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学位論文題目	Optical and carrier transport properties of Graphene Oxide(GO) based c-Si/PEDOT:PSS heterojunction solar cells （酸化グラフェンをキーマテリアルとした結晶 Si/ 導電性高分子接合太陽電池の光学的およびキャリア輸送特性に関する研究）
論文審査委員	委員長　教　授　白井　肇 委　員　教　授　酒井　政道 委　員　准教授　上野　啓司 委　員　准教授　柿崎　浩一

論文の内容の要旨

Solar cells based on crystalline silicon (c-Si) p-n junction offer high power-conversion efficiency η of 23-24%, but high temperature process of above 1000˚C is required. The c-Si based heterojunction solar cells with an intrinsic hydrogenated amorphous silicon (a-Si:H) thin layer (HIT) also offer high η values of 22-23% due to higher open-circuit voltage V_{oc} values and a better surface passivation. Here, low-pressure plasma CVD sputtering are used for the fabrication of a-Si:H and indium-tin-oxide (ITO) layers. The alternate approach using organic solar cells (OSCs) have been extensively studied due to their potential as a renewable, alternative source of electricity and their preference in low cost, light weight, mechanical flexibility, and easy processing conditions such as spin-coating. For the hole collection in common solar cells, spin-coated poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is often used to modify the ITO electrode in view of the superior injection/collection properties of the PEDOT:PSS/active layer compared to those of the ITO/active layer interface. But the efficiency of OSCs is not efficient. Recently, efficient c-Si/PEDOT:PSS junction solar cells have been reported. However, little studies on the optical properties and carrier transport in the c-Si/PEDOT:PSS junctions have been performed. In this thesis, the optical and carrier transport properties of the c-Si/PEDOT:PSS(GO) composite heterojunction solar cell devices are demonstrated by optical transmittance, current density-voltage-temperature (*J*-V-T) characteristics, and spectra response measurements. Through systematic studies on optical and carrier transport properties, we found that the GO addition into PEDOT:PSS increased the optical transmittance in the visible-infrared region and the film resistivity. The enhanced electric field at the c-Si/PEDOT:PSS(GO) interface suppressed the electron recombination at the anode. These findings imply that PEDOT:PSS(GO) composite is a possible material as a hole-collecting transparent conductive layer.

論文の審査結果の要旨

Poly(ethylene dioxythiophene):poly(styrene sulfonate)(PEDOT:PSS) is a conductive polymer and has been used as a hole injection layer or as transparent electrodes in organic solar cells (OSCs). There have also been several efforts to enhance the conductivities of PEDOT:PSS including thermal treatment, secondary doping of inert solvents such as ethylene glycerol, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), graphene oxide (GO), and ZnO. Recently, efficient c-Si/organic heterojunction solar cells with several molecule-doped conductive PEDOT:PSS have been reported. Thus, conjugated polymer is also possible candidate for the good passivation layer of dangling bonds at c-Si surface and p-n junction device. Recently, we have demonstrated efficient N-type c-Si(n-Si)/PEDOT:PSS heterojunction solar cells by adding graphene oxide (GO) showing a η of 10.3%. However, the role of the GO addition to conductive PEDOT:PSS is still open question for the photovoltaic performance.

In this thesis, to understand the role of GO addition to PEDOT:PSS, the optical, electrical, and photovoltaic properties of the c-Si/PEDOT:PSS:GO composite heterojunction devices are studied through spectroscopic ellipsometry (SE), optical transmittance, current density-voltage-temperature (*J*-V-T) characteristics, external quantum efficiency EQE, capacitance-voltage (*C*-V), and photoresponse decay measurements.

One-side polished CZ n-Si with a resistivity of 3-5 Ω•cm was used as a substrate. A functionalized GO used in this study was prepared by a modified Hummers method, a chemical oxidation method. The average size of GO flake sheets was 1-5 μm. The commercial product of PEDOT:PSS with a 5 wt% DMSO addition was used for the precursor. GO was highly soluble in an aqueous solution, and therefore, it was well dispersed in the PEDOT:PSS. The pristine PEDOT and PEDOT:PSS:GO composite mixture solutions were spin-coated on n-Si(100) wafer at 1500 rpm for 30s followed by thermal annealing. The two different device structures consisting of n-Si/GO/PEDOT:PSS heterojunction and c-Si/PEDOT:PSS:GO composite solar cells were studied. The *J*-V characteristics were measured in the dark and under light illumination using simulated solar light (AM1.5G, 100mW/cm^2). The η was calculated as $\eta = V_{oc} J_{sc} FF / P_{in}$, where J_{sc} was the short circuit current density and P_{in} was the incident light power. *FF* was determined by $FF = (V_m J_m)/(V_{oc} J_{sc})$, where V_m and J_m were voltage and current density in the maximum power point of the *J*-V curves in the fourth quadrant.

