High Temperature Sputtered TiO₂ Film as an Efficient Blocking Layer for the Dye-sensitized Solar Cells

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We investigated the carrier leakage blocking effect of the magnetron sputtered TiO₂ film insertion between transparent anodic electrode and porous TiO₂ film in the dye-sensitized solar cell (DSC), as a consequence of preventing the ionic short-circuiting of the electrolyte to the anodic electrode through porous TiO₂ film. The optimization of the deposition condition of the high temperature TiO₂ sputtering for the carrier leakage blocking is reported.

Key Words: Carrier Leakage Blocking, Sputtered TiO₂ Film, Rutile Crystalline Layer, Dye-sensitized Solar Cell

1 Introduction

The major performances of solar cells are the short-circuit current density (Jsc), the open-circuit voltage (Voc), and the fill factor (ff) of the I-V curves. The elemental materials, structures, and fabricating procedures, therefore, must be designed to maximize the Jsc, Voc, and ff. On the development of the performance of dye-sensitized solar cells (DSC), the key subject for Jsc increase is to improve the electric conductance and surface area of porous TiO₂ photoelectrode and to develop the dye materials. And the key subject to enlarge the Voc is to prevent the ionic short-circuiting of the electrolyte solution. Addition of 4-tert-butylpyridine (TBP) into electrolyte solution is the well known method to prevent the carrier leakage of the direct electron acceptance from the TiO₂ electrode with the avoidance of hole mediation to the optically excited dye. However, this method has not enough effect for the drastic improvement of the carrier leakage in DSC. As another method for the carrier leak block, it is tried to introduce the fine TiO₂ membrane by means of spray pyrolysis method between the TiO₂ porous membrane and conductive transparent electrode. However, even with high temperature sintering of fine TiO₂ membrane, the blocking effect cannot be satisfied for the actual applicable process of DSC.

On the other hand, dry processes such as sputtering method and CVD (Chemical Vapor Deposition) method for TiO₂ deposition are suitable for forming the higher quality and finer membrane having stable material properties than the wet process. Especially, the sputtering method can form a uniform and fine membrane for a large area at relatively low temperature and is expected to be used for every material. Consequently, it is thought that sputtering method is superior to prepare the blocking layer.

In this study, we investigated the carrier blocking effect of the introduction of the fine TiO₂ membrane for the improvement of the performance of DSC. The optimization of the deposition conditions of the magnetron sputtering of TiO₂ is reported in this paper.

2 Experimental

The blocking layer TiO₂ films were deposited by Ar RF magnetron sputtering (JEH-430RSC, JEOL) using a TiO₂ ceramic target (99.9 %, Kojundo Chemical Laboratory Co.) on FTO (fluorine-doped SnO₂) electrode deposited on borosilicate glass substrates (Solaronix, 10 ohm/sq, transparency 80 %). RF input power were 300 W and the gas pressure during the deposition was kept constant at 3.0 Pa. The film thickness was controlled to 200 nm. Porous TiO₂ membrane for dye adhesion was formed by the following procedure; colloidal paste (Ti-Nanoxide T, Solaronix) painting by Squeegee printing method on the sputtered TiO₂ film, drying in the air at room temperature, and sintering at 450 °C for 30 min. The thickness of the porous TiO₂ membrane was controlled to about 7 μm, inspected by surface texture measuring instrument (SURFCOM1400D, TOKYO SEIMITSU). The crystal structures of these films were analyzed by X-ray diffraction (XRD, RINT-2000, Cu Kα radiation, Rigaku) with 50 kV and 300 mA. The porous TiO₂ surface was derivatized by immersing in a 3 × 10⁻⁴ M ethanolic solution of the dye (Solaronix, N719) overnight, and consequently dried in the air.

The DSC cells were fabricated by clamping the dye coated porous TiO₂ electrode plate against the platinum layer coated FTO glass plate with filling the electrolyte (0.1 M LiI + 0.03 M I₂ + 0.6 M 1-propyl-3-dimethylimida- zolium iodide + 0.5 M t-Butylpyridine in acetonitrile) in the capillary space. The cell performances and the I-V characteristics, especially, were examined under the irradiation of the solar simulator (PEC-L 10, Pecell Technologies, Inc.), where the irradiating power were checked by a power meter (NOVA-PD300UV SH, OPHIR).
3 Results

