Infrared photovoltaic solar cells based on C_{60} fullerene encapsulated single-walled carbon nanotubes

R. Hatakeyama, Y. F. Li,[a)] T. Y. Kato, and T. Kaneko
Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan

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We have investigated the possibility of using single-walled carbon nanotubes (SWNTs) as the infrared energy conversion material based on the configuration of SWNT/Si heterojunction. The performance of solar cells based on SWNTs has been examined under illumination by the light with different wavelengths. Our experimental results confirm that SWNTs play a critical role in transforming the infrared light (1550 nm) into the electrical energy. The encapsulation of C_{60} fullerene inside SWNTs is found to significantly enhance the performance of solar cells through adjusting the Fermi level of SWNTs. © *2010 American Institute of Physics*.
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Carbon nanotubes (CNTs) are attracting much scientific interest in an application to photovoltaic energy conversion devices.[1,2] In particular, there has been a tremendous effort to develop solar cells based on CNTs during the past decade by either making the conjugated conducting polymers with single-walled CNTs (SWNTs) (Refs. 3–7) or fabricating heterojunctions based on CNTs and Si.[8–10] It is suggested that CNTs do not participate in the photogeneration process in the conjugated polymers. In the latter case, various kinds of CNTs including SWNTs, and double/multiwalled CNTs are used as photogenerator as well as transport layer of charge carriers. Additionally, SWNTs have been extensively used as the transparent electrodes for collecting charge carriers.[11–13] However, these previous studies have so far mainly focused on how the CNTs improve the efficiency of solar cells in a short wavelength (less than 1100 nm) range, and detailed investigations on their infrared properties of solar cells based on CNTs are still lacking. On the other hand, since a large portion of solar energy is above a wavelength of one micrometer, it is of crucial importance to harvest the infrared solar spectrum by using CNTs, especially SWNTs, due to their outstanding infrared properties.[14]

In this letter, we have systematically investigated the possibility of making infrared solar cells based on *n*-silicon and *p*-type pristine SWNTs or C_{60} encapsulated SWNTs (C_{60}@SWNTs) that serve as the energy conversion material. It is demonstrated that SWNTs can be used to convert the infrared light (1550 nm) into the electrical energy under the configuration of solar cells. Moreover, C_{60}@SWNTs are found to show the better power conversion efficiency than pristine SWNTs.

Pristine SWNTs were prepared by an arc discharge method using Fe/Ni as a catalyst. The synthesis of C_{60}@SWNTs was performed by a plasma-ion irradiation or vapor diffusion method.[15–18] The C_{60} fullerene inside SWNTs was characterized in detail by transmission electron microscope imaging (Hitachi HF-2000) and Raman spectroscopy.[20] The optical absorption spectra of SWNTs and C_{60}@SWNTs were taken with a V-7200 spectrophotometer. The solar cells were fabricated by spin coating nanotube films onto the *n*-type silicon (with resistance of $8-12\ \Omega$ cm) with a window ($1.5\times1.5\ \text{cm}^2$) on which an Au/Cr electrode with thickness of $\sim$250 nm was separated by a 100 nm SiO_2 insulator layer, as schematically shown in Fig. 1(a). A Ti layer as the bottom electrode was deposited on the back side of Si substrate by a sputtering method. The SWNT film on the Si substrate was characterized by atomic force microscopy (AFM), as shown in Fig. 1(b), where the network structure of SWNTs is clearly identified. Three kinds of light sources including a solar simulator, a Xe arc lamp (LSX-2510) with a wavelength of 390–1100 nm selected by a monochromator, and 1550 nm infrared light emitting diodes (LEDs) were used to measure the current-voltage (*I-V*) characteristics of solar cells.

