科学研究費助成事業　　研究成果報告書

平成 ２６ 年　 ６ 月　 ９ 日現在

機関番号：１２６０１
研究種目：若手研究(B)
研究期間：2011～2013
課題番号：２３７６０１８０

研究課題名（和文）ナノカーボン材料を利用した太陽電池作製と評価

研究課題名（英文）Fabrication and evaluation of solar cells employing nanocarbon materials

研究代表者
エイナルソン　エリック　ジー（Einarsson, Erik）

東京大学・工学（系）研究科（研究院）・講師

研究者番号：００５５３６０３

交付決定額（研究期間全体）：（直接経費）　3,400,000円、（間接経費）　1,020,000円

研究成果の概要（和文）：垂直配向単層CNT膜を温度制御した水蒸気にさらし，単層CNTがハニカムセル状に凝集しマイクロ・ハニカム構造を持つ膜自己集合した．成長した単層CNTの膜厚と水蒸気処理の条件によって様々なハニカム構造が得られる．この方法で作ったハニカム膜は，同じく炭素材料である透明伝導膜として使われているバッキペーパーより伝導性も透明度が高いことを明らかにした．

セル内では単層CNTが水平にシリコン基板と良好に接触する構造が自己組織化的に形成されることが分かった．この自己組織化ハニカム単層CNT膜をn型シリコン上に転写し，ヘテロ接合太陽電池を作成した．ドーピングなどを行わずに，5%程度の光変換効率が得られた．

研究成果の概要（英文）：By exposing vertically aligned single-walled CNT films to the vapor of a temperature-controlled water bath, the CNTs self-assembled into a micro-honeyomb structure. The obtained structure was dependent on the nanotube film thickness and the water vapor treatment parameters. We found that the honeycomb structure fabricated by this method exhibited higher transmittance and conductivity than another all-carbon material known as buckypaper.

We found that the single-walled CNTs in the honeycomb cell self-assembled into a flat layer that makes good contact with the underlying silicon substrate. We transferred the honeycomb onto an n-type silicon wafer, forming a heterojunction solar cell. Without doping or other treatment, we found the light conversion efficiency increased by approximately 5%.

研究分野：工学

科研費の分科・細目：機械工学・熱工学

キーワード：垂直配向単層カーボンナノチューブ　自己組織化　ヘテロ接合太陽電池

１．研究開始当初の背景

Single-walled carbon nanotubes (SWNTs) feature outstanding electronic, optical, mechanical, and thermal properties, and hence are considered one of most promising materials for next-generation optical and electronic devices. Indeed, SWNTs have been exploited for photovoltaic and photo-electrochemical cells encompassing all aspects. Currently, SWNT-Si solar cells with high power conversion efficiency (PCE) have emergent technological impact. Randomly oriented SWNT films (so-called "buckypaper") are most intensively investigated for this kind of solar cell. Efforts in improving the properties of randomly oriented SWNT films have improved the PCE and the fill factor (*FF*) substantially. However, these improvements have been realized by chemical modification of the buckypaper, resulting in poor stability. The gap between the superior properties of individual SWNTs and the mediocre performance of their micro/macroscale assembly is hindering the realization of their full potential. Carefully designed SWNT morphologies provide an alternative to efficiently organize the charge generation, separation, and transport at solar-cell interfaces.

Self-assembly is a high-yield, low-cost method that builds low-dimensional materials into 3D micro/macro architectures with various morphologies. Capillary forces have been used to direct the self-assembling of patterned arrays of nanowires, nanopillars, and multi-walled carbon nanotubes (MWNTs) into hierarchical networks. However, because of the hydrophobicity and significantly smaller diameter of SWNTs, wetting vertically aligned SWNTs (VA-SWNTs) results in a high-density bulk with millimeter-scale cracks rather than the hierarchical honeycomb-like network formed by MWNT arrays. So far, such a honeycomb structure of SWNTs has been achieved only by film-casting anionic shortened SWNTs −cationic ammonium lipid conjugates in organic solution− of which the complicated solution preparation induces defects and degradation of SWNTs.

２．研究の目的

Our goal with this research is to develop a simple, gentle self-assembly method by which SWNTs can be utilized in solar cell applications without suffering chemically induced damage or undesired doping.

