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Liquid-phase Deposition of Titanium Oxide Film on Silicon Substrate Mediated by Polydopamine

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Polydopamine (PDA) bearing surface catechol groups on a silicon wafer was used to induce the deposition of thin TiO_2 films from aqueous solution. Different deposition conditions, such as the concentration and pH of precursor solution as well as the deposition temperature, were adopted. It was found that the growth rate and crystalline phase can be controlled by these deposition parameters; moreover, the crystal growth and adhesion strength to the substrate of TiO_2 film can be promoted by PDA layer.

Liquid-phase deposition (LPD), as a typical aqueous low-temperature technique for deposition of oxide films, has been widely used for the preparation of SiO_2 and TiO_2.[1,2] The distinguishing characteristic of LPD is the composition of the aqueous solution, which is composed of metal–fluoride complexes [such as $(NH_4)_2TiF_6$] and boric acid (H_3BO_3) or aluminum metal. Thus, the hydrolysis of Ti–F complexes can be tuned by the following chemical reactions:

$$TiF_6^{2-} + 2H_2O \rightarrow TiO_2 + 6F^- + 4H^+ \tag{1}$$

$$H_3BO_3 + 4HF \rightarrow BF_4^- + H_3O^+ + 2H_2O \tag{2}$$

$$2Al + 12HF \rightarrow 2H_3AlF_6 + 3H_2 \tag{3}$$

The chemical nature of the substrate surface is another important factor for LPD. Organic self-assembled monolayers (SAMs) bearing special functional tail groups, such as –OH and $–SO_3H$, have been widely used to promote the deposition of different oxide films, such as TiO_2 and SnO_2.[3–5] Researches revealed that LPD was promoted due to an enhancement in nucleation by van der Waals or electrostatic attractions between the SAMs and the existing solid particles.[3–5] However, SAMs can only be formed on surfaces with special chemical composition, such as SiO_2, Au, etc.

Recently, polydopamine (PDA) is reported to be adhesive and can be attached to almost all material surfaces.[6] Moreover, the catechol groups on PDA can serve as active points to chelate with nanoparticles in aqueous solution.[6] So, herein, PDA is deposited onto the Si substrate to boost the growth of TiO_2. Moreover, to further increase the affinity between PDA and the substrate, the substrate is premodified by 3-aminopropyltriethoxysilane (APTES) SAMs. Thus, APTES–PDA was generated. The formation of APTES–PDA has been discussed in previous study.[7] So, the following discussions will be only focused on the deposition of TiO_2 films.

