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Oriented growth of thin films of titanium oxyfluoride at the interface of an air/water monolayer

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When a monolayer of dioctadecyldimethylammonium bromide is formed on the surface of mixed aqueous solutions of $(NH_4)_2TiF_6$ and H_3BO_3 with a B/Ti molar ratio below 1.5, oriented crystallites of NH_4TiOF_3 are produced and grown at the hydrophilic interface of the monolayer to yield a self-supporting thin film within a few days.

In recent years, soft solution chemistry has attracted a great deal of attention from the viewpoint of low energy-consuming material processing and morphological control of inorganic materials. In this area, crystalline metal oxides have been synthesized in the liquid phase *via* ligand-exchange (hydrolysis) equilibrium reactions of the corresponding metal fluorides at an ambient temperature.[1,2] For example, the overall reaction (1) for TiO_2 synthesis consists of three equilibrium reactions (2)–(4),[3–5] in which H_3BO_3 acts as an F^- scavenger and forces the equilibrium to shift to the product side. By this liquid-phase deposition (LPD) method, TiO_2 crystalline films are successfully prepared on a substrate at room temperature.[2]

$$[TiF_6]^{2-} + 3/2\,H_3BO_3 + 2H^+ \rightleftharpoons TiO_2 + 3/2\,HBF_4 + 5/2\,H_2O \quad (1)$$

$$[TiF_6]^{2-} + n\,H_2O \rightleftharpoons [TiF_{6-n}(OH)_n]^{2-} + n\,HF \quad (2)$$

$$H_3BO_3 + 4\,HF \rightleftharpoons HBF_4 + 3\,H_2O \quad (3)$$

$$[Ti(OH)_6]^{2-} + 2\,H^+ = TiO_2 + 4\,H_2O \quad (4)$$

So far, we have been investigating inorganic synthesis using (multi)layered organic films as reaction fields and templates.[6–10] On the other hand, Langmuir monolayers have been successfully employed to direct the growth of oriented arrays of inorganic salts and metal sulfides.[11–13] These results motivated the present study to combine the LPD reactions and an air/water monolayer as a template. As reported below, self-supporting thin films of NH_4TiOF_3, which acts as a stable intermediate in LPD synthesis of TiO_2, were produced at the interface of the air/water monolayer, and were dominated by (00*l*) oriented crystallites. The conversion of NH_4TiOF_3 into TiO_2 while retaining the orientation was also suggested.

The LPD solution used for the subphase was a mixed aqueous solution of ammonium hexafluorotitanium [$(NH_4)_2TiF_6$, 0.1 mol dm^{-3}] and boric acid (H_3BO_3, 0.1–0.3 mol dm^{-3}). An air/water monolayer of dioctadecyldimethylammonium bromide (DODMABr) was formed at 298 K on the surface of the LPD solution by spreading a 100 μl portion of a toluene–ethanol solution (9 : 1, v/v) of DODMABr (*ca.* 1 mg cm^{-3}). After evaporating the spreading solvent for 20 min, two-dimensional compression was performed by using a computer-controlled film balance (USI system Co. Ltd., FSD 110). The DODMA monolayer on pure water showed an expanded surface pressure-area (π–A) isotherm characteristic of a liquid phase. On the LPD solution, on the other hand, the monolayer exhibited a condensed π–A isotherm, suggesting that the cationic DODMA monolayer interacts with inorganic ionic species such as TiF_6^{2-} and borate ions.[14] The monolayer-assisted crystal growth was performed at a constant π value of 20 mN m^{-1}, which is in the middle of solidus region of the π–A isotherms. The monolayer of octadecyl alcohol (ODA) was formed in the same manner using a toluene solution of ODA, but the π–A isotherms were almost the same on either pure water or the LPD solution, indicating no interaction between the neutral monolayer and the ionic species. The products were characterized by X-ray diffraction (XRD, Rigaku LINT-2200), scanning electron microscopy (SEM; HITACHI Co. Ltd., S-2250N) and transmission electron microscopy (TEM; JEOL, JEM-2010 UHR) equipped with an energy dispersive X-ray spectrometer (EDX, Oxford Link ISIS).

In the $(NH_4)_2TiF_6/H_3BO_3$ LPD solutions, a white precipitate was produced at room temperature within a few days, and the main products were different below and above the stoichiometry of the overall reaction (1) (B/Ti = 1.5). At B/Ti $\geqslant$ 1.5, the main product was anatase-type TiO_2 [Fig. 1(b)], in agreement with a previous report.[2] The main product at 1 $\leqslant$ B/Ti < 1.5 was NH_4TiOF_3 [Fig. 1(a)],[15] with the oxyfluoride convertable into anatase TiO_2 either by treatment with aqueous H_3BO_3 or by air-calcination at 873 K for 1 h [Fig. 1(c)]. These results indicate that NH_4TiOF_3 is a stable intermediate in the LPD synthesis of TiO_2.

