Anatase Thin Films on Glass from the Chemical Vapor Deposition of Titanium(IV) Chloride and Ethyl Acetate

Shane A. O'Neill, Robin. J. H. Clark, and Ivan P. Parkin*

Christopher Ingold Laboratories, University College London, 20 Gordon Street,
London WC1H 0AJ, United Kingdom

Nicholas Elliott and Andrew Mills

Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham
Building, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

Received July 2, 2002. Revised Manuscript Received October 6, 2002

Thin (50−500 nm) films of TiO_2 may be deposited on glass substrates by the atmospheric pressure chemical vapor deposition (APCVD) reaction of $TiCl_4$ with ethyl acetate at 400−600 °C. The TiO_2 films are exclusively in the form of anatase, as established by Raman microscopy and glancing angle X-ray diffraction. X-ray photoelectron spectroscopy gave a 1:2 Ti:O ratio with Ti $2p_{3/2}$ at 458.6 eV and O 1s at 530.6 eV. The water droplet contact angle drops from 60° to <5° on UV irradiation. The deposited films bring about the complete photooxidation of a stearic acid overlayer following irradiation at 254 nm for 30 min. Both the drop in contact angle and the photooxidation described are critically important to the self-cleaning applications of anatase films on glass.

Introduction

It is apparent that titania (TiO_2) is the best photocatalyst with which to perform the degradation of organic micropollutants in aqueous media,[1] due to its high stability and relatively strong oxidizing power. It is able to utilize visible and/or near UV light and is inexpensive. It has long been known that the pigment titanium white (TiO_2) is responsible for the fading of colored pigments in paints.[2] Its attraction as a pigment for the paints industry comes from its high opacity, which arises from its high refractive indices, of 2.61 and 2.90 for rutile and 2.56 and 2.49 for anatase.[3] Because of its photo-oxidative properties, it was thought originally that TiO_2 would be unsuitable as a pigment in paint as its use resulted in slow degradation of the organic polymer of the paint.[4] However, it was found that such degradation could be prevented by coating the particles with a thin layer of an inert oxide such as alumina and amorphous silica, thereby maintaining the optical properties of titania, but reducing its propensity to photodegrade.

While titania has been widely used as a photocatalyst for water purification purposes, there is growing interest in its use as a thin, transparent film for the photodestruction of organic materials, thus creating a self-cleaning surface.[4] Additionally, titania films also show the remarkable property of having extremely low contact angles for water droplets. This enhances the self-cleaning efficiency of windows by encouraging sheeting of rain droplets. Thin films of this type could be employed in self-cleaning windows, a property that has been realized by Pilkington Glass with the launch of the world's first commercially available self-cleaning glass, Pilkington Activ.[5] Clear TiO_2 films require titania particles to be smaller than the wavelength of visible light, a requirement which precludes the use of commercially available TiO_2 in the form of Degussa P25, which has aggregate particle diameters in excess of 100 μm.

Sol−gel methods have been used previously to deposit thin, optically transparent films onto glass by hydrolysis of $Ti(O^iPr)_4$ followed by calcination at 500−600 °C.[6] The films produced by this method are not abraded when scratched with pencils and cannot be removed using Scotch tape; however, they can be scratched by brass or steel. They consist of large aggregates of anatase with TiO_2 crystallites of 3−21-nm diameter and are therefore clear. Degussa P25 films have also been deposited on glass substrates but, due to increased particle size, are light scattering; such films show good photocatalysis but are easily abraded, for example, by rubbing with a soft cloth.

Thin films of titania have also been deposited on glass substrates by physical and chemical vapor deposition.[7,8] Low-pressure chemical vapor deposition routes have also been used to grow TiO_2 on a variety of substrates such as silica, quartz, and glass.[9,10] Atmospheric pressure chemical vapor deposition (APCVD) has the ad-

---

* To whom correspondence should be addressed.

(1) Hoffman, M. R.; Martin, S. T.; Choi, W.; Bahneman, D. *Chem. Rev.* **1995**, *95*, 69.

