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学位論文題目	Study on Fabrication and Characterization of Porous Titanium Composite Counter Electrodes of Dye-sensitized Solar Cells (色素増感太陽電池用多孔質チタン対極の作製と評価に関する研究)
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論文内容要旨

Recently the development and utilization of a novel energy source has been one of the most important issues to build a sustainable society. This is due to the continuous depletion of our fossil fuels (gases, coals, and oil) and for ecological conservation reasons, as for last few years there is a tremendous change of global climate due to the global warming caused by the combustion of fossil fuel energy carriers gases, coals, and oils). The solar cell is one of the proposed various ideas and the dye-sensitized solar cells (DSC) have been attracting much attention because of its easy preparation, low cost, and relatively high energy conversion efficiency η . A DSC generally consists of a dye-coated titanium dioxide (TiO_2) particle layer on a transparent conductive oxide (TCO) glass substrate, an electrolyte containing iodide (I^-)/triiodide (I_3^-) ions and a counter electrode which is made of a TCO glass substrate covered with platinum (Pt) as shown in Fig.1. In order to enhance the performance and stability of a DSC, developing the new counter electrode (CE) have been given much importance. This is because the triiodide ions (I_3^-) are reduced at the electrolyte/counter electrode interface of the DSC, and therefore, a low resistive interface of electrolyte/counter electrode are required for the fast charge transportation of ions in the DSC. Generally, Pt/TCO is widely used as a counter electrode for a DSC. This conventional Pt/TCO counter electrode causes to a large series resistance effect on the DSC, resulting the decreases in the fill factor FF and photocurrent J_{sc} leading to deterioration in the energy conversion efficiency η of the DSC. The high sheet resistance of TCO and high interface resistance at electrolyte/counter electrode caused by the small surface area of plane Pt are responsible for this large series resistance of the DSC. Therefore, it is in need to develop a novel counter electrode with low resistance at the electrolyte/counter electrode interface and low sheet resistance of the DSC.

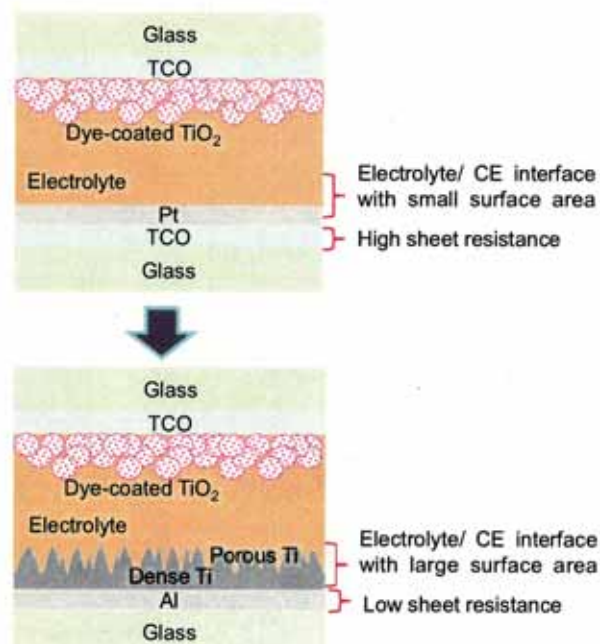


Fig. 1 Formation of new counter electrode (CE) for DSCs.

It was reported that a counter electrode of large surface area with high conductive film could reduce the interface resistance and sheet resistance, respectively.

In the present work, our plan was to fabricate and characterize a porous Ti composite counter electrode in place of conventional Pt/TCO counter electrode, and its application to DSCs as shown in Fig. 1. We fabricated the composite counter electrode by a multilayer structure of thin Pt/porous titanium (Ti)/aluminum (Al)/dense Ti/glass. Porous Ti has large surface area to reduce the resistance at electrolyte/counter interface, and high conductive film of Al could be a possible candidate to reduce the sheet resistance of the counter electrode, where dense Ti can act as an anti-corrosive layer of high conductive film of Al from its dissolution in the electrolyte solution of the DSC. Individual effect of all these elements (porous Ti, dense Ti, and Al) on the performance of the DSC was characterized and finally, it was our goal to establish the porous Ti composite counter electrode as an alternative of conventional Pt/TCO counter electrode from the view point of the improvement of the DSC performance by the counter electrode's activity and function.

