Deposition of Compact Hydrous Aluminum Sulfate Thin Films on Titania Particles Coated with Organic Self-Assembled Monolayers

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An organic self-assembled monolayer (SAM) was deposited on submicron-sized pigment-grade TiO_2 particles to create a highly hydrophilic surface comprised of sulfonate groups. Hydrous aluminum-containing thin films were uniformly deposited on the powder from aqueous solutions at 60–80 °C. The as-deposited films were in the form of boehmite ($AlO(OH)$) or hydrous Al sulfate, depending on the Al salts used in the starting solution. $AlCl_3$ solutions gave rise to porous films of needlelike crystalline boehmite, whereas mixed $Al_2(SO_4)_3/Al(NO_3)_3$ solutions led to compact, uniform, adherent, dense amorphous sulfate-containing films up to ~5 nm thick. The sulfate anion in solution is thought to promote nucleation and growth of a solid phase through its relatively strong electrostatic field. However, the sulfate anion is weakly bound, and the sulfate films can be partly leached of sulfur in neutral or weakly basic solutions at room temperature without sacrificing their compact nature.

I. Introduction

The polymorphs of titanium dioxide (TiO_2) have very high refractive indices: n_d for rutile and anatase are 2.76 and 2.52, respectively.[1] The high refractive index, together with excellent hardness, hiding power, and tint strength, make TiO_2 powder the most widely used white pigment in the plastic and paint industries; it is also used extensively in the paper industry. For practical use, however, TiO_2 pigments have to be first coated with an inert oxide, typically Al_2O_3 and/or SiO_2. This is necessary because TiO_2 is photochemically active and can degrade pigmented organic binders when exposed to sunlight or near-UV light for extended periods, particularly in the presence of moisture.[2] An ideal coating for TiO_2 should prevent contact between the active surface and degradable organic materials by encapsulating the pigment particles with an oxidation-resistant, nonporous thin film that can neutralize or hinder the diffusion of redox-active species from the TiO_2 surface. It is also desirable that the coating

improve the rheology of TiO_2 particles in aqueous or organic media. However, the coating must be transparent to visible light; that is, it must be sufficiently nonabsorbing and thin to avoid degrading the excellent brightness and whiteness of TiO_2, yet nevertheless insulate the pigment surface from the organic matrix.

Standard coatings for commercial TiO_2 pigments are aluminosilicate thin films with an Al-to-Si atomic ratio ranging from 1:1 to 4:1. These thin films are usually created by suspending TiO_2 powder in an aqueous slurry containing aluminate and silicate salts.[2,3] The pH is a critical parameter that affects the solubility and therefore the deposition rate of the coating. Usually, the pH is adjusted to the range 6–10 to allow hydrolysis and deposition to occur at a suitable rate. The as-deposited films are readily transformed to pure oxides by removing water during heat treatment at high temperature.[2]

Recently, self-assembled monolayers (SAMs) have attracted increasing attention, particularly for their potential applications in optical and electronic devices.[4] SAMs are ultrathin (1.5–3.0 nm), closely packed assemblies of long-chain hydrocarbon molecules. They are spontaneously formed by immersion of an appropriate

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(1) Kingery, W. D.; Bowen, H. K.; Ulmann, D. R. *Introduction to Ceramics,* 2nd ed.*;* John Wiley & Sons: New York, 1975.
(2) Solomon, D. H.; Hawthorne, D. G. *Chemistry of Pigments and Fillers;* John Wiley & Sons: New York, 1983.
(3) *Inorganic Pigments Manufacturing Process*, Gutcho, M. H., Ed.; Noyes Data Corp.: Park Ridge, New Jersey.
(4) Ulman, A. *An Introduction to Ultrathin Organic Films—from Langmuir—Blodgett to Self-Assembly*; Academic: Boston, MA, 1991.

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substrate into a solution of a surface-active material in an organic solvent. The spontaneous bonding of the organic molecules onto the substrate together with the strong van der Waals attraction among the alkyl chains are the driving forces for the formation of a highly ordered, close-packed SAM film.[4] Such SAM films can thus be used to control the surface or interfacial properties of solids, particularly because systematic modification of the SAM surface functionality is possible using straightforward chemistry. Important to the present context, SAMs have also been used to assist the deposition of oxide thin films from aqueous solution onto Si wafers and other substrates.[5-10] These studies were inspired by the biomineralization process, and are analogous to earlier studies on the deposition of inorganic materials onto Langmuir–Blodgett thin films.[11,12] Long-chain alkyl trichloro- or trialkoxy-silane monomers (i.e. $RSiX_3$, where X is chloride or alkoxy, and R is a carbon chain, which can bear different functionalities) lead to SAM formation on Si substrates by the creation of a siloxane network, which stabilizes the attachment of the SAM to the substrates. In cases where functionalized SAMs have been used to promote oxide deposition, colloidal forces between the SAM and oxide particles in metastable aqueous solutions are believed to promote the deposition of the thin oxide film.[6,9,10]

Although many studies have been performed on various flat substrates (glass, semiconductors, and metals),[4] much less work has been done on deposition of SAMs on particulate substrates. SAMs should have significant advantages over Langmuir–Blodgett technology when applied to the coatings of particles, or of substrates with complicated shapes. Margel et al.[13,14] have reported that alkylsilane SAMs could be successfully deposited onto particulate substrates such as SiO_2 and amorphous Fe nanoparticles to form a compact coating. The coated powders showed very different floatability and wettability behaviors compared with the noncoated powders and were characterized by various spectroscopies.