On the surface of LPD solution with B/Ti = 1, no product was formed in the absence of the DODMA monolayer, but pale violet-colored transparent films were formed within a few days in the presence of the monolayer. The floating films thus formed were transferred onto quartz substrates by scooping up or by horizontal dipping. SEM observation showed that the thickness of the film after 3 days was *ca.* 0.5 μm [Fig. 2(a)]; thickness at the sub-micron level was also suggested by the interference UV–VIS absorption spectrum. It is seen that the surface of the film at the air or monolayer side was smooth while that of the solution or crystal-growth side was rough and that morphology

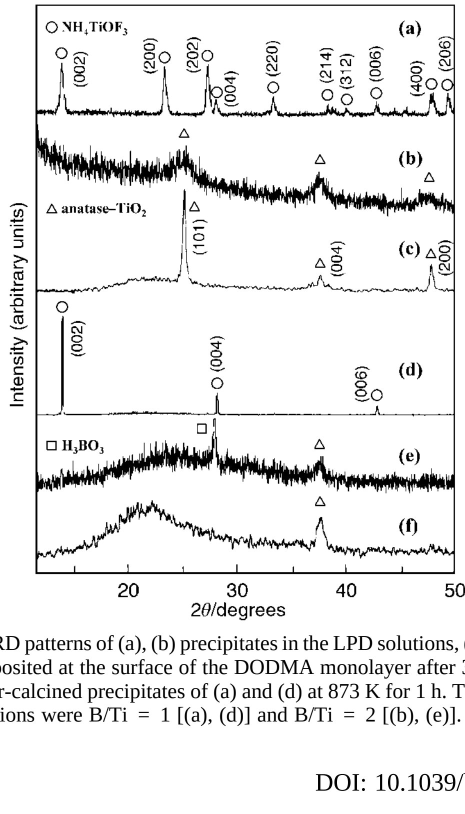

Fig. 1 XRD patterns of (a), (b) precipitates in the LPD solutions, (d), (e) thin films deposited at the surface of the DODMA monolayer after 3 days, and (c), (f) air-calcined precipitates of (a) and (d) at 873 K for 1 h. The solution compositions were B/Ti = 1 [(a), (d)] and B/Ti = 2 [(b), (e)].

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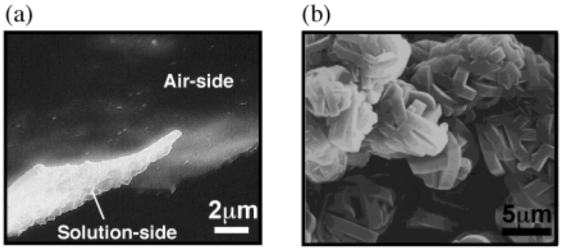

Fig. 2 SEM images of (a) NH_4TiOF_3 film deposited at the surface of DODMA monolayer and (b) NH_4TiOF_3 precipitate in the LPD solution. Solution composition: B/Ti = 1, deposition time: 3 days.

of the film was totally different from that of the precipitate [Fig. 2(b)]. XRD results on the quartz-supported films [Fig. 1(c)] showed that the crystalline product on the surface of solution (B/Ti = 1) was NH_4TiOF_3 *i.e.* the same as the precipitate from the same LPD solution but the NH_4TiOF_3 films was preferentially oriented with the (00*l*) crystal planes parallel to the solution surface.

In the presence of neutral octadecyl alcohol (ODA) monolayer, no crystalline product was observed on the solution surface, consistent with the suggestion from the π–A isotherm measurement that the ODA monolayer scarcely interacts with the ionic species. The result implies that electrostatic interaction between the cationic monolayer and inorganic species is indispensable to form stable and oriented NH_4TiOF_3 films. The importance of the electrostatic interaction was also confirmed by monitoring the deposition of NH_4TiOF_3 from the LPD solution (B/Ti = 1, pH = 4.5) with a QCM microbalance (Sogo Pharmaceutical Co., SF-105A). Here, three types of quartz resonators (AT cut, 9 MHz) with different Au electrodes (area: 0.34 cm^2) were used; bare, derivartized with mercaptoethylsulfonate (MES, anionic surface) and 2-amino-1-ethanethiol (AET, cationic at pH = 4.5). The amount of deposition of NH_4TiOF_3 was almost the same on the bare and anionic MES electrodes, while the amount on the cationic AET surface was much larger than those on the other two electrodes at the same immersion time; for example, deposited amounts on AET and bare electrodes were 300 ng and 50 ng after 2 h and 1100 ng and 200 ng after 6 h, respectively.