The composite counter electrode which we proposed consisted of the Pt, porous and dense Ti, and Al layers. The Al layer was deposited by the vacuum evaporation method. Immediately after deposition of the Al layer, the porous and dense Ti layers were deposited by the DC magnetron sputtering method without exposing the surface of the Al layer to an atmosphere. The DC power was fixed at 200 W. The structures of Ti layers were controlled by adjusting the argon (Ar) pressure. The porous and dense Ti layers were deposited at Ar pressures of 1 and 0.08 Pa, respectively. The porosity and the surface roughness of the porous Ti layer were controlled by a wet etching technique. The porous Ti surface was etched with a 1.36 % hydrofluoric acid solution (HF) (Stella Chemifa Co., Japan) for 4 s followed by immersion in a mixture of TiW-I (mixture of hydrogen peroxide and boric acid, chelating agent) and TiW-II (ammonia water) (Wako Pure Chemical Industries, Ltd., Japan) for 150 s. The thin Pt layer was deposited by the thermal decomposition of chloroplatinic acid (H_2PtCl_6). The 0.1 M of H_2PtCl_6 solution was spin coated on the porous or dense Ti layer at a rotation speed of 200 rpm for 5 s and the counter electrode was annealed at 400 °C for 15 min. In the case of preparing the conventional counter electrode, the 400-nm thick Pt film was deposited on the TCO substrate by the RF magnetron sputtering method. The structures of the counter electrodes were observed using a field emission scanning electron microscope (FE-SEM) (SU8000, Hitachi High-Technologies Co., Japan) and energy dispersive X-ray (EDX) spectroscopy. In order to form the photoelectrode, a mixture of TiO_2 (anatase) nanoparticles, polyethylene glycol (PEG), acetylacetone, triton x100, and H_2O (300 : 150 : 30 : 15 : 1000) were prepared. After it was milled for 6 hours, the paste was applied to the TCO glass substrates. The TCO glass substrate to which the TiO_2 paste was applied was annealed at 400 °C for 1 hour followed by at 500 °C for 30 min to form a TiO_2 nanoparticle layer of about 10 μm in thickness. The TiO_2 electrode was immersed in a 0.3 mM N719 dye solution diluted with tertiary butyl alcohol and acetonitrile for 24 hours to absorb the N719 dye molecules on the TiO_2 electrode surfaces. The iodide Γ /triiodide I_3^- redox couple electrolyte was injected into the gap between the two electrodes. A mask was placed on the DSCs during measuring the photovoltaic characteristics. The photovoltaic characteristics of the DSCs were measured at a sweep rate of 2 mV/s under illumination of light of AM 1.5 (100 mW/cm²).

Figure 2 shows the top-view and cross-sectional FE-SEM images of the Ti films deposited by the DC magnetron sputtering method at Ar pressures of (a) 0.08, (b) 0.5, and (c) 1 Pa. The insets in Fig. 2 exhibit top-view FE-SEM images. From Fig. 2, we can see that the structure of the Ti film depended strongly on the pressure of Ar gas. In the case of an Ar pressure of 1 Pa, the Ti film had the dendritic structure, and the boundary between dendrites can be clearly seen in Fig. 2(c), that is, the Ti film deposited at an Ar pressure of 1 Pa had a porous structure. On the other hand, the Ti film was homogeneous and dense when the Ar pressure was 0.08 Pa. The Ti film deposited at an Ar pressure of 0.5 Pa, which was a moderate condition had a medium (neither dense nor porous) structure. This indicates that we can control the structure of the Ti film through the Ar gas pressure of DC magnetron sputtering method.

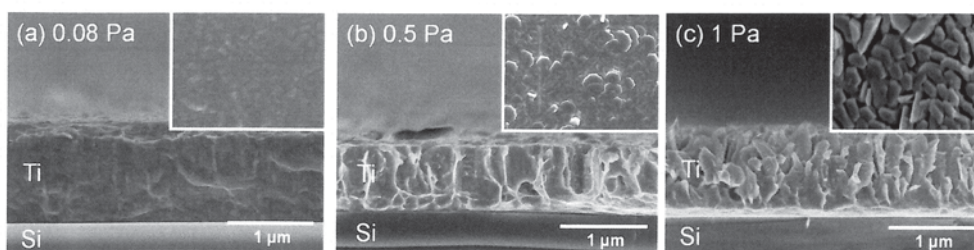


Fig. 2. Cross-sectional FE-SEM images of Ti films deposited by DC magnetron sputtering at Ar pressures of (a) 0.08, (b) 0.5, and (c) 1 Pa. The insets show top-views FE-SEM images.