In the work reported here, we demonstrate the feasibility of applying SAMs to alter the dispersability of pigment-grade TiO_2. First, the conditions for coating siloxy-anchored SAMs onto submicron TiO_2 powder have been established. Then, by using a sulfonate-functionalized SAM, aluminum hydroxide or basic aluminum sulfate thin films were precipitated onto the SAM-coated TiO_2 particles. The sulfonate functionality is derived from in situ oxidation of an initial thioacetate
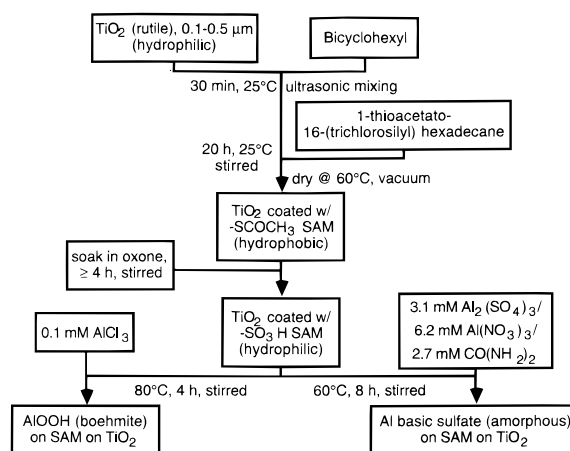
(5) Bunker, B. C.; Rieke, P. C.; Tarasevich, B. J.; Campbell, A. A.; Fryxell; G. E.; Graff, G. L.; Song, L.; Liu, J.; Virden, J. W.; McVay, G. L. *Science* **1994**, *264*, 48.
(6) Shin, H.; Collins, R. J.; De Guire, M. R.; Heuer, A. H.; Sukenik, C. N. *J. Mater. Res* **1995**, *10*, 692.
(7) Collins, R.; Shin, H.; De Guire, M. R.; Heuer, A. H.; Sukenik, C. N. *Appl. Phys. Lett.* **1996**, *6*, 860.
(8) Agarwal, M.; De Guire M. R.; Heuer, A. H. *Appl. Phys. Lett.* **1997**, *7*, 891.
(9) Agarwal, M.; De Guire, M. R.; Heuer, A. H. *J. Am. Ceram. Soc.* **1997**, *80*, 2967.
(10) Shin, H.; Agarwal, M.; De Guire, M. R.; Heuer, A. H. *Acta Mater.* **1998**, *46*, 801.
(11) Hughes, N. P.; Heard, D.; Perry, C. C.; Williams, R. J. P. *J. Phys. D: Appl. Phys.* **1991**, *24*, 146.
(12) Mann, S.; Archibald, D. D.; Didymus, J. M.; Douglas, T.; Heywood, B. R.; Meldrum, F. C.; Reeves, N. J. *Science* **1993**, *261*, 1286.
(13) Brandriss, S.; Margel, S. *Langmuir* **1993**, *9*, 1232.
(14) Rozenfeld, O.; Koltypin, Y.; Bamnolker, H.; Margel, S.; Gedanken, A. *Langmuir* **1994**, *10*, 3919.

Figure 1. Procedures for preparing coatings of boehmite or thin films of aluminum hydroxide/hydrous sulfate on TiO_2 powder. (Oxone: $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, in saturated aqueous solution at room temperature.)

functional group on the as-deposited SAM. The premise of this effort is that such mixed organic–inorganic bilayers may insulate pigmented organic binders from any TiO_2 redox activity better than conventional single aluminum hydroxide or aluminosilicate thin films. Another expectation is that the deposition of thin films on the SAMs will bring about more uniform, compact, and dense coatings.

II. Experimental Procedures

Film Deposition. Pigment-grade, submicron-sized, uncoated TiO_2 powders (DuPont, Wilmington, DE) were used as the "substrates" without further treatment. The procedures for coating this powder with siloxane-anchored SAMs and aluminum hydroxide or aluminum sulfate thin films are summarized in Figure 1. The as-received TiO_2 powder was mixed with toluene or bicyclohexane (BCH) in a beaker (10 mg TiO_2:1 mL solvent) and agitated in an ultrasonic bath for 30 min to break up any clusters in the as-received material. Due to the hydrophilic nature of the TiO_2 surface, the particles tended to agglomerate and to sink to the bottom of the beaker after sonication.

For 10 mg of TiO_2/1 mL BCH, 10 μL of octadecyltrichlorosilane (OTS) or 1-thioacetato-16-(trichlorosilyl)hexadecane (TA)[15] were added to the solution while stirring. To avoid rapid polymerization of the trichlorosilanes by over-exposure to water, the silanes were handled under a high-purity N_2 atmosphere prior to their addition to the powder slurry. SAM depositions were typically carried out with the solution open to the atmosphere while stirring for 20 h at room temperature. During this step, the particles tended to disperse in the nonpolar organic solution, implying a change in the initial hydrophilic surface of the TiO_2.

The SAM-coated powders were separated from the solution by centrifugation. They were repeatedly washed with dichloromethane and acetone (to remove any excess silane), and dried under reduced pressure at 60 °C to remove residual organic solvent. In contrast to the as-received powder, the powder thus treated was hydrophobic and could not be dispersed in or wetted by water.

In preparation for the deposition of an inorganic Al-containing film, a powder sample coated with TA was mixed with a saturated aqueous solution of oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2$-$SO_4$, a monopersulfate oxidizing agent) and stirred vigorously for at least 4 h to transform the hydrophobic thioacetate surface into one having a hydrophilic sulfonate functionality.[15] The sulfonate-functionalized TiO_2 powder was very hydrophilic

(15) Collins, R. J.; Sukenik, C. N. *Langmuir* **1995**, *11*, 2322.

and could be completely dispersed in water. It was extensively washed with double distilled water to remove any excess oxone and then stored under water.

Two solutions were used as sources for the Al-containing films: aqueous $AlCl_3$ (10^{-4} M) or a mixed aqueous $Al_2(SO_4)_3$ (0.0031 M)/$Al(NO_3)_3$ (0.0063 M) solution. All the chemicals used were reagent grade. The $AlCl_3$ solution did not result in compact films; our results are presented in the Appendix. The sulfate/nitrate solution was first developed by Brace and Matijevic to synthesize spherical aluminum hydroxide particles of narrow size distribution.[16] To prepare a stock solution, 4.163 g of $Al_2(SO_4)_3 \cdot 18H_2O$, 4.688 g of $Al(NO_3)_3 \cdot 9H_2O$ and 3.2 g of $CO(NH_2)_2$ (urea) were dissolved in 100 mL of distilled water. The solution was subsequently heated to 90 °C for 0.5 h and cooled to room temperature. Because some of the solution had evaporated, the final volume was readjusted to 100 mL. The stock solution was clear and remained stable for several weeks. To deposit the films, the stock solution was diluted 20 times. Because the dilute solution may hydrolyze and polymerize, only freshly prepared solutions were used for film deposition. The well-washed, SAM-coated TiO_2 powders (and powders without SAMs, as control specimens) were immersed in the Al salt solutions and stirred at elevated temperatures for various times. For powders, a temperature of 60 °C (for 8 h) was optimum for the sulfate/nitrate solution, whereas 80 °C for 4 h was optimum for the chloride solution. After this step, the TiO_2 particles were thoroughly washed with water and dried in an oven at 110 °C. Bulk precipitation from solutions lacking TiO_2 particles was also studied.

To study the *rate* of the film deposition and to facilitate transmission electron microscopic (TEM) examination of the film–substrate interface, SAM-coated single-crystal Si wafers (and uncoated wafers, as control specimens) were exposed to mixed aluminum sulfate/nitrate solutions under similar conditions as those used with the TiO_2 particles. The formation of sulfonated SAMs on Si wafers was carried out as reported previously.[6] For deposition of the Al-containing films, the only difference in procedure between coating flat and particulate substrates was that the latter were coated in a stirred solution at 60 °C, whereas the flat substrates were coated under quiescent conditions at room temperature. Depositions on the Si substrates were carried out for various immersion times (i.e., 0.5, 1.0, 2.0, 5.0, and 12.0 h).

Film Characterization. Fourier transform infrared (FTIR) spectra of the OTS and TA SAMs on rutile powder were recorded with a Perkin-Elmer 1600 FTIR spectrometer. KBr pellets were prepared from the powder samples. Liquid samples for IR analysis were placed between KBr plates.

