Nanojunction Material Effect on the Photoelectric Response of Single-Wall Carbon Nanotube Rectennas
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ABSTRACT: To optimize the performance of carbon nanotube (CNT)-based rectennas, we have studied the effect of metal work function on the photodetection characteristics. Two materials of conducting nanoprobes, namely, gold (Au) and platinum (Pt), have been used to form a rectifying diode at the interface with the CNT. The electrical and optical characteristics of single-wall carbon nanotubes (SWCNTs) dispersed on top of a SiO₂/Si substrate have been investigated using a conductive mode atomic force microscope (C-AFM). The I−V measurements performed for both diodes have exhibited an explicit rectification behavior with high sensitivity of a CNT-based rectenna to light. It has been observed that the lower work function metal (Au) leads to a higher on/off current ratio than the high work function metal (Pt). These experimental observations will be explained using the material characterization of the complete system along with representative energy-band diagrams.

INTRODUCTION

Nanoantennas are attracting a lot of attention due to the progress in nanomanufacturing techniques.1 One of the novel techniques to realize nanoantennas at a nanoscale is to utilize nanoprobes (or ultrasharp tips)2−4 that will be used to make physical contact with individual CNTs and form a nano-Schottky diode rectifier.5 Additionally, we have demonstrated the feasibility of designing an optical rectenna by engineering a rectifying diode at the interface between a metal nanoprobe of an atomic force microscope (AFM) and single-wall carbon nanotubes (SWCNTs).6 This has paved the way for more investigations, wherein, in this work, we study the effect of the metal type of the nanoprobe on the rectenna performance.

Carbon nanotubes can be visualized as rolled-up sheets of graphene. They are widely explored due to their outstanding electrical, physical, and mechanical properties, and nowadays, they are becoming materials of choice for transistors,7−9 gas sensors,10,11 optical sensors,12 light emitters,13,14 and MEMS/NEMS applications.15 In optoelectronics, the property that makes CNT a favorable material is the symmetric band structure near the Fermi level that leads to an efficient broadband absorption covering from ultraviolet to infrared.16,17

Moreover, the CNT-based photodetector will reduce the dark current18 and enhance the sensitivity due to the high surface-to-volume ratio of individual CNTs. High-performance photodiodes, with high infrared (IR) responsivity and detectivity, are fabricated using solution-processed CNTs via a doping-free technique and photovoltage as the signal.19

In this work, we have investigated the optoelectrical behavior of SWCNTs as nanorectennas using different coatings for the conducting materials of AFM probes. As we have demonstrated in our previous work, isolating an individual carbon nanotube is an essential requirement for testing light detection characteristics of SWCNT-based nanorectennas, since pristine CNTs as-synthesized are bundled. In our work, we use N-methyl pyrrolidone (NMP),
as a highly effective solvent for dispersing and debundling SWCNTs.20−23

Here, we show that the optical rectenna constructed by individually dispersing SWCNT on a silicon oxide substrate has optical characteristics that depend on the type of metal of the nanoprobe of C-AFM, which is in direct contact with the SWCNT. This is attributed to the change in the electrical structure of the nanoprobe/CNT nanodiode, as well as the effect of the adsorption of the optical light by the CNT. The measurements are done using C-AFM equipped with a white light source.

This light source is a broadband, halogen dimming light source that has a power of 50 W and a wavelength spectrum between 500 and 1000 nm. Our results are related to the properties of the 1D Schottky barrier determined by the energy alignment between the metal/CNT and the Si substrate.

