

# A Facile Layer-by-Layer Adsorption and Reaction Method to the Preparation of Titanium Phosphate Ultrathin Films

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Received March 24, 2005. Revised Manuscript Received May 6, 2005

A layer-by-layer adsorption and reaction method was developed for the preparation of titanium phosphate ultrathin films. By repetitive adsorption of hydrated titanium from aqueous  $\text{Ti}(\text{SO}_4)_2$  solution and subsequent reaction with phosphate groups, ultrathin films of titanium phosphate were fabricated. Regular film growth was verified by UV–vis absorption spectroscopy and quartz crystal microbalance measurements. The film composition is mainly  $\text{Ti}(\text{HPO}_4)_2$ , as confirmed by X-ray photoelectron spectroscopy and FT-IR spectroscopy. The as-prepared titanium phosphate films are uniform, highly stable, and their thickness can be well controlled by adjusting the number of adsorption–reaction cycles and pH value of  $\text{Ti}(\text{SO}_4)_2$  and phosphate salt solutions. The layer-by-layer adsorption and reaction method provides a facile way to prepare ultrathin films of titanium phosphate and other kinds of metal phosphates.

## Introduction

There is growing interest in developing techniques for preparing functional ultrathin inorganic films. On one hand, excellent properties of some inorganic materials can be derived from their size-dependent quantum effect in nanometer-thick films. These properties are not available for their corresponding bulk materials; on the other hand, facile ways for ultrathin film fabrication are a prerequisite to integrated functional film materials. Currently, physical methods such as vapor deposition techniques are frequently employed to prepare inorganic ultrathin films. Unfortunately, most of these techniques suffer from serious problems such as irregularity in the coverage and uniformity, difficulty in controlling film composition and thickness, and the narrow window for the choice of precursors.<sup>1</sup> In addition, these vapor deposition techniques require well-controlled environment and sophisticated pieces of equipment, which increase the cost of film production.

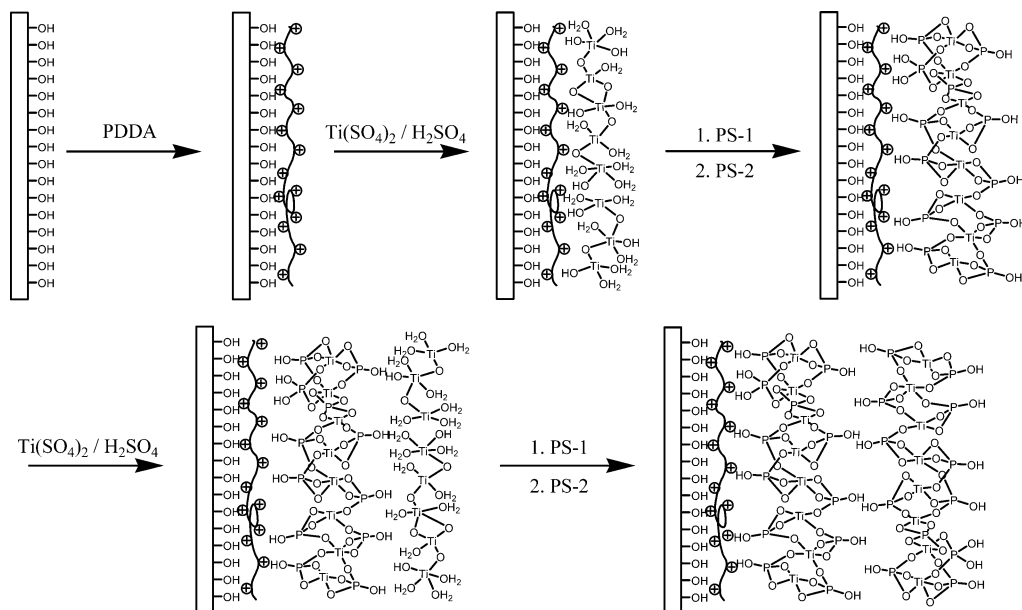
Solution-based film preparative techniques represent a simple and inexpensive alternative to vapor deposition techniques because no elaborated equipment is required.<sup>2</sup> Meanwhile, solution-based film preparative techniques are in general suitable for film fabrication on nonplanar surfaces.<sup>3</sup> There are several solution-based strategies for preparing uniform inorganic ultrathin films, for example, dip coating, chemical bath deposition, liquid-phase deposition, and so on, depending on the category standards used.<sup>4</sup> Among them, two essential solution-based film preparative methods for inorganic film fabrication, which work in a layer-by-layer