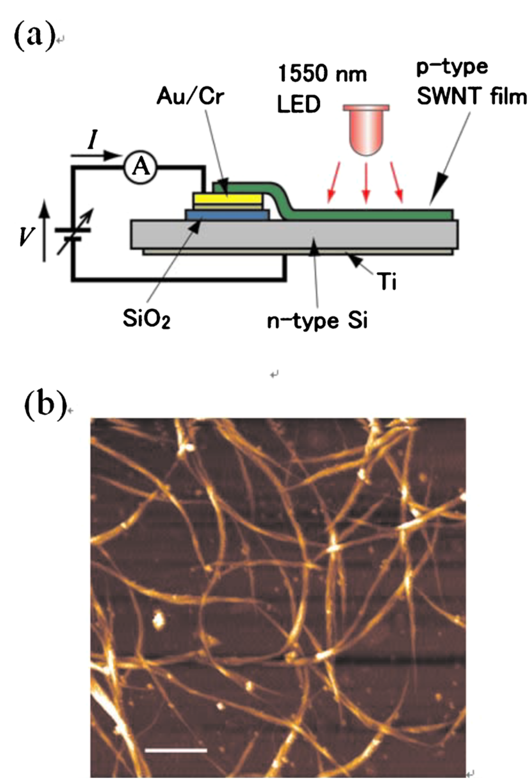

FIG. 1. (Color online) (a) Schematic illustration of infrared solar cell incorporating *n*-Si and *p*-type pristine SWNTs or C_{60}@SWNTs under illumination of 1550 nm LED. (b) An AFM image of SWNT network on the Si substrate (scale bar: 1 μm).

[a)]Author to whom correspondence should be addressed. Electronic mail: yfli@plasma.ecei.tohoku.ac.jp.

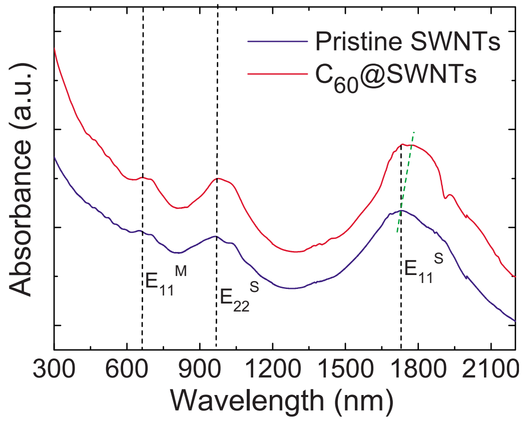

FIG. 2. (Color online) UV-vis-NIR optical absorption spectra of SWNT films of pristine SWNTs and C_{60}@SWNTs.

Figure 2 gives the ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra of pristine SWNTs before and after the C_{60} encapsulation. A broad peak in the range of ~1500–2100 nm can be assigned as the first van Hove transitions (E_{11}^{S}) in the semiconducting nanotubes based on their transition energy. Meanwhile the peaks in the range of ~900–1100 nm and ~600–750 nm can be attributed to the second van Hove transition (E_{22}^{S}) in the semiconducting SWNTs and the first transition (E_{11}^{M}) in the metallic SWNTs, respectively. The distinct spectral change upon the C_{60} encapsulation is clearly observed in the (E_{11}^{S}) region. The absorption peak at ~1723 nm in pristine SWNTs is redshifted to ~1766 nm for the C_{60}@SWNTs, indicating that the encapsulated molecules substantially affect the electronic structure of host SWNTs. This seems to be consistent with the band-gap narrowing effect of C_{60}@SWNTs described in previous literatures.[19]

In previous works, thin films of CNTs and Si have been wildly used to make the heterojunction solar cells, in which nanotubes are generally believed to play an important role as photogenerator.[8,10] However, it is definitely found in the present work that the main contribution of power conversion in the solar cell from CNTs is strictly dependent on the wavelengths of light. In order to clarify the above critical issue, comparative experiments have been performed by using a silver layer instead of SWNT film to fabricate solar cells in the same way. We have carefully compared the performance of solar cells based on SWNT/Si or C_{60}@SWNT/Si with that based on the Ag/Si Schottky barrier (supporting information). In both the cases, the devices are indicative of typical diodelike *I-V* characteristics. Under illumination by the solar simulator, the *I-V* curves shift downward and the observed open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) in solar cells in the presence of SWNTs are rather similar to those observed in solar cells based on Ag/Si.

