

Abstract

Studies of nano-carbon hole transport layer for high performance photovoltaic devices
by
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Low-dimensional nano-carbon materials including the form of zero-dimensional (0D) fullerenes, 1D nanotubes, and 2D graphene with extraordinary electronic and optoelectronic properties, provide a large impact on the research field of nanotechnology. The extreme electron confinement in the low-dimensional nano-carbon materials endows them with unique electronic structure and properties, which have been extensively studied from the viewpoint of fundamental studies and device applications.

Carbon nanotube is a very important member of low-dimensional carbon materials, because it has the superior characteristic of high carrier mobility, high specific surface area, high mechanical properties, and tunable bandgap. The fundamental researches on the optoelectronic applications have been extensively studied in the carbon nanotubes. Indeed, the photocurrent has been achieved in single-walled carbon nanotubes. The carbon nanotubes also show high electronic conductivity and have been used as the electrode and carrier transport layer in the opto-electronic devices. Furthermore, the carbon nanotubes have excellent elastic properties, which are very suitable for the flexible and portable optoelectronic devices.

In this thesis, I applied the carbon nanotube for the photovoltaic solar cell devices. I conducted the fundamental studies of photovoltaics of carbon nanotube solar cells with the combination of well-defined materials (crystalline silicon) and fabricated the carbon nanotube/Si heterojunction solar cells. In the carbon nanotube/Si heterojunction solar cells, I could not detect the obvious photocurrent contributions from carbon nanotubes, which suggests that the carbon nanotube work as a hole extraction/transport layer. Therefore, I found that the electrical conductivity of carbon nanotubes becomes very

important for improving the photovoltaic performance of the solar devices, because the carbon nanotube also works as a semi-transparent electrode in the devices.

First, I have started the studies of carbon nanotube/Si heterojunction solar cells using the sprayed single-walled carbon nanotube film, and studied *p*-carbon nanotube/*n*-Si heterojunction solar cells for understanding the series resistance effects and the photovoltaic mechanism of device. From the model and calculation, the resistance is recognized as the main culprit of the relatively low performance in solar cells. The enhancement of the conversion efficiency was realized by HNO₃ doping which decreased in the series resistance of the carbon nanotube network films and increased in the *p*-*n* junction density.

As a next step, I used high quality carbon nanotube thin film fabricated by the floating catalytic chemical vapor deposition method for further improvement of photovoltaic performance. The sheet resistance of carbon nanotube fabricated by this method is about 4 kΩ/sq with a transparency of 91% at 550 nm, which is much lower than sprayed nanotube film with the same transparency. The carbon nanotube/Si heterojunction solar cell using this high quality carbon nanotube films shows a photovoltaic conversion efficiency of 12% without post-processing. In addition, the high reproducibility of the photovoltaic performance of this type of device was clearly demonstrated, suggesting the superior potential of carbon nanotube solar cells.

I also investigated the photovoltaic performance of carbon nanotube-based solar cells using environmentally friendly, durable, and inexpensive materials such as MoO_x and ZnO, which work as antireflection layers for increasing the optical absorption, carrier dopants for a reduction of the series resistance, and effective carrier transport layers for the reduction of the Schottky barrier. The photovoltaic performance of *p*-carbon/*n*-Si and *n*-carbon/*p*-Si heterojunction solar cells was improved using multifunctional layers of MoO_x and ZnO, which resulted in very high photovoltaic conversion efficiency values of 17.0% and 4.0%, respectively. Finally, the photovoltaic performance of organo-lead iodide perovskite solar cells with efficient carbon nanotube/graphene oxide hole-transport layers was studied. A perovskite/carbon nanotubes/graphene oxide solar cell with a protecting layer of polymer exhibited a high photovoltaic conversion

efficiency of 13.3%, which was comparable to that of a perovskite solar cell containing a well-sued standard organic hole-transport layer. Moreover, it was demonstrated that the photovoltaic conversion efficiency value for the perovskite/carbon nanotube/graphene oxide/polymer decreased only slightly compared to that of the standard perovskite solar cell using organic hole transport layer in air condition. With their respective efficient carrier extraction/transport and electron-blocking properties, the combination of carbon nanotube and graphene oxide in the perovskite solar cell contributes to a reduction in carrier recombination losses and an increase in the open-circuit voltage, resulting in a high photovoltaic conversion efficiency.

These findings regarding the performance of carbon nanotube films as an efficient carrier transport layer shed new light on device physics and suggest that these materials have significant potential for use in optoelectronic applications.

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Chapter 1. Introduction

1.1. Background

Low-dimensional carbon materials

Carbon is an abundant element in nature, which has been studied extensively on their structure, texture, properties and applications.¹⁻⁴ Graphite, one of carbon allotropes, has an sp^2 -hybridized crystal structure with a honeycomb lattice.⁵⁻⁷ Graphene is a atomically thin flat monolayer of carbon atoms exfoliated from 3-dimensional (3D) graphite.⁸⁻¹² It can be not only wrapped up into 0D fullerenes but also rolled into 1D nanotubes.

Figure 1.1 shows atomic structures of low-dimensional carbon allotropes; fullerene (0D), carbon nanotube (1D), and graphene (2D), which was discovered in 1985,¹³ 1991,¹⁴ and in 2004,⁸ respectively. In the Fullerene, each large molecule of the fullerene family (C_n) consists of 12 pentagons and integer number of m hexagons ($m \neq 1$), conforming to the relation $m = \frac{n-20}{2}$ (Euler's theorem).¹⁵ C_{60} is a one of the most typical fullerene and a reactive molecule containing 30π -bonds, which can be used for the useful organic molecule for photovoltaic application.^{16, 17} [6, 6] - Phenyl - C_{61} Butyric Acid Methyl Ester (PCBM) is one of the famous derivative of fullerene which have been widely used in the organic solar cells for several-ten years.

The carbon nanotubes were firstly reported by Dr. S. Iijima and have been attracted much attention as the considerable research target on six-years after the first observation of C_{60} .¹⁴ The atomic structure of carbon nanotubes is described in terms of the tube chirality (chiral indices) which has significant implications on the materials properties,

such that nanotubes can be either metallic or semiconducting depending on the structure defined by the chirality (chiral indices).¹⁸ The carbon nanotubes offer tremendous opportunities for the fundamental research because of their unique electronic properties, thermal conductivity, and mechanical properties.^{4, 19-25} In particular, the excellent optoelectronic properties of carbon nanotubes combined with their low-density and flexible properties, offer the new application for light weight, flexible, and wearable devices.²⁶⁻²⁸

Graphene made from a atomically thin 2D sheet of sp^2 -hybridized carbon atoms, was first experimental exfoliated from graphite by Geim and co-workers at Manchester University in 2004.⁸ This experimental isolation of single atomically-thin layer graphene yielded access to large amounts of interesting physics on graphene. The initial stage of graphene studies including observations of ambipolar field effect, the anomalous quantum Hall effect, extremely high carrier mobility accelerates the graphene research.^{11, 29-31} These interesting properties attract the tremendous interests in the possible implementation of graphene in various kinds of devices, such as high-speed and radio frequency logic gates, thermally and electrically conductive reinforced composites, highly sensitive sensors, and transparent electrodes for displays and solar cells.³²⁻³⁵

The researchers have also explored the unique properties of other low-dimensional carbon materials such as chemically derived graphene.³⁶⁻³⁹ One of the most promising chemically functionalized products of graphene is graphene oxide (GO). The GO is a non-stoichiometric compound and has inhomogeneous structures. In the GO, a fraction of carbon is sp^3 hybridized and covalently bonded with oxygen, and the remaining carbon atoms form sp^2 hybridized clusters with various sizes,⁴⁰ which determine the optical and electronic properties of GO. Tunability of luminescent color by oxidation or

reduction makes GO attractive especially for applications as light-emitting devices as well as photovoltaics.^{39, 41, 42} All of these extraordinary optoelectronic properties indicates that the high potential of low-dimensional carbon materials represent tremendous opportunity for new application in the 21st century.

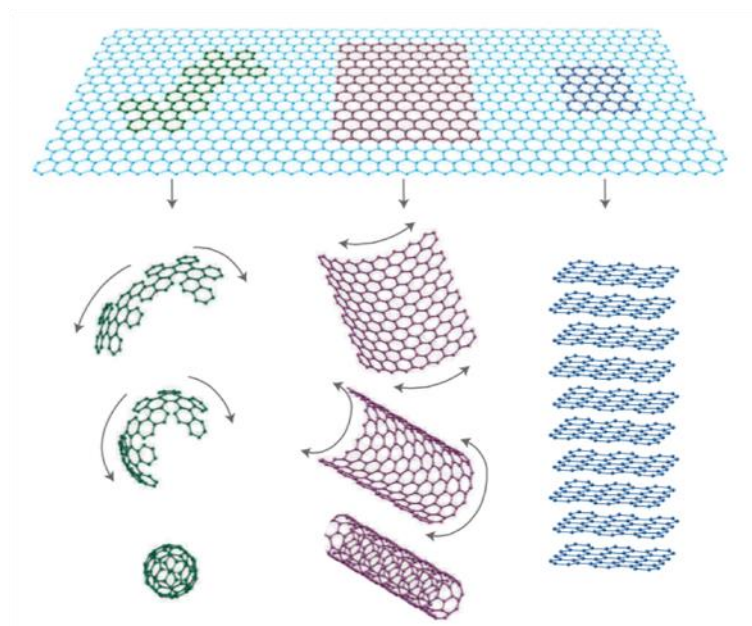


Figure 1.1 Structure of sp^2 carbon allotropes; fullerene, carbon nanotube, and graphene. The figure was taken from Ref.⁴³.

Photovoltaic devices

More than 100 years after the discovery of a photovlotage by Edmund Becquerel, the first photovoltaic device utilizing a p - n junction in crystal silicon was fabricated by Chapin, Fuller and Pearson in 1954.⁴⁴ The clean and huge solar light enegy can be directly converted to electrical energy by the photovoltaic devices, which would become an important energy source for solving the problems resulted from the conventional energy sources suhc as fossil fuel, however, the high production cost and low conversion efficiency make the solar cell difficult to commercialize for the power generation source at that time. In the 1970s, the crisis in energy supply led to a sudden

growth of interest in alternative sources of energy. Photovoltaics were a one of the subjects of intense interest. The new strategies for producing photovoltaic devices and low cost materials more were explored for improving the energy conversion efficiency. The routes for reducing cost including photoelectrochemical junctions,⁴⁵ and alternative materials such as polycrystalline silicon,^{46, 47} amorphous silicon,⁴⁸ 'thin film' materials⁴⁹ and organic conductors were extensively explored.⁵⁰ The new photovoltaic device structures for improving power conversion efficiency including tandem and intermediate-band designs were also proposed. From the 1990s, the interests in photovoltaics were expanded along with growing awareness of global warming and requirement of secure sources of electricity alternative to fossil fuels. In late the 1990s, the production of photovoltaic devices as solar panels was grown at a rate of 15-25% per year, which is driven by reduction of cost. The photovoltaics became competitive in place where the conventional electricity supply is expensive for remote low power applications.

In the 21st century, the photovoltaics devices still keep on the trend of high speed development. The application of new materials and structures in the photovoltaic devices accelerated the research and development of the devices.⁵¹⁻⁵³ Low-dimensional carbon material is one of the highest potential materials for the photovoltaics application in the near future because of their outstanding optoelectronic properties.⁵⁴

In this thesis, I will mainly focus on the photovoltaic devices using low-dimensional carbon materials, i.e. solar cells using 1D carbon nanotubes.^{55, 56} Recently, the 1D carbon nanotubes with high carrier mobility, tunable band gap and also good chemical stability have been extensively studied as the carrier transport layer in the organic solar cells and dye sensitized solar cells. Figure 1.2 shows one of the examples for use of solar cells that the carbon nanotubes were chemically modified and integrated into a dye

sensitized solar cell, in which the carbon nanotubes are not responsible for exciton generation but mainly in charge generation with the exciton dissociation and charge carrier transport.⁵⁷ Moreover, a typical carbon nanotube/Si heterojunction device similar to that of a single junction crystalline silicon solar cell with replacement of an Si emitter layer by a carbon nanotube thin film has been extensively studied,⁵⁸⁻⁶⁰ in which the carbon nanotubes are used for the purpose of photocurrent generation. The other attractive research is incorporating carbon nanotubes into organo-lead iodide perovskite solar cells as elements in P3HT for charge transport.

Even though the 1D carbon nanotubes have been widely used on the photovoltaics, some problems are still remained to solve for further improvement of performance of carbon nanotube photovoltaic devices, as follows. 1) Development of more efficient carrier doping for carbon nanotubes is required in order to reduce the series resistance loss, because the large sheet resistance in the carbon nanotube thin film greatly decreases the charge transport efficiency on the photovoltaic devices. 2) A high Schottky barrier at the interface of carbon nanotubes and the metal electrode limits the performance in carbon nanotube-based photovoltaic devices. The control of Schottky barrier using an efficient carrier transport layer should enable the delivery of a high photocurrent without carrier recombination loss.^{21, 61} 3) The charge transport mechanism and photocurrent generation condition in carbon nanotubes are still not clear.

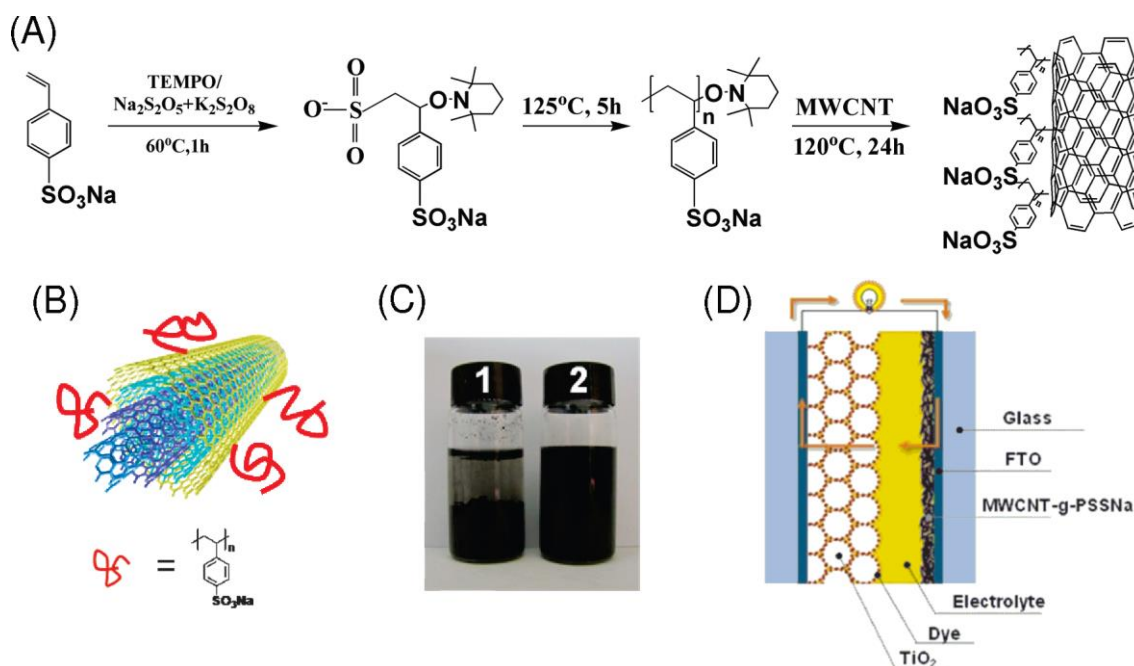


Figure 1.2 Chemically modified carbon nanotube electrode for dye sensitized solar cells. (A) Synthetic scheme of MWCNT-g-PSSNa, (B) structure of MWCNT-g-PSSNa, (C) photo images of, 1, pristine MWCNT and, 2, MWCNT-g-PSSNa in DI water, (D) schematic diagram of dye-sensitized solar cells. The concentration of both solutions was 1.25 mg mL⁻¹. The figure was taken from Ref⁵⁷

1.2. Chapter outline

In the following Chapter 2, the fundamental electronic properties of single-walled carbon nanotube (SWNT) and graphene oxide (GO) were introduced and the fundamentals of a solar cell were also described as an introduction. In Chapter 3, I investigated the photovoltaic performance in carrier-doped SWNTs/Si heterojunction solar cell. In Chapter 4, I studied the photovoltaic performance of SWNTs/Si solar cell using high quality and uniformity SWNTs fabricated by floating-catalytic (FC)-chemical vapor deposition (CVD). In Chapter 5, I demonstrated SWNTs/Si solar cell using the metal oxide layers by assisting the carrier transport properties. In Chapter 6, the SWNT/GO based organo-lead perovskite solar cells were investigated. As a

summary of this thesis, conclusion and outlook including suggested future works were provided in Chapter 7.

Chapter 2. Introduction of nano-carbon materials and photovoltaics

2.1. Graphene and Graphene oxide

Graphene have attracts enormous interest because of richness of optical and electronic properties. High carrier mobility, optical transparency, flexibility, robustness, and environmental stability endow graphene with wide applications on solar cells, light-emitting devices, photodetectors and ultrafast lasers.

2.1.1. Atomic structures of graphene

Figure 2.1a shows an atomic structure of graphene, where A and B are the sublattice and $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors of graphene ($|\mathbf{a}_1| = |\mathbf{a}_2|$). Graphene consists of carbon atoms aligned with honeycomb structure in a single atomic layer plane. This atomic structure can be defined by lattice vectors as,

$$\bar{\mathbf{a}}_1 = \frac{a}{2}(3, \sqrt{3}), \quad \bar{\mathbf{a}}_2 = \frac{a}{2}(3, -\sqrt{3}), \quad (2.1)$$

where $a = 1.42 \text{ \AA}$ is the carbon-carbon bond length (Figure 2.1a). Figure 2.1b shows a Brillouin zone of graphene, where the reciprocal-lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are given by

$$\bar{\mathbf{b}}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \bar{\mathbf{b}}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}). \quad (2.2)$$

The thickness of a single atomic layer (or monolayer) graphene sheet is $\sim 3.4 \text{ \AA}$,⁶² which corresponds to interlayer distance of graphite. Highly symmetric points in momentum space are named as K, K', M and Γ (Figure 2.1b). Particularly, K and K' points at the corners of the Brillouin zone called Dirac points are important for understanding the novel electronic structure, described in detail in Section 2.1.2.

Chemically derived graphene

Figure 2.2a and b shows a chemical structure and atomic model of graphene oxide (GO) sheet, respectively. Several types of oxygen functional group are covalently bound to the basal plane and sheet edges of graphene sheet. These oxygen functional groups make GO hydrophilic and soluble in water, which can be helpful for solution-processing.^{63, 64} This character is contrasting in that the precursor graphite is hydrophobic. As-prepared GO shows an insulating behavior, while graphene and graphite show metallic behavior. The procedures of chemical reduction in GO increases its conductivity up to semiconducting behavior. The functional groups in GO include mainly hydroxyl, epoxy and carboxyl groups.^{7, 38} The solubility of GO allows it to obtain a uniformly deposited thin film which has potential application of optoelectronics. The thickness of monolayer GO sheet is ~ 0.83 nm,⁶⁵ which is larger than plain graphene because of the oxygen functional groups.

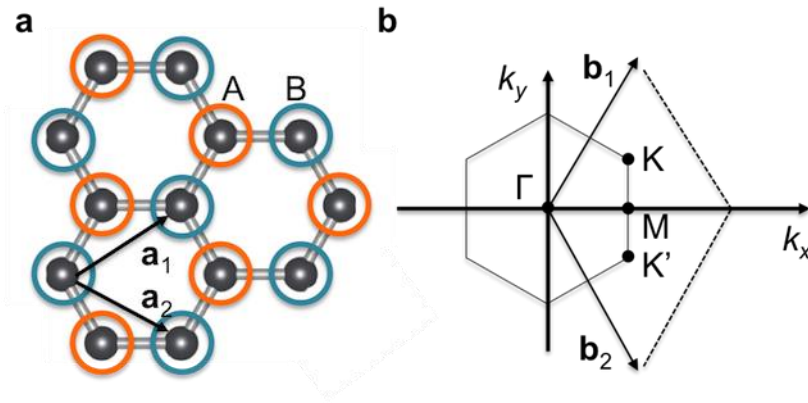


Figure 2.1 (a) Honeycomb lattice of graphene, where A and B highlighted by orange and blue circles are the sublattice. $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors of graphene. (b) The Brillouin zone of graphene, where highly symmetric points are named as K, K', M and Γ . $\mathbf{k}_x$ and $\mathbf{k}_y$ are momentum vector. The figure was taken from Ref ¹⁷⁴

High-resolution TEM image provides us insight into the morphology that largest portion of the layer is composed of clean well-crystallized graphene areas, where the

hexagonal lattice is remained (light gray color in Figure 2.2c). The average size of the well-crystallized areas is from 1 to 6 nm.^{40, 66} Remarkable amount of defects is observed within the crystallized areas (green color in Figure 2.2c).

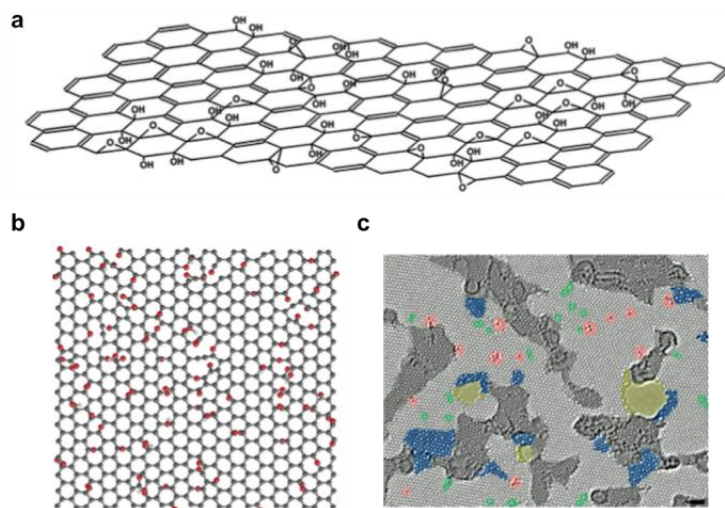


Figure 2.2 (a) Chemical structure of GO sheet according to the Lerf-Klinowski model (taken from Ref.⁶⁷). (b) Atomic model of morphology for single layer GO. Carbon, oxygen and hydrogen atoms are grey, red and white, respectively. (c) Atomic resolution, aberration-corrected high-resolution TEM image, with color added to highlight the different features. The defect free crystalline graphene area is displayed in the original light-gray color. Contaminated regions are shaded in dark gray. Blue regions are the disordered single-layer carbon networks, or extended topological defects, that identified as remnants of the oxidation-reduction process. Red areas highlight individual ad-atoms or substitutions. Green areas indicate isolated topological defects, that is, single bond rotations or dislocation cores. Holes and their edge reconstructions are colored in yellow. Scale bar corresponds to 1 nm. The figure was taken from Ref.⁶⁶.

2.1.2. Optoelectronic properties

sp^2 Hybridization

Isolated carbon atom has four valence electrons in 2s and 2p orbitals. When carbon atoms bind to each other, their 2s and 2p orbitals can mix with one another in sp^n ($n= 1, 2, 3$) hybridized orbitals. Graphene has the sp^2 configuration. In the configuration, the orbitals for one 2s and two 2p orbitals mix to form three in-plane covalent bonds with angle of 120° from each other, which is called σ bond as shown in Figure 2.3. Another valence electron is in the $2p_z$ orbital. The p_z electrons that remain perpendicular to the hexagonal network form delocalized π electron states as shown in Figure 2.3. The π electron states form valence and conduction energy bands nearby Fermi level, while the σ electron states are far from Fermi level, and not dominantly contribute to carrier transports and optical transitions.

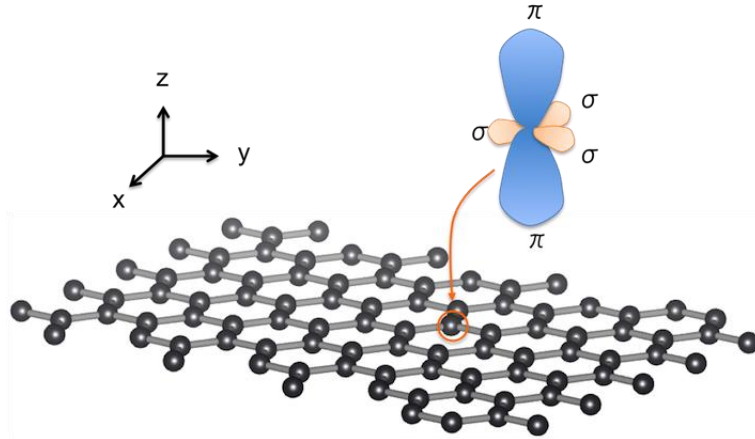


Figure 2.3 The σ and π orbitals of carbon atom in sp^2 honeycomb lattice. Reproduced from Ref.¹⁷³

Energy band structures

In graphene, the 2D energy dispersion is calculated by solving the eigenvalue problem for a Hamiltonian H and an overlap integral matrix S given by,⁶⁸

$$H = \begin{Bmatrix} \varepsilon_{2p} & -\gamma_0 f(k) \\ -\gamma_0 f(k)^* & \varepsilon_{2p} \end{Bmatrix} \text{ and } S = \begin{Bmatrix} 1 & sf(k) \\ sf(k)^* & 1 \end{Bmatrix}, \quad (2.3)$$

where ε_{2p} is the site energy of the 2p atomic orbital, γ_0 is the nearest neighbor C-C interaction energy, and s is the overlap integral. The function $f(k)$ is given by

$$f(k) = e^{ik_x a / \sqrt{3}} + 2e^{-k_x a / 2\sqrt{3}} \cos \frac{k_y a}{2}, \quad (2.4)$$

where k_x and k_y are momentum along x and y axis. $a = |\mathbf{a}_1| = |\mathbf{a}_2| = \sqrt{3}a_{C-C}$. The solution of the secular equation

$$\det[H - ES] = 0, \quad (2.5)$$

provides energy dispersion of graphene expressed by

$$E_{g2D}^{\pm}(k) = \frac{\varepsilon_{2p} \pm \gamma_0 \sqrt{|f(k)|^2}}{1 \mp s \sqrt{|f(k)|^2}}, \quad (2.6)$$

where the plus and minus in this equation correspond to bonding (π) and anti-bonding (π^*) state of the two atoms composing the unit cell, in which they yield valence and conduction bands. Figure 2.4 shows the full band structure of graphene and the zoom in of the energy bands close to one of the Dirac points. The linear energy dispersion nearby K or K' points are called Dirac cone (the inset of Figure 2.4). This energy dispersion near by Dirac point ($\mathbf{K}$ or $\mathbf{K}'$) can be expressed by

$$E_{\pm}(\mathbf{q}) \approx \pm \hbar v_F |\mathbf{q}|, \quad (2.7)$$

where the momentum $\mathbf{q} = \mathbf{k} - \mathbf{K}$ with $|\mathbf{q}| \ll |\mathbf{K}|$. In this region, the electron transport is essentially governed by Dirac's (relativistic) equation.⁶⁹ The charge carriers in graphene behave as massless Dirac fermions and enable us to access quantum electrodynamics.

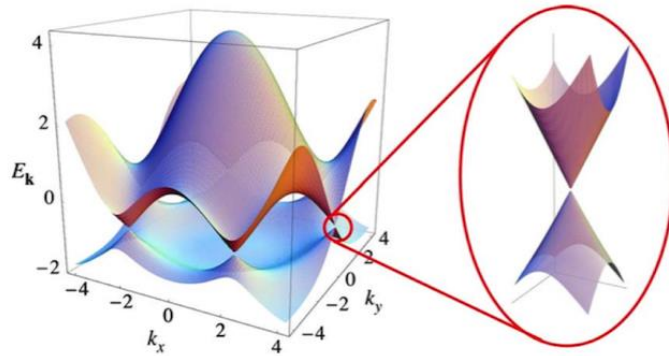


Figure 2.4 Energy dispersion (or energy of electron as a function of momentum) for the π and π^* bands in graphene. The inset shows the zoom in of the energy bands close to

one of the Dirac points (at the K or K' points). The figure was taken from Ref.⁹.

Induction of energy gap to graphene by chemical modification

One of motivations to use chemically derived graphene is introduction of energy gap to graphene that is absence of energy gap. Application of graphene to logic circuits has a fundamental limitation because of a modest on-off ratio in graphene based transistors. It originates from thermally excited carriers associated its zero gap. On the other hand, one can tune the energy gap of graphene oxide (GO), one of chemically derived graphene, and therefore controllably transform GO from an insulator to semiconductor and to a graphene-like semi-metal.⁷⁰ The electronic conductivity is governed by the ratio of sp^2 and sp^3 fractions, where π -states from sp^2 carbon are conducting, while sp^3 -bonded carbons are insulating.

2.2. Carbon nanotubes

Single-walled carbon nanotubes, with their unique crystal structures and chirality-dependent electronic and vibrational states, provide an ideal model for the exploration of one dimensional physics, as well as quantum engineered architectures for applications in optoelectronics

2.2.1. Atomic structures

The atomic structure of a single walled carbon nanotube (SWNT) can be expressed in the terms of the chiral vector¹⁹ which connects two crystallographically equivalent sites on a two dimensional graphene sheet. The chiral vector (C_h) is defined by the equation,

$$C_h = na_1 + ma_2, \quad (2.8)$$

where a_1 and a_2 are the unit vectors of the hexagonal honeycomb lattice of the graphene sheet in real place (Figure 2.5), and the integers (n, m) indices are the number of steps along the zig-zag carbon bonds. Figure 2.5 also shows the chiral angle θ

between the zig-zag $(n, 0)$ direction and the chiral vector (C_h). The nanotube diameter d_t is given by

$$d_t = \sqrt{3}a_{C-C}(m^2 + mn + n^2)^{1/2} / \pi = C_h / \pi, \quad (2.9)$$

where C_h is the length of C_h , a_{C-C} is the C-C bond length, and the chiral angle θ is given by

$$\theta = \tan^{-1}[\sqrt{3}n/(2m+n)]. \quad (2.10)$$

Here, chiral angle θ determines the amount of ‘twist’ in the nanotube and two limiting cases exist where the chiral angle is at 0° and 30° . These limiting cases are known as zig-zag (0°) and armchair (30°) based on the geometry of the carbon bonds around the circumference of the nanotube. All other conformations in which the C–C bonds lie at angles $0^\circ < \theta < 30^\circ$ are known as chiral.

The properties of carbon nanotubes are determined by the diameter d_t and the chiral angle θ . And the number of hexagons (N), per unit cell of a nanotube specified by integers (n, m) , is given by

$$N = 2(m^2 + n^2 + nm) / d_R \quad (2.11)$$

If $n-m=3dx$, $d_R=3d$, otherwise, $d_R=d$, here, d is defined as the largest common divisor of (n, m) , and x is an integer.

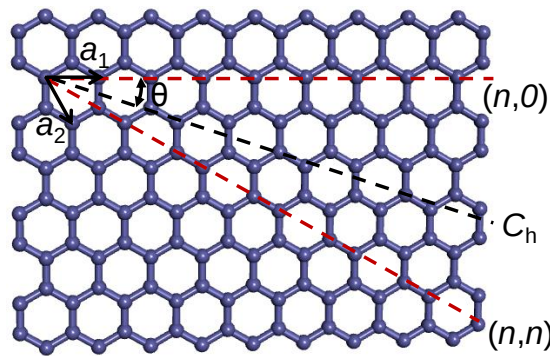


Figure 2.5 Schematic of a graphene sheet illustrating lattice vectors a_1 and a_2 , and the roll-up vector $C_h = na_1 + ma_2$. The zigzag $(n, 0)$ and armchair (n, n) tubes are indicated with red and black dashed lines.

