

Natural superhydrophilicity of sol–gel derived SiO₂–TiO₂ composite films

S. Permpoon · G. Berthomé · B. Baroux ·
J. C. Joud · M. Langlet

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Abstract Sol–gel SiO₂–TiO₂ mixed films have been deposited from a polymeric SiO₂ solution and either a polymeric TiO₂ mother solution (MS) or a derived TiO₂ crystalline suspension (CS). The chemical and structural compositions of MS and CS mixed films heat-treated at 110 or 500 °C have been investigated by Fourier transform infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. Water contact angle measurements show that TiO₂ rich MS films exhibit photo-induced superhydrophilicity, but cannot maintain a zero contact angle in the absence of UV light. In contrast, CS mixed films exhibit a natural and persistent superhydrophilicity for a large range of compositions. Superhydrophilic properties are analyzed in terms of enhanced acidity at the SiO₂–TiO₂ interfaces and discussed with respect to the chemical and structural composition of MS and CS films.

Introduction

Titanium oxide, preferentially in its anatase polymorphic form, exhibits a photo-induced superhydrophilicity under UV exposure. This behavior ensues from

surface oxygen vacancies (O₂), which are created through an oxydo-reduction of TiO₂ (Ti⁴⁺ + e⁻ → Ti³⁺ and 2O²⁻ + 2h⁺ → O₂) induced by photo-generated electron (e⁻)/hole (h⁺) pairs. Surface oxygen vacancies can then be saturated by OH groups, through a molecular or dissociative adsorption of atmospheric water, which yields a superhydrophilic surface, i.e., a surface showing a water contact angle of zero [1, 2]. A superhydrophilic surface has higher affinity toward water than toward carbon contamination. Therefore, contamination adsorbed on the surface can easily be cleaned by water, without the need of detergent, resulting in a self-cleaning surface. However, the photo-induced superhydrophilicity can be reversed to hydrophobicity when the surface is stored in the dark, owing to the replacement of hydroxyl groups by oxygen from air [1]. When considering practical aspects, a surface cannot permanently be irradiated by UV light, such as sunlight. Hence, an ideal self-cleaning surface requires two essential criteria, which are photoinduced superhydrophilic properties and their in-time persistence in the absence of UV light.

Machida et al. [3] have first reported that the addition of 10–30 mol% of SiO₂ into a TiO₂ film yields optimum photo-induced superhydrophilicity, which can be maintained for a certain time in the dark. Ren et al. [4] also reported that SiO₂–TiO₂ thin films have excellent superhydrophilicity and enhanced adhesion to the substrate. It was shown that the addition of SiO₂ not only improved the photoinduced superhydrophilicity of anatase but also its photocatalytic activity [5, 6]. Guan [7] studied the relationship between photocatalysis and photohydrophilicity for self-cleaning applications of composite SiO₂–TiO₂ films. He mentioned that the amount of SiO₂ in mixed SiO₂–TiO₂

S. Permpoon · G. Berthomé · B. Baroux · J. C. Joud
Laboratoire de Thermodynamique et de Physico-Chimie
Métallurgique, ENSEEG-INPG, Domaine Universitaire,
BP 75, 38402 Saint Martin d'Hères, France

M. Langlet (✉) · S. Permpoon
Laboratoire des Matériaux et de Génie Physique, INPG-
Minatec, 3 parvis Louis Néel, BP 257, 38016 Grenoble
Cedex 1, France
e-mail: Michel.Langlet@inpg.fr

films had different influences on the photocatalysis and photohydrophilicity. An optimum photocatalytic activity could be obtained by adding 10–20 mol% of SiO₂ in the films, whereas the addition of 30–40 mol% of SiO₂ yielded an optimum photohydrophilicity.

Besides, several works have shown that the addition of SiO₂ into TiO₂ films retards titania crystallization [8, 9]. Lee et al. [8] revealed that, during mixed film calcination, transformation from amorphous to anatase phase, as well as transformation from anatase to rutile phase, were shifted toward higher temperatures when increasing the SiO₂ content. Moreover, Yu et al. [10, 11] indicated that the SiO₂ addition had a suppressive effect on the crystal growth of TiO₂, because the contact between TiO₂ particles was barred by SiO₂ during the thermally activated growth process. Recently, Guan et al. [7, 12] have suggested that SiO₂ addition might increase the surface acidity of SiO₂–TiO₂ films, which would improve the hydroxyl content at the surface of composite films, resulting in enhanced photo-hydrophilic properties.

In the present work, mixed SiO₂–TiO₂ films were deposited using the sol–gel process. Precursor solutions containing various SiO₂ amounts were prepared from two different titanium precursor sols. A first TiO₂ sol was prepared using a standard sol–gel procedure [13], which required a high temperature post-deposition treatment to yield crystalline TiO₂ films. A second TiO₂ sol consisted of a suspension of anatase nanocrystallites, which was prepared using a specific sol–gel route [14]. In previous works, we showed that this suspension was compatible with the low temperature processing of optical grade photocatalytic [15] and photo-hydrophilic films [16]. In this article, SiO₂–TiO₂ composite films deposited from both kinds of TiO₂ sols have been investigated in the view of understanding and optimizing their superhydrophilic properties.

Experimental

Preparation of SiO₂–TiO₂ mixed films

Silica–titania mixed films containing 0–100 mol% of SiO₂ were deposited from mixtures of TiO₂ and SiO₂ precursor sols. A SiO₂ polymeric sol was prepared by diluting tetraethoxysilane (TEOS) in absolute ethanol, deionized water, and hydrochloric acid (HCl), according to a previously published procedure [17]. A concentrated sol was first prepared with a TEOS concentration of 2.35 M, a molar ratio H₂O/TEOS of 2.2, and a pH of 3.5. This solution was aged at 60 °C for 2 days. Then, it was diluted in

additional absolute ethanol to get a final TEOS concentration of 1.5 M.

TiO₂ precursor sols were prepared using two different sol–gel routes which were detailed elsewhere. A classical method yielded a polymeric mother solution (MS), which was prepared by mixing tetraisopropyl orthotitanate (TIPT) with deionized water, HCl, and absolute ethanol as a solvent [13]. TIPT concentration in the solution was 0.4 M, and the TIPT/H₂O/HCl molar composition was 1/0.82/0.13. The solution was aged at room temperature for 2 days before deposition or mixing with the SiO₂ sol. The second method relied on the preparation of a crystalline suspension (CS) of TiO₂ nano-crystallites in absolute ethanol [14]. This suspension was prepared from the MS using a multi-step procedure. The MS was firstly diluted in an excess of deionized water (H₂O/TIPT molar ratio of 90) and then autoclaved at 130 °C for 6 h. Autoclaving yielded the crystallization of TiO₂ particles in the liquid phase. An exchange procedure was then performed in order to remove water from the sol and to form a CS in absolute ethanol. The final TiO₂ concentration in ethanol was 0.24 M. For more data, the whole procedure has been described in a previous paper [14]. The final sol was composed of TiO₂ nanocrystallites of about 6 nm in diameter. Previous works showed that both MS and CS preparation conditions gave rise to very stable sols, which indicated that no gelation took place in MS sols, while no significant crystal aggregation took place in CS sols. Consequently, these sols could be stored for several weeks before being used for TiO₂ film deposition or SiO₂–TiO₂ mixed sol preparation.

