Effects of molybdenum oxide molecular doping on the chemical structure of poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) and on carrier collection efficiency of c-Si/PEDOT:PSS heterojunction solar cells

The effects of MoO$_3$ molecular doping in poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) (PEDOT:PSS) on the chemical structure and, in turn, on the carrier collection efficiency of c-Si/PEDOT:PSS heterojunction solar cells are demonstrated. Scanning electron microscopy revealed that the hydrophilic PSS polymer chain was intercalated into the interlayer van der Waals gap of MoO$_3$ flake sheets, which modified the chemical structure of PEDOT:PSS. MoO$_3$ exhibited intense photoluminescence in the 350-550 nm region, which enhanced the carrier collection efficiency of c-Si/PEDOT:PSS heterojunction solar cells with no significant changes. These findings suggest that the intense photoluminescence of MoO$_3$ and its light wavelength conversion contribute to the increased carrier collection efficiency.

1. Introduction

There has been tremendous interest in developing next-generation photovoltaics based on advanced materials such as quantum dots, semiconducting nanostructures and conjugated polymers.\textsuperscript{1-3} Crystalline silicon (c-Si) remains the basic material for high-efficiency stable photovoltaics, and it has recently been demonstrated that Si nanowire junctions and Si wire arrays from catalytic growth or electrochemical etching can improve light absorption.\textsuperscript{4-6} On the other hand, the integration of different nanostructures or polymers into Si-based photovoltaics has been explored widely, and many heterojunction structures have been reported, such as GaN nanorods epitaxially grown on n-type c-Si, InAs nanorods grown on p-type Si, and multiwalled nanotube (CNT) arrays grown in an anodized alumina template on Si substrates.\textsuperscript{7-9}

Highly conductive poly(3,4-ethylenedioxythiophene):poly (stylenesulfonate) (PEDOT:PSS) is often used to modify indium tin oxide (ITO) electrodes owing to its superior injection/collection properties by secondary doping of novel reagents such as graphene, graphene oxide (GO), CNTs, and metal oxide particles.\textsuperscript{10-13} It is also reported that PEDOT:PSS, GO, and metal oxide such as molybdenum trioxide (MoO$_3$) are good candidates for solution-processable hole-transporting materials that exhibits an intense photoluminescence (PL) emission in the 325-550 nm region and is expected to find application as a light wavelength conversion layer.\textsuperscript{14-17} Furthermore, the MoO$_3$ layer would presumably generate a strong inversion in Si by electrostatic repulsion, as in the cases of dielectric SiO$_x$ and Al$_2$O$_3$\textsuperscript{18-20} Thus, a high built-in voltage, $V_{bi}$, can be expected at the c-Si/PEDOT:PSS:MoO$_3$ composite interface.

In the present paper, we demonstrate the effect of luminescent MoO$_3$ molecular doping to conductive PEDOT:PSS on the chemical structure and external quantum efficiency (EQE) of n-type c-Si(100)/PEDOT:PSS heterojunction solar cells.
2. Experimental details

The c-Si wafer (CZ, 3-5 Ω·cm, 300 μm thickness) was cleaned by the RCA1 and RCA2 procedures. Highly conductive PEDOT:PSS (Clevios PH1000) with 5 wt% DMSO was used as a starting solution. MoO$_3$ (Kanto Kagaku Ltd. 99.99%) powder flake with an average size of 1.7 μm were used as a dopant. PEDOT:PSS:MoO$_3$ composite solutions with different MoO$_3$/PEDOT:PSS+MoO$_3$ (1, 3, 10, and 30 wt%) were stirred for 1h. As the PEDOT:PSS:MoO$_3$ solution was then stirred for 1h. Here, as the PEDOT:PSS solid content of PH1000 is around 1%, the dry weight ratios of MoO$_3$/PEDOT:PSS composite thin films were much higher than the values reported in present paper, for example, in the case of the 1 wt% composite, the real dry weight ratio of MoO$_3$/PEDOT:PSS was almost unity. A thin film was formed by spin-coating the precursor solution on RCA-cleaned c-Si wafers at 1000 rpm for 60 s, followed by thermal annealing at 140˚C for 30 minutes. Finally, a top Ag grid electrode was fabricated by pattern printing. The PEDOT:PSS:MoO$_3$ composite films were characterized using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and spectroscopic ellipsometry (SE). The PL spectra were measured using FluoroMax-3 (Horiba Jovin-Yvon) spectrophotometer.