fashion, are worthy to mention. The first method is surface sol–gel process which was originally developed by Kunitake and Ichinose for the preparation of metal oxide ultrathin films.<sup>5</sup> The surface sol–gel process to the preparation of ultrathin metal oxide films involves the sequential chemisorption of metal alkoxides and their hydrolysis. To date, surface sol–gel process has been successfully applied to the fabrication of Ti, Zr, Al, B, and Hf oxides on planar and nonplanar surfaces.<sup>1,5,6</sup> The second method is successive ionic layer adsorption and reaction (SILAR) process, which was developed by Nicolau for the preparation of sulfide thin films in the mid 1980s.<sup>7</sup> SILAR process combines the advantages of chemical bath deposition (CBD) and atomic layer deposition (ALD) in which the film preparation involves sequential introduction of precursors because of separated aqueous solutions used. As a result, SILAR avoids precipitation that occurred in CBD. In the past few decades, the SILAR method has been successfully used for film preparation of II–VI semiconducting materials such as ZnS, CdS, PbS, CuS, and  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ , as well as their combinations:  $\text{Zn}_{1-x}\text{Cd}_x\text{S}:\text{In}$  and  $\text{ZnS}:\text{Mn}$ .<sup>4,8</sup> The growth of various oxide films has also been demonstrated.<sup>4,9</sup>

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**Figure 1.** Schematic illustration of the stepwise growth of titanium phosphate ultrathin films. For simplicity, a single molecular layer of titanium phosphate is shown for each deposition cycle. A thicker titanium phosphate layer can be deposited per deposition cycle depending on the film growth conditions.

Inorganic phosphorus-containing materials have received much attention during the past decade.<sup>10,11</sup> Among these materials, titanium and zirconium phosphates were given special attention.<sup>11</sup> Titanium phosphates have been extensively studied with respect to their potential applications in areas such as ion exchange, intercalation, proton conduction, catalysis, electronics, optoelectronics, and so forth. Although layered,<sup>12</sup> open-framework,<sup>13</sup> and mesoporous<sup>14</sup> titanium phosphate has been successfully synthesized, they are usually in the form of powder. As a result, there are very few reports on the preparation of titanium phosphate ultrathin films. It is believed that the titanium phosphate in the form of ultrathin film will facilitate its applications because of its easy handling and integration with other functional materials. Very recently, Kuo et al. reported the preparation of amorphous titanium phosphate by low-pressure chemical vapor deposition using a mixture of titanium tetrachloride ( $\text{TiCl}_4$ ) and trimethyl phosphate ( $\text{P}(\text{O}-\text{CH}_3)_3$ ).<sup>15</sup> The use of chemical vapor deposition equipment makes the film preparation process complex. Therefore, a facile way to prepare ultrathin film of titanium phosphate (and other kinds of metal phosphates) is highly required.

In this paper, as an extension of SILAR method and surface sol-gel process, we developed a layer-by-layer adsorption and reaction method for the preparation of titanium phosphate ultrathin films. We demonstrate that amorphous titanium phosphate films can be prepared by repetitive adsorption of a substrate from aqueous  $\text{Ti}(\text{SO}_4)_2$  solution and subsequent reaction in aqueous phosphate salt (PS) solution. The growth of titanium phosphate multilayer films was confirmed by UV-vis spectroscopy, quartz crystal

microbalance (QCM) measurement, FT-IR spectroscopy, and X-ray photoelectron spectroscopy (XPS). Surface morphology was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The tailoring of film thickness and morphology by changing pH of PS and  $\text{Ti}(\text{SO}_4)_2$  solution was studied in detail. The generality of this method to prepare metal phosphate films was further demonstrated by the preparation of zirconium phosphate.

## Experimental Section

**Materials.** Titanium sulfate ( $\text{Ti}(\text{SO}_4)_2$ ), zirconium sulfate ( $\text{Zr}(\text{SO}_4)_2$ ), sodium hydrogen phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ), and sodium dihydrogen phosphate dehydrate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) were of analytical grade and purchased from Beijing Chemical Reagents Company. Poly(diallyldimethylammonium chloride) (PDDA) aqueous solution with a molecular weight of 100 000–200 000 and poly(methacrylic acid) (PMAA) aqueous solution with a molecular weight of ca. 6500 were purchased from Sigma-Aldrich. Deionized water was used in all experiments. The phosphate salt (PS) solution comprises 0.1 M phosphate ( $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ ) with its pH adjusted by the addition of HCl or NaOH.

**Film Preparation.** Quartz and silicon wafers were immersed in slightly boiled piranha solution (3:1 mixture of 98%  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$ ) for 20 min and were rinsed by a copious amount of water. Caution: Piranha solution reacts violently with organic material and should be handled carefully. To avoid the sulfur influence, silicon wafers for X-ray photoelectron spectroscopy (XPS) measurement were immersed in 30%  $\text{H}_2\text{O}_2$  for 1 day to obtain hydroxyl-terminated surface. The cleaned quartz and silicon wafers were immersed in PDDA aqueous solution (1.0 mg/mL) for 20 min to obtain a cationic ammonium-terminated surface and were ready for titanium phosphate multilayer deposition. Ag-coated quartz crystal microbalance (QCM) resonators were sonicated in ethanol and water and were dried by nitrogen gas. Then, they were immersed in an aqueous solution of PDDA to render the surface positively charged, as in the case of quartz and silicon wafers.

