Plasma Treatment of Semiconductor Electrode for the Improvement of Dye-sensitized Solar Cell

H. Yamane, S. Matsushima, H. Nakamura, K. Yamada

Department of Materials Science and Chemical Engineering,
Kitakyushu National College of Technology, Kitakyushu, Japan

Abstract: Dye sensitized solar cell was assembled using TiO\textsubscript{2} nanoparticle with argon-nitrogen plasma treatment and CuBi\textsubscript{2}O\textsubscript{4} sputtering electrode prepared by plasma irradiation. The electric property of the solar cell fabricated by plasma treated TiO\textsubscript{2} nanoparticle was improved because the physical and chemical property of TiO\textsubscript{2} particles affected from the nitrogen plasma treatment.

Keywords: Dye sensitized solar cell, TiO\textsubscript{2} nanoparticle, CuBi\textsubscript{2}O\textsubscript{4} sputtering

1. Introduction

Dye sensitized solar cell (DSC) having high efficiency with low cost was first reported by Grätzel et al. [1]. Figure 1 shows the schematic presentation of DSC. The semiconductor materials such as titanium dioxide (TiO\textsubscript{2}) were used for the electrode of DSC, and the property of DSC would be depended on this semiconductor electrode. In our previous work, the influence of TiO\textsubscript{2} electrode thin film treated directly by argon plasma to the light to electric energy conversion efficiency in DSC was investigated. We found the necessary to optimize the condition of plasma treatment to electrode for obtaining higher conversion efficiency in DSC [2-4].

On the other hand, another type of DSC, tandem type DSC composed of n type and p type semiconductor electrode was reported to improve the photovoltaic property of DSC [5].

In this paper, two types of DSC were constructed from plasma treated TiO\textsubscript{2} or CuBi\textsubscript{2}O\textsubscript{4} plasma sputtering electrode, and the mechanism of effect on the characteristics of DSC using plasma treated electrode tried to be found out.

2. Experiments

2.1. Sample preparation

TiO\textsubscript{2} nanoparticles (called P25, Degussa Co., Dusseldorf, Germany) and CuBi\textsubscript{2}O\textsubscript{4} were used as semiconductor electrode of DSC. CuBi\textsubscript{2}O\textsubscript{4} powder was prepared following the previous report [6]. The powder of CuO and Bi\textsubscript{2}O\textsubscript{3} were pounded in mortar with molar ratio 1 to 1. The grained powder was calcined in a furnace at 973 K for 24 hours. Finally, the coagulated CuBi\textsubscript{2}O\textsubscript{4} powder was pound up for characterization and constructing of DSC electrode.

2.2. Plasma treatment of TiO\textsubscript{2} nanoparticle

A round bottom flask type reactor was used for treating the particles with inductively coupled plasma generated by a radio frequency generator operating at 13.56 MHz. The particles evacuated for a day in the reactor were pretreated with argon plasma with the condition of 200 W discharge power at 15 Pa of argon gas for 45 min. After that, the particles were treated with nitrogen plasma at 200 W and 30 Pa with N\textsubscript{2} gas for 20 to 100 min.

2.3. Characterization of TiO\textsubscript{2} particles after plasma treatment

X-ray photoelectron spectroscopy (XPS) measurement of the film was carried out with a Shimadzu ESCA750 X-ray photoelectron spectrometer (Shimadzu Co., Kyoto, Japan) to determine changes in the surface structure after plasma treatments. XPS spectra were collected by exciting the particle without pre-treatment with a Mg K\textsubscript{a} X-ray source. Mg K\textsubscript{a} radiation was generated with a voltage of 8 kV and current of 30 mA. The spectrometer was calibrated using the Ag\textsubscript{3}d\textsubscript{5/2} core line. Specific surface area and pore size distribution of TiO\textsubscript{2} films were investigated by NOVA1200 (Yuasa Ionics Inc., Osaka, Japan). 5 mm x 5 mm size of TiO\textsubscript{2} thin film covered on slide glass was used for this measurement.

Figure 1 Schematic presentation of DSC.
2.4. Procedure of DSC assembled using TiO$_2$ electrode with plasma treatment

The thin film of semiconductor electrode for DSC was prepared by casting with screen-printing techniques on FTO glass plate using the TiO$_2$ paste concocted by blending of plasma treated TiO$_2$ particles with certain concentrations and poly (ethylene glycol): PEG which has 20,000 molecular weight in 1 mol/L acetic acid aqueous solution. On the other hand, several samples of TiO$_2$ paste could be prepared without PEG. TiO$_2$ casting films were annealed in air at 723 K for 30 min. This cast-anneal cycle was carried out for three times to prepare TiO$_2$ electrode.

