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Direct Synthesis of Anatase Films with ~100% (001) Facets and [001] Preferred Orientation

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Abstract

Anatase films exhibiting ~100% (001) reactive facets at the surface were grown hydrothermally on gold substrate from a homogeneous solution of TiF_4 and NaF. In addition to NaF, it was found that TiO_2 films with very similar properties could be prepared with the fluoride salts LiF, CsF, HF, NH_4F , and $\text{N}(\text{CH}_2\text{CH}_3)_4\text{F}$. The polycrystalline anatase films are continuous, approximately 1 μm thick, and evenly coat the substrate. The surface grain size is ~400 nm. Grazing angle XRD measurements show that the films exhibit a high degree of preferred orientation with the c-axis normal to the substrate surface. SEM images reveal that the grains span the thickness of the films. Annealing the films at 500 °C removes fluorine and causes crystallites within the grains to restructure as shown by SEM, XRD, and Raman spectroscopy. Supported anatase films grown from this one-pot method may serve as oxidative photocatalysts and electrodes for photoelectrochemical applications such as solar cells and hydrogen evolution.

Keywords

TiO_2 ; anatase; (001); preferred orientation; Raman; fluoride

Introduction

Anatase TiO_2 is one of the most versatile semiconducting transition metal oxides. It is straightforward to prepare by solution or vapor phase methods and the band gap of 3.2 eV enables a wide range of photochemical applications.^{1,2} For example, anatase decontaminates air and water photocatalytically under illumination with ultraviolet light.³ Dye-sensitized solar cells rely on films of sintered anatase nanoparticles to serve as the host for the light-harvesting dyes and the electron transport layer.^{1,2,4,5} For these and other emerging applications such as hydrogen evolution and lithium ion electrodes,⁶ performance depends critically on the mineral phase (anatase or rutile), particle size, and morphology.^{1,2,7} Advances in crystal engineering facilitate the fabrication of particles and films tailored with specific properties. In this work, we exploit the recognized role of fluoride in directing anatase crystal growth to synthesize supported films exhibiting a dominant polycrystalline {001} surface and a strong c-axis preferred orientation.

The computational and experimental study by Yang et al.⁸ was a seminal paper in which it was demonstrated that fluorine influences the anatase crystal morphology during growth. Fluorine binds to the {101} and {001} facets but lowers the surface energy of the minority

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Supporting Information. Supplemental SEM, XRD, and Raman data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

{001} surface relative to {101}.⁸ Thus, the crystal grows isotropically along the [100] and [010] zone axes leading to highly truncated bipyramid morphologies whose terminal surface is dominated by the {001} facets. In addition to fluoride, alcohols and amines also function as crystallographic controlling agents to promote the formation of truncated bi-pyramid shaped crystals. On the other hand, without F⁻ and at low pH, typical hydrothermal anatase preparations yield high surface area powders in which the particles have an octahedral shape enclosed by {101} facets.^{1,9} Recent theoretical^{10,11} and experimental^{12,13} work suggests that the {001} surface is more photochemically active than the {101} facets. Powders with {001} facets show higher photocatalytic activity compared to Degussa P25, a benchmark TiO₂ material.^{12,13} For applications such as water decontamination, high surface area powders are particularly effective, but this advantage must be balanced against the problem of separating the colloidal particles from the purified effluent. Practical platforms for solar or UV assisted photocatalysis will utilize anatase prepared as films and membranes.