The above similarity reveals that the main light-power conversion contributions of solar cells based on SWNT/Si may come originally from Si rather than SWNTs at short wavelengths. Furthermore, we have investigated the photoresponse of solar cells under illumination of mono wavelength from 400 to 1100 nm which is close to band-edge absorption spectra of Si (Ref. 20). As the wavelength increases over 850 nm, the solar cell based on Ag/Si exhibits a drastic decrease in the conversion efficiency in contrast to

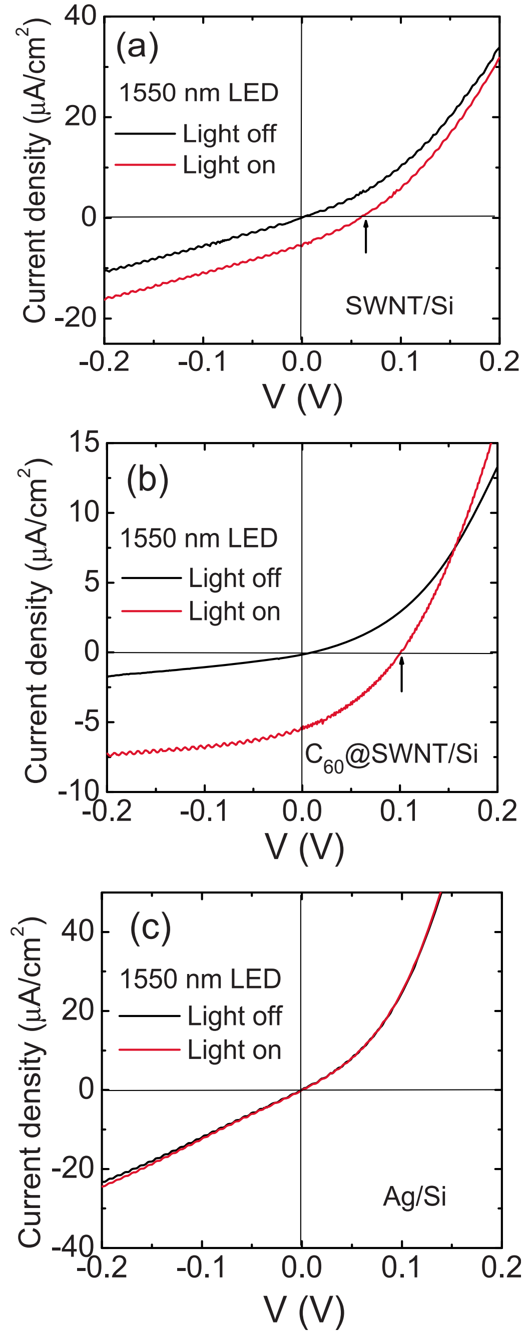

FIG. 3. (Color online) Current-voltage (*I-V*) characteristics of solar cells based on (a) SWNT/Si, (b) C_{60}@SWNT/Si and (c) Ag/Si measured in dark and under 1550 nm LED illumination.

that observed in the solar cell constructed with the SWNT film, suggesting that SWNTs as a low band-gap material play an essential role in enhancing the solar cell performance in the infrared wavelength range. Figure 3(a) displays the *I-V* characteristics of the SWNT/*n*-Si solar cell in dark and under 1550 nm LED illumination (~1.5 mW/cm^2). In the case of illumination, V_{oc} and J_{sc} are about 57 mV and 5.4 μA/cm^2, respectively. In contrast, the solar cell device based on the C_{60}@SWNT film shows much better performance in the open-circuit voltage. The *I-V* characteristics are shown in Fig. 3(b), where the V_{oc} substantially rises up to 100 mV, much higher than the case observed in Fig. 3(a), as a result of C_{60} encapsulation. In any case, the generated solar cell power from the 1550 nm light based on the SWNT/Si junc-