３．研究の方法

VA-SWNTs were synthesized on Co/Mo dip-coated Si/SiO_2 substrates using our conventional alcohol catalytic chemical vapor deposition (ACCVD) process. The high G/D ratio obtained by Raman spectroscopy demonstrates the SWNTs are of high quality. The average diameter of the VA-SWNTs is approximately 2 nm, and the film thickness is 5 ± 0.2 μm. After ACCVD synthesis, the VA-SWNTs were exposed to vapor from a hot water reservoir. After a fixed time, the substrate was turned over and dried in the ambient environment. Following this treatment the uniform VA-SWNT array had self-assembled into

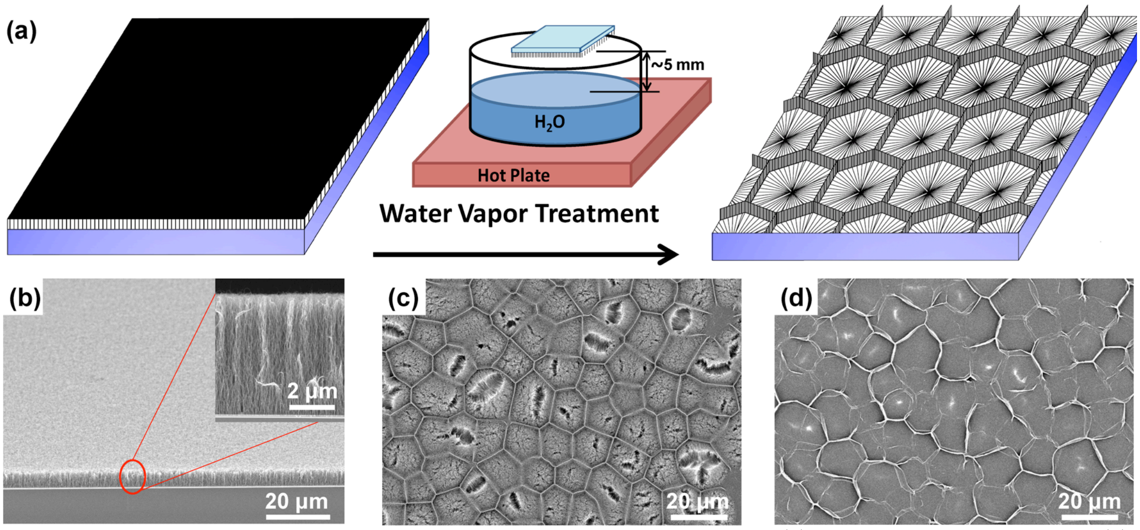

Figure 1: Water vapor treatment of the VA-SWNT array into a μ-HN. (a) Schematic of the process. (b) As-synthesized VA-SWNT with a uniform top surface. (c) Intermediate stage of the μ-HN formation. (d) Stable μ-HN formed after 30 iterations.

hexagonal frames, and by repeating these steps for 20 to 30 iterations the VA-SWNT array evolved into a micro honeycomb network (μ-HN). This process is shown in **Figure 1**.

４．研究成果

The liquid–solid interaction induced by the condensation and subsequent evaporation of water is the tool used to engineer the morphology of VA-SWNTs into a self-assembled μ-HN.

The μ-HN is a hierarchical hexagonal 3D network (Figure 2a) that consists of vertical SWNT walls and a randomly networked SWNT bottom. Each wall is a cross-linked high-density SWNT agglomeration (Figure 2Figure 2b), and the bottom of each honeycomb cell is a randomly oriented buckypaper that results from the collapse of SWNT alignment. The schematic of μ-HN is shown in Figure 2c. This is the most energetically favorable outcome because it uniformly divides the region into cells having minimal perimeter, that is, allows the largest number of SWNTs to collapse. Varying the water reservoir temperature and vapor exposure time of water vapor treatment results in different morphologies.

The self-assembled SWNT films can be transferred onto arbitrary substrates by a hot-water thermocapillary method. The SWNT-Si junction was formed after transferring the self- assembled SWNT film onto an *n*-type Si wafer (doping level ~10^{15} cm^{-3}), which has a 3 mm × 3 mm bare Si contact window in the center (Figure 3a). The current density–voltage (*J–V*) characteristics of the SWNT-Si solar cells fabricated with μ-HN, collapsed HN, and porous HN were obtained under 100 mA/cm^2 AM1.5G illumination (Newport) and dark conditions, as shown in Figure 3b. The pristine μ-HN SWNT-Si solar cell exhibited a high, stable *FF* of 72%, with an ideality factor of 1.71 over the 300–500 mV range (obtained from the slope of the quasi-linear part of the logarithmic scale *J–V* curve under dark conditions). To our knowledge, this ideality factor is the lowest reported thus far (i.e., closest to an ideal device). The PCE value of 5.91% was obtained immediately after the fabrication, and it gradually increased to 6.04% after 3 weeks under ambient conditions (Figure 3b).