(2) Keidel, E. *Farben-Ztg.* **1929**, *34*, 1242.

(3) Clark, R. J. H. *The Chemistry of Titanium and Vanadium*; Elsevier: Amsterdam, 1968; Chapter 9.

(4) Mills, A.; Le Hunte, S. *J. Photochem. Photobiol., A* **1997**, *108*, 1.

(5) Smith, A. *Int. Glass Rev.* **2001**, *1*, 29.

(6) Paz, Y.; Luo, Z.; Rabenberg, L.; Heller, A. *J. Mater. Chem.* **1995**, *10*, 2842.

(7) Takahashi, Y.; Matsuoka, Y. *J. Mater. Sci.* **1988**, *23*, 2259.

10.1021/cm020707f CCC: $25.00

Table 1. Conditions for Growth of TiO_2 by the APCVD Reaction of $TiCl_4$ and Ethyl Acetate

temp (°C)			gas flow ($dm^3\ min^{-1}$)							
coater	$TiCl_4$	EtOAc	$TiCl_4$	EtOAc	make up gas	run time (s)	phase seen by RM[a]	film thickness (nm) (SEM/UV)[b]	contact angle[c]	% degradation of stearic acid at 253 nm
660	68	42	0.2	0.2	7.5	30	anatase	500		25 after 12 min
600	68	42	0.2	0.2	7.5	30	anatase	500	33	35 after 60 min
550	68	42	0.2	0.2	7.5	30	anatase	450	12	100 after 60 min
500	68	42	0.2	0.2	7.5	30	anatase	450	10	69 after 60 min
450	68	42	0.2	0.2	7.5	30	anatase	400	8.5	100 after 60 min
400	68	43	0.2	0.2	7.5	30	anatase	300	11	30 after 60 min
500	68	43	0.4	0.4	7.1	30	anatase	500		
660	64	39	0.1	0.1	11	10	anatase	100	2.7	25 after 12 min
660	58	45	0.2	0.2	10.8	10	anatase	150	4.6	62 after 12 min
660	68	43	0.3	0.3	10.6	10	anatase	150	2.7	65 after 12 min
660	68	43	0.4	0.4	10.4	10	anatase	200	1.7	100 after 12 min

[a] RM = Raman microscopy. [b] SEM = scanning electron microscopy. [c] All films are preirradiated for 60 min at 254 nm prior to contact angle measurement. Film morphologies were all of the island growth “crazy paving”-type).

vantage over LPCVD routes in that it is inexpensive, gives fast growth rates, 100−1000 times that of LPCVD, and can be incorporated readily into modern float-glass production facilities. By contrast to sol−gel methods of synthesis, APCVD is not a batch process on the production scale. It also has the advantage over sol−gel methods of producing films of TiO_2 of greater mechanical robustness, which are ideal for applications such as self-cleaning windows. In this paper we report the synthesis and characterization of photoactive anatase films by a convenient APCVD reaction of $TiCl_4$ and ethyl acetate.