2.2.2. Optoelectronic properties

The n, m integers completely characterize nanotube chirality and thus determine the electronic band structure. The optical, mechanical and electronic properties of a carbon nanotube, therefore, strongly depend on the chirality.^{71, 72} The chirality rules in SWNTs are as follows: a) (n, m) tubes with $n-m = 3p$ (p is an integer) are metals; and b) (n, m) tubes with $n-m \neq 3p$, the nanotube is semiconducting with a band gap energy E_g . The band gap energy E_g dependent on the nanotube diameter d_t , the C-C nearest neighbor potential overlap integral, $V_{pp\pi}$, and the C-C bond distance d_{cc} is given by

$$E_g = 2V_{pp\pi}d_{cc}/d_t. \quad (2.12)$$

Thus armchair nanotubes (n, n) are completely intrinsically metallic ($E_g=0$ eV), while other one third of zigzag nanotubes are small band gap (1 -100 meV) metallic. All chiral nanotubes and the remaining two thirds of zigzag nanotubes are semiconducting with band gaps defined by equation 2.11. This results in the observation of 60% semiconducting with remaining 40% metallic carbon nanotubes.⁷³

The carbon nanotubes exhibit 1D electronic density of states (DOS) which is obtained by zone-folding of the 2D energy dispersion relations of graphene, described in equation 2.6. The 1D energy dispersion relations of a SWNT are given by

$$E_{\mu}^{\pm}(k) = E_{g2D}^{\pm}(k \frac{K_2}{|K_2|}) + \mu K_1, \quad (2.13)$$

where $-\frac{\pi}{T} < k < \frac{\pi}{T}$, and μ is integer. The 1D confinement of electrons into allowed

k -states gives rise to van Hove singularities in the DOS derived as,

$$D(E) = \frac{T}{2\pi N} \sum_{\pm} \sum_{\mu=1}^N \int \frac{1}{\left| \frac{dE_{\mu}^{\pm}(k)}{dk} \right|} \delta(E_{\mu}^{\pm}(k) - E) dk. \quad (2.14)$$

Figure 2.6 shows the schematic of the electronic DOS of SWNT. It is now known that the optical absorption spectra of nanotubes are entirely excitonic in nature and thus many-body effects with consideration of Coulomb interactions must be considered for an accurate description of the optical properties of nanotubes.⁷⁴ Therefore, the actual light energy required to produce a “ $v_i - c_i$ ” transition is $(E_{c_i} - E_{v_i}) + \text{binding energy } (eh) - \text{self energy } (ee)$, and leads to the experimental finding that E_{22}/E_{11} tends to a value of 1.8 with decreasing tube diameter, rather than the value of 2 as would be expected from simple density functional theory (DFT) calculations alone.⁷⁵

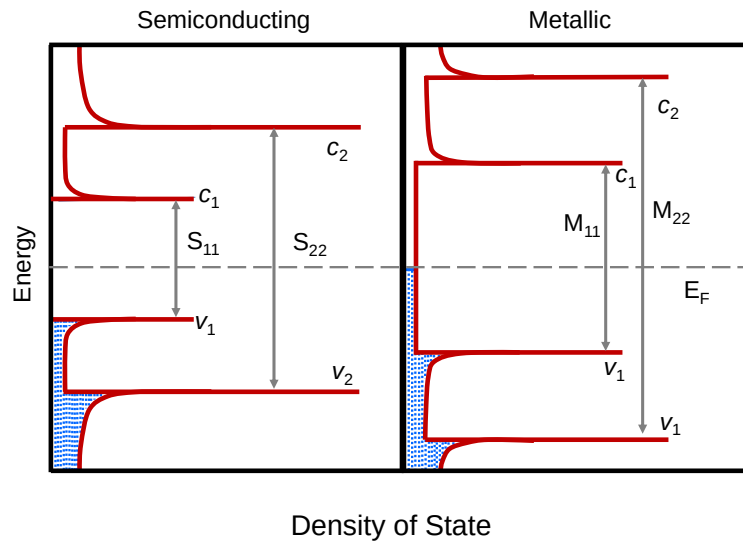


Figure 2.6 Schematic of the electronic density of states (DOS) of (a) semiconducting and (b) metallic SWNTs showing valence and conduction bands, v_i and c_i , and optically active electronic transitions, S_{ii} and M_{ii} .

The optical transition strongly occurs between the van Hove singularities (E_{ii}) due to the large DOS, which is determined by the (n, m) structure and diameter of SWNTs. Figure 2.7 shows the Hove optical transition energy between van Hove singularities as a function of nanotube diameter based on tight binding model without consideration of many-body effect.⁷⁶ This figure is called as ‘Kataura plot’. The optical transition energy

of semiconducting SWNTs is predicted as the simple relationship, $E_{gap} \propto 1/R \approx 0.6 \text{ eVd}^{-1} (\text{nm})$.

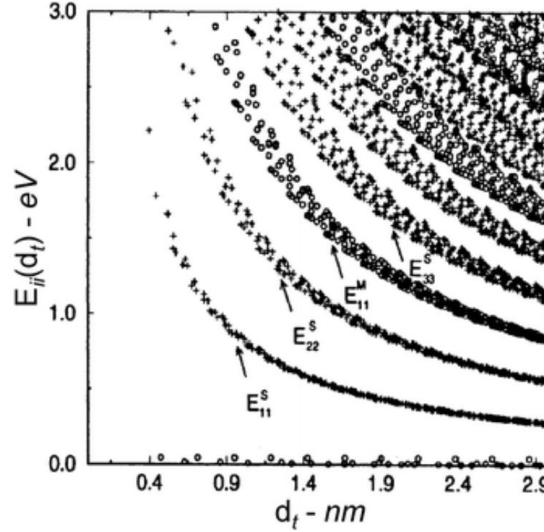


Figure 2.7 Typical “Kataura plot” displaying the calculated energy separations between van Hove singularities ii (refer to Figure 2.6) for all (n, m) SWNTs with a diameter between 0.4 and 3.0 nm. The crosses and open circles indicate semiconducting and metallic nanotubes, respectively. [Reprinted from ref.⁷⁷]

The “intrinsic” semiconducting SWNTs have a Fermi level in the middle of band gap. However the semiconducting SWNTs are exposed in air, they show hole-doped (p -type) characteristics because the SWNTs have only “surface” and the atoms and molecules are easily adsorbed on the surface of SWNTs. In air conditions, the physically adsorbed oxygen on the SWNTs has strong electron withdrawing nature and provides the holes for semiconducting SWNTs. Moreover, SWNTs can be chemically-doped p -type by electron-withdrawing species such as strong oxidizers,⁷⁸ oxidizing acids,⁷⁹ and n -type by electron-donating species such as alkali metals,⁸⁰ hydrazine, nitrogen-rich polymers⁸¹ and nitrogen-rich aromatic compounds. The substitutional doping by replacement of C atoms has also been demonstrated with boron (p -type) and nitrogen (n -type) in SWNTs.⁸² This raises the interesting prospect of all-carbon nanotube photovoltaics

based on *p-n* or *p-i-n* heterojunctions.

2.3. Fundamentals of photovoltaics

Photovoltaics based on the energy converted process from the solar light to electric power. The charge carriers (electrons and holes) are excited by the semiconductor materials by solar light in the photovoltaic devices. The generated charge carriers are separated in the built-in electric field and fed to an external-circuit as photogenerated current, as shown in schematic of Fig. 2.8. The performance of a photovoltaic device strongly depends on the absorbing materials and the how the charge carriers are effectively picked up in the external-circuit. I will explain the fundamental of solar cell in the following section.

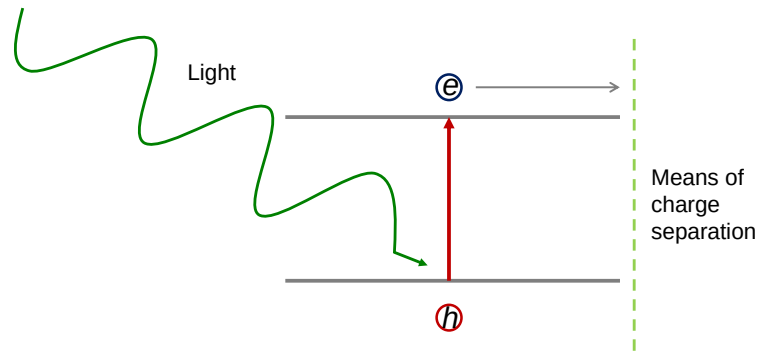


Figure 2.8 Simplified schematic of photovoltaic process in the cells, and the excitation and charge carrier separation of charged carriers.

2.3.1. Solar resource

Solar light includes wide range of electromagnetic waves from ultraviolet, visible and infrared regions. The radiated power density is 62 MW/m^2 at the sun's surface, but is reduced to 1353 W/m^2 at a point just outside the Earth's atmosphere. On passing through the atmosphere, the solar light is further absorbed and scattered by various atmospheric constituents so that the spectrum is attenuated and changed in spectrum after reaching the Earth's surface. Atomic and molecular oxygen, ozone and nitrogen

filter out light of wavelengths less than 300 nm, while water and CO₂ molecules mainly absorb the solar light in the infrared region and are responsible for the dips in the absorption spectrum at 900, 1100, 1400 and 1900 nm (H₂O) and at 1800 and 2600 nm (CO₂). The attenuation by the atmosphere is quantified by the ‘Air Mass’ factor (n_{AirMass}), which is defined as the ration of optical path length to Sun with optical path length vertically on the surface. The standard spectrum for temperature latitudes is Air Mass 1.5 (or AM 1.5), which is defined as the AM 1.5 spectrum normalized so that the integrated irradiance is 1000 W/m². Figure 2.9 shows the standard terrestrial (Air Mass 1.5) spectrum.

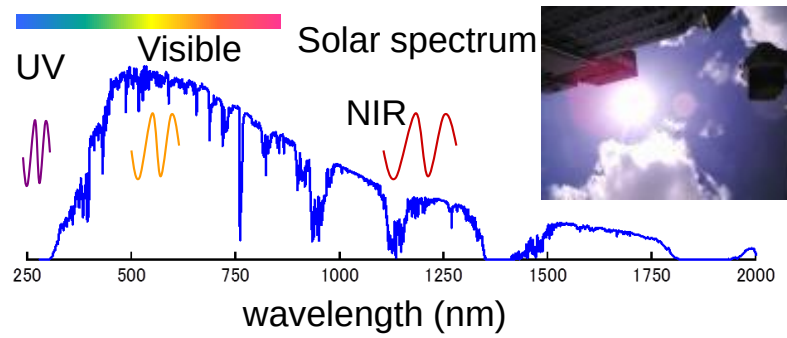


Figure 2.9 Standard terrestrial (Air Mass 1.5) spectrum of solar light.

2.3.2. Band structure of semiconductor

The band structure of a semiconductor crystal described by the energy-momentum ($E-k$) relationship, is usually obtained by solving the Schrödinger equation of an approximate one-electron problem as follows,

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(r)\right]\Psi(r, k) = E\Psi(r, k). \quad (2.15)$$

The Bloch theorem states that if a potential energy $V(\mathbf{r})$ is periodic in the direct lattice space, then the solutions for the wavefunction $\Psi(\mathbf{r}, \mathbf{k})$ of the Schrödinger equation should be written in the form,

$$\Psi(\mathbf{r}, \mathbf{k}) = u_{\mathbf{k}}(\mathbf{r}, \mathbf{k}) e^{i \mathbf{k} \cdot \mathbf{r}}, \quad (2.16)$$

where $\Psi(\mathbf{r}, \mathbf{k})$ and $u_{\mathbf{k}}(\mathbf{r})$ are periodic of the direct lattice. One can also show that the energy $E(\mathbf{k})$ is periodic in the reciprocal lattice from the Bloch theorem. It is sufficient to use only $\mathbf{k}$ in a primitive cell of the reciprocal lattice for a given band index to label the energy uniquely.

The energy bands of solids have been studied theoretically using a variety of numerical methods.^{83, 84} The three methods frequently used are the orthogonalized plane-wave, the pseudopotential, and the $\mathbf{k} \cdot \mathbf{p}$ method for semiconductors. Figure 2.10 shows typical energy-band structures of semiconductors. It should be noted that there is a forbidden energy range, in which the states for electrons (holes) cannot exist. The energy states (or energy bands) are existed above and below this energy gap. The upper bands are called as the conduction bands, and the lower bands as the valence bands. The energy separation between the top of the lowest conduction band and bottom of the highest valence band is called as the bandgap energy (E_g), which is one of the most-important parameters in semiconductor physics. There are the two-types of semiconductors as shown in Fig. 2.10(a) and (b). One is a direct bandgap semiconductor, in which the conduction band top and valence band top are at same $\mathbf{k}$ -space. Another is an indirect semiconductor, in which the conduction band top and valence band top are at different $\mathbf{k}$ -space.

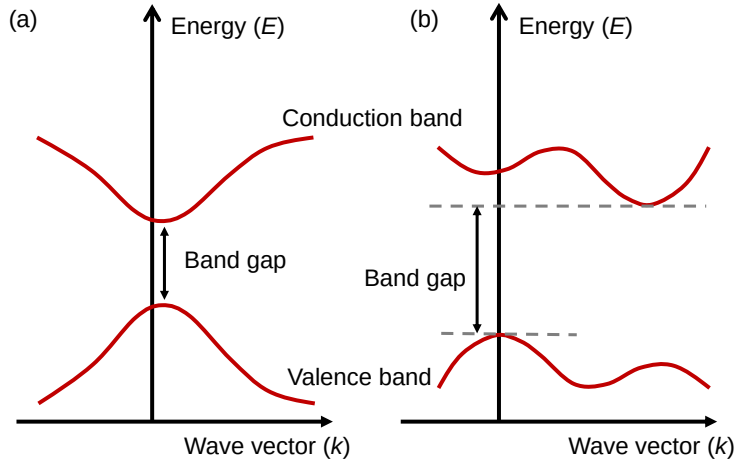


Figure 2.10 (a) and (b), Band structure diagram of direct and indirect band gap semiconductor.

2.3.3. Junctions

In a crystalline semiconductor, a junction between two electronically different materials provides an electrostatic force at the interface. The electrostatic force existing in equilibrium state forms an electric field (also called a ‘built-in’ field) due to compositional gradient. An electric field plays effective roles for charge separation since it always drives *p*-type and *n*-type carriers in opposite directions. The several conditions giving rise to charge separation for photovoltaic application in semiconductor are: 1) gradient in the vacuum level or work function, 2) gradient in the electron affinity, and 3) gradient in the band gap. I will describe the details of junctions.

Work function

The work function of a material is the potential energy required to remove the least tightly bound electron to the vacuum. The work function Φ_w is defined as

$$\Phi_w = E_{vac} - E_F. \quad (2.17)$$

Here E_{vac} and E_F are vacuum and Fermi level, respectively. Note that position of Fermi level within the band gap depends on the type of carrier doping and carrier density.

Since E_F is a constant in equilibrium condition, an electrostatic field must be established at the junction between two regions with different Φ_w due to the gradient in E_{vac} . One can form the heterojunction between a semiconductor and a metal or two semiconductors with different Φ_w .

Metal-Semiconductor junction

I suppose that the work function of an n -type semiconductor with Φ_n is smaller than that of metal with Φ_m . When they are connected each other as the metal/semiconductor heterojunction as “Shottckey junction”, the Fermi levels should line up with the difference of work function by $(\Phi_m - \Phi_n)$ between the semiconductor and metal, as shown in Fig. 2.11(a). The situation is much different in the case of p -semiconductor and metal interface, where the Φ_m is smaller than Φ_p . The contact becomes as is junction is the Ohmic contact. The Shottckey junction causes the exchange of charge carriers across the junction. The electrons flow from the semiconductor to the metal leaving positively fixed charge behind, and a negatively charge on metal, until the charge gradient is sufficient to prevent further flow. At this point the two sides are in thermal equilibrium condition. The energy of the conduction band edge in the semiconductor is lower than the metal at the interface and an electrostatic field develops close to the junction. The variation in electrostatic potential energy is represented by the change in E_{vac} in Fig. 2.11(a) and the field by the gradient of E_{vac} . The potential difference V_d is shared between the two materials according to their dielectric permittivities. At some distance from the interface of junction on either sides, the potential difference stops varying and the electric field falls to zero. This region is called the space charge region (space charge layer) of the junction.

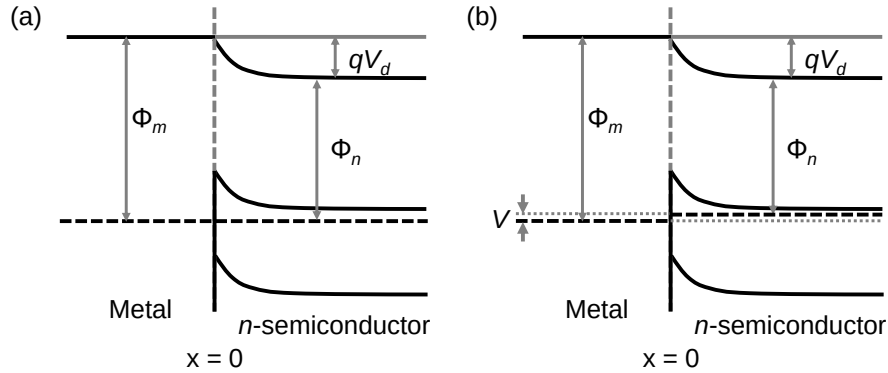


Figure 2.11 (a) Band diagram of n -type semiconductor-metal junction in equilibrium in the dark. (b) Band diagram of the semiconductor-metal junction under illumination at open circuit. The accumulation of photogenerated electrons in the semiconductor raises the Fermi level and generates a photovoltage, V .

If the semiconductor is illuminated by the light with higher photon energy than E_g , the electron-hole pairs are generated in the space charge layer in the semiconductor. The electrons and holes are spatially separated, as a consequence the electrons are accumulated in the semiconductor and the holes in the metal. The semiconductor will become negatively charged and the potential difference across the junction will be reduced, which giving rise to a photovoltage, V . The photovoltage V is equal to the difference in the Fermi levels of semiconductor and metal far from the junction.

p - n junction

There is another type of junction at the interface of p -type semiconductor/ n -type semiconductor as p - n junction. Figure 2.12 shows the schematic of p - n junction. An built-in electric field is established at the heterojunction due to the difference of work function by $(\Phi_p - \Phi_n)$, which drives photogenerated electrons towards the n -type semiconductor side and holes towards the p -type semiconductor side. The p - n junction

has the advantages over the Schottky barrier junction with low defect density and large built-in bias. Thus, the most of solar cell devices based on the semiconductor are designed and fabricated using p - n junction.

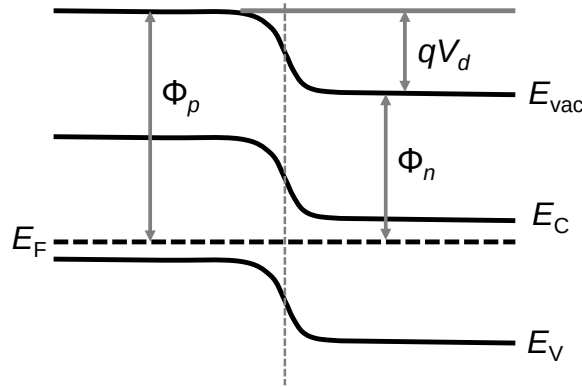


Figure 2.12 Band diagram of the p - n junction in equilibrium.

2.3.4. Important definitions in photovoltaics

The solar cell can replace of a battery in a simple electric circuit, as shown in Fig. 2.13. In the dark condition, the cell in the circuit of Fig. 2.13(a) is opened. When the circuit is switched by the light illumination, the excited electrons generate a potential difference (electro-motive force), which develops a voltage of the battery in circuit of Fig. 2.13(b). The voltage developed is called as the open circuit voltage V_{oc} , when the terminals are isolated. The current is the short-circuit current I_{sc} , when the terminals are connected. The short-circuit current density J_{sc} is the short circuit current on the unit of area (A), which is useful quantity for evaluating the performance of solar cell. For an load resistance R_L , the cell develops a voltage V between 0 and V_{oc} . and delivers a current density of $V=AJR_L$. J is determined by the current-voltage characteristic of the cell under illumination. Thus both V and J are determined by the illumination and the load.

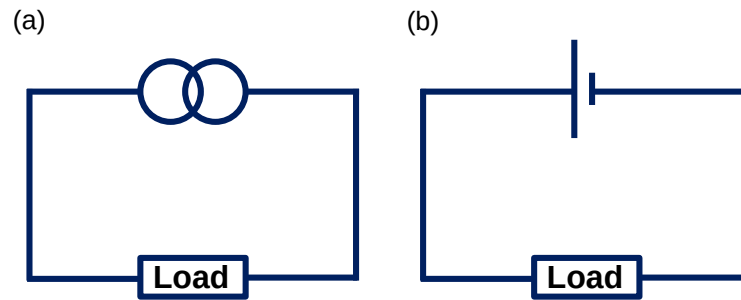


Figure 2.13 Solar cell as a battery in a simple circuit.

2.3.5. Basic principle

Mechanism

A photovoltaic converter is designed to convert the incident solar energy into electrochemical potential energy. The photons in the solar light are absorbed in the material and cause the promotion of an electron from conduction band to valence band in an excited state. The band gap is very important because it enables excited electrons to remain in higher energy levels for long enough to be exploited. When the electrons are excited across a band gap as shown in Fig. 2.14, the electrons (holes) quickly decay to the lowest available energy state in the conduction (valence) band in the order of 100 fs, but the decay across the band gap as recombination of electron-hole occurs relatively slow on the orders from nano-second to micro-second.

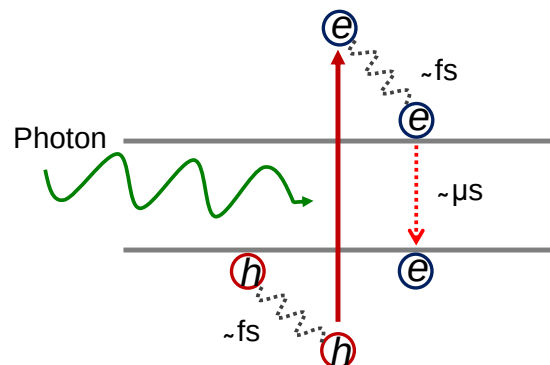


Figure 2.14 Promotion of an electron from valence band to conduction band by a photon energy of solar light. The thermalization of electrons (holes) to the band edges,

and recombination occur.

Power conversion efficiency

The optically excited electrons (holes) in the solar cell should be collected and extracted to the external circuit to complete the photovoltaic conversion process. The mechanism for charge carrier separation is required and the intrinsic potential asymmetry for electrons and holes drives the electrons (holes) away from their generated point in the cell. In ideal condition, the charge carriers are traveling without loss to an external circuit to form electricity current. The current density of the converter is described as,

$$J_{sc} = q \int_0^{\infty} \eta_c(E)(1-R(E))a(E)b_s(E)dE, \quad (2.18)$$

where $\eta_c(E)$ is the collected probability by the external circuit, $a(E)$ is the probability of absorption at a photon energy E , $R(E)$ is the probability of reflection, and $b_s(E)$ is the incident flux of photons normal to the flat surface of convertor. Then, the current density of the converter is also described as,

$$J_{sc} = q \int_0^{\infty} QE(E)b_s(E)dE, \quad (2.19)$$

where $QE(E)$ is the probability that an incident photon with energy E will deliver one-electron to the external circuit.

Here, I assume that all incident photons with energy $E > E_g$ are absorbed to promote one-electron to the excited state and spatially separated charge separation are perfectly collected by the external circuit. This gives the maximum photocurrent density as

$$J_{sc} = q \int_{E_g}^{\infty} b_s(E)dE. \quad (2.20)$$

I can also calculate the incident and extracted power from the photon fluxes. The incident power density by integrating the incident irradiance over the photon energy in

the solar light is described as

$$P_s = \int_0^\infty E b_s(E_s) dE. \quad (2.21)$$

I assumed that no potential is lost through resistances anywhere in the circuit for the output power. In this case, I describe as $P_{\text{output}} = J(V)V$. Thus, the power conversion efficiency is wrote as,

$$\eta = \frac{VJ(V)}{P_s}. \quad (2.22)$$

The maximum photovoltaic conversion efficiency is achieved at the voltage condition where the relationship described below is as,

$$\frac{d}{dV}(J(V)V) = 0. \quad (2.23)$$

Shockley and Queisser showed the detailed balance calculation to derive a fundamental limit of photovoltaic conversion efficiency (PCE) of a single junction solar cell.⁸⁵ Calculations have provided a PCE limit of $\sim 33\%$ (Shockley-Queisser limit), where this limit is based on the assumption that absorbed one-photon generates a single electron-hole pair (exciton) in semiconductor. SWNTs have been shown to exhibit multiple-exciton generation (MEG) from a single photon,⁸⁶ which provide a potential to exceed the Shockley-Queisser limit.

2.4. Carbon nanotubes for solar cells

Carbon nanotubes have attracted much attention both from fundamental physics and optoelectronic device applications, because intriguing physical and chemical properties such as high carrier mobility, tunable band gap, and high chemical stability endow them high potential for photovoltaic applications. In the photovoltaic devices, the carbon nanotubes could work as both the active layer to generate carriers and charge transport layer to conduct charge carriers, which is promising toward high performance solar cell

devices.

2.4.1. Charge carrier generation

I describe about the charge carrier generation in carbon nanotubes. Freitag *et al.* report the photoconductivity from individual semiconducting SWNTs.⁸⁷ The mechanism of photocurrent generation involves resonant excitation of E_{22} exciton state in the semiconducting SWNT. The novel phenomena of multiple electron-hole pair generation has also been reported in SWNTs, in which that efficient multiple carrier generation from a single hot E_{22} exciton occurs in the SWNTs.⁸⁶ However, the state of art single SWNT device might not form a realistic basis for technological viewpoint for solar cell, because of their low current outputs and small active area. Nevertheless, it has been recently demonstrated that a single carbon nanotube diode can be realized in such a way that it can be replicated a cascade solar cell.⁸⁸

Recently, carbon nanotubes and Si heterojunctions solar cells have been developed by taking advantage of the high mobility, conductive and transparent features of carbon nanotube. Ong *et al.*, reported the photocurrent response of SWNTs/Si heterojunction solar cell using SWNTs with a narrow chirality distribution.⁸⁹ The small peak of photocurrent response at E_{11} exciton band has been shown, which demonstrates that the SWNT contributes to the photo-conversion process not only as a charge separator/transporter/collector, but also as a light absorber in the SWNTs/Si heterojunction solar cell.

2.4.2. Charge transport

High carrier mobility of carbon nanotubes shows a great promising for carrier transport part in optoelectronic devices. Carbon nanotubes have been assembled into various components of organic solar cells to improve their efficiencies. Replacement of

the ITO transparent anode using a thin carbon nanotube layer has been investigated.⁹⁰ SWNTs modified with phthalocyanine-pyrene conjugates have also been reported by Guldi and coworkers in dye-sensitized solar cells.⁹¹

In the application of photovoltaics, carbon nanotubes were first used as the acceptor in the bulk heterojunction of polymer solar cells by Kymakis *et al.* They fabricated the polymer solar cells using blended P3OT with 1wt% CNTs.⁹¹ The J_{sc} and V_{oc} increased in the fabricated solar cells, because the addition of SWNTs introduced the internal polymer-nanotube junction for exciton dissociation and continuous paths for electron transport to cathode. The low efficiencies of SWNT-based solar cells can be associated with a few factors such as the presence of metallic SWNTs making short circuit, impurities, SWNT aggregation, and low charge carrier mobility in the polymer matrix.⁹² ⁹³ It was found that only semiconducting SWNT can contribute for the electron charge transfer by *ab initio* calculations of polymer-carbon nanotube heterojunctions.⁹⁴ The highly oriented and isolated SWNTs coated with a P3HT layer exhibited a high transfer ability,⁹⁵ which suggests that the controlling of SWNTs dispersion in the polymer is a critical issue for the photovoltaic performance. Nogueira *et al.*, tried to mitigate aggregation of SWNTs by the covalent functionalization with thiophene moieties and PCE of 1.48% was achieved by use of functionalized SWNT and P3OT polymer under 1.55 mW/cm² illumination.⁹⁶ Moreover, the electric field orientation of SWNTs can be achieved to reinforce these effects.⁹⁷

Ago *et al.* first reported the replacement of ITO electrode by carbon nanotubes in polymer solar cells.⁹⁸ The enhanced external quantum yield (EQE) was attributed to the interpenetrating network between polymer and multi-walled carbon nanotubes (MWNTs) and to the higher built-in electric field because of the higher work function of MWNTs (5.1 eV) with respect to ITO.⁹⁹ Wu *et al.* showing that the conductive thin

films made of high purity SWNTs could represent a promising alternative to ITO.¹⁰⁰ An improved PCE was reported, when a SWNT layer was substituted to the common ITO electrode.⁹⁰ However, the photovoltaic performance is very low because of the high sheet resistance of SWNT film. A transfer-printing method was used to produce low sheet resistance carbon nanotube films (200 Ω/sq) with high optical transmission of 85% in the visible range.¹⁰¹ Ultrasoother, high-quality, and highly uniform SWNT electrodes have been produced by ultrasonic spraying.¹⁰² Carbon nanotube electrodes are mainly proposed as hole collector to replace the ITO electrode in polymer solar cells. Moreover, the SWNT also can be a bottom electron collecting electrode in solar cells with an active layer made of P3HT and ZnO nanowires as electron acceptors.¹⁰³

The prototype of carbon nanotube photovoltaic device using carbon nanotube/Si heterojunctions was first fabricated by connecting individual carbon nanotube and Si nanowire in 1999.¹⁰⁴ The earliest success of application for macro-size solar cells based on carbon nanotubes/Si heterojunction was reported by Wei *et al.* in 2007.⁵⁸ Double-walled carbon nanotubes (DWNTs) were transferred onto *n*-Si, where nanotubes were served for both photocarrier generation and collection layer, as shown in Figure 2.15(a). Figure 2.15(b) shows the photovoltaic performance of a fabricated DWNTs/Si heterojunction solar cell. The PCE of only 1.3% was achieved in the DWNTs/Si heterojunction solar cell, however PCE is not so high due to high sheet resistance, low short-circuit current and low fill factor. Higher performance of carbon nanotube/Si heterojunction solar cells were fabricated by reducing the thickness of native silicon oxide on Si substrate.⁶⁰

Wadhwa *et al.* reported a novel method of improving carbon nanotubes/Si solar cells through electronic junction control by using an ionic liquid gate of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-BTI), as shown in Fig. 2.16. The device exhibited a PCE of 8.5% which was dynamically and reversibly adjusted between 4 and 11% by ionic liquid gating.¹⁰⁵ The mechanism of the electronic junction control was explained by considering the gate-induced modulation of the nanotube's Fermi level and the gate-modulated control of the interface dipole at the junction.

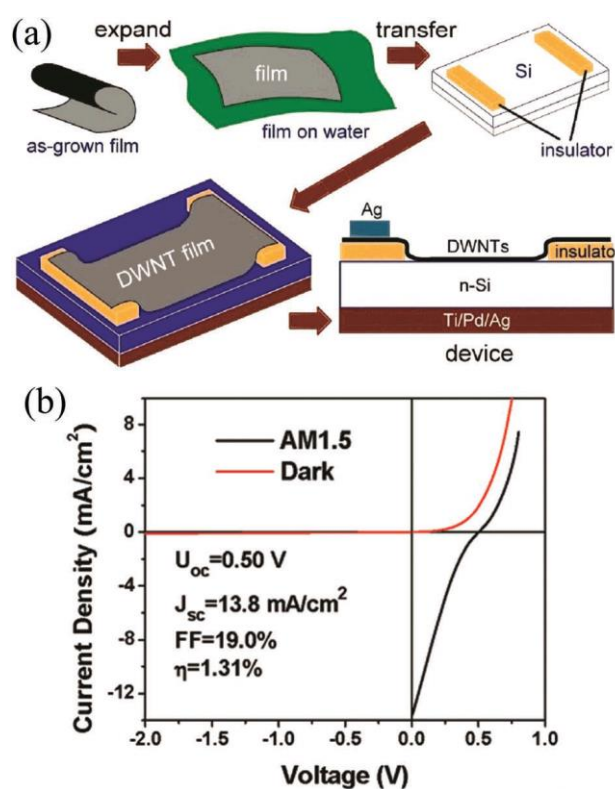


Figure. 2.15 (a) Illustration of the fabrication process of DWNT/ n -Si solar cell and (b) current density-voltage (J - V) curve of the solar cell. Adapted with permission. The figure was taken from Ref.⁵⁸

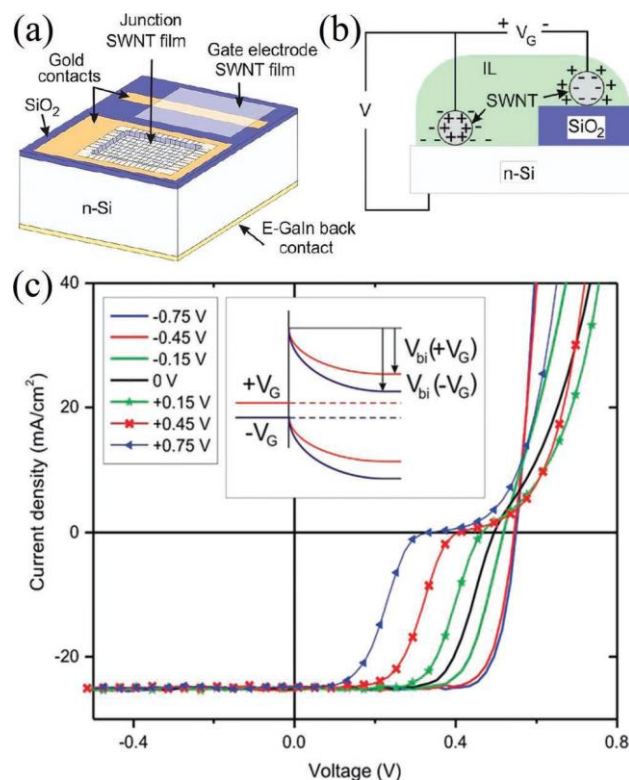


Figure. 2.16 (a) Schematic of electrically-gated heterojunction solar cell, (b) schematic of charge distribution during gated operation, and (c) J - V characteristics of the device with varying gate voltage. Inset shows the schematic of built-in potential V_{bi} change. The figure was taken from Ref.¹⁰⁵

Jia *et al.* achieved higher PCE of 13.8% by chemical doping method (0.5 M HNO₃) for nanotube film, as shown in Fig. 2.17. The untreated device exhibited a PCE of 6.2 %, while the treated devices using HNO₃ shows the large improvement of photovoltaic performance due to an increase in J_{sc} from 27 to 36 mA/cm² and coupled in FF from 0.47 to 0.72. Nitric acid doping of SWNT membranes has been shown to both decrease the tube-tube resistance and shift of Fermi level down towards the valance band (p -doping). These findings are used to explain to the observed increases in efficiency,¹⁰⁶ however the detail mechanism has not been fully cleared.

Shi *et al.* reported a high PCE of 15.1% for carbon nanotubes/Si solar cells using a

TiO₂ antireflection film.¹⁰⁷ A uniform TiO₂ layer was formed by spin-coating, and the carbon nanotubes were embedded within two TiO₂ layers. After the coating of the TiO₂ layer, the J_{sc} increased from 24.4 to 32.2 mA/cm² due to the anti-reflection effect of the TiO₂ layer and the PCE was improved to 15.1% from 8% after chemical doping by HNO₃/H₂O₂.

