

Carbon Nanotube Arrays for Photovoltaic Applications

R.E. Camacho, A.R. Morgan, M.C. Flores, T.A. McLeod, V.S. Kumsomboone, B.J. Mordecai, R. Bhattacharjea, W. Tong, B.K. Wagner, J.D. Flicker, S.P. Turano, and W.J. Ready

Vertically aligned periodic arrays of carbon nanotubes (CNTs) are used to create topographically enhanced light-trapping photovoltaic cells. The CNTs form the back contact of the device and serve as a scaffold to support the photoactive heterojunction. Molecular beam epitaxy is used to deposit CdTe and CdS as the p/n-type materials and ion-assisted deposition is used to deposit a conformal coating of indium-tin oxide as the transparent top contact. X-ray diffraction data shows (111) texture of the CdTe. Photocurrent produced “per cm² of footprint” for the CNT-based device is 63 times that of a commercially available planar single crystal silicon device.

INTRODUCTION

CdTe has been extensively investigated as a material for use in photovoltaic applications. The 1.45 eV band gap is nearly optimal for absorbing sunlight and for integration with a CdS window layer as a complementary heterojunction material.^{1,2} The theoretical efficiency for

CdTe-based solar cells is ~29%. However, the maximum reported efficiency is ~16%.³ Several studies have focused on improving the efficiency of CdTe-based solar cells by reducing crystal defects and optimizing interface properties between CdTe and its complementary cell material.⁴⁻⁸

Recently, fullerenes have been proposed for materials to be used in photovoltaic applications.⁹ The motivation for photovoltaic applications of fullerenes arises from the high photoconductivity values observed in C₆₀ and the strong acceptor properties of fullerenes.¹⁰ In this study, adherent and conformal heterojunctions between carbon nanotubes (CNTs) and CdTe/CdS/indium-tin oxide (ITO) thin films are formed to create novel photovoltaic cells.

See the sidebar for experimental procedures.

RESULTS AND DISCUSSION

A conformal thin film of CdTe with good adhesion to the multi-walled carbon

EXPERIMENTAL PROCEDURE

Vertically aligned carbon nanotube (CNT) arrays composed of multi-walled carbon nanotubes (MWCNTs) were grown via iron-catalyzed pyrolytic decomposition of hydrocarbon gases in a chemical vapor deposition (CVD) furnace between 700°C and 800°C for growth periods varying from 5 min. to 30 min. A combination of 100 sccm of C₂H₂, 1,000 sccm of CH₄, and 500 sccm of H₂ gasses were used for CNT synthesis. The CVD chamber was initially purged and later cooled under 1,000 sccm of argon flow.

During molecular beam epitaxy growth of CdTe and CdS, the CNT array temperature was varied from 250° to 400°C and CdTe source temperature was varied from 500° to 650°C. CdTe flux values during deposition were on the order of 10⁻⁶ Torr and growth time of CdTe varied from 90–105 min. CdS flux values and growth times were similar.

Indium-tin oxide (ITO) was deposited on the substrates using a Leybold APS1104 ion-assisted deposition system with advanced plasma source. The substrate temperature for deposition was 200°C and the ITO was deposited at a rate of 0.2 nm/s until a thickness of 150 nm was reached.

Samples were imaged with an LEO model 1550 thermionic field-emission scanning-electron microscope (SEM) both before and after thin film deposition. A Hitachi S-800 SEM was additionally used for imaging. X-ray diffraction characterization was performed with a Rigaku D/Max-11B X-Ray Powder Diffraction System.

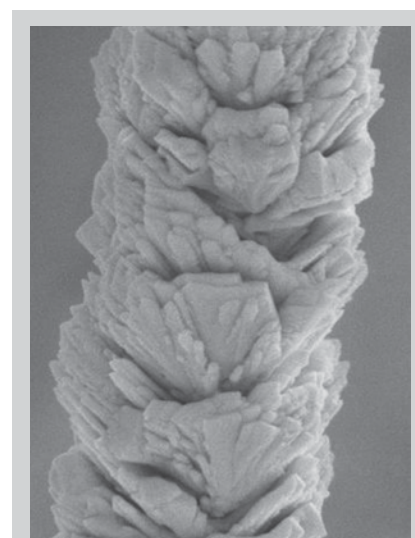
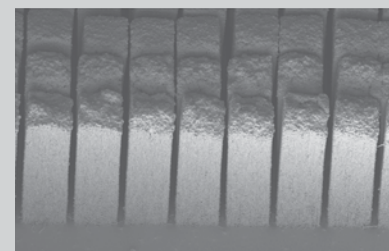
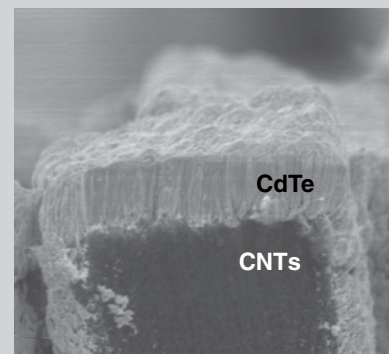