The final solutions were obtained by mixing MS or CS sols with various amounts of the SiO₂ sol. The mixed sol was stirred for 30 min before film deposition. SiO₂–TiO₂ mixed films were deposited at room temperature on (100) silicon wafers by spin-coating (300 μL of sol, spin-speed of 3,000 rpm). Prior deposition, the substrates were ultrasonically cleaned with ethanol for 3 min, then rinsed with distilled water, and dried with air spray. During room temperature film deposition, the solvent vaporized and alkoxide precursors reacted through the well-known hydrolysis/polycondensation sol–gel route yielding a xerogel film, i.e., a film constituted of metal–oxygen–metal polymeric chains with unreacted chain-end alkoxy and hydroxyl groups. As-deposited mixed films were subsequently heat-treated for 2 h at 500 °C for MS films and at 110 or 500 °C for CS films. Heat-treatments were performed in air and the samples were directly introduced in the pre-heated oven. After heat-treatment, the films were cooled to room temperature under ambient condition. Ellipsometric measurements

showed that the film thickness increased from 40 nm to 200 nm for a SiO₂ content ranging from 0 mol% to 100 mol%, which was related to the respective concentrations of the SiO₂ sol (1.5 M) and TiO₂ sols (0.4 and 0.24 M for MS and CS sols, respectively).

Characterizations

The films were characterized by Fourier transform infrared (FTIR) transmission spectroscopy in the range of 4000–250 cm⁻¹ with a resolution of 4 cm⁻¹ using a Bio-Rad FTS-165 spectrometer. Spectra were recorded in room atmosphere without any purging with an acquisition of 300 scans. The spectra were analyzed after subtraction of the bare substrate spectrum. TiO₂ films were studied by X-ray diffraction (XRD) with CuK_α radiation using a Siemens D-5000 diffractometer. A 2-theta range of [18–21] was scanned, with a step of 0.02° and an integration time of 22 s, in order to precisely study the (101) reflection of anatase. Surface analysis was performed by X-ray photoelectron spectroscopy (XPS) using a XR3E2 apparatus from Vacuum Generator employing an Mg K_α source (1253.6 eV). The X-ray source was operated at 15 kV for a current of 20 mA. Before collecting data, the samples were put in equilibrium for 24 h in an ultra high vacuum chamber (10⁻¹⁰ mbar). Photoelectrons were collected by a hemispherical analyzer at 30° take-off angle. Spectra were calibrated with C1s peak at 284.7 eV. All these studies were systematically performed on freshly deposited films. More punctually, XPS studies were also performed on films aged up to 6 weeks.

Surface hydrophilicity of the films was quantified from measurements of the water contact angle. Experiments were performed at 20 °C in an environmental chamber using a KRUSS G 10 goniometer connected with a video camera. Several water droplets of 0.5 μL volume were spread on the samples and water contact angles were measured at different points of the thin film surface for statistical purpose. The effects of film aging on the hydrophilic properties were analyzed using a same statistical procedure. During aging, the films were stored in a plastic box opaque to UV radiation, in such a way that aging effects only traduced natural hydrophilic properties of the films, i.e., did not traduce any photo-induced effects. The photo-induced film hydrophilicity was evaluated from the in-time variation of the water contact angle under UV light irradiation provided by a 100 W black light bulb with a light intensity of 21 mW/cm² (B-100AP, Ultraviolet Product Co. Ltd.). A 365 nm filter was used and the distance between the lamp and the sample was fixed at 5 cm.

Results and discussion

Chemical and structural composition of mixed films

Figure 1 shows FTIR spectra of pure MS and CS TiO₂ films. The MS TiO₂ film heat-treated at 500 °C exhibits two resolved bands at 430 and 260 cm⁻¹, which correspond to transverse optics (TO) vibration modes of anatase (Fig. 1a) [22]. The CS TiO₂ film heat-treated at 110 °C exhibits two weaker and broader but well resolved bands located at 430 and 300 cm⁻¹, together with a large shoulder on the high wavenumber side of the 430 cm⁻¹ band (Fig. 1c). The 430 cm⁻¹ band corresponds to the TO mode of anatase, while the large shoulder and the second band at 300 cm⁻¹ correspond to combinations of longitudinal optics (LO) and TO modes of anatase [14]. Previous transmission electron microscopy and XRD studies showed that CS films heat-treated at 110 °C were constituted of nanocrystallites of about 6 nm diameter, which were already present in the precursor CS sol, while MS films heat-treated at 500 °C were constituted of thermally grown nanocrystallites of 35 nm diameter. Size effects explain differences in the IR features illustrated in Fig. 1a and c [14, 15]. For the CS film heat-treated at 500 °C (Fig. 1b), the high wavenumber broad shoulder disappears and anatase bands noticeably sharpen and increase in intensity compared to bands observed for the film heated at 110 °C. These features indicate a structural ordering and an increase of the crystallite size [14, 15]. Accordingly, we showed in a previous paper that CS TiO₂ films heat-treated at high temperature underwent a thermally activated crystalline growth, occurring through atom diffusion at grain boundaries,

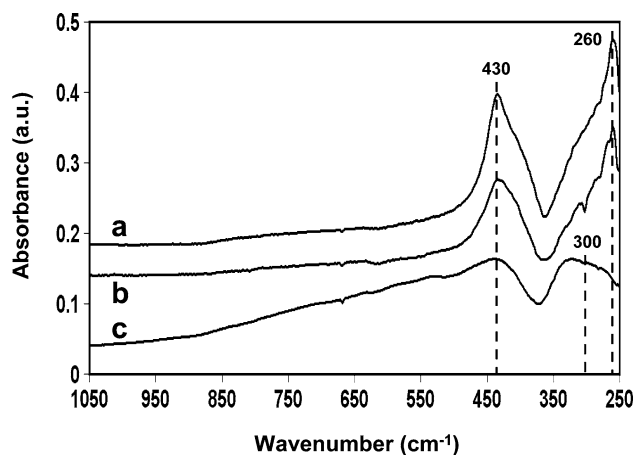


Fig. 1 FTIR spectra of (a) a pure MS TiO₂ film heat-treated at 500 °C, and pure CS TiO₂ films heat-treated at (a) 500 °C and (c) 110 °C

and that heat-treatment at 500 °C yielded crystallite of around 15 nm in diameter [15].

The IR spectrum of a pure SiO₂ film heat-treated at 500 °C exhibits the typical LO and TO vibration modes of silica (Fig. 2a). Three bands located at 460, 815 and 1,080 cm⁻¹ and a shoulder at around 1,200 cm⁻¹ are assigned to the rocking TO1 mode, symmetric stretching TO2 mode, asymmetric stretching TO3 mode, and LO3 mode of the intertetrahedral oxygen atoms in SiO₂, respectively [17]. A SiO₂ film heat-treated at 110 °C exhibits similar IR features (Fig. 2b). Besides, some weak shoulders appear on the LO3/TO3 bands, together with a new band centred around 950 cm⁻¹ and a slight shift of the TO2 band. Previous deconvolution studies allowed us assigning these features to residual Si–OR alkoxy and Si–OH hydroxyl groups [17], which indicates that hydrolysis and polycondensation reactions are not fully completed in SiO₂ films heat-treated at low temperature. Since these band and shoulder signatures are not observed in the spectrum of the film heat-treated at 500 °C, it can be concluded that this temperature is high enough to promote complete pyrolysis and release of residual alkoxy and hydroxyl groups, which agrees with previous studies [17].