A typical procedure for titanium phosphate multilayer preparation by a layer-by-layer adsorption and reaction method is schematically shown in Figure 1 and is described as follows: the ammonium-

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terminated substrates were immersed in an aqueous solution of 10 mM  $\text{Ti}(\text{SO}_4)_2$  dissolved in 0.1 M  $\text{H}_2\text{SO}_4$  (pH = 0.95) for 5 min. Then, the substrate was transferred to the first PS solution (noted as PS-1, pH = 4.0) for a few seconds, followed by immersing the substrate into the second PS solution (noted as PS-2, pH = 4.0) for 5 min. Finally, the substrate was dried with  $\text{N}_2$  flush. In this way, one layer of titanium phosphate was deposited on the substrate. Multilayer films of titanium phosphate could be prepared by repeating the above processes. By replacing  $\text{Ti}(\text{SO}_4)_2$  solution with  $\text{Zr}(\text{SO}_4)_2$  solution, zirconium phosphate ultrathin films could be prepared in the same way for titanium phosphate films.

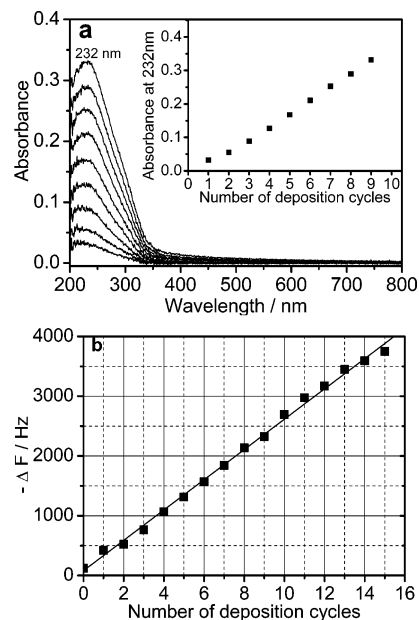
**Preparation of Titanium Phosphate Powder.** The titanium phosphate powder was prepared by adding 60 mg of  $\text{Ti}(\text{SO}_4)_2$  into 10 mL of 0.1 M PS solution (pH 4.0) under sonication ( $\text{PO}_4^{3-}:\text{Ti}^{4+} = 4:1$ ). Immediately, a white precipitate appeared. The sonication was continued for 30 min to make the reaction complete. Finally, the precipitate was separated by centrifugation, rinsed with copious water, and dried in an oven at 50 °C for 30 min.

**Characterization.** UV-vis absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. QCM measurements were taken with a KSV QCM-Z500 using quartz resonators with both sides coated with Ag ( $F_0 = 9$  MHz). Fourier transform infrared (FT-IR) spectra were collected on a Bruker IFS 66V instrument equipped with an MCT detector. Pellets of the titanium phosphate powder mixed with KBr and titanium phosphate films deposited on silicon wafer were used. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB Mark II (VG Company, U.K.) photoelectron spectrometer using a monochromatic Mg  $K\alpha$  X-ray source. Atomic force microscopy (AFM) images were taken with a Nanoscope IIIa AFM Multimode (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers. Scanning electron microscopy (SEM) observations were carried out on an XL30 ESEM FEG scanning electron microscope.

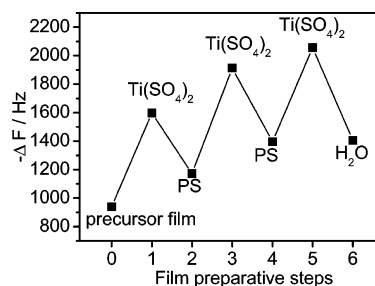
## Results and Discussion

### Preparation of Titanium Phosphate Ultrathin Films.

$\text{Ti}(\text{SO}_4)_2$  hydrolyzes easily to  $\text{TiO}_2$  precipitates in neutral and basic aqueous solutions. Aqueous  $\text{Ti}(\text{SO}_4)_2$  solution with the addition of 0.1 M  $\text{H}_2\text{SO}_4$  (with a pH of 0.95) can be stable without the formation of  $\text{TiO}_2$  precipitates for at least one month in a sealed vessel under ambient conditions. In an aqueous solution of  $\text{Ti}(\text{SO}_4)_2$ , several kinds of hydrated titanium ions exist, which can polymerize into titanium oxide chains with different lengths depending on the pH and concentration of the solution (for simplicity, we called them hydrated titanium).<sup>16,17</sup> If not stated, aqueous  $\text{Ti}(\text{SO}_4)_2$  solution with the addition of 0.1 M  $\text{H}_2\text{SO}_4$  and 0.1 M PS solution with pH of 4.0 adjusted with HCl were used as the dipping solutions for the preparation of titanium phosphate films. To enhance the adherence of the first layer of titanium phosphate film to the substrate surface, a substrate covered with PDDA was employed. Because of the desorption of the hydrated titanium layer during the immersion in PS solution, two separated PS solutions were adopted to avoid the contamination of the PS solution and to guarantee a uniform deposition process of titanium phosphate films. UV-vis spectroscopy and QCM measurements were employed to monitor the fabrication process of titanium



**Figure 2.** (a) UV-vis absorption spectra of titanium phosphate films with different layers. The number of layers is 1–9 from the bottom to the top. The inset shows the absorbance at 232 nm vs the number of titanium phosphate layers. (b) QCM frequency decrease ( $-\Delta F$ ) of successive growth of titanium phosphate films.



