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Fabrication and Characterization of Schottky Diodes using Single Wall Carbon Nanotubes

by Brandon E. Luquette and Barbara M. Nichols

ARL-TR-4534 **August 2008**

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
August 2008	Final	

4. TITLE AND SUBTITLE
Fabrication and Characterization of Schottky Diodes using Single Wall Carbon Nanotubes

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Brandon E. Luquette and Barbara M. Nichols

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: AMSRD-ARL-SE-RL
2800 Powder Mill Road
Adelphi, MD 20783-1197

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-4534

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Schottky diodes using single wall carbon nanotubes (SWNTs) were fabricated using palladium and aluminum source and drain contacts, respectively. SWNTs were grown on high resistivity silicon substrates with a thermal oxide layer using chemical vapor deposition and ferric nitrate catalyst. Multiple cleanroom processing steps were used to make the diodes which included the deposition of marker layers, oxygen plasma etch for selective nanotube removal, and electron beam evaporation of metal electrodes in two separate depositions. The diodes were designed in a coplanar waveguide (CPW) transmission line topology in order to facilitate RF testing. Electrical testing at the DC level was accomplished. Further investigation into the RF characterization of carbon nanotubes will allow for the incorporation of such devices into integrated circuit architectures.

15. SUBJECT TERMS
Carbon nanotubes, Schottky diodes

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	SAR	16	Barbara M. Nichols
U	U	U			19b. TELEPHONE NUMBER *(Include area code)* 301-394-0602

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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1. Background

Semiconducting single wall carbon nanotubes (SWNTs) possess unique electrical properties including carrier mobilities unrivaled in state of the art semiconductors (*1*) and the ability to carry high current densities (*2*). The ability to control these properties holds the promise for smaller, faster, denser, and more power efficient electronics. Accompanying the potential for higher performance voltage controlled current, SWNTs present an opportunity for high frequency applications. In order to harness the capabilities of this technology, fundamental functional devices must be fabricated and characterized. One fundamental device in microelectronic design is the two-terminal rectifier – the diode. One subset of the diode, particularly of interest for RF (radio frequency) applications such as receiver systems, is the Schottky diode.

Functionally realizing the Schottky diode using SWNTs is accomplished by depositing two different metals with differing work functions onto the nanotube to serve as the source and the drain. The operation of the diode is dictated by the interface of the metal contact and the nanotube. A Schottky barrier is formed at this interface due to the differences in the metal Fermi level and the valence/conduction band of the nanotube (*3*). The height of this barrier is dependent upon the work function of the metal used for the contact (*4*). By using a metal with a higher work function as a contact at one end of the nanotube, an ohmic contact is created. On the other end of the device, a metal with a lower work function than the nanotube is used to create a Schottky contact. The band diagram in figure 1 represents the device under forward bias. E_C is the conduction band edge, E_V is the valence band edge, and Pd and Al represent the relative work functions of palladium and aluminum with respect to the nanotube. Note SWNTs usually act as p-type semiconductors.

Electron transport through the barrier is achieved by thermonic emission (TE) as well as tunneling current. The TE current produces the rectifying I-V curve and dominates electron transport when the device is not gated (*5*). When a voltage is applied across the device, positive or negative depending on the channel doping, electron emission is increased due to increased electron energy, and current flow is established.

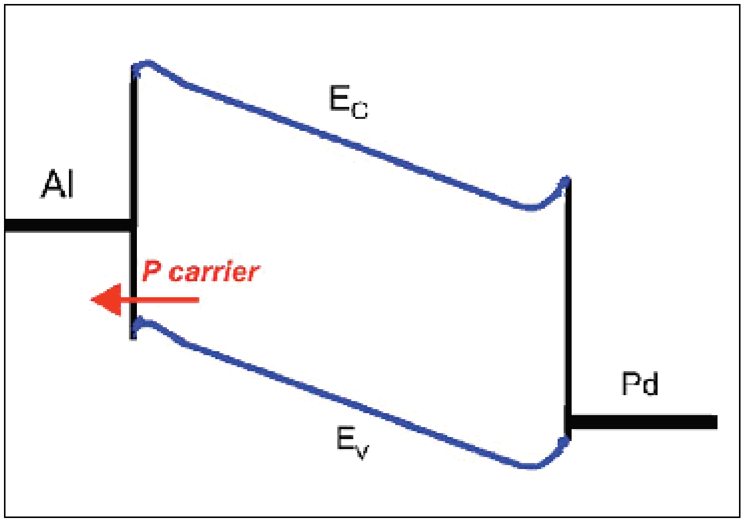

Figure 1. Band diagram illustrating Schottky barrier height dependence on the work function of metal contact. Diagram from reference 6.