The IR spectra of MS mixed films heat-treated at 500 °C exhibit typical bands of a SiO₂ network (Fig. 3a). The band intensities continuously decrease with decreasing the relative amount of SiO₂ in the films. For SiO₂ amounts up to 20 mol%, anatase bands are also observed (Fig. 3b). However, anatase bands appearing for MS mixed films heat-treated at 500 °C are weaker and broader than for a pure MS TiO₂ film (Fig. 1a), which indicates a lower crystallization degree and/or the presence of smaller TiO₂ crystallites [14]. For a SiO₂ concentration of 40 mol% or more, anatase

bands are replaced by a large single band lying between 500 cm⁻¹ and 250 cm⁻¹, which overlaps with the TO1 mode of silica (Fig. 3b). This broad band indicates that the films are composed of amorphous titania [14, 15]. The broad band decreases in intensity with decreasing the TiO₂ amount, and only the TO1 mode of silica can be observed for a film with 80 mol% of SiO₂. FTIR data suggest, therefore, that the crystallization and crystal growth of titania are impeded by the presence of a silica component in MS mixed films. This is presumably related to dilution effects within the SiO₂ network [3, 10]. Because contact between titanium species is barred by SiO₂, structural ordering and crystalline growth of TiO₂ particles are inhibited. IR spectra in Fig. 3a also evidence a strong band at around 950 cm⁻¹, which decreases in intensity when decreasing the SiO₂ content. However, this band is not observed for a pure SiO₂ film heat-treated at 500 °C (Fig. 2a). Thus, it cannot be assigned to silicon alkoxy and hydroxyl groups evidenced in Fig. 2b. Such a band is often mentioned in the spectra of mixed SiO₂–TiO₂ composites. It depicts the IR absorption of Si–O–Ti bonds [23, 24]. Usually, the room temperature sol-gel deposition of a SiO₂–TiO₂ xerogel film yields a mixed network constituted of Si–O–Ti polymeric chains, where Si⁴⁺ and Ti⁴⁺ cations are untimely distributed at the molecular scale. Si–O–Ti bonds in such a network yield IR absorption at around 950 cm⁻¹. Upon heat-treatment at high temperature, a SiO₂–TiO₂ phase separation can take place, which proceeds through the breaking of Si–O–Ti bonds and the formation of well separated Si rich and Ti rich regions. Ti–O–Ti units constituting Ti rich regions can in turn promote the formation of TiO₂ grains and their crystallization. Phase separation and TiO₂ crystallization are all the more likely to take place as the heat-treatment temperature is higher and/or the Ti amount greater [25–27]. FTIR spectra illustrated in Fig. 3a and b suggest that, in MS films heat-treated at 500 °C with a SiO₂ concentration of 40 mol% or more, phase separation occurs only partially, which agrees with previous results [25]. So-formed Ti–O–Ti units remain dispersed within the SiO₂ network, which impinges the growth and subsequent crystallization of TiO₂ grains. Such mixed films are thus amorphous and composed of Ti–O–Ti units within a SiO₂ network, where a large amount of Ti⁴⁺ cations are still distributed in their initial Si–O–Ti polymeric chain configuration. It should be mentioned that, compared to the spectrum of a pure SiO₂ film (Fig. 2a), the TO3 SiO₂ band of MS mixed films is shifted towards lower wavenumbers (Fig. 3a), which can partly be related to a partial overlapping of this band with the Si–O–Ti band.

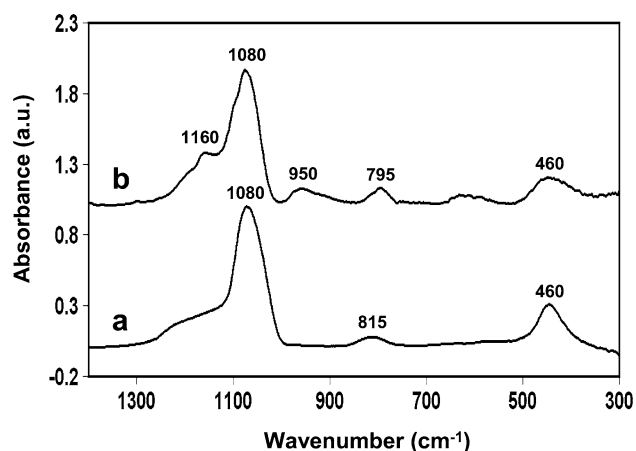
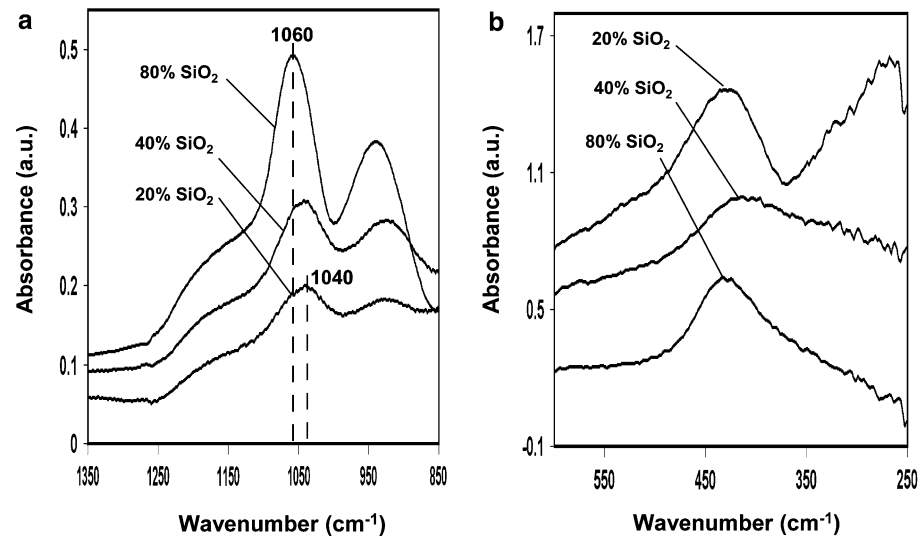


Fig. 2 FTIR spectra of pure SiO₂ films heat-treated at (a) 500 °C and (b) 110 °C

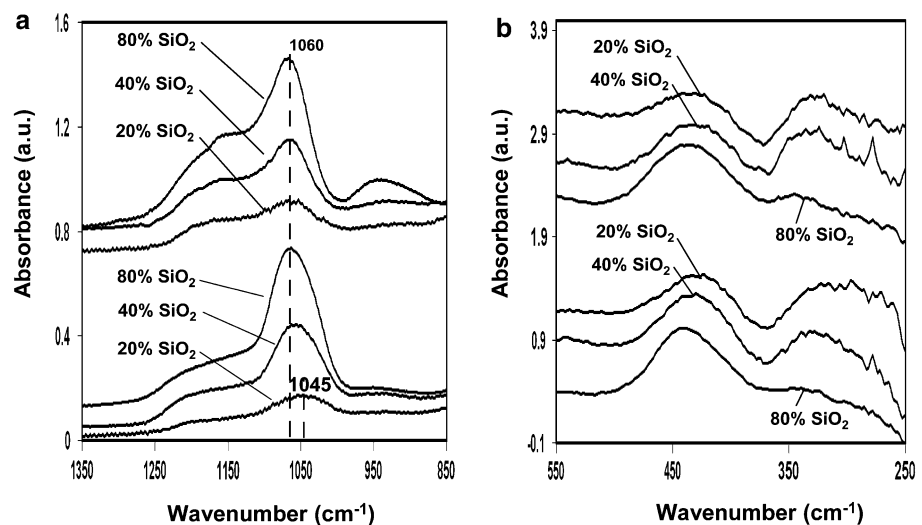
Fig. 3 FTIR spectra of MS mixed films heat-treated at 500 °C with different SiO₂ contents: (a) high wavenumber range and (b) low wavenumber range



The IR spectra of CS mixed films heat-treated at 500 °C exhibit typical bands of a SiO₂ network (Fig. 4a, bottom). Besides, bands of anatase crystallites are observed for any SiO₂-TiO₂ mixed compositions, provided that the TiO₂ amount be sufficient with respect to the FTIR sensitivity (Fig. 4b, bottom). Anatase bands decrease in intensity when decreasing the relative amount of TiO₂, while the TO1 vibration mode of silica becomes dominant. Let us note that for CS films, the presence of anatase crystallites at any SiO₂-TiO₂ composition does not rely on a thermally activated phase separation. It is related to the film deposition conditions that involve a TiO₂ CS. The broadness and position of the anatase bands observed for CS mixed films heat-treated at 500 °C (Fig. 4b, bottom) indicate that anatase crystallites are much smaller than in pure CS or MS TiO₂ films heat-treated

at 500 °C (Fig. 1a, b). Actually, anatase bands of a CS film heat-treated at 500 °C with 20 mol% of SiO₂ are very similar to those observed for a pure CS TiO₂ film heat-treated at 110 °C (Fig. 1c), which is composed of crystallites with a size of 6 nm. This observation suggests that the dilution of TiO₂ crystallites in a SiO₂ network inhibits the thermally activated growth of anatase crystallites in CS films. Contrary to MS mixed films, the Si-O-Ti band at 950 cm⁻¹ cannot be appreciated for CS mixed films, while the TO3 SiO₂ band still appears to be shifted toward lower wavenumbers when increasing the TiO₂ amount (Fig. 4a, bottom). Since this shift cannot be attributed to overlapping with the Si-O-Ti band, it might indicate a possible chemical modification of the SiO₂ network. While the spectrum of a pure CS TiO₂ film heat-treated at 500 °C exhibits sharper and more intense anatase bands