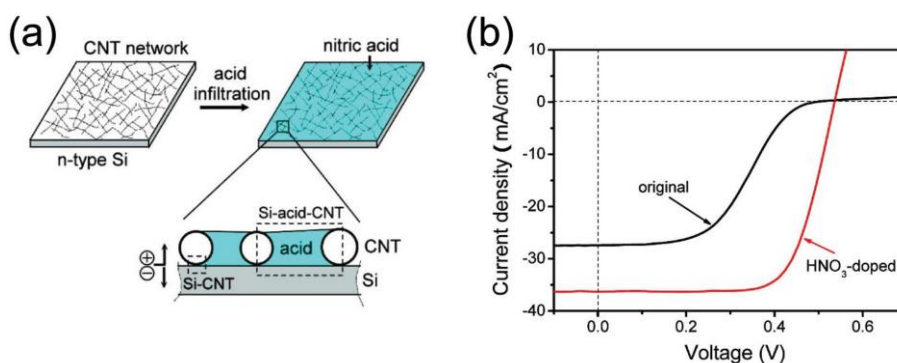


Figure 2.17 (a) Illustration of CNTs/Si solar cell and infiltration of nitric acid into the CNT network to form Si-acid-CNT photoelectrochemical units at the interface. (b) J - V curves of the CNTs/Si solar cell. After infiltration of nitric acid, the PCE of the solar cell in the wet state increased to 13.8% from 6.2%, owing to the enhancement in J_{sc} and FF. The figure was taken from Ref.¹⁰⁶

Chapter 3. HNO₃ doped single-walled carbon nanotube for Si solar cells

3.1. Introduction

In this Chapter, I describe the photovoltaic performance of SWNT/Si heterojunction solar cell and carrier doping effect of SWNT for the device performance.

The carbon nanotubes have attracted a great deal of interest for photovoltaic applications because of their excellent physical and electronic properties, including tunable band gap, high carrier mobility, and multi-carrier generation. The heterostructures of carbon nanotubes and silicon (Si) have been studied to realize highly efficient photovoltaic cells during ten years. Commonly available semiconductors SWNTs are unintentionally hole-doped, described in Chapter 2, which can be used for the *p-n* heterojunction solar cells combination with *n*-type Si. High conversion efficiency was achieved in the SWNTs/Si heterojunction solar cells because of the SWNTs efficient transport the hole extracted from the Si substrate. The *p*-type chemical doping of SWNTs with acid,¹⁰⁶ SCl₂O,¹⁰⁸ and gold (III) chloride hydrate¹⁰⁹ further enhances the photovoltaic conversion efficiency of SWNT/Si heterojunction solar cells. In the heterojunction solar cells, microscopic photovoltaic conversion processes by doping are complicated because the SWNT network contributes to photovoltaic processes of charge separation and charge transport. However, understanding the mechanism of doping effect in the carbon nanotube is very important not only for the photovoltaic applications but also for the fundamental researches.

In this Chapter, I will describe the fundamental photovoltaic performance of SWNT/Si solar cells and the enhancement of photovoltaic performance by carrier

doping effect in the carbon nanotube. Figure 3.1 shows the schematic of SWNT/Si heterojunction solar cells structure used in this chapter. The photovoltaic conversion efficiency of the cells without and with HNO_3 doping was studied and the enhancement mechanism of the different thickness SWNTs film was also investigated. The conversion efficiency strongly enhanced depending on the thickness of the SWNT network film. The thickness-dependent power losses of the cell were obtained from the analysis of current-voltage characteristics based on the equivalent circuit model. From these results, it was found that the enhancement of conversion efficiency by HNO_3 doping resulted from both an increase in the p - n junction density and a decrease in the series resistance of the SWNT network film due to an increase in the carrier density.

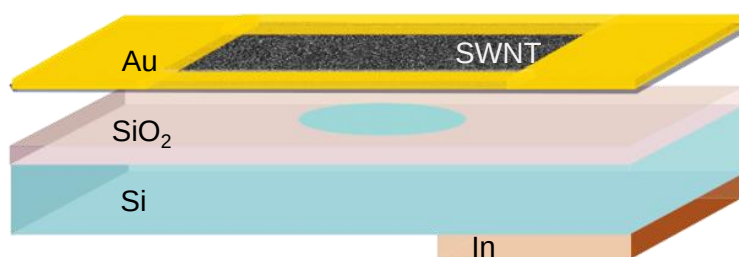


Figure 3.1 Schematic of SWNT/Si solar cell devices.

3.2. Preparation of carbon nanotube thin film for cells

For the fabrication of solar cells, CoMoCAT (6,5)-rich SWNTs were dissolved in dimethylformamide (0.25 mg/mL) and treated with a bath sonicator for 60 min and tip sonicator for 30 min. The solution was directly sprayed onto both n -type Si wafers ($\sim 10 \, \Omega \cdot \text{cm}$) and reference glass substrates using an air-brushing technique.^{108, 110} A Si wafer with a window ($\phi = 2 \, \text{mm}$) of a predeposited insulating oxide layer, and a reference glass substrate were placed side by side on a heating platform so that the resulting SWNT network films on both substrates were of the same thickness. The fabricated SWNT/ n -Si heterojunction solar cells were electrically contacted with Au

anodes on the SWNT side and with indium (In) cathodes on the Si side.

3.3. Experimental methods

3.3.1. Light transmittance measurements

Transmittance spectra of SWNT thin film were measured using a UV-vis spectrophotometer (Shimadzu, UV-1800), as shown in Figure 3.2. In the spectrophotometer, the excitation light source is a combination of deuterium (D_2) lamp and halogen lamp. The D_2 lamp and halogen lamp were employed in 200-340.8 nm and 340.8-1100 nm. White light from the lamps is cut into monochromatic light at the diffraction grating and split into two paths at the beam splitter. One path goes to the photodiode for the sample and the other path goes to the reference photodiode. Scanning the grating i.e. varying the excitation wavelength, the ratio of the light intensity transmitting through the sample and reference was measured to obtain absorption spectra. The scan rate of the grating was set as “middle speed” and the sampling pitch was set as 1 nm interval. We measured the transmittance spectrum of glass substrate as a baseline.

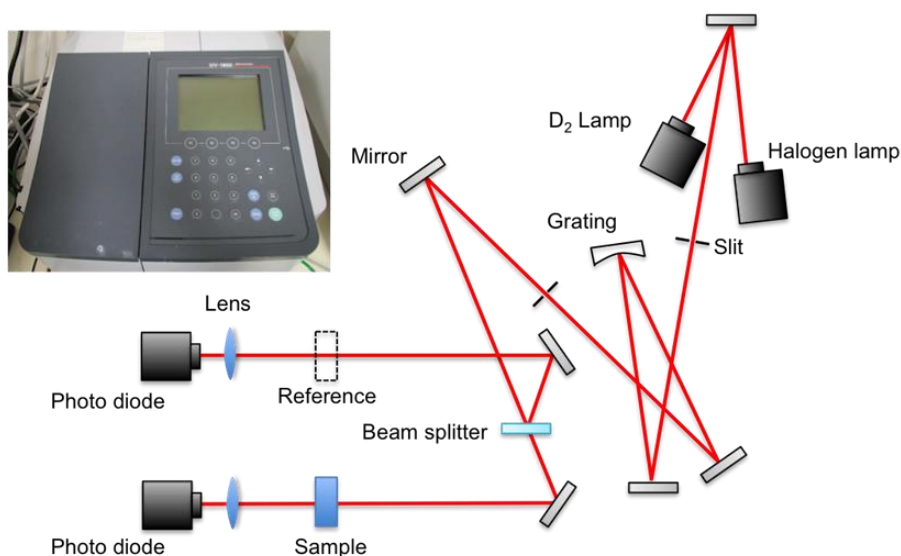


Figure 3.2 Photograph and schematic optical alignment of the UV-vis spectrophotometer. The figure was taken from Ref¹⁷⁴

3.3.2. Solar cell performance measurements

For photovoltaic testing, the devices were irradiated using a solar simulator (San-Ei Electric XES-40S1) with the AM 1.5 spectrum ($\sim 100 \text{ mW/cm}^2$), and current density–voltage (J – V) data were recorded using a digital multimeter (Keithley, 2400) shown in Figure 3.3. The AM 1.5 conditions for the solar simulator were confirmed using a standard cell (Bunkoukeiki, BS-500BK). The SWNTs/Si solar cells with a circle window of 2 mm were tested in the measurement of this chapter.

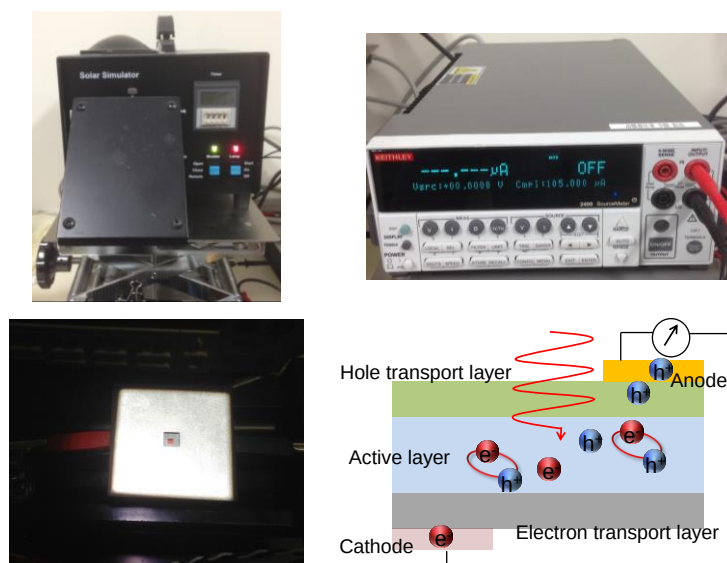


Figure 3.3 Photograph of testing set up of solar cells and schematic of principle of solar cells.

3.3.3. Four probe resistance measurements

The measurement of resistivity of carbon nanotubes thin film was conducted by a 1/2 Digit Multimeter (Keithley, 2100) combination with a four probe tester, as shown in Figure 3.4. In the measurement, the carbon nanotube film was coated on the glass substrate by spray method. The four probes are arranged along linearly. A constant current passes through the two probes and the potential drop across the middle two probes is measured. The resistance (R) of SWNT film is proportional to its length L and inversely proportional to the area of cross section A .

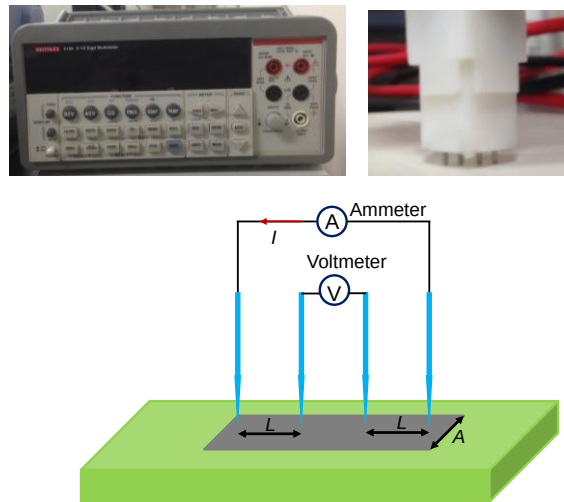


Figure 3.4 Photograph of surface resistance measurement set up and schematic of four probe method.

3.4. Sample characterization

Figure 3.5 shows the typical current density–voltage (J – V) characteristics of the SWNT/Si solar cells before (original, black curve) and after (doped, red curve) infiltration (doping) of HNO_3 in the network of SWNTs. Before HNO_3 infiltration, the photovoltaic conversion efficiency η , fill factor (FF), short–circuit current density (J_{sc}), and open–circuit voltage (V_{oc}) of the solar cells were approximately 3.4%, 44%, 17.2 mA/cm^2 , and 0.45 V, respectively. After HNO_3 (0.01 mol/L) doping, I confirmed that η of this cell increased up to 7.6%, and the parameters FF, J_{sc} , and V_{oc} increased to 67%, 21.2 mA/cm^2 , and 0.54 V, respectively. I confirmed that the transmittance of the SWNT film before and after HNO_3 doping with limited changes indicates that HNO_3 doping has a very small effect on the solar light incident density, as shown in Figure 3.6.

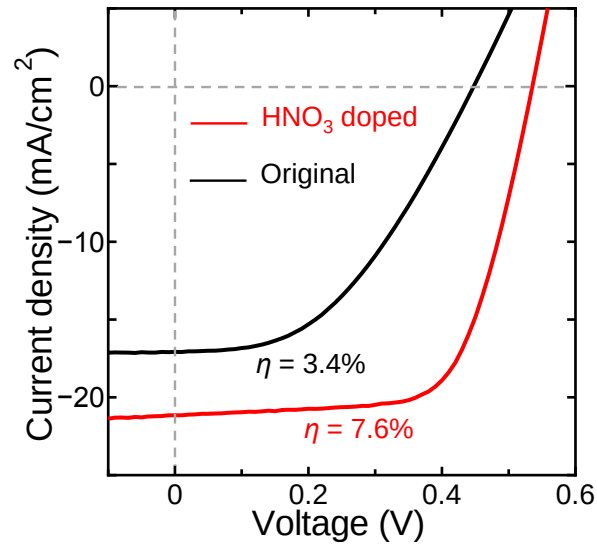


Figure 3.5 J - V characteristics of SWNT/Si heterojunction solar cell before (original, black curve) and after (doped, red curve) HNO_3 doping. Photovoltaic conversion efficiencies η of the cells before and after HNO_3 doping are indicated.

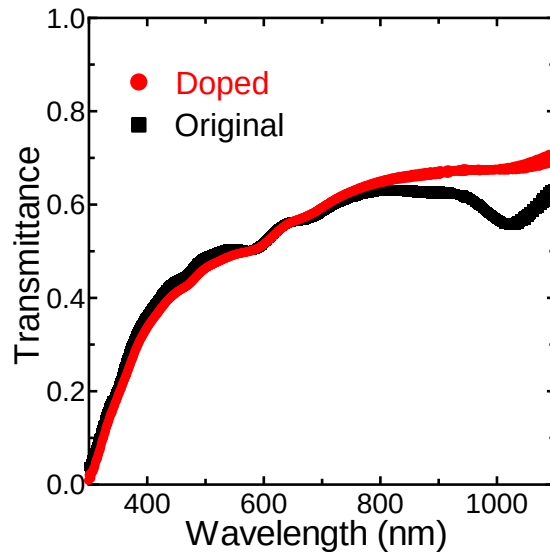


Figure 3.6 Optical transmittance spectra of SWNT/Si heterojunction solar cell before (original, black curve) and after (doped, red curve) HNO_3 doping. The absorption peaks (transmission dips) for the second subband transitions E_{22} are observed at about 1030 nm.

3.5. SWNTs thickness dependent performance

I fabricated many p -SWNT/ n -Si solar cells with different SWNT network film thicknesses that were characterized by the optical transmittance T at 550 nm. Figure 3.7(a) shows η of SWNT/Si cells before and after HNO_3 doping as a function of transmittance T , as indicated by the solid squares and circles, respectively. Before HNO_3 doping, η significantly increases with T from 20% to 70% (i.e., decreasing thickness) and significantly decreases with T above 70%. The maximum value of η is observed at $T \approx 70\%$. After HNO_3 doping, η drastically improves depending on T . The enhancement of the conversion efficiency defined as the difference before and after HNO_3 doping $\Delta\eta$ was calculated from these data. The inset of Figure 3.7(a) shows $\Delta\eta(T)$, and $\Delta\eta(T)$ also strongly depends on T of the SWNT network films of the devices, i.e., it increases with T , namely, with decreasing film thickness.

In Figure 3.7(b), I plotted J_{sc} of SWNT/ n -Si solar cells before and after HNO_3 doping as a function of T . Before HNO_3 doping, J_{sc} shows characteristic behavior of a linear increase with T until $T \approx 75\%$ and then decreases above 75%. This behavior of J_{sc} can be explained by both the carrier generation in the Si layer G and effective areal density of p - n junction S , as $J_{\text{sc}} \propto G \cdot S$.¹¹¹ The previously reported incident photon to charge carrier conversion efficiency (IPEC) spectrum has revealed that the optically generated carriers in the Si layer mainly contribute to the photovoltaic process in SWNT/Si solar cells.¹¹¹ In this case, the number of optically generated carriers is simply proportional to T , and the generation factor G is directly proportional to T . In contrast, S decreases with increasing T (i.e., decreasing thickness). As a result, $J_{\text{sc}}(T)$ of the cell before HNO_3 doping shows a characteristic maximum at approximately 75%.

By HNO_3 doping, the behavior of J_{sc} changes and shows a simple linear increase with T ,¹¹² as shown in Figure 3.7(b). We note that the transmittance of SWNTs in the visible

region did not change by HNO_3 doping, as shown in Figure 3.6. At the region of the first sub-band optical transition energy (E_{11}) around 1010 nm, I observed a small change in the transmittance corresponding to the net light transmittance less than 5%, which I can neglect in the following analysis. The simple linear increase in J_{sc} suggests that S drastically increases, and J_{sc} is dominated only by G described as $G \propto T$ after HNO_3 doping.

The inset of Figure 3.7(b) shows FF of the SWNT network films as a function of T . FF also depends on T and shows a maximum value at $T \approx 60\%$. FF is determined by the losses in the photovoltaic process resulting from the series resistance R_s ,¹¹³ shunt resistance R_{sh} ,¹¹⁴ and diode D . The dependence of the measured FF on T implies that the power losses also depend on T (i.e., thickness) of the SWNT network film.

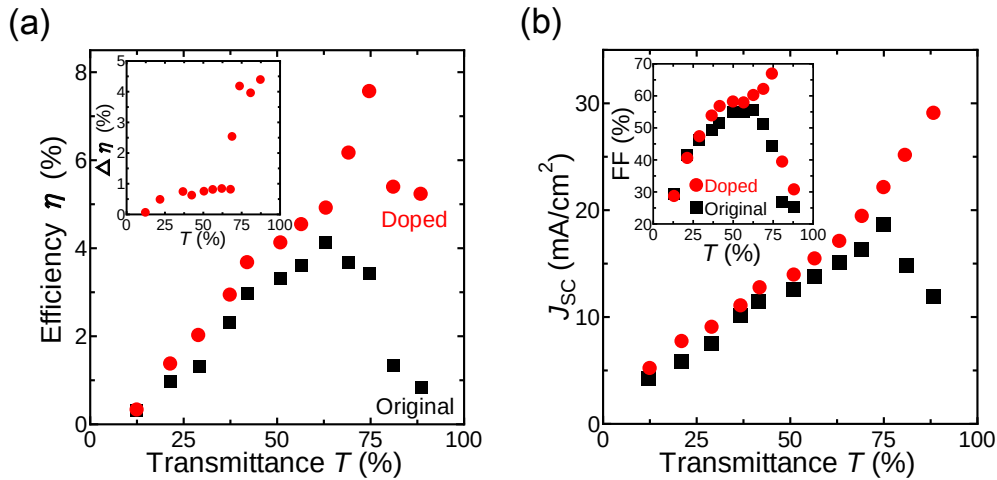


Figure 3.7 (a) Photovoltaic conversion efficiency η of the SWNT network film before (original, black squares) and after (doped, red circles) HNO_3 doping as a function of transmittance T at 550 nm. The inset shows the difference in efficiency before and after HNO_3 doping $\Delta\eta$. (b) Short-circuit current density of the solar cells J_{sc} before (black squares) and after (red circles) HNO_3 doping as a function of T . Inset shows the fill factor (FF) of the solar cells as a function of T .

3.6. Mechanism of SWNT/Si solar cells

The role of SWNTs in the devices is still controversial, even though the SWNT/Si solar cells exhibit high power conversion efficiency. This is because that the semiconducting SWNT exposed in air conditions is *p*-type due to oxygen adsorption and mixed with the metallic SWNTs. Two main mechanisms are proposed for how the SWNT/Si solar cells convert light to electrical power: 1) *p-n* heterojunction solar cell (Figure 3.8(a)), 2) metal-semiconductor Schottky junction solar cell (Figure 3.8(b)). The semiconducting SWNTs enable to form *p-n* junctions with *n*-Si, in which a diffusion process of photo-generated carriers occurs when *p*-SWNTs are placed in contact with *n*-type Si. The hole and electron will be injected into the *n*-Si and *p*-SWNTs, respectively. As a result of the charge diffusion, the electric neutrality will be broken and form a built-in field, which engenders a carrier drift. The injection of carriers would bend the energy band of SWNTs and Si. Thermal equilibrium is reached with the co-relationship of concentration difference of carriers and built-in field, while the dynamical movement of charge carriers still exists. In the Schottky junction solar cells, the situation is the similar with the *p-n* junction solar cell but the metallic SWNTs is used to instead of semiconducting SWNTs. Then main differences are the magnitude of the reverse saturation current and the switching characteristics.

I use high concentration of semiconducting nanotubes (90%, 6,5-CoMoCat) for the SWNT/Si solar cell. Because *p-n* junction in the solar cells is dominated, we therefore employed the *p-n* junction model here for analyzing the doping effects.

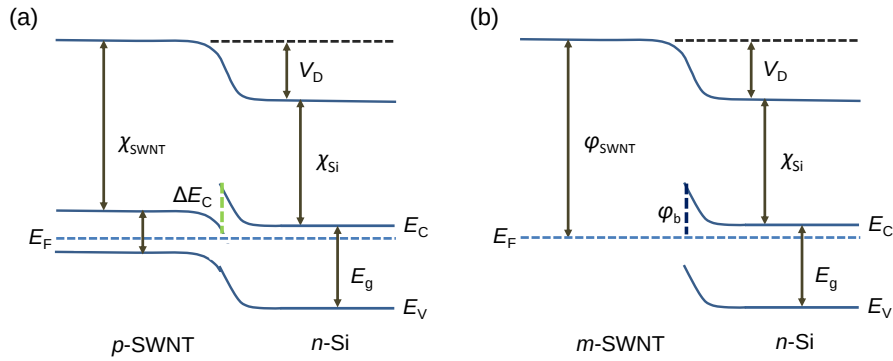


Figure 3.8 Energy-band diagrams of the SWNT/Si heterojunction. The SWNTs form two types of heterojunction on the Si substrates: a) p - n (semiconductor/semiconductor) junction and b) Schottky (metal/semiconductor) junction. χ_{SWNT} and χ_{Si} are the electron affinities of SWNTs and Si layer, respectively. ϕ_{SWNT} is the work functions of SWNTs. E_g represents the bandgaps. E_C and E_V are the conduction band energies and the valence band energies, respectively. E_F is the energy of the Fermi level. ΔE_C is the valence band energy difference between SWNT and Si. In the ideal thermal equilibrium diagram, ϕ_b is the ideal barrier height and V_D is the built-in potential barrier.

3.7. Equivalent circuit model of J - V curve

I analyzed the J - V curve using the equivalent circuit model to understand the photovoltaic conversion process and losses.¹¹⁵ The total current density J in the model can be described as:

$$J = J_0 \left\{ \exp\left(\frac{e(V - R_s J)}{nk_B T}\right) - 1 \right\} + \frac{V - R_s J}{R_{sh}} - J_{ph}, \quad (1)$$

where J_0 is the reverse saturation current density, e is the electron charge, $k_B T$ is the thermal energy, n is the diode ideality factor, and J_{ph} is the photocurrent density. The schematic diagram of the equivalent circuit model is shown in the inset of Figure 3.9. Figure 3.9 shows the experimental results of the typical J - V curves (solid lines) and calculated J - V curves (dotted lines) using eq. (1) before and after HNO_3 doping. The

fitted J – V curves produce the experimental J – V curves well. From the fitting procedure, the diode factor, R_s , and R_{sh} can be obtained.

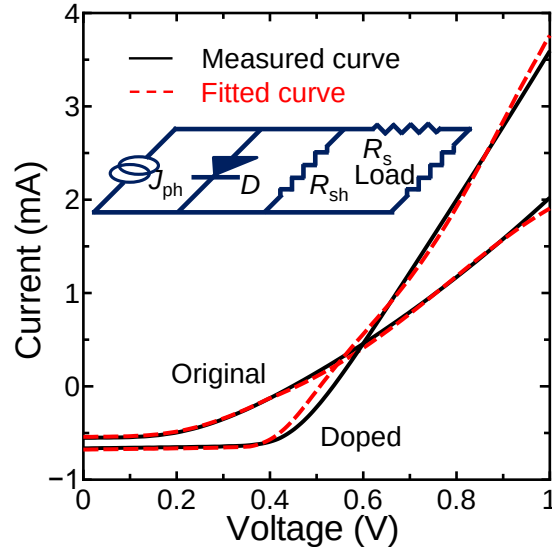


Figure 3.9 Experimentally obtained J – V curves (black solid line) and simulated ones (red dashed line) based on the equivalent circuit model. Inset shows the schematic diagram of the equivalent circuit model of a device connected with a load, series resistance (R_s), shunt resistance (R_{sh}), and a diode (D).

3.8. Series resistance effect in solar cells

Figure 3.10(a) shows the obtained R_s before and after HNO_3 doping as a function of T . R_s before HNO_3 doping shows a relatively higher value than that after HNO_3 doping and drastically increases with T above 70%. I note that R_s is drastically reduced at high transmittance and slightly decreased at low transmittance by HNO_3 doping, which is consistent with the observation of a strong reduction of the sheet resistivity by HNO_3 doping of the SWNT network films measured by the four-probe method. HNO_3 acts as an efficient p -type (hole) dopant for SWNTs.¹¹⁶ HNO_3 doping causes an increase in the hole density of the SWNT network films, which strongly reduces the resistivity of the film. In addition, the effective p – n junction density in the p –SWNTs/ n –Si heterojunction solar cells and J_{sc} , as shown in Fig. 3.7(b), increase with the hole density

of the SWNTs. From the detail analysis of J - V curve change, it is confirmed that the decrease of conversion efficiency comes from the decrease of FF of SWNTs film, which results from the increase of R_s .

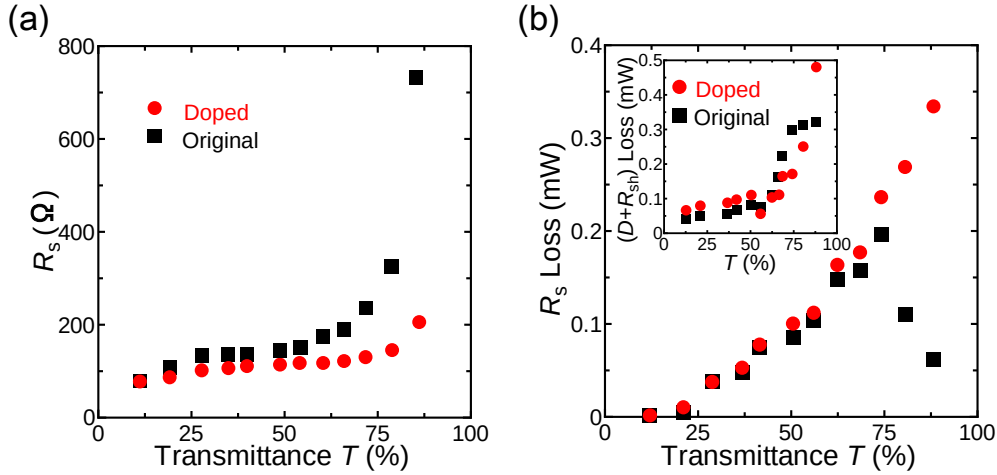


Figure 3.10 (a) Series resistance R_s before (original, black squares) and after (doped, red circles) HNO_3 doping as a function of T derived from the J - V curve analysis. (b) Transmittance T dependence of series resistance (R_s) loss. Inset shows the total shunt resistance and the diode ($R_{sh} + D$) loss with different T .

I calculated the power consumption resulting from the shunt, series, and diode losses using R_s , R_{sh} , I_{sc} , V_{max} , and I_{max} , where V_{max} and I_{max} are the load current and voltage of the solar cell, respectively. The inset of Fig. 3.10(b) shows the sum of the calculated shunt (R_s) and diode (D) losses before and after HNO_3 doping as a function of T . The sum of R_s and D losses ($D + R_s$) is nearly unchanged after doping, which suggests that the increase in the carrier density of the SWNTs by HNO_3 doping does not directly affect these losses. Figure 3.10(b) shows the calculated $R_s(T)$ loss before and after HNO_3 doping. Before HNO_3 doping, the R_s loss linearly increases with T until 75% and decreases above 75%, while it shows a simple linear increase after HNO_3 doping. The $R_s(T)$ loss at about 75% is strongly changed by HNO_3 doping because R_s is drastically decreased by HNO_3 doping, as shown in Fig. 3.10(a).

3.9. Theoretical calculation methods

Here, I discuss the enhancement mechanism of η of the SWNT/Si solar cells by HNO_3 doping with respect to the results presented in Figure 3.7. η before and after HNO_3 doping shows maximum behavior with an increase in T , but the transmittance (T) showing the maximum η shifts to a higher T value (thinner SWNT films) by HNO_3 doping. In order to understand this result, I consider the photovoltaic conversion of SWNT/Si heterojunction solar cells as a function of T (i.e., thickness) using G , S , and the ratio of power loss R_{loss} obtained from the power loss normalized by the total power consumption. The photovoltaic conversion efficiency as a function of T can be described as

$$\eta_{\text{cal}}(T) \propto G(T) \cdot S(T) \cdot (1 - R_{\text{loss}}(T)) \cdot V_{\text{oc}}, \quad (2)$$

where V_{oc} was found to be almost constant before and after doping. G and S in eq. (2) can be expressed as $G(T) = (1 - r_{\text{eff}}) \cdot T$, $S(T) = (1 - k^{-\log T})$, where r_{eff} is the effective reflectivity of the SWNT network films on the Si substrates, derived using the Maxwell–Garnet model,¹¹⁷ and k (≤ 1) is a parameter reflecting the probability that a p - n junction is not generated at the interface of the n -Si and SWNTs. The detailed calculations were shown in Appendix 1.

3.10. Modeling results

Since J_{sc} is proportional to G and S , I obtained the relative change of S as a function of T in Fig. 3.11(a) from J_{sc} and G as $S \propto J_{\text{sc}}/G$. It is found that $S(T)$ after doping becomes much larger than that before doping above T of 75%. The dashed curves in Figure 3.11(a) were obtained by fitting the function $S(T) = (1 - k^{-\log T})$. The experimental curves before and after the doping were excellently produced using the model with different parameters of k , where $k_{\text{before}} = 2 \times 10^{-7}$ and $k_{\text{after}} \approx 0$ were obtained. Considering that the k parameter is proportional to the probability that a p - n junction is

not formed at the interface of the Si and SWNT film, $k_{\text{after}} \approx 0$ means that the formation rate of the p - n junction at the interface is drastically improved in the high transmittance region by HNO_3 doping. η_{cal} determined using k_{before} and k_{after} produces the experimental data well for both before and after HNO_3 doping, as shown in Fig. 11(b) (solid lines). This result strongly suggests that the effective areal density of the p - n junction drastically increases in the high transmittance region by HNO_3 doping. Therefore, I attribute the significant change in $\eta(T)$ by HNO_3 doping not only to the reduction in the series resistance of the SWNT network films but also to the drastic improvement of the probability of generating a p - n junction at the SWNT/Si interface and the consequent increase in the effective areal density of the p - n junctions.

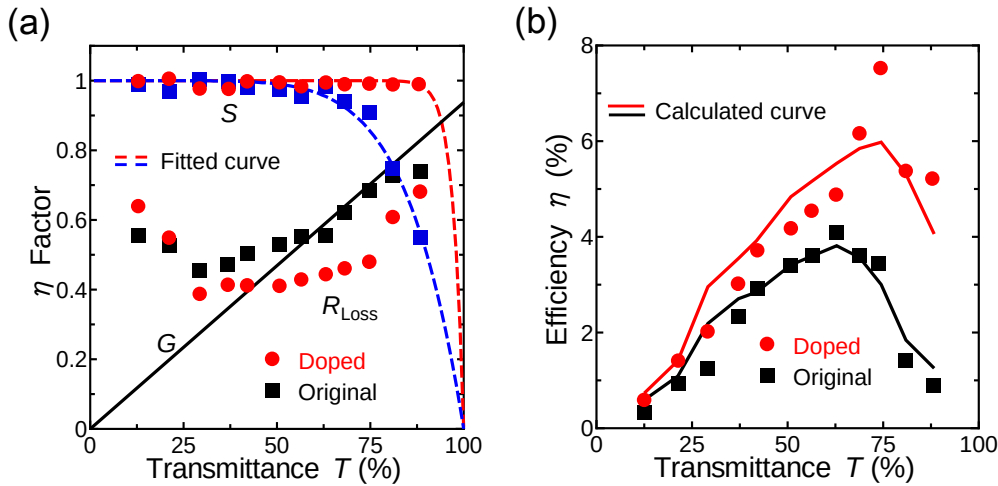


Figure 3.11 (a) Plots of photovoltaic conversion factors, generation of carriers (G), effective areal density of p - n junctions (S), and the power loss ratio (R_{loss}) as a function of T . (b) Experimental results of photovoltaic conversion efficiency η and simulated curves using eq. (2).

3.11. Chapter summary

In this chapter, I studied the enhancement mechanism of the photovoltaic properties of SWNT/Si heterojunction solar cells by carrier doping using HNO_3 . The photovoltaic

conversion efficiency of the cells enhanced strongly depending on the thickness of the SWNT network film. It was found that the enhancement of the conversion efficiency by HNO_3 doping resulted from not only a decrease in the series resistance of the SWNT network films, but an increase in the p - n junction density due to the carrier doping. These findings provide important insight for further improvement of the photovoltaic properties of carbon nanotube solar cells.