A PHI 5600 X-ray photoelectron spectrometer (XPS) was used to characterize the various samples. XPS measurements on the powders were conducted by pressing the sample onto a piece of In foil. All XPS peak energies were calibrated using the characteristic C1s peak at 284.6 eV. For study of the rate of film deposition, films deposited on Si wafers were subjected to XPS sputter depth profiling. The atomic concentration of Al, O, and Si were measured after each sputter cycle and plotted as a function of sputter time. The time of sputtering at which the Si profile rose to a constant level was taken as the time, t_s, required to sputter through the film. Values of t_s were converted to film thickness by comparison with a cross-sectional TEM micrograph of a 5-nm-thick film on a SAM-coated Si wafer.

A Hitachi S-4500 field-emission scanning electron microscope (SEM), a Philips CM-20 transmission electron microscope (TEM), and a JEOL 4000-EX high-resolution transmission electron microscope (HRTEM) were used to characterize the microstructure of the inorganic coatings. Noran energy-dispersive X-ray (EDX) spectrometers for microchemical analysis were available on both the SEM and TEM. Powder samples were dispersed on a TEM grid using methanol. Planar-view TEM observations were performed on flat Si
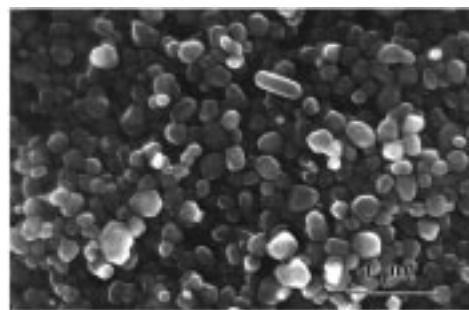

Figure 2. SEM micrograph of as-received TiO_2 powder.

samples, which were prepared by conventional backside ion thinning after hand-polishing down to 20–25 μm.

III. Results

Coating of SAMs onto TiO_2 Particles. The TiO_2 powder used in this study has the rutile structure, smooth surfaces, and a particle size range of 50–500 nm (Figure 2). As already noted, the uncoated powder was hydrophilic and could be readily dispersed in water using ultrasonic agitation or stirring. Aqueous suspensions of TiO_2 could be stabilized at a suitable pH (7–8). On the other hand, both the OTS- and TA-coated powders could be readily dispersed in an organic solvent like methylene chloride; these coated powders floated on the surface of water, indicating the high degree of encapsulation achieved by the SAMs.

Because of their large surface area, anhydrous TiO_2 powders readily adsorb moisture, and the resulting hydrated TiO_2 surfaces contain a variety of hydroxyl species.[17,18] Molecular H_2O can easily be removed by drying the powder in an oven at temperatures >100 °C, although surface hydroxylation survives to much higher temperatures. For SAM formation, a trace of water is important for forming the siloxane network that bonds the trichlorosilane-terminated surfactants to the substrate. In fact, if the powder is heat treated at 100 °C prior to coating or if the coating process was done without exposure to the ambient atmosphere, the SAM coverage was much worse (as evidenced by a weaker $-CH_2-$ signal in IR spectra, poorer dispersion in the organic solvent, and a lower XPS carbon signal) than for SAMs deposited on the as-received powder in an open system.

For both the coated and uncoated powders, IR spectra showed a broad absorption band around 3400 cm^{-1}. This band is assigned to Ti–OH and adsorbed/coordinated H_2O.[19] As expected, the intensity of this band decreased after coating the powder, which is consistent with a portion of the hydroxyl groups and the molecular H_2O being consumed during the coating process and with reduced amounts of physisorbed H_2O on the hydrophobic particles. Figure 3 shows the IR spectra between 2800 and 3100 cm^{-1} of the OTS and TA alkyltrichlorosilanes in the liquid state and when coated on the TiO_2 powder. (The spectrum of the uncoated powder has no absorption between 2800 and 3100 cm^{-1}.) The adsorption bands for OTS and TA around 2850 and 2920 cm^{-1}

(16) Brace, R.; Matijevic, E. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3691.

(17) Ritter, H. S. In *Pigment Handbook*; Patton, T. C., Ed.; Wiley-Interscience: New York, 1974; Vol. 3.
(18) Parfitt, G. D. *Prog. Surf. Membr. Sci.* **1976**, *11*, 181.
(19) Griffiths, D. M.; Rochester, C. H. *J. Chem. Soc.* **1977**, *73*, 1511.
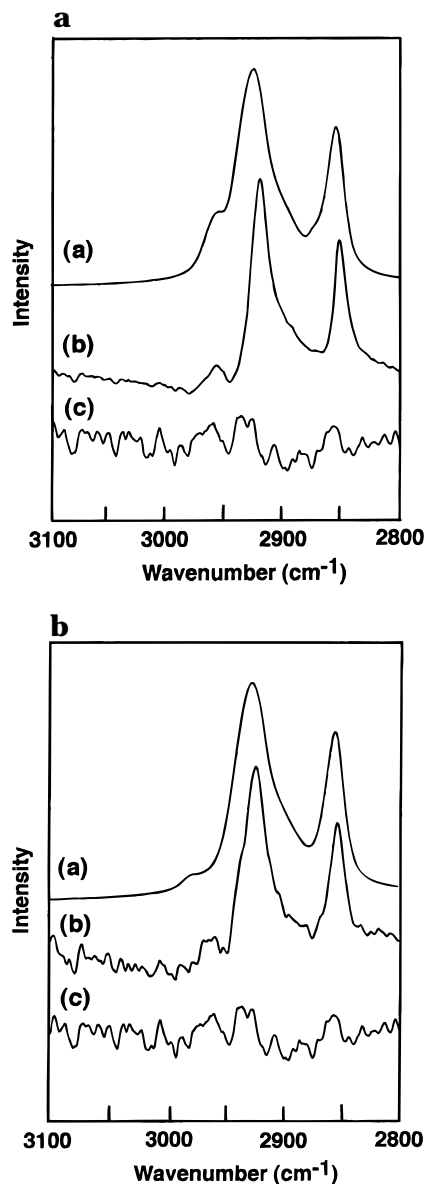
a

b

Figure 3. (a) Infrared spectra for (a) octadecyltrichlorosilane (OTS) in the liquid state, (b) OTS coated on TiO_2 powder, and (c) as-received TiO_2. (b) Infrared spectra for (a) thioacetate (TA) in the liquid state, (b) TA coated on TiO_2 powder, and (c) as-received TiO_2.