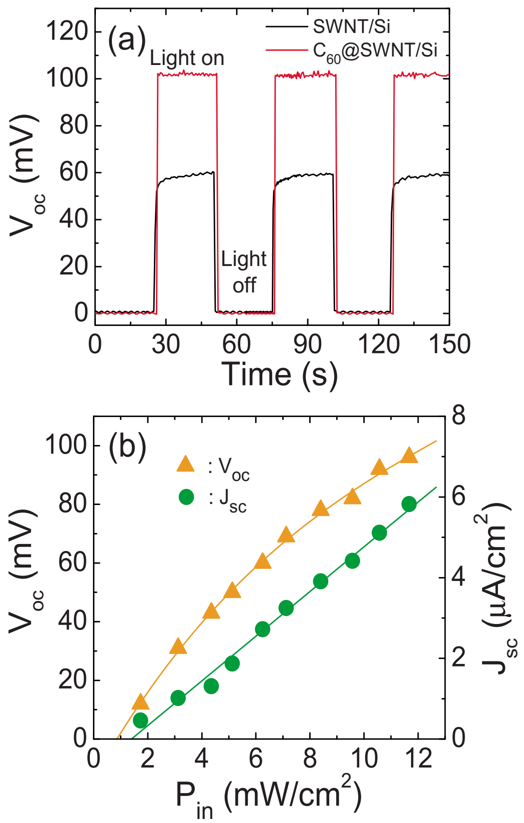

FIG. 4. (Color online) (a) V_{oc} measured as a function of time for SWNT/Si and C_{60}SWNT/Si solar cells. (b) V_{oc} and J_{sc} measured as a function of LED input power for a C_{60}@SWNT/Si solar cell.

tion is higher than that of Ag/Si solar cells by three orders of magnitude, as seen in Fig. 3(c). This result provides direct evidence for the participation of SWNTs in the photocurrent generation from the 1550 nm light owing to their low bandgap energy of ~0.7 eV.

Time resolved measurements are also performed in order to compare the photoresponse of C_{60}@SWNT/Si and pristine SWNT/Si solar cell devices, as shown in Fig. 4(a). Obviously, the photovoltage generation is reproducibly observed with response to light on-off cycles in both kinds of solar cells, and the value of V_{oc} shows an increase when C_{60} is present inside SWNTs. Our further experiments demonstrate that a similar trend in V_{oc} change has been observed in solar cells fabricated by using SWNTs or C_{60}@SWNTs with high coverage on the surface of Si. The increase in V_{oc} of the C_{60}@SWNT/Si solar cell might be explained by the charge-transfer effect between C_{60} and SWNT, which enhances the *p*-type transport characteristic.[16–18] As a consequence, the Fermi level shifts to the valence band in C_{60}@SWNTs relative to the case of pristine SWNTs. Therefore, the built-in potential in the *p*-*n* junction formed between *p*-type C_{60}@SWNTs and *n*-Si becomes higher due to the band structure modification of SWNTs, correspondingly yielding a large open-circuit voltage. Figure 4(b) gives the variations in V_{oc} and J_{sc} as a function of input power (P_{in}) of LED. Both V_{oc} and J_{sc} are found to increase almost linearly with increasing the input power, suggesting that the infrared light density exerts a significant effect on the photogeneration efficiency of SWNTs. In the present work, the power efficiency ($\eta = 1.49 \times 10^{-2}\%$) of the C_{60}@SWNT/Si solar cell is lower, which is possibly ascribed to the low density of deposited SWNTs. Although efficiencies of these SWNT-based devices have not yet reached those of organic or inorganic thin film solar cells, SWNTs having unique properties are believed to drive the development of infrared solar cells further in a promising way.

In summary, we have demonstrated that it is possible to use SWNTs as the infrared energy conversion materials based on the configuration of SWNT/Si heterojunction. The Si substrate is found to dominate the power conversion efficiency of SWNT/Si solar cells at wavelengths less than 1100 nm. On the contrary, SWNTs play a critical role in transforming the infrared light (1550 nm) into the electrical energy. The encapsulation of C_{60} inside SWNTs leads to a significant increase in the open-circuit voltage through adjusting the Fermi level of SWNTs and enhancing the build-in potential in the SWNT/Si junction. We believe that the photoconversion efficiency of our devices can further be improved by optimizing some factors such as the density of C_{60}@SWNTs, doping level of Si, and efficient electrode design, and so on.

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