2. Fabrication

The Schottky device fabrication layout consisted of 4 different photomask layers designed in collaboration with the Fuhrer research group at the University of Maryland. The first layer consisted of alignment markers for processing subsequent layers. The marker layer consisted of 10 Å titanium covered by 1000 Å of platinum. All metal deposition was done by e-beam evaporation. This metallization was chosen specifically to withstand the high temperatures of carbon nanotube growth (i.e., 800 – 1000 °C).

Metallization also played a role in determining what substrates were used in this work. Initially, the diodes were to be fabricated on single crystal quartz and fused silica substrates for RF testing purposes. However, repeated attempts at metal deposition of a marker layer resulted in poor adhesion to the quartz surface, most likely due to surface contamination on the wafers. While investigating this contamination issue, it was decided to use high resistivity silicon substrate (resistance greater than 10 kΩ/cm) with a thermal oxide layer grown as an alternative. This choice of substrate produced better adhesion while still providing a suitable substrate for RF testing.

The carbon nanotubes were grown on high resistivity silicon with a 5000 Å SiO_2 layer via chemical vapor deposition (CVD). A solution of ferric nitrate dissolved in isopropanol (60 µg /mL) was used as the catalyst. Growth was performed in a quartz tube at 875 ºC with a flow of hydrogen, methane, and ethylene gasses for 20 minute after a 45 minute anneal at 875 ºC in argon. Using this catalyst method and growth conditions, carbon nanotubes are sporadically distributed across the substrate. Tube growth and densities were verified using scanning electron microscopy (SEM).

Controlling the growth of nanotubes on the substrate is critical for electronic circuit design. It is preferable to know both the location and number of nanotubes in a device to predict electrical parameters such as characteristic impedance. In order to limit the nanotubes to the desired location between the two metal contacts, a procedure, using oxygen plasma etch which has been shown to remove carbon nanotubes grown by CVD (*7*), was developed to remove the unwanted nanotubes. A layer of photoresist was spun onto the substrates, and using the image reversal photolithography technique[1], squares were patterned to protect the predetermined sites of the metal-nanotube interfaces. An oxygen plasma etch (power: 200 W, O_2 flow: 20 sccm, time: 2 minutes) was performed on the substrate to clear all extraneous nanotubes not covered by photoresist. After the plasma treatment, the photoresist was dissolved with acetone, leaving only the protected tubes behind. Figure 2 shows a region of the substrate which was protected by photoresist in contrast to the surrounding area which was not covered in photoresist during the oxygen plasma etch.

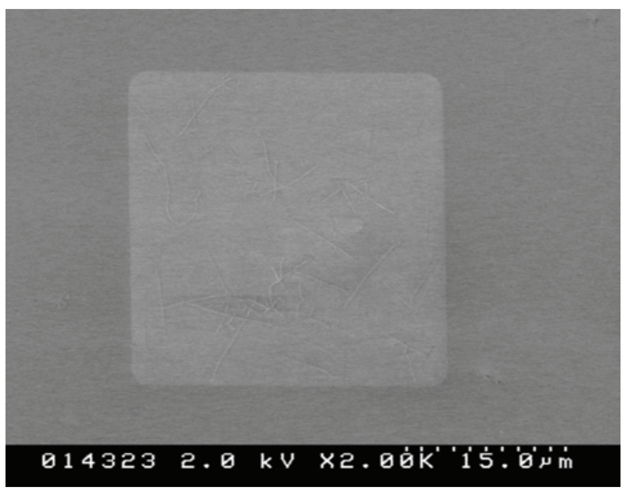

Figure 2. SEM image of photoresist protected tubes after the photoresist was dissolved.

Metallization of the electrodes was a crucial step in fabricating the diodes and required special processing to ensure success. Using standard photolithography processing resulted in poor lift-off, most likely due to slight photoresist overdeveloping. Overdeveloping leads to an angled photoresist profile instead of an abrupt vertical sidewall. This angled profile leads to metal "flashing" along the electrode. An example of this electrode profile can be seen in figure 3. Lift-off resist (LOR), a special resist material, was used in conjunction with AZ 5214E photoresist in order to produce well defined electrode edges and therefore a more reliable liftoff

[1]The image reversal process consists of spinning a special positive photoresist, AZ 5214E, which when processed under specific conditions acts as a negative photoresist. The overall result is a negative image of the mask pattern.

process. Metal liftoff was performed using MicroChem Remover PG, a special LOR stripping chemical, at 60 ºC. The distribution of the carbon nanotubes between contacts was determined by SEM.