Supported anatase films with a large percentage of {001} facets were prepared on titanium foil using the fluoride route. Polycrystalline films grew on titanium substrate with hydrofluoric acid by heating at 180 °C for 1 to 3 hours.^{14,15} One study used the anatase film to photocatalytically decompose azo dyes,¹⁴ while the other tested the anatase/Ti composite as a photoanode for water oxidation.¹⁵ Both studies reported high activity for their respective applications, which was attributed to the large fraction of exposed {001} facets. A study by Feng et al. showed that hydrolysis of (NH₄)₂TiF₆ at low pH yields sufficient fluoride to direct the growth of anatase nanosheets on fluorine-doped tin oxide substrates.¹⁶ At temperatures 150 °C, this procedure results in films with a more intense (101) diffraction peak indicating some texture compared to the powder pattern. Using a different approach, Wang et al. found that transparent, partially [001]-oriented anatase films could be prepared hydrothermally on functionalized borosilicate slides.¹⁷ The uniform polycrystalline films 100–200 nm thick were synthesized from a solution of TiCl₃, poly(vinylpyrrolidone), and sodium sulfate at 200 °C for three hours. The resulting octahedral shaped crystal grains exhibited a slight truncation along the [001] direction in the presence of ethylene glycol. In addition to solution phase syntheses, vapor deposition results in continuous anatase films. For example, Long et al. used pulsed laser deposition of Ti under 5 Pa of oxygen to prepare ~100% [001]-oriented anatase films on silicon substrates.¹⁸ These c-oriented nanoscale films were prepared using high substrate temperatures (>650 °C) and resulted in continuous films with small irregularly shaped grains (< 100 nm). Other vapor phase methods that resulted in anatase films include reactive pulse magnetron sputtering¹⁹ and plasma enhanced chemical vapor deposition.²⁰ These methods produced very uniform films but without apparent texture. Examination of the SEM and XRD film data obtained from different syntheses reveals an astonishing variety of film morphologies and textures. Despite this gain in understanding, the synthesis of films with specific morphology, texture, grain size and shape, composition, and presumably the optimum properties for a particular application, remains a considerable challenge.

In this paper, we report the results of our work on the fluoride-mediated synthesis of supported anatase films. By comparison to previous work,^{14–20} films prepared on gold substrates from an aqueous solution of TiF₄ and NaF are unique in their {001} surface morphology and extent of preferred orientation, especially for a low temperature hydrothermal synthesis approach. In addition, because HF is toxic and corrosive, we explored alternative sources of fluoride to direct anatase film growth. It was found that NH₄F, N(CH₂CH₃)₄F, LiF, CsF, and HF produced films similar to those obtained using NaF. Films dominated by reactive {001} facets have obvious photocatalytic and photoelectrochemical applications, and may serve as a model system for studying adsorbate and electron transfer processes. The {110} surface of rutile has been characterized extensively with respect to its photochemical processes, but suitable single crystals of

anatase are more difficult to obtain and have hindered comparable studies.²¹ Therefore, this efficient one-pot route to highly oriented anatase films with reactive {001} facets will present new opportunities to study surface dependent phenomena and stimulate advances in environmental and energy related applications.

Experimental

Materials Synthesis

Anatase films were grown on a gold-coated silicon substrate placed vertically in a Teflon liner and immersed in a solution consisting of 50 mM TiF₄ and 25 mM NaF. For every reaction, two substrates were placed in one reactor yielding identical films. The sealed Parr reactor was placed in a furnace and heated at a rate of 0.4°/min. to 120 °C. The reaction mixture was held at temperature for four hours and then cooled to room temperature (0.4°/min.). The pH of the solution before and after synthesis was 1.6 and 1.8, respectively. After washing the resulting film three times with deionized water, the film was dried overnight at 120 °C. One of the two films was annealed at 500 °C for three hours to remove water and fluorine. As-synthesized and annealed films were cleaved along the silicon substrate crystallographic plane by placing a scoring tool at the very edge of the wafer and applying pressure until the substrate split in two.

Gold was a serendipitous choice for the substrate and an outgrowth of our work on hybrid organic-inorganic materials based on self-assembled monolayers.²² To prepare the substrate, prime grade single-side polished p-type silicon (100) wafers were cleaned for 15 minutes in RCA-1 solution, rinsed with copious amounts of deionized water and ethanol, and dried under Ar. The wafers were placed in a bell jar, which was then evacuated, and subjected to a four-hour bakeout period. After the pressure was reduced to 10⁻⁷ torr, a wetting layer of chromium (5–10 nm) was evaporated onto the wafer surface. Then, gold was deposited at a rate of ~10 Å/s to a final thickness of 200 nm.

Anatase powder was synthesized using a modified literature method.⁸ Aqueous stock solutions of TiF₄ (100 mM) and HF (100 mM) were prepared. 5 mL of each solution and 5 mL of deionized water was added to a Teflon liner and placed in a Parr reactor. The mixture was heated at 180 °C for 4 hours. The resulting powder was washed three times with deionized water and dried at 120 °C in air before characterization. All chemicals were purchased from Sigma-Aldrich and used as received without further purification.

