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The influence of “small molecules” on properties of TiO_2 films prepared by sol–gel method

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ABSTRACT

The sol–gel method was used for preparation of TiO_2 sols without and with the addition of “small molecules” — acetylacetone and acetic acid. The TiO_2 films were made by dip-coating method in different time intervals after preparation of sols. Properties of film surface, such as morphology, rms-roughness and adhesion force were studied using atomic force microscopy (AFM). The contact angle of water and diiodomethane was measured for identification of polar and dispersion component of the surface free energy (SFE). From the obtained results, it can be seen that “small molecules” influence the morphology of films. During the first days after the sol preparation, there is the increase of roughness of films prepared from sols with “small molecules” but with the increasing time, the roughness decreases. There is no crystallization of films with acetylacetone. For films prepared from sols with acetylacetone, the polar component of SFE is lower than in the case of films prepared from sols without “small molecules” and with acetic acid. The “small molecules” decrease the stiffness and adhesion force mainly for films prepared several days after sol preparation. This influence is the result of complex effect of “small molecules” on processes occurring during preparation of films, from hydrolysis reaction over process of particle growth to thermal treatment.

1. Introduction

Titanium dioxide exhibits very important properties which make it attractive for preparation of films on different substrates. These coatings are useful for applications in various fields relating to superhydrophobics [1,2], optics [3], environment [4], photocatalysts [5], etc. The polar and dispersion component of surface free energy (SFE), adhesion forces and morphology and rms-roughness of surface are determining surface properties for mentioned applications of TiO_2 films. Polar component of SFE gives the information about the surface polarity. Dispersion component of SFE gives the information about roughness of surface or its porosity [6]. Morphology, topography and rms-roughness of surface are investigated in nano-level with AFM which also enables to determine the surface stiffness and adhesion forces. These properties enable to characterize the surface and look for the correlation between surface properties and properties required for application of TiO_2 films in mentioned fields [7,8]. Nowadays, these relations are studied intensively [1–5].

The sol–gel method is quite often used for preparation of TiO_2 films. This method enables to have the influence on final properties of prepared films by change of sol composition and preparation conditions, such as heating temperature [9–11]. Except for the changes in the ratio “TiO_2 precursor:water”, the composition of sols can also be changed by the addition of “small molecules”, such as ethylenediamine, acetic acid and acetylacetone [12–14] which have the influence on hydrolysis reactions of TiO_2 precursor and following condensation reactions which lead to formation of sol particles. The “small molecules” also influence the processes of aggregation, agglomeration and Oswald ripening. During the Oswald ripening, the large particles grow and they become dominant to small particles and it changes the size distribution of particles in sol [9,10,15]. The influence can also be seen during thermal treatment of films where “small molecules” have the influence on decomposition reactions. Then, this complex effect of “small molecules” influences the final surface properties of prepared TiO_2 films but it is important to say that the sufficient attention has not been paid to this problem.

This paper is focused on the study of the influence of sol composition on final surface properties of prepared TiO_2 films — morphology, rms-roughness, adhesion force, stiffness and surface free energy and its components. The changes of sol composition are carried out by addition of “small molecules”, such as acetylacetone and acetic acid. From the aspect of the elapsed time from sol preparation to film preparation, the influence of time on mentioned properties of TiO_2 films is also studied while the complex effect of “small molecules” is taken into account.

2. Experimental

Titanium(IV) isopropoxide (98%, $Ti(iPr)_4$), isopropanol (p.a., IPA), nitric acid (66%, HNO_3) and distilled water (H_2O) were used for

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preparation of TiO_2 sols. The acetylacetone (p.a., AcAc) and acetic acid (99%, AA) were used as "small molecules". Table 1 shows the molar composition of the solutions used for preparation of sols. The sols were prepared according to the scheme in Fig. 1.

The dip-coating technique was used for deposition of TiO_2 films on microscope slide glasses. This substrate was selected because it is a suitable material from the aspect of transparency which is required in many applications. The substrates were cleaned by the procedure described in [16] and withdrawn from the sol at a speed of 20 $mm \cdot min^{-1}$. The films were dried at 80 °C for 15 min, heated at 10 $°C \cdot min^{-1}$ and annealed at 400 °C for 50 min and then they were cooled freely. The films were prepared from sol immediately after sol preparation (0) and 1, 3, 7, 10 and 14 days after its preparation. In the following parts, this period of time is called the "elapsed time" from sol preparation to avoid the exchange of the given term with Oswald ripening which is often called "aging of sols". The prepared films were stored in an environment with relative humidity of 52.9%. Thickness of all prepared TiO_2 films was about 55 nm [17].

The surface of TiO_2 films was investigated using atomic force microscope NT-206 (Micro test Machines Belarus) operated in contact mode in the air at room temperature and relative humidity ~55%. The MikroMasch NSC11/AlBS cantilever with a spring force constant of 3 $N \cdot m^{-1}$ (measurement of morphology and topography) and 48 $N \cdot m^{-1}$ (measurement of adhesion force and stiffness) was used. The surface morphology and topography were evaluated by SurfaceXplorer 1.0.8.65 program according to the procedure described in [16].

