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Composition of the TiO_2 Film for Dye Sensitized Solar Cell (DSC) by AD Method

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TiO_2 thick films were prepared at room temperature by AD (aerosol deposition) method. The obtained films were a semiconductor and translucent at visible light range, which were important for TiO_2 electrode film used in dye sensitized solar cells (DSC). It was confirmed that these properties could be controlled by changing carrier gas. Moreover, the films had a light-scattering surface layer that was considered to be effective for improvement in DSC efficiency. For making porous films, films were made by the AD process using TiO_2 powder added with MgO fine powder followed by dissolving MgO particles in the films to make them porous. A dye used for DSC could be incorporated into the porous films. It was found that AD method was a promising process to make TiO_2 films for DSC.
Key words: dye sensitized solar cell (DSC), TiO_2 thick film, aerosol deposition (AD),

1. INTRODUCTION

Nowadays, dye sensitized solar cell (DSC) attracts attentions of many researchers as a new low-cost solar cell. It is very important for solar cells used for small-scale and dispersed type energy supply systems to achieve high efficiency with low-cost. The DSC is eagerly studied for practical use because of the cost. However the energy conversion efficiency of the DSC is still insufficient and improvement in the efficiency is needed. The DSC is mainly consists of five parts, electric conduction film (Fluorine doped tin oxide, FTO) glass, TiO_2 porous film, Ru light sensitive dye, iodine solution and opposite pole (FTO glass covered with Pt). Among all these parts, the TiO_2 porous film is the most important to achieve a high efficiency of DSC. TiO_2 porous film must adsorb many molecules of Ru dye which generate electrons. And the film property also concerns the amount of light absorbed by dye and the conduction of generated electrons. Generally, the TiO_2 porous films are prepared by sintering method at about 500 C. However, the reduction of electric conductivity of FTO by sintering restricts the efficiency and DSC with enough efficiency has not been prepared yet. And for full-plastic DSC, low temperature process is demanded for the process of the TiO_2 films.

Aerosol deposition (AD) method enables us to make various kinds of ceramic thick films at room temperature. And it also can be applied for TiO_2. So we think the AD method is a promising method to prepare TiO_2 film for DSC with high efficiency. However, as already stated, the TiO_2 film must be conductive, transparent and porous. These properties must be satisfied in AD method.

The ultimate objective of this study is to prepare TiO_2 thick film for DSC with high efficiency by AD method. In this paper, we have prepared TiO_2 films by AD method, evaluated the properties (conductivity and transparency) of the TiO_2 film and proposed a way to make the film porous.

2. EXPERIMENTAL

2.1 Preparation and characterization of TiO_2 film

A TiO_2 powder with rutile type structure was supplied from Showa Denko Co. Ltd. The diameter of a primary particle is about 500 nm. Using this powder, five kinds of samples were prepared on FTO glasses and slide glasses. In the sample II, III and IV, TiO_2 powder was annealed in nitrogen gas added with 3% of hydrogen gas to deoxidize the TiO_2 raw powder at different temperatures (deoxidization temperature). Powders to

Table I Preparation conditions of TiO_2 AD films

Sample	Materials powder condition		AD Condition			
	Deoxidization temp.	Dry temp.	Carrier gas	Flux	Scanning speed	Number of round trips
I	—	200℃	O_2	2.0 L/min	1.25 mm/sec	50
II	400℃	—				
III	500℃					
IV	600℃					
V	—	200℃	He			

* Deoxidization of raw powder was done in N_2 gas which involves 3% H_2 for 2 hours.

make samples I and V were dried at 200 C in air. In the AD method, oxygen was used for a carrier gas for samples I, II, III and IV. As for sample V, helium gas was used for a carrier gas. TiO_2 films were prepared under the conditions of 2.0 L/min flux of the carrier gas, 1.25 mm/sec of the scanning speed of substrate and 50 round trips in the scanning. The preparation conditions are summarized in Table I. Conductivity measurement was performed as follows: an In-Ga electrode was formed on the prepared sample, a voltage was applied in the film thickness direction to measure the sample resistance. The electrical conductivity is calculated from film thickness and electrode area. Transparency measurement was performed as follows: the surface of each sample was polished to control the film thickness at about 1 μm. And then transparency is measured by a visible light spectrometer using substrate as a standard. The measurement wavelength was from 300 nm to 800 nm, which was the absorption wavelength range of the dye for DSC.

