Improved Performance of Film Dye Sensitized Solar Cell Using Atmospheric Pressure Microplasma

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Abstract—This paper introduce the surface modification for film dye sensitized solar cells (film DSSCs) using atmospheric pressure microplasma as a damage less surface treatment process. The photo conversion efficiency was improved by about 0.3% - 0.6% after O2 or Ar microplasma treatment. Dye adsorption amount owing to the increase of OH bonds and surface defects on TiO2 surface were increased after both microplasma treatments. The effects of the microplasma treatments on DSSSs surface were analyzed by photovoltaic measurements, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) analysis.

Keywords—Microplasma, dielectric barrier discharge, dye sensitized solar cells, surface modification

I. INTRODUCTION

In 1991, Grätzel and O’Reagan reported the dye sensitized solar cells (DSSCs) which are based on titanium oxide [1]. The DSSCs are well known as cost-effective technology and high photo-conversion efficiency devices [2-7]. Solar energy conversion efficiency have been achieved up to 13% [8]. In recent years, film DSSCs have been gathered much attention. Film DSSCs have many advantages, the low-cost of raw materials, faster manufacturing time, and the designability owing to flexible substrates in comparison with silicon solar cells. Although many advances have been made in film DSSCs fabrication of late years, their photo-conversion efficiency remains lower than glass substrate DSSCs and Si-based solar cells. The lower photo-conversion efficiency of film DSSCs are owing to low calcination temperature compared with glass substrate DSSCs.

One method for the surface treatment for DSSCs is the chemical process [9-12]. This process is potentially harmful to the human body and the environment. Surface modification of DSSCs by various plasma treatments has been reported, to increase the solar conversion efficiency using RF-plasma [13-16], vacuum deposition [17-22], dielectric barrier discharge [23, 24], and plasma jet [25-27].

The plasma processes mentioned above were performed under extreme parameters: low pressure or high temperature and so on. By using atmospheric pressure plasma, there is advantage that a vacuum device is not required. This paper introduces improvement of the photo-conversion efficiency of film DSSCs using atmospheric pressure microplasma at room temperature. The binder-free titanium oxide paste which is used typically for film DSSCs was the target in this study [28, 29]. We report for the first time on the binder-free TiO2 pastes of film DSSCs that have been improved using atmospheric pressure microplasma as a post process.

II. EXPERIMENTAL SETUP

A. Microplasma Electrodes

Fig. 1 shows a schematic image of microplasma electrodes for surface modification of titanium oxide surface. The microplasma electrodes are perforated metallic plates covered with a dielectric layer. The dielectric constant is about $\varepsilon_r = 10^4$. These electrodes are faced each other with a spacer (thickness is 100 µm) as a small discharge gap. A relatively low discharge voltage (about 0.5-2.0 kV$_{0-p}$) is required to obtain a high-intensity electric field ($10^7$-$10^8$ V/m) due to this electrode structure [30, 31]. The diameter of electrode is φ60 mm. The electrodes have φ2 mm holes for the process gas flow and aperture ratio is 30%.

The microplasma was generated by applying a high voltage to microplasma electrodes. The active species such as radicals and ions generated by microplasma were flowed by the process gas and affected the target surface [32, 33].

An image of Ar microplasma is show in Fig. 2. Microplasma was generated around the holes. The discharge area can be limited by a spacer.
B. Protocol of Making Process of Film DSSCs

The binder-free titanium oxide paste for low temperature calcination (Peccell PECC-01-06) was used for preparing the working film DSSC’s electrode. The binder-free titanium oxide paste was coated on the ITO transparent film (Thickness is 100 µm) using a squeeze printing process. The TiO$_2$ electrode was calcined 15 min at 120°C in the air. The calcined TiO$_2$ electrodes were treated using atmospheric pressure microplasma. The plasma treated electrodes were immersed in a 0.3 mM N719 dye solution for 22 h. The counter electrode was used as the glass substrate coated with Pt. The TiO$_2$ electrode and the counter electrode were faced together and held with binder clips. The electrolyte (EL-A1 TOMYPURE) was used and injected between two electrodes. The area of TiO$_2$ film was set at 0.25 cm$^2$.

C. Experimental Setup

The experimental set up for surface modification of TiO$_2$ film on the indium tin oxide (ITO) transparent electrode using atmospheric pressure microplasma is shown in Fig. 3.

A neon-sign transformer (LECIP αNEON M-1H) is used as a power supply to apply an AC high voltage to the microplasma electrode. The sample and microplasma electrodes were placed into a chamber which volume was 1.0 L to control the ambient gas. O$_2$ gas (O$_2$ >99.9%) and Ar gas (Ar>99.999%) were used as process gases. The process gas was fed to microplasma electrodes from gas cylinder. The flow rate of both process gases was set at 5.0 L/min. Before carrying out each experiment, the process gases were flowed for about 1 min in the chamber. Thus, the effect of impurity components in the chamber was minimized. The distance between the grounded electrode and the sample was fixed to 1 mm. The treatment time was set at 15 min in all experiments.