Experimental Section

Nitrogen (99.99%) was obtained from BOC and used as supplied. Titania thin films were deposited onto SiO_2-coated standard float glass as supplied by Pilkington Glass Plc. (The silica layer acts as a barrier coating to prevent diffusion of ions from the bulk of the glass into the CVD film.) Atmospheric pressure CVD experiments were performed on 225 × 89 × 4 mm^3 glass substrates using a cold wall APCVD reactor. Full details of the reactor and the equipment used for film analysis have been published previously.[11] The glass was cleaned prior to use by being washed with distilled water, then 2-propanol, and finally petroleum spirits (40−60 °C) and then dried in air. The glass substrate was heated on a graphite block containing three Whatman cartridge heaters, the temperature of the block being monitored by a Pt−Rh thermocouple. The rig was designed so that four separate gas lines could be used, all of which were made of $^1/_4$-in.-diameter stainless steel except for the inlet to the reaction chamber and the exhaust line from the reaction chamber which was $^1/_2$ in. in diameter. Carrier gases were preheated to 150 °C by being passed along 2-m lengths of coiled stainless steel tubing inside a three-zone tube furnace. Gas temperatures were monitored in situ by Pt−Rh thermocouples. $TiCl_4$ (99.9%, Aldrich Chemical Co.) was used as supplied and placed into a stainless steel bubbler, which was heated by a heating jacket to 68 °C. The $TiCl_4$ was added to the gas stream by passing hot N_2 through the bubbler. Ethyl acetate was introduced into the gas stream by passing hot N_2 through the liquid, which was held at 50−80 °C. The apparatus was baked at 150 °C for an hour prior to each run. Deposition times were 30 s unless otherwise stated. The coated substrates were cooled to 200 °C before removal from the graphite block and were then handled and stored in air. The large substrates were cut into ca. 1 × 1 cm^2 squares for analysis by SEM, XPS, Raman, and UV studies; 2.5 × 2.5 cm^2 squares were used for X-ray diffraction, contact angle, and photocatalysis tests.

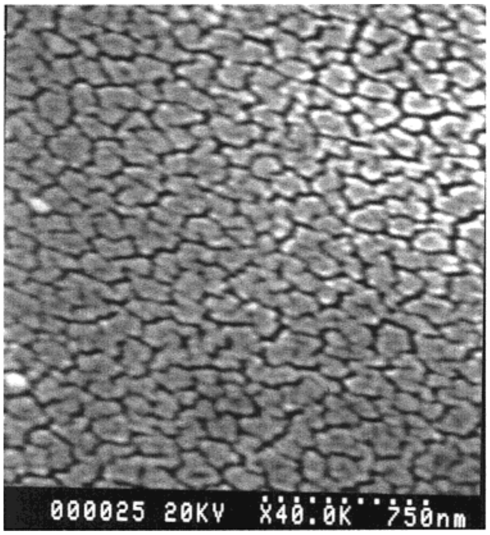

Figure 1. SEM micrograph of TiO_2 thin films deposited on glass at 500 °C.

Photocatalysis was assessed by destruction of a layer of a test organic chemical—stearic acid—on a 2.5 × 2.5 cm^2 square of TiO_2-coated glass which had been irradiated at 254 nm for 1 h prior to measurement. Stearic acid (7.5 μL of 0.4 mM solution in MeOH) was applied with a Hamilton syringe to the surface, which was then spun at 1500 rev min^{-1}. The transmission IR spectra of the glass coated with the stearic acid layer was quantified from 3000 to 2850 cm^{-1}. The glass coated with stearic acid was irradiated at 15-min intervals for up to an hour at 254 nm by two BDH germicidal lamps (8 W). The IR spectra of the residual film was monitored after each irradiation and the peak area quantified. Stearic acid was chosen as a test organic reagent as it was nonvolatile, gave an excellent C−H signature, and could be easily and reproducibly made by spin-coating. The 254-nm lamp was chosen for this photodegradation study as it is monochromatic (99.5% of the emitted energy at 254 nm), subbandgap, and readily available.

Results

All films deposited in this study have been grown from the reaction of titanium(IV) chloride with ethyl acetate

---

(8) Aarik, J.; Sammelsberg, V.; Uustare, T.; Ritala, M.; Leskela, M. *Thin Solid Films* **2000**, *370*, 163. Lee, Y. H.; Chan, K. K.; Brady, M. J. *J. Vac. Sci. Technol., A* **1995**, *13*, 596. Chen, Q.; Qian, Y.; Chen, Z.; Wu, W.; Zhou G.; Zhang, Y. *Appl. Phys. Lett.* **1995**, *66*, 1608. Kim, E. K.; Son, M. H.; Min, S. K.; Hon, Y. K.; Yom, S. S. *J. Cryst. Growth* **1997**, *170*, 803.

