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Dynamically and Continuously Tunable Infrared Photodetector Using Carbon Nanotubes

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Dynamically and Continuously Tunable Infrared Photodetector Using Carbon Nanotubes

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Abstract

This report details the progress made in realizing a tunable photodetector based on carbon nanotubes. Results are presented for the theory and modeling of the electronic and optical properties of carbon nanotubes, the fabrication of nanotube devices, their electrical testing, and their optoelectronic characterization. The effects of gamma and proton irradiation are also discussed.

CONTENTS

1. Introduction.....	7
2. Modeling of strain and doping effects on CNT electronic and optoelectronic properties.....	9
2.1 Modeling of strain effects	9
2.2 Modeling of doping effects.....	11
3. Fabrication of CNT devices and electrical characterization	13
3.1 Suspended CNT FETs.....	13
3.1 Suspended CNT Schottky diodes.....	14
4. Optoelectronic measurements of CNT devices.....	17
5. Radiation testing of cnt devices	19
6. Conclusions.....	20
7. References.....	21
Distribution [can go on an even or an odd page]	22

FIGURES

Figure 1. Calculated electronic and optical bandgap of a (17,0) CNT as a function of strain.....	10
Figure 2. Calculated electronic properties of a (10,0) CNT as a function of doping.....	11
Figure 3. Calculated optical properties of a (10,0) CNT as a function of doping.	11
Figure 4. SEM image of a suspended CNT FET made fabricated using nanoimprint lithography.	14
Figure 5. Transfer characteristics of a suspended CNT FET.....	14
Figure 6. SEM image of a suspended CNT Schottky diode.	15
Figure 7. Current-voltage characteristics of a CNT Schottky diode.....	15
Figure 8. Reverse-bias current in the dark and under illumination for a CNT Schottky diode. ...	17
Figure 9. Bolometric response of a CNT Schottky diode at forward bias.....	18
Figure 10. Transfer characteristic of a CNTFET before and after exposure to gamma irradiation.	19

NOMENCLATURE

DOE	Department of Energy
SNL	Sandia National Laboratories
CNT	Carbon Nanotube
FET	Field-Effect Transistor

1. INTRODUCTION

Infrared photodetectors play a key role across Sandia mission areas being used for example in space-based surveillance, thermal imaging, aerial surveillance, and non-destructive imaging of components. IR detectors rely on pixel arrays, each pixel having a dimension in the ten to twenty micron range. Pixels are often made of exotic semiconductors like $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ because the bandgap (and thus the sensitivity to different optical wavelengths) can be controlled by varying the composition x . However, once a composition is chosen, this fixes the sensitivity to a specific range of wavelengths leading to black-and-white detection. As everyday experience with human vision shows, color detection improves discrimination significantly, and the same applies to IR detectors. Thus one important need is dynamic multiwavelength detection in the IR. Current technology achieves two-color detection at the pixel level using a triple layer thin film approach, where two films with different compositions contact a common electrode layer. Unfortunately, this does not provide an obvious path for continuous multi-wavelength detection.

To address this issue, we proposed to utilize the unique properties of carbon nanotubes (CNTs) to demonstrate an infrared pixel with continuously and dynamically tunable absorption. The concept relies on the fact that the bandgap of CNTs is sensitive to strain, with a change of 100 meV per percent strain, as demonstrated experimentally and theoretically. By fabricating a CNT nanoelectromechanical (NEM) device, we proposed to control the strain applied to the CNTs and achieve tunability of the optical absorption. Such CNT NEMS have been demonstrated with resonant frequencies of tens of MHz, and can thus be rapidly tuned. Our experimental work was coupled with theory and modeling of the photophysics of strained CNT devices. Finally, we tested the radiation hardness of these devices.

This SAND report details the progress made in all facets of this project including many-body ab initio calculations, device fabrication, electrical testing, optoelectronic testing, and radiation testing.

2. MODELING OF STRAIN AND DOPING EFFECTS ON CNT ELECTRONIC AND OPTOELECTRONIC PROPERTIES

To further support the idea that strain can change the optical properties of CNTs, we developed a many-body approach based on the GW method and the Bethe-Salpeter equation to calculate the electronic and optical properties of strained CNTs. In addition, we realized that electrostatic gating of the CNTs to induce the strain, as proposed in the NEMS device would change the effective doping level of the CNTs. We thus calculated electronic and optical properties of the CNTs as a function of doping.

2.1 Modeling of strain effects

We performed our ab initio calculations on the semiconducting (11,0) and (17,0) CNTs for uniaxial strains from 0% to 5%. We start by investigating the ground-state properties (e.g. relaxed atomic structure, electron density) within Density Functional Theory (DFT). The DFT calculations are performed within the Local Density Approximation (LDA), using ab initio pseudopotentials in combination with a plane-wave basis set with a kinetic energy cutoff of 60 Ryd, in a supercell geometry with tube separation (center to center) of 1.8 nm. The atomic structure is relaxed until forces are smaller than 5 meV/Å for both the strained and unstrained cases.