Fig. 3 shows waveforms of O$_2$ microplasma discharge. The current spikes owing to streamer were observed in the discharge current. This phenomenon is the feature of dielectric barrier discharge [34]. The applied voltage of O$_2$ microplasma and Ar microplasma were set at 1.6 kV zero to peak and 0.6 kV zero to peak, respectively. The power consumption was calculated from the area of Lissajous figure. A 33 nF capacitor was connected between the grounded electrode and ground to measure the Charge-Voltage Lissajous figure of microplasma. The power consumption of O$_2$ microplasma and Ar microplasma were 3.8 W and 2.6 W, respectively.
The surface temperature characteristics of microplasma electrodes during treatment process shown in Fig. 5 were measured using a thermographic camera (Avio TVS-200) to evaluate the thermal effect of the film DSSCs. The surface temperature was under 40°C after 15 min discharge. The surface temperature is low enough not to affect the calcination of film DSSCs.

The current-voltage (I-V) characteristics and various parameters of the sample were measured under the Air Mass 1.5 solar light using a solar cell evaluation system (JASCO CEP-25BX). X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-3400) was used to analyze the chemical composition of the TiO$_2$ surface. Ultraviolet-visible absorption spectroscopy (UV-VIS, Shimadzu UV-1600PC) was used to measure the dye absorption amount. The TiO$_2$ surface before and after treatment was observed by Scanning electron microscopy (SEM, JEOL JSM-7001F).

III. RESULTS

A. Photovoltaic Measurements

Fig. 6 (a) and Table I show the comparison of I-V characteristics between control samples and O$_2$ microplasma treated samples. Five samples were treated simultaneously in each microplasma treatment experiment. Fig. 6 shows median sample of each treatment experiment. As shown in Fig. 6 (a), the short circuit current density ($J_{SC}$) and the solar conversion efficiency ($\eta_C$) of the control sample were 3.56 mA/cm$^2$ and 1.37%, respectively. After O$_2$ microplasma treatment, $J_{SC}$ and $\eta_C$ were increased to 4.80 mA/cm$^2$ and 1.99%, respectively.

Also, Fig. 6 (b) and Table II show the comparison of I-V characteristics between control samples and Ar microplasma treated samples. $J_{SC}$ and $\eta_C$ of the control sample were 3.81 mA/cm$^2$ and 1.53%. After the Ar microplasma treatment $J_{SC}$ and $\eta_C$ were increased to 4.79 mA/cm$^2$ and 1.87%, respectively. There was about 10% error at a maximum in control samples owing to simple manufacturing of film DSSCs. The open circuit voltage ($V_{OC}$) and fill factor (FF) between control sample and microplasma treated sample did not have significant changes before and after the treatment process.

B. Chemical Analysis of the TiO$_2$ Surface using XPS

Chemical bonds on TiO$_2$ surface were analyzed by XPS to evaluate the surface state. There are some reports on XPS analysis of TiO$_2$ surface treated by various kinds of plasma. In this study, Ar species or O$_2$ species generated by an atmospheric pressure microplasma mainly contribute to surface modification of the TiO$_2$ surface.

Fig. 7 shows XPS spectra of O 1s peaks on the TiO$_2$ surface before and after microplasma treatments. The O 1s spectra were divided into 2 peaks, Ti-OH peak and Ti-O peaks. Table III shows the atomic concentration of O 1s peak on the TiO$_2$ surface. The surface stoichiometry was determined by calculating the relative peak area as the ratio from the total area for each peak in XPS spectra. The Ti-OH peak in O 1s spectra was increased from 16.4 to 21.3% after O$_2$ microplasma treatment and was increased from 16.4 to 24.4% after Ar microplasma treatment, respectively. Improvement of hydrophilicity on TiO$_2$ surface was observed after both microplasma treatments.

![Fig. 6](image)

**TABLE I**

<table>
<thead>
<tr>
<th>Condition</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta_C$ (%)</th>
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<tbody>
<tr>
<td>Control</td>
<td>3.56</td>
<td>0.70</td>
<td>0.55</td>
<td>1.37</td>
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<tr>
<td>O$_2$ microplasma</td>
<td>4.80</td>
<td>0.74</td>
<td>0.56</td>
<td>1.99</td>
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**TABLE II**

<table>
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<tr>
<th>Condition</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta_C$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>3.81</td>
<td>0.74</td>
<td>0.54</td>
<td>1.53</td>
</tr>
<tr>
<td>Ar microplasma</td>
<td>4.79</td>
<td>0.74</td>
<td>0.55</td>
<td>1.87</td>
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</tbody>
</table>

**TABLE III**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic concentration [%]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Ti-OH</td>
</tr>
<tr>
<td>Control</td>
<td>16.4</td>
</tr>
<tr>
<td>O$_2$ microplasma</td>
<td>21.3</td>
</tr>
<tr>
<td>Ar microplasma</td>
<td>24.4</td>
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</table>
Fig. 8 shows XPS spectra of TiO₂ surface. The Ti 2p spectra have been analyzed for four peaks, Ti⁴⁺ 2p₁/₂, Ti⁴⁺ 2p₃/₂, Ti³⁺ 2p₁/₂, and Ti³⁺ 2p₃/₂. Table IV shows the atomic concentration of Ti 2p peaks on the TiO₂ surface. 4 peaks in Ti 2p spectra were grouped as Ti⁴⁺ site and Ti³⁺ site. The Ti³⁺ site in Ti 2p XPS spectra increased from 4.0 to 6.2% after O₂ plasma treatment and increased from 4.0 to 5.3% after Ar plasma treatment. Surface defect concentration was increased after both plasma treatments.