Chapter 4. FC-CVD based carbon nanotube film for Si solar cells

4.1. Introduction

In this Chapter, the carbon nanotube/Si heterojunction solar cells were investigated using network films of high quality SWNTs grown by atmospheric-pressure floating-catalyst chemical vapor deposition (FC-CVD). The optimization of the device window size and the thickness of SWNT films, a high photovoltaic conversion efficiency of greater than 12% was achieved for SWNTs/Si heterojunction solar cells without any postprocessing. The relationship of window size with the thickness of SWNT film for high conversion efficiency of SWNT/Si solar cells can be revealed.

The solar cells based on simple heterostructures of SWNTs and Si have been extensively studied as model devices.^{59, 89, 108, 109, 111} In the past few years, the photovoltaic performance of SWNT/Si heterojunction solar cells has been improved using postprocessing techniques and complicated device structures, such as carrier doping of SWNT films by the infiltration of acid described in previous chapter,¹¹⁸ controlling the electronic junctions using an ionic liquid electrolyte,^{105, 119} and coating the Si surface with an anti-reflection layer.¹⁰⁷ Photovoltaic conversion efficiencies of greater than 10% have been reported for these devices. However, the need to use complicated postprocessing techniques is impracticable for the application of SWNTs to large-scale solar cells. In addition, such techniques may lead to a low stable device. Hence, the development of a method for the production of high efficiency, stable SWNT/Si heterojunction solar cells that do not require postprocessing is strongly desired.

The physical properties of SWNT thin films strongly affect the photovoltaic performance of SWNT/Si heterostructure solar cells. It has been revealed that the SWNT film serves as a semitransparent carrier transport layer in these solar cell devices.¹²⁰ Hence, one of the major factors limiting the photovoltaic efficiency of previously reported SWNT solar cells may be related to the carrier transport properties of the films. It is thus expected that SWNT/Si heterostructure solar cells with these films that have high transparency and low sheet resistivity will improve photovoltaic conversion efficiencies.

In this Chapter, I report the results of our investigation of the photovoltaic properties of SWNTs/Si heterojunction solar cells using SWNT thin films fabricated using FC-CVD. A photovoltaic conversion efficiency of ~10% was obtained for solar cells using these high-quality SWNT thin films with both high transparency and low sheet resistivity. In addition, various cells with SWNT films of different active window sizes and thicknesses were examined to determine the effect of these characteristics on the transparency of these films. Because of the optimization of such device parameters and the utilization of a high-quality SWNT film, a high photovoltaic conversion efficiency of greater than 12% was achieved in a SWNT/Si heterojunction solar cell without any additional postprocessing, such as carrier doping. In addition, the high reproducibility of the photovoltaic performance of these devices in air was demonstrated. These are important insights for large scale carbon nanotube solar cells with high photovoltaic conversion efficiency.

4.2. Preparation of SWNT film by FC-CVD method

The SWNTs were grown using the FC-CVD method, as reported previously.^{121, 122} Carbon monoxide (CO) was the carbon source, and the catalyst particles were produced by the decomposition of ferrocene vapor. CO (100 sccm) was passed through a

temperature-controllable cartridge containing ferrocene powder. Additional CO (300 sccm) and CO₂ (3 sccm) were also introduced to the furnace, and the growth temperature was set at 850 °C. The SWNTs film was collected at room temperature on a membrane filter comprising cellulose acetate and nitrocellulose. The thickness of a SWNT film can be controlled by the collection time.

The *n*-Si substrates (1–10 Ω·cm) with window sizes (ϕ diameter) ranging from 1 to 3 mm were used for the solar cell devices. The native SiO₂ layer of the active window was removed using a buffered HF solution. The membrane filter containing the SWNT film was then placed on the Si substrate such that the film was in direct contact with the top surface of the substrate. A fiber wiper was then applied to the surface of the substrate with adequate pressure to release the film from the membrane filter and to create a connection between the film and the substrate. It was essential to place a drop of ethanol on the surface to ensure good contact between the films and the substrates and to densify the SWNT film.¹²³ Next, gold (Au) as the anode was coated around the SWNT film to enclose the active area, while Indium (In) onto the back side of the Si substrate as the cathode was made. The schematic of the detailed fabrication process of a SWNT/Si solar cell is also illustrated in Fig. 4.1.

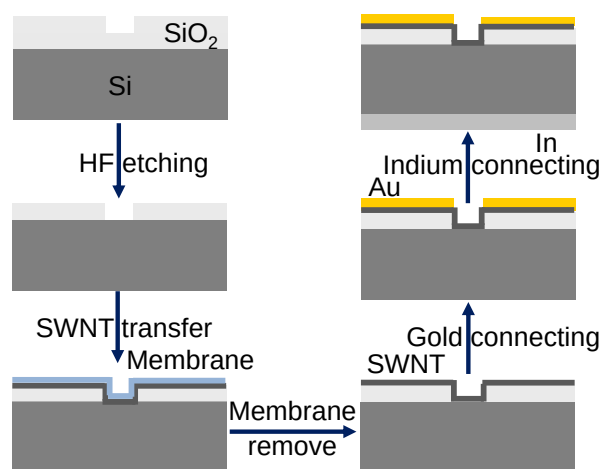


Figure 4.1 Illustration of detail fabrication process of a SWNT/Si solar cell involving

the following steps: 1) etching the oxide layer, 2) formation of SWNTs/Si contact and junction, 3) removing the membrane filter, 4) fabricating gold contact as a cathode, and 5) fabricating indium contact as an anode.

4.3. Characterization of FC-CVD SWNT film

The optical transmission spectra of the SWNT films on the glass substrates were measured using a UV/vis/NIR spectrophotometer (Hitachi, U-4100). To evaluate the photovoltaic properties of the devices, the SWNT/Si heterojunction solar cells were irradiated using a solar simulator (San-Ei Electric XES-40S1) under AM 1.5 conditions ($\sim 100 \text{ mW/cm}^2$), and the current density–voltage (J – V) data were recorded using a sourcemeter (Keithley, 2400). The AM 1.5 (100 mW/cm^2) conditions in the solar simulator were confirmed using a standard cell (Bunkoukeiki, BS-500BK). The sheet resistance of the SWNT network was measured using a digital multimeter (Keithley, 2100) connected to a four-probe collinear arrangement (Astellatech, SR4-S). To measure the ionization potential for the SWNT film, the photoelectron emission spectrum (RIKEN KEIKI, AC-3) was used.

The ionization potential of carbon nanotubes was measured by using the photoelectron emission spectrum. Figure 4.2(b) shows the basic principle of measurement of ionization potential. The photoelectron is emitted from the sample by a higher energy UV light irradiation and the number of emitted photoelectrons depends on the energy of UV light. If the energy of UV-light is larger than the energy difference between the valence band top and vacuum-level, the photoelectrons have enough energy to be emitted from the valence band. Therefore, the ionized potential can be measured by the number of detected photoelectrons as a function of energy.

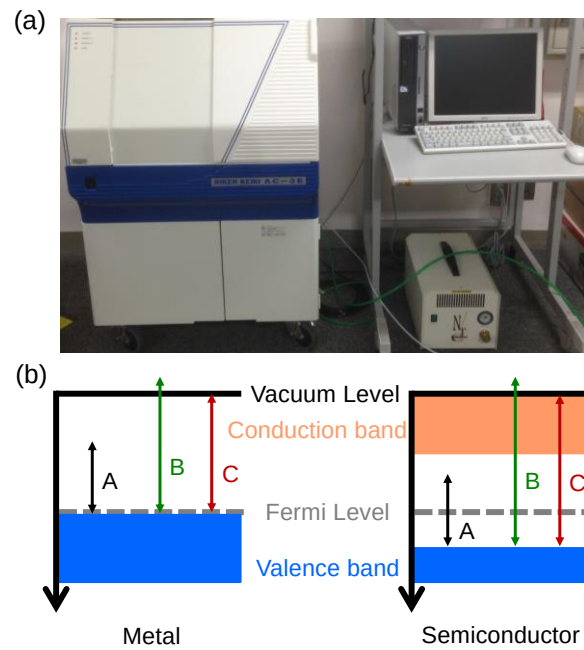


Figure 4.2 (a) Photograph of AC-3 instrument system. (b) Schematic of band gap of work function and ion affinity of metal and semiconductor, respectively. The transition A is the case that the incident UV light energy is low, B is the case that the incident light energy is larger than the difference between top of valence band and vacuum-level, and C is the case that energy difference of vacuum level and top of valence band is the same energy of UV light.

4.4. Sample characterization

Figure 4.3(a) shows photographs of uniform and large-area (12.56 cm^2) SWNT films fabricated using an atmospheric-pressure FC-CVD technique by feeding a carbon source gas with a catalyst precursor. This technique can control the thickness of SWNT films and is also useful for large-scale SWNT/Si solar cell applications. The SWNTs were collected at times of 12, 16, 20, 30, 40, and 60 min. The corresponding transmittance spectra of these films are shown in the inset of Fig. 4.3(b). The transmission value for each film at 550 nm (T) is indicated in the inset of Fig. 4.3(b).

Figure 4.2(b) shows the sheet resistances of the SWNT films as a function of T . The SWNT films fabricated by the FC-CVD method exhibit both low resistivity and high transparency, such as $2 \text{ k}\Omega/\square$ for $T = 80\%$, which is significantly superior to those of films prepared using a spray method.¹¹⁸ I evaluated the first sub-band transition energy of SWNTs, E_{11} , as 0.65 eV by optical absorption spectrum in Fig. 4.3(c) and determined the diameter of SWNTs ($\sim 1.6 \text{ nm}$) from previous reports.^{122, 124}

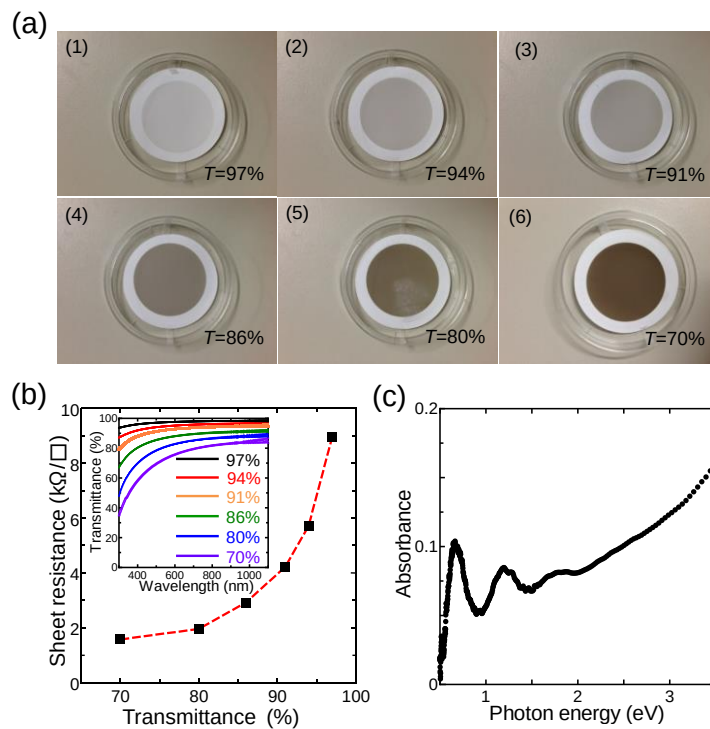


Figure 4.3 (a) Photographs of SWNT films with transmittance values $T = 97, 94, 91, 86, 80$, and 70% at 550 nm , respectively. (b) Sheet resistance of SWNT films as a function of T . Inset shows the transmission spectra of the SWNT films. (c) Absorption spectrum of SWNTs film.

4.5. Photovoltaic performance of cells depending on SWNTs thickness

The effect of the thickness of the SWNT film on the photovoltaic properties of SWNT/Si heterojunction solar cells was investigated. Figure 4.4(a) shows the J - V

curves of SWNT/Si heterojunction solar cells with an active window size (ϕ) of 2 mm fabricated using SWNT films with different thicknesses (transmission values T). The J – V curves for the SWNT/Si heterojunction solar cells drastically change as the transmittance of the SWNT film varies. On the basis of the evaluation of this series of J – V curves, it is found that the photovoltaic conversion efficiency η strongly depends on the thickness of the film (*i.e.*, the transmittance T). Figure 4.4(b) shows the values obtained for η , the fill factor (FF), the short-circuit current density (J_{sc}), and the open-circuit voltage (V_{oc}) as a function of T derived from the series of J – V curves. The photovoltaic conversion efficiency η increases as T decrease and reaches a maximum value at $T \approx 80\%$. In contrast, a negligible change in V_{oc} is observed, while the FF drastically increases as T decreases. In addition, J_{sc} drastically increases as T decreases in the high-transmittance region and moderately decreases as T decreases in the low-transmittance region. Thus, an increase in both FF and J_{sc} from 26.5 to 71% and from 18.9 to 26.9 mA/cm², respectively, contributes to the drastic increase in η from 2.5 to 10.6% from $T = 97$ to 80%. It should be noted that the photovoltaic conversion efficiency of the cell with a high -transparency and low -resistivity SWNT film prepared using FC-CVD ($T = 80\%$) reached a value of 10.6%, which is much larger than the value of 3.2% obtained for cells prepared using a spray method ($T \sim 80\%$), as shown in the previous Chapter.¹¹⁸

Figure 4.5(a) shows the J – V curves of SWNT/Si heterojunction solar cells with an active window size (ϕ) of 1 mm fabricated using SWNT films with different thicknesses (transmission values T). The tendency of the conversion efficiency variations is similar with 2 mm samples. Figure 4.5(b) shows the values obtained for η , the fill factor (FF), the short-circuit current density (J_{sc}), and the open -circuit voltage (V_{oc}) as a function of T derived from the series of J – V curves. The photovoltaic conversion efficiency η increases as T decrease and reaches a maximum value at $T \approx 90\%$. The similar

phenomenon is also shown in Fig. 4.6 and Fig. 4.7, the difference is the maximum value of conversion efficiency located at the different transmittance depending on the balance of series resistance and transmittance of SWNTs.

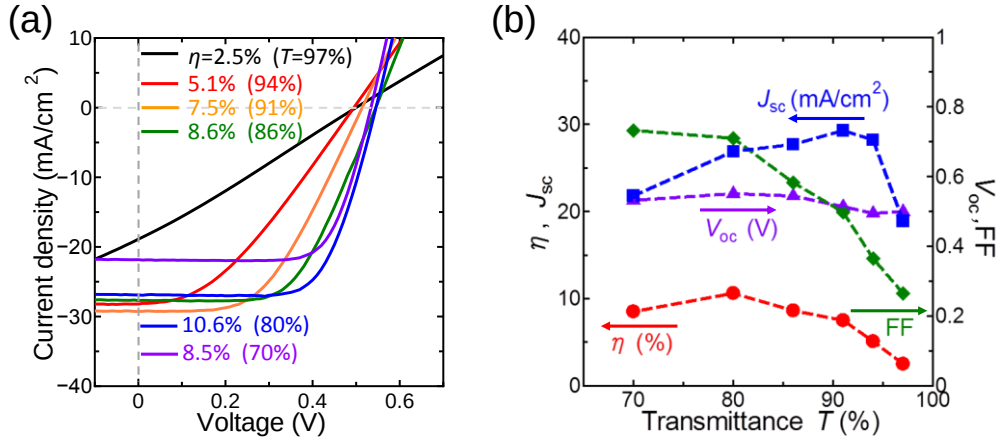


Figure 4.4 (a) Current density–voltage (J – V) curves for heterojunction solar cells with an active window size of 2 mm fabricated using SWNT films of various thicknesses (transmittance). The conversion efficiency of the solar cells and the corresponding transmittance values for the SWNT films are shown in the figure. (b) Values for η , FF, J_{sc} , and V_{oc} obtained from the J – V curves for each device as a function of T .

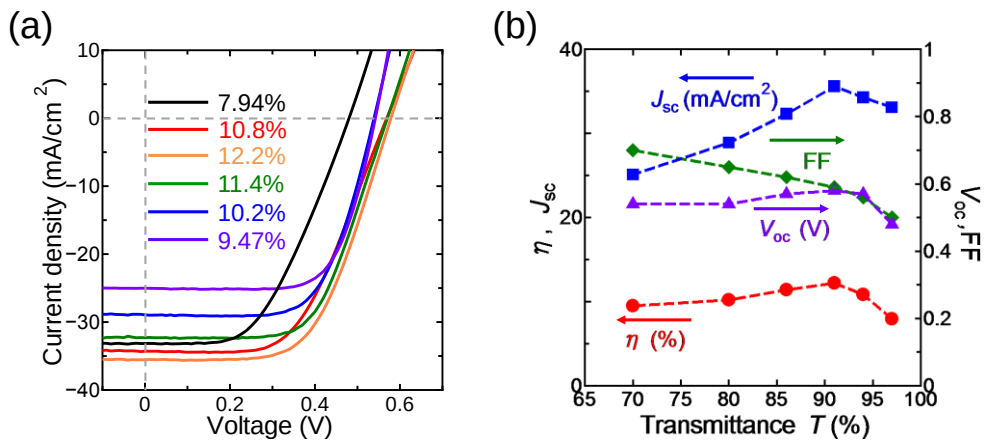


Figure 4.5 (a) Current density–voltage (J – V) curves for solar cells with 1 mm diameter active windows fabricated using SWNT films of varying thicknesses (transmittance).

(b) Values for η , FF, J_{sc} , and V_{oc} obtained from the J - V curves for each device as a function of T .

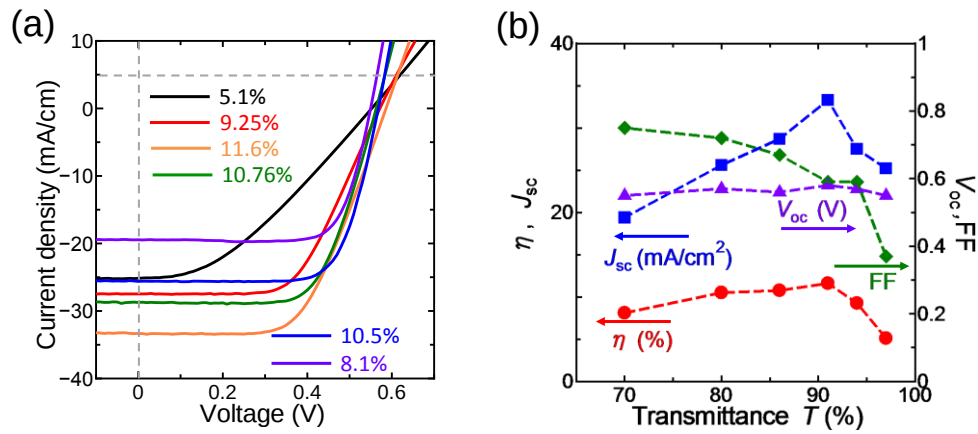


Figure 4.6 (a) Current density–voltage (J - V) curves for heterojunction solar cells with 1.5 mm diameter active windows fabricated using SWNT films of varying thickness (transmittance). (b) Values for η , FF, J_{sc} , and V_{oc} obtained from the J - V curves for each device as a function of T .

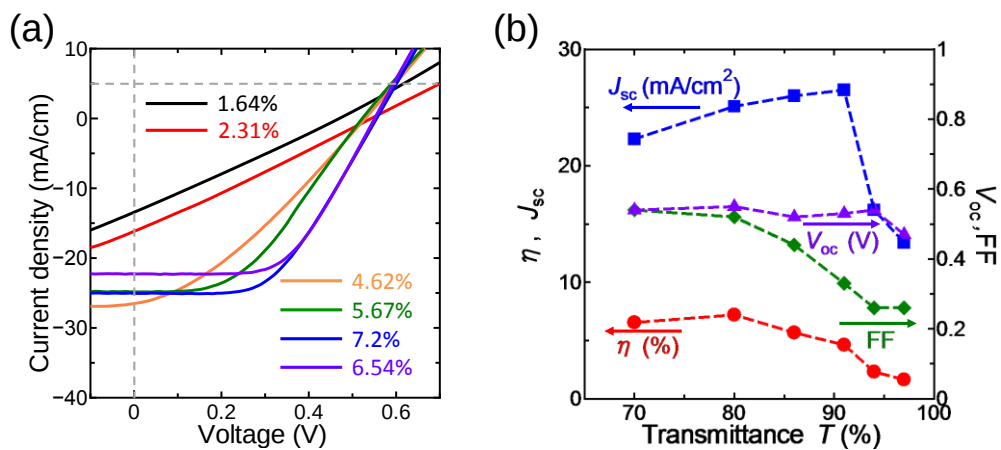


Figure 4.7 (a) Current density–voltage (J - V) curves for solar cells with 3 mm diameter active windows fabricated using networked SWNT films of varying thickness

(transmittance). (b) Values for η , FF, J_{sc} , and V_{oc} obtained from the J - V curves for each device as a function of T .

4.6. Active area dependent performance

Next, the change in the conversion efficiency of solar cells as a function of the window size and SWNT film transmittance was investigated. The SWNT/Si heterojunction solar cells with active window sizes (ϕ) ranging from 1 to 3 mm and SWNT films with transmittance (T) ranging from 70% to 97% were prepared (Figure 4.5-4.7). The photovoltaic conversion efficiencies of solar cells with SWNT films of different transmittance are shown in Fig. 4.8 as a function of the window size. The figure shows that the photovoltaic conversion efficiency increases as the active window size decreases, mainly because of a reduction in the effective series resistance, as discussed below. However, the optimized T values are different depending on the active window size. Thus, the optimized device parameters for SWNT/Si heterojunction solar cells ($\phi = 1$ mm and $T = 91\%$) are determined based on these results and are shown to provide a high conversion efficiency of 12.2%.

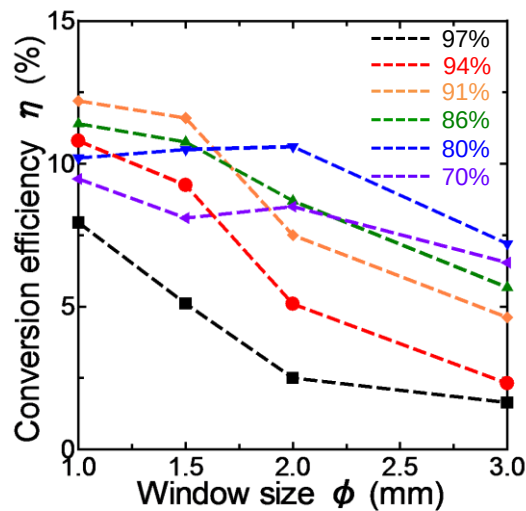


Figure 4.8 Photovoltaic conversion efficiency of solar cells with SWNT films of

various thicknesses as a function of the window size.

4.7. Series resistance effect in photovoltaic devices

Here, I discuss the photovoltaic conversion process of these SWNT/Si heterojunction solar cells. A diagram of energy levels of SWNT/Si heterojunction solar cells is shown in Fig. 4.9. According to the previous studies, it was found that the photogenerated electron and hole pairs (carriers) are mainly generated in the *n*-Si layer.¹¹¹ The electrons and holes are separated due to the band alignment at SWNTs and the Si interface, and these electrons and holes as photocarriers contribute to the photovoltaic properties of *p*-SWNT/*n*-Si solar cells.

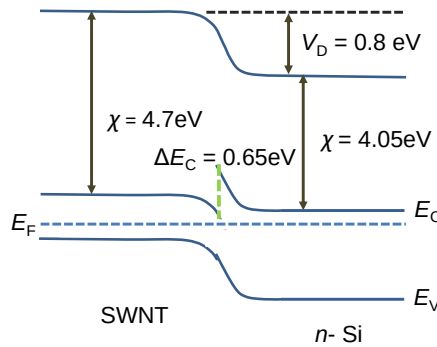


Figure 4.9 Band alignment diagram of SWNT/Si heterojunction.

The work-function and band gap of Si are about 4.52 and 1.12 eV,⁶⁰ respectively, and the Fermi level is about 0.2 eV below the conduction band. Figure 4.9 shows the band alignment diagram of SWNT/Si heterojunction determined by combining the previously reported results and measured work-function (in Fig. 4.10) and band gap of SWNT, where χ , E_C , E_V , and E_F are the electron affinity, conduction band, valence band and Fermi level, respectively. Both the built-in voltage (V_D) of 0.8 eV and barrier height of conduction band (ΔE_C) of 0.72 eV are shown in the band diagram. Figure 4.10 shows the photoelectron emission spectrum of SWNTs. The work-function of 5.05 eV is

determined by the intercept of the fitted linear line and the background level. The obtained work-function of 5.05 eV is consistent with the previously reported result.¹²⁵

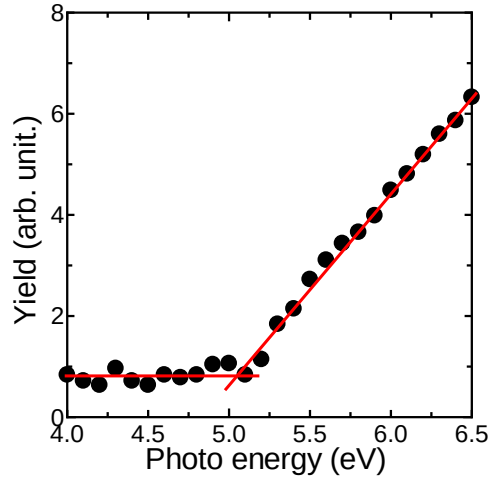


Figure 4.10 Photoelectron emission spectrum of SWNTs.

To gain further insight into the impact of the properties of the SWNT film on the photovoltaic performance of SWNT/Si heterojunction solar cells, the series resistance (R_s) of the optimized devices ($\phi = 1$ mm) fabricated by different thickness SWNT films was calculated using the J - V curve data and the following relationship:¹²⁶

$$I \frac{dV}{dI} = R_s I \quad (1)$$

Figure 4.11 shows that the series resistance increases as T increases (decreased thickness of the SWNT network film). This result suggests that the decrease in the FF with an increase in T (Fig. 4.4) is because of the increase in R_s . The plot of $I(dV/dI)$ for the device fabricated using a SWNT film with $T = 91\%$ as a function of I is shown in the inset of Figure 4.11(a). The value for $R_s (= 180 \, \Omega)$ corresponding to $1.41 \, \Omega \cdot \text{cm}^2$ is obtained from the slope of the line in the inset of Fig. 4 11(a). This low series resistance is mainly because of the high density and close connection of the SWNT network, which occurs because of Y-junction formation in the films fabricated using the FC-CVD

method.¹²²

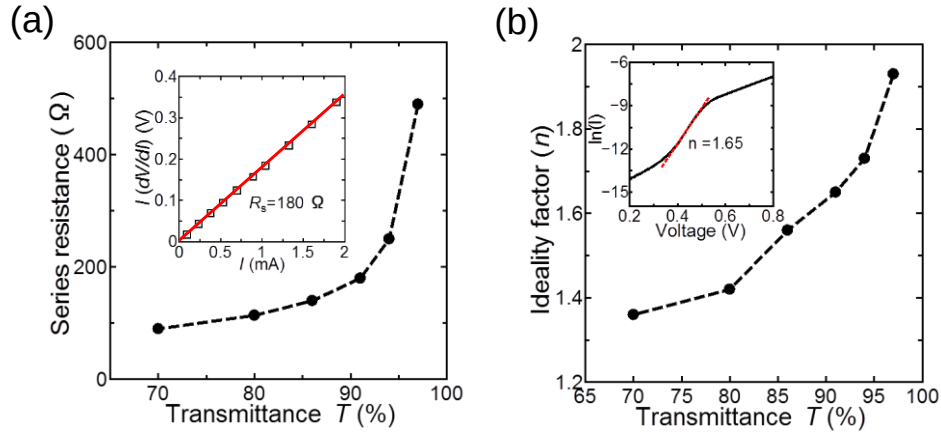


Figure 4.11 (a) Series resistance of the devices plotted as a function of the transmittance T . The inset shows $I(dV/dI)$ as a function of I for the device fabricated using the SWNT film with $T = 91\%$. The linear fitted result is shown as a solid line, and the slope of the fitted line corresponds to the cell series resistance. (b) Diode ideality factors as a function of the transmittance T . The inset shows the semilogarithmic plot of the J – V curve for the device fabricated using the SWNT film with $T = 91\%$. The linear fitted line is shown as the solid line.

The diode ideality factor (n) was also evaluated to investigate the carrier transport mechanism of the devices. This factor is determined under forward bias conditions using the relationship described below:

$$\frac{1}{n} = \frac{kT}{q} \cdot \frac{d \ln I_{\text{dark}}}{dV} \quad (2)$$

where q is the electronic charge, k is the Boltzmann constant, V is the applied voltage, and I_{dark} is the dark current. The plot of $\ln I_{\text{dark}}$ for the device fabricated using the film with $T = 91\%$ as a function of V is shown in the inset of Fig. 4.11(b). From the slope of this line, the diode ideality factor n is determined to be 1.65. Figure 4.11(b) shows the values for n obtained for the devices as a function of T . The figure shows that n moderately decreases from 1.93 to 1.36 as T decreases (*i.e.*, the thickness of the SWNT

film increases). These values are much smaller than those previously reported⁶⁰ and nearly the same as those of typical Si solar cells.¹²⁷ Based on these results, it can be concluded that n is related to the diffusion recombination process, accompanied by tunneling.¹²⁸ The moderate increase in n with increasing T is because of the increase in the sheet resistance of these films.¹²⁹

Figure 4.12(a) shows a typical J - V curve of the optimized SWNT/Si heterojunction solar cell ($\phi = 1$ mm) using the SWNT film with $T = 91\%$ under AM 1.5 conditions. The values for J_{sc} , V_{oc} , and FF extracted from the J - V curve are 30.2 mA/cm^2 , 0.586 V , and 70% , respectively, which result in a high photovoltaic conversion efficiency η of 12.5% . This value (12.5%) is higher than the previously reported value (10.5%)¹⁰⁵ and is the highest photovoltaic conversion efficiency for a SWNT/Si heterojunction solar cell fabricated using as-grown SWNTs without any carrier doping treatment as a postprocessing technique. Previous studies of the photovoltaic conversion process have revealed that the SWNT film mainly serves as a semitransparent carrier transport layer in SWNT/Si heterojunction solar cells.¹³⁰ Thus, the high photovoltaic conversion efficiency of greater than 12% is because of the high quality (low resistivity and high transparency) of the SWNT film.

The photovoltaic conversion efficiency of 20 solar cells fabricated using the optimized device parameters was then measured, and a remarkable reproducibility for η in the narrow range from 11.8% to 12.7% is observed, as shown in the inset of Fig. 4.12(a). The stability of the photovoltaic performance in the SWNT/Si heterojunction solar cell was also examined. Figure 4.12(b) shows the time evolution of the photovoltaic conversion efficiency η , J_{sc} and V_{oc} of the solar cell. The values for J_{sc} and V_{oc} nearly remain the same, while the FF moderately decreases with prolonged time, resulting in a modest decay in the photovoltaic conversion efficiency from 12.5 to

10.5% over 10 days. This decreased rate of 0.2% per day is much smaller than the previously reported value of $\sim 1.2\%$ per day for SWNT/Si solar cells doped with HNO_3 .¹⁰⁶ Thus, the optimized SWNT/Si solar cells fabricated using SWNT films grown by FC-CVD that have low resistivity and high transparency show both superior photovoltaic performance (conversion efficiency $> 12\%$) and high stability.

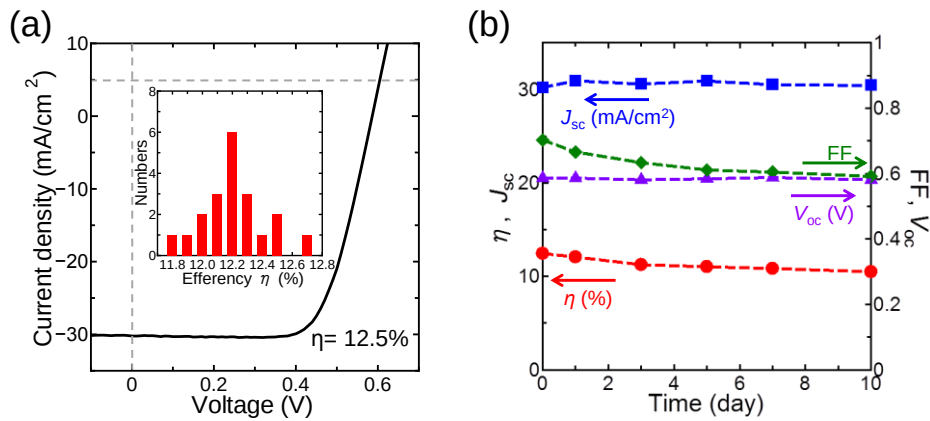


Figure 4.12 (a) Current density–voltage (J – V) curves for optimized SWNT/Si heterojunction solar cells fabricated with a window size of 1 mm using a SWNT film with $T = 91\%$. The inset shows a histogram of the variation in the photovoltaic conversion efficiency of the fabricated SWNT/Si solar cell devices. (b) Time evolution of the photovoltaic properties FF, V_{OC} , J_{SC} , and η of an optimally prepared device.

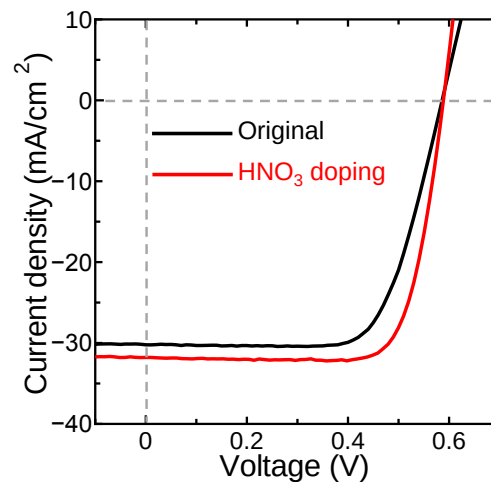


Figure 4.13 Current density–voltage (J – V) curves for original (black line) and HNO_3 -doped solar cells with 1 mm diameter active windows fabricated using

networked SWNT films with a transmittance of 91%.