Materials Characterization

Powder and grazing angle xray diffraction (gXRD) patterns were acquired with a Bruker D8 Advance diffractometer using Cu(K_α) radiation ($\lambda = 1.5406 \text{ \AA}$) and NaI scintillation detector. The diffractometer was equipped with a Goebel mirror and thin film receiving slit accessories to enable measurements at a grazing angle of 1°. Powder patterns were acquired in the Bragg-Brentano configuration. Diffraction patterns were acquired between 20–80° 2 θ with a data spacing of 0.02 at three seconds per point. Scanning electron microscopy (SEM) was performed with a Carl Zeiss Ultra55 field emission instrument. SEM images were acquired with an Everhart-Thornley or annular secondary electron detector at working distances of 3–5 mm and accelerating energy of 2 keV. An Oxford Instruments INCA 350 energy dispersive xray spectroscopy (EDS) system equipped with an XMax 80 mm² silicon drift detector was used to determine the composition of the as-synthesized and annealed films. An accelerating voltage of 7 keV was used at an analytical working distance of 8.5 mm. Raman spectra were acquired with a WITec alpha 300 R+ confocal system with an excitation wavelength of 532 nm and resolution of 2 cm⁻¹.

Results and Discussion

Figure 1 shows an optical image of the film that grows on a freshly evaporated gold surface in the presence of 50 mM $\text{TiF}_4(\text{aq})$ and 25 mM $\text{NaF}(\text{aq})$ at 120 °C for four hours. The film displays the effects of interference and is mechanically robust withstanding sonication in water for over an hour. The unpolished side of the silicon wafer also appears to support film growth, but the film adheres weakly to this side and readily flakes off with washing, handling, and sonication.

Grazing angle XRD

Figure 2 compares the diffraction pattern of the as-synthesized powder with the gXRD patterns of the film before and after annealing. The powder pattern displays the typical diffraction pattern of anatase (tetragonal, I_4/amd , JCPDS 21-1272). The film gXRD data show that only anatase is formed during the synthesis and is the only phase present after high temperature annealing. The gXRD pattern of the film differs significantly from that of the powder pattern. The most intense peak of the film is the (004) reflection at 37.84° while the most intense peak of the powder is the (101) reflection at 25.32° (2θ). A close inspection of the gXRD pattern of the as-synthesized film reveals that peaks corresponding to Miller indices with small or zero l -index such as the (101), (200), (211), and (220) reflections at 25.32° , 48.01° , 55.03° , and 70.33° , respectively, are absent or weak relative to the powder pattern. The gXRD peaks of the film at 37.80° and 53.86° 2θ corresponding to the Miller indices (004) and (105), respectively, are particularly intense. The gXRD data indicates a strong c -axis preferred orientation, which is confirmed by examination of the SEM images (vide infra).

The crystallographic preferred orientation (CPO) defined in equation 1 can be used to gain a semi-quantitative measure of the extent of (001) ordering of the film.²³ The terms I^X and I^Y refer to the intensity of two peaks from the diffraction pattern of the anatase film that are compared to the corresponding ratio from a reference, in this case the powder pattern. The most intense peaks that are present in both the film (004) and powder (101) patterns have 2θ values of 25.32° and 37.80° , respectively. Using equation 1, the CPO values are calculated to be 0.98 and 0.91 for the anatase film before and after annealing, respectively. That is, the extent of preferred orientation is nearly 100% for the as-synthesized film.

$$CPO(I^X/I^Y) = \frac{(I_{film}^X/I_{film}^Y) - (I_{ref}^X/I_{ref}^Y)}{(I_{film}^X/I_{film}^Y)} \quad \text{Eqn. 1}$$

The annealed film has a slightly lower CPO value of 0.91 due to the increased intensity of the (101) peak relative to (004). In addition, peaks that were weak or absent from the as-synthesized film – (200), (211), (220), (213), and (301) – are more intense after annealing. The gXRD data suggests that annealing introduces some disorder as fluorine and water are lost during annealing. Under conditions of F-depletion, the (101) surface becomes lower in energy than (001). Surface diffusion of atoms at domain boundaries may then lead to the growth of {101} facets at the expense of {001} facets resulting in an increase in the intensity of this and related diffraction peaks. A second possibility that accounts for the increased ‘powder’ character of the annealed film is that some of the initially deposited TiO_2 is amorphous. Heat treatment to 500 °C then converts the amorphous material to anatase, which has a random orientation with respect to the substrate surface. The amorphous TiO_2 , if present in the as-synthesized film, would be difficult to confirm due to the gXRD measurement geometry and the much larger fraction of crystalline material that lies above it.