The solar cell was assembled using the TiO$_2$ electrode immersed into ethanol solution with 0.3 M ruthenium dye for 2 days and FTO glass plate sputtered with Pt as counter electrode. The electrolyte solution composed with I$_2$ (0.04M), LiI (0.5M) and 4-t-butylpyrdine (0.58M) in acetonitrile was filled between these electrodes.

2.5. Procedure of tandem type DSC assembled using TiO$_2$ electrode with plasma treatment

The tandem type DSC using TiO$_2$ electrode as anode and CuBi$_2$O$_4$ electrode on Pt sputtered FTO glass substrate as cathode. CuBi$_2$O$_4$ electrode was prepared by plasma sputtering. Pt sputtered FTO glass plate and CuBi$_2$O$_4$ disk placed in doughnut-shape reactor were treated by Argon plasma with a discharge power from 100 to 200 W at 15 Pa of argon gas pressure for 5 min. The solar cell was assembled with same procedure described chapter 2.4, except for using CuBi$_2$O$_4$ sputtered electrode as cathode. XPS spectroscopy was carried out in order to confirm sputtering of CuBi$_2$O$_4$ on the FTO glass plate.

2.6. Measurement of photovoltaic properties of solar cells

Photovoltaic properties of assembled solar cell were investigated by current-voltage characteristics under irradiation with 500W xenon short cut lamp (UVL-500SX, Ushio, Inc., Tokyo, Japan) or simulated solar light under AM1.5G, 100 mW/cm$^2$ (PEC-L11, Peccell Technologies, Inc., Yokohama, Japan)

3. Results and discussions

3.1. Characteristics of TiO$_2$ nanoparticles after plasma treatment at N$_2$ atmosphere

Figure 2 shows the N 1s XPS spectra of TiO$_2$ nanoparticles before and after nitrogen plasma treatment using the round-bottomed flask-type reactor. N$_1$s peaks are not observed for pristine TiO$_2$ particles before the plasma treatment, whereas peaks around 399–402 eV, which are associated with the formation of nitrogen bonds such as N-N, N-H, and N-O-H, are clearly present for the plasma-treated particles. The spectra mean the new phase involving N molecules would be prepared on the surface of TiO$_2$ nanoparticles.

Figure 3 shows the pore size distribution of thin films from pristine TiO$_2$ nanoparticle or N$_2$ plasma treated one. The pore volume after plasma treatment was decreasing compared with no treatment film in small size region. On the other hand, the pore volume became larger at that of 100 nm. The specific surface area of each film was also investigated by BET method. The specific surface area of TiO$_2$ film with sintering was 61.62 m$^2$/g and that of plasma treated TiO$_2$ film was 41.53 m$^2$/g respectively.

Table 1 Electric property of DSC using the paste prepared from plasma treated TiO$_2$ particles with or without PEG.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>PEG (wt%)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>Voc (V)</th>
<th>f f</th>
<th>η (%)</th>
<th>Ad (nmol/µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
<td>16.6</td>
<td>0.725</td>
<td>0.634</td>
<td>7.66</td>
<td>5.36</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>18.5</td>
<td>0.713</td>
<td>0.473</td>
<td>6.24</td>
<td>4.10</td>
</tr>
<tr>
<td>50</td>
<td>40</td>
<td>16.5</td>
<td>0.734</td>
<td>0.556</td>
<td>6.73</td>
<td>4.59</td>
</tr>
<tr>
<td>80</td>
<td>40</td>
<td>16.1</td>
<td>0.718</td>
<td>0.498</td>
<td>5.77</td>
<td>4.11</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>17.2</td>
<td>0.715</td>
<td>0.466</td>
<td>5.72</td>
<td>3.17</td>
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<tr>
<td>50</td>
<td>0</td>
<td>18.7</td>
<td>0.752</td>
<td>0.617</td>
<td>8.67</td>
<td>5.24</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>19.6</td>
<td>0.727</td>
<td>0.563</td>
<td>8.01</td>
<td>4.66</td>
</tr>
</tbody>
</table>

Figure 2 N$_1$s spectra of TiO$_2$ nanoparticle before and after plasma treatment

Figure 3 Pore size distribution plot of TiO$_2$ nanoparticle before and after plasma treatment

Table 1 Electric property of DSC using the paste prepared from plasma treated TiO$_2$ particles with or without PEG.