**Figure 3.** Stepwise monitor of the layer-by-layer adsorption and reaction process of titanium phosphate films by QCM measurements. A precursor film of three-layer titanium phosphate film deposited on Ag-covered quartz resonator was used.

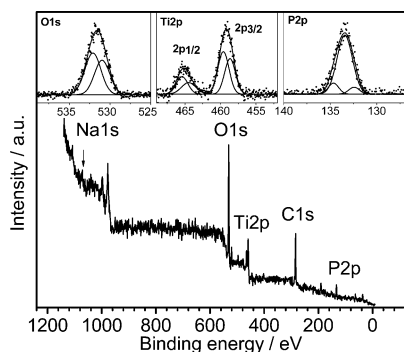
phosphate films. UV-vis absorption spectra of different layers of titanium phosphate films are shown in Figure 2a. All spectra have an absorption peak near 232 nm with a threshold at 343 nm, which are the typical spectral characteristics of titanium phosphate film material. The absorbance at 232 nm increases linearly with the increase of the number of titanium phosphate film deposition cycles, indicating a satisfactory deposition process with an almost equal amount of titanium phosphate deposited in each layer. As shown in Figure 2b, QCM frequency regularly decreases because of the successive deposition of titanium phosphate layers on the resonator. The frequency decrease for one layer of titanium phosphate deposition was  $253.5 \pm 3.8$  Hz.

The formation of the titanium phosphate, rather than  $\text{TiO}_2$  multilayer film, was first clarified by QCM measurements. As shown in Figure 3, when a Ag-coated QCM resonator covered with a precursor film of three layers of titanium phosphate was immersed into an aqueous solution of  $\text{Ti}(\text{SO}_4)_2$  for 5 min and dried directly without water rinse (steps 1 and 3), a frequency decrease of 699.4 Hz was detected. Then, the resonator was immersed in PS-1 and PS-2 solutions for 5 s and 5 min, respectively, followed by  $\text{N}_2$

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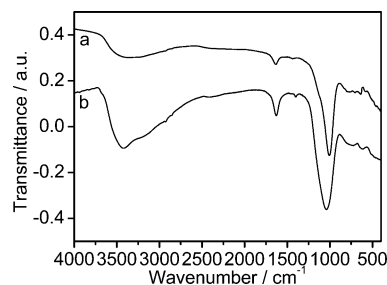




**Figure 4.** XPS spectra of an as-prepared six-layer titanium phosphate film.

drying (steps 2 and 4). A frequency increase of 471.1 Hz was obtained, indicating that part of the adsorbed hydrated titanium could be removed. A net frequency decrease of 228.30 Hz was finally obtained for one cycle of adsorption and reaction. This result is consistent with that in Figure 2b. As a comparison, when the substrate was immersed into  $\text{Ti}(\text{SO}_4)_2$  solution for 5 min and then transferred directly into deionized water for 5 min (steps 5 and 6), a net frequency decrease of 9.4 Hz was obtained after drying the resonator, indicating that almost all of the adsorbed titanium species was removed in water if no immersion in PS solution was applied. These results validate the hypothesis that hydrated titanium adsorbed on substrate surface reacts with phosphate to form an insoluble layer of titanium phosphate. When the substrate covered with hydrated titanium was immersed into PS solution, an interfacial reaction took place to form a layer of amorphous titanium phosphate.<sup>18</sup> The P–OH groups on the titanium phosphate layer ensure the adsorption of the next layer of hydrated titanium. Therefore, multilayer films of titanium phosphate can be fabricated, as shown in Figure 1. The deposition of hydrated titanium on the previous titanium phosphate layer is possibly based on coordination bonding and electrostatic interaction between P–OH and hydrated titanium. The removal of hydrated titanium in water in Figure 3 indicates that these interactions are quite weak. Both UV–vis spectra and QCM measurement show that 5 min is long enough for the adsorption of hydrated titanium and the subsequent reaction with PS. Therefore, 5-min immersion in aqueous  $\text{Ti}(\text{SO}_4)_2$  solution and 5-min reaction in the second PS solution was used for the preparation of titanium phosphate films.