Figure 1. A CdTe thin film well-adhered to a single CNT.



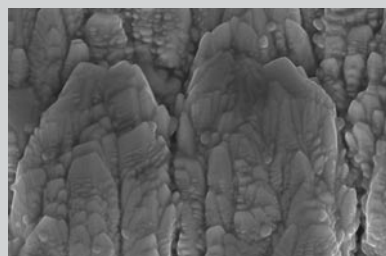
a



b
Figure 2. (a) A CdTe-coated CNT array. (b) Cross section of CNT array showing thick conformal CdTe coating on all sides.

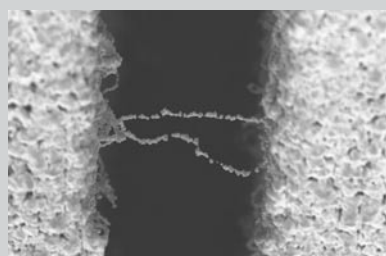
nanotube (MWCNT) arrays (Figures 1–3) was generated. The deposition process is not exclusively limited to line-of-sight and significant deposition of CdTe on both normal and orthogonal surfaces of the CNT arrays was observed.

The MWCNTs are not functionalized,

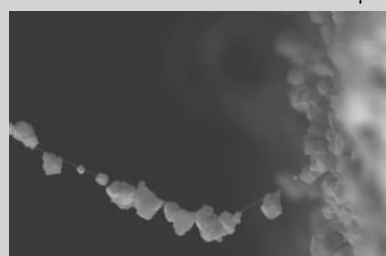


200 nm

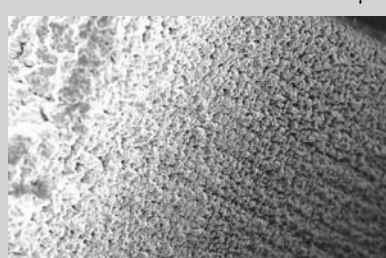
Figure 3. An enlargement of a CdTe surface adhered to CNT.



a 2 μm



b 1 μm



c 2 μm

Figure 4. (a) CdTe adhering to stray CNTs bridging between two CNT arrays. (b) Enlargement of right side of lower fibril from (a) showing excellent adhesion of sub-micrometer CdTe "popcorn" to CNT. (c) CdTe on sidewall of CNT array showing nucleation and adhesion to individual MWCNT "vines" that compose the arrays.

treated, or altered in any way prior to CdTe deposition. However, by altering the source and/or substrate temperatures and deposition times during molecular beam epitaxy (MBE), varying morphologies and coating thickness densities can be produced (Figure 4). X-ray diffraction (Figure 5) reveals that despite the polycrystalline appearance, the preferred orientation and texture of the CdTe microstructure is predominantly (111). Coatings of up to 12 μm in thickness were observed on the MWCNTs, though conformal coatings thinner than 500 nm have also been generated (Figure 1).

An ideal thickness for a planar CdTe photovoltaic device is between 2–4 μm. A benefit of the current work is that the light-trapping concept (Figure 6) effectively extends the dwell time of the incident photons in the material. Thus, photon absorption increases and as a result the photoactive layer can be made much thinner than what would be considered "ideal" for a planar structure. With a thinner CdTe layer, the photo-generated charge carriers have a shorter diffusion path to travel and thus avoid recombination which is a significant limiting factor for efficiency gains.