Fig. 4 FTIR spectra of CS mixed films with different SiO₂ contents: (a) high wave number range and (b) low wave number range. The films were heat-treated at 110 °C (top) and 500 °C (bottom)



(Fig. 1b) than that of a CS TiO₂ film heat-treated at 110 °C (Fig. 1c), which illustrates a thermal growth of anatase crystallites at 500 °C, IR spectra of mixed CS films heat-treated at 110 and 500 °C are rather similar (Fig. 4b, top and bottom). This similarity confirms that, in mixed CS films, the presence of a SiO₂ component inhibits the growth of TiO₂ crystallites at 500 °C. Beside SiO₂ vibration modes, the IR spectra of mixed CS films heat-treated at 110 °C (Fig. 4a, top) exhibit silicon alkoxy and hydroxyl signatures previously evidenced for a pure SiO₂ film heated at the same temperature (Fig. 1b). In particular, the alkoxy/hydroxyl band is observed at around 950 cm⁻¹ for SiO₂ rich films. However, compared to spectra of MS mixed films (Fig. 3a), this band is very weak. Besides, Figs. 2b and 4a indicate that, contrary to what is observed for MS films heat-treated at 500 °C, this band does not significantly increase in intensity when increasing the TiO₂ content from 0 mol% to 20 mol%. It can, therefore, be inferred that this band does not traduce the presence of Si–O–Ti polymeric bonds, which confirms that, contrary to MS mixed films, such bonds do not exist in CS mixed films. Fig. 4a (top) also shows that, contrary to MS and CS mixed films heated at 500 °C, CS films heat-treated at 110 °C do not display any significant shift of the TO3 SiO₂ band when increasing the TiO₂ amount.

X-ray diffraction measurements were performed on films heat-treated at 500 °C. The (101) reflection of anatase is clearly evidenced for MS and CS films with a SiO₂ amount in the range (0–20 mol%) and (0–40 mol%), respectively (insert of Fig. 5). Intensity of this reflection decreases with increasing the SiO₂ amount. This decrease is firstly due to a corresponding decrease in the TiO₂ amount. For MS mixed films, this

decrease also confirms FTIR data, showing that an increase in the SiO₂ content impinges the SiO₂–TiO₂ phase separation and the related TiO₂ crystallization. Accordingly, no anatase reflection could be observed for MS films with a SiO₂ content of 40 mol% or more. For CS mixed films, reflections of anatase were below the XRD sensitivity for a SiO₂ content of 60 mol% or more. However, because CS films were deposited from a TiO₂ CS, it is inferred that crystallites are also present for high SiO₂ contents. Insert of Fig. 5 also shows that intensity decrease of the (101) anatase reflection is accompanied with a noticeable peak enlargement, which depicts a crystallite size decrease with increasing the SiO₂ amount. The TiO₂ crystallite size was determined from the full width at half maximum (FWHM) of the (101) reflection using Scherrer's formula (Fig. 5). The crystallite size derived for MS films decreases from about 35 to 8 nm when increasing the SiO₂ amount from 0 mol% to 20 mol% and no size measurement could be performed for greater SiO₂ amounts. For CS films heat-treated at 500 °C, the crystallite size decreases from 15 nm to 6 nm when increasing the SiO₂ amount up to 10 mol%. This size does not appreciably vary for greater SiO₂ contents. Let us recall that the 6 nm size corresponds to that measured for pure TiO₂ CS films heat-treated at 110 °C. This observation confirms FTIR data showing that in CS mixed films, a very small content of SiO₂ is sufficient for suppressing the thermally induced growth of TiO₂ crystallites, whose size is maintained as before calcinations.

To summarize, FTIR and XRD data indicate that the crystallization degree of MS mixed films heat-treated at 500 °C decreases when increasing the SiO₂ concentration. Amorphous films are obtained for a SiO₂ amount of 40 mol% or more. Those amorphous films are constituted of Si and Ti rich regions interconnected with Si–O–Ti polymeric chains. In contrast, though the size of TiO₂ crystallites decreases when increasing the SiO₂ amount up to 10 mol%, CS mixed films are shown to be well crystallized, as far as the TiO₂ amount is great enough for allowing FTIR and XRD detection, and no Si–O–Ti chains can be evidenced.

Analysis of Si–O–Ti environments in MS and CS mixed films

X-ray photoelectron spectroscopy analysis was used for better investigating the surface chemical state of SiO₂–TiO₂ mixed films. Deconvolutions of *Ti2p* spectra showed that the contribution of Ti³⁺ cations could be neglected for pure TiO₂ films as well as mixed

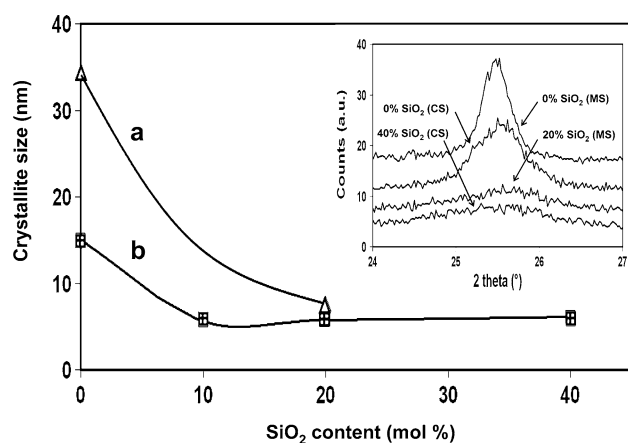


Fig. 5 Crystallite size variations versus SiO₂ content for (a) MS mixed films and (b) CS mixed films heat-treated at 500 °C. Insert shows corresponding XRD patterns

TiO₂–SiO₂ films (not illustrated here). *O1s* spectra of pure films were deconvoluted using a 10% Lorentzian/Gaussian function to estimate the relative contributions of Ti–O (or Si–O), O–H, and C–O components in pure TiO₂ and SiO₂ films heat-treated at 500 °C (Fig. 6). Deconvolutions have been performed by fixing a constant FWHM of 1.5 +/- 0.1 eV for each component. Since the relative intensity of the C–O component depicted for TiO₂ and SiO₂ films was very weak (less than 2%), it has not been illustrated in Fig. 6. This figure shows that *O1s* spectra of pure TiO₂ and SiO₂ films are essentially composed of a major component located at 529.9 (Fig. 6a) and 533.2 eV (Fig. 6b), which can be attributed to Ti–O and Si–O binding energies, respectively [18, 20]. Both spectra depict a secondary component located at higher energies, which can be ascribed to O–H groups linked to Si and Ti cations. The relative intensity of the O–H component is much greater for the SiO₂ film (32%) than for the TiO₂ film (12%). Since no hydroxyl groups could be evidenced by FTIR in the bulk of these films,

it is concluded that XPS data only traduce the presence of surface OH groups. The greater amount of surface OH groups depicted for the SiO₂ film illustrates the fact that a silica surface is naturally more hydrophilic than a titania one.