(9) Kukli, K.; Ritala, M.; Schuisky, M.; Sajavaara, T.; Keinonen, J.; Uustare, T.; Harsta, A. *Chem. Vap. Deposition* **2000**, *6*, 303. Fernandez, A.; Lassaletta, G.; Jimenez, V. M.; Justo, A.; Gonzalez-Elipe, A. R.; Herman, J. M.; Tahiri, H.; Ait-Ichou, Y. *Appl. Catal., B* **1995**, *7*, 49.

(10) Marco de Lucas, M. C.; Fabreguette, F.; Collin, S.; Bourgeois, S. *Int. J. Inorg. Mater.* **2000**, *2*, 255.

(11) Price, L. S.; Parkin, I. P.; Hardy, A. M. E.; Clark, R. J. H.; Hibbert, T.; Molloy, K. C. *Chem. Mater.* **1999**, *11*, 1792.

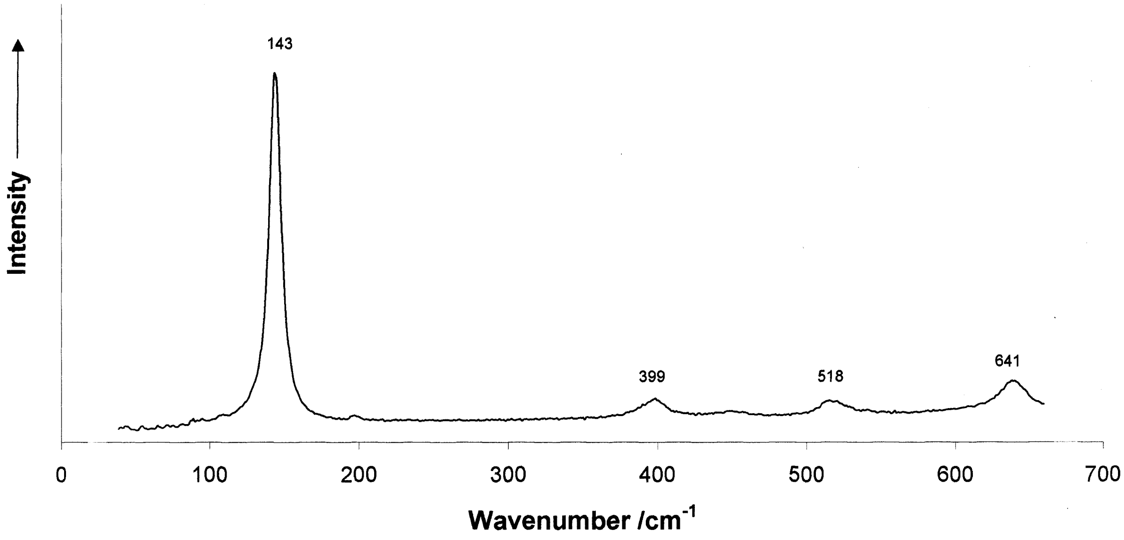

Figure 2. Raman spectrum of anatase TiO_2 deposited on glass at 500 °C.

