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Basic Study of Surface Modification for Film Dye Sensitized Solar Cells using Microplasma

大気圧マイクロプラズマによるフィルム型色素増感太陽電池の表面改質の基礎検討

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This paper introduces the process of improvement of the conversion efficiency of Film Dye Sensitized Solar Cell using microplasma under atmospheric pressure. The surface modification for titanium oxide transparent electrode was carried out with various active species generated between the microplasma electrodes. Titanium oxide transparent electrodes are investigated using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and electrochemical impedance spectroscopy (EIS). The photo conversion efficiency of film DSSCs was measured by solar cell evaluation system. The photo-conversion efficiency increases with about 0.6% after 15 min oxygen microplasma treatment.

1. Introduction

In 1991, Grätzel and O'Reagan reported the dye sensitized solar cells (DSSCs) which were based on titanium oxide. The DSSCs are well known as cost-effective technology and high photo-conversion efficiency devices [1]. Film DSSCs have many advantages, such as the use of low-cost raw materials, faster manufacturing time, and the designability owing to flexible substrates in comparison with silicon solar cell. Although many advances have been made in film DSSCs fabrication of late years, their photo-conversion efficiency remains still lower than the glass substrate DSSCs and the Si-based solar cells. The lower photo-conversion efficiency of film DSSCs are owing to low firing temperature compared with glass substrate DSSCs. Titanium on ITO film surface modification by various plasma treatments has been reported to increase the solar conversion efficiency using RF-plasma and plasma jet [2,3]. This paper introduces improvement of the photo-conversion efficiency of film DSSC using atmospheric pressure microplasma as a no damage process.

2. Experimental Method

The experimental setup for surface modification of Titanium oxide on ITO film is shown in Figure 1. The microplasma electrodes are perforated metallic plates covered with a dielectric layer and faced each other with a 100 μm spacer as a small discharge gap.

The Titanium oxide sample and the microplasma electrodes were placed into the chamber to avoid the impurities from ambient gas. The high-purity oxygen (>99.9%) gas was supplied from a gas cylinder as process gas. The gas flow rate was set at 5.0 L/min. The Distance between the grounded electrode and the titanium oxide sample was set at 1.0 mm. An AC high voltage was supplied by a neon-sign transformer (LECIP αNEON M-H1) to generate the microplasma. The applied voltage (V_{o-p}) was set at 1.56 kV, and the frequency of the power supply was set at 27.1 kHz.

The current-voltage (I-V) characteristics were measured under Air Mass 1.5 using a solar cell evaluation system (JASCO CEP-25BX). X-ray photoelectron spectroscopy (Shimadzu ESCA-3400) was used to analyze the chemical composition on the titanium oxide surface.

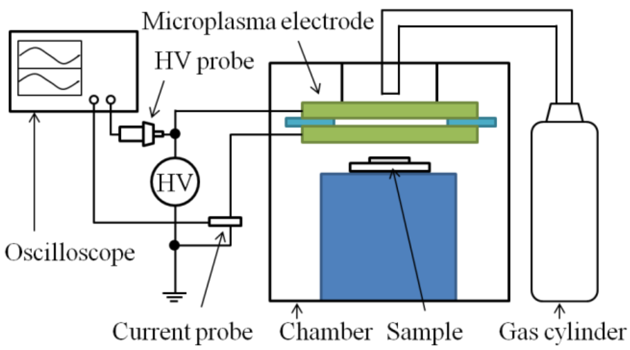

Fig. 1. Experimental setup for surface modification.

3. Result and discussion

3.1 *Photovoltaic measurement*

Figure 2 shows a comparison of I-V characteristics between untreated DSSC and treated DSSC. Treatment time was set at 15min. The relative humidity in the chamber was 0%. The short-circuit current density was increased with 1.15 mA/cm^2 compared with untreated DSSC. The photo-conversion efficiency was increased to 1.95 % from 1.36% after oxygen plasma treatment. Fill factor had a tendency to increase after oxygen plasma treatment.