The Scherrer formula, $D_v = K_\beta \lambda / \beta_S \cos \theta_B$, can be used to predict the volume weighted domain size, D_v , for coherent scattering.²⁴ In this expression, K_β is the Scherrer constant, λ the wavelength, θ_B is the Bragg angle, and β_S is the sample contribution to the integral linewidth in radians. Using the intense (004) peak for which $2\theta = 37.84^\circ$, $\beta_S = 0.261^\circ$ after correcting for instrument line-broadening contribution, and $K_\beta = 1.0$,²⁴ the crystallite size was calculated to be 35 nm before and after annealing. Contrary to our expectation that the crystallites would increase in size,^{25,26} the integral linewidths of all peaks were essentially the same before and after annealing. The domains or crystallites are much smaller than the grains that make up the bulk of the film.

Scanning Electron Microscopy

Figure 3 shows SEM images of the anatase film before and after annealing at 500 °C. The top-down view before annealing reveals the film to be an intergrown network of TiO₂ grains. The polycrystalline surface of the film exhibits crystal grains that are square in shape with rounded corners and an edge length of approximately 400 nm. The square facets are identified as the (001) surface on the basis of the anatase crystal symmetry (tetragonal, I_4/amd) and the strong [001] texture. The top-down view shows that not all of the (001) facets are parallel to the substrate, but their dominant presence at the surface suggests photochemical applications for these highly oriented films.

The film fractured along grain boundaries when the substrate was cleaved to expose the film cross-section revealing important characteristics about the internal structure of the film, Figure 3c. The anatase film is approximately 1.1 μm thick over the length of the substrate. The larger grains reach from the gold to the external surface and are oriented normal to the substrate. The narrow taper of the grains and the number of small particles at the gold interface support a competitive growth mechanism initiated by seeding of the gold surface.²⁷ Fluorine lowers the energy of the (001) surface and promotes isotropic growth along the [100] and [010] directions.⁸ Crystal grains compete for space growing outward along the [001] zone axis away from the gold surface. The grains with a growth direction perpendicular to the substrate surface ultimately dominate the film by growing laterally and longitudinally, thereby truncating grains that grow at more oblique angles.²⁷ The resultant TiO₂ grains acquire a wedge shape that is narrow at the gold substrate and expands toward the surface.

A consequence of this film growth model in which adjacent grains compete for space is that {101} facets have little chance to develop in comparison to studies that prepared isolated crystals.^{2,7} Film cross-sections occasionally reveal a grain that extends above the others (Figure 3c, inset). The angle formed at the intersection of the (001) plane and visible edge is $\sim 97^\circ$ whereas the angle at the intersection of the (001) and (101) planes is calculated to be 111.7° . The edges of the exposed grains represent the crystal growth directions (higher surface energy) and may correspond to (301) facets that intersect the (001) surface to form an angle of 97.6° or possibly {101} facets that are not fully developed. Based on additional observations of grain edges that intersect the surface {001} facets at film cross sections or defect spheres (*vide infra*), {101} facets are not prevalent under our film growth conditions.

High temperature annealing at 500 °C for two hours in air results in a number of changes to the anatase film (Figures 3d–f). Figure 3e reveals that small square or rectangular holes appear in the grain surfaces. In addition, fine cracks at grain boundaries lace the film's surface (Figure 3d). However, surface grain size, texture, and film thickness are virtually identical before and after annealing. The cross-section view (Figure 3f) shows that the film restructured during annealing. As a result, nanoscale voids formed within the grains. Annealing is known to increase the size of nanoscale anatase particles^{25,26} and it is possible

that the crystallites coarsened with temperature. However, grazing angle XRD does not support this hypothesis.