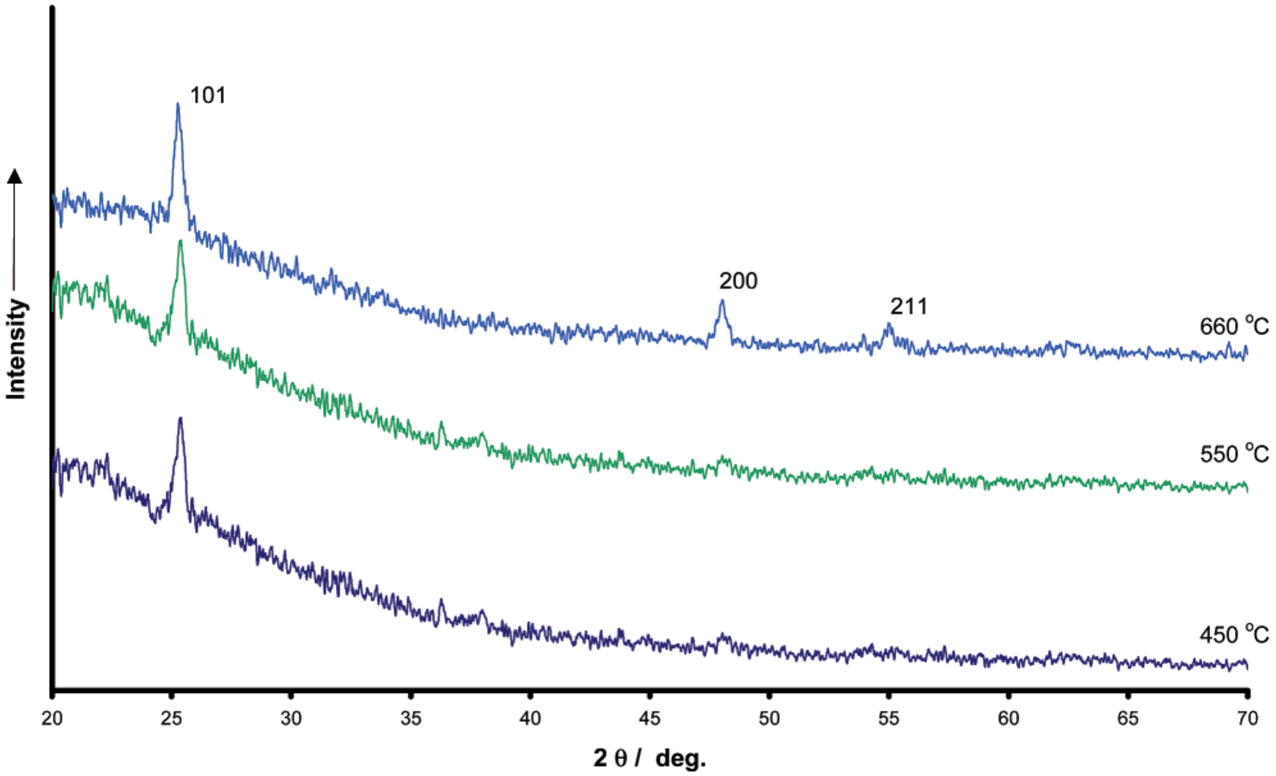

Figure 3. Glancing angle XRD patterns of TiO_2 films deposited on glass at 450, 550, and 660 °C.

as the co-oxygen source under APCVD conditions at various substrate conditions, deposition times, and precursor concentrations. These parameters affect the nature of the films produced. Deposition times greater than 60 s resulted in nonuniform films with optical interference patterns, as did increased precursor concentrations. Increased flows of ethyl acetate (0.8 dm^3 min^{-1} of N_2 or greater through ethyl acetate bubbler) yields titania films which are dark in appearance due to contamination with carbon. In general, it has been found that films grown at 500 °C for 30–60 s result in deposition of uniform, transparent coatings. A summary of properties of the TiO_2 thin films deposited in the APCVD reaction of $TiCl_4$ and ethyl acetate is given in Table 1.

All films deposited by the APCVD reaction of $TiCl_4$ and ethyl acetate at 500 °C were of uniform thickness along the entire length of the glass substrate as determined by UV–vis spectroscopy. All titania films deposited were unaffected by prolonged immersion in common solvents (acetone, toluene, methanol, and water) and mineral acids (2 and 6 M HCl, HNO_3) and could neither be removed by Scotch tape nor be abraded by a stainless steel scalpel. Films deposited with growth times of 10–30 s were transparent with minimal reflectance. Longer deposition times of the order of 120 s gave interference patterns on the glass in reflection. For film growth times in excess of 180 s, hazy films result due to the formation of larger particles and intense scattering. Refractive index measurements gave a value of 2.5 for the thickest