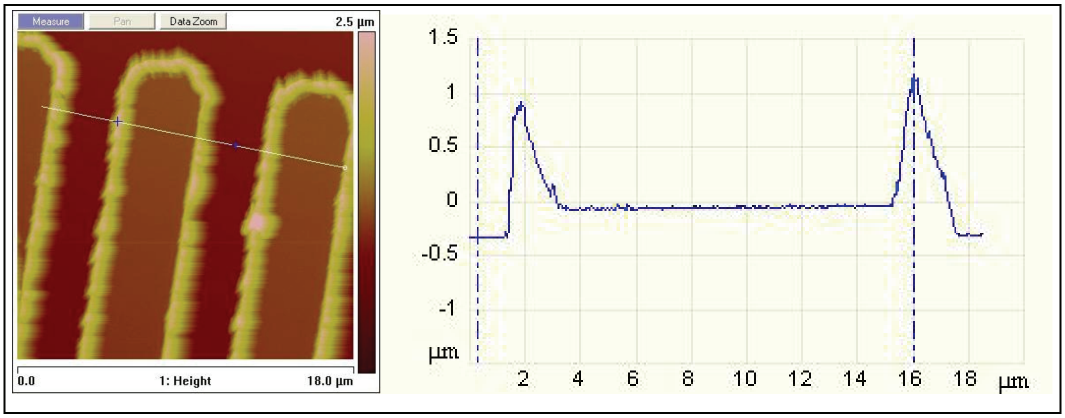

Figure 3. AFM images of metal contacts fabricated using standard photolithography showing the pronounced flashing at the edges.

Diode metallization required the use of two separate masks. The two contact metals chosen were palladium (Pd) and aluminum (Al) for the ohmic and the Schottky contacts respectively because of their work functions with respect to carbon nanotubes. SWNTs have a work function of approximately 4.9 eV, whereas Pd has a value of 5.12 eV and Al has a value of 4.27 eV (*6*). The metal thicknesses used for the contacts were 80 nm for Al and 20 nm for Pd with a 100 nm layer of Au on top for more robust contacts. Figure 4a shows the diagram of the electrodes, and figure 4b shows an actual SEM image of the fabricated electrodes. Figure 4c shows a schematic picture of the metal-nanotube interface, and figure 4d shows the metal-CNT interface of one of the fabricated devices.