The initial stage of precipitate and film formation was studied by TEM and EDX. Products in solution and on the surface were mounted on TEM micro-grids covered with a carbon ultrathin film (Oken Shouji Co. Ltd) by dropping the solution and scooping up, respectively. In the LPD solution with B/Ti = 1, discoid crystallites, *ca*. 400 nm diameter by 150 nm thickness, on average, were observed 1 h after the preparation of the solution. The atomic composition of the crystallites measured by EDX was close to that for NH_4TiOF_3 (Ti : O : F = 1 : 1.2 : 2.8). With increasing time, the crystallites grew, aggregated and eventually precipitated as irregularly shaped particles [Fig. 2(b)]. On the surface of the LPD solution (B/Ti = 1) with the DODMA monolayer, discoid crystallites of NH_4TiOF_3 with nearly the same size as in the solution were present after 1 h the majority being oriented with the circular plane parallel to the monolayer surface [Fig. 3(a)]: smaller crystallites with diameter below 50 nm were also observed. Electron diffraction [Fig. 3(c)] showed each discoid crystallite was a single crystal with the circular plane corresponding to the (00*l*) or *ab* plane of tetragonal NH_4TiOF_3. The amount and size of the crystallites increased at the monolayer surface with increasing time and a continuous thin film composed of nanoparticulates was eventually produced after 12 h [Fig. 3(b)]. With further time, the thickness of the film increased to, for example, 0.45 μm after 3 days and 0.64 μm after 5 days as estimated from the UV–VIS interference. The results clearly indicate that the oriented deposition of NH_4TiOF_3 discoids is a crucial step in the monolayer-assisted formation of oriented NH_4TiOF_3 films. It is also reasonable to propose that in the initial stage the discoid crystallites deposited at the monolayer surface with the *ab* plane preferentially parallel to the surface and act as seeds for the subsequent crystal growth.

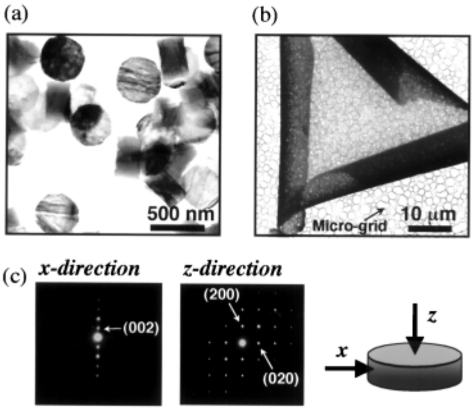

Fig. 3 TEM images of NH_4TiOF_3 crystallites deposited at a DODMA monolayer surface after (a) 1 h and (b) 12 h after the preparation of the monolayer. (c) Electron diffraction patterns of the crystallites of (a). Arrows indicate the direction of electron beam.

Monolayer-assisted LPD synthesis was also investigated for a B-rich LPD solution (B/Ti = 2), from which non-oriented anatase TiO_2 was precipitated [Fig. 1(b)]. The formation of the oriented NH_4TiOF_3 crystallites was observed by TEM electron diffraction measurements in the early stage up to 6 h. After 3 days, however, a weak XRD peak corresponding to the (004) peak of anatase TiO_2 was observed [Fig. 1(e)]. The absence of (101) and (200) peaks which are stronger than the (004) in non-oriented powder anatase indicates the presence of (00*l*) oriented crystallites in the film. In addition, when the (00*l*) oriented NH_4TiOF_3 film prepared from the B/Ti = 1 LPD solution was air-calcined at 873 K for 1 h, only the (004) XRD line of anatase TiO_2 was observed [Fig. 1(f)]: the broad peak around 2θ = 20–25° is due to the quartz substrate. These results suggest the possibility of synthesizing oriented TiO_2 films directly by the monolayer-assisted LPD method on a B rich solution or indirectly by heat-treatment of an oriented NH_4TiOF_3 film. Detailed investigation is in progress with respect to the conversion of NH_4TiOF_3 to TiO_2 with retention of orientation as well as the mechanism of the deposition and growth of oriented crystallites at the monolayer surface.

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15 The XRD pattern of NH_4TiOF_3 has been reported in JCPD 33-82 in the absence of crystallographic data. X-Ray and electron diffraction results in this study tentatively suggest a tetragonal unit cell with a = 0.7573(3) nm and c = 1.2647(6) nm.