**Chemical Composition of the Titanium Phosphate Films.** The surface chemical composition of the as-prepared titanium phosphate multilayer films was determined by XPS spectroscopy. The XPS spectra of a six-layer titanium phosphate film are shown in Figure 4. No peak for Si 2p was detected, indicating a thick and fully covered titanium phosphate film prepared. The absence of sulfuric element in XPS spectrum indicates that no  $\text{SO}_4^{2-}$  was incorporated in the film. Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> are present at binding energies of 465.3 and 459.2 eV, respectively. The Ti 2p<sub>3/2</sub> can be deconvoluted to two peaks at 458.7 and 459.6 eV with an atomic ratio of about 45 to 55. The first Ti ions are in an octahedral environment, and the second Ti ions are in a tetrahedral environment.<sup>18</sup> P 2p consists of three peaks at



**Figure 5.** FT-IR spectra of as-prepared titanium phosphate film (a) and titanium phosphate powder (b).

132.4, 133.4, and 134.7 eV, which corresponds to binding energies for  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ , and  $\text{H}_2\text{PO}_4^-$ , respectively.<sup>19</sup> The atomic ratio of  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ , and  $\text{H}_2\text{PO}_4^-$  is calculated to be 7:83:10. Therefore,  $\text{HPO}_4^{2-}$  is the main phosphoric element presented in the film. An unsymmetrical O 1s signal peak at 531.6 eV was observed, which can be deconvoluted to two peaks at 531.0 and 532.1 eV. The peak at 531.0 eV is the main assignment of O in Ti–O–P and P=O, while the other peak at 532.1 eV corresponds to O in P–O–H.<sup>20</sup> The fact that O 1s of  $\text{TiO}_2$  peaks at 530.1 eV was not detected in XPS measurement indicates that no Ti–O–Ti existed in the film.<sup>20</sup> The elemental ratio of Ti:P is 1:2.20 for the as-prepared titanium phosphate film. The XPS data support that the composition of the film is mainly  $\text{Ti}(\text{HPO}_4)_2$ , although free phosphate groups might be present in the film.

FT-IR spectrum of the as-prepared titanium phosphate film deposited on silicon wafer is given in Figure 5 (curve a). As a comparison, FT-IR spectrum of titanium phosphate powder prepared using the same solutions as for the preparation of titanium phosphate film is also given (Figure 5, curve b). The FT-IR spectrum of the film is exactly the same as that of its powder except for the wavelength number that is lower than  $660\text{ cm}^{-1}$ , which is caused by the poor transmittance of silicon wafer. It is believed that the broad peak at  $\sim 3400\text{ cm}^{-1}$  and the one at  $1635\text{ cm}^{-1}$  correspond to the surface-adsorbed water and hydroxyl groups.<sup>21</sup> A broad peak at  $885\text{--}1280\text{ cm}^{-1}$  is observed for titanium phosphate film. The peaks in this range are often the characteristic frequencies of antisymmetric/symmetric stretching frequencies of P–O and P–OH groups.<sup>22</sup> The very weak peak of phosphoryl (P=O) at  $1300\text{--}1400\text{ cm}^{-1}$  indicates that a little amount of free  $\text{PO}_4^{3-}$  is present in the titanium phosphate film, which is in agreement with the result of the XPS measurement.<sup>23</sup> As a comparison, the intensity of phosphoryl peak in titanium phosphate powder is relatively stronger than that in the film. As no distinctive peak at  $850\text{ cm}^{-1}$  was observed, which corresponds to the Ti–O–Ti stretching vibration of Ti ions, one can conclude that Ti ions are separated by phosphate.<sup>23,24</sup>

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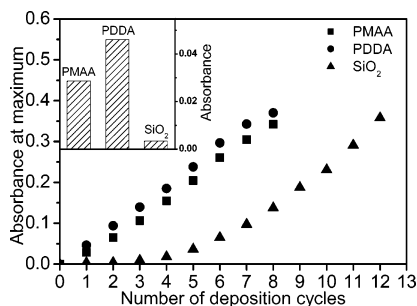
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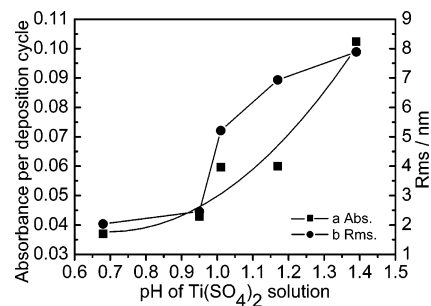


**Figure 6.** Maximum absorbance of the titanium phosphate films as a function of the number of layers deposited on PDDA-modified (●, absorbance at 230.5 nm) (a), PMAA-modified (■, absorbance at 229.5 nm) (b), and bare (▲, absorbance at 225 nm) (c) quartz substrates. The inset column shows the maximum absorbance of the first layer of titanium phosphate on these three substrates.

It was known that the P–O–P deformation vibration can produce a peak at about  $750\text{ cm}^{-1}$ .<sup>23–25</sup> The absence of this peak suggests that P–O–P is absent in the titanium phosphate film and powder. Therefore, we conclude that the FT-IR spectra support a Ti–O–P structure in the titanium phosphate film and powder. From the information given by XPS and IR spectra, we speculate that titanium phosphate film is mainly composed of  $\text{Ti}(\text{HPO}_4)_2$  in which free  $\text{PO}_4^{3-}$  is also incorporated. The titanium phosphate prepared in this way is amorphous because no diffraction patterns of crystallized titanium phosphate are observed in the X-ray diffraction spectra.

