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셀 폭에 따른 염료 감응형 태양전지의 표면저항 효과

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A surface resistance effect on the fabrication of Dye-sensitized Solar Cell with various widths

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Key words : sputter deposition(스퍼터링 증착), RF plasma(RF 플라즈마), Dye-sensitized solar cell(염료 감응형 태양전지), cell width(셀폭), internal resistance(내부저항)

Abstract : Sputter deposition followed by surface treatment was studied using reactive RF plasma as a method for preparing titanium oxide (TiO_2) films on the FTO (SnO_2: F) substrate for dye-sensitized solar cells (DSCs). Anatase structure TiO_2 films deposited by reactive RF magnetron sputtering under the conditions of Ar/O_2(5%) mixtures, RF power of 600W and substrate temperature of 400 ℃ were surface-treated by inductive coupled plasma (ICP) with Ar/O_2 mixtures at substrate temperature of 400℃, and thus the films were applied to the DSCs. We have chosen a solar cell width as a variable of a large-scaled DSCs and confirmed electric characteristics of an individual cell. As a result, the higher the internal resistance of DSC becomes, the wider the width gets. Internal resistance makes it difficult to collect photoelectron generated from dye. Ultimately up sizing DSC causes the increase of internal resistance and then has a bad effect on the cell characteristics.

1. INTRODUCTION

Nanocrystalline dye-senstitized solar cells (DSCs) are promising candidates for low-cost photovoltaic devices [1]. Several prototypes have been presented, but no large-scale production has yet appeared as a consequence of the many problems that these devices are still facing. It is claimed that the unique properties of the nanocrystalline DSCs stem from the ability to achieve an interaction of the dye and the electrolyte with all interconnected nanoparticles.

DSCs are based on a wide band-gap semiconductor material with a very large internal surface to which dye molecules are attached. Titanium oxide (TiO_2) is an important material in the construction of DSCs because of its large surface area, sufficient light absorption and high photoelectrical response as a porous photo-electrode material of DSCs [2]. The electron is excited from the valence band to the conduction band, when TiO_2 is irradiated with ultraviolet radiation of about 380 nm or less wavelength, and electron-hole pairs are created.

DSCs typically consist of a dye sensitized TiO_2 electrode in contact with an electrolyte and completed by an inert counter electrode. Remarkable progress regarding the efficiency of DSCs was made possible by employing porous nanocrystalline TiO_2 prepared by sol-gel methods. The porous network of the TiO_2 nanoparticles prepared by this technology result in extremely large surface area, greatly enhancing absorption of light as compared to a monolayer of dye adsorbed on a flat unstructured surface of the same size. However, the randomly porous structure of TiO_2 electrode gives rise to several undesired characteristics,

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such as low conductivity and charge density. Recently, DC magnetron sputtering technique has been used to deposit porous TiO_2 thin films with large surface area for use in DSCs. The sputtered films yielded a high photocurrent when incorporated into DSCs configuration, although energy conversion efficiency was not still high3).

Commercial solar cells like poly-crystalline Si solar cells have a current-collecting grid that was made by silver solder or conductive printing paste to reduce their high surface resistance. In the case of dye-sensitized solar cells, there are some precedents with the metal grid protected by resin or glass-ceramic to be not attacked from redox electrolyte4,5).

In this study, different square sizes of DSCs with various widths were especially investigated. The surface resistance, Isc, Voc and fill factor(FF) of DSCs were measured and discussed in association with the different widths

2. EXPERIMENTAL PROCEDURE

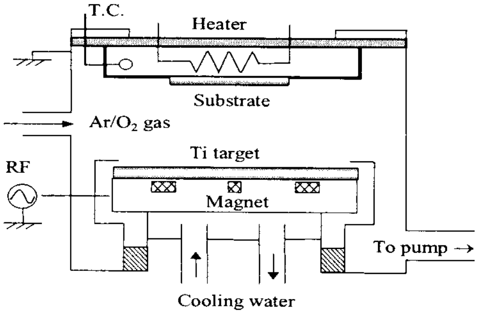

Fig. 1 Schematic diagram of RF magnetron sputter system

The process was roughly divided into two in this experiment. The primary process formed TiO_2 films of anatase crystal structure by the RF reactive magnetron sputter system as shown in Fig. 1. The secondary process was the plasma surface treatment using immersed type single-turn ICP. The RF magnetron sputter system can be briefly described as follows. The chamber was of stainless steel of internal diameter 300 mm. The RF power (P_{rf}) of 600 W was supplied to a TiO_2 target having diameter of 100 mm. The distance between the target and substrate was 150 mm.