The correlation between the sputtering temperature of the TiO₂ carrier blocking layer and the DSC cell performances were investigated for optimization of the deposition condition for carrier blocking. Figure 1 shows the I-V curves of the DSC with the sputtered TiO₂ blocking layer at 100, 300, and 480 °C, where the Ar gas pressure were fixed at 3 Pa during sputtering process to minimize the plasma damage in the TiO₂ layer. The energy conversion efficiency (η) of the DSC at each sputtering temperature is noted, respectively. As the result, η was improved at higher sputtering temperature. Figure 2 shows the dark I-V curves for the DSC chips. The leakage current at reverse bias was drastically reduced with the sputtered TiO₂ blocking layer, and the blocking effect was enhanced by the sputtering temperature rise. In order to investigate the temperature dependence of the blocking effect of the sputtered TiO₂ film, we inspected the crystalline quality of the sputtered TiO₂ films by XRD as shown in Fig. 3. At 100 °C, the sputtered film was amorphous with no peak attributable to crystal. Sputtered at 300 °C, many diffraction peaks corresponding to anatase crystal appeared, and peaks corresponding to rutile crystal also appeared at 480 °C sputtering. This result indicates that as temperature rise the crystallization of the sputtered TiO₂ film was enhanced. We had identified the same tendency of the crystallization of the sputtered TiO₂ films with Raman inspection.

According to this experimental result, we investigated the rearrangements from anatase to rutile of the low temperature sputtered TiO₂ films by post sintering process at 450 °C. At 1st step, TiO₂ was sputtered on FTO glass substrate at 300 °C. At the 2nd step, the sputtered film was sintered at 450 °C in the air. Figure 4 shows the XRD peaks of sputtered TiO₂ films of (a) sintered in bare surface, and of (b) sintered with surface coverage of porous TiO₂. This result indicates that there is no crystalline change of sputtered TiO₂ layer by the post sintering process at 450 °C to form the porous TiO₂ membrane.

4 Discussion

According to the above experimental results, we considered the mechanism of carrier blocking effect of sputtered TiO₂ layer in DSC. As presented in Figs. 1 and 2, the carrier blocking effects of sputtered TiO₂ were improved at higher temperature sputtering. Both of Jsc and Voc of DSC were expanded by the sputtering temperature rise.

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Fig. 1 Effect of substrate temperature during sputtering process on photocurrent-voltage characteristics of the dye-sensitized solar cells.

Fig. 2 Darkcurrent-voltage curves of the dye-sensitized solar cell with and without blocking TiO₂ layers prepared at different substrate temperature condition.

Fig. 3 XRD patterns of the TiO₂ blocking layers prepared at different substrate temperature condition.
The reason of Voc expansion can be considered as the result of increase of protection effect against ionic penetration from the electrolyte solution through the blocking layer by the crystallization progress as shown in Figs. 3 and 4. The sputtered TiO₂ film is consists of the columnar structure of several dozens micron size grains. The microscopic density for ion-proof may be improved by temperature rise at film deposition related to the surface migration length.

And the Jsc enlargement at higher temperature sputtering should be considered as the improvement of the electron transport characteristics in the sputtered TiO₂ blocking layer; in other words, the higher temperature sputtered TiO₂ blocking layer has the higher conductivity with lower recombination rate for the traveling electrons which were optically generated at dye material.

As a shown in Fig. 4, the crystal structure of the blocking layer covered with porous TiO₂ membrane would not change by the 450°C post annealing process. It indicates that sputtered TiO₂ blocking layer should be rutile crystalline for higher performance of DSCs.

Besides the better carrier characteristics of rutile TiO₂ than anatase, we consider the advantage of the rutile TiO₂ blocking layer as following; the optically generated electrons in dye materials should transport through porous TiO₂ membrane and blocking TiO₂ films to FTO anodic electrode, where the electron transport from porous TiO₂ anatase crystal (conduction band energy, E_c = 3.2 eV) to the rutile crystal (E_c = 3.0 eV) blocking layer may be improved than to the anatase crystal blocking layer.

**5 Conclusion**

DSC’s performances can be drastically improved by the leakage carrier blocking layer insertion by high temperature TiO₂ sputtering between porous TiO₂ membrane adsorbing dye and FTO transparent anodic electrode. The leakage blocking effects were appeared at the expansion of Jsc and Voc, and resulted in the increase of the energy conversion efficiency of the DSC. Such effects were enhanced by higher temperature sputtering of the TiO₂ film up to 480°C. From the XRD inspection, the higher temperature sputtered TiO₂ film has rutile crystalline structure, which may be suitable for the carrier leakage blocking.

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