The *O1s* spectra of MS and CS mixed films heat-treated at 500 °C with 40 mol% of SiO₂ are presented in Fig. 7. These spectra have been deconvoluted with respect to *O1s* peaks illustrated in Fig. 6. Since a multi-peak deconvolution would be very speculative, O–H components depicted in Fig. 6 have not been taken into account. Deconvolution spectra shown in Fig. 7 only rely on undeconvoluted peaks illustrated in Fig. 6, i.e., deconvolutions have been performed by fixing a constant FWHM of 1.5 +/- 0.1 and 1.9 +/- 0.1 eV for the Ti–O and Si–O components, respectively. Fig. 7 shows that, for both MS and CS mixed films, deconvoluted spectra are composed of two major peaks located at 530.5 +/- 0.1 eV and 532.3 +/- 0.1 eV, which correspond to Ti–O and Si–O components, respectively. It has to be underlined that similar decomposition spectra

Fig. 6 *O1s* XPS spectra of (a) a pure SiO₂ film and (b) a pure TiO₂ film heat-treated at 500 °C

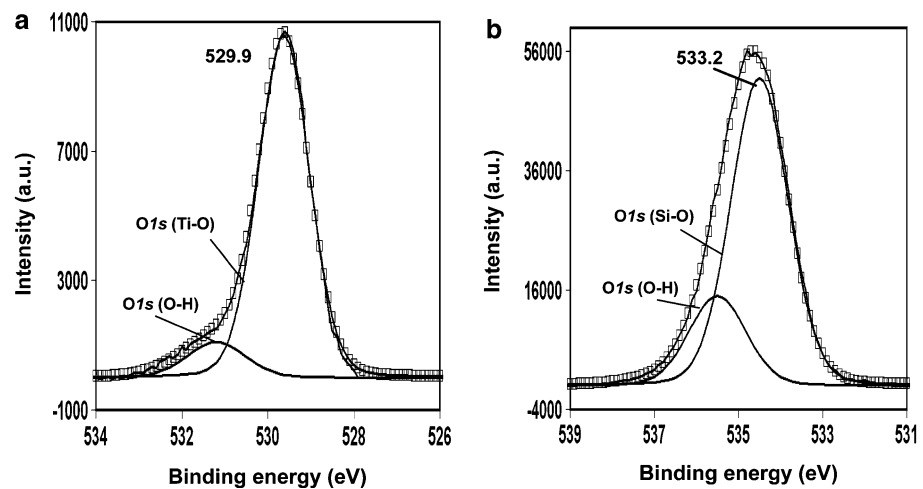
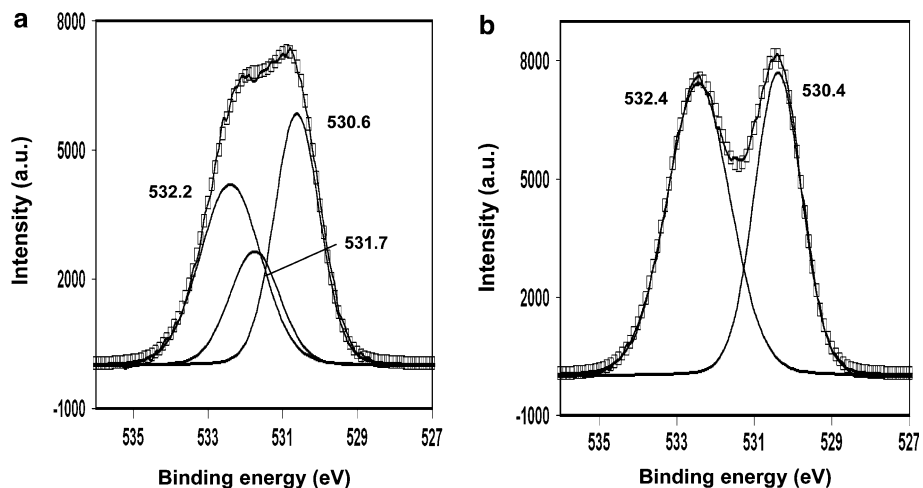


Fig. 7 *O1s* XPS spectra of (a) a MS mixed film and (b) a CS mixed film heat-treated at 500 °C with 40 mol% of SiO₂



were strictly reproduced after aging the mixed films for 2 weeks (not illustrated here), which seems to validate the reliability of our decomposition procedure. However, compared to pure films, Si–O and Ti–O peaks depicted for mixed films are shifted by about 1 eV and 0.5 eV towards lower and higher energies, respectively. Some articles devoted to the XPS analysis of SiO₂–TiO₂ interfacial systems mentioned such shifts [18, 20, 21], which would reflect a substitution of Si (Ti) atoms by less (more) electronegative and more (less) polarizable Ti (Si) atoms in a SiO₂ (TiO₂) host. Besides, for the MS mixed film, an optimized deconvolution of the *O1s* spectrum requires taking into account a third component located at around 531.7 eV, in between the Si–O and Ti–O peaks (Fig. 7a). No third component is necessary for the deconvolution of the CS spectrum (Fig. 7b). The existence of an intermediary *O1s* peak was mentioned by other authors for SiO₂–TiO₂ binary systems, and was ascribed to the binding energy of oxygen within a mixed Si–O–Ti environment [19, 23]. The presence (absence) of this intermediary peak can obviously be correlated to the presence (absence) of Si–O–Ti polymeric chains depicted by FTIR for MS (CS) mixed films.

On the one hand, XPS data confirm FTIR data showing that MS mixed films are partially constituted of Si–O–Ti polymeric chains, while such chains are not present in CS mixed films. On the other hand, shifts evidenced by XPS suggest that, in both kinds of mixed films heat-treated at 500 °C, a certain amount of Si⁴⁺ (Ti⁴⁺) cations might be incorporated within a TiO₂ (SiO₂) environment. These observations can be discussed as follows. It has already been mentioned that MS mixed films are initially composed of Si–O–Ti polymeric chains and that, after heat-treatment, a partial phase separation yields Si rich (SiO₂ network) and Ti rich (Ti–O–Ti units) regions, while Si–O–Ti residual chains can still remain. The 950 cm⁻¹ IR band and 531.7 eV XPS peak give evidence of such residual chains for a MS film heat-treated at 500 °C with 40 mol% of SiO₂. Besides, owing to incomplete phase separation, some Si⁴⁺ (Ti⁴⁺) interstitial cations can locally remain in the so-formed Ti (Si) rich regions, which would explain XPS shifts illustrated in Fig. 7a. It has been reported that Si⁴⁺ and Ti⁴⁺ cations located in Si–O–Ti chains are in 4-fold coordination, and Si⁴⁺ (Ti⁴⁺) cations locally remaining in the TiO₂ (SiO₂) rich regions essentially retain their initial 4-fold coordination [18, 24, 27, 28]. In the case of CS mixed systems, film formation involves the deposition of pre-formed anatase TiO₂ crystallites. Thus, as-deposited films are composed of well separated SiO₂ and TiO₂ regions without any Si–O–Ti polymeric chains. During heat-

treatment at a sufficiently high temperature, Ti⁴⁺ (Si⁴⁺) cations are likely to enter the silica (titania) network through an interfacial solid state diffusion process. Such a process is expected to produce interfacial regions where the SiO₂ (TiO₂) network is enriched with Ti⁴⁺ (Si⁴⁺) cations, which would be depicted by shifts of the *O1s* peaks illustrated in Fig. 7b. In the case of SiO₂–TiO₂ interfacial composite systems, Tanabe et al. have proposed a model [29] that has largely been employed in more recent works [6, 7, 12], postulating that Si⁴⁺ cations entering a TiO₂ host retain their initial 4-fold SiO₂ coordination, yielding interstitial SiO₄ units, while Ti⁴⁺ cations entering a SiO₂ host retain their initial 6-fold TiO₂ coordination, yielding interstitial TiO₆ units.

It should be mentioned that, contrary to XPS spectra, FTIR spectra seem to be weakly sensitive to the substitution of Ti⁴⁺ (Si⁴⁺) cations within a SiO₂ (TiO₂) host. However, two features have to be underlined. On the one hand, since in the case of CS mixed films heat-treated at 500 °C the shift of the TO3 vibration mode of silica cannot be related to an overlapping with the Si–O–Ti IR band, it might possibly depict the insertion of titanium within the SiO₂ network. Accordingly, such a shift was not observed for CS mixed films heat-treated at 110 °C, presumably because this temperature is not high enough to promote diffusion. On the other hand, the reduced crystallization degree and/or crystallite size of TiO₂ particles in mixed MS and CS films might not only ensue from dilution within the SiO₂ matrix, but might also express a crystallization inhibition provoked by the insertion of silicon within TiO₂ grains. Accordingly, it has been previously shown that interdiffusion mechanisms between glassy SiO₂ and crystalline TiO₂ films can promote the formation of amorphous SiO₂–TiO₂ interfaces [21].