Figure 1 shows that the bandgap of the (17,0) CNT as a function of strain, indicating a reduction of 115 meV/%. These values can be compared with those obtained from the simple tight-binding expression for small strains applied to zigzag CNTs where values of -108 meV/% are obtained. While DFT and TB calculations agree to a large extent, an open question is whether many-body effects can change the above picture. To address this question, we performed quasiparticle calculations using the GW approach. The electron self-energy $\Sigma=iGW$ is obtained within the G_0W_0 approximation, i.e. using the LDA eigenvalues and wavefunctions to construct the 1-particle Green's function G . The screened Coulomb interaction W is evaluated within the Random Phase Approximation and extended at non-zero frequencies using the Plasmon-Pole approximation. We have considered empty states up to an energy cutoff of ~ 60 eV, and we have used the 'static-remainder' technique to ensure convergence with respect to the number of empty states. Convergence with respect to k-point sampling has been achieved with 128 k-points in the one-dimensional Brillouin zone. Also, the Coulomb potential has been truncated, in order to prevent tube-tube interactions or periodic image effects due to the use of a periodic supercell.

Figure 1 shows the calculated GW gap as a function of strain. The dependence on strain is very similar to that obtained within LDA, with the gap decreasing linearly with strain. However, we find that strain effects are much more significant within GW: a reduction of 200 meV/% strain is found for both tubes. This enhanced effect is due to quasiparticle corrections to the LDA bandstructure.

Figure 1. Calculated electronic and optical bandgap of a (17,0) CNT as a function of strain.

We next turn to the optical properties. To calculate these, we start from the GW results and couple them with the BSE. Both the BSE and GW calculations were performed using the BerkeleyGW package. We solve the BSE for excitons within the static approximation for the dielectric screening and within the Tamm-Dancoff approximation for excitons. Having obtained the excitonic properties one can then obtain the optical response of CNTs using the standard approach. The optical bandgap is obtained from the QP bandgap after subtracting the binding energy of the lowest bright exciton, a quantity which results from the overall attractive electron-hole interaction between the (quasi)electron and the (quasi)hole forming the exciton.

Figure 1 shows the calculated optical absorption spectra including excitonic effects. It is immediately clear from this picture that the exciton energy Ω is strongly shifted by strain. Surprisingly, the dependence of the peak energy on strain is similar to that of the LDA gap, with a variation of about 100 meV/%. The implication is that the exciton binding energy depends on strain. In fact, we find that the binding energy decreases significantly with strain, with a variation on the order of 65 meV/%. Much like the decrease in the quasiparticle gap, the decrease in binding energy also stems from the change in dielectric screening upon applied strain. Indeed, the attractive interaction between the electron and hole forming the exciton is mediated by the screened Coulomb interaction W . As we discussed, with decreasing bandgap the dielectric screening gets enhanced, and thus the binding between electron and hole decreases. This effect in fact explains why the change in optical gap upon applied strain is similar to the obtained at the LDA level: it is due to cancellation of effects between QP self-energy corrections and excitonic effects.

2.2 Modeling of doping effects

We used the many-body *ab initio* technique described in section 2.1 to calculate the electronic and optical properties of a doped (10,0) CNT. Details of the methods and extended results can be found in Refs 1 and 2. One of the main results is the large reduction of the electronic bandgap upon doping of the CNT. Indeed, as Fig. 2 shows, the bandgap can be reduced by hundreds of meVs with experimentally-relevant doping. This effect is much stronger than in bulk materials due to the different screening in quasi-one-dimensional materials.

Figure 2. Calculated electronic properties of a (10,0) CNT as a function of doping.

The strong impact of doping is also found in the optical properties. Figure 3 shows the exciton binding energy as a function of doping for two of the excitons. Clearly, the binding energy is significantly reduced by doping. For example, the lowest energy exciton has a binding energy of 0.85 eV at zero doping, which can be reduced to as low as 0.2 eV at large doping.

Figure 3. Calculated optical properties of a (10,0) CNT as a function of doping.

The results of our modeling suggest that both strain and doping effects should be considered when analyzing the performance of suspended CNT devices when a gate bias is applied to bend the CNTs. More generally, our results indicate that many-body effects are important in CNTs, and should be included in device-level simulations of electronic and optoelectronic devices.