Figure 3 shows cross-sectional FE-SEM images of the porous Ti films on a Si substrate (a) after HF treatment, (b) after TiW-I-II treatment, and (c) after HF treatment followed by TiW-I-II treatment (HF+ TiW-I-II treatment). A comparison between Figs. 2(c) and 3(a) indicated that HF treatment slightly dissolved the surface of the porous Ti film to widen the gap between each dendrite. In the case of TiW-I-II treatment, the surface of dendrites was slightly roughened as shown in Fig. 3(b). On the other hand, HF+ TiW-I-II treatment drastically changed the surface roughness and porosity of a porous Ti film, as shown in Fig. 3(c), although the structural changes were small when HF and TiW-I-II were separately used. HF treatment damaged the surface of dendrites, and the damaged layer was effectively removed by TiW-I-II to enable the formation of porous Ti film with a rough surface. The rough porous Ti film has a large surface area to reduce series resistance at the interface between the electrolyte and counter electrode of a DSC.

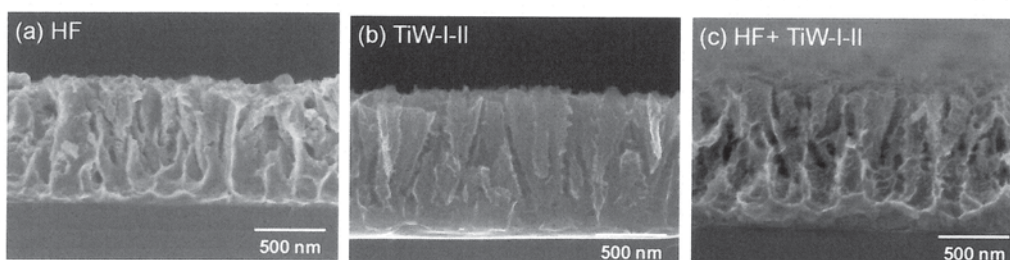


Fig. 3. Cross-sectional FE-SEM images of Ti films (a) after HF treatment, (b) after TiW-I-II treatment, and (c) after HF + TiW-I-II treatment.

Figure 4 shows the formation and application of porous Ti composite counter electrode to a DSC. From Fig. 4(a), we can clearly see that the Pt/porous Ti/dense Ti/Al/glass multilayer structure was formed. Pt was deposited by the thermal decomposition of H_2PtCl_6 to stabilize counter electrode activity. Figure 4 (b) shows the energy dispersive X-ray (EDX) spectra of the top, middle and bottom of the porous Ti layer after the deposition of Pt. The inset in Fig. 6(b) shows the collection area of each EDX spectrum. A peak due to Pt was clearly observed in the EDX spectra of the porous Ti layer independently of the position, indicating that Pt was homogeneously deposited on the porous Ti surfaces by the solution process, as shown in Fig. 4 (b). Figure 4 (c) shows the photovoltaic characteristics of DSCs using a Pt/porous Ti/dense Ti/Al/glass counter electrode and a conventional Pt/TCO counter electrode. We can see that the Pt/porous Ti/dense Ti/Al/glass counter electrode functioned stably as a counter electrode without the dissolution of Al in an electrolyte; this indicates that the dense Ti layer completely protected the Al layer against the electrolyte, and that a DSC with the Pt/porous Ti/dense Ti/Al/glass counter electrode showed a slightly higher open circuit voltage ($V_{oc} = 0.65$ V), higher short-circuit current density ($J_{sc} = 6.1$ mA/cm²), higher fill factor ($FF = 0.65$),

and better conversion efficiency ($\eta = 2.6\%$) than those of a DSC with a conventional Pt/TCO counter electrode

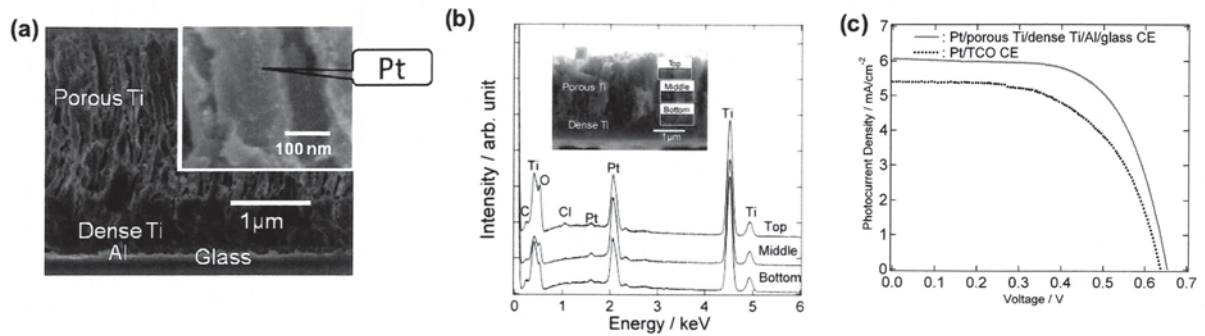


Fig. 4. (a) A cross-sectional FE-SEM image of the porous Ti composite counter electrode, where the inset shows the deposited thin Pt on the porous Ti layer, (b) EDX spectra of the porous Ti layer after deposition of Pt, and (c) the comparison of the photovoltaic characteristics of DSCs using a Pt/porous Ti/dense Ti/Al counter electrode and using a conventional Pt/TCO counter electrode, respectively.