A SWNT/Si heterojunction solar cell was also investigated by HNO_3 doping. Figure 4.13 shows the solar cell with and without HNO_3 doping. The optimized SWNTs/Si heterojunction solar cell exhibits a very high photovoltaic conversion efficiency of 14.5%.

4.8. Chapter summary

In this Chapter, SWNT/Si heterojunction solar cells prepared using high quality SWNT films with low resistivity and high transparency fabricated by the FC-CVD method were investigated. The optimum device structure was determined to consist of a 1 mm diameter window and a SWNT film with $T = 91\%$, and a photovoltaic conversion efficiency of 12% was obtained for a SWNT/Si heterojunction solar cell prepared without postprocessing using this structure. In addition, the high reproducibility of the photovoltaic performance of this type of device was clearly demonstrated, suggesting the superior potential of carbon nanotube solar cells. These are also important steps for large scale carbon nanotube solar cells with high photovoltaic conversion efficiency.

Chapter 5. Metal oxide layers assisted carbon nanotube/Si solar cells

5.1. Introduction

Several crucial issues remain to be solved for further improvement of the performance of carbon nanotube photovoltaic devices and to enable the shift from fundamental research to application development. First, a high Schottky barrier at the interface of the carbon nanotubes and the metal electrode limits the performance in carbon nanotube-based photovoltaic devices. Control of the Schottky barrier using an efficient carrier transport layer should enable the delivery of a high current without carrier recombination loss.^{21, 61} Second, more efficient carrier doping for carbon nanotubes is required in order to reduce the series resistance loss of the conversion efficiency. Third, solar light management within the device structure of carbon nanotube solar cells is required in order to enhance efficient photocarrier generation.

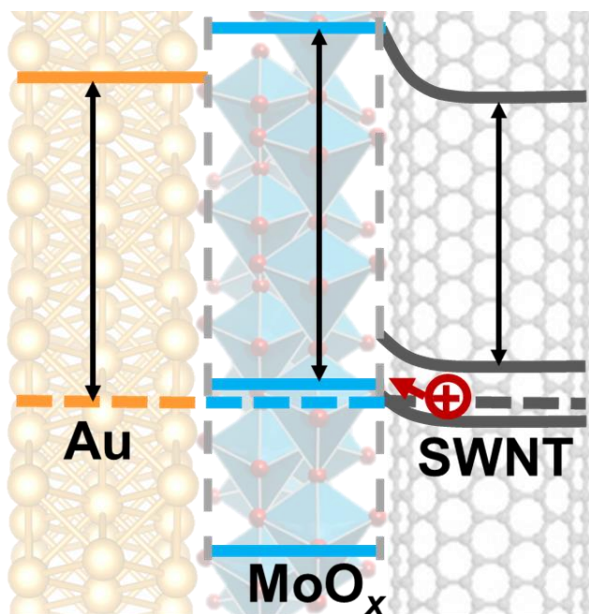


Figure 5.1 Band gap alignments of the MoO_x-SWNT/Au interfaces. MoO_x reduces the barrier between Au and SWNT for better carrier transport.

A high Schottky barrier at the interface of the semiconducting layer and the metal contact limits the performance of photovoltaic devices. Regarding this problem, it is expected that the metal oxides MoO_x and ZnO would play an important role in reducing the Schottky barrier for efficient carrier transport in photovoltaic devices based on carbon nanotubes. The metal oxides also serve as antireflection layer and efficient carrier dopant, which contribute to a reduction in the loss of incident solar light and increase the photocurrent, respectively.

In this Chapter, I describe about improvement in the photovoltaic performance of carbon nanotube-based solar cells containing environmentally friendly, durable, and inexpensive MoO_x and ZnO metal oxide layers. The MoO_x and ZnO layers play multiple roles as antireflection, carrier doping, and efficient carrier transport layers, as shown in the schematic of band alignment of Fig. 5.1 in the carbon nanotube-based solar cells. The photovoltaic performance of SWNT/Si hybrid solar cells is improved using these multifunctional MoO_x and ZnO layers, with high photovoltaic conversion efficiencies (PCE) of 17.0% and 4.0% achieved for p -SWNT/ n -Si and n -SWNT/ p -Si devices, respectively. The value of 17.0% is the highest yet reported for the PCE of p -SWNT and 4.0% of the conversion efficiency is also very high to the n -SWNT hybrid solar cells. These findings regarding the use of metal oxides as multifunctional layers suggest that metal oxide layers could improve the performance of various electronic devices based on carbon nanotubes.

5.2. Device fabrication and characterization

The fundamental procedure of device fabrication in p -SWNT/ n -Si solar cells is almost same as that in the previous chapter. I introduced the MoO_x layer as multi-functional layers in the device structure, as shown Figure 5.2. The MoO_x layer were deposited via thermal evaporation of MoO_3 at a rate of 0.5 nm/s and base pressure

of 5×10^{-6} Torr. SWNT films with window sizes (ϕ : diameter) of 1.0 mm were used. Each SWNT film was then connected to the Au anode, while each *n*-Si substrate was connected to an indium (In) cathode.

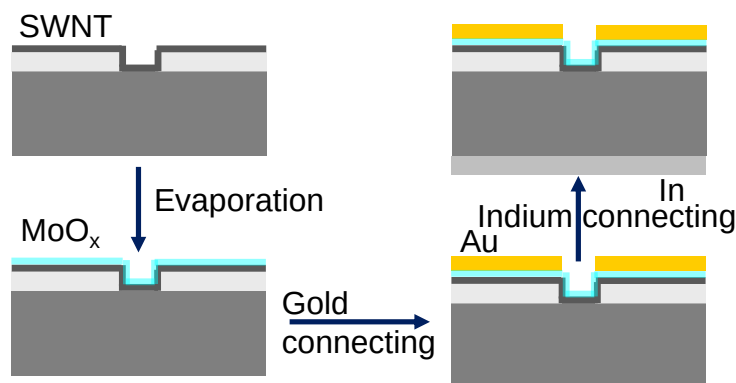


Figure 5.2 Illustration of detail fabrication process of a MoO_x-SWNT/Si solar cell: 1) formation of SWNTs/Si contact and junction, 2) Evaporation of MoO_x on the SWNTs/Si substrate, 3) fabricating gold contact as a cathode, and 5) fabricating indium contact as an anode. The fabrication of SWNT/Si heterojunction is the same with Chapter 4.

For the incident to photon conversion efficiency (IPCE) measurements, the devices were tested using a monochromated Xenon arc light system (Zolix LSP-X150). The microstructure of SWNT films and cross-sectional structures of the devices were characterized using a scanning electron microscope (SEM, JEOL JEM-6500F).

Reflectivity measurement

Optical materials such as carbon nanotube films can be evaluated by measuring the optical reflectivity. The reflectivity of SWNTs film on the substrate was measured by UV/Vis spectrometer with near-normal incidence reflectivity attachment as shown in Fig. 5.3, where the incident angle is 5° .

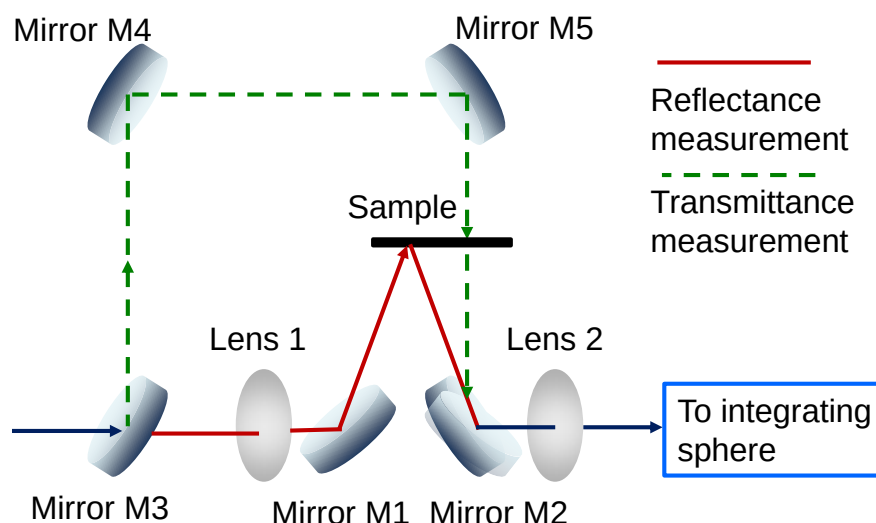


Figure 5.3 Schematic of transmission and reflectivity measurement. The transmittance and reflectance measurement is selected by putting in/pulling out the mirror M3 and switching over the mirror M2. The optical path is transmittance measurement is indicated by dashed line. The transmittance is measured with the mirror M3 inserted and the mirror M2 switched to the transmission side. The optical path in reflectance measurement is indicated by solid line.

Quantum efficiency measurement

The quantum efficiency of a solar cell is the value that the how large the incident photons from the solar light are converted to photocurrent. Thus, the measurement of quantum efficiency as a function of incident light wavelength is called as incident photon to current conversion efficiency (IPEC). If the quantum efficiency of solar cell is integrated over the whole solar spectrum range, the amount of current that the device produced by exposed to sunlight can be evaluated. There are two types of quantum efficiency of a solar cell; external quantum efficiency (EQE) and internal quantum efficiency (IQE). EQE is the ratio of the number of charge carriers collected by the solar cell to the number of incident photons, while IQE is the ratio of the number of charge carriers collected by the solar cell to the number of photons that are absorbed by the cell.

Figure 5.4 (a) and (b) show schematic of IPCE measurement and photographs of IPEC measurement system for the external quantum efficiency measurement.

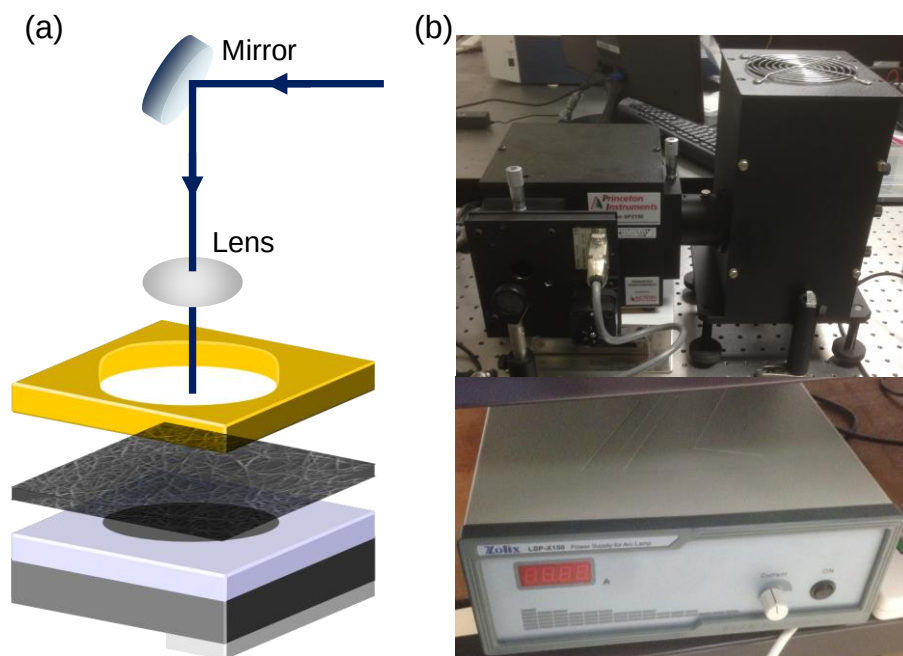


Figure 5.4 (a) Schematic of optical alignment for IPEC measurement and (b) photograph of IPCE measurement set-up.

Scanning electron microscope

Scanning electron microscope (SEM) is used for investigating the surface morphology of materials. The block diagram of SEM is shown in Fig. 5.5. An electron optical system consists of an electron gun, a condenser lens and an objective lens, a scanning coil, and other components. The electron optical system and specimen are kept in high vacuum condition. The electron gun produces an electron beam and the electron beam bombards the specimen. As a result, secondary electrons are emitted from the specimen surface. The secondary electrons are detected by photomultiplier tube and amplified electronic signals are transformed to a video scan-image that can be seen on a monitor or to a digital image. The topography of specimen surface, therefore, can be observed by two-dimensional scanning of electron probe over the surface.

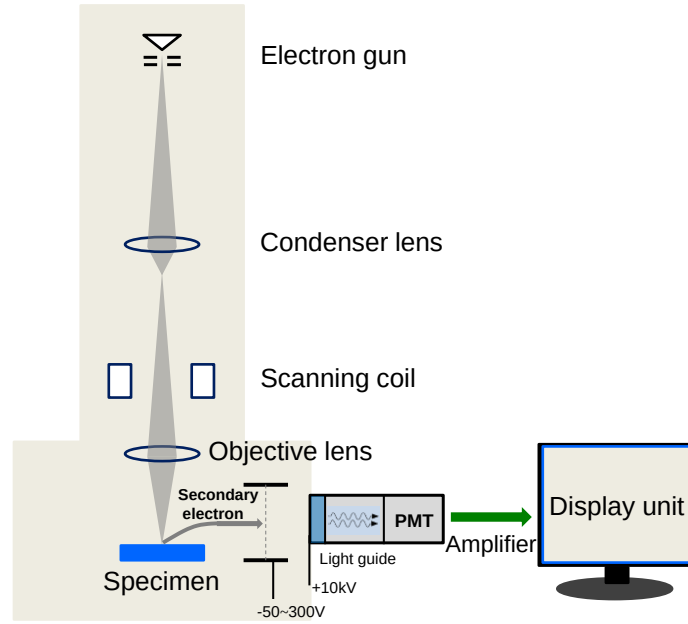


Figure 5.5 Schematic of scanning electron microscope (SEM).

Resistivity measurement of nanotube film

The contact resistance of semiconductor SWNT/Au (R_c) and sheet resistance of SWNT (R_{sheet}) were measured by the transfer length method (TLM).² I transferred the pristine SWNTs film and MoO_x-SWNTs film (with 2 mm width and 20 mm length) onto the glass substrate and evaporated Au contact pads using the mask technique. Inset of Figure 5.6 shows the schematic of TLM measurements, where the distances (d) of the contact pads are 1, 2, 3, and 5 mm, and the length (L) and width (W) of contact pads are 2 and 2 mm, respectively. I measured the total resistance (R_{tot}) tested by the two-probe method between Au pads as a function of d and plotted the data in Figure 5.6. The total resistance is described as

$$R_{\text{tot}} = 2R_c + R_{\text{sheet}} \frac{d}{W}. \quad (5.1)$$

I can evaluate the values of R_c and R_{sh} using the least-square fitting method. The contact resistance is equivalent to the resistance of an additional length of SWNTs sheet, and

this equivalent length is called the current transfer length (L_T), and is given by

$$L_T = \frac{R_c W}{R_{\text{sheet}}}. \quad (5.2)$$

Moreover, the specific contact resistance ρ_c is defined as

$$\rho_c = R_{\text{sheet}} L_T^2. \quad (5.3)$$

The reduction of the series resistance caused by the SWNT sheet resistance can be measured using¹³¹

$$R_1 = \frac{1}{8\pi} \rho_{\text{sheet}} / t, \quad (5.4)$$

where R_1 , t , and ρ_{sheet} are the series resistance, the SWNTs film thickness, and SWNTs sheet resistivity, respectively.

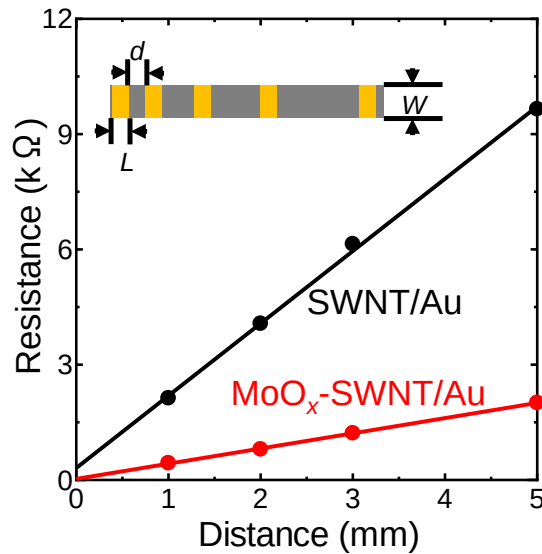


Figure 5.6 Total resistivity (R_{tot}) as a function of distance d for SWNT/Au (black circles) and MoO_x-SWNT/Au (red circles). The solid lines show the fitted results using Equation (5.1) with a least-square fitting method. Inset shows the schematic of the TLM measurements.

5.3. Theoretical calculations

5.3.1. Analysis of the J – V curves

The J – V curves were analyzed using the equivalent circuit model to understand the photovoltaic properties of the prepared devices.

The total current density J in this model can be described as follows.

$$J = J_0 \left\{ \exp\left(\frac{e(V - R_s J)}{nk_B T}\right) - 1 \right\} + \frac{V - R_s J}{R_{sh}} - J_{ph}, \quad (5.5)$$

where J_0 is the reverse saturation current density, e is the electron charge, n is the diode ideality factor, $k_B T$ is the thermal energy, R_s is the series resistance, R_{sh} is the shunt resistance, and J_{ph} is the photocurrent density.

5.3.2. Doping and hole conductive effects

I have evaluated photovoltaic power loss to understand the photovoltaic properties of solar cell from the change of series resistance (1.), shunt resistance (2.) and diode loss (3.) from the equivalent circuit model.

1. The loss of series resistance can be described as,

$$P_s = I_{\max}^2 R_s, \quad (5.6)$$

where P_s is the consumption power of series resistance, $I_{\max}$ is the photocurrent at maximum power point, and R_s is the series resistance. The increase of PCE by the change of the consumption power can be evaluated as,

$$\Delta\eta = \frac{P_1 - P_2}{P_{in}} \times 100\%, \quad (5.7)$$

where $\Delta\eta$ is the increase of PCE, P_1 and P_2 are the power consumptions before and after MoO_x coating, respectively, and P_{in} is the input power.

The MoO_x coating also increases the shunt resistance, which reduces the loss from

the shunt current leakage. The loss of shunt resistance can be described as,

$$P_{sh} = U_{sh}^2 / R_{sh}, \quad (5.8)$$

$$U_{sh} = U_{max} + U_s, \quad (5.9)$$

$$U_s = I_{max} R_s, \quad (5.10)$$

where P_{sh} , U_{sh} , and I_{sh} are the shunt resistance consumption power, shunt voltage, and shunt current, respectively, U_{max} and I_{max} are the load voltage and current, respectively, and U_s is the series voltage.

3. The power of diode is calculated as

$$P_D = U_D I_D, \quad (5.11)$$

$$U_D = U_{max} + U_s, \quad (5.12)$$

$$I_D = I_{sc} - I_{sh} - I_s, \quad (5.13)$$

where P_D , U_D , and I_D are the consumption power of power, diode voltage, and current flow through diode, respectively. U_D and I_{sc} are the load voltage and open circuit current, respectively.

5.4. Structure of solar cells

Figure 5.7(a) and (b) show schematics of the p -SWNT/ n -Si heterojunction solar cells without and with a MoO_x layer, respectively. In the p -SWNT/ n -Si heterojunction solar cell with the MoO_x layer, the MoO_x layer is evaporated on the SWNT network film, and then a gold (Au) contact is coated using the mask of the active window area. The MoO_x layer is considered to consist of two parts, one between the SWNT film and the Au contact, and one only in contact with the SWNT film in the window area of the solar cell.

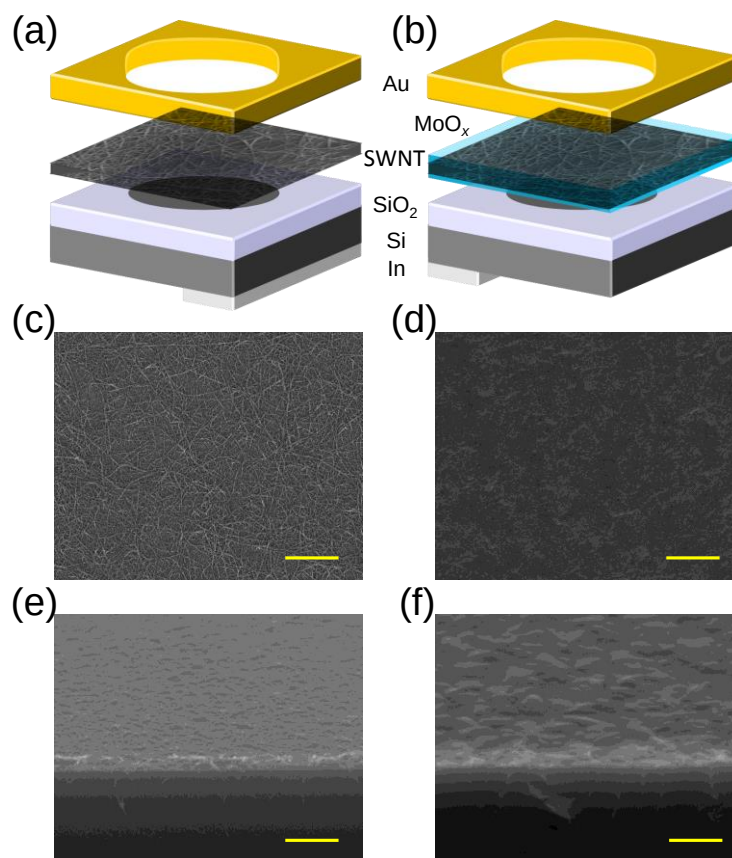


Figure 5.7 Schematics of the solar cell devices and characterization of the SWNT network film. (a), (b), Schematics of the pristine-SWNT/Si and MoO_x-SWNT/Si solar cells, respectively. (c), (d), Top view SEM images of the SWNT network film on an Si wafer and the SWNT film with an MoO_x layer, respectively. (e), (f), Cross-sectional SEM images of the pristine-SWNT/Si and MoO_x-SWNT/Si solar cells, respectively. Scale bar in each figure is 1 μm .

Figure 5.7(c) and (d) show SEM images of the SWNT network film without and with a MoO_x coating. The average diameter of the SWNTs is determined to be 1.6 nm from the absorption spectrum of the film which shown in Fig. 5.8.¹²² The SWNT film without the MoO_x coating exhibits a spider web-like structure consisting of interconnected nanotube bundles with diameters ranging from several to tens of nanometers. After evaporation of MoO_x for 60 seconds, the SWNT network film is covered by a very thin

MoO_x layer. Figure 5.7(e) and (f) show cross-sectional views of the SWNT/Si layers, which are used to determine the thickness of the MoO_x layer. A textured surface structure is observed for the SWNT/Si with the MoO_x layer (Figure 5.7 (f)), and the average thickness of the MoO_x layer was determined to be approximately 30 nm. Notably, as the deposition time increased, the MoO_x layer on the SWNT film becomes flat. SEM images of SWNT films coated with thicker MoO_x layers are shown in Fig. 5.9.

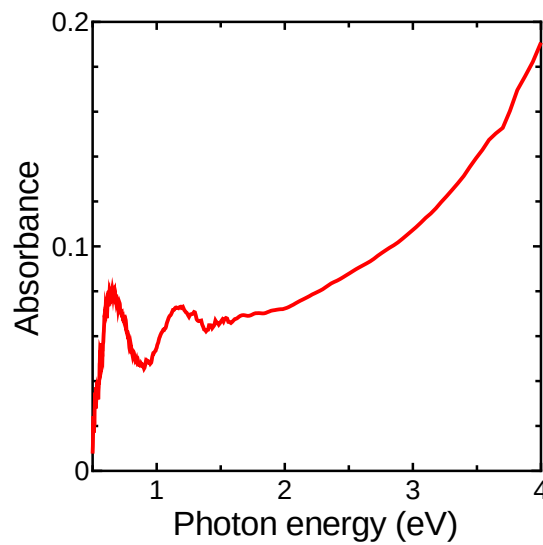


Figure 5.8 Absorption spectrum of the SWNT network film deposited on a glass substrate. We see that the absorption peaks for the first and second subband transitions E_{11} and E_{22} are observed at 0.67 and 1.15 eV, respectively. The average diameter of this SWNT network film is estimated to be approximately 1.6 nm from the empirical Kataura plot.¹²⁴

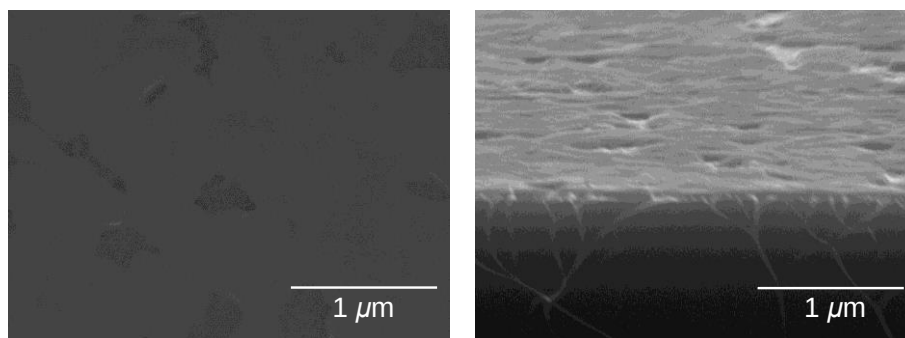


Figure 5.9 Top view and cross-sectional SEM images of an MoO_x-SWNT/Si solar cell. The MoO_x layer was thermally vapor deposited for 60 nm.

5.5. Photovoltaic performance of solar cells

The current density–voltage (J – V) characteristics of p -SWNT/ n -Si solar cells under Air Mass (AM) 1.5 conditions are shown in Fig. 5.10(a). Typical photovoltaic behavior is observed, as shown in the figure. The J – V curve of pristine-SWNT/Si solar cell (black solid line) exhibits a short-circuit current density (J_{sc}) of 27.9 mA/cm², an open-circuit voltage (V_{oc}) of 0.57 V, and a fill factor (FF) of 69%, resulting in a PCE (η) of 11.1%. In contrast, the J – V curve for the solar cell containing the MoO_x coated SWNT film-(MoO_x-SWNT/Si) exhibits a very high J_{sc} value of 36.6 mA/cm², which is close to the maximum value reported for Si solar cells¹³² and the highest short-circuit current density for hybrid solar cells using crystalline Si and other nanomaterials. This short-circuit current density value is associated with a V_{oc} of 0.59 V and an FF of 78%, resulting in a very high value for the η of 17.0%, which is a 1.5-fold increase in the PCE compared to that of the pristine-SWNT/Si solar cell. It should be noted that the thickness of the MoO_x layer (approximately 30 nm) is optimized for the MoO_x-SWNT/Si solar cell shown in Fig. 5.11. This very high η of 17.0% is the highest value reported to date for carbon-based solar cells, including SWNT/Si solar cells. Furthermore, the J – V curves for the p -SWNT/ n -Si solar cells in Fig. 5.10(a) are well reproduced by the fitted curves calculated using the equivalent circuit model.

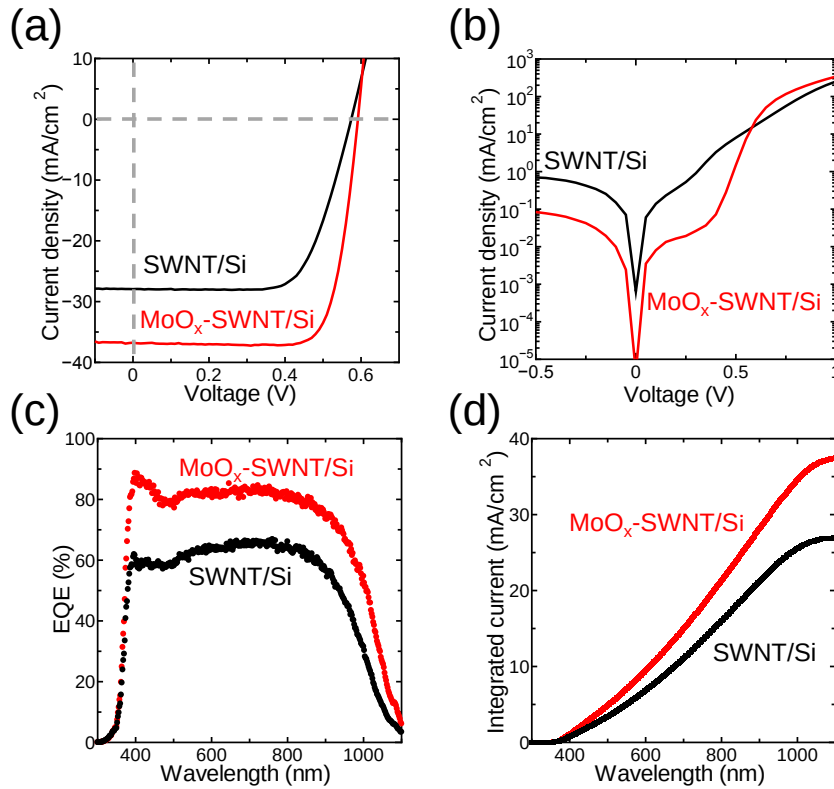


Figure 5.10 Photovoltaic properties of the solar cell devices. (a) J - V curves for an SWNT/Si solar cell recorded under AM 1.5G (solid lines) and dark (dashed lines) conditions before (black lines) and after (red lines) vapor deposition of an MoO_x layer. (b) Log-plot of the dark current before (black line) and after (red line) MoO_x coating. (c) IPCE spectra before (black line) and after (red line) MoO_x coating. (d) Calculated integrated photocurrent under AM 1.5G irradiation before (black line) and after (red line) MoO_x coating.

Table 5.1 Parameters for the p -SWNT/ n -Si solar cells without and with the MoO_x coating. The analysis is presented in Fig. 5.12.

Sample	J_{sc} (mA/cm ²)	FF (%)	V_{oc} (V)	η (%)	n	R_s (Ω)	R_{sh} (K Ω)
SWNT/Si	27.9	69	0.57	11.1%	1.24	360	8
MoO _x -SWNT/Si	36.6	78	0.59	17.0%	1.08	117	20

Figure 5.12 shows the experimental results for typical J - V curves with (black circles) and without (red circles) an MoO_x layer and the fitted J - V curves (solid lines) obtained using Eq. (5.1). The fitted curves well reproduce the experimental results. The parameters, including the saturation current density (J_{sc}), FF, the open-circuit voltage, the PCE (η), the diode ideality factor (n), the series resistance (R_s), and the shunt resistance (R_{sh}), obtained from the J - V curve analysis are shown in Table 5.1. The parameters for the shunt resistance, series resistance, and diode ideality factor are much improved for the MoO_x -SWNT/Si solar cell. I also investigated the PCE variations of five solar cells fabricated with the optimized device parameters. The very small variation of PCE in the range from 15.8 to 17.6% is observed as shown in the Table 5.2. The J - V characteristics for both the pristine-SWNT/Si and MoO_x -SWNT/Si solar cells clearly exhibit diode properties. However, the MoO_x -SWNT/Si solar cell showed much better diode properties with a lower reverse leakage current and a three orders higher rectification ratio compared to those of the pristine-SWNT/Si solar cell, which suggests a reduction of the series resistance and an increase in the shunt resistance with addition of the MoO_x coating in the SWNT/Si solar cell. An increase in the dark current under forward bias conditions above 0.5 V is also observed. This result indicated that the hole extraction efficiency is improved due to the MoO_x coating^{133, 134}, which will be discussed below. Moreover, the diode ideality factor n ($=1.08$) for the MoO_x -SWNT/Si solar cell is lower than that of the pristine-SWNT/Si ($=1.24$). This low value for the diode ideality factor is an indication of efficient transport characteristics with minimum interfacial recombination in the MoO_x -SWNT/Si solar cell.

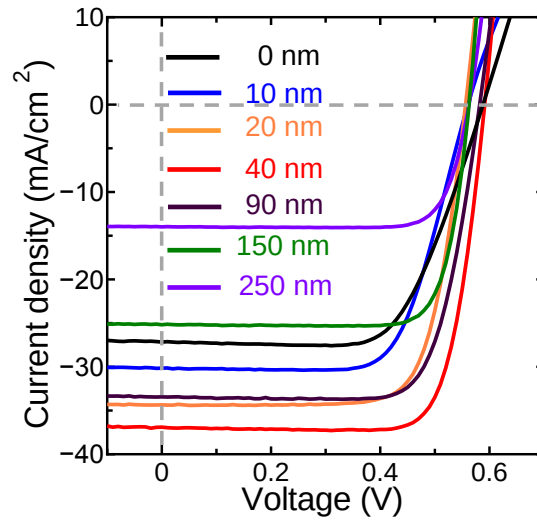


Figure 5.11 J - V curves for MoO_x -SWNT/Si solar cells as a function of the MoO_x layer thickness.

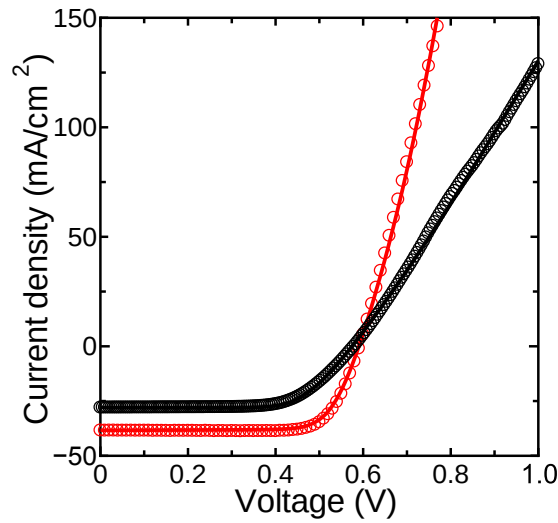


Figure 5.12 Experimentally obtained J - V curves before (black circles) and after (red circles) MoO_x coating of the SWNT film in p -SWNT/ n -Si solar cells. The J - V curves calculated using Eq. (5.3) are shown as solid lines.