A temperature controller and heater controlled the substrate temperature. Cooling water is circulated through the target and chamber to prevent overheating during deposition. At first, the chamber was exhausted vacuum to 210^{-6} Torr or less. The temperature of the 20mm20mm FTO substrate was maintained at 400°C. The Ar/O_2(5%) with 5:1 pressure ratio gas was introduced to 18 mTorr, and the P_{rf} of 600W was applied to target. And hence, the deposited TiO_2 films were taken out of the chamber to confirm the structure and thickness of the films.

Many studies have been reported on modifying the surface properties of TiO_2 by various methods, including chemical processes (aquageria, degreasing, and RCA protocol) and physical treatments using oxygen or argon plasma6). Among them, Ar/O_2 plasma was considered as a promising treatment because it results in the highest work function, the lowest sheet resistance and the smoothest surface7). Consecutively, a procedure of the plasma surface treatment is indicated as second process. The prepared TiO_2 films were dye-sensitized with a dye solution. Before immersing into the dye solution, the films were plasma-treated to remove physisorbed impurities and promote surface activity. The TiO_2 films are reset in an ICP chamber, which was described in detailed in our previous report8), and the Ar/O_2 mixtures were introduced to a total pressure of 18 m Torr and P_{rf} of 400W was applied, and plasma surface treatment was performed for 1 h. The temperature of the substrate was made to be 400°C.

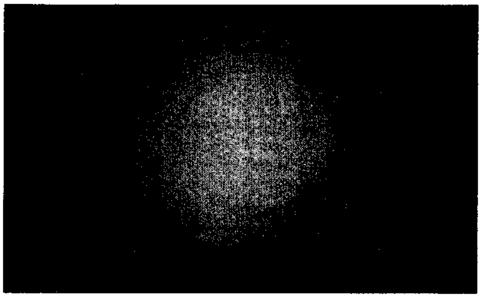

Fig. 2 Plasma image taken for surface treatment

Fig. 2 shows the images of plasma taken for surface treatment, in which the Ar/O_2 plasma was covered the TiO_2 surface. After the plasma treatment, the resulting TiO_2 properties were investigated by X-ray diffractometry (XRD), Scanning electron microscopy (SEM).

In this study, we designed DSCs with an active area of same height and the different width. To confirm the influence of electronic flow by surface resistance, we chose the width of a cell as the variable.

That is, the width of DSC was changed as a variable for large-sized solar cell. The height of an active area for all DSCs is 60[mm] and the width makes differentto 1, 3, 5, 7, 10, 20[mm] respectively. And we expected effect that increases in surface resistance.

Table. 1 An active area of DSC for measurements

	Width[mm]	Height[mm]
A	1	60
B	3	″
C	5	″
D	7	″
E	10	″
F	15	″
G	20	″

Table 1 represents an active area of DSCs used in this study. Electrical Properties of DSCs for experiment was measured by Keithlley 2420 source meter on Solar Simulator (100mW/cm^2).

FTO glass with approximately 8.3Ω/cm^2 of sheet resistance is cleaned and prepared in advance. TiO_2 paste is coated by screen printing method on it. And then it is sintered for 30 minutes at 450℃. The dye of cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)(N3) dissolved on ethanol is adsorbed on the nano-porous TiO_2 electrode film manufactured through the previous process. The Pt catalyst is coated by RF sputtering method. The working and counter electrode are sealed by the adhesive (SolaronixSA, Amoil 4) in a sandwich. The gap between two electrodes is filled with the electrolyte (Iodolyte TG-50). And then DSCs for experiment is completed after sealing the hole to fill up the electrolyte. Fig. 3 and photo. 1 shows structure and an appearance of DSCs for experiment.