2.2 Preparation of porous TiO_2 film

Porous TiO_2 films were prepared by dissolving MgO in the composite films of TiO_2 and MgO prepared by AD method. The raw powder was prepared by mixing TiO_2 powder (Showa Denko Co., Ltd.) and MgO powder (Kyowa Kagaku Co., Ltd.). The diameter of a primary particle of the MgO powder was about 900 nm. The mixing of powders was carried out in a ball mill with ethanol for 24 hours. The mixing ratios of TiO_2 and MgO were 70:30, 80:20, 90:10 and 95:5 wt%. After mixing, slurry was dried and the powder thus obtained was sieved with mesh size of 180 μm. Furthermore, the mixed powders were dried at 200 C for 1 weak before using in the AD process. The deposition condition of the composite thick films is as follows: 4.0 L/min of the flux of helium carrier gas, 1.25 mm/sec of the scanning speed of substrate and 50 round trips in the scanning.

MgO particles in the composite films were dissolved in water at 80 C for 2 hours followed by drying at 200 C for 5 minutes to make porous films. The films thus obtained were immersed in the Ru dye ethanol solution of $5x10^{-4}$ mol/l for 24 hours.

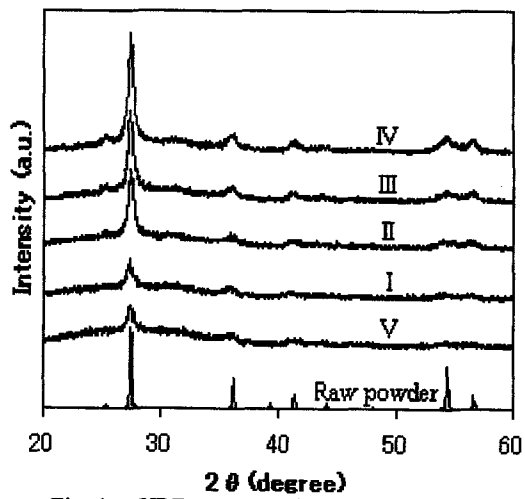


Fig. 1. XRD patterns of the TiO_2 AD films and the raw powder

3. RESULTS AND DISCUSSION

3.1 Property of TiO_2 film

XRD profiles of TiO_2 films are shown in Fig. 1. All samples were identified as rutile type TiO_2 which was the same as raw powder. Broad peaks in the XRD profiles indicated that the crystalline size of the TiO_2 was reduced and strains were induced in the films, which is a characteristic feature of AD process.

Table II shows conductivity (σ) of TiO_2 films prepared in this study. We tried to increase the conductivity (σ) of the films by employing TiO_2 raw powders annealed in a deoxidizing atmosphere. However, it was found that the conductivity showed lower values even if the films were annealed at higher temperature. This indicated that the defects induced by deoxidization of raw powders did not contribute to the conductivity of TiO_2 films prepared by AD process. On the other hand, the conductivity of TiO_2 films markedly increased when helium was used as a carrier gas. The conductivity of sample V was 90.9×10^{-7} S/cm, which is over 10 times of the conductivity of sample I (8.70×10^{-7} S/cm). The high conductivity of TiO_2 is due to the deoxidization of Ti ions in TiO_2 and the generation of oxygen vacancies for charge compensation. It should be noted that the reduction of TiO_2 is more effective in helium carrier gas than the annealing in reducing atmosphere.

Table II Conductivity (σ) of TiO_2 films (1V applied)

Sample	Deoxidization temp. of TiO_2 raw powder	Carrier gas	σ ($\times10^{-7}$S/cm)
I	—	O_2	8.70
II	400°C		7.19
III	500°C		5.85
IV	600°C		2.19
V	—	He	90.9

Figure 2 shows current (I) *vs.* voltage (V) curves of samples. It was found that the I vs. V curves of the TiO_2 films showed a non-ohmic behavior. The In-Ga electrodes used in this study usually form an ohmic contanct with n-type oxide semiconductors like TiO_2. The non-ohmic behavior shown in Fig. 2 may be due to the electron transport behavior in TiO_2 films.