Table 5.2 Variation of photovoltaic performance of SWNT/Si solar cell with MoO_x coating.

Samples	J_{sc} (mA/cm ²)	FF	V_{oc} (V)	η (%)
No. 1	36.6	0.78	0.59	17.0
No. 2	35.8	0.76	0.58	15.8
No. 3	34.5	0.80	0.59	16.3
No. 4	37.1	0.80	0.59	17.6
No. 5	36.9	0.79	0.59	17.2

Next, the effects of incorporation of the MoO_x coating in the SWNT/Si solar cell are further investigated to understand the improvement in the photovoltaic properties. Figure 5.10(c) presents the spectra of the incident photon to current conversion efficiency (IPCE) for the pristine-SWNT/Si and the MoO_x-SWNT/Si solar cells. A broad and flat value of approximately 65% in the spectrum of the original pristine-SWNT/Si cell is observed from 400 to 900 nm, which corresponds to the wavelength range for light absorption by Si and suggested that the Si substrate plays a role in the solar light absorption and photocarrier generation of the cell,^{109, 111} and the SWNT mainly works as the efficient carrier separation, collection, and transport layer.¹⁰⁹ In contrast, the IPCE spectrum of the MoO_x-SWNT/Si solar cell exhibits a large increase in the external quantum efficiency (EQE) and surpassed 80% in the wavelength region from 400 to 900 nm. Figure 5.10(d) shows the integrated currents calculated using the overlap between the EQE spectrum and the AM 1.5G solar photon flux for each cell. The calculated integrated photocurrent yields current densities of 27 mA/cm² in the pristine-SWNT/Si and 36.5 mA/cm² in the MoO_x-SWNT/Si solar cell. Notably, these results are consistent with the photocurrent densities determined from the J - V curves, as shown in Fig. 5.10(a).

5.6. Role of MoO_x in photovoltaic devices

A dramatic improvement in the photovoltaic performance of the SWNT/Si solar cell due to the inclusion of an MoO_x coated SWNT film is demonstrated. The MoO_x layer inserted between the SWNT film and the Au anode serves as an effective hole transporting layer. Moreover, the MoO_x layer on the SWNT network film in the active window functions as an antireflection layer for solar light and a carrier dopant for the SWNTs. A detailed analysis of the physical mechanisms involved in the improvement of photovoltaic performance using an MoO_x coated SWNT film is presented below.

5.6.1. Hole transport

Some materials inserted between semiconducting hole generation layers and anodes can increase the hole extraction/injection efficiency for optoelectronic devices through the reduction of the Schottky barrier at the interface. The semiconducting SWNT film with a diameter of 1.6 nm has band gap of about 0.9 eV by considering of the exciton binding energy.¹³⁵ The work function of the SWNTs is determined to be 4.7 eV.¹³⁶ Due to the difference in the work functions of the SWNTs and Au (5.3 eV),¹³⁷ an interface dipole layer is formed at the SWNT/Au-anode interface until the valence band edge of the SWNTs aligned with the Fermi level of the Au anode, accompanied with large band bending, as shown in Fig. 5.13(a). This pin effect involved in the alignment of the valence band edge and the Fermi level has been observed using scanning tunneling spectroscopy.¹³⁷ With the MoO_x coating, however, the interaction between the MoO_x layer and the SWNT film leads to significant changes in the electronic structure of the SWNT surface and as a consequence, modification of the surface potential. The MoO_x layer has a higher work function than the ionization energy of the SWNTs and is close to the Fermi level of the SWNTs, which enables efficient hole transfer from the SWNTs to the Au anode via the MoO_x layer. MoO_x films have been frequently observed to function as hole transport layers in organic semiconductor/Au interfaces.¹³⁸ The change

in the band alignment due to the insertion of the MoO_x layer promotes photocarrier extraction from the SWNTs to the Au anode, leading to a significant increase in the short-circuit current density and a reduction of the net R_s value. Therefore, MoO_x as an effective hole transport layer enhances photovoltaic performance by preventing current leakage and consequent counter-diode formation,¹³⁹ which is also reflected in Fig. 5.13(b).

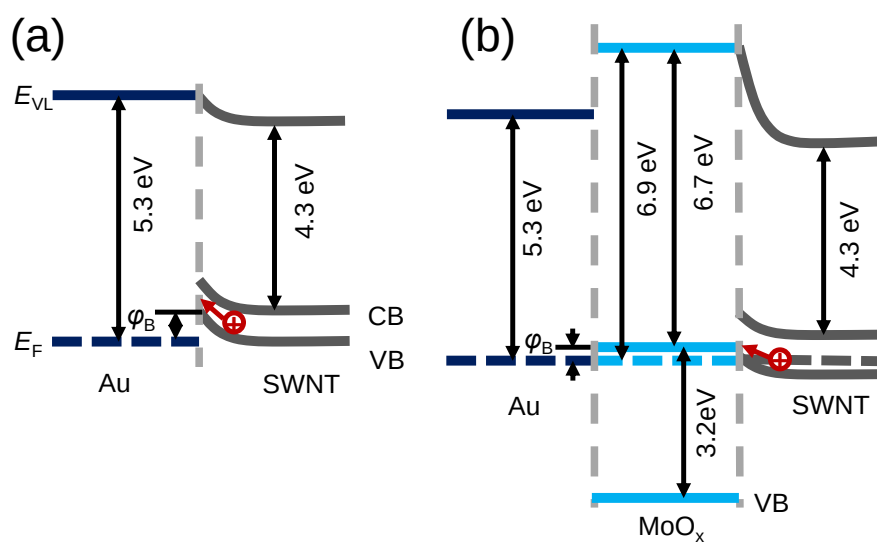


Figure 5.13 Multifunctional performance of MoO_x as a hole transport. (a), (b), Band gap alignments of the pristine-SWNT/Au and the MoO_x -SWNT/Au interfaces, respectively.

To reveal the role of the MoO_x film as a hole transport layer, a p -SWNT/ n -Si solar cell with a MoO_x layer between the SWNT film and the Au anode is fabricated and shown in Fig. 5.14.

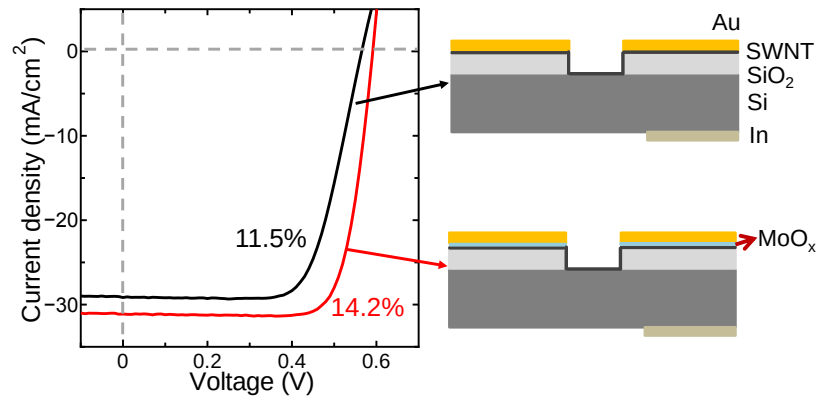


Figure 5.14 J - V curves for p -SWNT/ n -Si solar cells without (black line) and with insertion of an MoO_x layer (red line) only between the SWNT film and the Au contact. Schematics of the device structures are shown in the figure.

Table 5.3 The obtained values of R_c , R_{sheet} , L_T , and ρ_c for SWNT/Au and MoO_x -SWNT/Au.

Sample	R_c (Ω)	R_{sheet} ($\Omega/\square$)	L_T (cm)	ρ_c ($\Omega \cdot \text{cm}^2$)
SWNT/Au	155	3760	0.008	0.24
MoO_x -SWNT/Au	19	790	0.005	0.02

SWNT/Si solar cells with and without insertion of an MoO_x layer between the SWNT network and the Au contact were fabricated to understand the effects of the MoO_x as a hole transport layer. Figure 5.14 presents the J - V curves of the pristine-SWNT/Si and MoO_x -SWNT/Si solar cells. The pristine-SWNT/Si solar cell is found to have a J_{sc} of 29.4 mA/cm^2 , an FF of 65%, and a V_{oc} of 0.58 V, which resulted in a η of 11.2%. For the MoO_x -SWNT/Si solar cell, the J_{sc} , FF, and V_{oc} were 31 mA/cm^2 , 78%, and 0.59 V, respectively, and a high η of 14.2% is obtained. The large enhancement in the PCE mainly result from an increase in the short-circuit current density and FF values, because the MoO_x layer plays a crucial role in reducing the energy barrier for charge carrier (hole) extraction and transport over the interface between the SWNT film and

the Au contact. Because of the effect of hole transport layer, the conduct resistance and recombination loss will be reduced. The conduct resistance was measured by the transfer length method and the experimental data can be well reproduced for SWNTs/Au and MoO_x-SWNT/Au, as shown in Fig. 5.5. We can evaluate the values of R_c and R_{sh} with using least-square fitting method. The obtained values of R_c , R_{sheet} , L_T and ρ_c are shown in Table 5.3. The obtained current transfer length without MoO_x coating is almost same value with that reported previously.¹⁴⁰ The drastic decreases of both L_T and ρ_c are observed by MoO_x coating, which mainly caused by the decrease in the effective barrier height at the SWNT/Au interface by MoO_x as a hole transport layer.¹⁴¹

I also calculate the gain from the reduction of recombination and diode loss. With considering Eq. (5.8)-(5.11) and Eq. (5.12)-(5.14), the increase of PCE by shunt resistance and reduction of diode loss was determined as of 1.46% and 0.09%, respectively, by MoO_x coating. Based on these result, we concluded that the PCE value increases because the MoO_x layer acts mainly as a hole extraction layer and reduces the Schottky barrier height at the interface between SWNT film and the Au anode.

5.6.2. Anti-reflection

Next, the reflectance spectra of the pristine-SWNT/Si and MoO_x-SWNT/Si solar cells is obtained in order to evaluate the ability of MoO_x layer to act as the antireflection layer, as shown in Fig. 5.15. The reflectivity (R) of the pristine-SWNT/Si solar cell is approximately 30%, mainly because of the high refractive index of Si in the wavelength region from 400 to 1000 nm. The reflectivity of the MoO_x-SWNT/Si solar cell, however, is substantially lower over the entire spectral region from 300 to 1100 nm (<20%). This decrease in the reflectivity contributed to an increase in the solar light absorption and generation of photocarriers in the Si substrate, resulting in an enhancement of the

short-circuit current density of the cell.

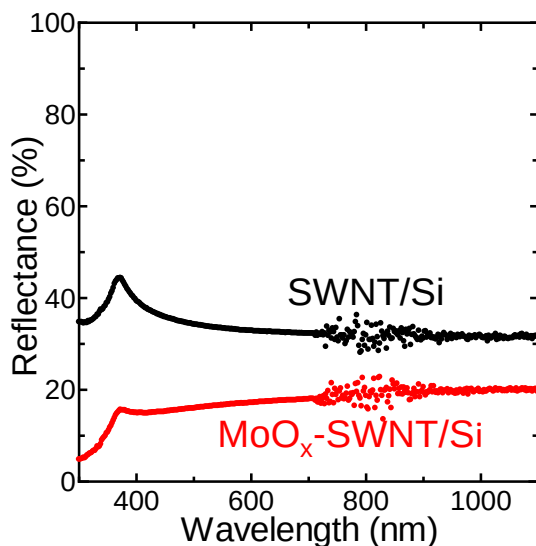


Figure 5.15 Reflectance spectra of the pristine-SWNT/Si (black line) and MoO_x-SWNT/Si (solid line) solar cells.

SWNT/Si solar cells with and without an MoO_x layer were fabricated only on the active area of the devices (red dashed square part in Fig. 5.16). The short-circuit current density and PCE of the pristine-SWNT/Si solar cell are 29 mA/cm² and 11.6%, respectively. For the MoO_x-SWNT/Si solar cell; however, the short-circuit current density J_{sc} drastically increases to 35 mA/cm², which results in a high value of 14.6% for the PCE. The significant increase in the short-circuit current density and PCE is due to the deposition of the MoO_x on the active area of the cell as an antireflection layer for solar light and a carrier dopant for the SWNT network.

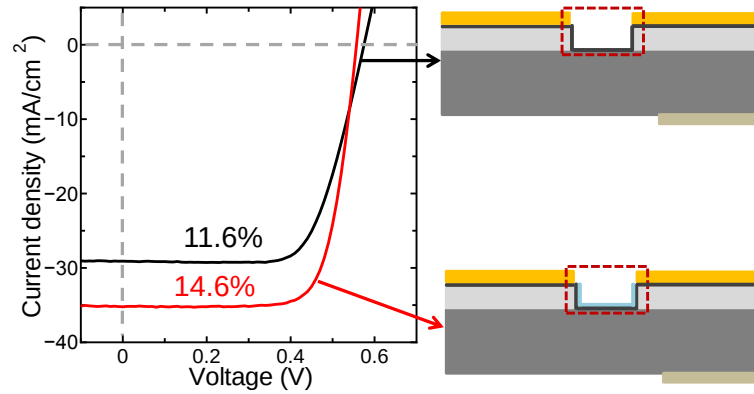


Figure 5.16 J - V curves for the p -SWNT/ n -Si solar cells before (black line) and after (red line) the deposition of an MoO_x layer only on the active area. Schematics of the device structures are shown in the figures on the right.

The antireflection effect is also confirmed by evaluating the internal quantum efficiency (IQE) using the relationship $\text{IQE} = \text{EQE}/(1 - R)$. The IQE was then evaluated to understand the carrier doping effect of MoO_x for the SWNT film. Figure 5.17 shows the IQE of the pristine-SWNT/Si (black solid line) and MoO_x -SWNT/Si (red solid line) solar cells. The IQE for the MoO_x -SWNT/Si solar cell is nearly identical to that of the pristine-SWNT/Si from 400 to 700 nm, but is greater above 700 nm. The increase in the short current density is calculated using the difference in the reflectivity of the pristine-SWNT/Si and the MoO_x -SWNT/Si as follows:

$$\Delta J = q \int \eta_c(E)(R_a - R_b)a(E)b_s(E)dE, \quad (5.14)$$

where q is the electron charge, $\eta_c(E)$ is the collected probability at a photon energy E , R_a and R_b are the reflectivity of the SWNT/Si systems before and after MoO_x coating, respectively, $a(E)$ is the absorption, and $b_s(E)$ is the spectral photon flux density at E . The increase in the current density calculated using Eq. (5.14) is 5.9 mA/cm^2 , which is nearly the same as the experimentally obtained value of 6 mA/cm^2 (Figure 5.16).

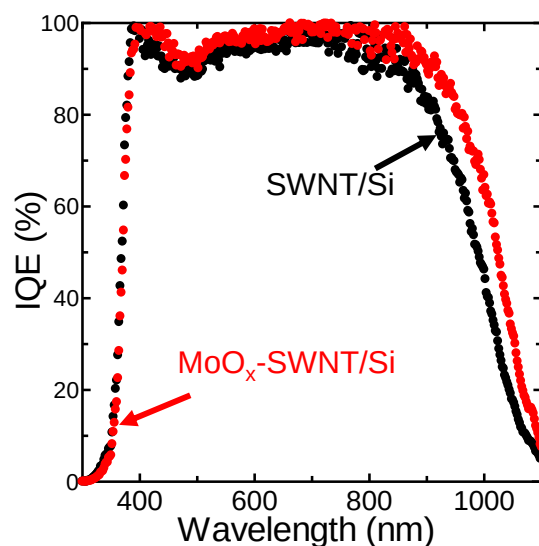


Figure 5.17 Internal quantum efficiencies (IQE) of the pristine-SWNT/Si (black line) and MoO_x-SWNT/Si (red line) solar cells.

The calculated IQE spectrum of the MoO_x-SWNT/Si solar cell is nearly coincident with that of the pristine-SWNT/Si, which strongly suggested that a reduction in the reflectivity contributes to an increase in the EQE in the MoO_x-SWNT/Si solar cell. The MoO_x layer reduced the effective refractive index mismatch between Si and air, because MoO_x has an intermediate refractive index ($n_0 = 2.2$).¹⁴² This decrease in the reflectivity of the MoO_x-SWNT/Si solar cell reduced the loss of solar light and increased photocarrier generation and was due to the fact that the MoO_x layer acts as an antireflection layer.

5.6.3. Carrier doping effect

The MoO_x also plays a role as a carrier dopant for the SWNTs. Figure 5.18 shows the $I(dV/dI)$ plots for the pristine-SWNT/Si and MoO_x-SWNT/Si solar cells as a function of the current (I). The series resistance (R_s) of the solar cells without and with the MoO_x

coating is evaluated from the slope of this plot, and the resistance of the MoO_x-SWNT/Si solar cell (=244 Ω) is found to be significantly lower than that of the pristine-SWNT/Si (=360 Ω). The decrease of series resistance is also confirmed by the independent two-probe method. Hole doping for the SWNTs in the MoO_x-SWNT occurs because the ionization energy of SWNTs is lower than the work function of the MoO_x layer, and thus the series resistance decreased.¹⁴³ We also confirm the effect of hole-doping for SWNTs by MoO_x layer for Raman spectra (Figure 5.19). The Raman spectra of SWNT network films were measured before and after MoO_x layer coating. The Raman peak at ~1600 cm⁻¹ corresponds to the G-band of SWNTs. The remarkable high frequency shift of the G-band (~3 cm⁻¹) is observed because of the presence of the MoO_x layer coating. The high frequency shift of the G-band suggests the presence of the hole doping for SWNTs; this is consistent with the previously reported result.¹⁴³ Therefore, an SWNT/Si solar cell with an MoO_x layer only on the active window (Figure 5.16) was fabricated to evaluate the antireflection layer and hole doping effects of the MoO_x layer. Based on the *J*-*V* curves obtained for this MoO_x-SWNT/Si solar cell, the value of *J*_{sc} is found to be increased by approximately 6.5 mA/cm² in the MoO_x-SWNT/Si solar cell compared to that of the cell without the metal oxide layer. Furthermore, in the IQE spectra, an increase in the IQE is also observed for the cell with the MoO_x layer, indicating the effective hole doping achieved by the addition of the MoO_x coating. The reduction of series resistance caused by sheet resistance of SWNT was also measured by the Eq. (5.4). We can calculate the series resistances from sheet resistance component as 150 ± 5 and 31 ± 3 Ω for SWNT/Au and MoO_x-SWNT/Au.

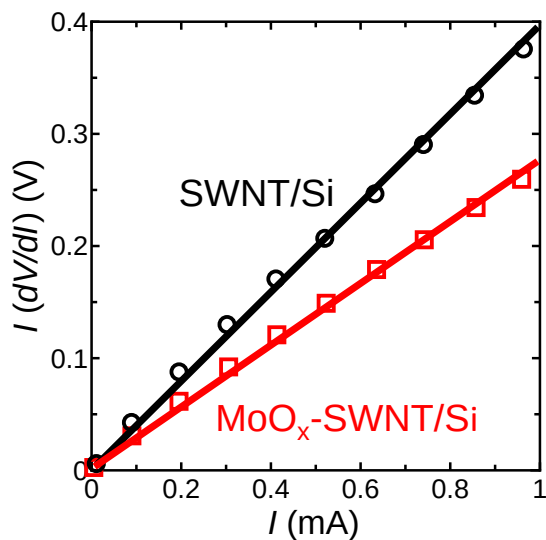


Figure 5.18 $I(dV/dI)$ plots of the pristine-SWNT/Si (black line) and MoO_x -SWNT/Si (red line) solar cells as a function of the current I .

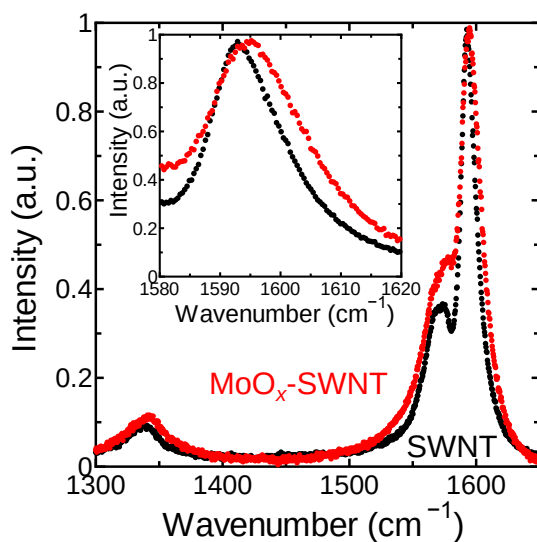


Figure 5.19 Raman spectra of SWNT network films without (black dot line) and with (red dot line) the MoO_x coating deposited by evaporation. Inset shows the zoom of the Raman spectra from 1580 to 1620 cm^{-1} .

We evaluated the contribution of MoO_x coating for the increase of PCE, quantitatively. The possibility of surface passivation by MoO_x coating was also checked

(Figure 5.20).^{144, 145} The minority carrier lifetimes of SWNT on *n*-Si substrate with and without MoO_x layer were measured by microwave-photo-conductivity decay method (μ -PCD) to understand the effect of surface passivation of Si substrate. The minority carrier lifetimes of with MoO_x layer (MoO_x-SWNT/Si) and without MoO_x layer (SWNT/Si) are estimated as 61 and 68 μ s from the measured decay curves, respectively, and almost do not change by the MoO_x coating. This result indicates that the MoO_x layer does not dominantly affect the surface passivation of the *n*-Si substrate. The increase of PCE by the MoO_x coating is estimated from the change of series resistance, shunt resistance and diode loss from the equivalent circuit model,¹⁴⁶ and reflection loss of solar light.

The series resistance including the components of sheet resistance of SWNT film and contact resistance between SWNT and Au interface drastically decreases from 360 (2.83) to 117 Ω (0.92 $\Omega \cdot \text{cm}^2$), which results on the total improvement of PCE about 2.08% by sheet resistance and contact resistance reduction by MoO_x coating. In order to further understand the contributions by the sheet resistance and contact resistance component, the series resistances reduced by sheet resistance and contact resistance were measured by the method described in section 5.3, which results on the increase of PCE as 0.95 and 1.13%, respectively. The PCE increases of 1.46% from decrease of shunt resistance and 0.09 % are evaluated due to the reduction of recombination loss and increased the reduction of diode loss. Moreover, the estimated reduction of reflected solar light by the anti-reflection effect increase the current density of 5.9 mA/cm², which results on the improvement of PCE as about 2.25%. The evaluated total increase of 5.9% is well consistent with the experimentally observed improvement of PCE in the device by the MoO_x coating, as shown in Fig. 5.10(a). These quantitative results strongly support that the MoO_x working as a dopant and hole transporting layer, and anti-reflection layer, drastically improves the photovoltaic performances of SWNT/Si

solar cells.

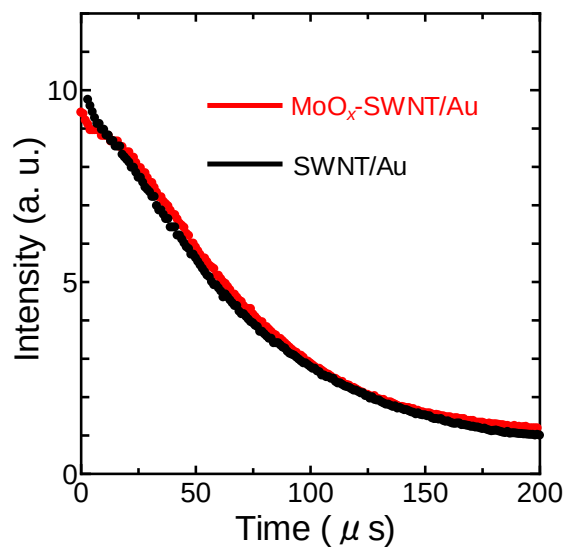


Figure 5.20 Carrier decays of SWNT/Si without and with MoO_x coating.

5.7. Variation of device performance

A statistic distribution of 60 devices is shown in Fig. 5.21. The high value of conversion efficiencies and small distribution of SWNT/MoO_x/Si solar cell mainly from 15.8 to 17.8% proves a high reproducibility of the photovoltaic devices. From the Gaussian fitting, the $16.8 \pm 0.3\%$ of solar cells was obtained.

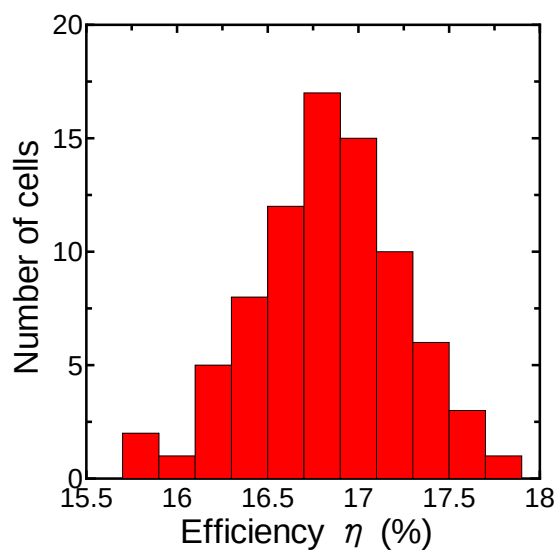


Figure 5.21 Photovoltaic efficiencies of 80 MoO_x-SWNT/Si solar cells.

5.8. *n*-SWNT/*p*-Si solar cells with ZnO layer

Finally, to determine if a similar improvement in photovoltaic performance could be achieved for a cell based on the *n*-type carbon nanotubes, similar experiments were performed using an *n*-SWNT/*p*-Si solar cell with ZnO insertion layers. The *n*-SWNT/*p*-Si solar cells with and without a ZnO layer between the SWNT network film and the electrode were fabricated. Details of the fabrication procedure are provided as follows: An aqueous solution of β -nicotinamide adenine dinucleotide (NADH, 90 mM, 10 μ L) was deposited on the SWNT network film for *n*-type doping in the glove box. An aqueous colloidal ZnO solution was prepared as previously reported⁵ and spin-coated on the SWNT film as a multifunctional layer. The detailed device structure for the *n*-SWNT/*p*-Si solar cell is shown on the middle of Figure 5.22.

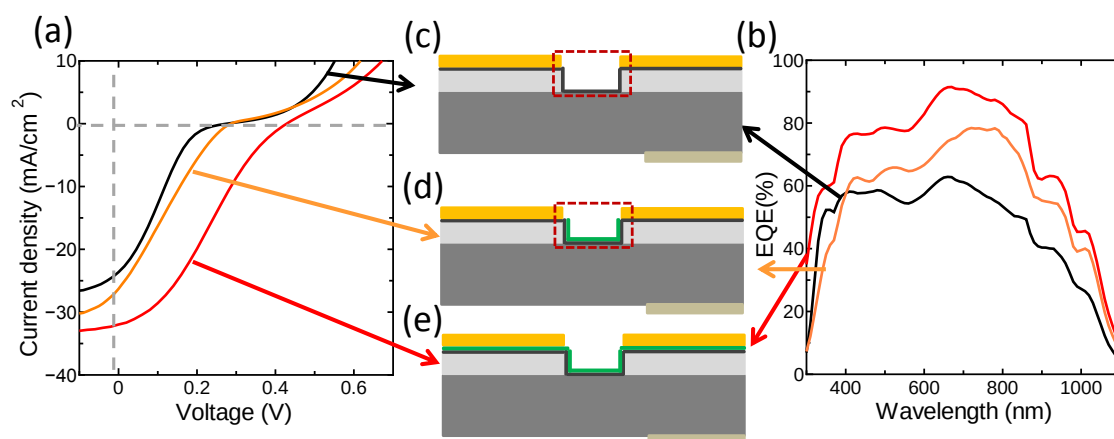


Figure 5.22 (a) *J*-*V* curves and (b) IPCE spectra of different structure of *n*-SWNT/*p*-Si heterojunction solar cells. The schematic of device structures are shown in the figure, original (black line), ZnO deposited as anti-reflection layer (orange line), and as a multifunctional layer (red line).

The morphology of a ZnO-coated NADH doped SWNT film is shown in Fig. 5.23. Nanorods with a size of several tens of nanometers can be observed to uniformly cover the substrate. From the cross-sectional SEM image, the thickness of the ZnO layer and the NADH film are estimated to be approximately 70 and 20 nm, respectively.

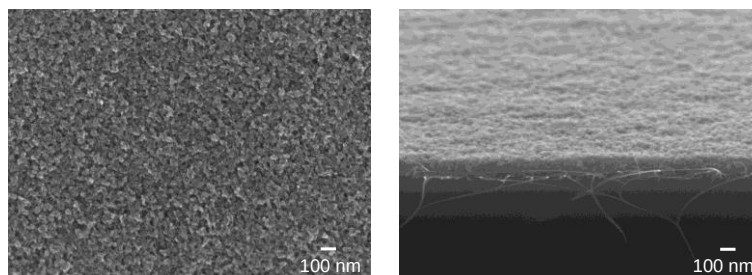


Figure 5.23 Top view and cross-sectional SEM images of *n*-SWNT/*p*-Si solar cells after spin-coating of ZnO.

Figure 5.24 shows the J - V characteristics of the *n*-SWNT/ *p*-Si (solid black line) and ZnO-SWNT/Si (red solid line). Even for the *n*-SWNT/*p*-Si cell without the ZnO layer, the PCE determined from the J - V curve is 1.3%. Moreover, a drastic increase in the PCE to 4.0 % is observed for the ZnO-SWNT/Si cell. (Table 5.4) The enhancement of the PCE resulted from an increase in the short-circuit current density and FF in the *n*-SWNT/*p*-Si solar cell fabricated with the ZnO-coated SWNT film. The increased short-circuit current density results from a reduction in the loss of the solar light reflectance, an efficient extraction of the electrons to the contact, and a decrease in the series resistance of the SWNTs. Moreover, the FF increases because of a reduction in the series resistance with the increase in the carrier doping. These results indicated that similar to MoO_x, the ZnO layer plays several roles, acting as an antireflection layer, a carrier dopant, and an electron transport layer and leads to a drastic improvement in the photovoltaic performance of the *n*-SWNT/ *p*-Si solar cells.

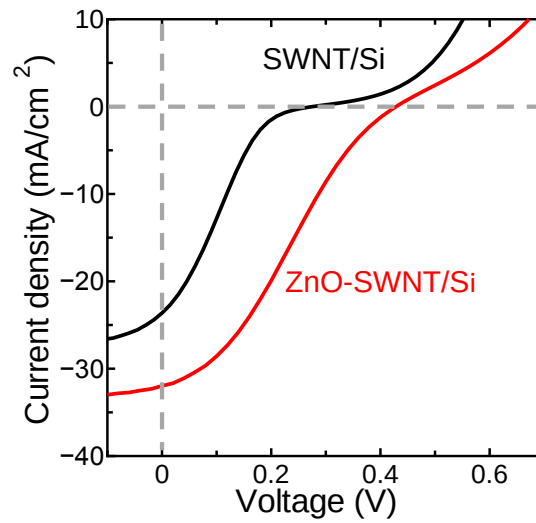


Figure 5.24 J – V curves for the n -SWNT/ p -Si solar cells without (black line) and with (red line) a ZnO layer.

Table 5. 4 Parameters for the n -SWNT/ p -Si solar cells without and with a ZnO coating.

^a ZnO coating on the n -SWNT/ p -Si solar cell as an antireflection layer.

^b ZnO coating on the n -SWNT/ p -Si solar cell as antireflection and electric transport layers.

Sample	J_{sc} (mA/cm ²)	FF (%)	V_{oc} (V)	η (%)
n - SWNT/ p -Si	23.6	20%	0.28	1.3
ZnO-SWNT/Si ^a	26.2	22%	0.29	1.7
ZnO-SWNT/Si ^b	31.9	29%	0.43	4.0

5.9. Chapter summary

We investigated the photovoltaic performance of carbon nanotube-based solar cells using environmentally friendly, durable, and inexpensive materials such as MoO_x and ZnO, which work as antireflection layers for increasing the optical absorption, carrier dopants for a reduction of the series resistance, and effective carrier transport layers for the reduction of the Schottky barrier. The photovoltaic performance of p -SWNT/ n -Si

and *n*-SWNT/*p*-Si heterojunction solar cells was improved using multifunctional layers of MoO_x and ZnO, which resulted in very high PCE values of 17.0% and 4.0%, respectively. We expect that metal oxides such as MoO_x and ZnO will contribute to improvement of device performance not only for photovoltaics but also other optoelectronics. Our finding also reveals new aspects of device physics and the potential for optoelectronic applications based on carbon nanotubes.

Chapter 6. Perovskite solar cells using carbon nanotubes/graphene oxide

6.1. Introduction

In this Chapter, we demonstrated that single-walled carbon nanotubes/graphene oxide buffer layer greatly improves the photovoltaic performance of organo-lead iodide perovskite solar cells. The carbon nanotubes/graphene oxide layer works as efficient hole extract and transport layer, and electron blocking layer. Furthermore, the great improvement of photovoltaic performance stability in the perovskite solar cells using carbon nanotubes/graphene oxide/polymethyl methacrylate was demonstrated in comparison with that using a typical organic hole transport layer of 2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene.