**Influence of Substrate Modification on Titanium Phosphate Deposition.** It is necessary to investigate on what kind of surface titanium phosphate can be deposited by this method. Three kinds of surfaces investigated are bare quartz, cationic PDDA-modified quartz, and anionic PMAA-modified quartz. Bare quartz wafer was treated with piranha solution to render its surface hydroxyl groups. The PDDA-modified quartz slide was achieved by immersing the piranha solution-treated quartz in 1 mg/mL PDDA aqueous solution for 20 min. A subsequent immersion of the PDDA-modified substrate in 1 mg/mL PMAA aqueous solution for 20 min can get the PMAA-modified substrate. The deposition process of titanium phosphate films on these three substrates was investigated by UV–vis spectroscopy. As shown in Figure 6, in all cases, the linear deposition process with the same slope was found except for the first several layers of titanium phosphate deposited on bare quartz wafer. The same slope indicates that the amount of titanium phosphate deposited per deposition cycle is equal for these three substrates, while the beginning several layers reflect the influence of the surfaces. The column figure in the inset is indicative of the amount of titanium phosphate deposited in the first layer. One can see that PDDA-modified quartz gets the maximum amount of titanium phosphate while the bare quartz gets the minimum.

The amount of titanium phosphate deposited is supposed to be determined by the amount of hydrated titanium strongly adsorbed on the substrate surface. With more hydrated titanium strongly adsorbed, more titanium phosphate can be obtained after reaction in PS solutions. Hydrated titanium

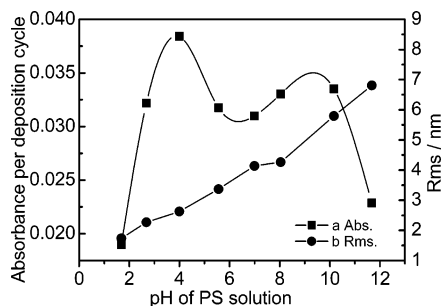


**Figure 7.** The amount of titanium phosphate deposited per deposition cycle (a) and the rms of the as-prepared titanium phosphate film (b) as a function of pH of aqueous  $\text{Ti}(\text{SO}_4)_2$ . The concentration of  $\text{Ti}(\text{SO}_4)_2$  is 10 mM. The pH of PS solution is 4.0.

in an acidic aqueous solution is positively charged. Physic-sorption is the main driving force for the adsorption of hydrated titanium on PDDA-modified surface. Carboxylic acid groups in PMAA coordinate with titanium, and coordination interaction is the main driving force for adsorption of hydrated titanium on PMAA-modified surface. The adsorption of hydrated titanium on PDDA- and PMAA-modified surfaces is strong. Therefore, the amount of hydrated titanium deposited is large. Because the  $\text{pK}_a$  of surface silanols is about 7,<sup>26</sup> the surface of bare quartz is positively charged when immersed in aqueous  $\text{Ti}(\text{SO}_4)_2$  solution (with a pH of 0.95). The adsorption of hydrated titanium on bare quartz surface is based on the coordination interaction of hydrated titanium with surface Si–OH groups, which is weak and a small amount of titanium phosphate can be deposited. The already deposited titanium phosphate layers can facilitate the subsequent adsorption of hydrated titanium, and gradually a linear deposition process was reached on bare quartz wafer.

**Fine Tailoring Film Deposition Process.** The properties of aqueous titanium salts are pH dependent, which will produce an influence on titanium phosphate film preparation. The amount of titanium phosphate deposited per deposition cycle and the surface root mean roughness (rms) of the as-prepared titanium phosphate films were investigated along with changing the pH of the PS and  $\text{Ti}(\text{SO}_4)_2$  solutions.

The amount of titanium phosphate deposited per deposition cycle was measured by UV–vis absorption spectroscopy and was averaged by eight cycles of titanium phosphate deposition. Figure 7 (curve a) shows the influence of pH of  $\text{Ti}(\text{SO}_4)_2$  solution upon the amount of titanium phosphate deposited. With the increase of pH from 0.68 to 1.39, the amount of titanium phosphate deposited per deposition cycle increases. In 10 mM  $\text{Ti}(\text{SO}_4)_2$  with the addition of  $\text{H}_2\text{SO}_4$ , hydrated titanium ions polymerize to form soluble hydrated titanium oxide chains. The polymerization is pH dependent. With the increase of pH, hydrated titanium oxides with longer chains form in solution,<sup>16,17</sup> which in turn leads to a larger amount of hydrated titanium deposition. Therefore, with the increase of pH of  $\text{Ti}(\text{SO}_4)_2$  solution, a greater amount of titanium phosphate is deposited after the subsequent reaction with PS solution. Because of the increased amount of titanium phosphate deposited per deposition cycle with the increase