EXPERIMENTAL MEASUREMENTS

Dispersing Single-Wall CNTs (SWCNTs). The precursor material used in this experiment is the SWCNT powder with the chirality (7,6), ≥77% carbon as SWCNT, and 5 nm diameter in average from Sigma-Aldrich. N-Methyl-2-pyrrolidone (NMP) is used for the dispersion of these SWCNTs from the powder. The SWCNT solution dispersion was reported in our previous work.6 For our rectenna, we used an n-Si substrate with a SiO$_2$ layer of a 2.31 nm thickness, as measured using the spectroscopic ellipsometry technique. For the application of CNTs as a rectenna, CNTs must be dispersed separately on the oxide layer to eliminate the direct contact with the substrate and the photoeffect from the Si substrate.24 After cleaning the substrate with acetone, isopropanol, and distilled water consecutively, a SiO$_2$/Si sample with dimensions of 1 cm × 1 cm was initially treated in oxygen plasma for 10 min to improve the hydrophilic nature.
of the top surface and increase the adhesion between the SWCNT solution and the substrate. Just after treatment of the substrate surface, the diluted CNTs were drop-casted on the SiO2/Si surface at room temperature and dried in a vacuum oven at 120 °C for 4 h, as shown in Figure 1a. In this work, we used the same concentration as reported previously6 since no aggregates have been reported to be present below 0.02 mg/mL that is considered as the nanotube dispersion limit in NMP.23

Measurement Methodology and CNT Characterization. Figure 1 shows the schematic diagram of the sample preparation and the electrical measurements carried out using a conductive mode atomic force microscope (C-AFM). Figure 1a shows the well-diluted and well-dispersed CNTs in the deionized water. Figure 1b shows the schematic diagram of the AFM for the measurement of electrical characteristics using gold (Au)-coated and platinum (Pt)-coated nanoprobes. Using this AFM setup, we identified the individually dispersed CNTs by performing air-mode topography and then carried out the electrical measurement on the specific CNT by turning the light on and off.

The physical dimensions of the metal-coated probes used in this work and those of CNTs are analyzed using the field emission scanning electron microscope (FESEM) micrographs. Figure 2 shows the SEM images of Au probes and Pt probes, respectively. Both probes have shown almost similar nanoprobe apex sizes with a diameter of around 25 nm. The inset of Figure 2a,b shows the energy dispersive X-ray spectroscopy (EDX) peaks of Au, Pt, and Si, which infer the Au- and Pt-coated Si cantilever and probe. Since the main focus of this work is to study the effect of the nanoprobe material on the I−V characteristics on the CNTs, therefore, we choose inert metals like Au and Pt probes with a nearly equal probe apex. The equal size of the conductive probes will help to exclude the effect of nanoscale size on the electrical measurements. Hence, the observed change in I−V characteristics will mainly depend on the different work functions of nanoscale probes. Figure 2c shows the SEM images of the individually dispersed CNTs on the SiO2/Si substrate. These individual CNTs are achieved by appropriate dilution of a CNT solution in deionized water. The scale bar of the CNT’s SEM image clearly shows the 5 nm radius of the CNT, while one can clearly observe the individually dispersed CNTs on the SiO2/Si substrate. Figure 2d shows the current mapping topographic image of a bunch of CNTs on the SiO2/Si substrate; this shows that the CNTs are conductive and the current response is due to the existence of CNTs on the surface. The C-AFM-based topographic image is carried out by applying a +0.5 V constant voltage on the substrate during the scanning of the conductive tip on the sample.