The adhesion force were calculated considering that the adhesion force F_{ad} is a combination of electrostatic force F_{el}, the van der Waals force F_{vdW}, the meniscus or capillarity force F_{cap} and forces of chemical bonds or acid–base interaction F_{chem} ($F_{ad} = F_{el} + F_{vdW} + F_{cap} + F_{chem}$) and at ambient conditions, the water neck is formed between AFM tip and substrate due to capillary condensation and adsorption of thin water films at surfaces. Then the adhesion force can be calculated on the basis of difference between minimum and zero line of force-displacement curve [18].

The stiffness was calculated considering that when the tip is in contact with substrate, it can be written [18,19]:

$$D = Z_p + Z_c + \delta \qquad (1)$$

where D is displacement between tip and substrate, Z_p is piezo deflection, Z_c is cantilever deflection and δ is deformation of sample. In contact $D = 0$ and if system is in equilibrium, also $k_s\delta = k_cZ_c$, where k_s, k_c are sample stiffness, cantilever stiffness, respectively. Using substitution, we can obtain:

$$k_cZ_c = -\frac{k_ck_s}{k_c + k_s}Z_p = -k_{eff}Z_p. \qquad (2)$$

The slope of force-displacement curve is a measure of the stiffness of sample (k_{eff}). If the sample is much stiffer than the cantilever, that is for $k_s >> k_c$, then $k_{eff} \approx k_c$, whereas $k_{eff} \approx k_s$ when $k_s << k_c$, i.e., when the sample is much more compliant than the cantilever.

The polar γ_s^p and dispersion γ_s^d component of surface free energy (SFE) of prepared TiO_2 films were calculated on the basis of Fowkes theory [6]. At first, the contact angle Θ for the solid is measured using the dispersion liquid. Then, γ_s^d is calculated from equation:

$$\gamma_s^d = 0.25\gamma_l(1 + cos\Theta)^2 \qquad (3)$$

where γ_l is SFE for dispersion liquid for which $\gamma_l = \gamma_l^d$. Next, the contact angle Θ_p is measured using the liquid for which $\gamma_l = \gamma_l^d + \gamma_l^p$. Using the determined value of γ_s^d and Θ_p, the quantity of γ_s^p can be calculated from the following equation:

$$\gamma_s^p = \left\{0.5\gamma_l\left(1 + cos\Theta_p\right) - \left(\gamma_s^p\,\gamma_1^d\right)^{0.5}\right\}^2 / \gamma_1^d \qquad (4)$$

The polar and dispersion component of SFE were calculated from the measurement of contact angle using diiodomethane and distilled water. The diiodomethane was chosen as dispersion liquid ($\gamma_l = \gamma_l^d = 50.8\ mJ \cdot m^{-2}$) and water was chosen as the liquid with the dominant polar component ($\gamma_l^d = 21.8\ mJ \cdot m^{-2}$, $\gamma_l^p = 51.0\ mJ \cdot m^{-2}$) [20]. The measurement of contact angle was carried out by sessile drop technique. Ten drops of liquid with a volume of 10 µl were dropped on each TiO_2 film.

The crystallization of TiO_2 in thick films was studied using PANalytical Empyrean X-ray diffractometer (CuKα radiation). Thick films were prepared at the same conditions of withdrawing, drying and heating. The procedure of deposition and drying was performed four times. The thickness of these films was about 220 nm.

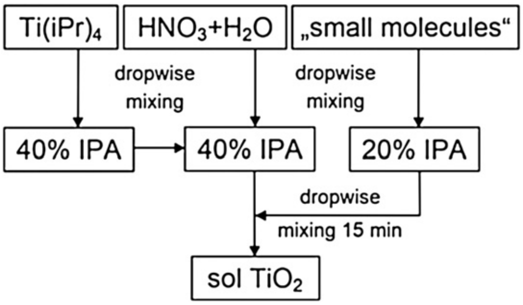

Fig. 1. The scheme of sol preparation.

Table 1
Molar composition of solutions used for preparation of sols.

Sol	Component					
	$Ti(iPr)_4$	AcAc	AA	HNO_3	H_2O	IPA
TiO_2(1)	0.05	0	0	0.090	0.210	0.65
TiO_2(7)	0.05	0.12	0	0.054	0.126	0.65
TiO_2(1) + AA	0.05	0	0.03	0.080	0.190	0.65

3. Results

As it can be seen in Fig. 2, on the surface of films with acetic acid, the size of bumps has increasing tendency along with elapsed time from sol preparation. The surface of films with acetylacetone is practically smooth without large bumps and it is not changed in dependence to elapsed time. The rms-roughness of films without "small molecules" decreases with elapsed time and it is in the range from 2.7 to 1.7 nm. The "small molecules" cause the small decrease of rms-roughness. However, the films prepared after the 1st and the 3rd day from the sol preparation exhibit considerably higher rms-roughness (Fig. 3).

In Fig. 4, it can be seen that when the elapsed time increases, the adhesion force considerably increases up to 7 days for films without "small molecules". Over this day, the values of adhesion force are not changed. For the film with acetylacetone prepared after the 1st day, the adhesion force is considerably lower in comparison to immediately prepared film. Other increase in time does not have any influence on the adhesion force. The similar tendency is observed for the film with acetic acid but the value of adhesion force decreases until the 7th day. Compared to films without "small molecules", the adhesion force between AFM tip and film surface is considerably lower for films prepared from sol with acetylacetone except the film prepared immediately (the adhesion force is the same as without acetylacetone). The similar tendency was observed for films prepared from sol with acetic acid after the 3rd day from sol preparation. The comparison of the adhesion force of