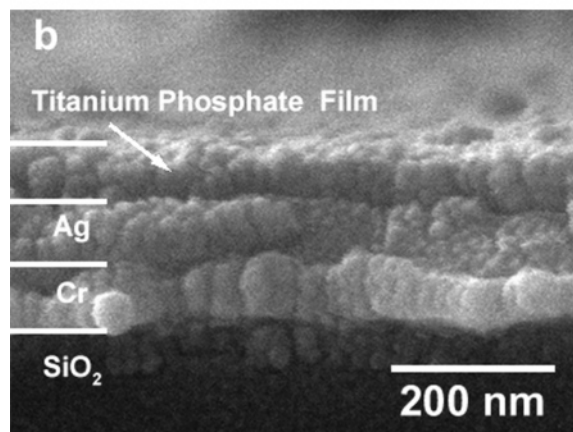
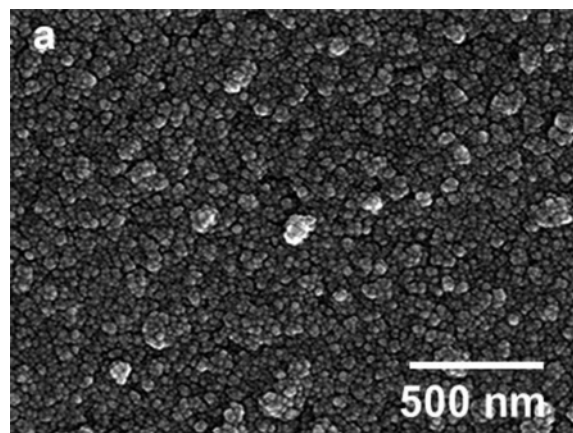
**Figure 8.** The amount of titanium phosphate deposited per deposition cycle (a) and the rms of the as-prepared titanium phosphate film (b) as a function of pH of PS solution. The concentration of  $\text{Ti}(\text{SO}_4)_2$  is 10 mM with a pH of 0.95 adjusted by addition of  $\text{H}_2\text{SO}_4$ .

of pH of  $\text{Ti}(\text{SO}_4)_2$  solution, the rms of the as-prepared film also increases, as shown in Figure 7 (curve b).

Figure 8 (curve a) shows the amount of titanium phosphate deposited per deposition cycle along with the change of pH of PS solution. With the pH of PS solution increasing from 1.68 to 11.68, the average amount of titanium phosphate deposited per deposition cycle exhibits a saddle-backed curve with one peak at  $\text{pH} \sim 4.0$  and another subpeak at  $\text{pH} \sim 9.0$ . The maximum absorbance occurred at  $\text{pH} 4.0$  with a value of 0.038 while the minimum absorbance at  $\text{pH} 1.68$  with a value of 0.019. The amount of hydrated titanium adsorbed on the substrate is the same for all samples because of the same aqueous  $\text{Ti}(\text{SO}_4)_2$  solution used. When the substrate with a layer of hydrated titanium is immersed into PS solution, two processes proceed which compete with each other. One is the desorption of hydrated titanium from the solid substrate because the hydrated titanium is loosely bound to the substrate surface, as evidenced by the removal of hydrated titanium in deionized water. The other is the reaction of hydrated titanium with PS to form insoluble titanium phosphate layer. The desorption of hydrated titanium is pH dependent. In the pH range of 1–4, the solubility of hydrated titanium decreases with the increase of pH in water.<sup>27,28</sup> Therefore, solubility of hydrated titanium is the dominant factor which governs the amount of titanium phosphate deposited. When the pH of PS solution exceeds 10, the solubility of hydrated titanium increases with the increase of pH.<sup>27,28</sup> This fact explains that the amount of titanium phosphate deposited per deposition cycle decreases with the increase of pH between 10 and 12.

Further investigation is required to fully understand the deposition process of titanium phosphate between pH 4 and 10. At present, we think that the deposition process might be co-controlled by the reaction rate of hydrated titanium with phosphate groups and solubility of hydrated titanium. The slower the reaction takes place, the thinner the film can be prepared. As shown in Figure 8 (curve b), irrelevant to the amount of titanium phosphate deposited per deposition cycle, the rms of the as-prepared films increases with the increase of pH of PS solution.