3. Results and discussion

Figure 1(a) shows the SEM image of MoO$_3$ particles in conductive PEDOT:PSS. The inset shows the crystal structure of MoO$_3$. MoO$_3$ exhibits a layered structure consisting of vertex-sharing chains of distorted MoO$_6$ octahedra that share edges with two similar chains to form layers. The distortion gives rise to very short “Mo=O” bonds at the apical octahedral positions that terminate the top and bottom of the double-octahedral oxide sheets.

![SEM images and EDX maps](image)

FIG 1 SEM images (a-c) and EDX maps (d-f) (corresponding to the circled region in Fig. 1 (a)) of MoO$_3$ particle in PEDOT:PSS. Inset illustrates crystal structure of MoO$_3$ where red and gray spheres denote O and Mo atoms, respectively; (b) and (c) show the novel hair-like structure. (d), (e), and (f) are the EDX maps for Mo, O, and S, respectively, in MoO$_3$ doped PEDOT:PSS.

The resultant two-dimensionally bonded layers are stacked in a staggered arrangement and held together by weak van der Waals forces. A variety of large guest species can be intercalated into the interlayer van der Waals gap. The SEM image shows a hairlike projections around the MoO$_3$ flake sheets with an average diameter of 15~20 nm which is much smaller than the typical mean size of PEDOT particles embedded in PSS chains. EDX maps of Mo, O, and S for the PEDOT:PSS:MoO$_3$ (3 wt%) composite are shown in Figs. 1(d)-(f). Notably, the EDX image of Mo was almost consistent with that of S despite the use of MoO$_3$, and even though S was distributed homogeneously. This implies that
the sulphur in PEDOT and/or PSS is coordinated preferentially in MoO$_3$ particle. In addition, the average $d$ spacing of the collected composite powder, as calculated from the four 060 reflections in the XRD spectra, was 0.9-1.1 nm, i.e., larger than that of pristine MoO$_3$ (0.6 nm). Furthermore, XPS revealed that the 3d binding energy corresponding to S=O in PSS decreased less for higher MoO$_3$ concentrations. These findings suggest that the concentration ratio of PEDOT to PSS increased. Thus, the PSS chain was intercalated into the MoO$_3$ flake sheet, modifying the chemical structure of PEDOT:PSS conjugated polymer.

Figure 2 shows the PL spectra of pristine MoO$_3$ and PEDOT:PSS:MoO$_3$ composite films at room temperature and the excitation PL (PLE) spectra for the 400 nm emission. Optical micrographs of PEDOT:PSS with and without MoO$_3$ doping are shown as well. An intense broad band PL emission at 350-500 nm having a maximum peak at around 390-400 nm was observed, and its intensity increased with MoO$_3$ doping concentration. Thus, the UV light at 310-345 nm was absorbed and efficiently showed an intense broadband PL emission at ~400 nm. In fact, the MoO$_3$-doped PEDOT:PSS micrograph was deep purple, owing to the intense PL emission at 350-550 nm from MoO$_3$. These results suggest that MoO$_3$ may potentially be used for absorbing light at short wavelengths and then emitting at longer wavelengths (350-550 nm), which would enhance the carrier collection efficiency of c-Si/PEDOT:PSS solar cells.