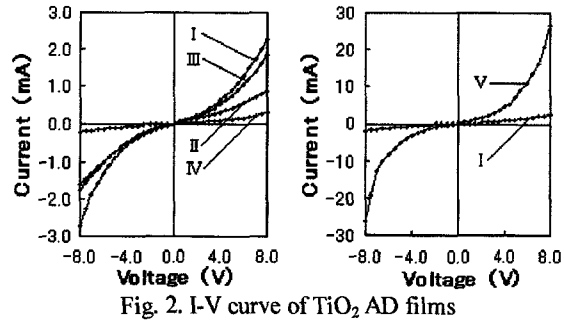


Fig. 2. I-V curve of TiO_2 AD films

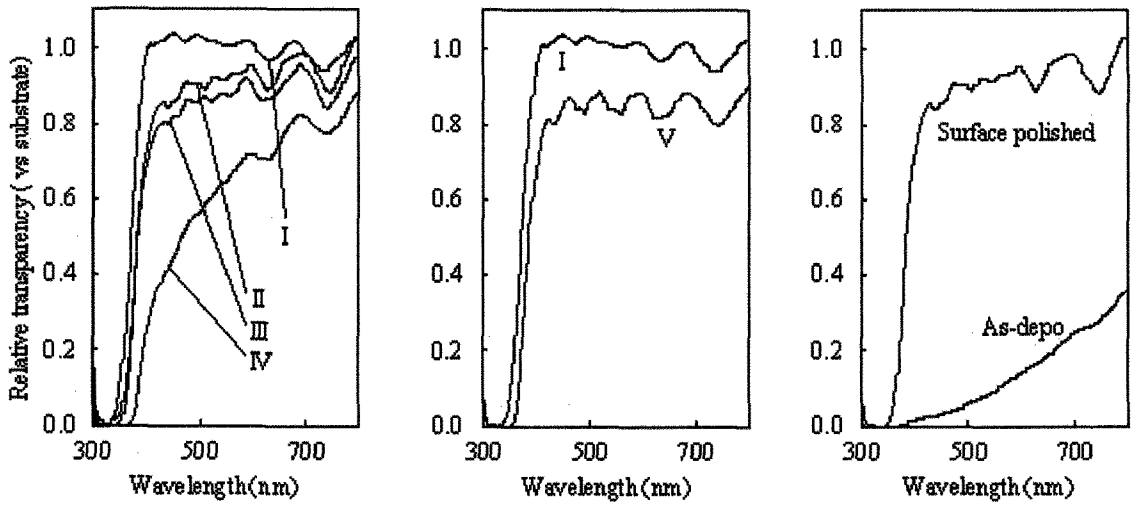


Fig. 3. Transparency of TiO_2 AD films prepared in this study
(a) Deoxidization temperature effect (b) Carrier gas effect (c) Surface polishing effect

Figures 3 (a) and (b) shows relative transparency of TiO_2 films prepared as a function of wavelength of light. The highest transparency was obtained in the sample I. It was an amazing result that the TiO_2 films prepared at room temperature by the AD method showed almost perfect transparency even though the sintering was not carried out. The transparency of the films decreased with increasing deoxidization temperature. This is due to the formation of defects such as reduction of Ti ions and oxygen vacancies, which did not contribute the conductivity of TiO_2 films. It should be noted that the absorption curve of sample V was different from those of sample II to IV, indicating that the defects induced in the films prepared using helium as a carrier gas were different from those induced in the deoxidization of raw powders. This result is consistent with that of conductivity shown in Table II and Figure 2. In Figure 3 (c), transparency before and after polishing was compared. The transparency markedly improved by polishing. Figure 4 shows the surface morphology of a TiO_2 film before polishing. Submicron sized grains were observed. These grains scattered light to reduce the transparency. The surface scattering seemed to be effective for improvement of DSC efficiency.