Figure 3 shows the X-ray diffraction (XRD) and Raman spectroscopy results, which are used to analyze crystallinity and nanostructured material properties of a bunch of CNTs used in this work. Figure 3a shows the XRD spectrum of the CNT powder where the Bragg angle (2θ ≈ 26°) is the fingerprint of single-wall CNTs with a d002 value of 0.3506 nm.25 In addition to this major XRD peak, the other peak with smaller intensity at an angle of 2θ ≈ 43° corresponds to (100) of a single-wall CNT.25 Figure 3b shows the Raman spectrum of the SWCNT described by a defined high-intensity peak G
CNT-SiO₂-Si, by switching the light on and off the D peak (1327.31 cm⁻¹ peak along with a few defects is determined by the intensity of the I peak). The curves showed overlapping. From this, it is evident that the response to light is only evident when the CNT is illuminated at a lower turn-on voltage of −0.5 V. Moreover, for a Pt-based photodiode, the rectification behavior is not clearly shown without illumination. While after illumination, a clear rectification behavior is shown with a relatively high current at a turn-on voltage of −0.5 V. The inset of Figure 4 shows the semilog scale plot of the electrical characteristics for better visualization of the rectification behavior and the photoeffect. A typical light response of the rectenna, made of Au-CNT-SiO₂-Si and Pt-CNT-SiO₂-Si, by switching the light on and off with 0.1 Hz has been shown in Figure 5, at a fixed applied voltage of −1.0 V. The typical on/off ratio of a Au-based photodiode is 38, while it is only about 3 in the case of a Pt-based rectenna. It can be readily inferred that the current in the case of the Pt-based rectenna is much smaller than in the case of the Au-based rectenna in the forward bias; this difference is more prominent when the light is on, with a much higher on/off current ratio for the Au/CNT-based rectenna. This effect is evident from the rectangular current profile shown in Figure 5. The relatively higher on/off current ratio in the case of the Au-based rectenna indicates a much higher sensitivity of the Au-CNT-SiO₂-Si rectenna structure. When the nanoprobe/CNT rectenna is illuminated, electron oscillation is produced inside the junction of metal–CNT in a similar way to oscillation inside the antenna. This is correlated to a modulation of the Fermi level at the barrier of the diode. As has been shown in our previous work, when the devices are illuminated, electron oscillation is produced inside the antenna. This oscillation causes a modulation of the Fermi level at the barrier of the diode that will be translated as a shift in the (I–V) curve. Moreover, due to the sharp tip end, the area of contact between the tip apex and CNTs is much less than the tip radius, and this ensures that an enhancement of the electric field is observed at the interface of the contact of the sharp tip and the CNT only, as it has been shown in our previous work using finite element simulation. It has also been demonstrated that the response to light is only evident when the probe is placed on a single CNT, not directly on the substrate, even though the light illuminates a wide area of the sample. The difference in the current value between the Au-based rectenna and the Pt rectenna can be understood in the light of the energy-band diagram for Au/CNT/SiO₂/Si and Pt/CNT/SiO₂/Si structures, as shown in Figure 6, which explains the difference in the electrical response between the two rectennas. The alignment of Fermi levels across the interfaces requires more bending in the Si (bulk) side in the case of Pt contact compared to Au contact on the surface with the CNT. As a result, a less negative voltage (forward bias) is needed to raise the bulk conduction band for electrons to tunnel from the Si conduction band through the thin oxide layer to the CNT, and then electrons drift to the Fermi level of the nanoprobe. In the reverse bias, due to the existence of a wide barrier at the CNT/SiO₂/Si interface, a minimal current is observed.

When the CNT is illuminated with light, the absorbed photons at the resonance frequency lead to an increase in the energy of the electrons on the conduction band of CNT, and hence they would have enough energy to go over the forward Schottky barrier into the nanoprobe side at a lower threshold (turn-on) voltage $V₂$, where $V₂ < V₁$ (in the dark case), as shown in Figure 7. Moreover, some light effect can be attributed to the electron–hole pairs photogenerated across the small energy-band gap of the SWCNT. Furthermore, as Au has a lower work function than Pt, a smaller barrier is created at the junction with the CNT. This results in more current at the forward (negative) bias. This can be explained from the structure of a forward bias Schottky barrier.