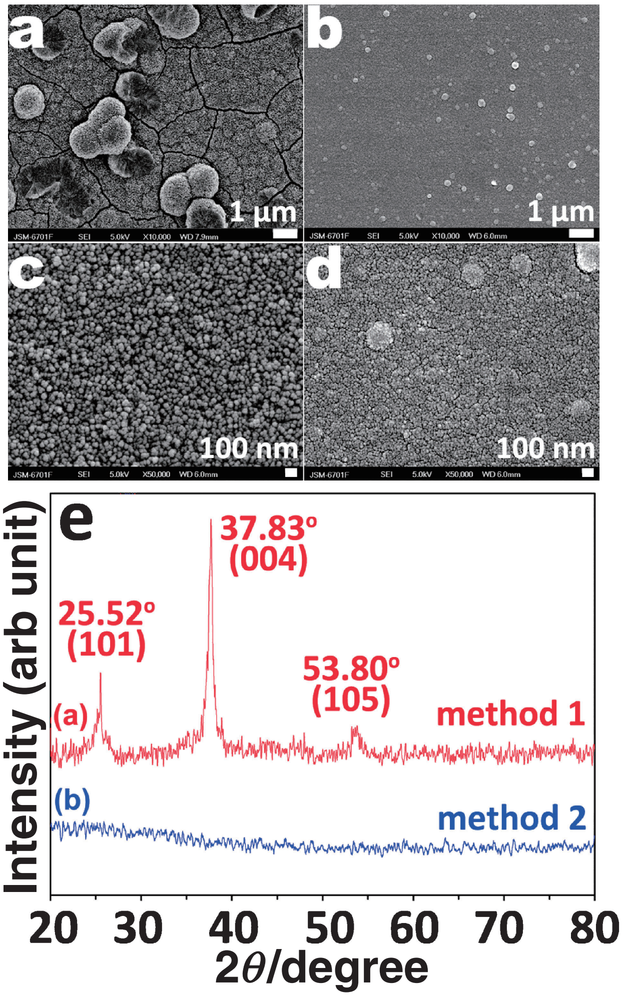

Figure 1. Morphologies of TiO_2 obtained by method 1 (a, c) and method 2 (b, d); XRD profiles of the deposited films (e). The substrate is PDA-modified Si wafer.

The TiO_2 films were prepared by two different methods. For method 1, APTES–PDA-modified Si substrates were immersed into a freshly prepared aqueous solution of 0.05 M $(NH_4)_2TiF_6$ and 0.15 M H_3BO_3 with a pH of 2.88 at 50 °C for 6 h. For method 2, the precursor solution of 0.10 M $(NH_4)_2TiF_6$ and 0.30 M H_3BO_3 with a pH of 3.88 was kept at 20 °C for 6 h. The acidity of the solution was adjusted by adding HCl solution (1 M). Then, the samples were ultrasonicated in water for 5 min and blown dry with N_2. For comparison, bare Si wafer cleaned by piranha solution [$v(98\%\ H_2SO_4):v(30\%\ H_2O_2) = 3:7$] was also used as substrate to induce the TiO_2 deposition.

Morphologies of the as-deposited TiO_2 films on PDA and bare Si substrates were provided in Figure 1 and Supporting Information; SI,[20] respectively. It is clearly seen that the films are composed of nanoparticles. As shown in Figures 1c and 1d,

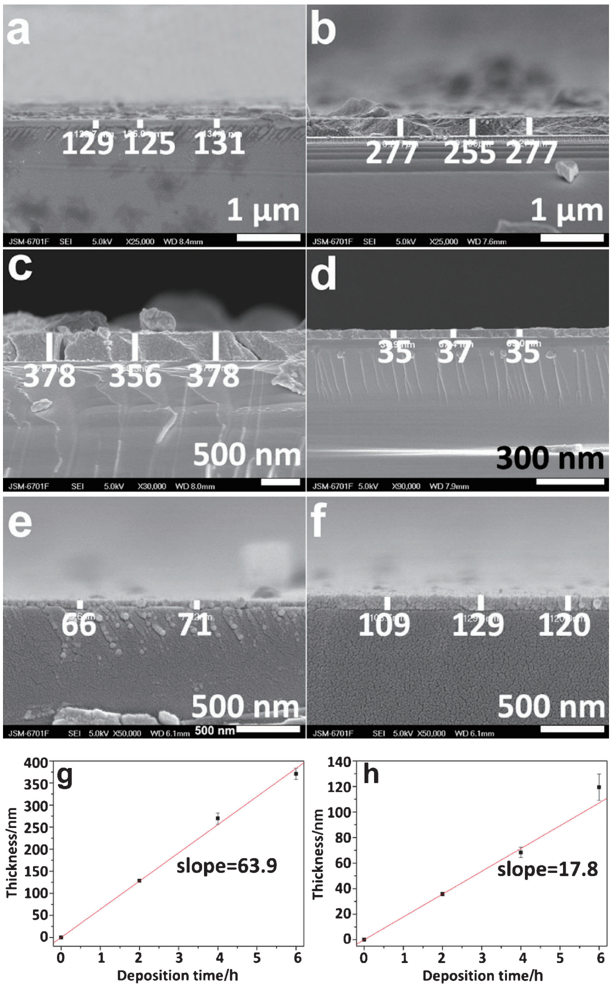

Figure 2. Cross-sectional views for the as-deposited films under different deposition time of 2 (a, d), 4 (b, e), and 6 h (c, f) by method 1 (a–c) and method 2 (d–f); Thickness-versus-deposition time curves for method 1 (g) and method 2 (h).