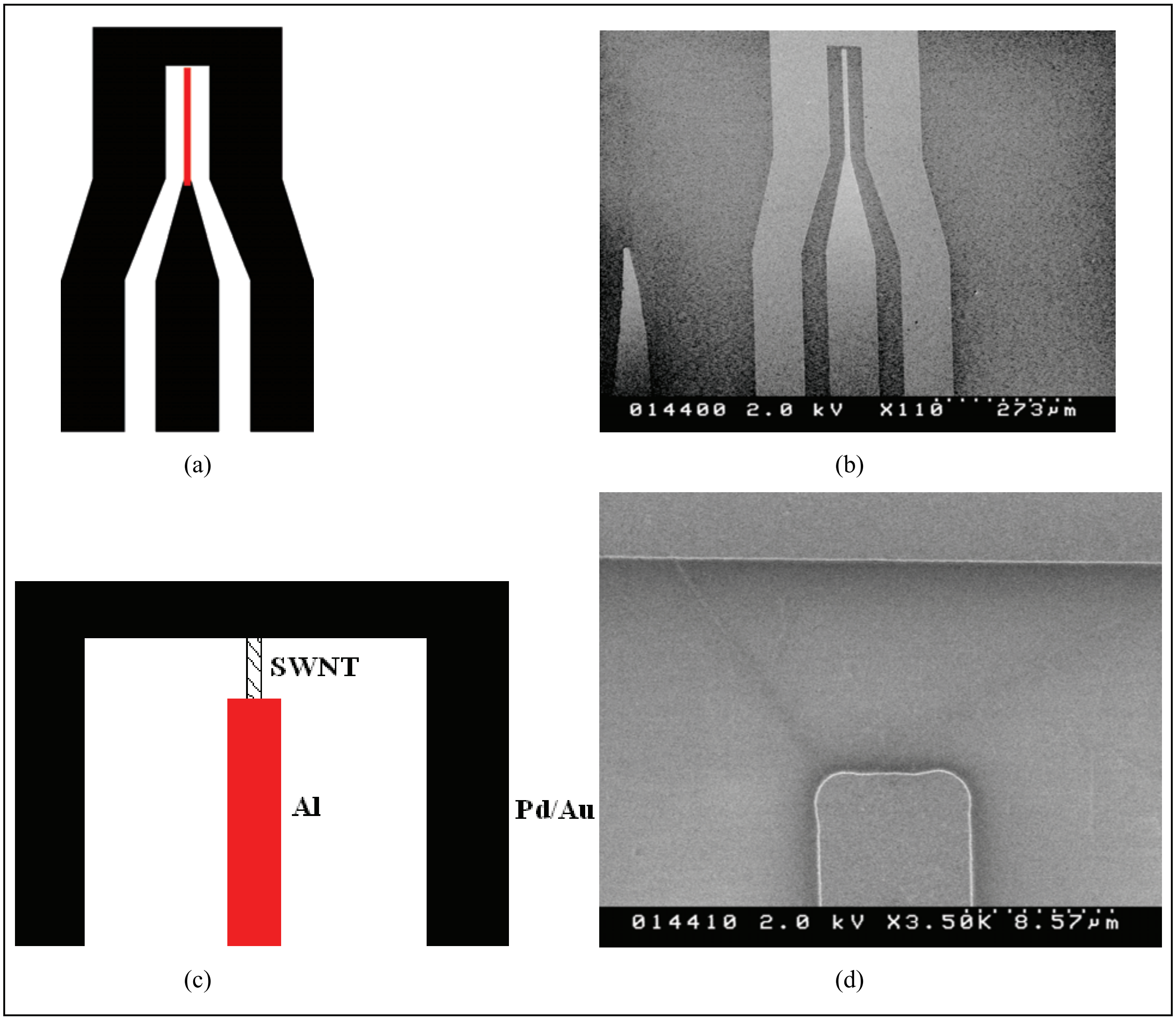

Figure 4. (a) Diode layout: The inner electrode represents the signal electrode (red – Al). The outer electrodes represent the ground electrodes (black – Pd/Au), (b) SEM image of the diode layout, (c) Schematic picture of device setup, and (d) SEM image of electrode-nanotube interface (top contact: Pd/Au, bottom contact: Al).

3. Electrical Testing

The electrode was designed in a coplanar waveguide topology (CPW) for 150 µm pitch probes. CPW was chosen because of its high frequency response as well as its measurement precision and repeatability. Due to the relatively unknown RF characteristics of carbon nanotubes, especially in the GHz frequency range (*8*), as well as the inability to predict the number and individual characteristics of nanotubes in a device, the electrodes were tapered in an attempt to provide usable impedance matching. High contact resistances are typical in metal-nanotube interfaces, and the number of nanotubes in a device affects its impedance. These conditions provide significant challenges for electrode design. Developmental work in AC characterization of SWNTs as well as in controlled growth is still required to obtain proper impedance matching in such a device (*9*).

Devices were tested (at DC) using a Keithley 4200 semiconductor characterization system. All measurements were taken at room temperature in air. The signal pad and one of the ground pads were probed in order to test the nanotubes bridging the Al and Pd electrodes. Rectification was verified by sweeping the voltage across the device from –2 to 5 V.

The mask layout contains 64 diodes per sample with varying gap lengths ranging from 5 to 20 μm. Two samples were processed for testing. During electrical testing, 5 useable devices were identified. Figure 5 shows the forward and reverse characteristics for one of these devices. The turn on voltage for this device occurs at 1.1 V.

