

Fabrication of Photodetectors using Transparent Carbon Nanotube Films

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Abstract

Carbon nanotubes are promising nanoscale materials for novel electrical, mechanical, chemical, and biological device and sensors based on its outstanding properties. Single walled carbon nanotubes can be either semiconducting or metallic material depending on its structures. However, controlling the structure is quite challenging with current technologies. For the network formation of the single walled carbon nanotubes, single walled carbon nanotube films, the properties of individual single walled carbon nanotubes are ensemble averaged and show uniform physical and electrical properties. Also it is transparent, flexible, and conductive. Therefore, it has attracted great research attentions and as a result, several applications of the single walled carbon nanotube films have been demonstrated. In this study, the metal-semiconductor-metal photodetector using the single walled carbon nanotube films are fabricated. The fabrication methods from the network synthesis to the photodetector device fabrication are demonstrated. The fabrication methods are vacuum filtration for the synthesis of single walled carbon nanotube films and typical semiconductor fabrication techniques for the fabrication of metal-semiconductor-metal photodetector device. Also the photoelectrical properties of the fabricated photodetector are discussed.

Keywords: *Carbon nanotubes, Single walled carbon nanotube films, Photodetector, Metal-Semiconductor-Metal photodetector*

1. Introduction

Carbon nanotubes (CNTs) have attracted great research attentions due to its outstanding electrical, physical, mechanical, chemical properties. Based on its excellent properties, CNTs are promising nanoscale materials for novel electrical, mechanical, chemical, and biological devices and sensors.[1, 2] Depending on the number of walls, CNTs are categorized into single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs). SWCNTs are composed with one wall and MWCNTs are composed with more than one wall. MWCNTs are electrically metallic material, but SWCNTs can be either semiconducting or metallic material based on its structures such as diameter and chirality. Three types of SWCNTs structures are possible such as armchair, zigzag, and chiral structures depending on its chirality. It is also known that the bandgap of semiconducting SWCNT is inversely proportional to their diameter. Typical growth methods of CNTs are the arc discharge, laser vaporization, and chemical vapor deposition methods.[2] However, controlling of the CNT structures such as diameter, chirality, location, and direction is very challenging with current technologies.

In the network formation of SWCNTs, SWCNT films, variations in diameter and chirality of individual SWCNTs are ensemble averaged and yield uniform physical and electrical

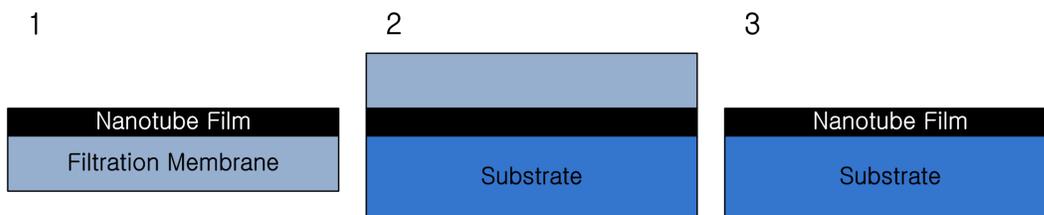
properties.[3-6] The SWCNT films have 3-Dimensional interwoven SWCNTs and it is optically transparent, electrically conducting, and mechanically flexible. Several applications of CNT films have been demonstrated. In optoelectronic and photovoltaic applications, the CNT films are promising materials as contact for light-emitting diodes (LEDs), organic solar cells, and electrochromic devices. In addition, thin film transistors, flexible microelectronics, and chemical sensors are possible applications of the CNT films.[7-19] To utilize the CNT films for the applications, it is required to develop the fabrication techniques. In this study, Metal-Semiconductor-Metal (MSM) photodetector using SWCNT films were demonstrated. The MSM photodetector has a simple structure which has 2 layers of a metal electrode layer and a semiconductor substrate layer, therefore it is relatively easy to fabricate. The photoelectric mechanism of the MSM photodetector is that, when light is illuminated on the device, electron and hole pairs are created in the semiconductor substrate and photocurrents start to flow between the metal electrodes. The fabrication techniques used in this study are typical semiconductor fabrication techniques such as photolithography and plasma etching. The synthesis of SWCNT films is also discussed to provide ideas of overall procedures of the fabrications. Moreover, photoelectric properties of the fabricated MSM photodetector were characterized and discussed to compare it to other typical MSM photodetectors.