EDS line-scan spectra acquired on the as-synthesized film cross-section show an approximately even distribution of fluorine from the film surface to the substrate. The film composition was estimated to be $\text{Ti}_{1.00}\text{O}_{1.88}\text{F}_{0.23}$ assuming that fluoride partially substitutes for oxygen by coordinating to Ti^{4+} . Additional oxygen (2.9 wt.%) is attributed to water (see Supporting Information Table S1). Infrared spectroscopy shows a broad intense band at 3200 cm^{-1} and weaker band at 1633 cm^{-1} attributable to the stretching and bending vibrational modes of hydroxyl groups (both water and Ti-OH), respectively (Supporting Information, Figure S1). The composition of the film after annealing is $\text{TiO}_{1.84}\text{F}_{0.04}$ with a trace amount of fluorine, which was detected within 100 nm of the external surface. Water and Ti-OH are removed by heat treatment as shown by the IR spectrum. An annealing temperature of $500\text{ }^{\circ}\text{C}$ is sufficient to eliminate fluorine from the film but heating times longer than three hours are required for complete removal. EDS did not detect sodium in the as-synthesized or annealed films.

Our hydrothermal synthesis method results in an oriented polycrystalline anatase film that uniformly coats the surface of the gold substrate. However, the surface is also populated with anatase spheres (Supporting Information, Figure S2) approximately $4\text{ }\mu\text{m}$ in diameter. The spheres are partially intergrown to the surface but most can be removed by sonication in water for several minutes. The crystal grains at the surface of the spheres have the same size and shape as the grains of the film. The cross-sectional view shows that each grain has a wedge shape terminated by a (001) facet. Annealing restructures the grains and introduces voids into the spheres. Other researchers used the fluoride route to prepare anatase particles with a spherical morphology similar to those shown here.^{28,29}

Raman Spectroscopy

Raman spectra of the films before and after annealing are shown in Figure 4. The films exhibit peaks characteristic of the six phonon scattering modes ($A_{1g} + 2B_{1g} + 3E_g$) of crystalline anatase.³⁰ No peaks attributable to rutile are observed. The as-synthesized film exhibits the $E_g(1)$, $E_g(2)$, $B_{1g}(1)$, $B_{1g}(2)+A_{1g}$, and $E_g(3)$ bands at 148, ~192, 400, 510, and 630 cm^{-1} , respectively. The Raman bands of the annealed film were observed at 141, ~196, 393, 515, and 635 cm^{-1} . The $B_{1g}(2)$ and A_{1g} bands differ in resonant frequency by only 6 cm^{-1} and overlap in both spectra.²⁹ The linewidth narrows after annealing by approximately 10 cm^{-1} for all bands (Table S1). The average linewidths before and after annealing are 36.4 cm^{-1} and 26.4 cm^{-1} , respectively, which are larger than bulk anatase, 7 cm^{-1} .³¹

The blueshift and broader width of the Raman bands of the unannealed film may be explained by stoichiometry or nanoscale effects. Anatase and rutile powders with less than the stoichiometric amount of oxygen exhibit broad Raman bands compared to powders annealed at $700\text{ }^{\circ}\text{C}$ under an oxygen atmosphere.^{32–34} Before annealing, fluorine substitutes for oxygen in the as-synthesized anatase film as shown by EDS. Annealing in air removes F and restores the oxygen stoichiometry to TiO_2 resulting in a narrower $E_g(1)$ band with a Gaussian width of 23 cm^{-1} at 141 cm^{-1} . Alternatively, the linewidth and band position may be attributed to nanosize effects – small crystallites within larger grains – that lead to phonon confinement. Characteristic features of phonon confinement observed for the $E_g(1)$ band include a broad red-shifted peak and asymmetric lineshape that is broader on the low-energy side.^{35–37} These spectral characteristics are typically observed for anatase particles $< 10\text{ nm}$ in size. Grazing angle XRD measurements show that $D_V = 35\text{ nm}$ before and after annealing. Therefore, phonon confinement is not the main line-broadening and peak shift mechanism. The $E_g(1)$ peak position after annealing at 141 cm^{-1} is characteristic of crystalline anatase but the width, 23 cm^{-1} , is relatively broad. Although non-stoichiometry

effects contribute significantly to peak broadening of the as-synthesized films, other effects such as structural defects or strain may also contribute to the linewidth of the annealed film.

The anatase spheres were found to have spectra with somewhat different peak intensity ratios (Figures S3 and S4) but the peak positions and linewidths before and after annealing were virtually identical to the films (Table S1). The spheres also exhibited a more intense fluorescent background before annealing similar to the films. The background fluorescence apparently decreases after annealing once fluorine is removed from the film and the oxygen stoichiometry is restored to TiO_2 .