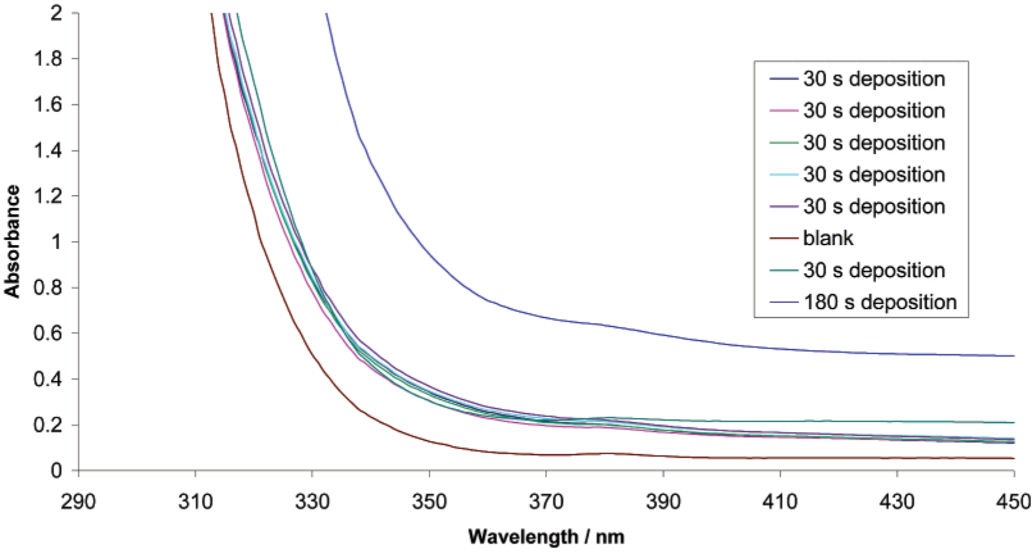

Figure 4. UV–vis spectra of TiO_2 thin films grown by the APCVD reaction of $TiCl_4$ and ethyl acetate, showing the reproducibility of the film thickness.

films—comparable to that of anatase (2.56 and 2.49). Growth rates were typically 0.5 μm min^{-1} at a substrate temperature of 500 °C, as determined by SEM. The films were shown to be uniform, with "crazy paving"-type morphology which is consistent with an island-type growth pattern as shown in Figure 1. The optical properties of the films were determined by transmittance and reflectance measurements in the region 300–1200 nm, the films showing good transmittance (60–90%) with minimal reflectance.

The composition of each deposited film was assessed by XPS, the bulk composition being found to differ from that of the surface. The contamination of the surface with carbon, due to exposure to air (CO_2 adsorbed), could be removed by Ar^+ bombardment to form a clean layer of titanium and oxygen in the expected elemental ratio of 1:2. The binding energies of the Ti $2p_{3/2}$ and O 1s were 458.6 and 530.6 eV, respectively, values which are typical of that for anatase and equal to those given in the literature.[12]

Raman microscopy has proved to be effective in the analysis of TiO_2 thin films deposited on glass by the APCVD reaction of $TiCl_4$ and ethyl acetate. In all deposition conditions and temperatures the APCVD reaction of $TiCl_4$ and ethyl acetate yields the anatase form. Characteristic Raman bands at 143, 198, 398, 515, and 640 cm^{-1} were observed, which agree with the literature values and assignments, viz. 143 cm^{-1} (B_{1g}), 198 cm^{-1} (A_{1g}), 398 cm^{-1} (B_{1g}), and 515 and 640 cm^{-1} (E_g) as shown in Figure 2.[13] Raman microscopy can readily yield spectra from titania films formed in growth times of only 10 s, whereas glancing angle XRD fails to provide meaningful data on films <200-nm thick. Notably, no rutile TiO_2 was formed, even at the highest deposition temperature.

