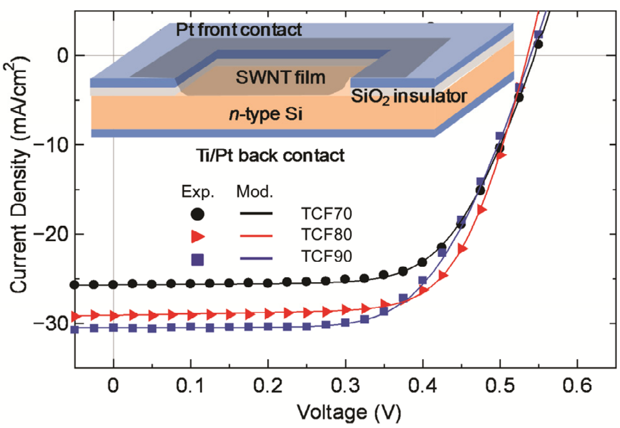
論文の内容の要旨

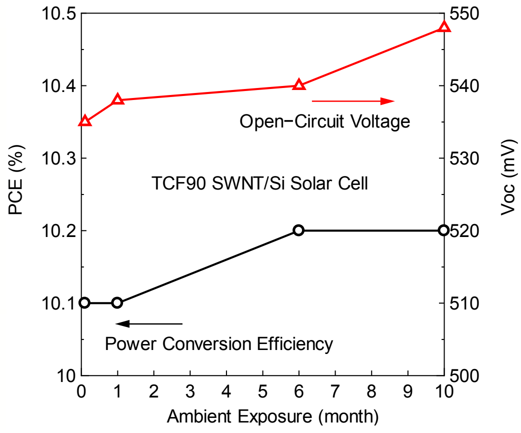
論文題目　　CVD growth control and solar cell application of single-walled carbon nanotubes

