

PHOTOCHEMICAL PROPERTIES OF ULTRATHIN TiO₂ FILMS PREPARED BY CHEMICAL VAPOR DEPOSITION

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(Received May 3, 1989)

Summary

Thin films of TiO₂ were prepared on fused silica and titanium substrates by chemical vapor deposition (CVD) using Ti[OCH(CH₃)₂]₄ under conditions of anatase formation. The UV-visible transmission spectrum of the film deposited on the fused silica substrate showed an absorption edge 30 nm shorter than that of anatase powder. This blue shift may be attributed to size quantization, *i.e.* the film may consist of extremely small TiO₂ particles. The absorption edge shifted to slightly longer wavelength upon heating the film in air at high temperatures. The photocatalytic property of the film was examined using the photodeposition reaction of silver from aqueous AgNO₃. The silver photodeposition rate increased with the calcination temperature, maximizing at around 400 °C and then decreasing at higher temperature. To compare the photocatalytic property with the photoelectrochemical property, photocurrents were measured in a KOH solution using the film deposited on the titanium substrate. They decreased after calcination at temperatures above 400 °C. Compared to bulk TiO₂, the wavelength dependence of the current was shifted to considerably shorter wavelengths, in agreement with the absorption spectrum.

1. Introduction

Materials and preparation methods for thin films have received considerable attention recently since such films have potential applications for new devices, including integrated circuits in electronics. TiO₂ thin films have been widely used as photoanodes in photoelectrochemical cells and can be easily

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prepared by CVD using organotitanium compounds such as titanium tetraisopropoxide [1]. Hardee and Bard [2, 3] have studied the preparation and the photoelectrochemical properties of CVD TiO_2 . Takahashi *et al.* [4 - 7] have studied in more detail the CVD conditions for preparing anatase and rutile films and examined their morphology and various properties.

In the present study, we prepared a thin film of very small particles of TiO_2 on a fused silica substrate by CVD and measured its absorption spectrum and the photocatalytic activity for the deposition of silver metal from aqueous AgNO_3 solution. We also demonstrated the usefulness of characterizing thin, optically active films using photoelectrochemistry. Photocurrents in a photoelectrochemical cell were monitored, using the CVD film on titanium, to examine the relationship between photocatalytic activity and photocurrent. The results were compared with those obtained in studies of the photocatalytic properties of fine TiO_2 powder prepared by hydrolysis of titanium tetraisopropoxide. We present evidence that the layers formed here contain extremely small particles.

2. Experimental details

The CVD apparatus was similar to that of Hardee and Bard [2]; the vessels of $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ and water were maintained at about 50 °C and the substrate was heated to about 170 °C. Dry nitrogen or argon was used as a carrier gas. The substrate was a fused silica plate (10 mm × 20 mm) which had been washed by sonication with detergent and rinsed with ethanol prior to CVD. A titanium disc (12.5 mm diameter, about 1 mm thick) was also used as a substrate to make a photoelectrode. The disc was polished first with emery paper, then with diamond paste, and finally was buffed to a mirror finish. The substrates were rotated slowly during CVD to ensure fairly uniform CVD films. With the fused silica substrate, however, interference rings appeared under white light due to uneven film thickness. The TiO_2 films were calcined in air for 3 h at various temperatures to investigate the change in photoactivity.

The absorption spectra of the CVD films deposited on the fused silica substrate were recorded on a UV-visible spectrometer in the transmission mode. The diffuse reflection spectrum of anatase (Merck) was recorded as a reference. Photodeposition of silver on the film from aqueous AgNO_3 solution was carried out in a fused silica photocell which was illuminated with a 500 W xenon lamp. The rate of silver deposition was measured by a spectrophotometric method using 500 nm light; the absorbance of the deposited silver was recorded at appropriate intervals of illumination. The titanium disc with its CVD film was connected to a copper wire using silver paint and epoxy resin. The photocurrent *vs.* the applied potential in a 0.1 M KOH solution was measured in a three-electrode system equipped with a platinum counter electrode and a standard calomel electrode (SCE) as a reference. The illuminated area of the electrode was 0.35 cm². The light

source was a 1000 W Hg-Xe high pressure lamp. The action spectra of the photocurrent were measured with a grating monochromator.

3. Results and discussion

Thin TiO₂ film deposited on a carefully cleaned fused silica substrate appeared smooth and transparent, much like single crystal TiO₂. As it grew, the film was stable through at least the first four interference rings (each ring corresponds to roughly 500 nm). Further CVD resulted in cracking and peeling. When heated in air at temperatures above 500 °C, a thick film with more than three interference rings cracked but did not peel off. Cracking was avoided by heating the film at about 400 °C after the development of each interference ring and then returning it to the apparatus for further CVD. Films with four - six interference rings did not crack or peel off the substrate when prepared in this way.

