Graduate School of Advanced Science and Engineering
Waseda University

博　士　論　文　概　要
Doctoral Thesis Synopsis

論　文　題　目
Thesis Theme

Scale up and performance enhancement of carbon nanotube/silicon heterojunction solar cell using molybdenum oxide layer

酸化モリブデン層によるカーボンナノチューブ/シリコンヘテロ接合太陽電池 の大面積化と高性能化

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Solar energy is one of the most important types of energy in the world and is clean and renewable. Solar cell is a device designed to convert solar energy directly into electrical power by the photovoltaic effect. At present, the silicon (Si) solar cells dominate the worldwide photovoltaics market owing to their high-power conversion efficiency (>20%), abundant resources for Si, superior stability (>20 years) and long lifetime. However, manufacturing Si solar cells involves high temperature (~900 ℃) diffusion process and toxic boron/phosphorous gas precursor. a-Si:H/Si heterojunction cells have been developed that can be fabricated at lower temperature, still using toxic gases. The carbon nanotube (CNT)/Si heterojunction solar cell has been developed to lower the cost by directly replacing the a-Si:H (n^+ or p^+) layer with CNT thin film. The CNT/n-Si heterojunction has benefits including simple solution-based process. However, the CNT/Si heterojunction solar cell has poorer stability and lower efficiency than the conventional Si solar cell. Importantly, it is unlikely to reach industrial production due to the difficulty of scaling up of the active area without decreasing its efficiency. In this study, the CNT/n-Si heterojunction solar cell is developed with designs on the cell structure and the fabrication process that are compatible with scale up.

Chapter 1 begins with the background of the Si solar cell, including the physical principle of solar cell operation and the Si heterojunction solar cell fabrication. Then it summarizes the advances and current progress in the CNT/n-Si heterojunction solar cell as well as the challenges for its scalable production. It also reviews the properties of the MoO_x layer and current applications in the CNT film. Compared with the conventional Si heterojunction solar cell, the CNT/n-Si heterojunction solar cell has lower efficiency, poorer stability, and smaller active area. Therefore, it is crucial to introduce some technologies to the CNT/n-Si solar cell for performance enhancement and scalable fabrication such as efficient doping for CNT film and light absorption improvement by additional antireflection coating (ARC) layer via simple, quick, and controllable processes. The potential application of CNT film in flexible solar cell is also proposed. And the importance of integration of the previously developed technologies including rapid vapor deposition of 10 μm-thick crystalline Si film, fabrication of high-quality CNT films, application of metal grid electrodes, combination of MoO_x with CNT film, and coating of ARC layer is discussed toward high performance/cost ratio of the heterojunction solar cells.

Chapter 2 focuses on p-type doping of the CNT film in the CNT/n-Si heterojunction solar cell by spin-coating MoO_x precursor. Doping of the CNT films can enhance the photovoltaic (PV) performance because it can increase the charge carrier density of the CNT film and reduce the sheet resistance and enlarge the built-in potential at the CNT/n-Si heterojunction for more efficient electron/hole separation. Various strong oxidizing agents such as HNO_3 and $SOCl_2$ have been reported as effective hole dopant for CNT film. However, these dopants suffer from instability or volatility in ambient conditions. Compared with these oxidizing agents, transition metal oxides like MoO_x are drawing increasing research interest due to their high work function and stability against volatility. Importantly, the solution-processable MoO_x as an effective hole transport layer has been widely applied in the organic solar cells. But there are no reports that use a solution-processable MoO_x for doping of the CNT layer in the CNT/Si solar cells. Herein, a significant improvement in the performance of the CNT/n-Si solar cell by applying solution-processable MoO_x precursor is demonstrated. The power conversion efficiency (PCE) increases to 10.0%, which is a 39% increase from the pristine CNT/n-Si cell (7.2%). By investigating the effect of the MoO_x on the CNT/n-Si solar cells, it is found that the MoO_x acts as both an efficient chemical dopant for the CNT film and an ARC, which resulted in a reduction in the series resistance and an enhancement of the short-circuit current density of the cell. The stability is a key consideration for the solar cell. Therefore, the stability of the MoO_x-CNT/n-Si solar cell under ambient condition is examined and compared with those of the pristine CNT/n-Si solar cell and the PEDOT:PSS/n-Si solar cell. The device with the MoO_x coating shows considerable stability, maintaining the PCE at 80% of its original value for two months in air without any protective layer. The above experiments are carried out based on the small solar cell (active area of 0.0314 cm^2). Finally, the use of the MoO_x precursor to scale-up the active area of solar cell is explored. However, the efficiency decreases with increasing active area due to the non-uniform MoO_x layer that is caused by the highly hydrophobic surface of the CNT film.