Table 1. Adhesion strength to the substrate and crystal phase of deposited TiO_2 film

No.	Substrate	Method	Adhesion strength[a] /min	Crystalline phase
1	Bare Si	1	≈5	Amorphous
2	Bare Si	2	>3	Amorphous
3	PDA-modified Si	1	>3	Anatase
4	PDA-modified Si	2	>3	Amorphous

[a] The adhesion strength was reflected by the ultrasonication process. The listed number is the enduring time before being broken.

the diameter is about 40 nm for method 1, about 20 nm for method 2. The particle size difference can be attributed to the hydrolysis conditions. Specifically, the deposition temperature for method 1 is higher, so the hydrolysis and condensation between the hydrolysate are supposed to be more vigorous. Thus, larger particles are obtained. Moreover, it is obvious that the TiO_2 film obtained by method 1 is cracked. This phenomenon has been observed elsewhere and can be ascribed to the shrinkage during post drying process.[8] It is inferred that the TiO_2 film obtained by method 1 is thicker. To prove this assumption, the cross section of the deposited film was observed by field emission scanning electronic microscopy (FE-SEM) (Figure 2). It can be seen from Figure 2c that the TiO_2 film obtained by method 1 records a thickness of 370.8 nm, which is much higher than that of TiO_2 film obtained by method 2 (Figure 2f, 119.4 nm). From above discussions, it is supposed that the crack formation is thickness-dependent. In other words, for liquid-phase deposited films, when the thickness is greater than a critical value, the crack formation is inevitable.[8] Fortunately, such critical value has been detected in our present study with a deposition time of 4 h at 50 °C (270.0 nm, Figure 2b, the top view SEM image was provided in SI[20]).

The thickness-versus-deposition time curves were plotted in Figures 2g and 2h based on the cross section observations. The deposition rate, reflected by the slope of the fitted line, for method 1 is much higher. This is in accordance with the nanoparticle size difference as discussed above and can also be due to the intensive hydrolysis of $(NH_4)_2TiF_6$ at higher deposition temperature. It is reported that the degree of supersaturation of the liquid deposition system has a strong influence on the film growth rate.[8] High supersaturation should increase the rates of nucleation and growth of solid, which may lead to increased growth rate of the film. In aqueous hydrolyzing systems, supersaturation of a solution can be tuned by temperature, concentration of the precursor, and pH. Here, the higher temperature of method 1 (50 °C vs. 20 °C) was apparently the dominant factor among the three.

The crystalline phase of the deposited film was assessed by XRD, and the results are summarized in Table 1. The related XRD patterns are also provided (Figure 1e and SI[20]). The as-deposited films are amorphous except the one deposited on PDA by method 1 (Entry 3, Table 1). The film exhibits anatase phase and crystal planes (004) are found to be highly oriented with a strongest intensity at 37.83°.[3,8,9] However, the film deposited on bare Si substrate by the same method (i.e., method 1) is amorphous. This shows that PDA can promote the crystal growth of TiO_2 for method 1. For method 2, TiO_2 films deposited on either PDA or bare Si substrate, are amorphous. This suggests that the low deposition temperature of method 2 tends to generate randomly oriented particulates, which are supposed to be adhered to the substrates to form TiO_2 films.

A simple ultrasonication process (100 W, 40 kHz) in water was adopted to evaluate the adhesion strength between the TiO_2 film and the substrate. As results showed, the deposited TiO_2 films on PDA (Entries 3 and 4, Table 1) and bare Si substrate by method 2 (Entry 2, Table 1) remain intact even after 3 h ultrasonication. However, TiO_2 deposited on bare Si substrate by method 1 (Entry 1, Table 1) exhibits poor adherence, and there leaves almost nothing on the substrate after 5 min ultrasonication. The reason for the difference between Entries 1 and 2 has been discussed elsewhere.[8] Specifically, TiO_2 formed in the precursor solution is supposed to be positively charged because that the pH (2.88 for method 1, 3.88 for method 2) is below the isoelectric point of TiO_2 (reported values of which range among 5.6,[10] 5.9,[11] and 6.2[12]). So, the formed TiO_2 will be assembled onto a negatively charged surface. The isoelectric point of SiO_2

