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
prepared by CVD using organotitanium compounds such as titanium tetra-

isopropoxide [1]. Hardee and Bard [2, 3] have studied the preparation and

the photoelectrochemical properties of CVD TiO₂. 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

TiO₂ on a fused silica substrate by CVD and measured its absorption spec-

trum and the photocatalytic activity for the deposition of silver metal from

aqueous AgNO₃ solution. We also demonstrated the usefulness of charac-
terizing thin, optically active films using photoelectrochemistry. Photocurr-
cents 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 TiO₂ powder prepared by hydrolysis

of titanium tetra-isopropoxide. 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 Ti[OCH(CH₃)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, inter-

ference rings appeared under white light due to uneven film thickness. The

TiO₂ 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 AgNO₃

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 depo-
sited silver was recorded at appropriate intervals of illumination. The tita-
nium 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
3. Results and discussion

Thin TiO$_2$ film deposited on a carefully cleaned fused silica substrate appeared smooth and transparent, much like single crystal TiO$_2$. 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 TiO$_2$ 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 TiO$_2$ 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 TiO$_2$/Ti gave distinct XRD peaks assigned to titanium, but no peaks corresponding to crystalline TiO$_2$. 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 TiO$_2$ 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 TiO$_2$ 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 $R < 200$ Å. In fact, little or no shift is observed with colloids in which the particle size is 100 Å or less [13 - 15]. Moderate blue shifts (0.2 - 0.6 eV) have been found with ultrathin (5 - 10 Å) TiO$_2$ films grown on porous Vycor Glass [16], and particles grown inside the 13 Å 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 Å 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$_2$. 
A TiO₂ 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 TiO₂. 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 TiO₂ 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 TiO₂ (anatase) prepared by hydrolysis of titanium tetra-2-propoxide is used for the photoreduction of the silver ion in aqueous Ag₂SO₄, 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 AgNO₃ [20]. Comparing powders and films, the difference in the calcination temperature required to give maximum activity is consistent with different particle sizes. For TiO₂ 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 TiO₂, which is restored by the reduction. The lower activity of the CVD film was not enhanced by reduction, probably because Ti³⁺ ion formation was very limited at the surface.
Figure 4 shows the photocurrents vs. the applied potential curves for the electrodes of the CVD TiO₂ 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 TiO₂. 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 TiO₂ 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
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. 39177001724. This joint research was also aided by an NSF grant to JMW, INT-850009449.

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