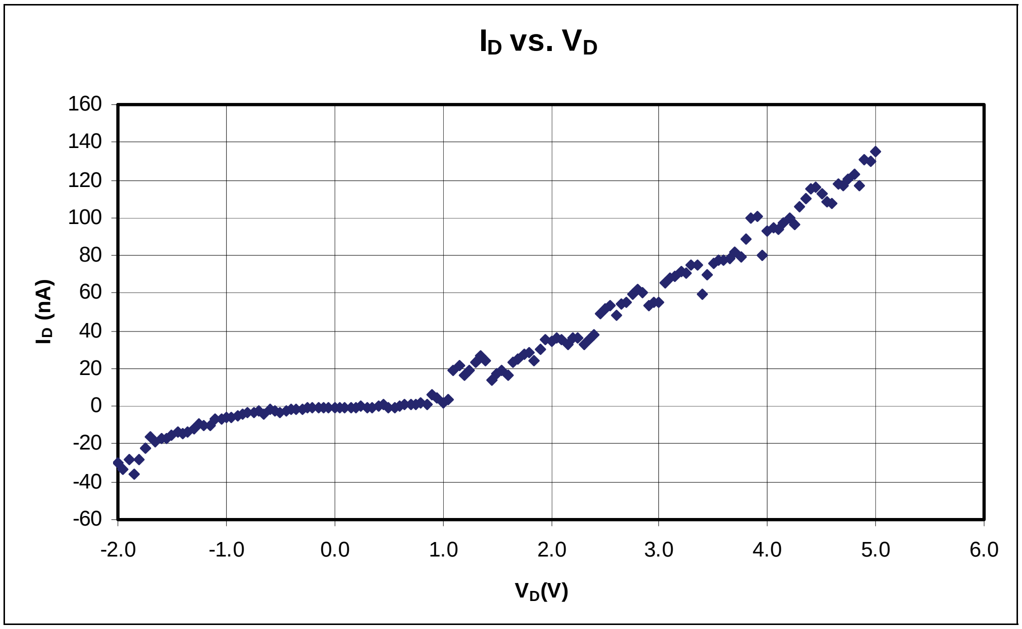

Figure 5. Diode DC I-V curve showing both the forward characteristic and reverse breakdown. The turn on voltage for the device occurs at 1.1 V. The ideality factor for this device is 1.80.

This behavior was then compared to the characteristic equation governing diode behavior, as seen in equation 1. The equation describes the drain current, I_D, through the diode with respect to the voltage across it, where I_S is the saturation current, n is the ideality factor, and V_T is the thermal voltage. The results were then benchmarked by calculating the ideality factor n for the tested diodes. A value of 1 for n represents an ideal diode, and n generally falls between 1 and 2 for functional diodes. Under low bias, up to 500 mV, ideality factors for the diodes averaged 1.80.

$$I_D = I_S\left[\exp(\frac{v_D}{nV_T}) - 1\right] \quad (1)$$

The results presented here are similar to other CNT diode properties previously reported, but with some differences. These ideality factors are higher than previously achieved values for in-house fabricated diodes using Au and Al contacts, which showed values between n = 1.1 to 1.2 (*10*). When compared to previous devices fabricated using the same contact metallization (Al/Pd), turn on voltages for the devices in this work were roughly 1 V greater (*6*). Better yield and further investigation into factors contributing to the formation of the Schottky barrier is needed in order to better compare the results conclusively. As our process is optimized and reproducibility increases, it is suspected that these issues will be better understood.

4. Discussion

At this stage of RF diode design development, efforts should be focused to increase yield in order to provide a sufficient sample size to adequately characterize these devices. After yield is increased and device performance is understood, the frequency response of these devices should be explored. It is expected the cutoff frequencies could extend well into the GHz regime due to the high mobilities reported for SWNTs (*9*).

In addition to cutoff frequency, power transmission in these diodes should also be analyzed. Power transmission measurements, such as RF to DC power conversion efficiency, could give valuable insight into the RF response of the devices as well as the current electrode design. As the AC response of SWNTs is better understood, other parameters of the diode such as input impedance should be defined, and a small signal equivalent circuit model should be developed.

Once these parameters of the devices are determined, these diodes could be used in a variety of applications including detectors, frequency multipliers, and nanoscale rectifying antenna (rectenna) designs. Improved performance at the device level, as is expected by using devices fabricated with multiple SWNTs, will increase the overall performance for these circuit applications.

5. Conclusion

Schottky diodes using single walled carbon nanotubes were fabricated using cleanroom processing techniques and their DC characteristics were tested. The devices fabricated during this research have provided objective evidence of achieving CNT-based Schottky diodes using Pd and Al metal contacts. The fine tuning of these devices will lead to optimization for various applications. Research to determine the optimal conditions required to improve yield, along with the design of suitable device architectures and development of the necessary test environments, are the next step in achieving the potential of carbon nanotube based electronics.

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10. Luquette, B. E.; Nichols, B. M. *Fabrication and Characterization of Schottky Diodes using Single Walled Carbon Nanotubes*; US Army Research Laboratory Summer Technical Report, August 2007.

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