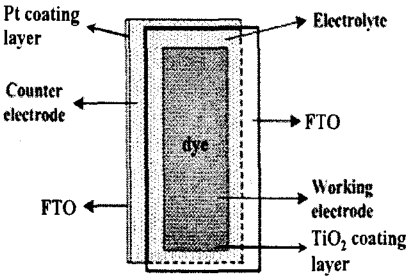

Fig. 3 Structure of DSC for measurements

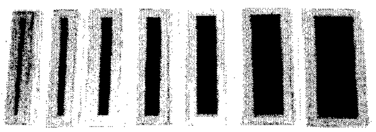

Photo.1 The DSC for measurements

3. RESULT AND DISCUSSION

Structural characterization of the plasma-treated TiO_2 films was performed by XRD and the result was shown in Fig. 4.

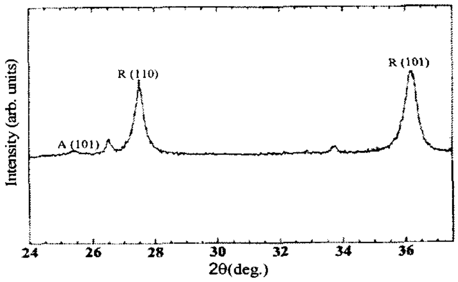

Fig. 4 XRD spectra for plasma-treated TiO_2 film. A: Anatase, R: Reflection

The result showed a prominent peak assigned to anatase (101), as well as two peaks due to the rutile (1 1 0) and (1 0 1) reflections. The film after plasma treatment displayed an expectedly weak anatase peak.

Surface morphologies were studied with SEM. Fig. 5 (a) and (b) show the SEM images on the surface and cross section of the prepared TiO_2 film, respectively. The micrograph gives clear evidence for the growth of TiO_2 crystal. As seen from Fig. 5 (a), rough surfaces with well-rounded particle were apparent, and the particle size of about 25 nm could be confirmed. In Fig. 5 (b), the micrograph in the cross section shows that the crystals developed in a pillar shape at the top of the film.

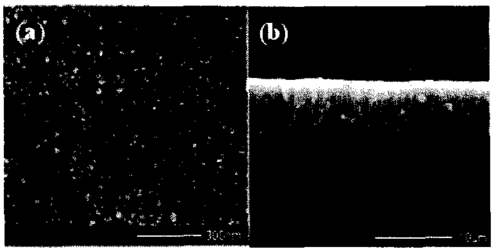

Fig. 5 SEM images of the untreated TiO_2 film. (a) Surface (b) Cross section

Fig. 6 TEM image of the plasma-treated TiO_2 film

Fig. 6 shows TEM image of the TiO_2 film prepared by sputter deposition followed by surface treatment. Closer look to the TEM images indicates that the size of TiO_2 particles is about 25 nm. Subsequently, the TiO_2 films made on these experimental bases exhibited the BET specific surface area of $95m^2/g$ and the pore volume of $0.3cm^2/g$.

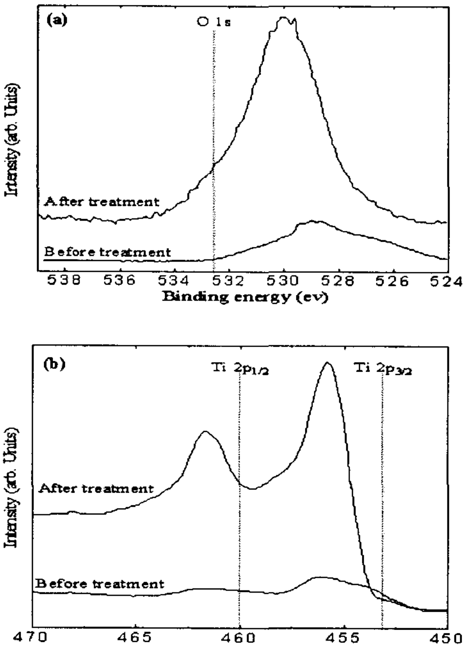

Fig. 7 XPS spectra of O 1s and Ti 2p on the TiO2 film surface before and after plasma treatment. (a) O 1s spectra (b) Ti 2p spectra

XPS is useful in elucidating surface chemistry, which may be responsible for electrochemical characteristics of the TiO2 film. Spectra of O 1s orbital and Ti 2p orbital before and after plasma treatment are respectively shown in Fig.7 (a) and (b). From XPS spectra, significant increase in oxygen and titanium on the TiO2 surfaces was detected. The chemical shift of both O 1s orbital and Ti 2p orbital was carried out in high binding energy side. XPS measurements clearly indicate a change in chemical composition on the plasma-treated TiO2 film. The results demonstrate that a significant surface oxygen enhancement occurred by removal of the surface impurities. Oxidative treatments incorporate more oxygen onto the surface, and the electrochemical characteristics correlates well with the oxygen addition.