The TiO₂ deposited on the titanium substrate appeared more uniform than that on the fused silica substrate, since the interference rings were not so clear. After 1 - 1.5 cycles of the color change the film was heated in air at about 400 °C for more than 10 min and then submitted to further CVD. This produced a thick film that was stable when heated at temperatures below about 650 °C, but peeled off at temperatures above 800 °C.

X-ray diffraction (XRD) of the film on the fused silica substrate showed very broad, difficult-to-resolve peaks from which it was impossible to determine whether the CVD TiO₂ was anatase or rutile in form, probably because the film is amorphous or contains extremely small particles of the oxide. After calcining at temperatures below 500 °C, the TiO₂/Ti gave distinct XRD peaks assigned to titanium, but no peaks corresponding to crystalline TiO₂. We suppose that any crystallinity would be anatase, since CVD of titanium tetraisopropoxide gives only anatase under conditions of slow deposition rate and low temperatures used here [4 - 6]. An attempt was made to measure the thickness of the CVD film on fused silica using an interference-type film thickness meter, but the result was ambiguous, since the precise refractive index of anatase was not known and the substrate was transparent. However, our results suggest that the film (with less than three interference rings) used in the photoactivity measurements was of the order of 1 μm thick.

The absorption spectra of the CVD film on fused silica showed an absorption edge near 360 nm, at a more than 30 nm shorter wavelength than for TiO₂ powder (anatase) (Fig. 1). The absorption edge shifted to even shorter wavelengths if the film was thinner. This blue shift of the spectrum is basically attributable to size quantization [8], *i.e.* the film consists of extremely small TiO₂ particles. Quantum size effects in semiconductor particles arise from a "particle in a sphere" correction to the optical band-gap, given by [8, 9]:

$$E_g = (\hbar^2/8R^2)[1/m_e^* + 1/m_h^*] - e^2/R + \text{polarization terms} \quad (1)$$

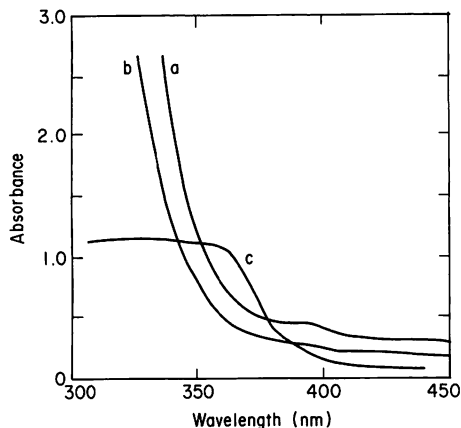


Fig. 1. Absorption spectra of the CVD TiO_2 film deposited on a fused silica substrate at 170°C (a, center; b, edge of the film) and diffuse reflection spectrum of anatase powder (c).

where R is the particle radius and m_e^* and m_h^* represent the effective masses of electrons and holes. For bulk TiO_2 , estimates of m_e^* and m_h^* of 8 - 110 and 0.01 electron masses, respectively, have been made [10 - 12]. The large m_e^* and small m_h^* values are a consequence of narrow titanium 3d and wide oxygen 2p bands in bulk TiO_2 . If these values are applied to small TiO_2 particles, the m_h^* term is expected to dominate E_g and observable blue shifts (less than 0.2 eV) should occur with $R < 200 \text{ \AA}$. In fact, little or no shift is observed with colloids in which the particle size is 100 \AA or less [13 - 15]. Moderate blue shifts (0.2 - 0.6 eV) have been found with ultrathin (5 - 10 \AA) TiO_2 films grown on porous Vycor Glass [16], and particles grown inside the 13 \AA diameter large cages in zeolite L [17]. Takahashi *et al.* [5] have observed a similar blue shift (0.3 - 0.5 eV) in their CVD TiO_2 study and, using a scanning electron microscope, they found that their film consisted of columnar crystals of anatase [6]. The blue shift we observe in CVD films on fused silica is comparable to these. We estimate the effective average particle diameter is about 10 \AA under the assumption that the substrate gives little effect on the electronic structure of CVD TiO_2 . The spectrum shifted to slightly longer wavelength upon heating the film to 500°C (Fig. 2), consistent with sintering and growth of the crystals. Above 500°C the spectrum remained unchanged, indicating no further sintering of the particles.

The photodeposition of silver metal over the film in aqueous AgNO_3 was followed by measuring the visible light transmittance of the film. The increase in absorbance caused by the silver photodeposition was greatest at the beginning of illumination and declined with time (Fig. 3). Fahrenholtz and Trozzolo [18] have employed a similar method with photodeposition on single crystal TiO_2 and observed a linear time dependence of the absorbance. Thus, the photochemical properties of the CVD film are somewhat different from those of single crystal TiO_2 .