（単層カーボンナノチューブの CVD 合成制御と太陽電池応用）

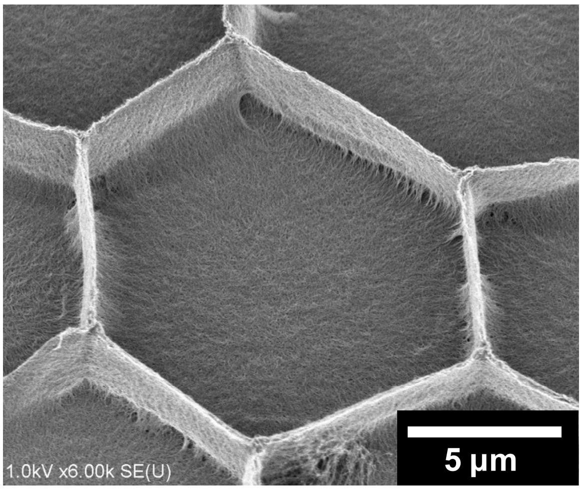
氏　　名　　崔　可航

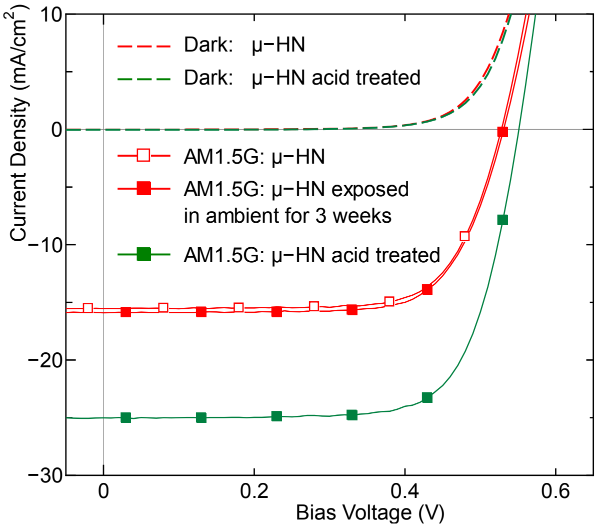
Single-walled carbon nanotubes (SWNTs) possess excellent optical, electrical, mechanical and thermal properties as well as chemical stability. Specifically, for the light harvesting application, SWNTs have the superiorities in terms of the wide spectrum of absorption ranging from near-infrared to visible wavelength, high electrical conductivity at high transparency as well as the multiple exciton generation. Combined with earth abundance and chemical stability, the SWNT is supposed to be a very promising candidate for next-generation solar cell applications. However, three main challenges have hindering the full exploitation of SWNTs for the solar cell applications: (1) The SWNTs synthesized on substrates or by floating catalysts have too large diameter. The reduction of the diameter of SWNTs from 2 nm to 1 nm would lead to the increase of the band gap from 0.5 eV to 1.2 eV which is possible for the applications of solar cells. However, this has not been achieved so far. This is the challenge at the nanoscale. (2) The one-dimensional SWNTs do not grow into a three-dimensional bulk like conventional semiconductors. The gap between the properties of SWNT assemblies and the individual SWNTs is the challenge at the microscale. (2) Before the first two challenges are solved, the technique of amounting SWNTs to photovoltaic devices needs further investigation and understanding, which could be categorized into the challenge at the macroscale. This doctoral thesis aims at controlling the structures and properties of single-walled carbon nanotube (SWNTs) at the macroscale, microscale and nanoscale level for the applications of high-performance solar cells.



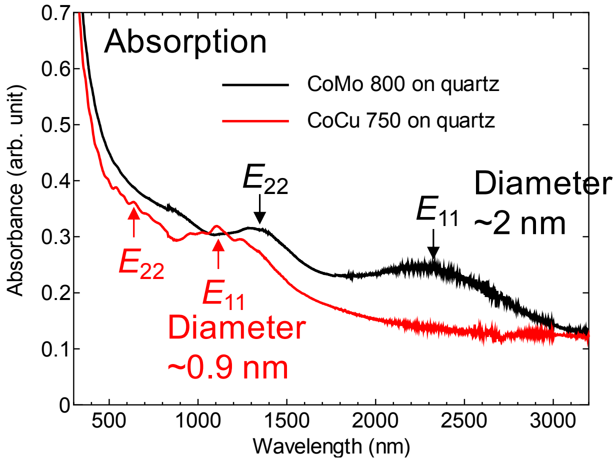


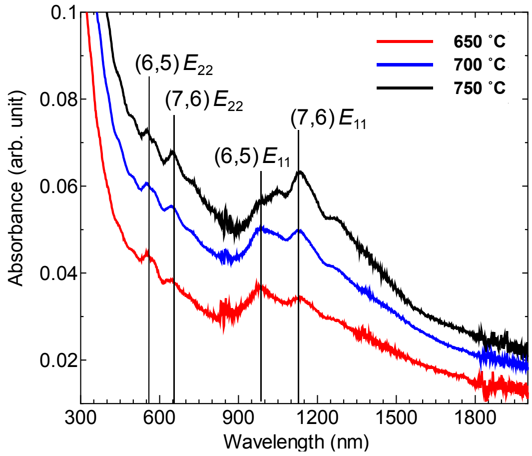
Recently the SWNT/Si solar cells are drawing emerging attentions owing to their simple and efficient structure. The power conversion efficiencies (PCEs) of SWNT/Si solar cells have been improved an order of magnitude during last five years. However, the so-far-reported peak PCEs of the SWNT/Si solar cells were all suffered from degradation, which is hindering their further applications. The SWNT/Si solar cells could lose almost 50% PCE after hours in air, and even with protection, the PCE still degraded by 20%. This could be attributed to that the peak PCEs were boosted by nitric acid or gold salt doping which were very instable. Another issue remained controversial is the working mechanism of the SWNT/Si solar cells. Initially, the SWNT/Si solar cell was proposed as a *p-n* heterojunction. Based on this hypothesis, (6,5) enriched SWNTs were used to further increase the built-in potential. However, the incident photon conversion efficiency (IPCE) spectrum of the SWNT/Si solar cells showed no obvious relationship with the SWNT absorption spectrum. In addition, the efficiency of graphene/Si solar cell became comparable with that of the SWNT/Si solar cell. The SWNT/Si solar cells were considered as a Schottky-barrier junction. One characteristic that could distinguish the *p-n* junction and the Schottky-barrier junction is the effect of the interfacial oxide layer. For a conventional Schottky-barrier junction, inserting an interfacial oxide layer between the metal electrode and semiconductor would eliminate the pinning of Fermi level and thus improve the PCE, while the opposite case applies for a *p-n* junction. Until now, both significant improvement and degradation of the PCEs were obtained after the removal of the interfacial oxide layer. These contradictory results call for more solid experimental proof for the further understanding of the SWNT/Si solar cells. By using the excellent optical and electrical of the pristine SWNTs with long bundle length, we present the single-walled carbon nanotube/silicon (SWNT/Si) solar cells of 11% power conversion efficiency (PCE) without doping. The PCEs of the fabricated solar cells even slightly increased after 10-month ambient exposure without any external protection. The open-circuit voltage of the SWNT/Si solar cells under low light intensities down to 10 mW/cm^2 demonstrated characteristics of the ideal *p-n* junction model. The mechanism was discussed through the effect of varying the interfacial oxide layer thickness between the SWNTs and Si on the solar cell performance. The high efficiency and stability demonstrated in this study make SWNT/Si solar cells one of practical choices for next generation energy system.