2. Experiment

2.1 Synthesis of SWCNT films

The details of SWCNT films synthesis procedures can be found in REF [3]. In brief, the SWCNTs used in this study were grown by a pulsed laser vaporization growth method. At the beginning of the fabrication, the as-grown SWCNTs were purified by HNO_3 . The purified SWCNTs were dispersed in surfactant solution which has Triton X-100 surfactant, NaOH, and DI water. The SWCNTs in surfactant solution were ultrasonicated for further dispersion. The SWCNTs in surfactant solution were then vacuum filtered onto a filtration membrane. As a result, the SWCNTs were deposited as a thin film on the membrane and the thickness was controlled by the SWCNTs concentration in the surfactant solution and volume of the solution filtered. The films were transferred onto a substrate by placing the films' side against the substrate and some pressures were applied on the back side of the filtration membrane. And the sample was dried in an oven. It was found that the SWCNT films were well adhered to the substrate after drying. Finally, the filtration membrane is dissolved in acetone, leaving only the SWCNT films adhered to the substrate. Figure 1 shows schematic diagrams of SWCNT films synthesis procedures. Figure 1.1 shows the SWCNT films formed on the filtration membrane after the vacuum filtration. Figure 1.2 shows the transferring the SWCNT

Figure 1. The schematic diagram of synthesis SWCNT films.



films and the filtration membrane on the substrate. The substrate can be various materials such as glass, silicon, and GaAs which was adopted for this study. Figure 1.3 shows the

transferred SWCNT films onto the substrate. Figure 2 is the AFM image of the synthesized SWCNT films. We can check the texture of the SWCNT films from the image.

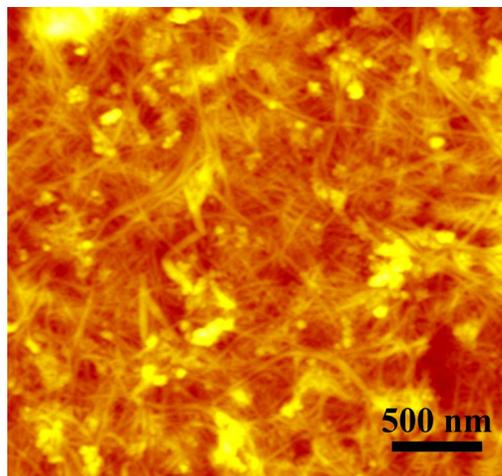


Figure 2. The AFM image of synthesized SWCNT films.

2.2 Patterning SWCNT films

Figure 3 shows the schematic diagram of patterning SWCNT films. First, photoresist, S1813, was spin coated on the SWCNT films and baked on a hot plate in air. The sample was then UV exposed and dipped into a developer. To remove any remaining developer, the sample was rinsed in DI water several times. Patterning the SWCNT films was done by O₂ plasma. The details of patterning procedures using inductively coupled plasma reactive ion etching system (ICP-RIE) was described in REF [20]. Briefly mentioning of the study, by using electron beam lithography, O₂ plasma, and ICP-RIE system, submicron (lateral dimension down to ~50 nm) features were achieved. The major advantage of ICP-RIE system is that it is possible to control a plasma density and ion energy during an etching process almost separately. Also it is possible to get relatively low pressure, high plasma density, large physical component, more anisotropic patterns, and faster etch rates depending on the parameters of the system. In the study, several factors of etching SWCNT films were systematically studied. Decreasing the substrate power decreased the SWCNT films and photoresist etch rates significantly. Decreasing the chamber pressure of ICP-RIE system increased the SWCNT films and photoresist etch rates and increased the etch selectivity between the SWCNT films and the photoresist which was used as etching masks. Also it was found that increasing the chamber pressure did not affect much on the etch rates of the SWCNT films and the photoresist. Increasing the helium flow rate which cools down the substrate during an etching process did not affect much on the etch rates of the SWCNT films and photoresists. Figure 4 is the AFM image of the etched SWCNT films using the developed etching techniques. The brighter areas are SWCNT films and the darker area is etched area, GaAs substrate. The texture of SWCNT films can be checked in the image. The dots on the darker area, substrate, are possibly the catalyst nanoparticles used for the SWCNTs growth.