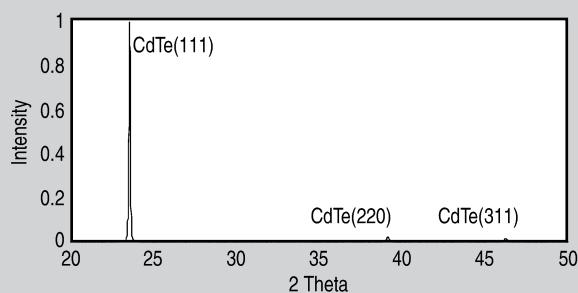
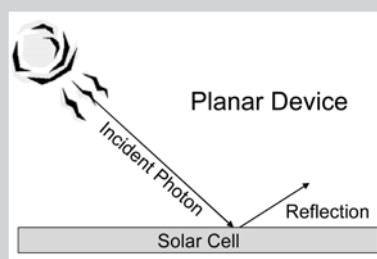
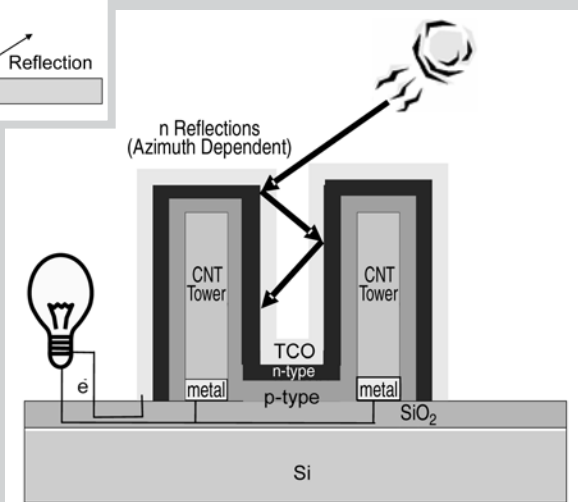


Figure 5. X-ray diffraction data showing that the deposited CdTe upon the CNT array is predominantly (111).



a



b

Figure 6. (a) A planar device offers only one opportunity to absorb an incident photon. (b) The periodic CNT array offers multiple absorption opportunities.

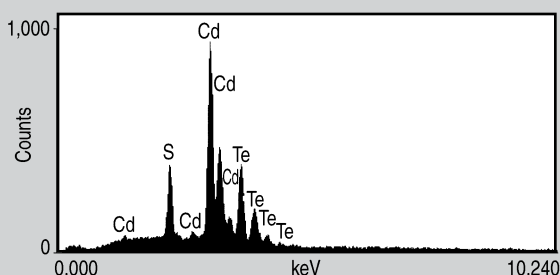


Figure 7. Energy-dispersive x-ray data of a CdTe/CdS heterojunction atop CNTs.

CdS ($E_g = 2.43$ eV) serves as a window layer for the photovoltaic device and is necessarily quite thin (150 nm) for optimum performance. Scanning-electron microscopy (SEM) images generally do not reveal significant changes in the microstructure following CdS deposition via MBE, but energy dispersive x-ray spectroscopy (EDS) confirms the presence of both CdTe and CdS (Figure 7) as the heterojunction necessary for photocurrent generation. Indium-tin oxide serves as the transparent top contact for the CNT-based device. The adhesion of ITO to the CNT structures is highly conformal, as shown in Figure 8.

A variety of CNT-based devices were tested via a Filmetrics 205 spectrometry system with a Hamamatsu L7893 halogen lamp (Figure 9). For comparison purposes, a commercially available silicon cell was also tested. This test allowed for a measure of the absorbance of photons of various wavelengths. The various CNT-based devices did not contain an anti-reflection (AR) coating, yet showed

significant absorption (generally 98.5% to 99.5%) across a broad range of wavelengths. The AR-containing silicon cell absorbed maximally at 560 nm, but exhibited significant reflection out of the sample off of this tuned point (as high as 55% which is not shown due to the vertical scale).

The CNT-based photovoltaic cells were next compared to the commercially available mono-silicon reference cell using a solar simulator with a D50 fluorescent bulb (luminescence = 1.15 W/cm²). The tubular light source was masked to simulate a point source in order to gauge the response of the planar cell and CNT-based cells to variations in azimuthal angle. For the planar cell, maximum performance was achieved with an orthogonal “high noon” position. This performance degraded as the azimuthal angle was adjusted away from the normal (Figures 10 and 11). Contrast this with the performance of the light-trapping CNT-based device that has a maximum efficiency when the photons impinge the surface at 45°. Performance doubles from ~3.5% to ~7% when going from the “high noon” orthogonal incidence to a 45° arrangement (Figures 12 and 13).

