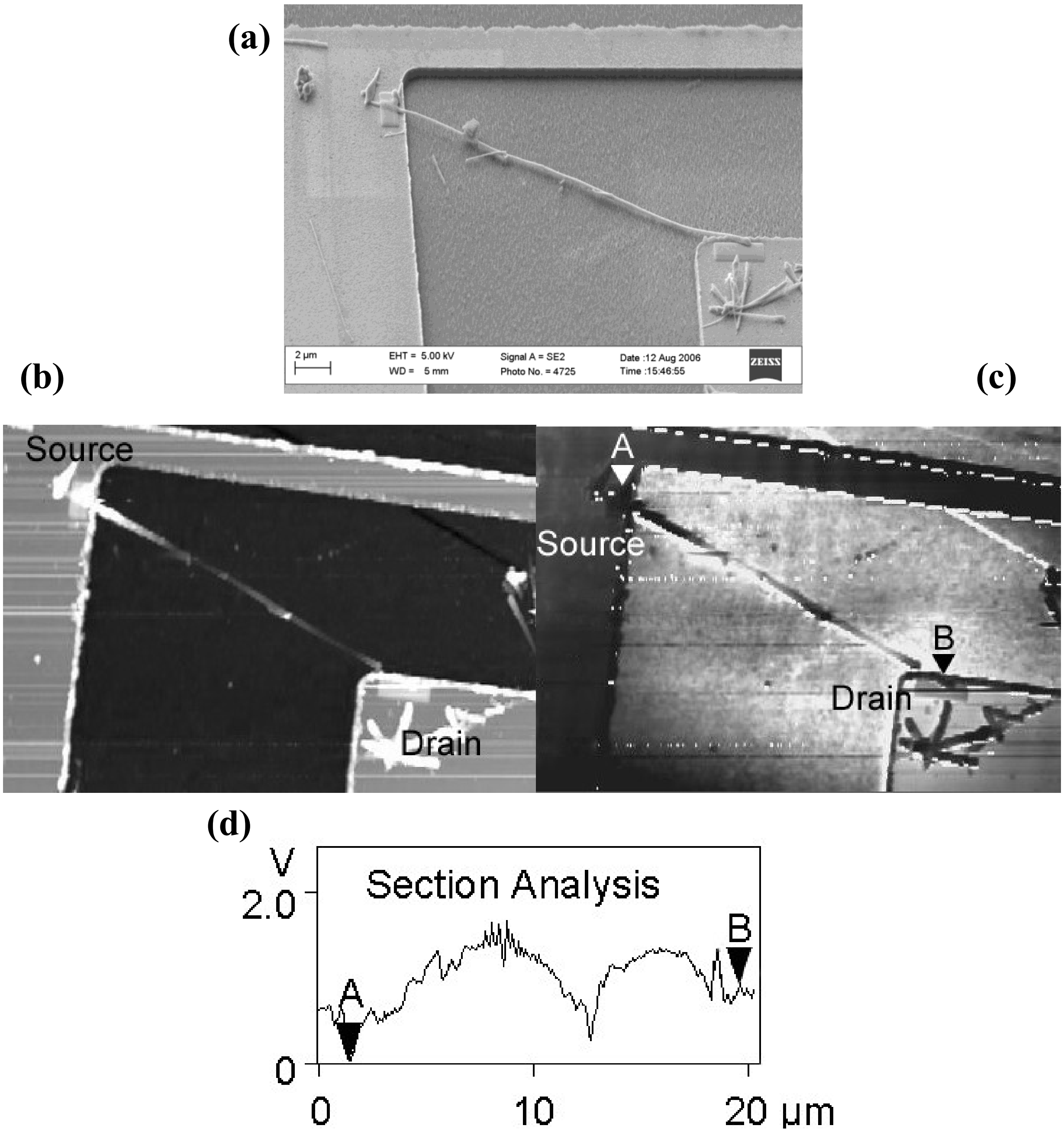


Fig. 7. (a) SEM image, (b) topography image, and (c) surface potential image of a suspended ZnO nanowire FET. The platinum deposits from the FIB at the electrodes are visible. (d) Section analysis of the surface potential along the suspended nanowire.

V. Conclusion

In conclusion, n-type single crystal ZnO NWs were synthesized by a vapor trapping CVD process. The NWs were used to fabricate suspended NW FET devices. The NW contact with Au electrodes was greatly improved by annealing and metal deposition with a FIB. The suspended ZnO NW FET was implemented as a gas sensor for the detection of NO_2. Although the NW FET showed sensitivity to the gas by means oxygen adsorption, the sensitivity of the suspended device to NO_2 was found to be much lower than that of the nonsuspended devices studied previously. SPM in tapping mode was used to study the surface potential distribution of the suspended NW. The NW surface potential section analysis showed a semi-erratic distribution possibly to due to flexing of the NW and maybe contact with the underlying oxide surface. Further investigation into the mechanical properties of the suspended NW may shed some light on the results. Additionally, continued work will further reveal the intrinsic properties of suspended ZnO nanowires and explore their device applications.

Acknowledgements

Device fabrication was performed at the Integrated Nanosystems Research Facility at the University of California, Irvine. Many of the SEM images and FIB work done at the Zeiss Center of Excellence at the University of California, Irvine. The author would like to thank Jia Grace Lu, CJ Chien and Joseph Fan for their help in guiding and assisting in this research. Also, thanks to the IM-SURE staff and the National Science Foundation for funding this research.

Works cited

Chang, P.-C.; Fan, Z.; Wang, D.; Tseng, W.-T.; Chiou, W. -A.; Hong, J.; Lu, J. G. "ZnO nanowires synthesized by vapor trapping CVD method." Chem. Mater. 16 (2004): 5133-5137.

Fan, Z.; Wang, D.; Chang, P.; Tseng, W. -Y.; Lu, J. G. "ZnO Nanowire Field Effect Transistor and Oxygen Sensing Property." Applied Physics Letters 85 (2004): 5923-5925.

Fan, Z.; Lu, J. G. "Electrical properties of ZnO nanowire field effect transistors characterized with scanning probes." Applied Physics Letters 86 (2005): 032111.

Fan, Z.; Lu, J. G. "Zinc Oxide Nanostructures: Synthesis and Properties." Journal of Nanoscience and Nanotechnology 5 (2005): 1561-1573.

Fan, Z.; Lu, J. G. "Chemical sensing with ZnO nanowire field-effect transistor." IEEE Transactions on Nanotechnology 5 (2006): 393-396.

Henrich, Victor E.; Cox, P. A. The Surface Science of Metal Oxides. Cambridge: Cambridge University Press, 1996.

Hu, J.; Odom, T. W.; Lieber, C. M. "Chemistry and physics in one dimension: synthesis and properties of nanowires and nanotubes." Acc. Chem. Res. 32 (1999): 435-445.

Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, Ph. "Single- and multi-wall carbon nanotube field-effect transistors." Appl. Phys. Lett. 73 (1998): 2447-2449.