($V_{oc} = 0.63$ V, $J_{sc} = 5.4$ mA/cm², $FF = 0.55$, $\eta = 2.0\%$). The improvement of the conversion efficiency was mainly associated with a larger fill factor and a higher short-circuit current. The large surface area of the porous Ti counter-electrode decreased the resistance of the reduction process at the electrolyte/counter electrode interface and the use of the Al layer in place of a TCO layer also decreased the sheet resistance. Our results indicate that it is very important to introduce the porous and high-conductive materials to the counter electrode of a DSC and that the porous Ti and the Al layer with the protective layer were promising materials for the CE of the DSC.

論文審査結果の要旨

近年、地球規模の環境問題がさげられる中、再生可能エネルギー源である太陽光を電力に効率よく変換する高性能太陽電池の開発が活発になっている。その中で色素増感太陽電池（DSC）は、低コスト化が可能で、比較的高い変換効率が得られる太陽電池として注目されている。しかしながら、現在、DSCの変換効率はシリコン太陽電池に比べ低く、実用化に向けた性能向上が求められている。DSCは、色素吸着した酸化チタン電極、電解液、及び、対極より成るが、著者は、DSC性能向上のために対極の構造に注目した。まず、DCマグネトロンスパッタの堆積条件によって、堆積されるチタン薄膜の構造を多孔質から緻密な膜まで自在に制御できることを見出し、それをDSCの対極へ応用することを提案した。そして、電解質による腐食のために対極として使用できなかった低抵抗アルミニウム電極を緻密なチタン薄膜で被覆することによってその使用を可能とし、対極のシート抵抗が低減し、DSCの変換効率が向上することを実験的に明らかにした。さらに、多孔質チタン薄膜をチタン被膜の上に重ね堆積することにより、対極の表面積の増大による変換効率の向上が実現できることを実験的に示した。本論文は、これらの研究成果を取りまとめたもので、全文5章より成る。

第1章は序論である。

第2章では実験手法について述べている。本研究で用いたDCマグネトロンスパッタ装置は、真空蒸着とDCマグネトロンスパッタリングとを真空一貫で行うことができる。そのため、アルミニウム薄膜の蒸着後、膜表面を大気に曝すことなくチタン薄膜を重ね堆積でき、夾雑物のない膜界面を実現できる。また、本章には、作製した対極の特性を評価するためのDSCの作製方法の詳細が記述されている。

第3章では、DCマグネトロンスパッタによるチタン薄膜の堆積と構造制御、及び、溶液処理による多孔質チタン薄膜表面の粗さ制御について述べられている。著者は、DCマグネトロンスパッタを用いてチタン薄膜を堆積する際、導入アルゴンガスの圧力が低い（0.1 Pa程度）ときには緻密なチタン薄膜が堆積し、一方、高い（1 Pa程度）ときには多孔質チタン薄膜が堆積することを見出した。また、溶液処理により、多孔質チタン薄膜表面の粗さを制御できることを示した。これらの成果は、チタン金属を電気電子材料として活用する場合に有用な知見である。

第4章では、多孔質チタン薄膜や緻密なチタン薄膜で覆われたアルミニウム薄膜を対極へ応用したときの効果を評価している。対極には電解質に対する耐腐食性が要求され、通常、耐腐食性の弱いアルミニウムを用いることができない。そこで、著者は、第3章で述べた緻密なチタン薄膜をアルミニウム薄膜電極の保護膜として利用することを提案した。チタン被膜付アルミニウム電極を対極に用いることにより、これまでDSCにおいて通常用いられている白金薄膜/酸化スズ/ガラスの三層構造電極に比べ2桁程度小さいシート抵抗を実現し、変換効率が向上することを実験的に示した。この結果は、緻密なチタン薄膜がアルミニウムの保護膜として有効に機能することを示している。さらに、表面粗さを増大した多孔質チタン薄膜を重ね堆積した対極を用いることにより、変換効率が1.5倍に増大することを明らかにした。これらは、高変換効率DSCを実現する上で極めて有用な知見である。

第5章は結論である。

以上要するに本論文は、DCマグネトロンスパッタによって多孔質から緻密な膜までの多様な構造のチタン薄膜を形成できること、さらに、それらのチタン薄膜はDSCの対極材料として活用できることを示した。これらの成果は、今後のDSCの開発において極めて有用であり、電気電子材料工学、電子工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。