are due to the $-CH_2-$ stretching modes, whereas the absorption at 2960 cm^{-1} for OTS (Figure 3a) is due to the $-CH_3$ stretching mode.[13] The band at 2920 cm^{-1} is particularly sensitive to the degree of structural order of the SAM and has been used to evaluate similar coatings on other solid surfaces.[20−23] Comparing the liquid silane spectra with those of the coated TiO_2 powders, the 2920 cm^{-1} band has obviously narrowed for both SAM-coated powders. Similar phenomena have also been observed with SAM-coated SiO_2 and amorphous Fe powders.[13,14] The methylene peak shifted from 2923 to 2917 cm^{-1} for the OTS-coated TiO_2 and from
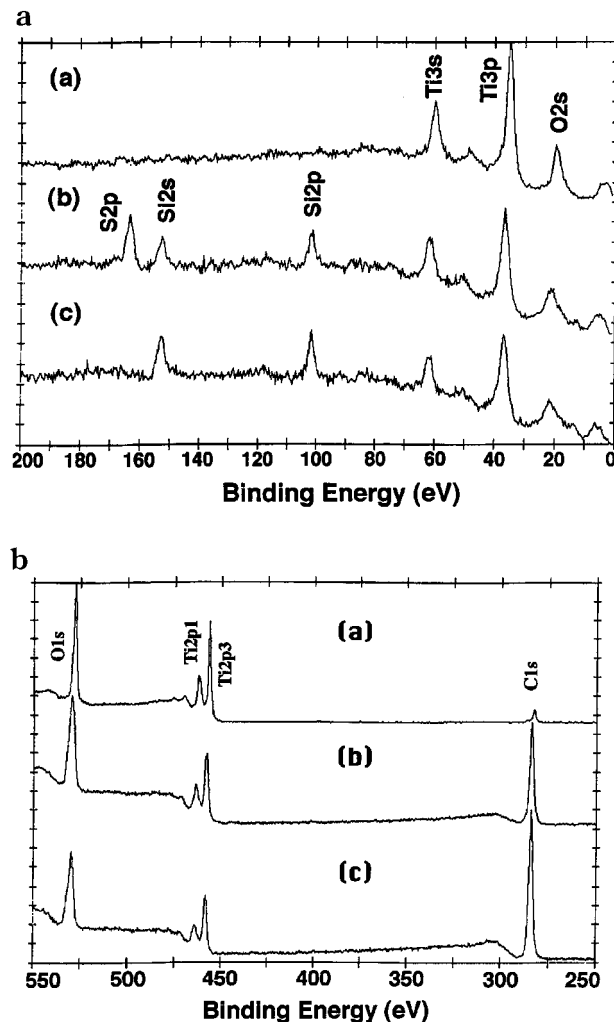
(20) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *99*, 235.

(21) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465.

(22) Pomerantz, M.; Segmuller, A.; Netzer, L.; Sagiv, J. *Thin Solid Films* **1985**, *132*, 153.

(23) Tillman, N.; Ulman, A.; Schildkraut, S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136.

a

b

Figure 4. The XPS spectra for TiO_2 powders: (a) uncoated TiO_2; (b) TiO_2 coated with TA SAMs; (c) TiO_2 coated with OTS SAMs; the ranges 0−200 eV (Figure 4a) and 250−550 eV (Figure 4b) are shown separately for clarity.

2923 to 2920 cm^{-1} for TA-coated TiO_2. Such frequency shifts are consistent with the transformation of the alkyl chain from a liquid state to a more compact, ordered, and solid-like film on the powder substrate. By this measure, there is a high level of order in the OTS SAM films and a lesser degree of order in the TA SAM films.

Figure 4 shows XPS spectra for as-received and SAM-coated powders. No changes occurred in the XPS spectra of the coated powders with repeated washing. The Ti signal was still detectable because the SAM coating was not thick enough to completely absorb all substrate-generated photoelectrons. (We also observe an XPS signal from the substrate in SAMs on Si wafers.) No Cl peaks were detected for the coated powder, showing that the Cl on the $RSiCl_3$ chain was completely replaced. Although the uncoated powder showed a weak C peak at 284.6 eV, presumably from some ambient contamination, the coated powders showed much stronger C peaks (see curves b and c of Figure 4b), as expected for TiO_2 powders well covered by the SAM alkyl chains. In contrast to the uncoated TiO_2, both Si and S peaks were observed for the TA-coated TiO_2 (curve b of Figure 4a), whereas Si peaks (but not S) were detected on the OTS-coated TiO_2 (curve c of Figure 4a). The Si peaks are due to the Si anchoring
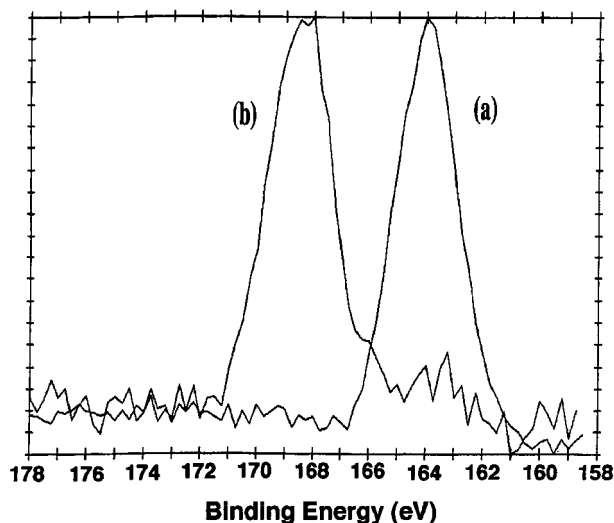
Figure 5. The S2p XPS spectra of SAM-coated TiO_2 powders: (a) TA SAM; (b) after oxidation of TA SAM to a sulfonate functionality.
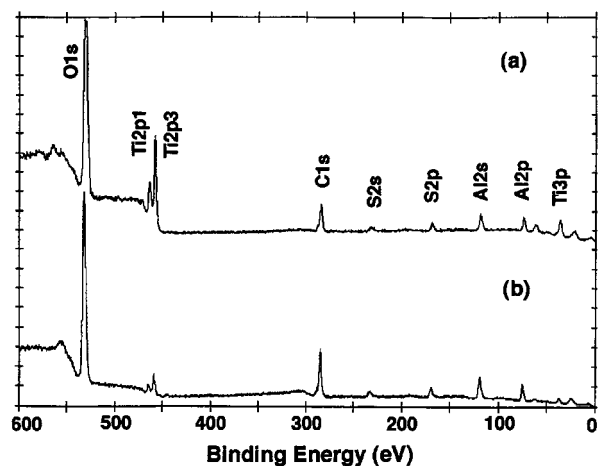

Figure 6. The XPS spectra for the basic aluminum sulfate-coated TiO_2 powders: (a) bare (uncoated) powder after immersion at 60 °C for 4 h in the sulfate/nitrate solution; (b) powders coated with sulfonate SAMs after identical exposure to the sulfate/nitrate solution.

end of the surfactants, whereas the S peaks come from the functional group at the projecting end of the TA-bearing SAM.

As reported previously,[7,15] the thioacetate moiety can be readily oxidized to a sulfonate moiety. The XPS spectra in Figure 5 show the shift of the S2p peak for the powder by ∼4.5 eV to higher energies when the thioacetate group is oxidized, just as on the planar substrates reported earlier.[7,15] The completeness of this oxidation, despite the uncontrolled surface morphology of the TiO_2 particles, is noteworthy. Once the sulfonate is formed, the coated powder becomes very hydrophilic and can be readily dispersed in water to form a homogeneous suspension.