Table 1 shows the characteristics of DSC using nitrogen plasma treated TiO₂ particles depended on the treatment time. Furthermore, TiO₂ electrode was prepared from TiO₂ paste with PEG, or some paste without PEG. In the TiO₂ electrode using paste including PEG, short-circuit current density $J_{sc}$ and open circuit voltage $V_{oc}$ were not inclined to change with plasma treatment, whereas fill factor $ff$, conversion efficiency $\eta$ and amount of adsorbed dye per area $Ad$ decreased with increasing plasma treatment time. On the other hand, these parameters of DSC prepared using the TiO₂ paste without PEG was improved compared with using the paste with PEG.

From the results, $J_{sc}$ of DSC increased (in the case of without PEG) using plasma treated TiO₂ whereas the amount of adsorbed dye decreased with increasing of treatment time. The reason why this effect would be increasing the electron diffusion coefficient due to forming the stronger junction among the nitrogen plasma treated TiO₂ particle. XPS spectra (Figure 1) shows N-containing surface layer was produced by plasma treatment in TiO₂ particle, and this layer could make the particle fuse easily in the sintering process, therefore the particles could connect each other smoothly. The reduction of specific surface area for the sintered TiO₂ film after nitrogen plasma treatment elucidates this phenomenon. This work defined the strong influences to the characteristics of DSC using TiO₂ electrode treated by nitrogen plasma treatment changing the physical and chemical property of TiO₂ particles.

3.3 Property of tandem type DSC using TiO₂ and CuBi₂O₄ electrode.

The advantage of n/p tandem type DSC is that solar light could be used for electric conversion more effectively. By introducing the p type semiconductor having lower energy band gap, the solar cell would be expected to absorb longer wavelength light compared with only using sensitized dye. Furthermore, the open circuit voltage of DSC was also elevated by addition of p type semiconductor with valence band lower than reduction potential of iodide. In this study, CuBi₂O₄ was used as p type semiconductor.

Figure 4 shows Cu₂p and Bi₄f XPS spectra of FTO glass substrate after CuBi₂O₄ sputtering process at several discharge powers of irradiation. The peaks related Cu molecules around 935 eV, and Bi molecules around 160 eV appeared in the spectra of each sample. It was confirmed that CuBi₂O₄ could be sputtered on FTO substrate by plasma irradiation. Figure 5 shows I-V curve and Table 2 describes the electric property of n/p tandem type DSC using TiO₂ electrode as anode and CuBi₂O₄ electrode on Pt sputtered FTO glass substrate as cathode prepared by plasma sputtering depended on generating discharge power. In this result, the working of DSC could be confirmed in spite of introducing p type semiconductor into the DSC system. However, the open circuit voltage $V_{oc}$ and conversion efficiency $\eta$ were decreasing with increasing of the discharge power of plasma irradiation from the I-V curves. Plasma sputtering with high discharge power fabricated large amount of CuBi₂O₄ on the substrate. The backward electron transfer generated in CuBi₂O₄ electrode connected electrolytes would cause negative effects for DSC. For improvement of DSC property, the plasma sputtering condition of CuBi₂O₄ should be optimized to prevent the backward electron transfer or other negative effects.

Table 2 Electric property of tandem type DSC fabricated by CuBi₂O₄ sputtering electrode.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$ff$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>3.26</td>
<td>0.683</td>
<td>0.649</td>
<td>1.45</td>
</tr>
<tr>
<td>100W</td>
<td>2.86</td>
<td>0.645</td>
<td>0.551</td>
<td>1.03</td>
</tr>
<tr>
<td>150W</td>
<td>2.88</td>
<td>0.615</td>
<td>0.525</td>
<td>0.93</td>
</tr>
<tr>
<td>200W</td>
<td>1.71</td>
<td>0.604</td>
<td>0.537</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Figure 4 Cu₂p and Bi₄f XPS spectra of CuBi₂O₄ sputtered on FTO glass plate.
4. Conclusions

Two kind of dye-sensitized solar cell were assembled using TiO$_2$ nanoparticle with argon-nitrogen plasma treatment and CuBi$_2$O$_4$ sputtering electrode prepared by plasma irradiation. The property of the solar cell with plasma treated TiO$_2$ nanoparticle was improved because the particles could connect each other smoothly in sintering due to the active N-containing surface layer produced by nitrogen plasma treatment. However, the tandem type DSC using CuBi$_2$O$_4$ sputtered electrode could not get improvement of electric property, because of backward electron transfer generating in the CuBi$_2$O$_4$ layer. The plasma sputtering condition of CuBi$_2$O$_4$ should be optimized to prevent the backward electron transfer.

References

**Figure 5** I-V curve of DSC and tandem type DSC fabricated by CuBi$_2$O$_4$ sputtering electrode depended on the discharge power of plasma irradiation.