Self-assembly is a high-yield and low-cost method that builds low-dimensional materials into three-dimensional 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, due to 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. We propose a water vapor treatment to direct the formation of single-walled carbon nanotubes (SWNTs) into a self-assembled micro-honeycomb network (μ-HN) for the application to SWNT-Si solar cells. The μ-HN consists of vertical aggregated SWNT walls and a buckypaper bottom. This hierarchical structure is much easier to prepare and has competitive optical and electrical properties compared with buckypaper. Varying the water reservoir temperature and vapor exposure time of water vapor treatment results in different morphologies. The pristine μ-HN SWNT-Si solar cell shows a record-high fill factor of 72% as well as a power conversion efficiency (PCE) of 6% without optimizing the diameter or height of the vertically aligned SWNTs. The FF represents the quality of a solar cell, and is one of three parameters characterizing solar cell performance along with V_{oc} and J_{sc}. The significant improvement in FF and ideality factor over previously reported values is attributed to the hierarchical μ-HN, which simultaneously enhances carrier separation, collection and transport. The dense, cross-linked SWNT walls in the μ-HN act as efficient conduction pathways, essentially serving as a micro-grid electrode to collect the charge carriers generated from the adjacent micro-honeycomb cells. The micro-grid configuration in the μ-HN significantly shortens the minimum carrier diffusion path, resulting in more efficient photocurrent collection. In the solar cells fabricated using collapsed HN and porous HN, the micro-grid configuration still exists, which leads to the quite high FFs. The PCE remains stable for weeks in ambient condition, and a PCE exceeding 10% is achieved in the dry state after dilute nitric acid treatment.





We synthesized the vertically aligned SWNT with average diameter as small as 0.9 nm directly on the substrate for the first time. The band gap of the 0.9 nm-diameter SWNTs is 1.1 eV, which is possible to be used for solar cell applications without post-processing techniques, such as separation and dispersion. The key to realize such a small diameter is by using cobalt and copper bimetallic nanoparticle catalysts. When the CVD temperature is decreased to 650 ˚C, the majority of chiralities of the as-synthesized SWNTs is limited to (6,5) and (7,5), which are supposed to the most useful SWNTs for solar cell applications.

To sum up, this doctoral thesis has made original contributions on controlling the structures and properties of single-walled carbon nanotube (SWNTs) at the macroscale, microscale and nanoscale level for the applications of high-performance solar cells: (1) Air-stable high-performance SWNT/Si solar cell with 11% efficiency has been realized for the first time; (2) The self-assembled microhoneycomb network of SWNTs has been proposed and realized for the first time; (3) The vertical-aligned and random-oriented SWNTs with the average diameter of 0.9 nm have realized for the first time.