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論文の内容の要旨

In this thesis, c-Si/Organic heterojunction (HOT) solar cell with solution-processed transparent conductive polymer such as PEDOT:PSS has been investigated, because a single junction of c-Si/PEDOT:PSS works as a photovoltaic device providing low-cost, high-performance solar cell alternative to conventional silicon solar cell. A power conversion efficiency, η has already reached at 10-13% by optimizing the PEDOT:PSS film thickness and the resistivity of silicon substrate without exploiting any light harvesting technique such as textured-Si, AR coating layer, or back-surface field (BSF). The key findings of this work are:

1) The uniform deposition of PEDOT:PSS on textured c-Si by chemical mist deposition: To improve the photovoltaic performance of c-Si/PEDOT:PSS solar cell, texturing of silicon has been performed for efficient light management. But uniform deposition of PEDOT:PSS on textured-Si by spin coating is a challenge. To this aim, chemical mist deposition (CMD) method has been employed for uniform deposition of PEDOT:PSS on textured c-Si substrate. The deposition of PEDOT:PSS has been investigated in terms of cavitation frequency *f*, solvent, flow rate of nitrogen, substrate temperature T_s, and substrate dc bias V_s as variables for efficient c-Si/PEDOT:PSS heterojunction solar cells. The high-speed-camera and differential mobility analysis characterizations reveals that the average size and flux of PEDOT:PSS mist depend on *f*, type of solvent, and V_s. Film deposition occurs when positive V_s is applied to the c-Si substrate at T_s of 30–40°C, whereas no deposition of films occurs with negative V_s, implying that the film is deposited mainly from negatively charged mist. The uniform deposition of PEDOT:PSS films occurs on textured c-Si(100) substrates by adjusting T_s and V_s. The adhesion of CMD PEDOT:PSS film to c-Si has greatly been enhanced by applying substrate dc bias V_s compared with that of spin-coated film. This provides lower carrier recombination at improved Si/PEDOT:PSS interface. The CMD c-Si/PEDOT:PSS heterojunction solar cell device on 2×2cm^2 textured c-Si(100) exhibits a power conversion efficiency, η of 11.0% with better uniformity of the solar cell parameters. Furthermore, η has been increased to 12.5% by the use of isotropically textured-Si and an AR coating layer of molybdenum oxide, MoO_x formed by CMD. These findings suggest that CMD with negatively charged mist has great potential for the uniform deposition of organic

and inorganic materials on textured c-Si substrates by suitably adjusting T_s and V_s.

2) The improvement of transport property of PEDOT:PSS by Nafion: The solar cell performance has been further improved by increasing the conductivity of PEDOT:PSS by incorporating guest molecules such as Nafion. In this work, the chemistry of amphiphilic perfluorosulfonic copolymer-Nafion coated conductive PEDOT:PSS and its effect on the photovoltaic performance of c-Si/PEDOT:PSS heterojunction solar cells have been demonstrated. The highly hydrophilic sulfonate group of insulating, chemically stable Nafion interacts with PSS in PEDOT:PSS, which reduce the coulombic interaction between PEDOT and PSS. The highly hydrophobic fluorocarbon backbone of Nafion favorably interacts with hydrophobic PEDOT of PEDOT:PSS. These factors give rise to the extension of π-conjugation of PEDOT chains. Silver paste used as a top grid electrode diffuses into the Nafion layer and contacts with underneath Nafion-modified PEDOT:PSS layer. As a consequence, solution-processed Nafion-coated c-Si/PEDOT:PSS heterojunction solar cells exhibit a higher power conversion efficiency of 14.0% with better stability for light soaking rather than that of the pristine c-Si/PEDOT:PSS device by adjusting the layer thickness of Nafion. These findings originate from the chemical stability of hydrophobic fluorocarbon backbone of Nafion, diffusivity of silver paste into Nafion and contact with PEDOT:PSS, and functioning of Nafion as an antireflection layer.