Chapter 3 is about the development of a rapid vapor deposition method of the MoO_x layer for CNT film in the CNT/n-Si solar cell, targeting more uniform deposition of the MoO_x layer on the CNT film. Previously, the MoO_x layer is deposited on the CNT/n-Si solar cell most frequently by evaporation of MoO_3 powder. Here, the MoO_x layer is prepared by thermal evaporation using a Mo boat that was pre-oxidized by heating in air. The MoO_x layer enhanced the PCE significantly from 6.7% to 11.2% for a small cell (active area of 0.0314 cm^2). For the large cell fabrication, it is essential to have a metal grid on the CNT film, but the meal grid directly contacts with n-Si through the pores in the CNT film. The MoO_x deposited on the CNT film fills the pores in the CNT film, thus working as a blocking layer between the metal grid and n-Si. The MoO_x layer also serves as dopant for the CNT film and functions as an ARC. Based on these, the MoO_x-CNT/n-Si solar cells with an active area of ~4 cm^2 are fabricated and the PCE is enhanced significantly from 0.98 % to 3.88%. However, this method is too quick to control the MoO_x thickness carefully.

Chapter 4 reports an improved method for the vapor deposition of MoO_x on the CNT film. Here, the MoO_x is evaporated by heating a Mo wire in O_2/Ar gas, and the deposition rate of MoO_x is adjusted at about 3 nm/min by controlling the feed of O_2. This method has another advantage of the ease of scaling up for industrial production by setting multiple wires. Based on these, a CNT/n-Si solar cell is designed with a scaled-up active-area of ~4 cm^2. This results in an efficiency of 5.4% by introducing MoO_x layer as physical blocking layer, and spin-coating PMMA as an additional ARC layer. The MoO_x layer thickness is optimized to ensure that the MoO_x layer can act as an effective physical blocking layer and keep the CNT electrically contacted with the top metal grid. Moreover, thermal annealing is applied to the MoO_x layer, the annealing condition including temperature and time is carefully adjusted, and the mechanism for the PV performance enhancement is studied. Based on this, a PCE of 9.3% is achieved, that is improved further to 10.2% with the assistance of the ARC layer of PMMA. Finally, the band alignment and dark log*J*-*V* characteristics are analyzed to understand the role of MoO_x in solar cell. These achievements will promote the practice application of the CNT/n-Si solar cell.

Chapter 5 summarizes the conclusions and perspectives. This study discusses the scale-up and performance enhancement of the CNT/n-Si heterojunction solar cell using the MoO_x layer. Three methods are developed to achieve this goal, including spin-coating of MoO_x precursor solution, rapid vapor deposition (<1 min) of MoO_x layer, and vapor deposition of MoO_x using Mo hot wire in O_2/Ar atmosphere. Finally, by optimizing the process conditions and the solar cell structures, the MoO_x-CNT/n-Si solar cell with an active area of ~4 cm^2 and a PCE of 10.2% is obtained with the assist of the PMMA coating as the ARC layer. Moreover, the future plans are discussed. By integrating with existing technologies such as rapid vapor deposition of the 10 μm-thick crystalline Si film, quick coating of CNT thin film, vapor deposition of MoO_x thin film by multiple Mo hot wires in oxygen atmosphere, Ag grid electrodes and the ARC layer will be combined to achieve high performance/cost ratio of the MoO_x-CNT/n-Si heterojunction flexible solar cells.

List of research achievements for application of Doctor of Engineering, Waseda University

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Presentation	3. Xiaoxu Huang, Hisashi Sugime, Suguru Noda*, "Performance enhancement of carbon nanotube/Si heterojunction solar cell by solution-processed MoO_3 layer," 18th Asian Pacific Confederation of Chemical Engineering Congress (APCChE 2019), PE322, Sapporo Convention Center, Sapporo, Japan, Sep. 25, 2019 (poster).
	4. Xiaoxu Huang, Hisashi Sugime, Suguru Noda*, "MoO_x layer with bar electrodes for enlarging active area and improving efficiency of carbon nanotube/n-Si heterojunction solar cells," 10th A3 Symposium on Emerging Materials: Nanomaterials for Electronics, Energy and Environment, P-16, Sungkyunkwan University, Korea, Oct. 27, 2019 (poster).