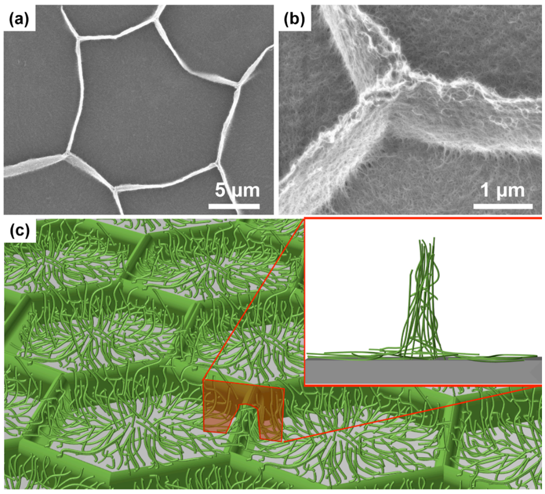

Figure 2: (a) An individual honeycomb cell. (b) Magnified image of the hierarchical structure of μ-HN. (c) Schematic of the μ-HN, with inset showing the hierarchical assembly.

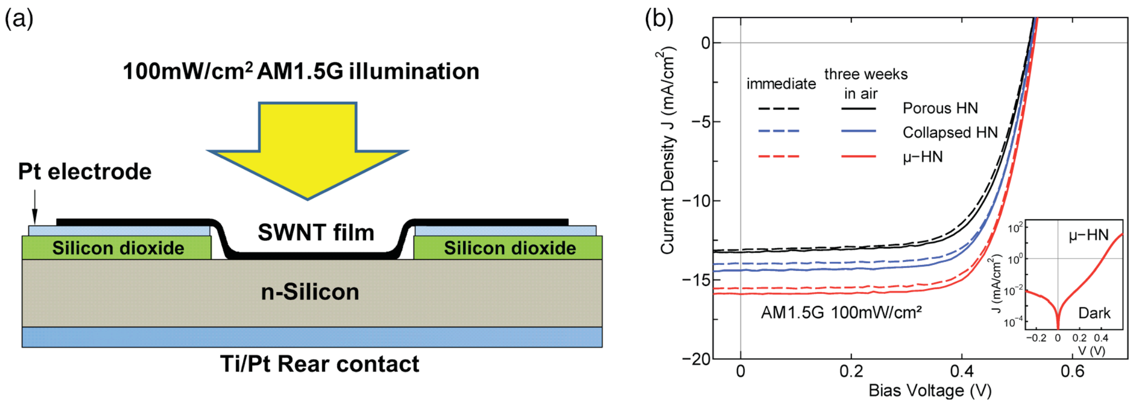

Figure 3 (a) Schematic of SWNT-Si solar cell. (b) *J–V* characteristics of the solar cells fabricated with μ-HN, collapsed HN, and porous HN. Dashed and solid lines denote values obtained within 3 hours of fabrication (immediate) and after being exposed to ambient air for 3 weeks after fabrication. Inset shows the log scale *J–V* curve under dark conditions.

In summary, we report a simple water vapor treatment to engineer the structure of VA-SWNTs into a micro honeycomb network (μ-HN). The hierarchical μ-HN consists of dense walls and a buckypaper bottom, which simultaneously increases the optical transmittance and decreases the sheet resistance. Employing the μ-HN in a SWNT-Si solar cell results in both high photoconversion efficiency and high fill factor. These results were obtained without any efforts made to optimize the SWNT chirality, diameter, or length. We believe the hierarchical μ-HN is very promising for applications of SWNT-Si solar cells.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計 4 件）

1. K. Cui, T. Chiba, S. Omiya, T. Thurakitseree, P. Zhao, S. Fujii, H. Kataura, E. Einarsson, S. Chiashi, S. Maruyama, "Self-Assembled Micro-Honeycomb Network of Single-Walled Carbon Nanotubes for Solar Cell", J. Phys. Chem. Lett., (2013), 4, 2571–2576. DOI: 10.1021/jz401242a]

2. P. Zhao, B. Hou, X. Chen, S. Kim, S. Chiashi, E. Einarsson, S. Maruyama, "Investigation of Non-Segregation Graphene Growth on Ni via Isotope-Labeled Alcohol Catalytic Chemical Vapor Deposition", Nanoscale, (2013), 5, 6530–6537. DOI: 10.1039/C3NR01080E

3. P. Zhao, A. Kumamoto, S. Kim, X. Chen, B. Hou, S. Chiashi, E. Einarsson, Y. Ikuhara, S. Maruyama, "Self-Limiting Chemical Vapor Deposition Growth of Monolayer Graphene from Ethanol", J. Phys. Chem. C, (2013), 117, (20), 10755–10763. DOI: 10.1021/jp400996s

4. R. Xiang, B. Hou, E. Einarsson, P. Zhao, S. Harish, K. Moriyama, Y. Miyauchi, S. Chiashi, Z. Tang, S. Maruyama, "Carbon atoms in ethanol do not contribute equally to formation of single-walled carbon nanotubes during CVD synthesis", ACS Nano, (2013), 7, (4), 3095–3103. DOI: 10.1021/nn305180g

〔学会発表〕（計 10 件）

1. E. Einarsson, T. Thurakitseree, A. Kumamoto, C. Kramberger, S. Chiashi, Y. Ikuhara, S. Maruyama, “Precursor-dependent reversible diameter modulation of vertically aligned single-walled carbon nanotubes”, NT13: Fourteenth international conference on the science and application of nanotubes, 2013 年 6 月 24 日～2013 年 6 月 28 日, Espoo, Finland.