3) The enhanced hole blocking capability at rear Si/cathode interface by $Ba(OH)_2$ as hole blocking layer: In this endeavor, the potential of solution-processed barium hydroxide, $Ba(OH)_2$ as a hole blocking layer on the photovoltaic performance of c-Si/PEDOT:PSS heterojunction solar cells has been presented. The UPS study shows that $Ba(OH)_2$ layer reduces the work function of Al cathode from 4.21 eV to 4.10 eV. PCE of the $2{\times}2cm^2$ size solar cell is increased from 12.8 for pristine to 13.6% using a 2-nm-thick $Ba(OH)_2$ layer between c-Si and cathode interface. The PCE is further improved to 14.3% with a short-circuit density J_{SC} of 30.27 mA/cm^2, an open-circuit voltage V_{OC} of 0.632 V, and a fill factor *FF* of 0.75 using a $Ba(OH)_2$ layer between c-Si/cathode and TAPC as a protection layer on top of the device with a remarkable higher stability for air storage compared to the pristine device. This stability improvement originates from the fact that water penetration into the PEDOT:PSS films is effectively blocked by strong ionic interaction between sulfonate anions and protonated bulky TAPC, which in turn, can impede oxidation of this polymer as well as PEDOT:PSS/c-Si interface to a greater extent over time.

4) The efficient back-PEDOT:PSS/c-Si solar cell using $Ba(OH)_2$ as HBL and Nafion as passivation layer: In this attempt, the effect of $Ba(OH)_2$ hole blocking interlayer and Nafion passivation layer on the photovoltaic performance of promising back-PEDOT:PSS/c-Si heterojunction solar cells has been investigated. The backPEDOT or back-contact device structure is preferable to increase the PV performance with higher reliability, suppress the UV damage to front PEDOT:PSS face and remove the optical loss on top grid electrode. In the device, a ~2-nm-thick spin coated $Ba(OH)_2$ has been used as a hole blocking layer at textured Si/Al interface. Nafion has been used as a passivation layer on front Si surface. The PCE of back-PEDOT:PSS/c-Si solar cells is increased from 4.4% for pristine to 8.1 % with better stability for air storage using $Ba(OH)_2$ layer in front c-Si/Al interface together with Nafion as a passivation layer. This remarkable increase in PCE mainly originates from the increased J_{SC} from 23.78 mA/cm^2 to 33.40 mA/cm^2, and V_{OC} from 0.536V to 0.573V, which is due to the efficient hole-blocking and enhanced electron injection capability of solution-processed $Ba(OH)_2$ layer and Nafion as an effective passivation layer for silicon. The stability of the backPEDOT:PSS/c-Si devices is mainly determined by the stability of Nafion passivation over time.

論文の審査結果の要旨

Recently, solution-processed crystalline Si(c-Si)/Organic heterojunction “HOT” (c-Si heterojunction with organic thin layer) solar cell with highly transparent and conductive conjugated polymer poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has been extensively studied. Power conversion efficiency (PCE) of this type of HOT solar cell has reached at 10-13% by adjusting the solvent, the film thickness of PEDOT:PSS, and the resistivity of c-Si substrate without exploiting any light harvesting technique such as textured-Si, AR coating layer, or back-surface field (BSF). However, for further increase in the solar cell performance and reproducibility, several component technologies should be taken into account, which include a) efficient light trapping, b) improved carrier transport property of PEDOT:PSS, c) reduction of contact resistance of c-Si/cathode interface, d) back surface field and so on. To solve these issues, the following items have been studied in this thesis:

Chapter 1: Introduction and motivation

Recent progress of c-Si based photovoltaics is reviewed and the objective of this study is introduced.

Chapter 2: Uniform deposition of PEDOT:PSS on textured c-Si by CMD

In general, textured c-Si is used in c-Si photovoltaic to enhance the light harvesting capability. However, as far as spin coat is used, non-uniform coating of PEDOT:PSS and weak adhesion were observed. To this issue, I attempted to deposit PEDOT:PSS on textured c-Si by chemical mist deposition (CMD) method. In this chapter, the deposition of PEDOT:PSS has been investigated in terms of cavitation frequency *f*, type of solvent, flow rate of nitrogen, substrate temperature T_s, and substrate dc bias V_s as variables. The high-speed-camera and differential mobility analysis characterizations reveals that the average size and flux of PEDOT:PSS mist depend on f, type of solvent, and V_s. Film deposition occurs when positive V_s is applied to the c-Si substrate at T_s of 30–40°C, whereas no deposition of films occurs with negative V_s, implying that the film is deposited mainly from negatively charged mist. The uniform deposition of PEDOT:PSS films occurs on textured c-Si(100) substrates by adjusting T_s and V_s.