Glancing angle X-ray diffraction studies on films grown at 450, 550, and 600 °C with deposition times of 30 s or greater showed the films to be crystalline and to consist of the anatase polymorph. Films deposited for periods of 10 s were found to be too thin for X-ray diffraction studies. Figure 3 shows the X-ray diffraction pattern of the thin films at various temperatures. In XRD θ–2θ scan measurements, peaks were observed at 25.3°, 38.7°, 48.1°, and 55.1°, which confirm that the TiO_2 films were composed of anatase, corresponding to the (101), (112), (200), and (211) facets, respectively. A sharp peak at 25.3° is ascribed to anatase (101) and the broad pattern in the same region is ascribed to the substrate SiO_2.[14] Tetragonal cell constants were determined as $a = 0.378(2)$ nm and $c = 0.951(2)$ nm and agree with previous literature values.[15] Qualitatively, the films have crystallite sizes in the region of 25–75 nm, as determined by line-broadening studies, with the larger crystallites being observed at the higher deposition temperatures. However, such figures should be treated with caution as they do not take into account strain effects.

There is a stark contrast between the contact angles of water droplets for pre- and post-UV-irradiated TiO_2 on glass. Pre-UV-irradiated samples have contact angles >60°, which is comparable with that of plain glass and characteristic of a hydrophobic surface. Upon irradiation for 30 min at 254 nm the contact angle drops below 2° for some samples, thereby highlighting the superhydrophilicity of TiO_2 films deposited by APCVD. The contact angle increases if the sample is kept in the dark and, after 48 h, the preirradiation values of the contact angle are restored. However, storage in a well lit room or exposure to sunlight maintains the low contact angles for months. It is this property which has fuelled the renewed interest in TiO_2 for self-cleaning applications, particularly in building materials and glass and as antifogging agents on mirrors. The reason for the low contact angle of sol–gel-derived titania surfaces has been linked to the formation of surface Ti(III)–OH moieties which can effectively hydrogen bond to water.

---

(12) Fernández, A.; Caballero, A.; González-Elipe, A. R. *Surf. Int. Anal.* **1992**, *18*, 392.

(13) Burgio, L.; Clark, R. J. H. *Spectrochim. Acta, Part A* **2001**, *57*, 149. Ohasaka, T.; Izumi, F.; Fujiki, Y. *J. Raman Spectrosc.* **1978**, *7*, 321.

(14) Nehishi, N.; Takeuchi, K. *Thin Solid Films* **2001**, *392*, 249.

(15) JCPDS, International Centre for Diffraction Data, 1995 [21-1272].

Destruction of a layer of a test organic chemical—stearic acid—on the TiO_2 film was used to assess preliminary photocatalytic efficacy. All of the TiO_2 films studied show 35−100% removal of the stearic acid layer after 60 min of irradiation at 254 nm. UV−vis absorption studies show an increase in the rate of photo-oxidation of stearic acid with an increase in the thickness of the TiO_2 film up to a certain point. In some cases complete destruction of stearic acid was achieved within 12 min. The films grown with a 10-s deposition time had thicknesses from ca. 50−100 nm, dependent on the flow of nitrogen carrier gas through the bubbler. The 100-nm-thick film grown at 660 °C showed the greatest self-cleaning efficacy with the lowest contact angle (1.7°) and fastest destruction of stearic acid (Table 1). Films with greater thickness, ca. 250 nm, grown at 500−600 °C gave higher contact angles (9°−33°) and slower rates of photodestruction of stearic acid. Notably, plain glass, not coated with TiO_2, showed no loss of the stearic acid overlayer, even after 12 h of irradiation at 254 nm.