**RESULTS AND DISCUSSION**

**Photoelectric Response of CNT Rectenna Devices.**

To assess the performance of the CNT-based rectenna, similar measurement conditions and procedures have been implemented on the two types of devices on different CNTs dispersed on the surface of the SiO₂/Si substrate. In our measurements, a voltage sweep between −1.0 and 1.0 V has been applied on the substrate while maintaining the AFM probe grounded. The probe has direct contact with the CNT, which is placed on the substrate. To complete the circuit, the second contact is made between the sample holder and the back of the substrate, which is scratched and covered with silver conductive paint to form an Ohmic contact. Figure 4 shows typical I–V curves of Au and Pt-based rectennas. For reproducibility validation, the measurements have been repeated on the same CNT several times with and without the light illumination; the curves showed overlapping. From the I–V curve, a clear rectification behavior is shown for both rectenna structures. However, a higher current in the case of a Au-based rectenna has been observed in the forward (negative) bias with a turn-on voltage of −0.65 V. This current increases drastically when illuminating the rectenna at a lower turn-on voltage of −0.5 V. Moreover, for a Pt-based photodiode, the rectification behavior is not clearly shown without illumination. While after illumination, a clear rectification behavior is shown with a relatively high current at a turn-on voltage of −0.5 V. The inset of Figure 4 shows the semilog scale plot of the electrical characteristics for better visualization of the rectification behavior and the photoeffect. A typical light response of the rectenna, made of Au-CNT-SiO₂-Si and Pt-CNT-SiO₂-Si, by switching the light on and off with 0.1 Hz has been shown in Figure 5, at a fixed applied voltage of −1.0 V. The typical on/off ratio of a Au-based photodiode is 38, while it is only about 3 in the case of a Pt-based rectenna. It can be readily inferred that the current in the case of the Pt-based rectenna is much smaller than in the case of the Au-based rectenna in the forward bias; this difference is more prominent when the light is on, with a much higher on/off current ratio for the Au/CNT-based rectenna. This effect is evident from the rectangular current profile shown in Figure 5. The relatively higher on/off current ratio in the case of the Au-based rectenna indicates a much higher sensitivity of the Au-CNT-SiO₂-Si rectenna structure. When the nanoprobe/CNT rectenna is illuminated, electron oscillation is produced inside the junction of metal–CNT in a similar way to oscillation inside the antenna. This is correlated to a modulation of the Fermi level at the barrier of the diode. As has been shown in our previous work, when the devices are illuminated, electron oscillation is produced inside the antenna. This oscillation causes a modulation of the Fermi level at the barrier of the diode that will be translated as a shift in the (I–V) curve. Moreover, due to the sharp tip end, the area of contact between the tip apex and CNTs is much less than the tip radius, and this ensures that an enhancement of the electric field is observed at the interface of the contact of the sharp tip and the CNT only, as it has been shown in our previous work using finite element simulation. It has also been demonstrated that the response to light is only evident when the probe is placed on a single CNT, not directly on the substrate, even though the light illuminates a wide area of the sample.

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Figure 5. (a) Light response of the Au/CNT/SiO₂/Si device at a reading voltage of (−1 V) and (b) light response of the Pt/CNT/SiO₂/Si device at a reading voltage of (−1 V).
diode at the interface between the metal probes and CNT, where the thermionic ionic current is dominant and can be expressed as follows\textsuperscript{29,30}

\[
I(V) = A^* T^2 e^{-\frac{q\phi_b}{kT}} e^{-\frac{qV}{kT}} (1)
\]

where \(A\) is the area of the Schottky diode, \(A^*\) is the effective Richardson coefficient, \(T\) is the absolute temperature, \(q\) is the fundamental electronic charge, \(\phi_b\) is the barrier height, \(k\) is Boltzmann’s constant, and \(V\) is the applied voltage.

For the same substrate, the difference between the two devices is the metal type used. From what has been reported in the literature, 5.05,\textsuperscript{31} 5.3, and 5.7 eV correspond to the work functions of CNT, Au, and Pt, respectively. The barrier height \(\phi_b\) at the interface between the CNT and the metal is higher in the case of Pt than in the case of Au with values of 1.095 and 0.695 eV, respectively, as also shown in Figure 6. This will lead to a higher current value in the case of Au compared to Pt. This is in agreement with our measurements that showed a lower current in the case of Pt-based devices.

**CONCLUSIONS**

In this work, we have investigated the photoelectric response of CNT-based nanorectennas for different metal nanoprobe materials in the C-AFM. The measurements exhibit a clear rectification behavior at the interface between the metal/CNT with a higher current observed in the case of a Au metal
The authors declare no competing financial interest.

Author Contributions
M.R. conceived the idea, supervised the experimental work, and wrote the paper; L.T. and Y.A. performed sample preparation, electrical and physical characterizations, and the manuscript drafting, with equal contribution; and B.M. contributed to data analysis, manuscript editing, and secured funding. All authors reviewed the paper.

Notes
The authors declare no competing financial interest.

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Figure 7. Schematics of the energy-band diagram of (a) Au/CNT/SiO₂/Si in the dark case and (b) Au/CNT/SiO₂/Si in the case where there is light. The turn-on voltage in (b) is less than in (a), as the absorbed light by the CNT results in higher energy carriers that can overcome the forward Schottky barrier at a lower voltage.
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