Formation of Basic Aluminum Sulfate Thin Films. Deposition of Al-containing thin films from aqueous solutions depends on solution conditions (temperature, pH, and the type and concentration of starting Al salts) and the surface composition. The solution conditions define the solubility of any potential solid phase and therefore determine the nucleation rate. We observed light scattering by very small particles when the sulfate/nitrate precursor solution was illuminated with a He−Ne laser (633 nm wavelength). We also observed slight cloudiness developing ∼20 min after dilution. We believe that the presence of such Al-containing ultrafine particles in solution is involved in the formation of hydrous Al-containing coatings, similar to our findings of deposition of ZrO_2- and Y_2O_3-containing films on Si wafers.[6,9,10] These latter systems demonstrated that sulfonate-bearing SAM surfaces can promote deposition either by attracting fine particles that have grown in the solution (homogeneous deposition) or by attracting complexes in the solution to form nuclei on the surface (heterogeneous deposition). The net attraction results from van der Waals and electrostatic interactions. The sulfonate group is a strong acid and thus readily deprotonates, even in acidic environments. The sulfonated SAM surface, as a result, is negatively charged, causing an electrostatic attraction for positively charged particles such as ZrO_2 and Y basic carbonate.[9,10] This attraction can add to the van der Waals interaction between the particles and the SAM

to promote film deposition. A similar effect was observed in this study.

Figure 6 shows XPS survey scans for films deposited after 4 h from the mixed sulfate/nitrate solution onto TiO_2 powders. The films deposited in the presence of the sulfonate SAM (spectrum b in Figure 6) gave rise to much weaker Ti substrate signals than the films deposited on bare substrates (spectrum a), indicating formation of a more uniform compact coating in the presence of the SAM. Semiquantitative analysis of the films deposited on sulfonate SAM films using the PHI XPS software indicated an Al:S ratio of 3:2; this will be discussed further later. The films that formed on SAMs on TiO_2 powders after 8 h (Figure 7b) were uniform, compact, and ultrathin (<10 nm). The inset EDX spectrum shows Al and S peaks, in addition to the main Ti and O peaks. (Note that the Cu peak in this spectrum arose from the Cu grid used to suspend the powders, whereas the weak but detectable Si peak arose from the anchored siloxane group of the SAM.) The films deposited on bare TiO_2 powders after 8 h (Figure 7a) were thinner (≤3 nm) and only barely continuous, and the EDX spectrum in the inset shows a weaker Al signal than in Figure 7b. The relative thicknesses of the films on the bare and SAM-coated powders were estimated by comparing the intensity ratio of Al K_α to Ti K_β X-rays; this ratio on the SAM-coated TiO_2 was about twice that of the film on bare TiO_2, confirming that a thicker film had formed on the SAM-coated TiO_2 powder.

Films deposited onto Si wafers from the sulfate/nitrate solution exhibited similar characteristics to those films formed on TiO_2 powders. Specifically, films deposited on SAM-coated wafers showed no XPS signal from the underlying Si substrate, implying complete coverage by the Al-containing film. (Films on SAM-coated Si are discussed in more detail later.) In contrast, significant Si XPS signals were sometimes detected through the coatings on bare Si wafers. Good adhesion of the films, both on bare and on SAM-coated Si wafers, was demonstrated by a simple tape test: XPS analysis of a piece of Scotch tape, pressed onto the film and then peeled off, revealed no Al or S on the tape.
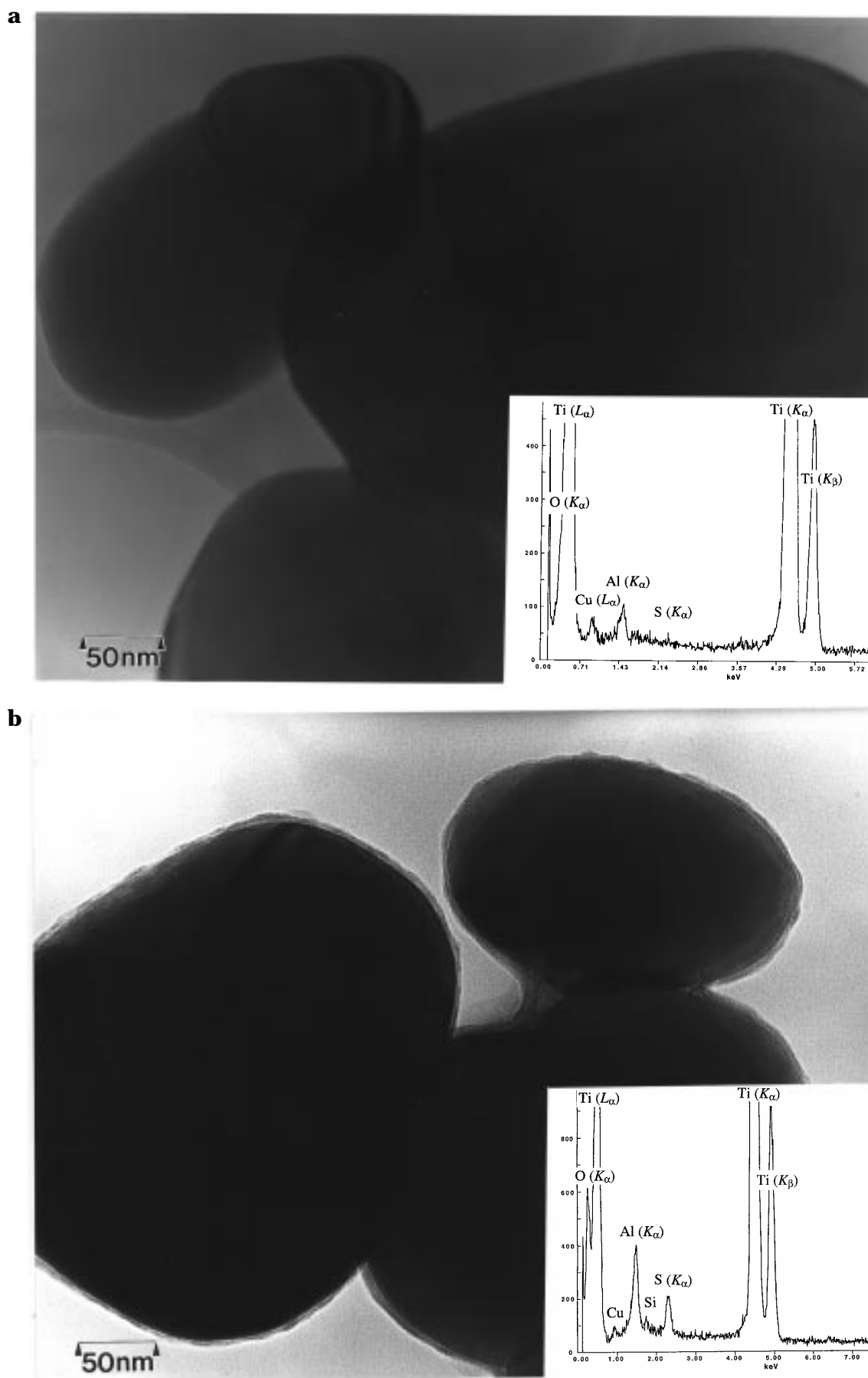
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Figure 7. The TEM micrographs of TiO₂ particles after 8-h immersion in aluminum sulfate/nitrate solution at 60 °C: (a) without prior SAM coating; (b) with prior SAM coating. The insets in (a) and (b) are EDX spectra.
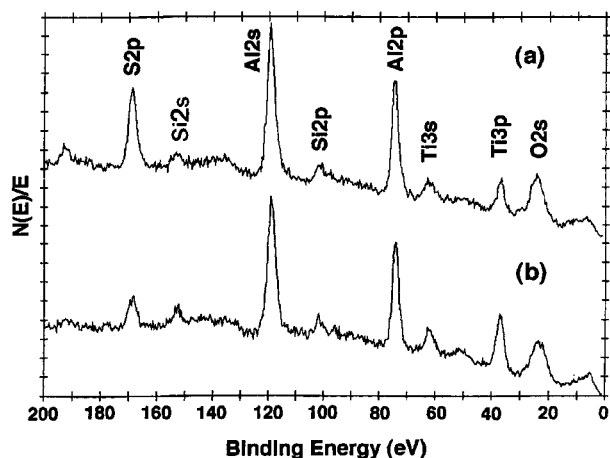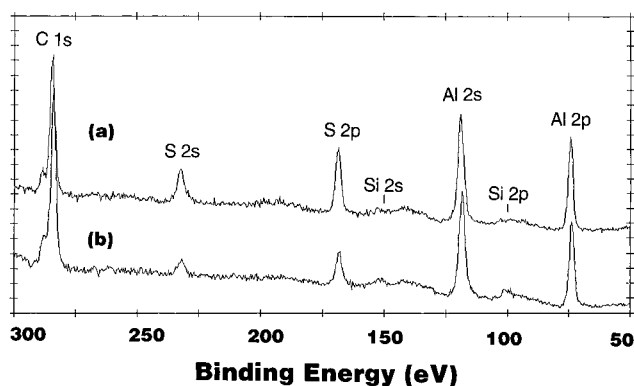
Figure 8. The XPS spectra of aluminum basic sulfate coatings on sulfonate SAM-coated TiO_2 powder (a) before and (b) after leaching in pH 7.0 solution for 25 min. The sulfur remaining in the leached film is associated (at least in part) with the SO_3H-terminated SAM.

