Available online at www.sciencedirect.com

ScienceDirect

Applied Surface Science 254 (2007) 1405–1414

applied surface science

www.elsevier.com/locate/apsusc

Morphology and natural wettability properties of sol–gel derived TiO_2–SiO_2 composite thin films

M. Houmard [a,b,*], D. Riassetto [b], F. Roussel [c], A. Bourgeois [d], G. Berthomé [a], J.C. Joud [a], M. Langlet [b]

[a] *LTPCM, INPG, BP 75, 38402 Saint Martin d'Hères, France*
[b] *LMGP, INPG–Minatec, BP 257, 38016 Grenoble Cedex 1, France*
[c] *CMTC, INPG, BP 75, 38402 Saint Martin d'Hères, France*
[d] *SOPRA-SA, 26 rue Pierre Joigneaux, 92270 Bois Colombes, France*

Received 19 April 2007; received in revised form 12 June 2007; accepted 29 June 2007

Abstract

Previous studies suggest that granular interfaces induce a natural and persistent super-hydrophilicity in TiO_2–SiO_2 composite thin films deposited by sol–gel route. This effect enables to consider self-cleaning applications that do not require a permanent UV exposure, whereas such a permanent exposure is necessary for pure TiO_2 films. In this study, TiO_2–SiO_2 composite thin films have been deposited from a TiO_2 anatase crystalline suspension and different SiO_2 polymeric sols. Wettability studies show that a suitable control of the TiO_2–SiO_2 mixed sol formulations noticeably enhances persistence of the natural super-hydrophilicity in composite films. It is shown that, beside granular interface effects, modifications in the composite film morphologies can noticeably influence wettability properties.

Keywords: Super-hydrophilicity; TiO_2–SiO_2 thin films; Sol–gel; Self-cleaning surfaces

---

1. Introduction

Titanium oxide, preferentially in its anatase polymorphic form, exhibits a photo-induced super-hydrophilicity under UV exposure. This behaviour ensues from surface oxygen vacancies (O_2^*), which are created through an oxydo-reduction of TiO_2 ($Ti^{4+} + e^- \rightarrow Ti^{3+}$ and $O^{2-} + 2h^+ \rightarrow (1/2)O_2^*$) 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 super-hydrophilic surface, i.e. a surface showing a water contact angle of zero or near zero [1,2]. A super-hydrophilic 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 super-hydrophilicity rapidly vanishes when the surface is stored in the absence of UV exposure [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 photo-induced super-hydrophilic properties and their in-time persistence in the absence of UV light.

In previous works, it has been observed that SiO_2 addition in TiO_2 films enables to increase in-time persistence of the photo-induced super-hydrophilicity [3,4]. More recently, we have shown that TiO_2–SiO_2 granular interfaces can also favour a natural and persistent super-hydrophilicity of sol–gel composite films without the need of any UV light [5]. In this study, an optimal persistence of the natural super-hydrophilicity was observed for a composite film of molar composition $60TiO_2$–$40SiO_2$, deposited from a TiO_2 anatase crystalline suspension and a SiO_2 polymeric sol, and subsequently heat-treated for 2 h at 500 °C. Numerous works have shown that TiO_2–SiO_2 composites exhibit an enhanced acidity, which makes them particularly attractive for catalytic applications [4,6–15]. This property would be induced by the formation of deprotoned

---

* Corresponding author at: LTPCM, INPG, BP 75, 38402 Saint Martin d'Hères, France.
E-mail address: manuel.houmard@ltpcm.inpg.fr (M. Houmard).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.06.072

TiO_x^- and/or protoned SiO_x^+ unities at TiO_2–SiO_2 granular interfaces. Our recent results suggest that these unities might also favour a molecular or dissociative water adsorption, which would induce enhanced wettability properties leading to a natural and persistent super-hydrophilicity of TiO_2–SiO_2 composite films. In our previous work, we also studied TiO_2–SiO_2 mixed films, deposited from TiO_2 and SiO_2 polymeric sols, and subsequently heat-treated for 2 h at 500 °C [5]. For these films, it was observed that any TiO_2–SiO_2 phase separation did not occur for a SiO_2 content of 20 mol% or more, which means that any TiO_2–SiO_2 granular interface did not exist. Accordingly, such films did not present any natural super-hydrophilicity, which was considered to be new evidence that such a property relies, at least partially, on the presence of TiO_2 grains and existence of TiO_2–SiO_2 granular interface. Furthermore, we have also shown that, when TiO_2–SiO_2 composite films are deposited from a TiO_2 crystalline suspension, they include a crystalline TiO_2 component that makes them photo-active. Thus, once super-hydrophilic properties start disappearing owing to a progressive carbon contamination, the photo-activity of composite films allows an easy super-hydrophilicity photo-regeneration through a rapid UV light exposure. It is thus inferred that an ideal composite film should (i) be composed of a SiO_2 component that yields natural super-hydrophilic properties, and (ii) exhibit a maximal TiO_2 content that yields a fast and efficient super-hydrophilicity photo-regeneration.