**Structural Characterization of Titanium Phosphate Films.** The surface morphology of the titanium phosphate



**Figure 9.** Surface SEM (a) and cross-sectional SEM (b) images of the as-prepared titanium phosphate films deposited on Ag-coated quartz crystal resonator.

film was investigated by SEM. Figure 9 a and b shows the surface SEM and cross-sectional SEM images of a 15-layer titanium phosphate film deposited on a Ag-coated QCM resonator. As can be seen from Figure 9a, the surface of titanium phosphate film is uniform. The film comprises tiny particles with an average diameter of  $22.1 \pm 3.8$  nm. The film has a constant thickness of about  $54.1 \pm 7.2$  nm, corresponding to a thickness of  $3.6 \pm 0.5$  nm for one titanium phosphate layer. The film deposited on the double sides of QCM resonator gave a total frequency decrease of 3750.4 Hz. The density of the film can be calculated by using eq 1:<sup>29</sup>

$$\rho \text{ (g/cm}^3\text{)} = -\frac{\Delta F \text{ (Hz)}}{2 \times 18.32d \text{ (nm)}} \quad (1)$$

Herein,  $\rho$  is the density of the titanium phosphate film,  $\Delta F$  is the frequency shift of QCM, and  $d$  is the thickness of the film measured by SEM. The film density of titanium phosphate film is  $1.89 \pm 0.25$  g/cm<sup>3</sup>. This value means the as-prepared titanium phosphate film has a porous structure, as can also be recognized from the SEM image shown in Figure 9a. The thickness of titanium phosphate film can be well controlled by changing the pH of  $\text{Ti}(\text{SO}_4)_2$  and PS solution used. Combined with the data shown in Figures 7 and 8, one can calculate that the thickness of one layer of

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titanium phosphate can be tailored between 1.8 and 9.6 nm if the variation in film density is neglected. Meanwhile, we found that by replacing the PS-1 solution with 0.1 M  $\text{H}_2\text{SO}_4$  in a typical preparative process, a smoother titanium phosphate film with rms of  $\sim 0.8$  nm and layer thickness of  $\sim 0.8$  nm per deposition cycle can be obtained. Importantly, the as-prepared titanium phosphate films are mechanically stable in solvents such as water, acetone, and carbon tetrachloride under sonication.

**Extension of the Layer-by-Layer Adsorption and Reaction Method to the Preparation of Zirconium Phosphate Films.** The above-developed method to prepare titanium phosphate ultrathin films was applied to the preparation of zirconium phosphate films to examine its generality to prepare other kinds of phosphate inorganic films. By using 10 mM  $\text{Zr}(\text{SO}_4)_2$  with the addition of 0.1 M  $\text{H}_2\text{SO}_4$  (with a pH of 0.85) and 0.1 M PS solution (with a pH of 4.0), zirconium phosphate ultrathin films were successfully prepared in the same way as for titanium phosphate films. The preparative process of zirconium phosphate films on a Ag-coated QCM resonator was monitored by QCM measurements. QCM frequency linearly decreases with the increase of number of deposition cycles, indicating a regular deposition process of zirconium phosphate films. The average frequency change for one layer of zirconium phosphate is  $214.7 \pm 16.9$  Hz. XPS spectrum confirms that the as-prepared zirconium phosphate film is mainly composed of  $\text{Zr}(\text{HPO}_4)_2$ . The SEM image of the as-prepared zirconium phosphate film shows the film comprises tiny particles with an average diameter of  $32.7 \pm 5.3$  nm. The average thickness for one layer of zirconium phosphate is about 4.3 nm, as determined by the cross-sectional SEM image of a 10-layer zirconium phosphate film (with a total thickness of  $43.3 \pm 9.1$  nm).

### Conclusions

It is established from the present results that the layer-by-layer adsorption and reaction method enables solution-based preparation of amorphous titanium phosphate films

with nanometer scale control of film thickness. The regular film growth is achieved by repetitive adsorption of hydrated titanium and subsequent reaction with phosphate groups. The as-prepared titanium phosphate films are uniform, highly stable, and their thickness can be controlled by adjusting the number of adsorption–reaction cycles and pH value of  $\text{Ti}(\text{SO}_4)_2$  and phosphate salt solutions. Titanium phosphate films can be, in principle, deposited on surfaces with complicated morphologies. The film preparative process is simple and no elaborate equipment is required. The flexible preparative method enables the introduction of secondary elements into the phosphate films, which will enrich the functionalities of the resultant films. Another important feature of the layer-by-layer adsorption–reaction method is its generality to prepare various kinds of metal phosphate films. Zirconium phosphate films were successfully prepared by repetitive adsorption in aqueous  $\text{Zr}(\text{SO}_4)_2$  and subsequent reaction in phosphate salt solution. The preparation of other kinds of phosphate inorganic thin films by this method is also under investigation. These films will find applications as optical films, ion exchanger, catalytic materials, and so on.

**Acknowledgment.** This work is supported by National Natural Science Foundation of China (NSFC Grant No. 20304004), Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (FANEDD Grant No. 200323), and Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT Grant No. IRT0422). The very helpful comments from reviewer #65 are greatly acknowledged.

**Supporting Information Available:** AFM image of as-prepared titanium phosphate films prepared by replacing PS-1 solution with 0.1 M  $\text{H}_2\text{SO}_4$ , QCM frequency decrease ( $-\Delta F$ ) of successive growth of zirconium phosphate films, XPS spectra of as-prepared zirconium phosphate film, and SEM image of the as-prepared zirconium phosphate films deposited on Ag-coated quartz crystal resonator. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

CM050646W