—Communication—

Preparation of TiO_2 Film by the Sol-Gel Method and its Application to Photoelectrochemical Electrodes

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1. INTRODUCTION

Titanium(IV) oxide has been considered to be one of the most potential n-type semiconductors applicable to photoelectrochemical electrodes for solar energy conversion into other forms of energy such as H_2 gas and electricity, since it was demonstrated to offer an inert photoelectrochemical anode free from deterioration during illumination by Fujishima et al.(1). However, as long as single crystal or polycrystal TiO_2 (rutile) is concerned, its practical application to the solar energy conversion seems to be far from reality, because of its low efficiency.

In the present paper the so-called sol-gel method(2) has been applied to prepare TiO_2 film on the nesa glass substrate. The dip-coating method using sol makes it possible to obtain a large area of thin films on the substrate with quite ease(3). Moreover, it is of great interest to note that the gel film thus obtained can have a large specific surface area, which might have great effects on the photoelectrochemical behavior when applied to photoelectrodes.

2. EXPERIMENTAL

Titania sol was prepared by mixing $\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$, anhydrous $\text{C}_2\text{H}_5\text{OH}$ and H_2O in a manner shown in Fig.1. Amounts of each chemical used are shown in Fig.1.

Titania gel film was obtained by dipping a nesa glass substrate in the TiO_2 sol and subsequently pulling it up at a constant speed ($\sim 0.15 \text{ mm s}^{-1}$). The resulting TiO_2 gel film was subjected to heat treatment at 500°C for 10 min. By repeating the above operation, a thick film up to about $2 \mu\text{m}$ could be obtained.

Photoelectrochemical properties of the TiO_2 film were measured in $0.05 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ solution using a potentiostat with three electrodes: besides a TiO_2 photoanode a Pt plate of $35 \times 25 \text{ mm}^2$ and S.C.E. were employed as a counter and a reference electrode, respectively. A 500 W xenon lamp was adopted to illuminate the TiO_2 electrode. Impedance analyses for the TiO_2 electrode were also performed using a lock-in amplifier at a fixed frequency (1015 Hz).

Fig.1 Preparation of TiO_2 film on a nesa glass substrate.

3. RESULTS AND DISCUSSION

The TiO_2 gel film heated at 500°C was found to be in the anatase form. Heating at temperatures higher than 500°C to get rutile form could not be made because of the softening of the nesa glass used. Figure 2 shows polarization curves of TiO_2 film electrodes with different thicknesses taken at scan rate of 10 mV s^{-1} under and without illumination. Without illumination it is not until the potential reaches about 2 V (vs. SCE) irrespective of the film thickness that the current probably due to oxygen evolution becomes detectable. On the other hand, under illumination the photoelectrochemical (PEC) current starts to flow at about $-0.5 \sim -0.3 \text{ V (vs. SCE)}$ and saturates above $0.5 \sim 1.0 \text{ V (vs. SCE)}$, where vigorous evolution of gases was observed on the both TiO_2 anode and Pt cathode. The shape of photocurrent - potential curves observed for the TiO_2 film electrode is very similar to that for a single crystal TiO_2 (rutile) electrode(1), although the present TiO_2 film is in the anatase form. It is also clearly seen from Fig.2 that the PEC current strongly depends on the film thickness. Figure 3 shows the variations of the PEC current with the TiO_2 film thickness at bias potentials of 0.5 , 1.0 and 1.5 V (vs. SCE) . At any bias potentials the PEC current increases with increasing film thickness, reaches a maximum at the thickness of about $1.8 \mu\text{m}$ and then falls with further increase in film thickness. It is noteworthy that the TiO_2 film electrode of $1.8 \mu\text{m}$ thick shows a maximum PEC current as high as 14 mA cm^{-2} at the bias potential above 1.5 V (vs. SCE) .

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Fig.2 Photocurrent-Potential curves for TiO_2 film electrode.

Fig.3 Plots of current vs. TiO_2 film thickness.

Fig.4 Mott-Schottky plot.

Figure 4 shows typical Mott-Schottky plots conducted for the TiO_2 film electrode of $1.8 \mu\text{m}$ thick under illumination and in the dark. From Fig.4 two important features are evident: (1) a marked flat band shift is caused by illumination, while the slope remains almost invariant, (2) a negative deviation from the linearity is obvious on the cathodic side.

Figure 5 shows the variations of the flat band potentials V_{fb} in the dark and under illumination, and their difference (the flat band shift ΔV_{fb}) with film thickness. The change of V_{fb} with the thickness in the dark is probably due to too thin film compared to the space charge layer. The maximum ΔV_{fb} is found to correspond to the maximum PEC current. The decrease in the PEC current at thickness of $2.25 \mu\text{m}$ may be explained by an increase in the resistance of TiO_2 film, as seen from Fig.6, which was determined by the impedance analysis of the electrode by assuming a simple equivalent circuit consisting of series of resistance and capacitance. It is also obvious from Figs.5 and 6 that ΔV_{fb} is not caused mainly by the IR drop, if any. Therefore, it is reasonable to conclude that the observed large value of ΔV_{fb} is due to the potential change in the Helmholtz layer caused by hole trapping in the surface states under illumination as shown previously (4,5). According to them it has been shown that the more the surface states, the larger the ΔV_{fb} value. The negative deviation on the Mott-Schottky plot on the cathodic side clearly indicates that the surface state becomes major contribution to the total capacitance over the Helmholtz layer in this region. It may be assumed that the high surface state density of the TiO_2 film electrode arises from its characteristic gel-derived structure with a large surface area and many surface defects.

Fig.7 shows the variation of the depletion layer thickness with the TiO_2 film thickness, which shows a minimum at $1.8 \mu\text{m}$. However, the thickness of about 10 nm is much less than generally expected ($\sim 1 \mu\text{m}$). This fact suggests that the underestimated surface area is used for calculation of the depletion layer thickness.

A detailed discussion will be made elsewhere.

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Fig.5 Plots of V_{fb} and ΔV_{fb} vs. TiO_2 film thickness.

Fig.6 Plot of resistance vs. TiO_2 film thickness.

Fig.7 Plot of d vs. TiO_2 film thickness.