The final benefit demonstrated is the production of photocurrent. By measuring the maximum amount of current produced and normalizing to the “foot-print” of the photovoltaic device, it was found that the commercially available

planar silicon device produced 0.7 mA/cm², while the CNT-based device produced 44.4 mA/cm². Thus, the light-trapping CNT device yields ~63-fold improvement in photocurrent production per unit area.

CONCLUSIONS

This effort demonstrated for the first time that a heterojunction photovoltaic cell can be created using CNTs as a conductive scaffolding coated with semiconducting materials. The p/n-type materials formed a coating that is adherent and conformal. Due to the light-trapping nature of the CNT-based device, thinner than “optimal” (for a planar device) CdTe layers can be used to reduce undesirable carrier recombination. Molecular beam epitaxy was used to grow CdTe and CdS thin films, while ion-assisted deposition was used to deposit a conformal coating of ITO as the transparent top contact. X-ray diffraction data showed a strong (111) structure of CdTe. Electrical testing via a solar simulator shows significant series resistance losses are present in the structure. Efficiency is shown to double from 3.5% at an orthogonal “high noon” azimuthal angle to 7% at a 45° solar incidence. In addition, the cells are very compact (~1 cm²) due to the light-trapping topographic surface. This study was successful in demonstrating conditions required for CdTe/CdS/ITO thin film growth on CNT arrays for photovoltaic applications.

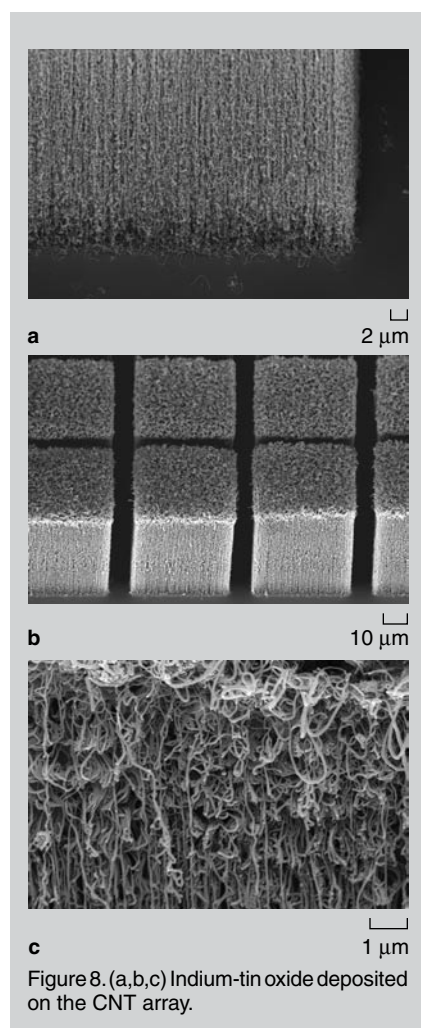


Figure 8. (a,b,c) Indium-tin oxide deposited on the CNT array.

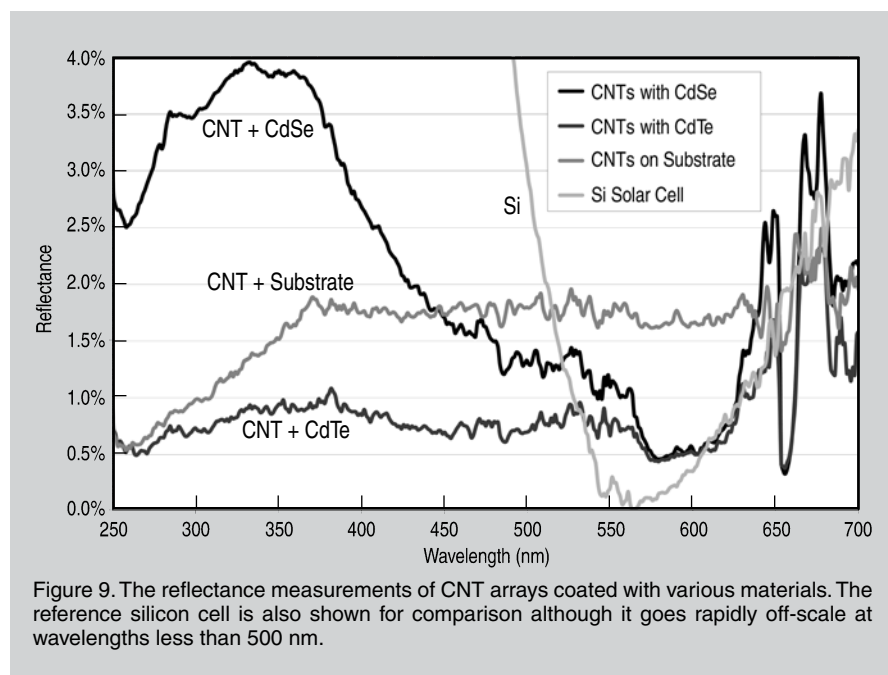


Figure 9. The reflectance measurements of CNT arrays coated with various materials. The reference silicon cell is also shown for comparison although it goes rapidly off-scale at wavelengths less than 500 nm.