Studies of solar cells based on the organo-lead halide perovskites $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been attracting much interest.¹⁴⁷⁻¹⁴⁹ Organo-lead halide perovskites with a direct bandgap play important roles in solar cells not only as strong light harvesters, but also as efficient carrier conductors because of their large absorption coefficients and high charge carrier mobilities.¹⁵⁰⁻¹⁵² Perovskite solar cells constructed of mesoporous scaffolds, perovskite light absorbers (such as $\text{CH}_3\text{NH}_3\text{PbI}_3$), and organic hole transport layers have exhibited outstanding performance to date and are leading to revolutionary research on photovoltaic devices.¹⁵³ Continuous improvement and engineering of interfaces,¹⁴⁸ solvents,¹⁵⁴ and materials¹⁵⁵ during the past five-years have led to a significant increase in the power conversion efficiencies (PCEs) of perovskite solar cells from the first reported value of 3.8 to >20%.^{156, 157} However, there remain many issues to solve such as their instabilities of both perovskite and organic transport layers in the

atmosphere toward the realistic application of organo-lead halide perovskite solar cells.^{149, 158}

Studies of carbon nanotubes as electrodes, hole transport layer, and dopants in perovskite solar cells have been also reported.¹⁵⁹⁻¹⁶¹ However, shunt current leakage can occur in porous SWNT networks due to the conduction band (CB) bottom of semiconducting SWNTs (~ 4.1 eV from vacuum level) is lower than that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (~ 3.9 eV), which can lead to large photovoltaic losses due to recombination between electrons in the carbon nanotubes and holes in the Au anode. Figure 6.1 shows the recombination mechanism of carriers in carbon nanotubes and at the anode. Such recombination losses greatly reduce the short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}), thus limiting the application of SWNTs in solar cells. To improve performance, an electron-blocking material must be introduced as a barrier layer. Graphene oxide (GO) is one of an environmentally friendly and solvent-dissoluble electron-blocking layers.¹⁶² Therefore, it is anticipated that a combination of SWNTs with efficient carrier transport abilities and the GO with a strong electron-blocking capability should function as an efficient carrier-transport layer for organo-lead iodide perovskite solar cells. Moreover, polymer such as polymethyl methacrylate (PMMA) with highly stable, and mechanical flexibility, is expected to form a compact layer with these nano-carbon materials (SWNTs and GO) by strongly crosslinking to protect the perovskite layer from oxygen and moisture.

In this chapter, we describe the application of SWNT/GO/PMMA thin film as hole conductive protecting layer in perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) solar cell. The application of nano-carbon materials (SWNT/GO) as efficient selective carrier-transport layers greatly enhances the PCEs of perovskite solar cells. The PCE of a perovskite solar cell measured through a $2 \times 2 \text{ mm}^2$ mask drastically increased from 3.3% in a cell without an

SWNT/GO/PMMA layer to 13.3% in a cell with an SWNT/GO/PMMA layer under Air Mass (AM) 1.5 conditions. Moreover, the stability in air of the PCE of a perovskite solar cell containing an SWNT/GO/PMMA was greater than that of a perovskite solar cell with a typical organic hole-transport layer of 2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD).

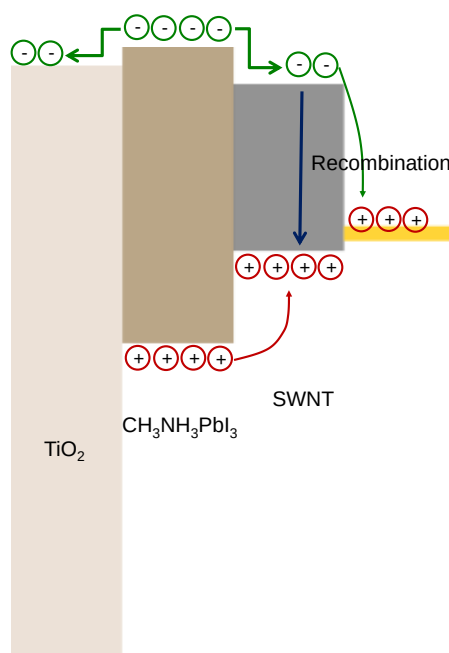


Figure 6.1 The recombination mechanism of carriers in carbon nanotubes and at the anode.

6.2. Device fabrication

FTO was purchased from Asahi Glass Co., Ltd., Japan. PbI_2 and mesoporous titanium oxide (PST-18NR) were purchased from Tokyo Chemical Industry Co., Ltd., PMMA was purchased from Sigma Aldrich Co., Ltd. Dehydrated ($\text{H}_2\text{O} < 8$ ppm) *N,N*-dimethylformamide (DMF), 2-propanol, and chlorobenzene purchased from Wako Chemical Co., Ltd., were used after drying. All other chemicals and reagents were purchased from Wako Chemical Co., Ltd and used as received unless noted otherwise.

SWNT films were grown using the FE-CVD and shown in Fig. 6.2.^{121, 123, 163} CO (200 s.c.c.m.) used as the carbon source was passed through a temperature-controlled cartridge containing ferrocene powder catalyst particles. Additional CO (200 s.c.c.m.) and CO₂ (3 s.c.c.m.) were then introduced to the furnace at a growth temperature of 850 °C. The SWNT films were collected at room temperature on a membrane filter comprising cellulose acetate and nitrocellulose. The SWNT film thickness was controlled by varying the collection time.

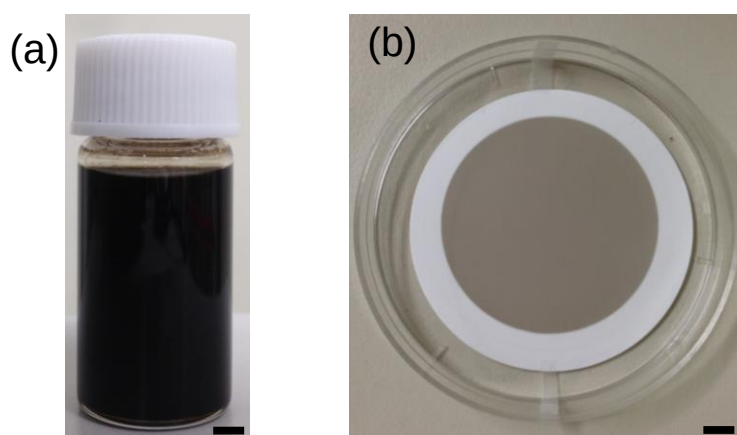


Figure 6.2 (a) and (b) Photographs of the graphene oxide (GO) solution and single-walled carbon nanotube (SWNT) film, respectively. The GO modified by octadecylamine (ODA) was well-dispersed in the chlorobenzene solution at a concentration of 5 mg/mL. The SWNT film had a transmission of 70% at a wavelength of 550 nm. The scale bar in each figure represents 0.5 cm.

The chemically modified GO was prepared by following previously reported procedures.¹⁶² The GO (10 mg) and ODA (100 mg) were mixed and dissolved in 1,2-dichlorobenzene (DCB, 5mL) under intermittent ultra-sonication at room temperature. The dispersion (3 mL) was mixed with THF (15 mL), and the resultant solution was sonicated and then centrifuged at 15000 rpm for 1 h to separate the sediment from the supernatant. The separated, functionalized GO was washed once using ethanol (10 mL) and then three times using THF (1 mL), and finally dried under

vacuum at room temperature. The prepared GO flakes chemically modified GO with ODA were then weighed and dissolved in chlorobenzene which was shown in Fig. 6.2. Figure 6.3 shows the Raman spectra of the GO before and after ODA modification, confirming that no changes in the innate properties of the GO occurred during the procedure.

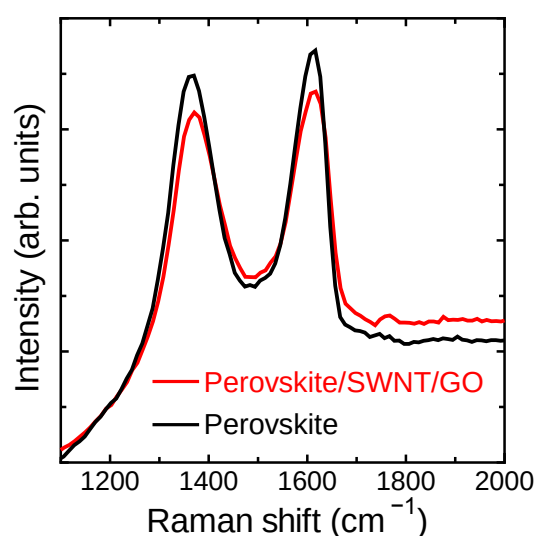


Figure 6.3 Raman spectra of the GO before (black line) and after modification using ODA (red line). The two Raman peaks at 1600 and 1380 cm⁻¹ correspond to the G and D peaks, respectively. There is only a small change in the Raman spectrum of the GO after ODA modification, indicating that the GO structure is not affected during the modification process.

Patterned and cleaned transparent conducting oxide substrate (FTO, 25 mm × 25 mm, Asahi Glass Co., Ltd., Japan) was covered with a 20–40 nm-thick TiO₂ compact layer via spray pyrolysis of titanium diisopropoxide bis (acetylacetonate) (75wt% in 2-propanol, Tokyo Chemical Industry Co., Ltd., Japan) solution in ethanol (0.05 M) at 450 °C. Subsequently, the substrate was immersed in a solution of TiCl₄ (440 μL, special grade, Wako Pure Chemical Industries Ltd., Japan) in 100 mL of water at 70 °C for 30 min, followed by rinsing twice with distilled water. The substrate was sintered at

500 °C for 20 min. The mesoporous TiO₂ layer was formed by spin-coating an ethanol suspension of a TiO₂ paste (PST-18NR, particle diameter ca. 20 nm) followed by drying at 125 °C and annealing at 500 °C.

In an Ar-filled glovebox, a 1.0 M solution of PbI₂ in DMF (70°C) was spin-coated on the mesoporous TiO₂ substrate (slope 5 s, 6500 rpm, 5 s, slope 5 s), followed by drying at 70 °C for 1 h. Subsequently, the resulting yellow film was dipped in a 0.06 M solution of CH₃NH₃PbI₃ in 2-propanol for 40 s and then immediately annealed on a hot plate at 70 °C for 1h.

The SWNT film on the membrane filter was placed in direct contact with the top surface of the active layer. A fiber wiper was then applied to the substrate with adequate pressure to release the SWNT film from the membrane filter and create a connection between the film and the substrate. The prepared GO solution (5 mg/mL in chlorobenzene) and PMMA (40 mg/mL in chlorobenzene) were each subsequently and sequentially spin-coated on the substrate at a rotation speed of 4000 rpm for 30 s, followed by drying for 30 min at 70 °C. Finally, a gold layer (80 nm) was thermally deposited on the hole-transporting layer.

6.3. Experimental methods

6.3.1. Photoluminescence spectroscopy

The main technique for photoluminescence (PL) measurement is using a microscope to focus the laser excitation source to a submicron spot on the sample. The sample absorbs the excitation photons and generates the emission (PL). The emitted photons are collected through a suitable filter which can cut the reflectance of excitation photons into a grating spectrometer, where the emission spectrum can be produced.

The schematic of a typical PL apparatus used in this study is shown in Figure 6.4, where an objective (Mitutoyo Corp, M Plan Apo NIR 100×/NA 0.42 $f=200$) is used to focus the excitation source on the sample and to collimate the PL signals from the sample. For convenience, I have divided this set up into several subsystems: (1) Super continuum light source followed by a monochromator was used for PL measurements of perovskite. (2) Optical system 1 was used for focusing the excitation beam onto the sample (pumping). (3) PL collection was performed by the optical system 2, (4) PL signals were detected by a monochromator with liq. N₂ cooled CCD camera. The PL was corrected using λ^2 correction (appendix 2).

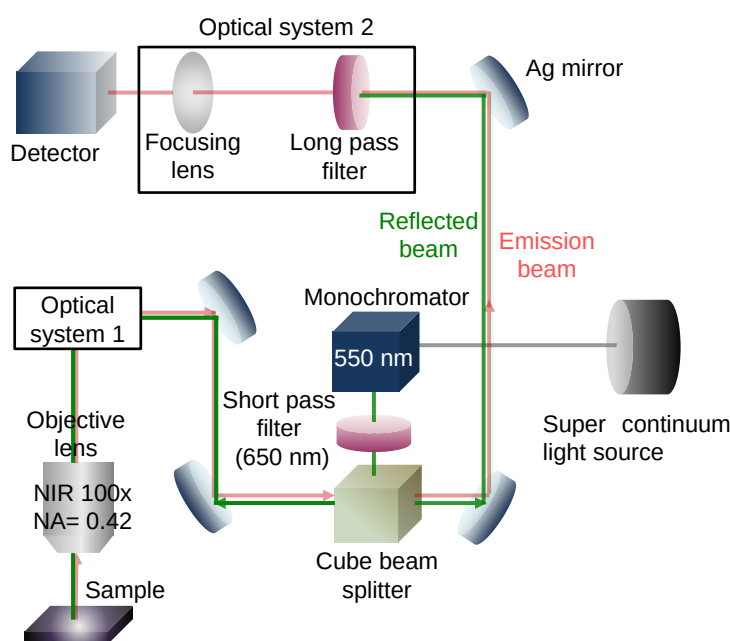


Figure 6.4 Schematic of a typical PL setup for investigating a sample. “Optical system” include a series of filters relevant to the measurement requirements.

Time-resolved PL measurements were carried out using time-correlated single photon counting (TCSPC) techniques which is one of the most widely used for emission lifetime measurements. In TCSPC measurements, the samples are excited with a periodic light source. After each excitation pulse, the time delay between a single emitted photon and a reference trigger pulse is recorded and a histogram of the time

delays is generated (Figure 6.5(a)). This histogram of number of occurrences versus time delay reconstructs the PL dynamics. Because of the counting concept, TCSPC is a technique that is inherently highly linear over many orders of magnitude. Most TCSPC modules operate in a reversed start/stop configuration (Figure 6.5(b)), that is, the single photon detector pulse starts a timer that is stopped by a subsequent trigger pulse provided by the laser source.

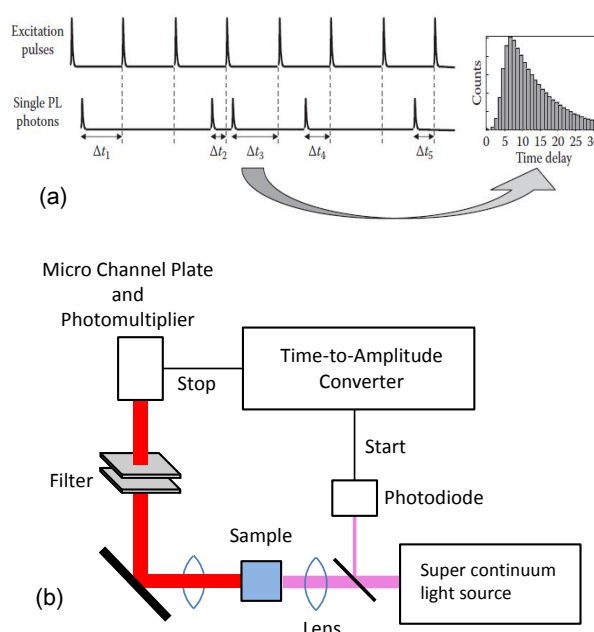


Figure 6.5 (a) In TCSPC, the time delays of single emitted photons are recorded and used to generate a histogram¹⁶⁴. Reproduced from Ref¹⁶⁴ (b) Schematic of the functioning of a TCSPC module.

6.3.2. Raman spectroscopy

Raman spectra were obtained using a Raman spectrophotometer (Ramantouch and inVia Raman Microscope) with a 100x magnification objective lens (Leica, TU Plan Flur 100X, numerical aperture 0.90) shown in Figure 6.6. The sample of GO was prepared by drop casting of the GO solution on SiO₂/Si substrates. The excitation light source is the diode laser with 2.33 eV photon energy. The sample was optically excited

with 400 μW laser power for 60s. The diffraction grating has 1800 grooves/mm and the grating scan type was set as “extended” to scan the grating in a wide range. In Raman spectroscopy, the energy difference between the energies of incident and Raman scattering light is measured as Raman shift. The Raman scattering is induced by interaction between incident photon and phonon (or lattice vibration). The Raman shift provides the information on lattice structures of materials.

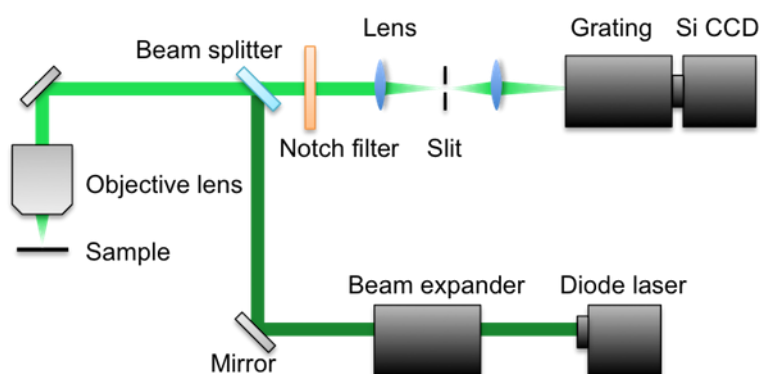


Figure 6.6 Schematic representation of the Raman spectroscopy. The figure was taken from Ref ¹⁷⁴

6.4. Perovskite solar cell devices

Figure 6.7(a) shows the device architecture for the perovskite($\text{CH}_3\text{NH}_3\text{PbI}_3$)/SWNT/GO/PMMA solar cells used in this study. The organo-lead iodide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$) were fabricated on the compact TiO_2 layers via the standard method described in the experimental section. The SWNT thin film, which had a transmission of approximately 70% at a wavelength of 550 nm, was then transferred to the perovskite layer. Next, the GO modified by octadecylamine (ODA) was spin-coated on the SWNT film to construct the SWNT/GO layer. Note that GO penetrates in the SWNT network to form the composite structure of SWNT/GO. Finally, PMMA was spin-coated on the SWNT/GO layer to maintain the environmental stability of the device.

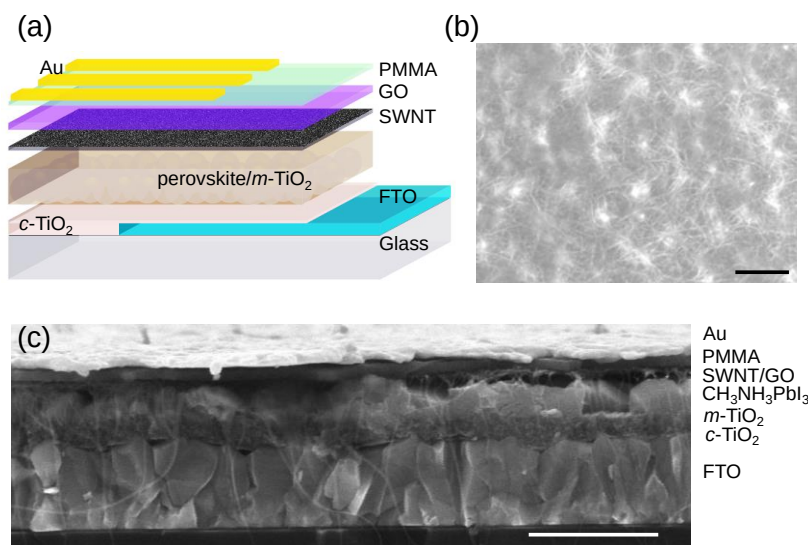


Figure 6.7 Schematics and SEM images of solar cell devices. (a) Schematic of an organo-lead iodide perovskite/SWNT/GO solar cell. (b) Top-view SEM image of an SWNT film on a perovskite thin film. (c) Cross-sectional SEM image of a perovskite/SWNT/GO solar cell. The scale bar in each figure is 1 μm .

Figure 6.7(b) and (c) show a top-view scanning electron microscopy (SEM) image of the SWNT thin film and a cross-sectional SEM image of the solar cell device, respectively. The SWNT film exhibits a spider web-like structure consisting of interconnected nanotube bundles with diameters ranging from several to tens of nanometers. The typical thicknesses of the compact TiO₂, mesoporous TiO₂, and CH₃NH₃PbI₃ layers are approximately 25, 200, and 300 nm, while those of the SWNT/GO and PMMA layers are approximately 15 and 100 nm, respectively.

The current density–voltage (J – V) characteristics of a perovskite/SWNT/GO/PMMA solar cell under Air Mass 1.5 conditions are shown in Fig. 6.8(a). The J – V curve of the solar cell exhibits a short-circuit current density (J_{sc}) of 20.1 mA/cm², an open-circuit voltage (V_{oc}) of 0.95 V, and a fill factor (FF) of 61%, resulting in a PCE (η) of 11.7%,

which is one of the highest values for perovskite solar cells containing an inorganic buffer layer.^{165, 166} Variation in the photovoltaic performance of 25 perovskite/SWNT/GO/PMMA solar cells was also investigated. The inset in Fig. 6.7(a) shows a histogram of the PCE values, which varies only slightly in the range from 9.2% to 11.7% and has an average value of $10.5 \pm 0.8\%$.

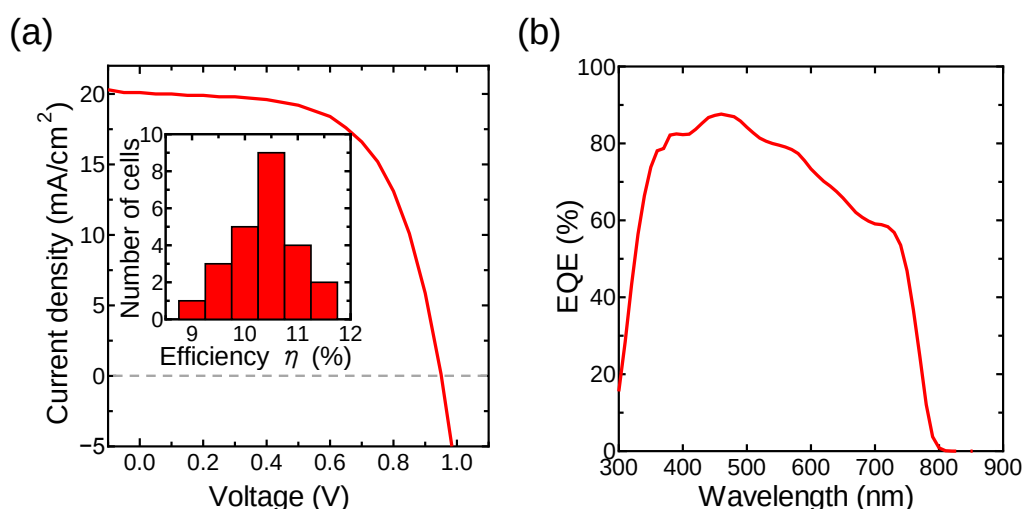


Figure 6.8 Photovoltaic performance of solar cell devices. (a) Typical J - V curve for a perovskite/SWNT/GO solar cell. The inset shows a histogram of the device performance for 25 perovskite/SWNT/GO solar cells. (b) IPCE spectrum of a perovskite/SWNT/GO solar cell.

Figure 6.8(b) shows the spectrum of the IPCE for a perovskite/SWNT/GO/PMMA solar cell. The IPCE response from ~ 300 to ~ 780 nm suggests that the perovskite layer plays a role in both solar light absorption and photocarrier generation in solar cell,¹⁴⁷ while the SWNT/GO layer mainly functions as an efficient carrier dissociation, collection, and transport layer. This is also supported by the absorption spectra for perovskite and perovskite/SWNT/GO (see Figure 6.14). The integrated current is also calculated using the overlap between the EQE spectrum and the AM 1.5G solar photon flux for the cell. Note that the calculated integrated photocurrent yield for the current

density is 19.5 mA/cm^2 , which is consistent with that of the photocurrent density ($\sim 20 \text{ mA/cm}^2$) determined from the J - V curve in Fig. 6.8(a).

The GO layer plays an important role in improving the photovoltaic properties of the cell. The J - V curves of perovskite solar cells without a hole-transport layer and with SWNTs, SWNT/GO, and SWNT/GO/PMMA layers are investigated to understand the roles of each layer, as shown in Fig. 6.9. The perovskite solar cell directly contact with the Au anode, denoted as free in Fig. 6.9, exhibits a PCE of 3.3% due to low J_{sc} and V_{oc} values (Table 6.1), which mainly results from large recombination losses at the interface of the perovskite layer and the anode and the low built-in voltage.¹⁵⁰ The SWNT layer serves to assist photogenerated carrier extraction/transport and separates the perovskite layer from the anode. After insertion of the SWNT layer, therefore, the PCE of the perovskite solar cell increased from 3.3 to 4.9%, a 50% increase mainly attributes to an increase in the J_{sc} value due to more efficient charge transport and suppression of carrier recombination. The series and shunt resistances evaluated from the J - V curve are also improved upon insertion of the SWNT layer, as shown in Table 6.1, suggesting that efficient hole transport and suppression of carrier recombination occurred in the cell. However, the SWNT thin layer barely separates the light absorber ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and the electrode (Au), do not exhibit substantial charge carrier selectivity.¹⁶⁷ Thus, the J_{sc} and V_{oc} values are still much lower than those in organo-lead iodide perovskite solar cells with spiro-OMeTAD organic hole transport layers.

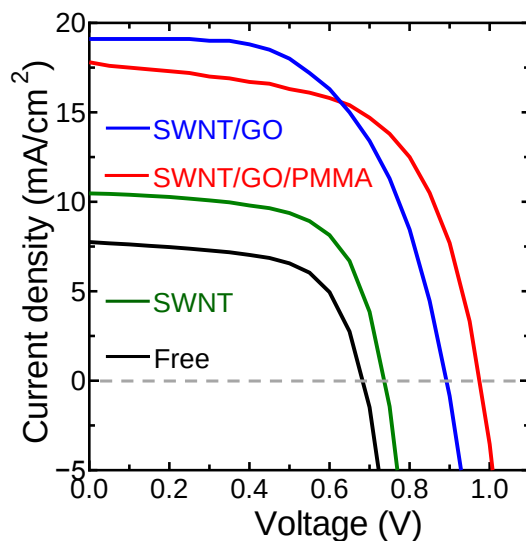


Figure 6.9 Photovoltaic properties of solar cells with various hole-transport layers. J – V curves of a hole-transport layer-free perovskite solar cell (black solid line) and perovskite solar cells with SWNT (green solid line), SWNT/GO (blue solid line), and SWNT/GO/PMMA (red solid line) layers.

The perovskite solar cell using the bi-component SWNT/GO buffer layer exhibits a two-fold higher PCE of 9.8% compared to that of the cell with only an SWNT layer (perovskite/SWNT; Fig. 6.9) due to higher J_{sc} (19.1 mA/cm²) and V_{oc} (0.89 V) values, which is the first report of about 10% by using SWNT/GO as a hole transport layer in organic solar cells as far as we know. This experimental result implies that the built-in potential (V_{bi}) across the device drastically increases upon insertion of the GO layer.¹⁶⁸ Figure 6.10 shows the large bandgap of a major portion of the GO (~3 eV), which is associated with the interfacial dipole moment between the SWNT/GO and perovskite active layers, may be the origin of the enhanced V_{bi} of the cell structure.¹⁶⁹ The turn-on voltage of perovskite solar cell containing GO is larger than that without GO, indicating that the built-in-voltage greatly improved by GO layer (Figure 6.11).¹⁶⁸ The large increase in the J_{sc} value from 10.5 to 19.1 mA/cm² (an increase of 82%) suggests that the GO acts as an electron-blocking layer and substantially improves the carrier

transport selectivity in the SWNT network. The top PMMA layer is utilized to protect the active layer from exposure to moisture, because humidity is known to decrease the performance of perovskite solar cells.¹⁵⁹ As can be seen in Fig. 6.9, the addition of the PMMA layer to the perovskite/SWNT/GO solar cell also contributes to a further increase in the PCE to 10.4% with enhancement of V_{oc} , possibly due to a further decrease in carrier recombination losses. Furthermore, the photovoltaic performance of perovskite solar cells with the GO, PMMA, and GO/PMMA layers is investigated to understand the role of these layers; the J - V curves of these solar cells are shown in Fig. 6.12.

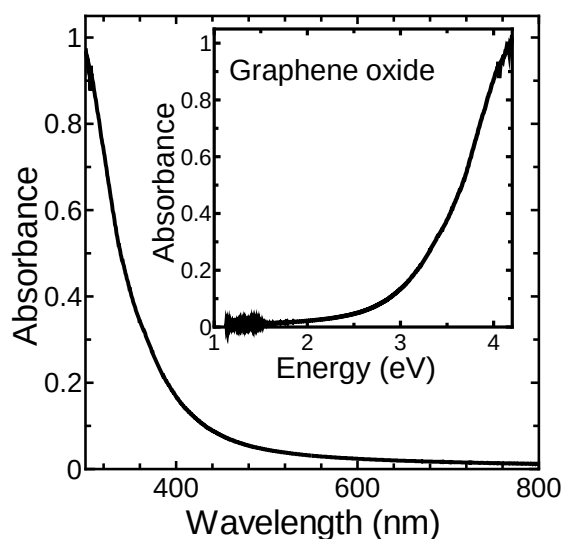


Figure 6.10 Optical absorption spectrum of the GO. The inset shows the same absorption spectrum as a function of the photon energy. A drastic increase in absorption occurred at approximately 3 eV, indicating that the optical gap for the major portion of the GO was approximately 3 eV.

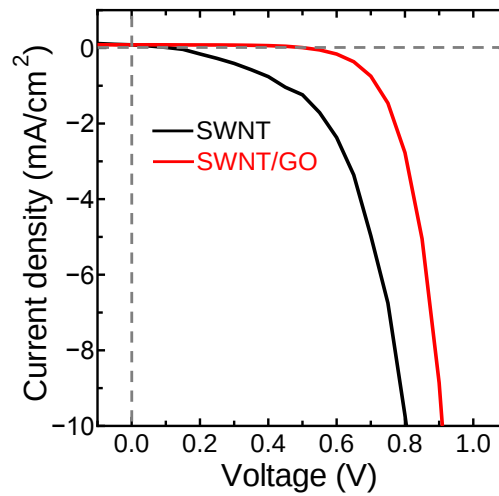


Figure 6.11 The J - V characteristics of perovskite solar cells using SWNT and SWNT/GO transport layer under dark conditions, which shows the increase of turn-on voltage from about 0.3 to 0.7 V by the introduction of GO.

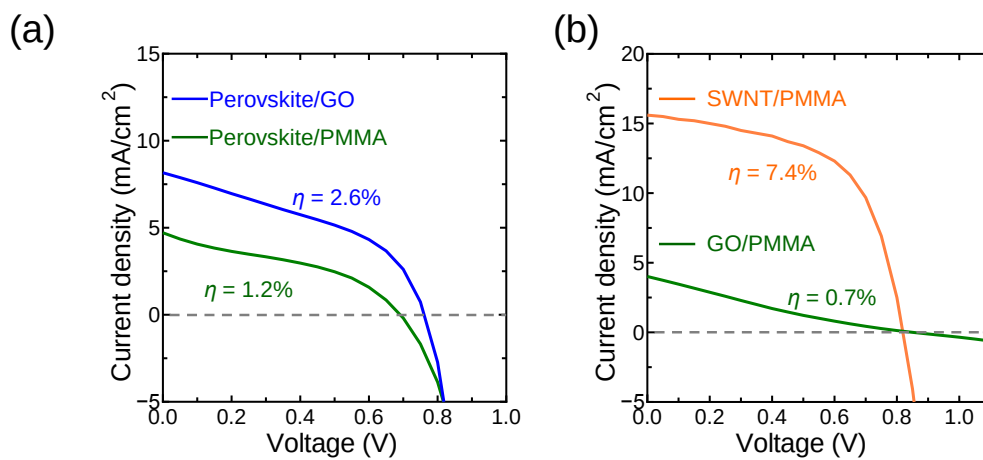


Figure 6.12 (a) J - V curves of perovskite/GO and perovskite/PMMA solar cells (b) J - V curves of perovskite/SWNT/PMMA and perovskite/SWNT/GO/PMMA solar cells.

The J - V curves of perovskite solar cells with various hole-transport layers were measured in order to understand the role of each layer. Figure 6.12 shows the J - V curves for perovskite solar cells with the GO (perovskite/GO) and PMMA (perovskite/PMMA) layers. The PCEs of the perovskite/GO and perovskite/PMMA

were relatively low at 2.6% and 1.2%, respectively. The detailed photovoltaic parameters from the J – V curves are shown in Table 6.2. The lower PCE values for the perovskite/GO and perovskite/PMMA cells compared to those of the perovskite/SWNT cell (4.9%, Figure 6.9) are attributed to the large series resistance loss due to the lower electronic conductivity of the GO and PMMA (see R_s in Table 6.2).

Table 6.1 Device parameters for the perovskite solar cells with no transport layer (layer-free) and with SWNT, SWNT/GO, and SWNT/GO/PMMA layers. The parameters η , R_s , and R_{sh} in the table indicate the PCE, series resistance, and shunt resistance, respectively.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)	R_s (Ω)	R_{sh} (k Ω)
Free	7.74	0.68	0.63	3.32	279	16.4
SWNTs	10.47	0.73	0.64	4.9	176	23.2
SWNTs/GO	19.1	0.89	0.57	9.8	267	8.4
SWNTs/GO/PMMA	17.7	0.97	0.60	10.4	215	10.1

Table 6.2 Parameters of perovskite solar cells with PMMA, GO and SWNT layer. R_s and R_{sh} are series and shunt resistance, respectively.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)	R_s (Ω)	R_{sh} (k Ω)
PMMA	4.71	0.69	0.38	1.24	1241	4.7
GO	8.16	0.76	0.42	2.63	459	4.2
GO/PMMA	4.0	0.85	0.20	0.7	8396	4.4
SWNT/PMMA	15.6	0.82	0.58	7.4	168	7.2

Figure 6.12 shows the J – V curves for perovskite solar cells with GO/PMMA (perovskite/GO/PMMA) and SWNT/PMMA (perovskite/SWNT/PMMA) layers. The detailed photovoltaic parameters evaluated from these J – V curves are also shown in Table 6.2. The PCE of the perovskite/GO/PMMA is low at 0.7%, also due to the very large series resistance loss (see R_s in Table 6.2). The PCE of the

perovskite/SWNT/PMMA cell is much higher, however, at 7.4%, but still lower than those of the perovskite/SWNT/GO (9.8%) and perovskite/SWNT/GO/PMMA (10.4%) cells (Figure 6.9). The lower J_{sc} and V_{oc} values for the perovskite/SWNT/PMMA cell without a GO layer (see in Table 6.2) compared to those for the cell with the GO layer can be attributed to relatively large carrier recombination losses and the low built-in potential.