In summary, FTIR, XRD, and XPS data depict noticeably different mechanisms, depending on whether mixed films are deposited from MS or CS sols. Chemical and structural properties of MS mixed films heat-treated at 500 °C rely on the extent of a thermally induced phase separation mechanism. Above certain SiO₂ content, an incomplete phase separation yields amorphous MS films, which are partly constituted of mixed Si–O–Ti environments where Ti⁴⁺ and Si⁴⁺ cations would be in 4-fold coordination. Chemical and structural properties of CS mixed films heat-treated at 500 °C rely on a thermally induced interdiffusion process. This process would yield SiO₂–TiO₂ interfaces constituted of Si⁴⁺ cations in 4-fold coordination within a TiO₂ host environment and Ti⁴⁺ cations in 6-fold coordination within a SiO₂ host environment. The

consequences of this conclusion will be discussed in details in the last section.

Hydrophilic properties of SiO₂–TiO₂ MS and CS films

Figure 8 depicts the natural water contact angles measured on freshly prepared SiO₂–TiO₂ MS and CS films heat-treated at 110 and 500 °C. It is interesting to note that freshly prepared TiO₂ films present hydrophilic properties comparable to that of a pure SiO₂ film heat-treated at 500 °C. These films exhibit a natural contact angle of around 15–20°. All mixed MS films heat-treated at 500 °C have a similar contact angle of around 20–30° (Fig. 8a). Small variations observed for the different film compositions are out of the topic of this article. For CS films heat-treated at 110 °C, a water contact angle of around 15° is measured from 0 mol% to 20 mol% of SiO₂ content (Fig. 8b). The contact angle sharply increases up to 70° when the SiO₂ content exceeds 20 mol%. Such behavior can be related to an incomplete oxidation of the SiO₂ component in these films, i.e., residual silicon alkoxy groups depicted by IR data for a low temperature heat-treatment (Figs. 2b and 4a) can detrimentally affect the film hydrophilicity. In contrast, at any SiO₂–TiO₂ composition mixed CS films heat-treated at 500 °C show a water contact angle of 0°, which indicates a natural superhydrophilicity (Fig. 8c).

We have investigated the photo-induced hydrophilicity of mixed MS and CS films heat-treated at 500 and 110 °C, respectively, i.e., films showing no natural superhydrophilicity. The results indicate that mixed MS and CS films with 0–20 mol% of SiO₂ exhibit photohydrophilicity. For these films, a 0° water contact angle is reached after an UV exposure of 30 min or less (Fig. 9). When the SiO₂ content exceeds 20 mol%, the

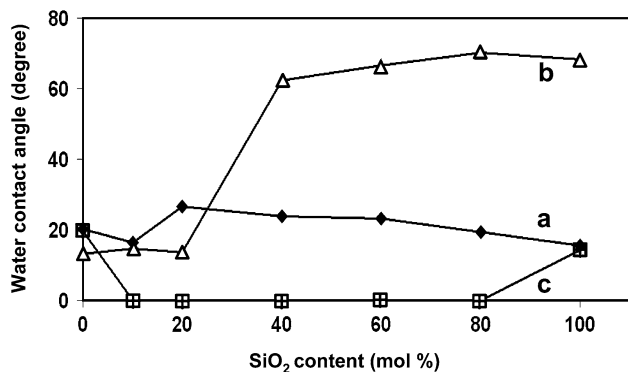


Fig. 8 Natural water contact angle variations versus SiO₂ content for (a) MS mixed films heat-treated at 500 °C, and for CS mixed films heat-treated at (b) 110 °C and (c) 500 °C

MS and CS mixed films lose their photo-induced hydrophilicity, i.e., no significant contact angle decrease is observed after a 2 h UV exposure (not illustrated here). On the one hand, the lack of photohydrophilicity in SiO₂ rich MS films heat-treated at 500 °C presumably relates to the lack of any crystalline TiO₂ component, as shown by FTIR and XRD data. Accordingly, we previously indicated that a photo-induced superhydrophilicity required well crystallized (anatase) TiO₂ particles [16]. On the other hand, though CS mixed films heat-treated at 110 °C are composed of crystalline TiO₂ particles, their lack of photohydrophilicity is presumably related to the presence of residual silicon alkoxy groups, whose amount increases when increasing the SiO₂ content. After exposure to UV radiation, MS films heat-treated at 500 °C and CS films heat-treated at 110 °C were aged in a dark place for 8 weeks and their contact angle was measured with respect to aging time (Figs. 10 and 11).

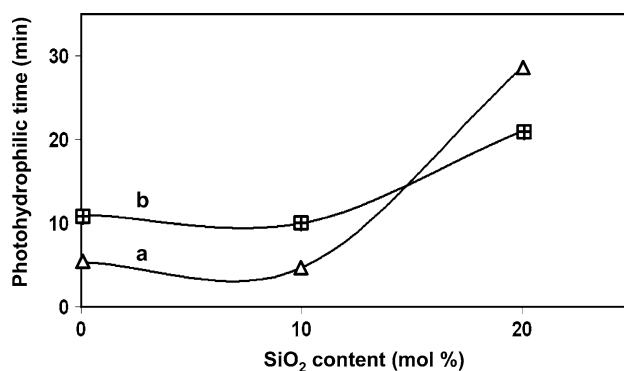


Fig. 9 Variations of the photohydrophilic time (i.e., UV exposure duration required to reach a zero contact angle) versus SiO₂ content for (a) MS mixed films heat-treated at 500 °C and (b) CS mixed films heat-treated at 110 °C

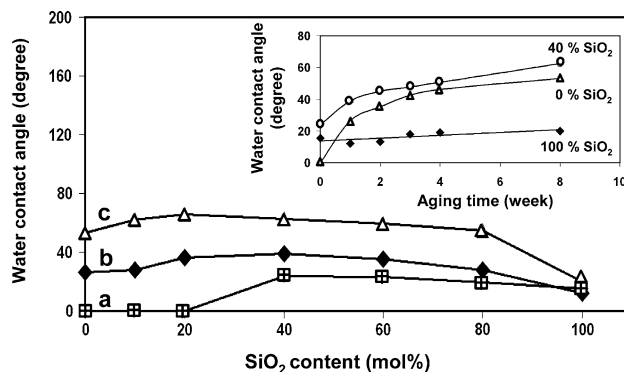


Fig. 10 Water contact angle variations versus SiO₂ content for MS mixed films heat-treated at 500 °C (a) without subsequent aging, and after aging in air for (b) 1 week and (c) 8 weeks. Films containing a TiO₂ component were preliminarily exposed to UV irradiation before aging (see text). The insert shows similar variation versus aging time for compositions of particular interest

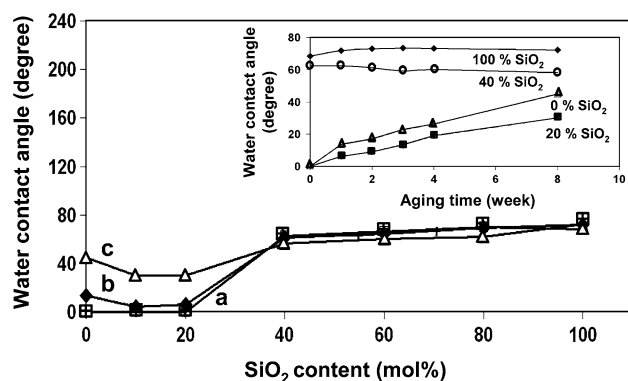


Fig. 11 Water contact angle variations versus SiO_2 content for CS mixed films heat-treated at 110°C (a) without subsequent aging, and after aging in air for (b) 1 week and (c) 8 weeks. Films containing a TiO_2 component were preliminary exposed to UV irradiation before aging (see text). The insert shows similar variation versus aging time for compositions of particular interest

All films containing a TiO_2 component exhibit a gradual contact angle increase with time. In particular, TiO_2 rich films rapidly lose their photo-induced hydrophilicity. In contrast, a pure SiO_2 film heat-treated at 500°C , though not superhydrophilic, exhibits a very slow contact angle increase over a period of 8 weeks aging (Fig. 10), which confirms the natural hydrophilicity of a silica surface.