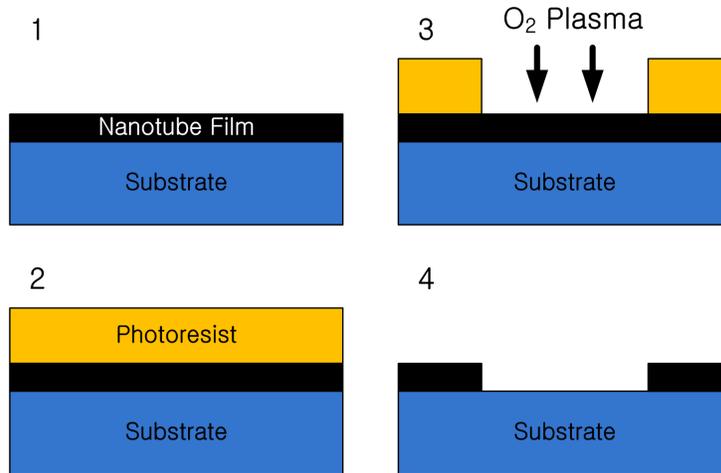


Figure 3. The schematic diagram of etching SWCNT films using O₂ plasma. The as-prepared SWCNT films (Figure 3.1) were spin coated by photoresist, S1813, (Figure 3.2). The sample was exposed by UV light and developed. To etch the SWCNT films using the photoresist as masks, the ICP-RIE system was used and O₂ plasma during the etching process etched the SWCNT films away. (Figure 3.3) The last step is removing the remained photoresists by acetone. (Figure 3.4)

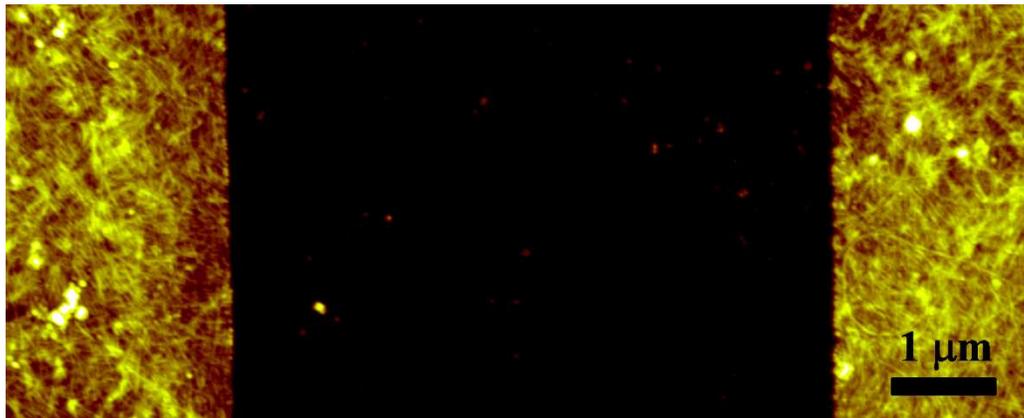


Figure 4. The AFM image of etched SWCNT films. The brighter areas are patterned SWCNT films, the texture of SWCNT films was shown, and the darker area is the substrate. The dots on the substrates are possibly the catalyst nanoparticles used for the growth of SWCNTs.

As shown in the image, the SWCNT films are selectively etched and the designed patterns of SWCNT films were achieved.

2.3 Fabrication of Metal-Semiconductor-Metal photodetector

To fabricate the SWCNT films MSM photodetector, the GaAs substrate which is a direct bandgap semiconductor was used as the semiconductor substrate and the SWCNT films were used as the metal electrodes. Figure 5 shows the fabrication procedures of the MSM photodetector using the SWCNT films. First, SiN isolation layer was deposited on the GaAs substrate. The SiN isolation layer was located between SWCNT films and GaAs substrate to eliminate parasitic leakage paths and reduce the dark current of the photodetector. (See figure 5.2 and figure 5.8)