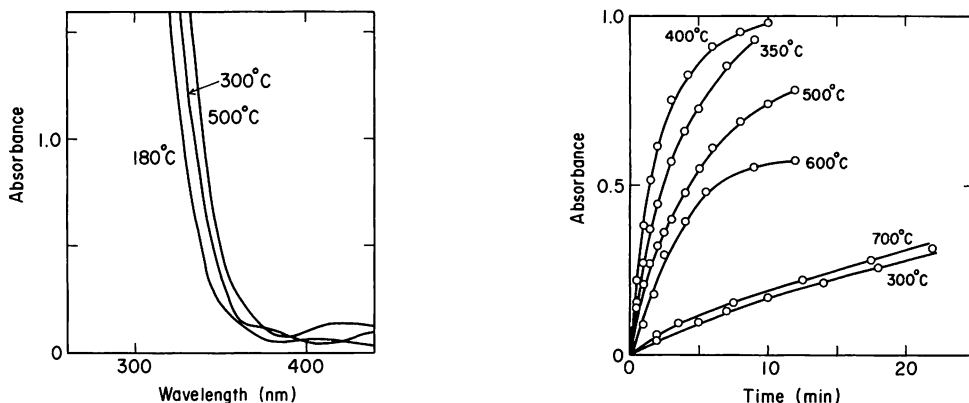


Fig. 2. Red shift of the absorption spectrum of the CVD film on fused silica upon heating in air.

Fig. 3. Time dependence curves of the absorbance resulting from the photodeposition of silver metal on the CVD film on fused silica immersed in aqueous AgNO_3 with xenon lamp irradiation. Temperature denotes the temperature at which the TiO_2 film was calcined.

A TiO_2 thin film was also prepared by painting an isopropanol solution of titanium tetra-2-propoxide over a fused silica substrate, followed by heating to 400°C in air to form a cloudy fine powder of TiO_2 . Like the CVD film, this film showed a non-linear time dependence of the absorbance. The departure from linearity increased with film thickness. Thus, the photochemical properties of the CVD film are much like those of the film composed of fine TiO_2 powder.

As shown in Fig. 3, heating in air caused the subsequent rate of silver photodeposition to first increase, then maximize near 400°C and decrease. Although a mechanism for the increase in photoactivity by calcination is not yet understood, a change in surface states may be a contributing factor. As expected, since the photoreduction of the silver ion is accompanied by the oxidation of water, bubbles (probably of oxygen) were observed on active CVD films after prolonged illumination.

When powdered TiO_2 (anatase) prepared by hydrolysis of titanium tetra-2-propoxide is used for the photoreduction of the silver ion in aqueous Ag_2SO_4 , its photocatalytic activity is very low but increases after calcination at 500°C and decreases for calcination above 800°C [19]. The same results were obtained using aqueous AgNO_3 [20]. Comparing powders and films, the difference in the calcination temperature required to give maximum activity is consistent with different particle sizes. For TiO_2 powder, the loss of photocatalytic activity induced by the high temperature calcination was restored by reduction in hydrogen at 700°C [20]. The activity drop can be explained in term of a decrease in the carrier density of TiO_2 , which is restored by the reduction. The lower activity of the CVD film was not enhanced by reduction, probably because Ti^{3+} ion formation was very limited at the surface.

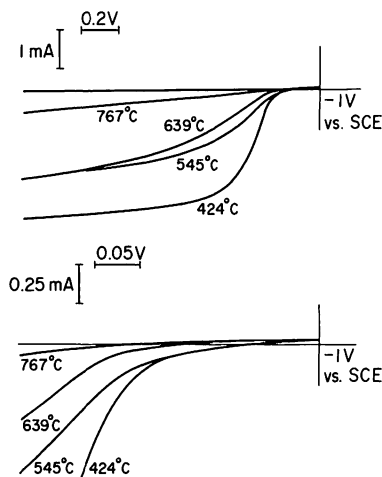


Fig. 4. Photocurrent *vs.* applied potential curves for the CVD film on the titanium substrate in a 0.1 M KOH solution. The onset regions are magnified in the lower figure. Temperature denotes the temperature at which the film was calcined.