Beside granular interface effects, other physico-chemical and structural properties can also influence wettability properties of TiO_2–SiO_2 composite films. In particular, morphological properties (surface roughness, open porosity) are an important aspect to consider. Thus, in the present state, a better comprehension of the super-hydrophilicity observed in TiO_2–SiO_2 composite films requires complementary studies. In this new work, composite films with a $80TiO_2$–$20SiO_2$ molar composition have been deposited from a TiO_2 anatase crystalline suspension and four SiO_2 polymeric sols of various formulations. We have studied how the sol formulations influence the formation mechanisms of composite films, their morphological properties, and their natural wettability that is finally discussed with respect to their morphology.

2. Experimental

2.1. Preparation of TiO_2–SiO_2 composite thin films

Silica–titania composite films containing 20 mol% of SiO_2 were deposited from mixtures of TiO_2 and SiO_2 precursor sols. First, a polymeric mother solution (MS) was prepared by mixing tetraisopropyl orthotitanate (TIPT) with deionized water, hydrochloric acid, and absolute ethanol as a solvent [16]. TIPT concentration in the solution was 0.4 M, and the TIPT/H_2O/HCl molar composition was 1/0.82/0.13. The solution was aged at room temperature for 2 days before use. Then, a crystalline suspension (CS) of TiO_2 nano-crystallites in absolute ethanol was prepared from the MS using a multi-step procedure that has been previously published [17]. Briefly, the MS was firstly diluted in an excess of deionized water (H_2O/TIPT molar ratio of 90) and autoclaved at 130 °C for 6 h. Autoclaving yielded the crystallization of TiO_2 particles diluted in the aqueous medium. An exchange procedure was then performed in order to remove water from the sol and to form a CS in absolute ethanol. The final TiO_2 concentration in ethanol was 0.24 M. The CS was composed of TiO_2 nano-particles crystallized in the anatase phase with a diameter of about 5–6 nm. Previous works have shown that CS preparation conditions give rise to a very stable sol, which indicates that no significant crystal aggregation takes place during aging at room temperature [17]. Consequently, this suspension can be stored for several weeks before being used for pure TiO_2 film deposition or TiO_2–SiO_2 mixed sol preparation.

Silica sols studied in this work were formulated in order to vary their reactivity and consequently modify the structure of Si–O–Si chains constituting the SiO_2 network. These modifications were expected to influence the physico-chemical and morphological properties of composite films deposited from different sols and finally induce variations in their hydrophilic properties. SiO_2 polymeric sols were prepared by diluting tetraethoxysilane (TEOS) in absolute ethanol, deionized water and hydrochloric acid (HCl) [18]. Concentred sols were first prepared with a TEOS concentration of 2.35 M by varying the H_2O/TEOS molar ratio (R_w) and pH. These solutions were aged at 60 °C for 2 days. Then, they were diluted in additional absolute ethanol to fix the desired final TEOS concentration (C). Four silica sols, labelled S1–S4, have been formed, whose formulations are presented in Table 1. Finally, these sols were mixed with the TiO_2 suspension to obtain four series of $80TiO_2$–$20SiO_2$ mixed sols, which were used for composite film deposition.

Mixed sols were stirred for 30 min, after what TiO_2–SiO_2 films were deposited at room temperature on (1 0 0) silicon wafers by spin-coating (300 μL of sol, spin-speed of 3000 rpm). Prior deposition, the substrates were cleaned with ethanol, then dried with air spray. During room temperature film deposition, the solvent vaporized and silicium alkoxide precursors reacted with TiO_2 crystallites according to mechanisms that are discussed in Sections 3.1 and 3.2. As-deposited films were then heat-treated for 2 h at 500 °C. Heat-treatment was performed in air and the samples were directly introduced in the pre-heated oven. After heat-treatment, the films were cooled under ambient conditions (temperature, hygrometry). Thicknesses of resulting composite films varied between ca. 40 and 70 nm depending on the

Table 1
Formulation of silica sols S1, S2, S3, and S4: TEOS concentration (C), pH, and H_2O/TEOS molar ratio (R_w)

Silica sol	C (mol/L)	pH	R_w
S1	1.5	3.5	2.2
S2	0.24	3.5	2.2
S3	0.24	3.5	1
S4	0.24	2	0.5