6.5. Role of carbon nanotubes

Figure 6.13(a) shows the energy levels of a perovskite/SWNT/GO solar cell, where the bandgaps for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and semiconducting SWNT films (diameter: 1.6 nm) were approximately 1.6¹⁷⁰ and 0.9 eV,¹⁶³ respectively. Band alignment is important for understanding the carrier dissociation process and determines the built-in field in a cell. Insertion of the SWNT layer causes an increase in the J_{sc} values, as shown in Fig. 6.9, which suggests that the SWNT functions as an efficient carrier dissociation and hole extraction layer in the band alignment. PL spectroscopy provides insightful information on the charge carrier extraction properties of solar cells. $\text{CH}_3\text{NH}_3\text{PbI}_3$ is a highly luminescent material, thus, the quenching of its PL intensity with a hole-conducting material is used as a measure of the charge extraction ability of the perovskite layer. Figure 6.13(b) shows the PL spectra of perovskite and perovskite/SWNTs thin films which were corrected by the λ^2 correction (Appendix 2). The PL spectrum of the perovskite film shows an intense peak at ~768 nm (1.61eV), which is in good agreement with absorbance spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ which was shown in Fig. 6.14. In contrast, the PL intensity of this peak in the perovskite/SWNT spectrum is drastically decreased. The large PL quenching in the perovskite/SWNT thin film suggests that the SWNT layer plays an effective role in charge carrier dissociation and extraction across the interface between the perovskite and SWNT layers.

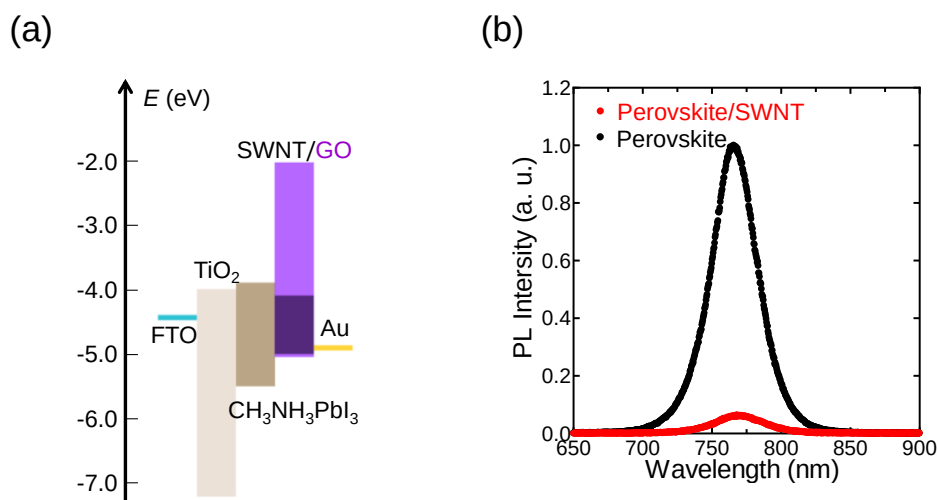


Figure 6.13 (a) Band alignment in a perovskite/SWNT/GO solar cell. (b) PL spectra of perovskite (solid black line) and perovskite/SWNT thin films (solid red line).

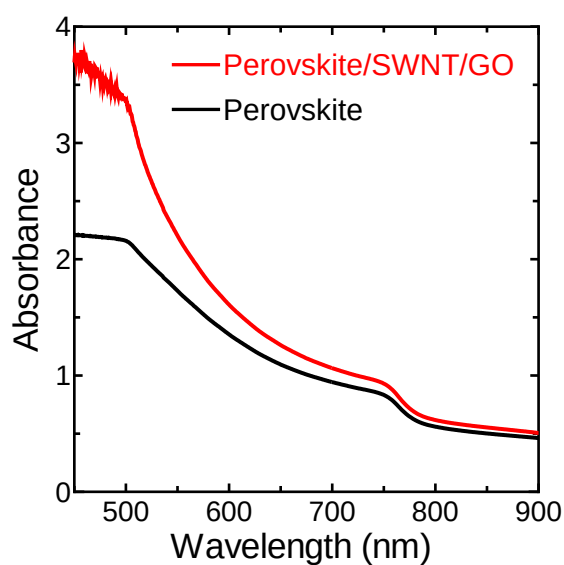


Figure 6.14 Optical absorption spectra of a perovskite thin film (black solid line) and a perovskite/SWNT/GO film (red solid line).

6.6. Time-resolved PL measurement

Time-resolved PL spectroscopy was performed to evaluate the crystallization of the lead-iodide perovskite layer and probe the charge dissociation assisted by the SWNT

and GO layers. Figure 6.15 shows the PL decay curves of just the lead-iodide perovskite film ($\text{CH}_3\text{NH}_3\text{PbI}_3$), the perovskite film covered by an SWNT layer (perovskite/SWNT), and the perovskite film covered by a GO layer (perovskite/GO) under low power conditions of $1.5 \mu\text{J}/\text{cm}^2$ with excitation at 550 nm. The single exponential PL decay of 6.1 ns in the perovskite film indicates the high crystalline quality of the samples.¹⁷¹ The shorter PL decay times of 1.35 and 0.83 ns in perovskite/GO and perovskite/SWNT were evaluated using a fitting analysis for the PL decay curves. The shorter PL decay time of perovskite/GO and perovskite/SWNT compared to that in the perovskite film are consistent with the experimentally observed PL quenching in the perovskite/SWNT (Fig. 6.13(a)). The PL decay times drastically decreased in the lead-iodide perovskite covered by the SWNT thin film due to efficient charge extraction from the perovskite layer by the SWNTs. Time-resolved PL spectroscopy results further support the good carrier extraction ability of SWNTs in the perovskite/SWNT hybrid structure.

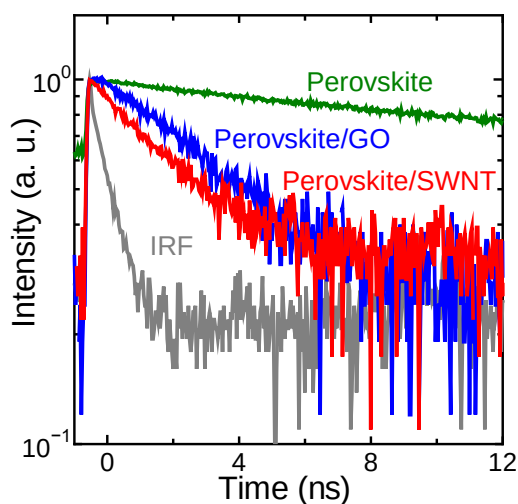


Figure 6.15 PL decay profiles of perovskite (solid green line), perovskite/GO (solid blue line), and perovskite/SWNT/GO (solid red line) films. The instrumental response function (IRF) in this experiment (solid gray line) is also shown.

6.7. Role of graphene oxide

Insertion of the GO layer leads to increases in the J_{sc} and V_{oc} values, as shown in Fig. 6.9, suggesting that the GO functions as an efficient electron-blocking layer and increases the built-in potential in the band alignment. The theoretically predicted V_{oc} maximum for perovskite solar cells has been determined to range from 1.32 to 1.34 V.¹⁷² SWNTs, which have a narrower bandgap than perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$), cannot block the electron leakage and reduce the recombination losses at the interface, and therefore, a relatively low V_{oc} value of 0.73 V is obtained. In contrast, the much larger bandgap of the GO compared to those of the perovskite and SWNTs may enable the GO to serve as an effective electron-blocking layer. The energy barrier between the perovskite and GO layer effectively limits electron diffusion, preventing carrier recombination loss at the anode and increasing the V_{oc} (160 meV) value from 0.73 V for the control device to 0.89 V.

6.8. Comparison of SWNT/GO and spiro-OMeTAD based devices

6.8.1. Power conversion efficiency

The photovoltaic performance of perovskite solar cells with SWNT/GO/PMMA and spiro-OMeTAD organic hole transport layers was then compared. Note that the organo-lead iodide perovskite used to fabricate the two cells was taken from the same production batch. Figure 6.16 shows the J – V curves for the perovskite cell with spiro-OMeTAD (perovskite/spiro-OMeTAD) and the cell with the SWNT/GO protected by a PMMA layer (perovskite/SWNT/GO/PMMA). The perovskite/SWNT/GO/PMMA cell exhibits a high PCE of 13.0% with the J_{sc} of 19.4, V_{oc} of 0.92V and FF of 0.72, respectively. Its photovoltaic performance is comparable to that of the perovskite/spiro-OMeTAD cell with a PCE of 12.8% (J_{sc} , V_{oc} , and FF values of 20.2 mA/cm^2 , 0.98 V, and 0.65, respectively). The similar PCE values for the perovskite/SWNT/GO and perovskite/spiro-OMeTAD cells suggest that SWNT/GO

layers may have practical applications in perovskite solar cells, but also indicates that there is further room for improvement of the performance of perovskite/SWNT/GO cells.

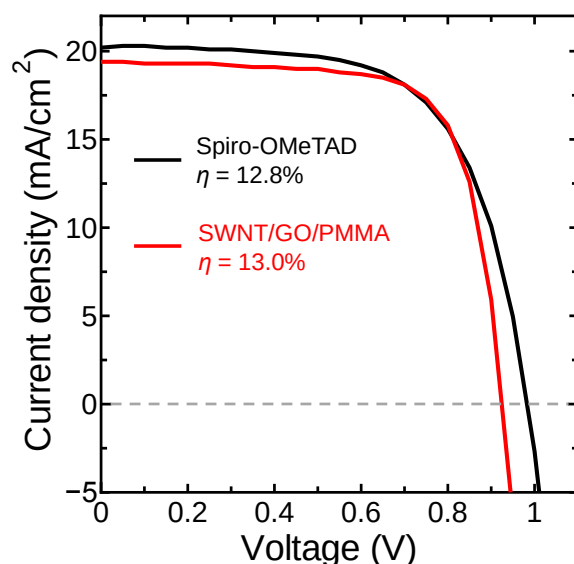


Figure 6.16 J - V characteristics of perovskite solar cells with a spiro-OMeTAD hole-transport layer (black solid line) and an SWNT/GO layer (red solid line) obtained under $100 \text{ W} \cdot \text{cm}^{-2}$ (AM 1.5G) illumination using a $2 \times 2 \text{ mm}^2$ mask.

6.8.2. Stability of device performance

The stability of photovoltaic properties is an important factor in the performance of perovskite solar cells, and was thus also investigated for the perovskite/SWNT/GO/PMMA solar cell. Figure 6.17 shows the changes in the PCE values, i.e., the stabilities of the perovskite/SWNT/GO/PMMA and perovskite/sprio-OMeTAD solar cells stored in air conditions (humidity: 70–80%, temperature: 298 K), as a function of time. Each solar cell was evaluated in air for ten days at two-day intervals. The PCE of the perovskite/sprio-OMeTAD solar cell clearly declines from 10.5 to 5.8% during the ten days. Here PCE decay is defined by $\Delta\eta = (\eta_0 - \eta_t)/\eta_0$, where η_0 and η_t are the PCE at the start and after ten days, respectively. The perovskite/sprio-OMeTAD solar cell exhibits significant degradation

($\Delta\eta\sim 45\%$) in performance by the tenth day in air. In contrast, the perovskite/SWNT/GO cell exhibits very stable performance, with the PCE value changing only slightly from 10.5% to 10.0% by the tenth day ($\Delta\eta\sim 5\%$). This result is attributed to the PMMA layer, which functions as an effective barrier to moisture and oxygen penetration and prevents degradation of the organo-lead perovskite. In addition, the SWNT/GO layer is more stable than sprio-OMeTAD. The perovskite/SWNT/GO solar cells with thicker PMMA layers are more stable. However, their PCE values are lower due to the insulating nature of PMMA; thicker layers prevent efficient carrier transport from the perovskite layer to the anode. Importantly, both high photovoltaic performance and stability of the perovskite/SWNT/GO solar cell can be achieved by choosing an appropriate thickness for the PMMA layer.

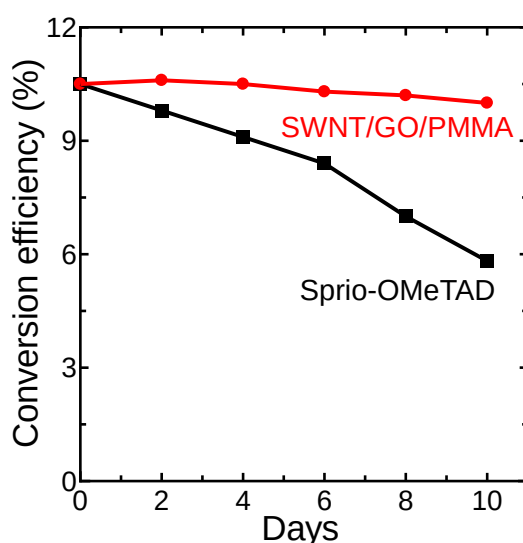


Figure 6.17 Performance stability of the perovskite/SWNT/GO (red circles) and perovskite/sprio-OMeTAD (black squares) solar cells stored in air (humidity: 70–80%, temperature: 298 K) as a function of time. The stability in air was evaluated every two days for ten days.

The stability of the photovoltaic performance of perovskite/SWNT/GO solar cells protected by PMMA layers of different thicknesses was also evaluated in air (humidity:

70–80%, temperature: 298 K). The J – V curves before and after exposure to air for 10 days are shown in Fig. 6.18, respectively. Drastic decreases in the PCE values and significant degradation of the photovoltaic performance are observed for the perovskite/SWNT/GO solar cells with thinner PMMA layers (30 and 40 nm). In contrast, almost no decrease in the PCE values and photovoltaic performance degradation is observed after 10 days for the perovskite/SWNT/GO solar cells with thicker PMMA layers (60, 90, and 160 nm).

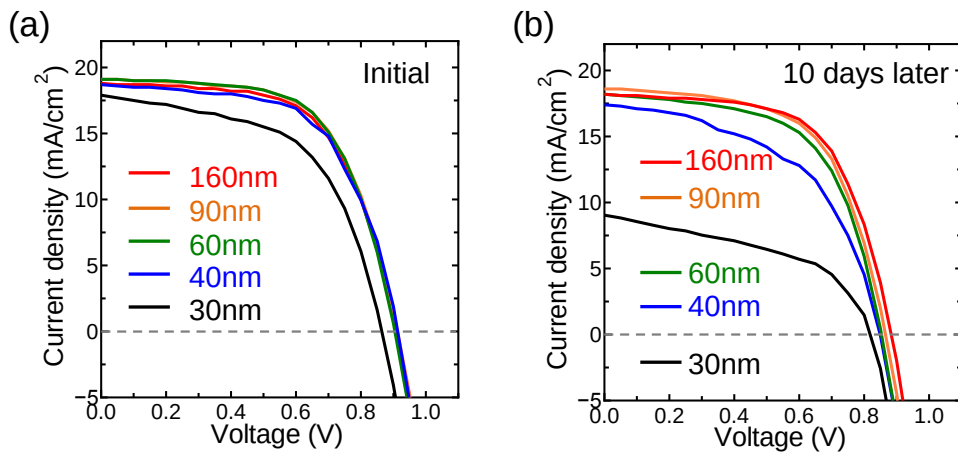


Figure 6.18 (a) and (b) J – V curves of perovskite/SWNT/GO solar cells protected by PMMA layers of different thicknesses before and after exposure to air for 10 days.

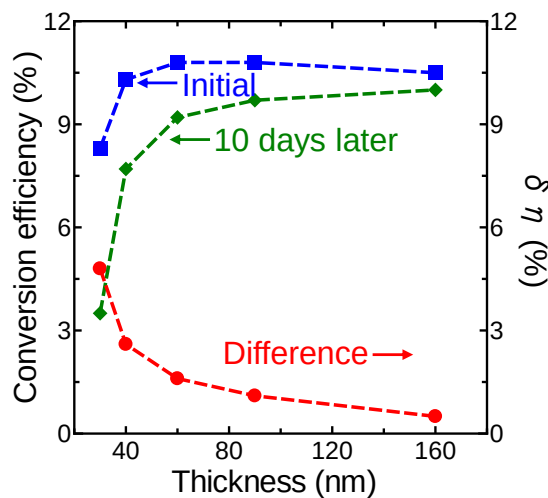


Figure 6.19 PCEs of perovskite/SWNT/GO/PMMA solar cells before (blue squares)

and after exposure to air for 10 days (green rhombuses). The difference of the PCE value ($\delta\eta$) in initial and after 10 days is also shown (red circles).

Figure 6.19 shows the PCEs as a function of PMMA layer thickness before and after exposure to air for 10 days. The difference of the PCE value ($\delta\eta$) is also shown in Fig. S8. The $\delta\eta$ drastically decrease with increasing PMMA layer thickness. The degradation of photovoltaic performance is much reduced with thicker PMMA layer, as also shown in Table 6.3

Table 6.3 PCEs value of solar cells as a function of layer thickness before and after exposure to air for 10 days, and the difference of PCE value ($\delta\eta$) in initial and after 10 days.

Thickness Efficiency	30 nm	40 nm	60 nm	90 nm	160 nm
η_0 (%)	8.3	10.3	10.8	10.8	10.5
η_t (%)	3.5	7.7	9.2	9.7	10.0
$\delta\eta$ (%)	4.8	2.6	1.6	1.1	0.5

Figure 6.20 shows the top view of Au coated SWNTs network with thin PMMA layer. The bundles of SWNTs are protruded on the surface, which plays an important role for electronic connection to electrode layer. Figure 6.20(b) and (c) shows cross sectional SEM images of a SWNT film covered by PMMA layer with thickness of ~ 100 nm and SWNT/PMMA/Au layer with PMMA layer thickness of ~ 80 nm, respectively. It is seen that the SWNTs can connect to Au in the cross-sectional images, indicated by arrows. The electrical connection covered by insulating PMMA layer comes from the characteristics network structure of SWNTs.

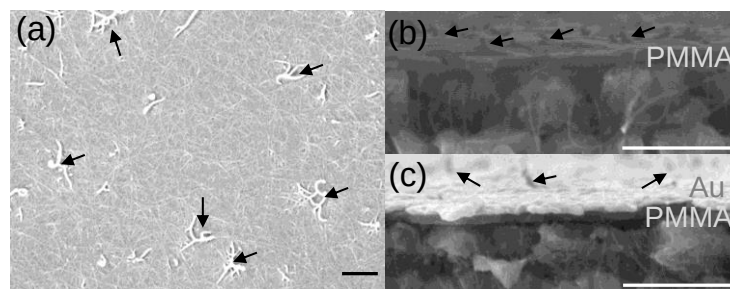


Figure 6.20 (a) Top view SEM image of Au coated SWNTs network with thin PMMA layer. (b) and (c) Cross sectional SEM images of SWNT network covered by PMMA layer with thickness of ~ 100 nm and SWNT/PMMA/Au layer with PMMA layer thickness of ~ 80 nm. Black arrows indicate the SWNTs and the scale bar in each figure represents $1\ \mu\text{m}$.

6.9. One step method for high efficiency

Finally, In order to further improve the power conversion efficiency of perovskite/SWNT/GO/PMMA solar cells, we tried to modify the interfacial connection between SWNT and perovskite layer. The experiment is same with sequential deposition method except the perovskite layer fabrication which is as follows: In a glove box filled with an inert gas, a $1.1\ \text{M}$ solution of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ in DMSO (room temperature) was deposited on the mesoporous TiO_2 films by spin-coating (slope $1\ \text{s}$, $1000\ \text{rpm}$ $40\ \text{s}$, slope $1\ \text{s}$, $0\ \text{rpm}$. $30\ \text{s}$, slope $5\ \text{s}$, $5000\ \text{rpm}$ $20\ \text{s}$, slope $5\ \text{s}$: At the last $5\ \text{s}$ of spin-coating, $0.5\ \text{mL}$ of toluene was slowly dropped on the rotating substrate.). The resulting transparent film was annealed on a hot plate at $100\ ^\circ\text{C}$ for $10\ \text{min}$ to form perovskite layer ($250\ \text{nm}$).

Figure 6.21(c) shows perovskite solar cells with an SWNT/GO layer obtained under $100\ \text{W}\cdot\text{cm}^{-2}$ (AM 1.5G) illumination (red line) and in dark condition (black line) using a $2 \times 2\ \text{mm}^2$ mask. A PCE of $13.3\ \%$ is observed for the perovskite/SWNT/GO/PMMA solar cell. The enhanced PCE resulted from a short-circuit current density (J_{sc}) of 19.4

mA/cm^2 , an open-circuit voltage (V_{oc}) of 0.95 V, and a fill factor (FF) of 72%. A drastically increased FF comes from the improved connection between SWNT and perovskite. Figure 6.21(a) and (b) show the perovskite fabricated by one step method and sequential deposition method, respectively. Good flatness is shown in Fig. 6.21(a). These results indicated that the photovoltaic performance of perovskite/SWNT/GO/PMMA solar cells can be improved with modification of the interface or structures.

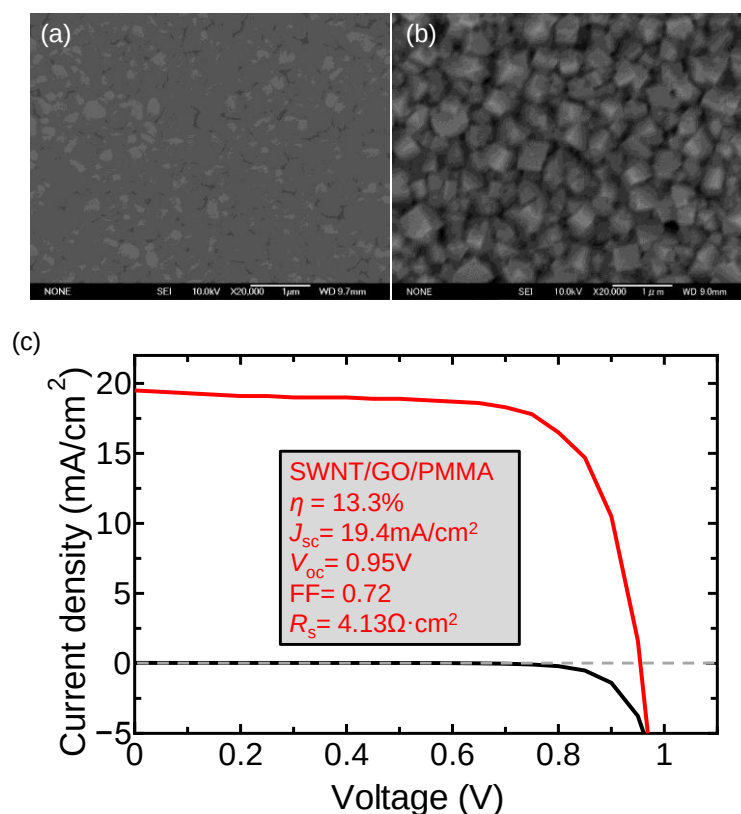


Figure 6.21 Top view of SEM images of one step method, (a) and sequential deposition method (b), fabricated perovskite substrate. (c) J - V characteristics of perovskite solar cells with an SWNT/GO layer obtained under $100 \text{ W} \cdot \text{cm}^{-2}$ (AM 1.5G) illumination and dark using a $2 \times 2 \text{ mm}^2$ mask.

6.10. Chapter summary

The photovoltaic performance of organo-lead iodide perovskite solar cells with efficient SWNT/GO hole-transport layers was studied. A perovskite/SWNTs/GO solar cell with a protecting layer of PMMA exhibited a high PCE of 13.3%, which was comparable to that of a perovskite solar cell containing a spiro-OMeTAD organic hole-transport layer. Moreover, it was demonstrated that the PCE value for the perovskite/SWNT/GO/PMMA decreased only slightly compared to that of the perovskite/spiro-OMeTAD in air condition. With their respective efficient carrier extraction/transport and electron-blocking properties, the combination of SWNTs and GO in the perovskite solar cell contributes to a reduction in carrier recombination losses and an increase in the open-circuit voltage, resulting in a high PCE. These findings regarding the performance of SWNT/GO films as an efficient carrier transport layer shed new light on device physics and suggest that these materials have significant potential for use in optoelectronic applications.

Chapter 7. Conclusions

In this thesis, I have investigated the carbon nanotubes as for photovoltaic materials and applied for Si heterojunction solar cell and organo-lead iodide perovskite solar cells.

First, I prepared SWNT thin film by a spray method and studied p -SWNT/ n -Si heterojunction solar cells for understanding the series resistance effects and the photovoltaic mechanism of device. From the model and calculation, the resistance is recognized as the main culprit of the relatively low performance in solar cells. The enhancement of the conversion efficiency was realized by HNO_3 doping which decreased in the series resistance of the SWNT network films and increased in the p - n junction density. As a next step, I used high quality SWNT thin film fabricated by the FC-CVD method for further improvement of photovoltaic performance. The sheet resistance of carbon nanotube fabricated by FC-CVD is about 4 $\text{k}\Omega/\text{sq}$ with a transparency of 91% at 550 nm, which is much lower than sprayed nanotube film with the same transparency. The SWNT/Si heterojunction solar cell using FC-CVD SWNT films shows a photovoltaic conversion efficiency of 12% without post-processing. In addition, the high reproducibility of the photovoltaic performance of this type of device was clearly demonstrated, suggesting the superior potential of carbon nanotube solar cells.

I also investigated the photovoltaic performance of SWNT-based solar cells using environmentally friendly, durable, and inexpensive materials such as MoO_x and ZnO , which work as antireflection layers for increasing the optical absorption, carrier dopants for a reduction of the series resistance, and effective carrier transport layers for the

reduction of the Schottky barrier. The photovoltaic performance of *p*-SWNT/*n*-Si and *n*-SWNT/*p*-Si heterojunction solar cells was improved using multifunctional layers of MoO_x and ZnO, which resulted in very high PCE values of 17.0% and 4.0%, respectively. Finally, the photovoltaic performance of organo-lead iodide perovskite solar cells with efficient SWNT/GO hole-transport layers was studied. A perovskite/SWNTs/GO solar cell with a protecting layer of PMMA exhibited a high PCE of 13.3%, which was comparable to that of a perovskite solar cell containing a spiro-OMeTAD organic hole-transport layer. Moreover, it was demonstrated that the PCE value for the perovskite/SWNT/GO/PMMA decreased only slightly compared to that of the perovskite/spiro-OMeTAD in air condition. With their respective efficient carrier extraction/transport and electron-blocking properties, the combination of SWNTs and GO in the perovskite solar cell contributes to a reduction in carrier recombination losses and an increase in the open-circuit voltage, resulting in a high PCE.

These findings regarding the performance of SWNT films as an efficient carrier transport layer shed new light on device physics and suggest that these materials have significant potential for use in optoelectronic applications.

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Scientific contributions

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Awards

1, MNC 2014 Young Author's Award, 27th International Microprocesses and Nanotechnology Conference, Nov. 2014, Oral presentation.

2, Student award in Institute of Advanced Energy, Kyoto University, Mar. 2016.

Appendix

Appendix1 Physics of k with respect to the areal density of p - n junctions

Here I describe the detailed physical meaning of the parameter k with respect to the effective areal density of p - n junctions. I consider that the SWNTs are coated on the n -Si substrate using the airbrushing technique. The ratio of SWNTs in contact with the n -Si substrate w is defined as

$$w = \frac{N_{\text{cov}}(1)}{N_{\text{all}}}, \quad (\text{A1})$$

where $N_{\text{cov}}(1)$ is the area covered by SWNTs with one-time spraying, and N_{all} is the total active area on n -Si of the solar cell device. I define the probability $p(n)$ that a certain part of the Si substrate is coated with SWNTs after the n -th coating during airbrushing. $p(1)$ should equal w for the first coating, and $p(2)$ should be $(1 - w)w$ for the second coating. Then, after the n th-coating, it should be $(1 - w)^{n-1}w$. I can therefore obtain an equation for $p(n)$ of SWNTs as

$$p(n) = 1 - (1 - w)^n. \quad (\text{A2})$$

Next, we consider the formation of a p - n junction between p -SWNTs and the n -Si substrate. I assume that a part of SWNTs in contact with the n -Si substrate can form p - n junctions, and the ratio of SWNTs that act as p - n junctions at the interface is defined as a ($0 \leq a \leq 1$), where this value depends on the carrier density in the SWNTs. The effective areal density of the p - n junction S_{pn} can be express as

$$S_{\text{pn}} = S_0[1 - (1 - aw)^n]. \quad (\text{A3})$$

where S_0 is the active area of the Si substrate. On the other hand, the transmittance T depending on the air-brushing time can be described as

$$T(n) = 10^{-cn}, \quad (\text{A4})$$

where c is a constant and cn is equal to the absorbance. We can obtain the relationship

$$n = -\frac{1}{c} \log T. \quad (\text{A5})$$

From eqs. (3) and (4), normalized S ($=S_{pn}/S_0$) can be described as

$$S = [1 - (1 - aw)^{-1/c \log T}]. \quad (\text{A6})$$

I use the parameter k instead of $(1 - aw)^{1/c}$ to simplify the equation to

$$S = 1 - k^{-\log T}. \quad (\text{A7})$$

Here S is the effective areal density of p - n junction, and k is related to the probability that the SWNTs in contact with the substrate do not form a p - n junction.

Appendix2 λ^2 correction

I define the experimentally light intensity $I(\lambda_{av})$, where λ_{av} , the average wavelength is measured with the spectral band width $\Delta\lambda \equiv \lambda_2 - \lambda_1$ ($\lambda_2 > \lambda_1$) which is determined by the slit width of a standard monochromator, $\lambda_{av} = (\lambda_1 + \lambda_2)/2$,

$$I(\lambda_{av}) = \int_{\lambda_1}^{\lambda_2} f(\lambda) d\lambda. \quad (\text{A8})$$

Here, $f(\lambda)$ is the real spectrum as a function of the wavelength λ . When $\Delta\lambda$ is sufficiently small,

$$I(\lambda_{av}) \approx f(\lambda_{av}) \Delta\lambda, \quad (\text{A9})$$

Using a standard monochromator in experiments, I obtain optical spectra with constant $\Delta\lambda$ for all λ because $\Delta\lambda$ is determined by the slit width. Thus, $I(\lambda_{av})$ closely corresponds to the real spectrum $f(\lambda)$.

Now I consider to replace the x-axis (λ_{av}) of the spectra $I(\lambda_{av})$ with the corresponding photon energy E_{av} which is defined as $E_{av} = (E_1 + E_2)/2$, where $E_1 = A/\lambda_1$ and $E_2 = A/\lambda_2$. When $\Delta\lambda$ is small, E_{av} can be approximated by A/λ_{av} . A is a constant and $A = 1239.8$ nm·eV for λ and E in the units of [nm] and [eV]. Here, $E_1 > E_2$ and the band width in

photon energy $\Delta E \equiv E_1 - E_2$. The experimental spectrum $I_e(E_{av})$ as a function of E_{av} which we want to obtain is expressed as,

$$I_e(E_{av}) = \int_{E_2}^{E_1} g(E) dE, \quad (A10)$$

where $g(E)$ is the real spectrum as a function of photon energy. When ΔE is sufficiently small constant, I obtain

$$I_e(E_{av}) \approx g(E_{av}) \Delta E. \quad (A11)$$

Note that ΔE cannot be constant for the data measured using a standard monochromator because $\Delta \lambda$ is constant for all the data points. So I cannot get the correct spectra as a function of E just by replacing the x-axis values of λ to E using the relationship $E = A/\lambda$.

Considering the one-to-one correspondence of (λ_1, λ_2) and (E_1, E_2) , the experimentally detected light intensity at a certain λ_{av} (and also at E_{av}) should be same,

$$I(\lambda_{av}) = I_e(E_{av}). \quad (A12)$$

With this, I obtain

$$g(E_{av}) \Delta E = f(\lambda_{av}(E_{av})) \Delta \lambda(E_{av}) \quad (A13)$$

Thus, I obtain

$$g(E_{av}) = f(\lambda(E_{av})) \frac{\Delta \lambda(E_{av})}{\Delta E_{av}} \quad (A14)$$

In the limit of $\Delta \lambda \rightarrow 0$ and $\Delta E \rightarrow 0$, with rewriting $E_{av} = E$,

$$g(E) = f(\lambda(E)) \left| \frac{d\lambda(E)}{dE} \right| = f(\lambda(E)) A E^{-2} = f(\lambda(E)) \frac{\lambda(E)^2}{A} \propto f(\lambda(E)) \lambda(E)^2 \quad (A15)$$

Therefore, for the experimental data,

$$I_e(E) \propto I(\lambda(E)) \lambda_{av}(E)^2 \quad (A16)$$

The above relation suggests that I can obtain $g(E)$ by multiplying $f(\lambda)$ with λ^2 for the corresponding E calculated by $E = A/\lambda$. This is the reason of the “ λ^2 correction”.