3. FABRICATION OF CNT DEVICES AND ELECTRICAL CHARACTERIZATION

3.1 Suspended CNT FETs

Suspended CNT FETs are fabricated using a transfer process where the CNTs are “stamped” from one wafer, the CNT “donor” wafer, onto the electrodes which are fabricated on the “acceptor” wafer. Using the stamping method the CNTs are never exposed to contaminating resist or harsh chemicals like etchants. Moreover, the CNTs on the donor wafer could conceivably be annealed to reduce defects, which requires temperatures higher than Au can tolerate, and the process would remain CMOS compatible.

The donor wafer is fabricated using the following procedure: The CNTs are purchased from a vendor, typically Cheap Tubes, dispersed in Sodium Taurodeoxycholate (1%STDC) with ultrasonication, and purified using ultracentrifugation. The purified CNTs are removed from the top two thirds from the centrifuge vial after ultracentrifugation. The solution is concentrated by centrifuging overnight using Optiprep-density gradient medium as a stop layer. The concentrate solution is enriched in semiconducting CNTs using density gradient ultracentrifugation (DGU). UV-Vis absorption spectroscopy reveals that the process results in an enrichment of up to 90% in semiconducting CNTs. The fraction of mostly semiconducting CNTS solution is then spin coated on the wafer, which has a thermal oxide (SiO_2) pretreated with the self assembled monolayer APTES. After spincoating the individual CNTs are distributed radially from the center of the wafer in a controllable density on the surface. The donor wafer is rinsed in acetone, isopropyl alcohol, and deionized water to remove the surfactant.

The electrodes on the acceptor wafer are patterned using shadow-mask photolithography, in which the photoresist is patterned into a shadow mask. To make the shadow mask, an undercut, liftoff resist (LOR 1A or LOR 20B, Microchem) is used under a conventional photoresist (Shipley 1805, Microchem, or NR9-1000PY, Futurex). The Au metal is deposited with a 5 nm Cr adhesion layer using electron beam evaporation. The e-beam evaporation is directional, so that the shadow mask acts as a stencil to pattern the Au and the Au electrodes never touch the photoresist. After deposition the photoresist is lifted off, leaving clean Cr/Au features. This process is used first to pattern 100 nm thick wiring to the source and drain electrodes and then 500 nm tall Au pillars on top of the wiring. An Ar plasma descum may be used to further clean the electrodes before stamping.

In the stamping process, the finished donor and acceptor wafers are divided into quarters or dies, taped together, and placed in a Nanonex NX-2000 nanoim print lithography tool. The tool presses the wafers together at 150 – 300 PSI and heats them to 150° C for three minutes. During this process the malleable Au pillars are slightly deformed (squashed), with more deformation at high pressure. A pre-anneal eliminates the deformation; however the deformation may be essential to the CNT transfer.

The stamping process results in nearly all of the CNTs pressed underneath the pillars being transferred from the donor wafer SiO_2 substrate to the acceptor wafer Au, because the CNT adhesion is much better on the Au. There is a finite probability for CNTs in the electrode gap between pillars to be transferred. Secondary electron SEM with a low accelerating voltage ($V \leq 2$ kV) and fast scanning can distinguish between CNTs that touch the substrate (partially suspended) and CNTs that extend from electrode to electrode without touching the substrate

(completely suspended) through the contrast change that occurs when the CNT contacts the insulating substrate. An example device fabricated using the above technique is shown in Fig. 4.

Figure 4. SEM image of a suspended CNT FET made fabricated using nanoimprint lithography.

The electrical characteristics of such devices were measured in a probe station. Figure 5 shows the transfer characteristics for one CNTFET device. The FET is ON at negative gate bias and OFF at positive gate bias, with an ON/OFF ratio greater than 1000. In addition, while there is some hysteresis in the two sweeps, it is much reduced from devices on substrates. These measurements indicate that high-quality devices can be fabricated with the nanostamping technique.

Figure 5. Transfer characteristics of a suspended CNT FET.

3.1 Suspended CNT Schottky diodes

Device fabrication was carried out by combination and permutation of individual steps so as to eliminate artifacts. These steps included: a) wafer functionalization, b) nanotube deposition by spin coating, c) photolithography and metallization, d) liftoff, e) dry etching, f) wet etching, and g) electrode annealing. Step details are as follows: a) Wafer functionalization: Heavily doped Si wafers capped with 900Å or 10,000Å of SiO₂ were Piranha cleaned and treated with solutions of (3-Aminopropyl)triethoxysilane (APTES) in ethanol. b) Nanotube deposition: Dilute aqueous