The adhesion of CMD PEDOT:PSS film to c-Si has greatly been enhanced by applying substrate dc bias V_s compared with that of spin-coated film. The CMD PEDOT:PSS/c-Si heterojunction solar cell devices on textured c-Si(100) in $2\times2\mathrm{cm}^2$ exhibits an PCE of 11.0% with better uniformity of the solar cell parameters. Furthermore, PCE has been increased to 12.5% by adding an AR coating layer of molybdenum oxide MoO_x formed by CMD. These findings suggest that CMD with negatively charged mist has great potential for the uniform deposition of organic and inorganic materials on textured c-Si substrates by suitably adjusting T_s and V_s.

Chapter 3: Improved transport property and stability for air storage of PEDOT:PSS by guest molecule

In this chapter, the chemistry of amphiphilic perfluorosulfonic copolymer Nafion-coated conductive PEDOT:PSS and its effect on the carrier transport and photovoltaic performance of PEDOT:PSSc-Si heterojunction solar cells have been demonstrated. The highly hydrophilic sulfonate group of insulating, chemically stable Nafion interacts with PSS in PEDOT:PSS, which reduce the coulombic interaction between PEDOT and PSS. The highly hydrophobic fluorocarbon backbone of Nafion favorably interacts with hydrophobic PEDOT of PEDOT:PSS. These factors give rise to the extension of π-conjugation of PEDOT chains. Silver paste used as a top grid electrode diffused into the Nafion layer and contacted with underneath Nafion-modified PEDOT:PSS layer.

As a consequent, solution-processed Nafion-coated PEDOT:PSS/c-Si heterojunction solar cells exhibits a higher power conversion efficiency of 14.0% with better stability for light soaking rather than that of the pristine PEDOT:PSS/c-Si device by adjusting the layer thickness of Nafion. These findings originate from the chemical stability of hydrophobic fluorocarbon backbone of Nafion, diffusivity of silver paste into Nafion and contact with PEDOT:PSS, and Nafion as an antireflection layer.

Chapter 4: Enhanced hole blocking capability at rear Si/cathode interface:

In this chapter, the potential of solution processed barium hydroxide, $Ba(OH)_2$ as a hole blocking layer on the photovoltaic performance of c-Si/PEDOT:PSS heterojunction solar cells has been presented. The UPS study shows that $Ba(OH)_2$ layer can reduce work function of Al cathode from 4.21 eV to 4.10 eV. The XPS study reveals the thermal stability of the layer. The power conversion efficiency (PCE) of the $2\times2cm^2$ size solar cell increases from 12.8 to 13.6% using a 2-nm-thick $Ba(OH)_2$ interlayer between c-Si and cathode interface. The PCE is further increased to 14.3% with a short-circuit density J_{SC} of 30.27 mA/cm^2, an open-circuit voltage V_{OC} of 0.632 V, and a fill factor *FF* of 0.75 using a $Ba(OH)_2$ interlayer between c-Si/cathode and 4,4′-Cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)benzenamine] (TAPC) as a protection layer on top of the device with a remarkable higher stability for air storage compared to the pristine device.

Chapter 5: Efficient back-PEDOT/c-Si solar cell using $Ba(OH)_2$ as HBL and Nafion as passivation layer

In this chapter, the promising the back-PEDOT/c-Si device structure using several component technologies has been introduced. The increased the PV performance with higher reliability is realizable with the use of back-PEDOT or back-contact device structure to suppress the UV damage to front PEDOT:PSS face and to remove the optical loss on top grid electrode. In the device, a 2-nm-thick spin coated $Ba(OH)_2$ has been used as a hole blocking layer at textured Si/Al interface. Nafion has been used as a passivation layer on front Si surface. PCE of back-PEDOT:PSS/c-Si solar cells also increases from 4.4 to 8.1 % with better stability for air storage using $Ba(OH)_2$ interlayer in front c-Si/Al interface together with Nafion as a passivation layer. This remarkable increase in PCE mainly originates from the increased J_{SC} from 23.78 mA/cm^2 to 33.40 mA/cm^2, and V_{OC} from 0.536V to 0.573V, which is due to the efficient hole-blocking and enhanced electron injection capability of solution-processed $Ba(OH)_2$ layer and Nafion as an effective passivation layer for silicon. The stability of the back-PEDOT:PSS/c-Si devices is mainly determined by the stability of Nafion passivation over time.

Chapter 6: Conclusion and remaining issue

In this chapter, the study on interface and hole transport layer for efficient c-Si/Organic heterojunction (HOT) solar cells is summarized together with remaining issue to further increase the photovoltaic performance and stability.