First, the photovoltaic performance of n-Si/PEDOT:PSS heterojunction solar cells with and without inserting a GO layer at the interface was studied. η increased from 8% of the pristine PEDOT:PSS to 9% by adjusting the GO layer thickness of 2.4 nm. Further increase of GO layer thickness, however, increased the series resistance and deteriorated the photovoltaic performance. The *C*-V measurement also revealed that the V_{bi} increased by inserting a GO layer at the n-Si/PEDOT:PSS interface. Thus, the insertion of GO layer at the n-Si/PEDOT:PSS interface is effective to improve the photovoltaic performance. These findings originated from the suppression of the recombination efficiency of dark electron and photo-generated hole at the anode.

Second, we extended the study on the n-Si/PEDOT:PSS:GO composite heterojunction solar cells. The optical and carrier transport properties of n-Si/PEDOT:PSS composite solar cells were investigated with different GO contents. η increased from 6.6% for the pristine PEDOT:PSS to 8.3% for the n-Si/PEDOT:PSS:GO(12.5 wt%) composite diode. The optical transmittance of PEDOT:PSS:GO composite films increased in the entire wavelength of 350-1000 nm by adjusting the GO content. The optical transmittance was in the range of 85-90% at the entire wavelength regions at a GO content of a 12.5 wt%. These results suggest that the charge collection ability of the buffer layer is enhanced and the PEDOT:PSS:GO composite play a role of both hole transport layer and transparent conductive layer. To better

understand the carrier transport properties of n-Si/PEDOT:PSS:GO composite heterojunction diodes, the *J*-V-T, *C*-V, and transient photocurrent measurements were performed for corresponding diodes. The forward and reverse dark current densities decreased with increasing GO content owing to the GO being a highly resistive material. The *J*-V-T characterization revealed that the defect related current transport is dominant with increasing GO content. The transient photocurrent measurement was performed for corresponding diodes to clarify the hole transport property. The two different excitation wavelengths of 355 and 1064 nm by pulse YAG laser were used for the measurement. Here, the measured current mainly originate from the hole transport through organic, c-Si/organic heterojunction and bulk n-Si and their contributions can be clarified by using different excitation wavelengths. The currents decayed exponentially with a single time constant for both wavelengths. For the longer wavelength of 1064 nm, the slower single decay curves were observed with a longer time constant. On the other hand, the use of 355 nm excitation showed both plateu and slower decay time constants for GO added diodes. These findings suggest that the current decay included mainly the information of c-Si/organic interface. The time constant was larger for the GO added PEDOT:PSS diode rather than the pristine PEDOT:PSS diode. The plateu region was observed at the initial stage and the current decayed with a longer time constant when the GO content increased. These results originate from the generation of additional shallow centers by the addition of GO. On the other hand, the current decayed with longer time constant than those by 355 nm, which showed a maximum at a GO content of 12.5 wt% for the 1064 nm excitation. These results imply that the current decay is ruled by trapping and detrapping processes through shallow and deep electron trapping states. Thus, the hole transport was improved by suppressing the electron and hole recombination due to the additional long lifetime electron trapping states.

- Graphene oxide (GO) is a possible material as a hole-transporting layer and a transparent conductive layer in the c-Si/PEDOT:PSS heterojunction solar cells.

- Efficient photovoltaic performance of n-Si/GO/PEDOT:PSS and n-Si/PEDOT:PSS:GO composite heterojunction solar cells showing a power conversion efficiency of 9-11% was obtained.

- Role of GO addition to PEDOT:PSS is the suppression of the carrier recombination of dark-electron and photo-generated hole at the anode due to the increased shallow electron trapping states at the n-Si/PEDOT:PSS.