The photoelectric efficiency was calculated with respect to the solar spectrum through a calibration of the Light Drive 1000 lamp with direct sunlight. The overall efficiency of a photovoltaic cell can be calculated from the expression.

$$\eta = \frac{J_{sc} V_{oc} FF}{P_s}$$

where Jsc is the integral photocurrent density (current obtained at the short-circuit conditions, divided by the area of the cell), Voc is the open-circuit voltage, FF is the fill factor (related to the series resistance for a practical solar cell), and Ps is the intensity of the incident light. Fig. 8 illustrates the current-voltage-power characteristics of the DSCs made of this TiO2 material.

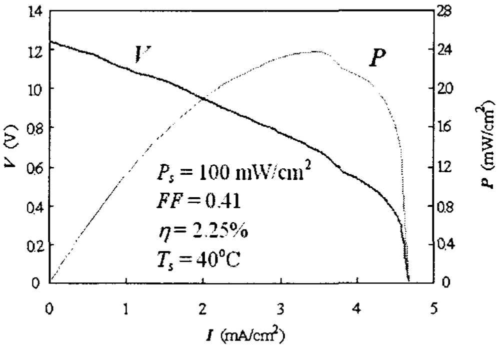

Fig. 8 I-V-P characteristics of a DSC based on TiO2 film

Fig. 9 shows a current per a unit area [cm2] according to the DSCs with different width. The graph decreases overall as the increase of the width of DSCs. The current density is the highest at 1[mm] of the width of DSC and falls sharply at 3[mm]. And then it decreases gradually as increasing the width of DSC to 5, 7, 10, 15, and 20[mm].

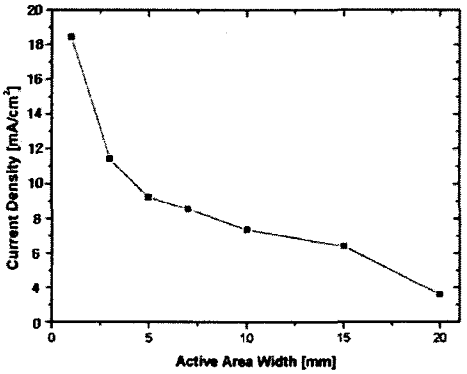

Fig. 9 The active area width Vs Current Density of Dye-sensitizedsolar cell samples

The photoelectron generated from dye is transported to FTO conductive glass through the TiO2 surface by the diffusion and the trap-detrap process. At that time, the electron collecting comes to be difficult according as the increase of surface resistance and the electron is difficult to flow smoothly in internal cell. We confirm that the increase of surface resistance has a bad effect on cell properties.

In this study, the sputter deposition followed by surface treatment was studied using reactive RF plasma as a method for preparing TiO2 films on FTO coated glass substrate for DSCs. The TiO2 films made on these experimental bases exhibited the BET specific surface area of $95m^2/g$, the pore volume of 0.3cm2/g and the TEM particle size of "25 nm. The DSCs made of this TiO2 material exhibited an energy conversion efficiency of about 2.25 % at 100 mW/cm2 light intensity. Consequently, we believe that the optimization between the specific surface area and photocurrent density of TiO2 films by the surface treatment was found to give rise to the improvement of energy conversion efficiency of DSCs, and the surface properties of the TiO2 significantly affect performance of DSCs.

4. CONCLUSION

We investigated electrical properties of the dye-sensitized solar cell in proportion to up sizing DSC after we had leaded to increase surface resistance by the change of width. As a result, current density [mA/cm^2] of DSC was gradually decreased according to the increase of the width.

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