ACKNOWLEDGEMENTS

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R.E. Camacho, B.J. Mordecai, A.R. Morgan, and M.C. Flores are undergraduate students, T.A. McLeod and V.S. Kumsomboone are research assistants, R. Bhattacharjea is a systems analyst, W. Tong is senior research scientist, B.K. Wagner is a principal research scientist, J.D. Flicker is a graduate student, S.P. Turano is a research engineer, and W.J. Ready is senior research engineer at Georgia Tech Research Institute, 929 Dalney St., Room 123 Baker Building, Atlanta, GA 30332. W.J. Ready may be reached at fax: (404) 407-9036; e-mail jud.ready@gtri.gatech.edu.

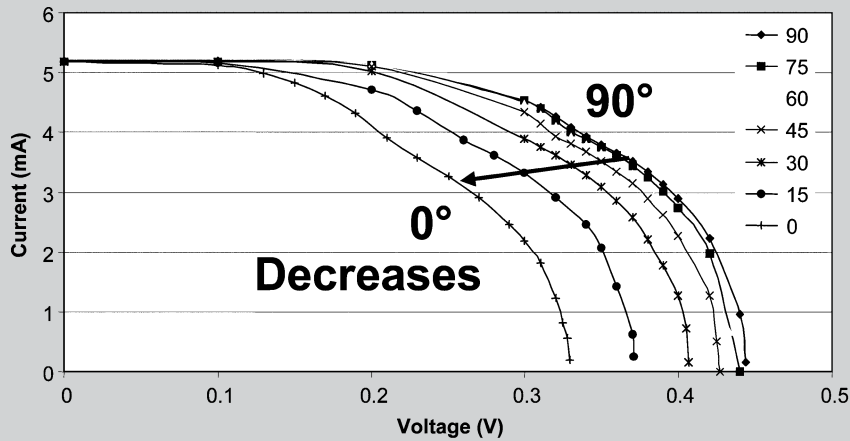


Figure 10. The I-V curve for a commercially available silicon cell. Performance decreases as the angle of incidence moves away from "high noon."

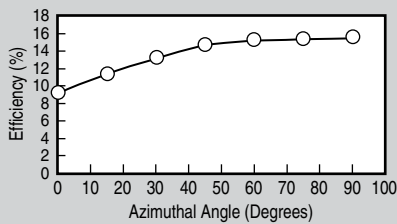


Figure 11. The corresponding decrease in efficiency for a planar cell with respect to azimuthal angle.

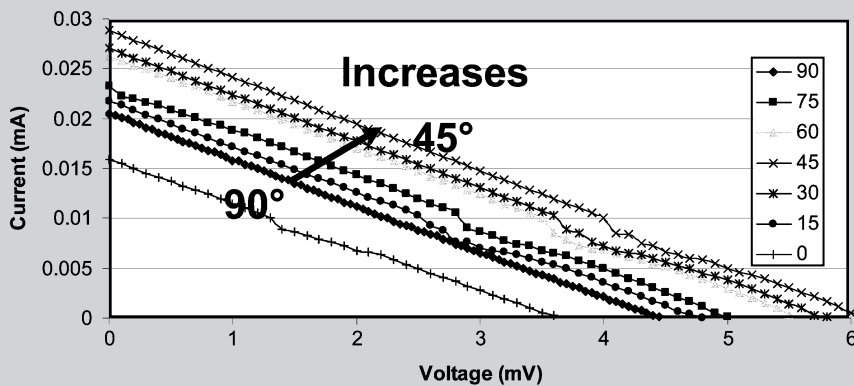


Figure 12. The I-V curve for CNT-based cell. Performance increases as the angle of incidence moves toward 45° from "high noon."

Figure 13. The corresponding increase in efficiency for CNT-cell with respect to azimuthal angle.