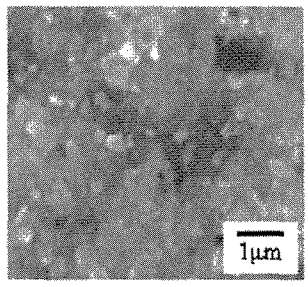
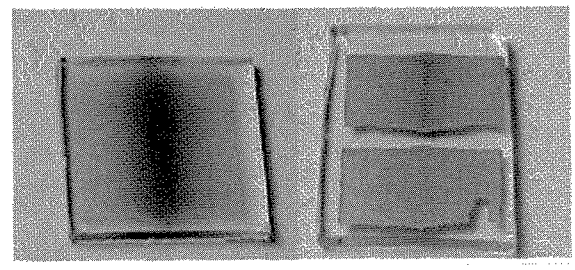


Fig. 4. Surface structure of as-deposited TiO_2 film

3.2 Preparation of porous TiO_2 film

Composite films were prepared using TiO_2-MgO mixtures as raw powders. However, dense films could not be obtained when the mixing ratio of TiO_2:MgO was 70:30, 80:20 and 90:10 because the agglomeration of powders were enhanced with increasing MgO content. Dense films were obtained only when the powder with the mixing ratio of 95:5 was used. The MgO particles were first tried to dissolve using diluted HCl but whole films were peeled off the substrate. Immersing in water at 80 C was an optimum condition to dissolve only MgO particles. After this process, the film was soaked in Ru dye solution for 24 hours. Figure 5 shows the change of film color after soaking. Red color indicates the dye was adsorbed in the film and the change in color was observed only for the composite films after dissolving MgO particle. This indicates that porous films indispensable to make DSC were successfully prepared from the composite film. We have not prepared the real solar cell using this film in this study. It will be a future work.



(a) (b)

Fig. 5. (a) photograph of as-deposited TiO_2 film
(b) photograph of the composite film after immersing in Ru dye for 24 hours

4.CONCLUSION

TiO_2 thick films were prepared by the AD method.

Crystalline films of rutile were formed on a glass substrate but the crystallinity was markedly reduced in comparison with the raw powder. The TiO_2 films showed semiconductivity but the deoxidization of raw TiO_2 powder reduced the conductivity. The usage of helium a carrier gas increased the conductivity about ten times, indicating that the carrier gas affected the defects of TiO_2 films. TiO_2 films with the transparency as same as substrate were obtained by AD method without sintering. The absorption curve of the film prepared using helium as a carrier gas was different from those prepared using deoxidized powders, indicating that the defects induced in both films were different. Composite films of TiO_2 and MgO was also prepared and MgO particles in the films were dissolved in water to make porous film. The porous film thus obtained adsorbed Ru dye by immersing in the dye solution.

REFERENCES

[1] H. Arakawa, *Functional Materials*, 20, 41-52 (2000).
[2] H. Sumino, S. Murai and S. Mikoshiba, *Toshiba review*, 56, 7-10 (2001)
[3] H.Arakawa and H. Ishizawa, *Functional Materials*, 22, 40-47 (2002).
[4] A. Konno, G.R.Asoka Kumara, M. Okuya and S. Kaneko, *Functional Materials*, 6, 26-33 (2003).
[5] Y. Nishikitani, *Functional Materials*, 6, 34-42 (2003).
[6] Y. Saito and S. Yanagida, *Powder and Industry*, 35, 36-43 (2003).
[7] S. Yanagida, *Applied Physics*, 73, 1509-18 (2004).
[8] H. Arakawa, *Applied Physics*, 73, 1519-24 (2004).
[9] K. Saito, T. Taima, M. Chikamatsu, K. Hara, Y. Yoshida and K. Yase, *Applied Physics*, 73, 1525-30 (2004).
[10] T. Miyasaka, *Applied Physics*, 73, 1531-35 (2004).
[11] S. Baba and J. Akedo, *Journal of the American Ceramic Society*, 88, 1407 (2005)
[12] Y. Imanaka and J. Akedo, *Electronic Components and Technology Conference*, 1614-1621 (2004)

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