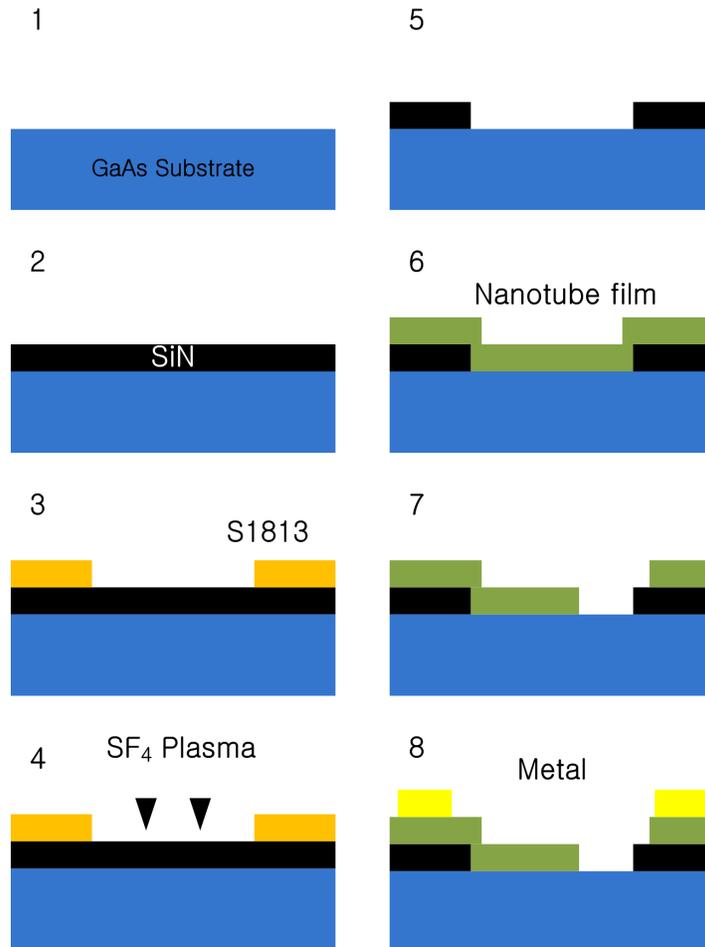


Figure 5. The schematic diagram of the the MSM photodetector fabrication procedures using the SWCNT films. (1) The GaAs direct bandgap semiconductor was used as the semiconductor substrate. (2) The SiN isolation layer was deposited on the GaAs substrate to eliminate parasitic leakage paths and reduce the dark current of the photodetector. (3) The active window was opened by photolithography and (4) the plasma etching of the unmasked SiN area using SF₄ plasma. (5) The sample was then dipped into acetone to remove any remaining photoresists. (6) The SWCNT films were prepared and deposited on the substrate by the vacuum filtration method (7) The deposited SWCNT films were etched using O₂ plasma by ICP-RIE system. (8) The metal electrodes were deposited and patterned on the SWCNT films by photolithography, electron beam evaporation, and lift-off processes.

To open the active window to get lights on the semiconductor substrate, photoresist, S1813, was spin coated, exposed in UV light, and developed in developer. (Figure 5.3) After rinse the sample in DI water, it was put into a plasma etching system and the unmasked SiN area was etched away by SF₄ plasma. (Figure 5.4) The sample was then dipped into acetone to remove any remaining photoresists. (Figure 5.5) By using the vacuum filtration method mentioned previously, SWCNT films were prepared and deposited on the substrate. (See figure 1 and figure 5.6) The deposited SWCNT films were etched and patterned by the developed method mentioned previously. (See figure 2 and figure 5.7) The pattern of the SWCNT films is interdigitated fingers shape to efficiently collect photocurrents from the semiconductor substrate. For convenient electrical measurements, metal electrodes were deposited and patterned on the SWCNT films. To deposit metal contacts on the SWCNT films, photoresist, S1813, was spin coated on the sample, exposed by UV light, and developed. Finally, Cr/Pd metal contacts were electron beam evaporated on the whole sample and lift-off process was subsequently conducted. (Figure 5.8)

3. Results

Figure 6 shows the fabricated MSM photodetector using SWCNT films and MSM photodetectors using typical metals. The later sample, control sample, was prepared for comparisons of photoelectric properties. Cr and Pd were used for the control sample as metal electrodes and GaAs was used as substrate. In the figure 6.1, the interdigitated fingers are SWCNT films to collect photocurrents from the GaAs semiconductor substrate and two large pads (yellow color) on both sides of the sample are metal (Cr/Pd) electrodes for convenient electrical probing. The rectangular box in the center of the device shows the active window to get lights reaching on the semiconductor substrate. To systematic analysis of the device, several samples with different dimensions were fabricated. The details of photoelectric properties of SWCNT films MSM photodetector were described in REF [21]. In brief, the effects of the device geometry on the photoelectric properties of the SWCNT films MSM photodetector were studied. The Schottky barrier height between SWCNT films and GaAs substrate, and comparisons between SWCNT films MSM photodetector and typical metal MSM photodetectors were provided as well.