solutions were pipetted onto functionalized or electrode- containing wafers spun at 2000 RPM. The wafers were copiously rinsed with DI water and dried with nitrogen. c) Photolithography and metallization: The shadow mask bridges are formed by exposing a negative tone photoresist deposited on a rapidly developing liftoff resist. Following sufficient development, the bridges are freed. The substrate is rinsed with DI water and dried with nitrogen. Deposited electrodes were usually 15 nm to 30 nm thick. The large workfunction electrode was often deposited on a very thin adhesion layer. d) Liftoff: N-Methyl-2-pyrrolidone (NMP) typically at elevated temperature (70°C to boiling) was used to remove the liftoff resist and bridges from the substrate. e) Dry etching: A brief O₂ plasma descum was used to ensure substrate cleanliness for devices in which nanotubes were deposited following lithography. f) Wet etching: A 5:1 (DI water:HF) buffered oxide etch was used to remove a few hundred nanometers of SiO₂ from beneath the nanotube channel in the suspended devices. After the etch, the wafer was transferred to a DI water bath, an isopropanol bath, and dried with nitrogen. g) Electrode annealing: Electrodes of some devices were annealed at 300-400° in Ar or vacuum in order to improve electrode-substrate adhesion in devices that underwent wet etching, or electrode-nanotube contact resistance in devices where the nanotubes were deposited on top of the electrodes.

Figure 6. SEM image of a suspended CNT Schottky diode.

The I-V curve for a CNT Schottky diode is shown in Figure 7, clearly showing rectification, with a low reverse-bias leakage current. We have realized many such devices using a combination of metals for the ohmic and Schottky contacts.

Figure 7. Current-voltage characteristics of a CNT Schottky diode.

4. OPTOELECTRONIC MEASUREMENTS OF CNT DEVICES

To measure the optoelectronic properties of the Schottky diodes, we used Scanning Photocurrent Microscopy (SPCM). Figure 8 shows the dark current and photocurrent of the device presented in Figs 6 and 7 under reverse bias, at room temperature. The laser spot was centered at the position of maximal response determined by SPCM, near the Cr contact. Note that the behavior of the photocurrent as a function of reverse bias differs dramatically from what is observed in bulk photodiodes. In bulk devices, illumination results in an I-V curve that resembles the dark current curve shifted downward by a constant current at each point: the I-V curve rapidly saturates at small reverse bias and remains saturated until breakdown occurs at large reverse bias. In contrast, the I-V curve under illumination in Fig. 8 increases rapidly at small reverse bias and does so continuously at larger fields, never saturating. We find this remarkable behavior to be characteristic of all the supported and suspended photodiodes that we fabricated. This is an important result because it suggests that photocurrent enhancement might be important in CNT diodes, which could lead to improved photodetector sensitivity. For example, preliminary theoretical work that we have performed suggests that the enhancement is due to the generation of multiple electron-hole pairs per incoming photon, which could significantly improve efficiency. This is a research area that deserves more attention in the future.

Figure 8. Reverse-bias current in the dark and under red illumination for a CNT Schottky diode.

We also considered the change in the forward-bias I-V curve for Schottky diodes, as shown in Fig. 8. There, it can be seen that the photocurrent under illumination is larger than the dark current. This is unusual because for a bulk diode, we expect a uniform downshift of the I-V curve. By comparing these measurements with measurements of the I-V curves in the dark but under heating at different temperatures, we concluded that light absorption in the diode leads to significant heating of the nanotube, which leads to a strong bolometric effect. Thus, these devices are not only interesting for direct photocurrent generation as discussed above, but also for applications that rely on bolometers.

Figure 9. Bolometric response of a CNT Schottky diode at forward bias.

5. RADIATION TESTING OF CNT DEVICES

The radiation hardness of FET devices consisting of individual CNTs was tested under gamma and proton irradiation. A number of devices were fabricated and electrical measurements were performed before and after radiation exposure. We found that regardless of the type of radiation or the dose, almost all of the devices still functioned as transistors post-exposure. An example for a device exposed to gamma irradiation is shown in Figure 10, where it can be seen that the subthreshold swing is unchanged before and after irradiation. However, we have observed that often there can be a reduction of the ON state current after exposure, although additional experiments are needed to verify the correlation with radiation exposure.

Figure 10. Transfer characteristic of a CNTFET before and after exposure to gamma irradiation.

6. CONCLUSIONS

This work has demonstrated the CNTs possess unique properties for optical detection, and has identified new phenomena that deserve further scientific exploration. For example, it was demonstrated that bandgap renormalization due to doping is particularly strong in CNTs, and this should be included in future modeling of CNT devices. We also demonstrated new fabrication approaches to make two and three-terminal CNT devices, which can be supported on a substrate or where the CNTs can be suspended. Finally, optoelectronic measurements have identified two new exciting phenomena, multiple electron-hole pair generation and a bolometric effect, that are exciting and should be explored both fundamentally and also for device applications.

7. REFERENCES

1. C. D. Spataru and F. Léonard, *Phy. Rev. Lett.* **104**, 177402 (2010).
2. C. D. Spataru and F. Léonard, *Chem. Phys.*, in press.

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