Figure 9. The XPS spectra of aluminum basic sulfate coatings on sulfonate SAM-coated silicon wafers (a) before and (b) after leaching in pH 7.0 solution for 25 min.

The SO_4^{2-} anion in the basic aluminum sulfate film can be partially leached with a neutral or weakly basic solution, consistent with the SO_4^{2-} being loosely bound in the film. The XPS spectra in Figures 8 and 9 show that the S content significantly decreased after 25 min of washing in distilled water whose pH had been adjusted (with dilute NaOH) to 7.0. This result was true for Al-bearing coatings on both TiO_2 particles (Figure 8) and on silicon wafers (Figure 9). The observed Al/S ratios (corrected for absorption differences) after leaching were variable, with the maximum leached ratio being 6.5. Cross-sectional HRTEM micrographs of the as-deposited and leached films on Si wafers (Figure 10) indicate that the leached films were somewhat thinner (~20%) than the as-deposited films, consistent with the XPS data, but retained a uniform and compact morphology.

The rate of film growth on flat Si surfaces was measured using sputter depth profiling calibrated against cross-sectional TEM observations of actual film thickness (e.g., Figure 10a). Figure 11 shows a typical depth profile for Al, O, and Si for a film deposited in 12 h, and Figure 12 shows film thickness versus deposition time. The films grew to 5 nm in 1 h, after which growth apparently stopped.
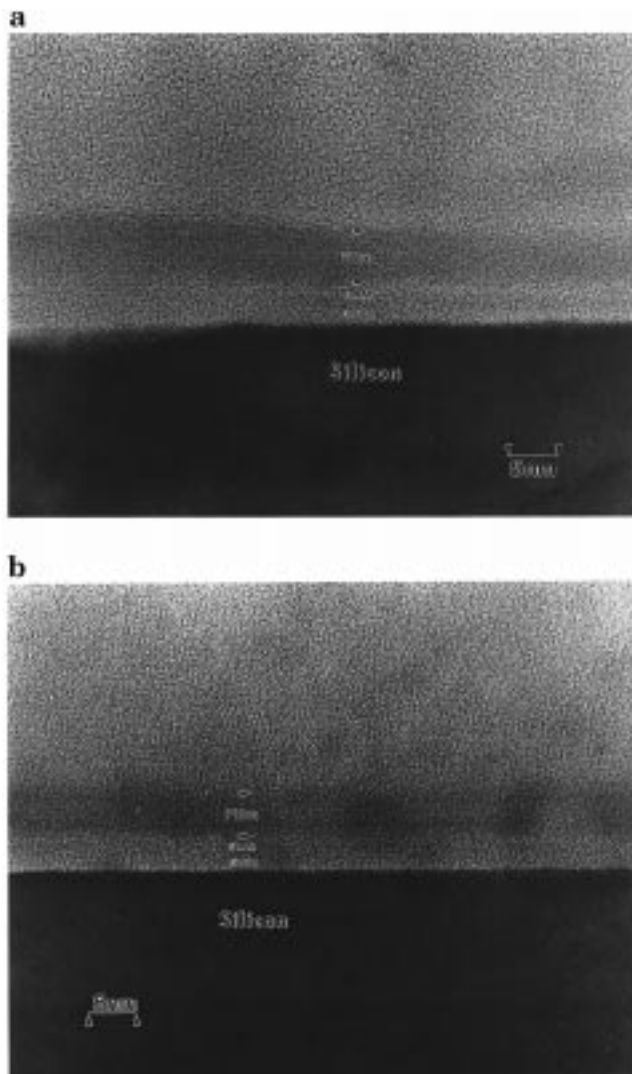

Figure 10. The HRTEM micrograph of (a) as-deposited and (b) leached films of basic aluminum sulfate films on SAMs on Si.
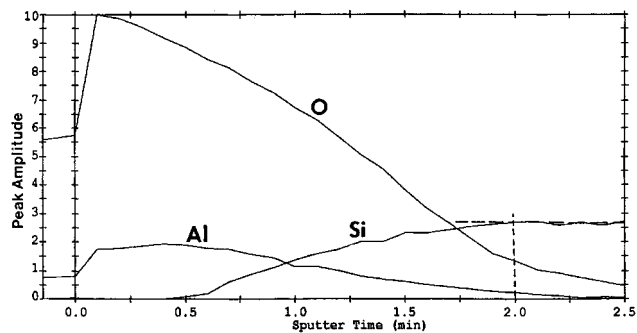

Figure 11. The XPS depth profiles of aluminum basic sulfate thin film on Si wafer showing the attenuation of Al and O, and the increase of the Si signal, as the film is sputtered away.