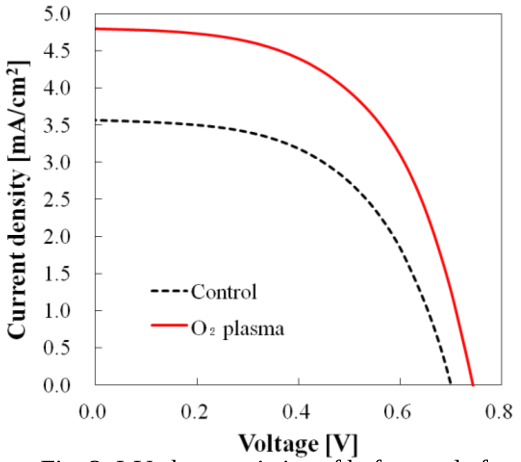

Fig. 2. I-V characteristics of before and after the microplasma treatments.

3.2 *XPS analysis*

Chemical bond analysis on the titanium surface was carried out by XPS. Ti 2p and O 1s XPS spectra of the titanium oxide sample surface treated for 15 min with oxygen plasma are shown in Figs. 3 and 4.

Figure 3 shows the XPS spectra of Ti 2p on the TiO_2 surface after the oxygen plasma treatment (15 min). The Ti 2p spectra were analyzed for four peaks. The surface stoichiometry was determined by calculating the relative peak area as the ratio of the total Ti 2p and O 1s in XPS spectra. The Ti^{3+} surface state in Ti 2p XPS spectra increased from 4.0 to 6.2% after 15 min of oxygen plasma treatment. The $Ti^{4+} \rightarrow Ti^{3+}$ reduced reaction could be observed at the TiO_2 sample surface. Part of the TiO_2 surfaces was changed to Ti_2O_3. This surface reaction determined the increase of the electric conductivity of the DSSSCs sample surface and consequently, the solar conversion efficiency was improved. O 1s XPS spectra were measured as well as Ti 2p to investigate the surface reaction. Figure 4 shows the XPS spectra of O 1s. The OH peak in O 1s was increased from 16.4 to 21.3% after 15 min of oxygen plasma. Hydrophilic property of titanium oxide surface was increased after plasma treatment. The increase of OH bonds contributed to the increase dye adsorption [4].

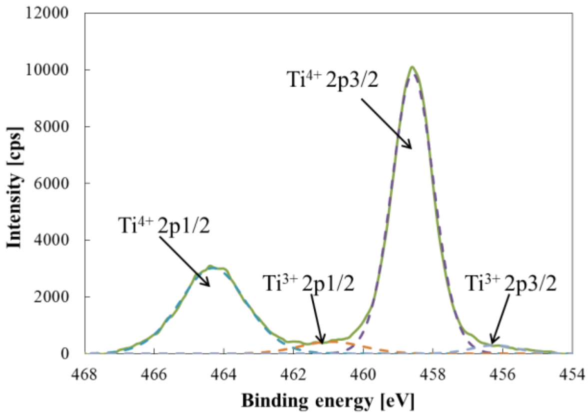

Fig. 3 Ti 2p spectra of titanium oxide on ITO film. after oxygen plasma treatment.

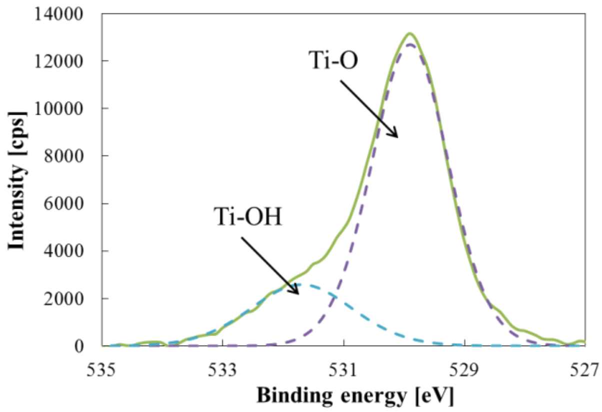

Fig. 4 O 1s spectra of titanium oxide on ITO film. after oxygen plasma treatment.

4. Conclusion

The surface modification using microplasma was carried out as no damage process. The I-V characteristics were measured to investigate the improved performance of film DSSCs. The surface state on titanium oxide film was evaluated by the XPS. The conversion efficiency was improved about 40% after oxygen plasma treatment. The XPS analysis showed increase of Ti^{3+} peaks and OH bonds on the titanium oxide film surface. The increase of OH bonds contributed to the increase dye adsorption and current density.

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