Fluoride Source

One of the objectives of this work was to test various fluoride sources that are comparatively less toxic and corrosive than HF for their ability to direct the growth of anatase films. In addition to NaF, we found that LiF, CsF, NH_4F , $\text{N}(\text{Et})_4\text{F}$, and HF produced anatase films with similar surface morphology. The films were synthesized for four hours at 120 °C with reagent concentrations of 50 mM for TiF_4 and 25 mM in the additional fluoride source. All of the preparations resulted in continuous polycrystalline anatase films. As for NaF, the film surfaces are composed of square grains with a high percentage of (001) facets. Figures that compare SEM and gXRD images of these films are shown in the Supporting Information (Figures S5 and S6). Table 1 compares values for the average grain size at the surface, thickness, and crystallographic preferred orientation of the as-synthesized films. Additional fluoride in the form of HF yields the thickest film 1.14 μm with an average surface grain size of 630 nm, but with the largest variation in edge length, 140 nm. The other cations produce films with smaller average grain size and film thickness. An inspection of the table shows that all of the films exhibit a strong [001] texture relative to the substrate as indicated by CPO values between 0.97–0.99.

Some notable differences in the film surface arise because of the different cations. For example, the anatase film synthesized with CsF as the crystallographic controlling agent is punctuated with voids that extend almost to the gold surface. Interestingly, EDS did not detect cesium in the as-synthesized film despite its apparent effect on the film surface. All of the films had some anatase spheres of approximately the same size on the surface, but the number of defects differed depending on the cation. The films synthesized with tetraethylammonium fluoride, ammonium fluoride, and hydrofluoric acid have fewer spherical defects while those prepared with alkali cations have a much larger number. The similarity of the film characteristics synthesized with different fluoride salts suggests that the positive counter ion plays a relatively minor role in the formation of anatase films.

Summary

The unique feature of the current study is the one-pot synthesis of supported anatase films that exhibit a high degree of c-axis preferred orientation and a surface morphology dominated by {001} facets. Studies that utilize these films for oxidative photocatalysis are in progress. A key feature of these films is that the grains span the film thickness. Photoelectrochemical applications may benefit from this film structure since electron transport may be more efficient compared to sintered powders that have a multitude of grain boundaries. One of the key issues that will be addressed in future work is the influence of the morphology and structure of the films on the conductivity before and after annealing. We have also shown that a number of different fluoride sources (NaF, LiF, CsF, NH_4F , $\text{N}(\text{Et})_4\text{F}$, HF) can be used as crystallographic controlling agents with similar results. Annealing results in changes to the composition and morphology of the films. In addition to loss of fluorine and water, the crystallites within the grains restructure without increasing their apparent size. In order to optimize anatase films for particular applications, we are

exploring the effects of temperature, fluoride concentration, pH, synthesis time and substrate material on the anatase film morphology, texture, and other physical properties.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Photograph of the film 1.1 μm thick grown on a gold substrate. The length of a side is ~ 25 mm.

Figure 2. Comparison of (a) anatase powder prepared using the fluoride route to (b) as-synthesized and (c) annealed (500 °C, 3 hour) films. The peaks marked by '*' are due to the gold substrate. Diffraction patterns are to scale and offset for clarity.

Figure 3. SEM images of the anatase film prepared from TiF_4/NaF aqueous solution at 120 °C for four hours. Top-down views of the films are shown (a,b) before and (d,e) after annealing. Film cross-sections before and after annealing are shown in panels (c) and (f), respectively.

Figure 4. Raman spectra of the anatase film (a) before and (b) after annealing at 500 °C in air. Arrows indicate the ordinate for each spectrum.

Table 1

Comparison of the anatase film thickness, surface grain size, and extent of crystallographic preferred orientation (CPO) as a function of additional fluoride source.

Fluoride Source ^a	Thickness (μm)	Grain size (nm)	CPO value
NaF	1.09	380 (90) ^b	0.968
LiF	0.90	370 (50)	0.988
CsF	0.94	390 (90)	0.984
NH ₄ F	0.83	420 (60)	0.976
N(Et) ₄ F	0.85	370 (80)	0.988
HF	1.14	630 (140)	0.992

^aThe concentrations of TiF₄ and additional fluoride salt were 50 mM and 25 mM, respectively.

^bEstimated error based on more than 10 measurements.