The film growth kinetics were superficially similar to those seen for TiO_2 and ZrO_2 films,[9,10] in which the rate of film growth also decreases with time. In the case of ZrO_2, the film thickness plateaus at ~40 nm. As is argued in ref 10, the growth kinetics are believed to be dominated by the rate of production of colloidal particles in solution because the energy per unit volume is sufficient to form a cohesive film only for very small particles. Thus, Ostwald ripening in solution and the
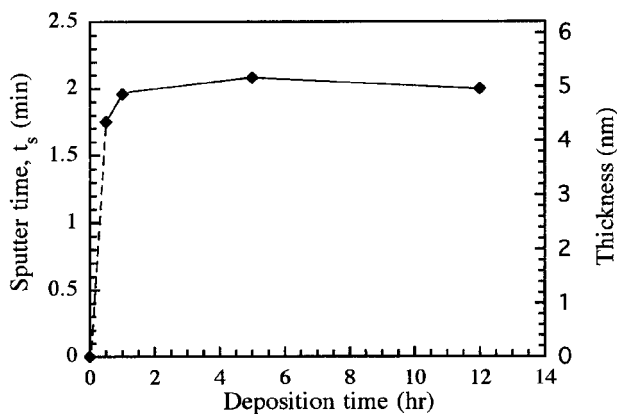
Figure 12. Sputter time and film thickness versus deposition times. The films were deposited on flat SAM-coated Si substrates, as described in the text.
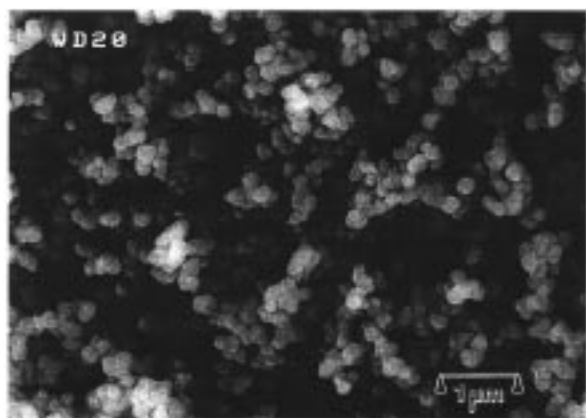

Figure 13. The SEM micrograph of precipitate collected from solution after aging at 60 °C for 8 h.

formation of large agglomerates can lead to cessation of film growth.

Bulk Precipitation. For further insight into the nature of the aluminum sulfate coating, "bulk" precipitates were formed in the sulfate−nitrate solution in the absence of TiO_2 particles using identical conditions as for film coating. The precipitate was allowed to form at 60 °C for 8 h, washed with distilled water, and dried at 110 °C. An SEM image (Figure 13) of the precipitate shows particles 150−200 nm in diameter. Semiquantitative XPS analysis gave an Al/S ratio of 2.9, which is close to the ratio found in the thin films. However, although very fine particles present in the solution early in the deposition may have been attracted to the substrates, as observed in other systems,[6,9,10] the particles shown in Figure 13 are too large to have contributed to the formation of the thin (5 nm) films on the TiO_2 powder and Si substrates.

The IR spectrum of the powder of Figure 13 is shown in Figure 14. This spectrum reveals strong broad absorption bands between 3100 and 3600 cm^{-1} and a sharp absorption band at 1650 cm^{-1}, features that indicate the presence of H_2O in the material. The strong absorption at 1100 cm^{-1} is assigned to the antisymmetric stretching mode of SO_4^{2-}, and the shoulder at ~1000 cm^{-1} may be due to symmetric stretching. The strong broad band centered at 625 cm^{-1} is assigned to Al−O vibrations. These features in the IR spectrum are
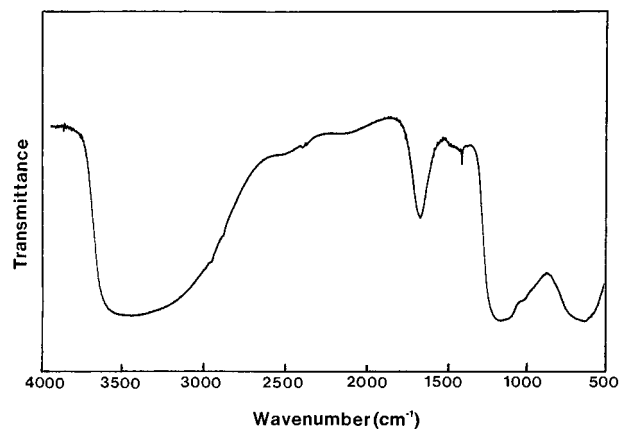

Figure 14. The IR spectrum of the precipitate shown in Figure 13. The absorption bands centered at 3300, 1650, 1100, and 625 cm^{-1} and the shoulder at 1000 cm^{-1} are characteristic of Al basic sulfate.[24]

consistent with the precipitate being a basic aluminum sulfate.[24]

IV. Discussion

We believe that the films that were formed on the TiO_2 particles and the Si wafers consist of the same phase as was formed by Brace and Matijevic.[16] They did not identify the particular basic sulfate that had formed in their experiments, but reported Al/S ratios of 2.2−3.5. In fact, complexes of the composition $Al_4(OH)_{10}(SO_4)$ have been suggested [25,26] as precursors to precipitation of aluminum sulfates.

In an attempt to prepare spherical particles with narrow size distribution from $AlCl_3$ solutions, Scott and Matijevic[27] obtained needlelike boehmite particles. However, structureless, uniform aluminum hydrous oxide particles were successfully prepared using $Al_2(SO_4)_3$ solutions,[16] confirming that SO_4^{2-} anions play an important role in the morphology of hydrous aluminum precipitates. In fact, Brace and Matijevic[16] studied the effect of SO_4^{2-} concentration on the formation of Al-containing sols. With a given Al^{3+} concentration and at low SO_4^{2-} concentration, the particle size of the sol was too small to show light scattering. The particle size increased as the SO_4^{2-} concentration increased, until the sol became coagulated and settled. These results clearly indicate that the SO_4^{2-} anion promotes growth of nuclei and precipitation of the particles that have grown to a certain size in a supersaturated solution.