First, regarding the effects of the device geometry on the dark current characteristics of the fabricated SWCNT films MSM photodetectors, increasing the spacing between the fingers of the SWCNT films decreased the number of fingers in identical active window size and finger widths. The decrease of numbers of fingers resulted in decrease of dark current of the device. The increasing of the width of the SWCNT films fingers and the spacing between the fingers were resulted in decreasing of the dark current. Also it was found that the width of the SWCNT fingers is roughly independent with the dark current if the widths of the fingers were beyond certain values due to the current crowding effect at the edges of the SWCNT films fingers. Also the current crowding effect was demonstrated by MEDICI simulations in the study. When the width of SWCNT films fingers and the spacing between the fingers were fixed, the increasing of the size of active window was resulted in the increasing of the dark current of the photodetectors.

The photoelectric properties with light illumination were studied as well and it showed that the dark current of the SWCNT films MSM photodetector was decreased compared to the metal MSM photodetector and the photocurrent are comparable for both samples. The results showed that a normalized photocurrent-to-dark current ratio [NPDR] for the SWCNT films

MSM photodetector was significantly improved compared to the typical metal MSM photodetector. The reduced dark current of the SWCNT films photodetector was possibly due to the porous structure of the SWCNT films which is different than the planar structure of the metal electrodes. Also the contact between the SWCNT films and the GaAs substrate was characterized. By the measurements of the dark current at various temperatures and the determination of major carrier of the device, the Schottky barrier height was found as ~ 0.54 eV at temperatures above 260 K. If an ideal MS junction is assumed, the workfunction of SWCNT films was extracted as ~ 4.6 eV which is in agreement with the values of workfunction previously reported.[22, 23]

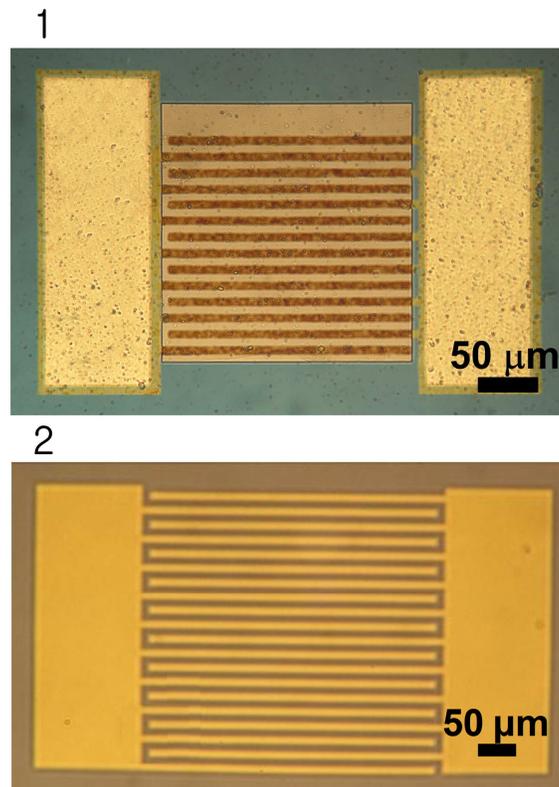


Figure 5. The optical images of (1) the fabricated SWCNT films MSM photodetector and (2) the fabricated metal MSM photodetector.

4. Conclusions

In summary, the fabrication of MSM photodetector using SWCNT films was successfully demonstrated. The fabrications including the synthesis of SWCNT films and the fabrication of photodetector device using the SWCNT films were discussed to give overall ideas of fabrication procedures. Moreover, photoelectric properties of the fabricated MSM photodetector were characterized and discussed. This work provides the fabrication procedures of MSM photodetectors using the SWCNT films and it can be helpful for utilizing the SWCNT films in some other applications such as sensors and electronics.