Figure 3(a) shows the current density-voltage ($J$-$V$) curves obtained under AM1.5 100 mW/cm$^2$ simulated solar light (Bunkoukeiki CEP-25BX) for c-Si(100)/PEDOT:PSS:MoO$_3$ composite heterojunction solar cells with different MoO$_3$ doping concentrations. The inset is a schematic of a c-Si/organic heterojunction solar cell. The effective area of each cell was 5×5 mm$^2$. $\eta$ was calculated via $\eta = V_{oc} J_{sc} FF P_{in}$, where $V_{oc}$ is the open-circuit voltage, $J_{sc}$ is the short-circuit current density, $FF$ is the fill factor, and $P_{in}$ is the incident light power. $FF$ is determined via $FF = (V_m J_m)/(V_{oc} J_{sc})$, where $V_m$ and $J_m$ are, respectively, the voltage and current density in the maximum power in the fourth quadrant of the $J$-$V$ curves. The reverse and forward dark currents were suppressed to below the values for a pristine PEDOT:PSS diode. $\eta$ increased to 11.01% with a $J_{sc}$ of 29.4 mA/cm$^2$, a $V_{oc}$ of 0.552 V, and an $FF$ of 0.683 at a MoO$_3$ concentration of 1 wt%.
$J_{sc}$ increased with MoO$_3$ doping concentration up to 3 wt%. However, $V_{oc}$ and $FF$ decreased markedly with further increase in MoO$_3$ concentration, due to the increased series resistance, $R_s$. The $1/C^2$-$V$ plot at 1 MHz also showed a relatively high $V_{oc}$ of 0.9-1 eV, resulting in a higher $V_{oc}$ than that of pristine PEDOT:PSS. The EQE and difference EQE (DEQE) spectra for solar cells with different MoO$_3$ doping concentrations are shown in Fig. 3(b). Here, the DEQE values are relative to that of a pristine c-Si/PEDOT:PSS solar cell, DEQE was found to be positive over the entire wavelength region of 350-1200 nm for a MoO$_3$ concentration of 1-3 wt%. At high MoO$_3$ doping concentrations of up to 10-30 wt%, DEQE was markedly enhanced in the 350-550 nm regions, with a shorter wavelength shift, but the values in the infrared region of 900-1200 nm were negative. It has been reported that polar solvent such as MeOH and ethylene glycol modify the chemical structure of PEDOT:PSS and that the phase separation of PEDOT-PSS enhances the hole mobility of PEDOT:PSS by increasing conduction path network of PEDOT chains. These findings suggest that the increased EQE in the 350-550 nm region of c-Si/PEDOT:PSS:MoO$_3$ composite heterojunction solar cells is due to the PL emission of MoO$_3$.

The PLE and PL spectra of pristine MoO$_3$ are shown in Fig. 4(a). The EQE and DEQE spectra of c-Si/PEDOT:PSS solar cells with and without a 30 wt% MoO$_3$ doping and spectroscopic sensitivity of sunlight are also included. The PL spectra at 360-510 nm can be ascribed to the intense near-band-edge (NBE) emission due to the free-exciton recombination and visible light emission by transitions of excited optical centers in the deep levels (DLs). The UV absorption between 310-345 nm led to visible PL emission in the 360-510 nm range. This visible wavelength region corresponds to those of the increased DEQE for c-Si/PEDOT:PSS:GO composite solar cells.

The reflectance spectra for PEDOT:PSS:MoO$_3$ composite films, as determined by SE spectra analysis, are shown in Fig. 4(b). The reflectance spectra in the UV region corresponding to the absorption of c-Si decreased slightly by MoO$_3$ doping, but no significant changes were observed. AFM revealed that the degree of RMS roughness was 3-9 nm ($5\times5$ μm$^2$), which is less than that of light trapping. Thus, the improved EQE in the
350-550 nm region does not result from MoO$_3$ acting as an anti-reflection layer but from the enhanced optical absorption in this region owing to the PL emission from MoO$_3$. The RMS roughness of the thin film examined by AFM was around 9 nm, up to a MoO$_3$ doping concentration of 10 wt%, which is negligibly small for a light-harvesting structure, as compared with that of textured Si(100). However, the EQE in the infrared region of 900-1200 nm deteriorated at a MoO$_3$ doping concentration above 10 wt% due to the increased optical reflectivity.

4. Conclusions
We studied the effect of MoO$_3$ molecular doping to conductive PEDOT:PSS on the chemical structure and photovoltaic properties of c-Si/PEDOT:PSS heterojunction solar cells. The MoO$_3$ molecular doping modified the chemical structure of PEDOT:PSS by the intercalation of PSS into the van der Waals gap of MoO$_3$ sheets. These changes enhanced the photovoltaic performance of the c-Si/PEDOT:PSS solar cells. η increased up to 11.0%. The UV absorption and intense PL emission at 350-550 nm increased the carrier collection efficiency in c-Si/PEDOT:PSS heterojunction solar cells.

References
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