The intensity of the C1s XPS peak (284.7 eV) was normalized with respect to the total intensity of O1s , Ti2p , and Si2p peaks, for pure TiO_2 and SiO_2 films as well as for MS and CS films with 40 mol % of SiO_2 . All the films were heat-treated at 500°C . Since FTIR and XPS data showed that the amount of alkoxy groups and C–O bonds was negligible, it is inferred that this normalized intensity essentially reflects the atomic percentage of carbon contamination at the film surfaces. Let us recall that the films were put in equilibrium for 24 h in ultra high vacuum before collecting XPS data. The vacuum atmosphere can influence the natural contamination by promoting partial carbon desorption, which in turn relies on the respective surface reactivity and carbon affinity of each sample. Thus, carbon contamination depicted by XPS cannot strictly be correlated to hydrophilic properties of the films. Fig. 12 indicates that the initial carbon contamination, measured on freshly prepared films, is the most severe for a pure TiO_2 film. When adding 40 mol% of SiO_2 into a MS film, the contamination slightly decreases but remains more important than for a pure SiO_2 film. In contrast, the initial contamination of a mixed CS film is much weaker than for a mixed MS film and appears to be similar to that of a pure SiO_2 film. The carbon contamination of these films was

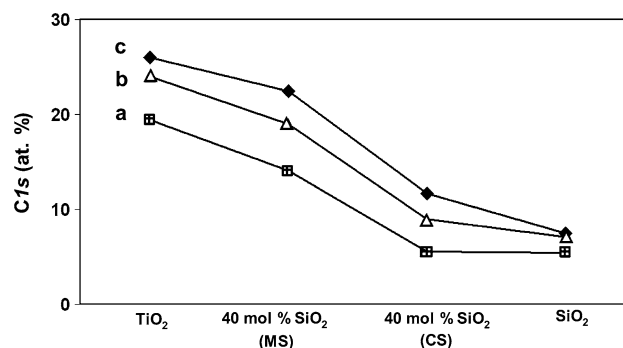


Fig. 12 Variations of the C1s atomic percentage for various films heat-treated at 500°C : (a) freshly prepared films, and films aged in air for (b) 2 weeks and (c) 6 weeks

evaluated over time for an aging period in air of 6 weeks. Fig. 12 shows that aged films follow a tendency similar to that observed for freshly deposited films. For a pure SiO_2 film, the carbon contamination increases very weakly with aging time. For the three other films containing a TiO_2 component, contamination significantly increases and the CS film with 40 mol% of SiO_2 still exhibits the lowest contamination. The differences in contamination evolution evidenced for a pure SiO_2 film and for pure or mixed MS films seem to correlate the contact angle evolutions of these films with aging time (Fig. 10), which would indicate that the loss of hydrophilicity depicted for MS films relates to their carbon contamination increase. As indicated in introduction, since the SiO_2 film is naturally hydrophilic, it is less prone to be contaminated and keeps a low water contact angle for a long time.

Since CS mixed films exhibited a natural superhydrophilicity and appeared to be less contaminated than MS films during aging in air, a special attention was paid to the superhydrophilicity persistence of these films. For this study, no UV exposure was performed before aging. Fig. 13 shows that, for a pure TiO_2 CS film, the contact angle gradually increases with aging, similarly to what is observed for a pure MS film. In contrast, all mixed CS films maintain their natural superhydrophilicity for a period of 1 week to more than 4 weeks, depending on the film composition. To the best of our knowledge, such natural and persistent superhydrophilic properties of mixed SiO_2 – TiO_2 films had never been reported before. The longest superhydrophilicity persistence is observed for a film with 40 mol% of SiO_2 , which can be related to the slow carbon contamination illustrated for this film in Fig. 12. It is worthwhile mentioning that, after aging for 8 weeks, this film still exhibits a carbon contamination weaker than that of a freshly prepared TiO_2 film and that of a freshly prepared mixed MS film with 40 mol%

of SiO_2 (Fig. 12). This observation suggests that the natural superhydrophilic properties of mixed films and their in-time persistence rely on a carbon contamination threshold. Since they can maintain carbon contamination below a certain threshold, CS mixed films exhibit a natural and persistent superhydrophilicity, while naturally more contaminated MS films cannot maintain any superhydrophilicity. However, even best films are observed to lose their natural superhydrophilicity after a certain aging period (Fig. 13). In order to test whether superhydrophilicity could be recovered through a photo-induced mechanism, the CS mixed film with 40 mol% of SiO_2 was exposed to UV radiation after 8 weeks aging. Fig. 14 shows that the water contact angle, which was 18° after aging, falls down to 0° after some minutes of UV exposure. The recovered superhydrophilicity could maintain for several additional weeks of aging, after what the contact angle was observed to increase again. A new UV exposure yields

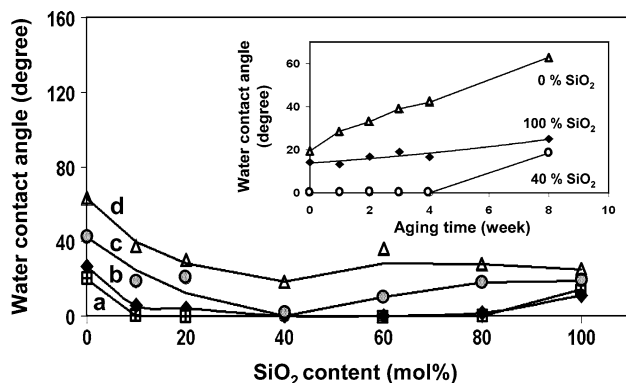


Fig. 13 Water contact angle variations versus SiO_2 content for CS mixed films heat-treated at 500°C (a) without subsequent aging, and after aging in air for (b) 1 week, (c) 4 weeks, and (d) 8 weeks. No UV irradiation was performed before aging. The insert shows similar variation versus aging time for compositions of particular interest

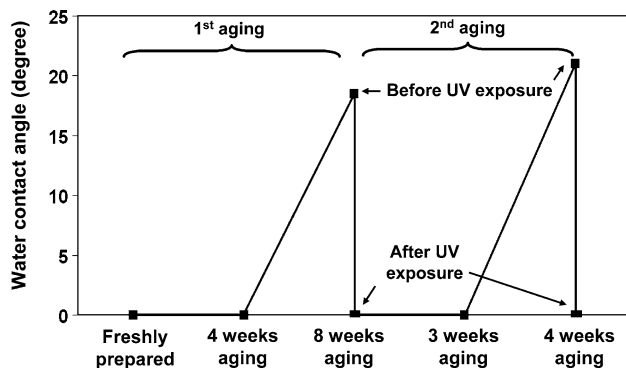


Fig. 14 Variations of the water contact angle versus aging time and UV exposure sequences for a CS mixed film heat-treated at 500°C with 40 mol% of SiO_2

ded once again recovering the superhydrophilicity. From a practical point of view, this result is very important, because it suggests that, thanks to the combination of natural and photo-induced properties, this film can maintain superhydrophilicity for a very long time, provided that UV irradiation be performed periodically. Long-term self-cleaning applications can thus be envisaged. On the one hand, photo-induced properties of this film are obviously related to the fact that it is composed of TiO_2 crystallites. On the other hand, it can be postulated that natural hydrophilicity of the SiO_2 component favors persistent superhydrophilic properties of mixed CS films. However, two arguments indicate that those properties do not entirely rely on the presence of a SiO_2 component. Firstly, a pure SiO_2 film does not exhibit any superhydrophilicity. Secondly, for a same amount of 40 mol% of SiO_2 , a MS mixed film does not show any natural superhydrophilicity, while a CS mixed film exhibits a natural and persistent superhydrophilicity. It is, therefore, concluded that natural properties of CS films partially rely on an additional property.