It is likely that bridging of polymeric hydroxylated Al complexes by sulfate ions is responsible for the formation of the compact films observed here. SO_4^{2-} ions are thought to promote polymerization of the hydrolyzed species, whereas Cl^- ions do not readily coordinate to form polynuclear complexes. Thus, due to its lower electrostatic field, the Cl^- anion promotes nuclei growth less efficiently than does the SO_4^{2-} anion. The weaker bridging force afforded by Cl^- as a monoan-

(24) Sack, M. D.; Tseng, T. Y.; Lee, S. Y. *Am. Ceram. Soc. Bull.* **1984,** *63,* 301.
(25) Singh, S. S. *Can. J. Soil Sci.* **1969,** *49,* 383.
(26) Brosset, C.; Biedermann, G.; Sillen, L. G. *Acta Chem. Scand.* **1954,** *8,* 1917.
(27) Scott, W. B.; Matijevic, E. *J. Colloid Interface Sci.* **1978,** *66,* 447.

ion (as opposed to a sulfate dianion) can still allow formation of many nuclei in the $AlCl_3$ solutions, but the slow growth rate is probably the cause of the needlelike morphology of the boehmite we observed. Such differences between anions are expected from the observed coagulation values,[28] which vary in the order SO_4^{2-} > Cl^- > NO_3^-, a ranking that is consistent with their electrostatic field strength and the double negative charge of the sulfate ion.

Brace and Matijevic[16] succeeded in forming aluminum sulfate sols containing nearly monodisperse spherical 0.5–0.6 μm particles by aging (at temperatures $\geq$ 90 °C) sulfate-containing solutions of Al salts with an initial pH of 4.1. However, stable sols could only be retained at pH 9.7. In a typical experiment, an aged sulfate sol was poured while hot into a cold NaOH solution at pH 9.7, adding additional base as needed to keep the pH constant. Without such stabilization, the sulfate sols redissolved on cooling. During this stabilization, the S was largely removed from the spherical particles (the $[Al^{3+}/SO_4^{2-}]$ ratio went from ~3 to >100). That S could be leached upon digestion of aluminum sulfate particles at pH 9.4 had also been reported by Willard and Tang,[29] whose data are in essential accord with the XPS analysis of our leached films.

According to this latter study, the Al/S molar ratio varies with the final pH attained; a precipitate obtained at low pH had a higher SO_4^{2-} content than did precipitates formed at higher pH. The Al/S ratio dramatically increased as the pH increased, and the sulfate was essentially lost when the pH approached 9.4.

Our sulfate depositions behaved somewhat differently. As shown in Figures 8 and 9, sulfate can be significantly leached from the deposits in neutral solutions in <1 h at room temperature. Significant dissolution of the Al-containing coating cannot be occurring because the ratio of the intensity of the Al peak to that of the substrate (Al/Ti in Figure 8, Al/Si in Figure 9) in the as-deposited materials were only slightly greater than in the leached films. Our results are also generally consistent with the ~10% reduction in particle diameter reported upon conversion of the sulfate sols to hydrous oxide sols by Brace and Matijevic.[16] Our TEM observation of the leached coatings on flat Si wafers (Figure 10) showed a 20% film thickness reduction after the sulfate had been leached, while the compact nature of the original coating was maintained.

V. Conclusions

Methyl-, thioacetate-, and sulfonate-terminated SAMs were formed on pigment-grade TiO_2 particles. The methyl- and thioacetate-terminated SAMs changed the wetting characteristics of the normally hydrophilic TiO_2 powder to hydrophobic. Oxidation of the thioacetate-terminated surface to a sulfonate functionality restored a hydrophilic character to the powder surface.

On the sulfonated surface, hydrous aluminum sulfate thin films could be deposited from aqueous solutions of a mixed aluminum sulfate/nitrate solution. The typical thickness of as-deposited films was 5 nm; this thickness
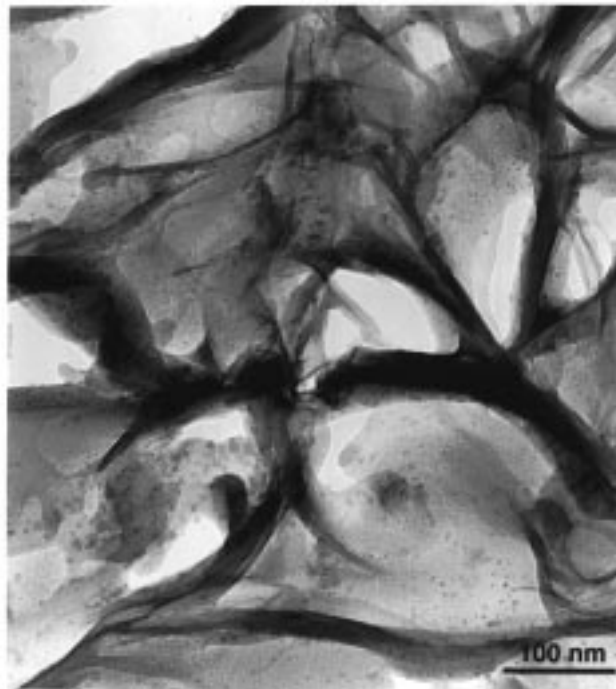
(28) Reed, J. S. *Introduction to the Principles of Ceramic Processing,* John Wiley & Sons: New York, 1988.

(29) Willard, H. H. Tang, N. K. *J. Am. Chem. Soc.* **1937**, *59*, 1190.

Figure 15. The TEM micrograph (plan view) of boehmite [AlO(OH)] film deposited from 0.1 mM $AlCl_3$ solution at 80 °C in 1 h on sulfonate SAM-coated silicon. The film has a very open microstructure with pores up to a few hundred nanometers in diameter.

Table 1. Identification by Electron Diffraction of the Film, Deposited from Aqueous $AlCl_3$ Solution (10^{-4} M) at 80 °C for 1 h, as Boehmite [AlO(OH)]

d spacings (Å) determined from electron diffraction pattern	d spacings (Å) for boehmite [AlO(OH)][a]	relative intensity[a]	$\{h\,k\,l\}$[a]
3.17	3.164	65	1 2 0
2.38	2.346	55	0 3 1
1.88	1.860	30	0 5 1
	1.850	25	2 0 0
1.47	1.453	16	2 3 1
1.34	1.312	16	2 5 1
1.16	1.161	4	1 10 0

[a] Joint committee on Powder Diffraction Standards, Swarthmore, PA, Powder Diffraction File No. 21-1307 (Boehmite).

was reached in 1 h, after which film growth apparently stopped. These films were structureless, adherent, and compact. With no initial SAM coating, the films on the TiO_2 particles were very thin ($\leq$3 nm) and barely continuous. The sulfate anion can be partly leached with a neutral or weakly basic solution, leaving the compact film unchanged. Leached films were ~20% thinner than the as-deposited films.

VI. Appendix

A film deposited on a Si wafer from 10^{-4} M $AlCl_3$ solution at 80 °C in 1 h (Figure 15) was porous and needlelike and was identified as boehmite [AlO(OH)] by electron diffraction (see Table 1). Because the film lacked compactness and was of poor adherence (a piece of Scotch tape, pressed onto the film deposited on a Si wafer and then peeled off, had picked up Al and O as revealed using XPS), no further investigations of film growth from $AlCl_3$ solutions were performed.

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