References

- [1] McEuen, P. L. and Park, J. Y., Electron transport in single-walled carbon nanotubes. *Mrs Bulletin*, 2004. 29(4).
- [2] Dresselhaus, M., Dresselhaus, G., and Avouris, P., *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*. 2001: Springer.
- [3] Wu, Z. C., Chen, Z. H., Du, X., Logan, J. M., Sippel, J., Nikolou, M., Kamaras, K., Reynolds, J. R., Tanner, D. B., Hebard, A. F., and Rinzler, A. G., Transparent, conductive carbon nanotube films. *Science*, 2004. 305(5688).
- [4] Snow, E. S., Novak, J. P., Campbell, P. M., and Park, D., Random networks of carbon nanotubes as an electronic material. *Applied Physics Letters*, 2003. 82(13).
- [5] Zhou, Y. X., Hu, L. B., and Gruner, G., A method of printing carbon nanotube thin films. *Applied Physics Letters*, 2006. 88(12).
- [6] Bekyarova, E., Itkis, M. E., Cabrera, N., Zhao, B., Yu, A. P., Gao, J. B., and Haddon, R. C., Electronic properties of single-walled carbon nanotube networks. *Journal of the American Chemical Society*, 2005. 127(16).
- [7] Ozel, T., Gaur, A., Rogers, J. A., and Shim, M., Polymer electrolyte gating of carbon nanotube network transistors. *Nano Letters*, 2005. 5(5).
- [8] Seidel, R., Graham, A. P., Unger, E., Duesberg, G. S., Liebau, M., Steinhoegl, W., Kreupl, F., and Hoenlein, W., High-current nanotube transistors. *Nano Letters*, 2004. 4(5).
- [9] Bradley, K., Gabriel, J. C. P., and Gruner, G., Flexible nanotube electronics. *Nano Letters*, 2003. 3(10).
- [10] Snow, E. S., Campbell, P. M., Ancona, M. G., and Novak, J. P., High-mobility carbon-nanotube thin-film transistors on a polymeric substrate. *Applied Physics Letters*, 2005. 86(3).
- [11] Blanchet, G. B., Subramoney, S., Bailey, R. K., Jaycox, G. D., and Nuckolls, C., Self-assembled three-dimensional conducting network of single-wall carbon nanotubes. *Applied Physics Letters*, 2004. 85(5).
- [12] Valentini, L., Armentano, I., Kenny, J. M., Cantalini, C., Lozzi, L., and Santucci, S., Sensors for sub-ppm NO₂ gas detection based on carbon nanotube thin films. *Applied Physics Letters*, 2003. 82(6).
- [13] Oakley, J., Wang, H., Kang, B., Wu, Z., Ren, F., Rinzler, A., and Pearton, S., Carbon nanotube films for room temperature hydrogen sensing. *NANOTECHNOLOGY*, 2005. 16(10).
- [14] Novak, J. P., Snow, E. S., Houser, E. J., Park, D., Stepnowski, J. L., and McGill, R. A., Nerve agent detection using networks of single-walled carbon nanotubes. *Applied Physics Letters*, 2003. 83(19).
- [15] Snow, E. S., Perkins, F. K., Houser, E. J., Badescu, S. C., and Reinecke, T. L., Chemical detection with a single-walled carbon nanotube capacitor. *Science*, 2005. 307(5717).
- [16] Lee, K., Wu, Z., Chen, Z., Ren, F., Pearton, S. J., and Rinzler, A. G., Single wall carbon nanotubes for p-type ohmic contacts to GaN light-emitting diodes. *Nano Letters*, 2004. 4(5).
- [17] Pasquier, A. D., Unalan, H. E., Kanwal, A., Miller, S., and Chhowalla, M., Conducting and transparent single-wall carbon nanotube electrodes for polymer-fullerene solar cells. *Applied Physics Letters*, 2005. 87(20).
- [18] Aguirre, C. M., Auvray, S., Pigeon, S., Izquierdo, R., Desjardins, P., and Martel, R., Carbon nanotube sheets as electrodes in organic light-emitting diodes. *Applied Physics Letters*, 2006. 88(18).
- [19] Rowell, M. W., Topinka, M. A., McGehee, M. D., Prall, H. J., Dennler, G., Sariciftci, N. S., Hu, L. B., and Gruner, G., Organic solar cells with carbon nanotube network electrodes. *Applied Physics Letters*, 2006. 88(23).
- [20] Behnam, A., Choi, Y., Noriega, L., Wu, Z. C., Kravchenko, I., Rinzler, A. G., and Ural, A., Nanolithographic patterning of transparent, conductive single-walled carbon nanotube films by inductively coupled plasma reactive ion etching. *Journal of Vacuum Science & Technology B*, 2007. 25(2).
- [21] Behnam, A., Johnson, J., Choi, Y., Noriega, L., Ertosun, M. G., Wu, Z. C., Rinzler, A. G., Kapur, P., Saraswat, K. C., and Ural, A., Metal-semiconductor-metal photodetectors based on single-walled carbon nanotube film-GaAs Schottky contacts. *Journal of Applied Physics*, 2008. 103(11).
- [22] Barone, V., Peralta, J. E., Uddin, J., and Scuseria, G. E., Screened exchange hybrid density-functional study of the work function of pristine and doped single-walled carbon nanotubes. *Journal of Chemical Physics*, 2006. 124(2).
- [23] Shan, B. and Cho, K. J., First principles study of work functions of single wall carbon nanotubes. *Physical Review Letters*, 2005. 94(23).