Discussion: acidity effects in SiO_2 – TiO_2 films

Some articles recently reported on enhanced photo-induced properties of SiO_2 – TiO_2 composites, which were attributed to the acidity of Si–O–Ti bonds [6, 7, 12]. We believe that the natural superhydrophilicity of our films can also be discussed in terms of enhanced acidity. It has been known for a long time that many binary metal oxides exhibit highly acidic properties [29, 30]. It was demonstrated that SiO_2 – TiO_2 composites are of particularly high acidic strength [31]. Accordingly, these composites have often been considered for catalytic applications [5, 6, 28, 32]. Tanabe et al. have proposed a model that reliably predicts which kind of binary oxide systems can show enhanced acidity [29]. This model attributes acidity to the charge imbalance that develops along M–O–M' heterolinkages (where M and M' are different cations). Such a charge imbalance is related to the differences in cation valence and coordination number at the site of substitution of the minor component cation, which is assumed to retain its original coordination number when entering the host environment while surrounding oxygen atoms are in the host coordination. Because the charge imbalance must be satisfied, Bronsted (Lewis) acidic sites are expected to form when the charge imbalance is negative (positive).

For a binary system composed of SiO_2 (4-fold coordination of Si^{4+}) and TiO_2 regions (6-fold coordination of Ti^{4+}), Tanabe et al. have shown that two

situations should be considered [29]. When silicon can enter the TiO_2 lattice as a minor component, because Si^{4+} cations retain their 4-fold coordination, $\text{SiO}_4^{4/3}$ units are formed. Lewis acidity is thus assumed to appear owing to an excess of localized positive charge. When titanium can enter the SiO_2 network as a minor component, because Ti^{4+} cations retain their 6-fold coordination, TiO_6^{-2} units are formed. Bronsted acidity is thus assumed to appear because these units may be compensated by two protons to keep the electric neutrality.

These arguments can in turn be applied to describe the surface hydrophilicity of our films. For MS mixed films heat-treated at 500 °C, FTIR, XRD, and XPS measurements indicated that, above a certain SiO_2 concentration, phase separation occurred only partially and no TiO_2 crystallization took place. For such amorphous mixed films, a large amount of Ti^{4+} cations were still distributed in their initial Si–O–Ti polymeric chain configuration. In such films, Ti^{4+} and Si^{4+} cations are inferred to be in 4-fold coordination. Thus, according to the Tanabe's model, no particularly enhanced acidity is expected because tetravalent cations in 4-fold coordination do not create any charge imbalance. Accordingly, MS SiO_2 – TiO_2 films did not show any natural superhydrophilicity and their photohydrophilicity could be observed only for low SiO_2 (i.e., high TiO_2) contents compatible with a SiO_2 – TiO_2 phase separation and subsequent crystallization of TiO_2 particles.

In the case of CS mixed films, phase separation was naturally achieved during room temperature deposition because these films were derived from a sol constituted of TiO_2 crystallites. In that case, FTIR and XPS spectra did not evidence any significant contribution of Si–O–Ti polymeric chains. For these films, it is inferred that very few Ti^{4+} cations are in 4-fold coordination. Moreover, provided that the post-deposition heat-treatment be performed at sufficiently high temperature, an interfacial diffusion mechanism might take place, which would promote diffusion of Si^{4+} (Ti^{4+}) cations into the TiO_2 crystalline lattice (the SiO_2 network) yielding localized $\text{SiO}_4^{4/3}$ (TiO_6^{-2}) units. According to the Tanabe's model, acidic sites may be created to compensate the charge imbalance, i.e., minor $\text{SiO}_4^{4/3}$ units in the TiO_2 lattice would show Lewis acidity, while minor TiO_6^{-2} units in the SiO_2 network would promote Bronsted acidity by compensating their excess negative charge with a surrounding proton. Consequently, $\text{SiO}_4^{4/3}$ Lewis sites present at the film surface might promote the molecular or dissociative adsorption of water present in the ambient atmosphere by capturing OH^- ions of H_2O molecules,

while Bronsted sites might be formed at the film surface through the reaction of TiO_6^{-2} units with H^+ cations of H_2O molecules, thus promoting the dissociative adsorption of water. In both cases, the enhanced amount of OH groups at the film surface can in turn promote natural superhydrophilicity. In the present state, it is not yet clear whether superhydrophilicity is predominantly induced by Lewis or Bronsted sites, or by the conjoint presence of both kinds of acidic sites. It is worthwhile mentioning that best superhydrophilic properties were obtained for a 40 mol% content of SiO_2 , which might correspond to the highest amount of $\text{TiO}_2(\text{Si}^{4+})$ and/or $\text{SiO}_2(\text{Ti}^{4+})$ acidic sites.

It is not excluded that natural superhydrophilic properties can also be obtained with MS mixed films. However, such properties would require a high temperature heat-treatment necessary to promote an efficient SiO_2 – TiO_2 phase separation, a TiO_2 crystallization, and a Si^{4+} (Ti^{4+}) diffusion within the TiO_2 lattice (the SiO_2 network). Besides, no superhydrophilic properties were evidenced in the case of CS mixed films heat-treated at 110 °C. It can first be inferred that, at this temperature, silicon alkoxy groups were not fully decomposed, which could detrimentally influence hydrophilic properties of these films. It is also inferred that the 110 °C temperature was too low to promote the Si^{4+} or Ti^{4+} diffusion within host environments. These observations suggest, therefore, that the formation of naturally superhydrophilic composite films at a reasonably low temperature (500 °C in this work) essentially relies on 1/a film deposition from a TiO_2 CS, and 2/a sufficiently high temperature heat-treatment necessary to promote thermal interdiffusion of Si^{4+} or Ti^{4+} cations.

Conclusion

Sol-gel SiO_2 – TiO_2 mixed films have been deposited from a polymeric SiO_2 solution and either a polymeric TiO_2 MS or a TiO_2 CS. The chemical and structural compositions of mixed films heat-treated at 110 or 500 °C have been investigated in relation to their hydrophilic properties. FTIR, XRD, and XPS characterizations show that MS mixed films partially undergo a SiO_2 – TiO_2 phase separation during heat-treatment at 500 °C. For TiO_2 rich MS films, this phase separation yields the crystallization of anatase particles, while films with a SiO_2 content greater than 20 mol% remain amorphous and consist of Si rich and Ti rich regions interconnected with Si–O–Ti polymeric chains. In contrast, these chains are not observed in CS mixed films heat-treated at 110 or 500 °C, and these films are

constituted of anatase crystallites dispersed within a SiO₂ matrix.

Water contact angle measurements show that TiO₂ rich MS films exhibit photo-induced superhydrophilicity, which is attributed to the presence of crystalline anatase particles in the films. However, these films cannot maintain a zero contact angle in the absence of UV light owing to carbon contamination of their surfaces. CS mixed films exhibit a natural and persistent superhydrophilicity for a large range of compositions. The superhydrophilicity persistence relies on a combination of natural and photo-induced properties. Photo-induced properties are related to the presence of anatase crystallites, which arise from a film deposition procedure involving a CS. Natural superhydrophilic properties have been attributed to an enhanced acidity at SiO₂–TiO₂ interfaces, which involves a post-deposition heat-treatment at sufficiently high temperature necessary to promote thermal diffusion of Si⁴⁺ or Ti⁴⁺ cations within TiO₂ or SiO₂ hosts. Natural and persistent superhydrophilic properties allow envisaging long-term self-cleaning applications.

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