Discussion

The APCVD reaction of $TiCl_4$ with ethyl acetate is shown to provide a simple means for depositing thin films of TiO_2 on glass substrates. Deposition time and substrate temperature influence the physical appearance of the films. Those deposited at 550−660 °C exhibit interference patterns, indicating nonuniform deposition onto the substrate, whereas those deposited at 500 °C result in films of uniform thickness. Anatase alone was deposited in all systems investigated, no chlorine contamination being detected in the XPS spectra. Ethyl acetate is a very convenient source for the introduction of oxygen in this APCVD process. It was chosen because it is widely used in organic chemistry and in industry. Notably, no film could be grown just from reaction of the $TiCl_4$ and residual oxygen in the system (either from the reactor or from traces in the nitrogen carrier gas). Comparative studies with water as a co-oxygen source invariably formed hazy, nonuniform films because of excessive gas phase reaction. Compared to the previously published LPCVD routes to TiO_2,[8,9] the APCVD system investigated here gives faster growth rates and under optimum conditions uniform films without chlorine and carbon contamination. Notably, the anatase films have excellent self-cleaning potential with low contact angles, good photocatalytic response, mechanical toughness, and chemical resistance. Compared with sol−gel-derived films, they are very mechanically robust and also do not have the haze associated with large particle sizes.

Growth of TiO_2 films at 500 °C has been shown to be very reproducible, as films deposited under identical conditions had identical UV−vis absorption spectra (Figure 4). Film thickness can be increased in a number of ways, viz. increasing the deposition time, by increasing the flow through the bubblers, thereby increasing the precursor flow to the heated substrate, and by increasing the bubbler temperature to increase the vapor pressure of the materials within the bubbler. These changes in film thickness can be detected by changes in the UV−vis spectra and by SEM measurements, such that films from ca. 50−500 nm could be made reliably. The rate of degradation of a stearic acid overlayer was found to be dependent upon the thickness of the TiO_2 film. Interestingly, a film thickness of ca. 100 nm corresponded to the greatest photocatalytic activity. Changes in crystallinity also appear to affect the photo-oxidative properties of films grown by the APCVD reaction of $TiCl_4$ and ethyl acetate. Films of equal thickness but deposited at different temperatures show different rates of destruction of stearic acid, the more crystalline films grown at the higher temperatures being the more effective.

Un-irradiated TiO_2 films are hydrophobic with contact angles typically greater than 60°, but on irradiation at 254 nm, they become hydrophilic with the contact angles dropping to 1° in some cases. Once having been irradiated and then placed in the dark for 48 h, the contact angle reverts to the original values. Superhydrophilicity occurs when the photon which hits the TiO_2 causes one of the less tightly bound oxygen atoms to be ejected, creating a vacancy which reacts with a water molecule, to create a hydroxyl group, that is, a Ti−O−H group, on the surface.[16] This moiety is highly hydrophilic, more so than its environs, and with just a 30-min exposure to UV irradiation, the TiO_2 surface becomes superhydrophilic.[16] The drop off in contact angle when stored in the dark is related to the fact that the titanium surface is slowly oxidized in air, a process which removes the Ti−O−H groups. Further exposure to sunlight or UV radiation in air quickly re-establishes the Ti−O−H-terminated surfaces and restores the low contact angle. Notably, the thinner APCVD-derived films showed the lowest contact angle measurements and the greatest photoactivity for the destruction of stearic acid. This may be associated with a comparatively high surface area for the thin films, as the films grew by an island growth mechanism, that is, in columns not as a continuous film (Figure 1).

Conclusions

TiO_2 has been deposited by the APCVD reaction of $TiCl_4$ and ethyl acetate on glass substrates between 400 and 660 °C. These films consist under optimum growth conditions of mechanically robust, nanocrystalline, non-scattering, photoactive anatase—making them ideal for self-cleaning glass applications. Film growth by the APCVD process has been shown to be reproducible with uniform coatings deposited at 500 °C covering the entire substrate. Optimal film thickness (100 nm) for the enhancement of the photo-oxidation of stearic acid can be readily achieved by modification of the precursor flow rate and the deposition time.

Acknowledgment. The EPSRC is thanked for Grants GR/M/95059 and GR/M/82592 to I.P.P. and R.J.H.C. Pilkington Glass is thanked for the glass substrates. Mr. Kevin Reeves, Institute of Archaeology, UCL, is thanked for help in acquiring SEM images.

CM020707F

---

(16) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431.