C. Estimation of Dye Adsorption Amount

There are several reports of surface defect and electron transfer in the DSSCs [35, 36]. The photo generated electrons can easily flow through surface defect toward ITO surface rather than the bulk surface. The TiO₂ surface Ti³⁺ site may play an important role to transfer the electrons. Also, the Solar cell electron life time tend to be longer owing to the increase of Ti³⁺ surface defect. It is considered that these effects may improve the performance of film DSSCs [15, 37].

C. Estimation of Dye Adsorption Amount

The dye adsorption amount was measured by UV-VIS. The adsorbed sample was soaked to the sodium hydroxide solution to dissolve the N719 dye. The adsorption amount was calculated from calibration curve. The dye adsorption was increased after both plasma treatments as shown in Fig. 9. Five samples were treated by each microplasma treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic concentration [%]</th>
<th>Ti⁴⁺</th>
<th>Ti³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>4.0</td>
<td>96.0</td>
<td></td>
</tr>
<tr>
<td>O₂ microplasma</td>
<td>6.2</td>
<td>93.8</td>
<td></td>
</tr>
<tr>
<td>Ar microplasma</td>
<td>5.3</td>
<td>94.7</td>
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</table>
The dye adsorption consists of ester bonds between hydroxide groups on TiO$_2$ surface and carboxy groups of N719 dye as shown in Eq. 1 [38].

$$\text{Ti-OH} + \text{COOH-R} \rightarrow \text{Ti-OOC-R} + \text{H}_2\text{O} \quad (1)$$

Chemical modification of hydrophilic group occurred and improved the hydrophilicity on TiO$_2$ surface. TiO$_2$ surfaces tend to make more ester bonds after both microplasma treatments. Increase of dye adsorption amount contributed to current density.

D. SEM Analysis

As shown in Fig. 10, images of the TiO$_2$ surface before and after treatment were taken by FE-SEM. The magnification was set at 30000 times. No significant change on the TiO$_2$ surface was observed for both plasma processes. After plasma treatment using atmospheric pressure microplasma, the TiO$_2$ surface was not changed in physical appearance such as etching effect but only in chemical composition.

IV. DISCUSSION

O$_2$ microplasma treatment and Ar plasma treatment improved the performance of film DSSCs owing to the increase of current density. XPS results showed the increase of Ti-OH peak and Ti$^{3+}$ site. Increase of Ti-OH peak improved the hydrophilicity on TiO$_2$ surface. The surface changes of the TiO$_2$ surface could be considered the effect of active species in O$_2$ or Ar microplasma. The impurities in the chamber could generate active species such as OH radicals. This phenomenon contributes to the surface modification, when pure O$_2$ and Ar gas were used as process gases. Dye adsorption amount was increased after both microplasma treatments. Since, the bonds between TiO$_2$ surface and the N719 dye is consisted of the ester bonds. An increase of OH bonds tends to make more ester bonds and increase the dye adsorption amount.

Therefore, the photo generated electron was increased and current density was improved. After both microplasma treatments, surface defect concentration (Ti$^{3+}$ site) was increased. Ti$^{3+}$ site can operate more effectively the electron diffusion and extend the photogenerated electron’s lifetime. SEM analysis showed no significant changes such as etching effect. Physical effect was not contributed to the increase of dye adsorption amount.

V. CONCLUSION

Surface modification of film DSSCs using atmospheric pressure microplasma was carried out and the following conclusions were obtained:

1. The conversion efficiency was improved by about 0.6% after 15 min of O$_2$ microplasma treatment. After 15 min of Ar microplasma treatment, the conversion efficiency was improved by about 0.3%. The current density was increased after both treatments. Increase of current density contributed to the improvement of the film DSSCs performance.

2. XPS analysis showed that OH peak increased in the TiO$_2$ surface. Chemical modification of hydrophilic
group occurred and improved the hydrophilicity on TiO₂ surface. Increase of dye adsorption amount owing to chemical modification of hydrophilic group was observed after both microplasma treatments.

3. XPS analysis showed that Ti³⁺ site increase in the TiO₂ surface. This change showed the defect content occurred on TiO₂ surface. Ti³⁺ site may play an important role to inject electron to conduction band of TiO₂ film.

4. SEM analysis showed no significant changes before and after microplasma treatment. Physical appearance such as etching effect was not obtained.

REFERENCES