Figure 4 shows the photocurrents *vs.* the applied potential curves for the electrodes of the CVD TiO_2 film on titanium in 0.1 M KOH. In agreement with the photoactivity of the CVD film on fused silica, the photocurrent decreased with an increase in calcination temperature. The photocurrent onset potential undergoes a slight positive shift with increasing calcination temperature. This may indicate the shift of a flat band potential of TiO_2 . Figure 5 shows the photocurrent action spectra at 0.1 V (SCE) (the photocurrent values are not corrected for light intensity). When the calcination temperature is lower than 550 °C, the photocurrent onset wavelength is shifted to a notably shorter wavelength than standard TiO_2 electrodes, in agreement with the absorption spectra (Fig. 1) of the CVD film on fused silica. The onset wavelength, however, shifted to a considerably longer wavelength when the film was calcined at temperatures above 639 °C, though

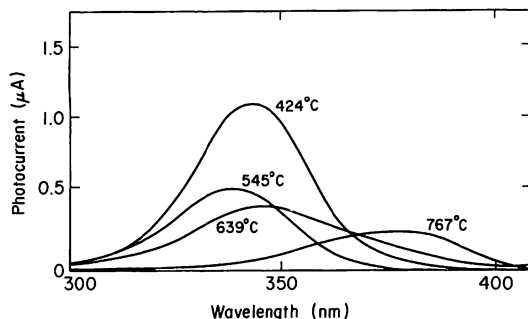


Figure 5. Wavelength dependence of the photocurrent for the film on titanium at 0.1 V (SCE) in a 0.1 M KOH solution (the photocurrent is not corrected for light intensity). Temperature denotes the temperature at which the film was calcined.

the absorption edge of the film on fused silica was not changed by heating at temperatures above 500 °C after calcination at 500 °C. This large shift may be due to the oxidation of the titanium substrate, which produces TiO₂ (rutile) between the CVD TiO₂ and the substrate and may lead to sintering and/or a change in the TiO₂ crystal form in the film.

In summary, the results of the present study show that thin TiO₂ films prepared by CVD have photochemical properties very similar to those of fine TiO₂ powder. These effects are attributable to size quantization effects. These results are reasonable, since scanning electron microscopy has revealed that such CVD films are composed of small TiO₂ particles [6]. The films, however, differ from the powders in that the particle size is much smaller and their structure and photochemical properties are influenced by the substrate. On a fused silica substrate, sintering of the TiO₂ thin film into particles appears to be suppressed even at high temperature. On the titanium substrate, on the other hand, a thick film is more stable than on the fused silica substrate, and the film properties are changed by calcination at high temperature owing to the oxidation of the substrate.

Acknowledgments

Support of this research by the Gas Research Institute is gratefully acknowledged. One of the authors (SS) was supported by the Japanese Ministry of Education, Science and Culture, Grant-in-Aid for Special Project Research No. 391770001724. This joint research was also aided by an NSF grant to JMW, INT-850009449.

References

- 1 E. T. Fitzgibbons, K. J. Sladek and W. H. Hartnig, *J. Electrochem. Soc.*, **119** (1972) 735.
- 2 K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.*, **122** (1975) 739.
- 3 K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.*, **124** (1977) 215.
- 4 Y. Takahashi, K. Tsuda, K. Sugiyama, H. Minoura, D. Makino and M. Tsuiki, *J. Chem. Soc. Faraday Trans. 1*, **77** (1981) 1051.
- 5 Y. Takahashi, A. Ogiso, R. Tomoda, H. Minoura and M. Tsuiki, *J. Chem. Soc. Faraday Trans. 1*, **78** (1982) 2563.
- 6 Y. Takahashi, H. Suzuki and M. Nasu, *J. Chem. Soc. Faraday Trans. 1*, **81** (1985) 3117.
- 7 H. Minoura, M. Nasu and Y. Takahashi, *Ber. Bunsenges. Phys. Chem.*, **89** (1985) 1064.
- 8 L. E. Brus, *J. Chem. Phys.*, **80** (1984) 4403.
- 9 L. E. Brus, *Nouveau J. Chim.*, **11** (1987) 123.
- 10 H. Yahia, *Phys. Rev.*, **130** (1963) 1711.
- 11 R. G. Breckenridge and W. R. Hosler, *Phys. Rev.*, **91** (1953) 793.
- 12 F. A. Grant, *Rev. Mod. Phys.*, **31** (1959) 646.
- 13 N. M. Dimitrijevic, D. Savic, O. I. Micic and A. J. Nozik, *J. Chem. Phys.*, **88** (1984) 4278.
- 14 D. Duonghong, J. Ramsden and M. Graetzel, *J. Am. Chem. Soc.*, **104** (1982) 2977.

- 15 A. Henglein, *Ber. Bunsenges. Phys. Chem.*, *80* (1982) 241.
- 16 M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis and E. Giamello, *J. Phys. Chem.*, *89* (1985) 5017.
- 17 J. S. Krueger and T. E. Mallouk, paper in preparation.
- 18 S. R. Fahrenholtz and A. Trozzolo, *J. Am. Chem. Soc.*, *94* (1972) 283.
- 19 S. Nishimoto, B. Ohtani, H. Kajiware and T. Kagiya, *J. Chem. Soc. Faraday Trans. 1*, *81* (1985) 61.
- 20 S. Sato and T. Kadowaki, to be published.