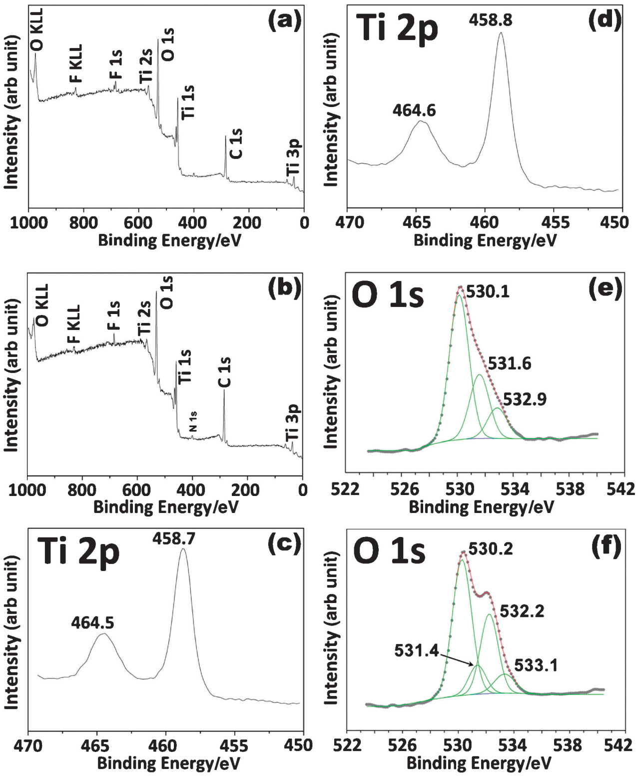

Figure 3. XPS of the as-deposited films obtained by method 1 (b), (d), and (f) and method 2 (a), (c), and (e).

(i.e., the oxide surface of Si) ranges from 1.8[13] to 2.7.[14] That is, the surface of bare Si substrate will be negatively charged at pH 3.88 of method 2 and less so at pH 2.88 of method 1. So, the adhesion strength for Entry 1 in Table 1 is lower. For Entries 3 and 4, the good adhesion may result from the strong chelation between catechol group and the TiO_2 particles, just as discussed in our previous study.[15]

The as-deposited films were further investigated by XPS (Figure 3). Expected Ti and unexpected N/F signals were observed in the survey spectra (Figures 3a and 3b), which can be ascribed to the deposited titanium oxide and the residues of $(NH_4)_2TiF_6$ as well as its partial hydrolysis products, respectively. To further characterize the titanium oxide, Ti 2p (Figures 3c and 3d) and O 1s (Figures 3e and 3f) spectra were examined. The binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ for the deposited films were observed to be at 458.7 (+0.1) and 464.5 (+0.1) eV, respectively, which are very close to the reported values for Ti^{4+} in TiO_2.[4,16] High resolution of O 1s spectra exhibited asymmetric line shapes and were deconvoluted into three peaks. The binding energy of 530.1 (+0.1) eV is lower than neutral oxygen molecules (531.0 eV) and is characteristic of Ti–O bonding as reported for TiO_2,[4,16] suggesting that oxygen is negatively charged possibly through the formation of chemical bonds with Ti^{4+}. The peak located at 531.4 (+0.2) eV is believed to be the surface hydroxy groups,[17,18] which are supposed to be formed in the aqueous solution during preparing procedures. The peak located at 532.9 (+0.2) eV is generally believed to be the O–C species by reason of the atmospheric contamination.[19] For TiO_2 film obtained by method 1, signal at 532.2 eV appeared. This value is almost the same as that of O 1s in PDA (532.3 eV, see Supporting Information[20]), suggesting that the signal is most likely to be resulting from the exposed PDA, which was facilitated by the cracks of TiO_2 film, as clearly shown in Figures 1a and 2c.

In conclusion, TiO_2 was deposited on different substrates under different deposition conditions. It is found that the growth of the film can be affected by the deposition conditions and the substrates. To be specific, TiO_2 films obtained by method 1 is thicker and rougher; while, the film obtained by method 2 is thinner and smoother. Moreover, for method 1, PDA can promote the adhesion strength and crystal growth of TiO_2 film.

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