2. K. Cui, T. Chiba, E. Einarsson, S. Chiashi, S. Maruyama, “Self assembled micro-honeycomb network of single-walled carbon nanotubes for heterojunction solar cells”, NT13: Fourteenth international conference on the science and application of nanotubes, 2013 年 6 月 24 日～2013 年 6 月 28 日, Espoo, Finland.

3. S. Maruyama, T. Thurakitseree, C. Kramberger, K. Ogasawara, S. Chiashi, E. Einarsson, “Diameter controlled CVD growth of nitrogen-incorporated single-walled carbon nanotubes”, IWEPNM 2014, 2014 年 3 月 08 日～2014 年 3 月 15 日, Kirchberg in Tirol, Austria

4. T. Thurakitseree, C. Kramberger, S. Chiashi, E. Einarsson, S. Maruyama, “CVD growth control of single-walled carbon nanotubes by nitrogen”, 4th A3 symposium on Emerging Materials: Nanomaterials for Energy and Electronics, 2013 年 11 月 10 日～2013 年 11 月 14 日, Jeju, 韓国

5. K. Cui, T. Chiba, E. Einarsson, S. Chiashi, S. Maruyama, “Self Assembled Micro-Honeycomb Network of Single-Walled Carbon Nanotubes for Heterojunction Solar Cells", JSAP-MRS Joint Symposia, 2013 年 9 月 16 日～2013 年 9 月 20 日，同志社大学・京都府京田辺市

6. S. Maruyama, K. Cui, E. Einarsson, S. Chiashi, "Self-Assembled Micro Honeycomb Network of Single-Walled Carbon Nanotubes for Heterojunction Solar Cells”（招待講演），International

Conference on Nanoscience and Technology China, 2013 年 9 月 05 日～2013 年 9 月 07 日，北京・中国

7. S. Maruyama, K. Cui, T. Chiba, E. Einarsson, S. Chiashi, "Self Organized Micro-Honeycomb Network Structure of Single-Walled Carbon Nanotubes for Photovoltaic Devices" (招待講演), ASME 2013 Summer Heat Transfer Conference, 2013 年 7 月 14 日～2013 年 7 月 19 日, Minneapolis, USA

8. S. Maruyama, K. Cui, T. Chiba, E. Einarsson, S. Chiashi, "Self Assembled Micro-Honeycomb Network of Single-Walled Carbon Nanotubes for Heterojunction Solar Cell", 1st Carbon Nanotube Thin Film Applications Symposium (CNTFA13), 2013 年 6 月 29 日～2013 年 6 月 29 日, Tallinn, Estonia.

9. K. Cui, T. Chiba, E. Einarsson, S. Chiashi, S. Maruyama, "Self-Assembled Micro Honeycomb Network of Single-Walled Carbon Nanotubes for Heterojunction Solar Cell", 7th International Workshop on Metrology, Standardization and Industrial Quality of Nanotubes, 2013 年 6 月 29 日～2013 年 6 月 29 日, Tallinn, Estonia.

10. E. Einarsson, T. Thurakitseree, A. Kumamoto, C. Kramberger, S. Chiashi, Y. Ikuhara, S. Maruyama, "Precursor-dependent reversible diameter modulation of vertically aligned single-walled carbon nanotubes", 7th International Workshop on Metrology, Standardization and Industrial Quality of Nanotubes, 2013 年 6 月 29 日～2013 年 6 月 29 日, Tallinn, Estonia.

〔図書〕（計 1 件）

1. E. Einarsson and S. Maruyama, "Synthesis of carbon nanotubes for photonic applications" in *Carbon Nanotubes and Graphene for Photonic Applications*, S. Yamashita and J.H. Choi (Eds.), Woodhead Publishing, Cambridge, 2013.

〔産業財産権〕

○出願状況（計 0 件）

名称：
発明者：
権利者：
種類：
番号：
出願年月日：
国内外の別：

○取得状況（計 0 件）

名称：
発明者：
権利者：
種類：
番号：
取得年月日：
国内外の別：

〔その他〕

ホームページ等
http://www.photon.t.u-tokyo.ac.jp/

６．研究組織

(1)研究代表者

エイナルソン　エリック　ジー
（EINARSSON, Erik G）
東京大学大学院工学系研究科・講師
研究者番号：00553603

(2)研究分担者

（　　）

研究者番号：

(3)連携研究者

（　　）

研究者番号：