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Novel fabrication method for $Si_{1-x}Ti_xO_2$ thin films with graded composition profiles by liquid phase deposition

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A novel technique for the direct synthesis of $Si_{1-x}Ti_xO_2$ thin films with graded composition profiles has been studied in aqueous solution, in which the $(NH_4)_2SiF_6$ solutions were added into the $(NH_4)_2TiF_6$ master solution under time- and rate-controlled reaction conditions: the composition of the films in the direction of the film thickness was successfully controlled over a wide range by this technique.

Materials in which the composition and/or the microstructure vary in one specific direction have recently attracted much interest as functionally graded materials (FGMs).[1,2] Thin films of FGMs are of particular practical interest because the physical and chemical properties of the films can be varied in the direction of film thickness, and thus the films possess exciting possibilities for various electronics and photonics applications. Gradient-type films have also been used as coating materials for improvement of mechanical and thermal properties of the base materials. A wide variety of fabrication methods for thin films of FGMs has been proposed, including physical, chemical and mechanical techniques.[3–5] However, few methods for preparing gradient mixed metal oxide films have yet been developed because the preparation of non-conductive metal oxides is difficult using conventional methods. Although Zhao *et al.* prepared a $Ti_{1-x}V_xO_2$ solid solution using the sol–gel technique,[6] the as-prepared films consisted of multi-layered oxide films with different compositions (stepwise structures) and gradient mixing of the film composition could be achieved only by high temperature post-annealing. A direct deposition technique is thus desirable for the preparation of thin films in which the film composition and structure can be precisely controlled.

Recently, direct deposition using ligand-exchange hydrolysis of a metal-fluoro complex and the F^- consumption reaction with boric acid or aluminium metal (liquid phase deposition process, LPD) has been developed for the preparation of metal oxide thin films, *e.g.*, titanium oxide,[7] silicon oxide,[8,9] vanadium oxide,[10,11] and iron oxyhydroxide films.[12] Using this technique, metal oxide films are coated on various kinds of substrates with complex shapes and large surface areas. Since the film deposition process proceeds through heterogeneous nucleation in an aqueous solution which is a typical homogeneous mixing system, composite films can readily be prepared by using mixed solutions containing objective species (typically metal ions). Thus, it is a promising technique for the direct preparation of multicomponent and/or multilayered metal oxide films.[13,14]

Herein, we describe an experimental study involving a new approach for the direct preparation of gradient-type $Si_{1-x}Ti_xO_2$ thin films by using the LPD method. The films obtained were found to be amorphous and consist of SiO_2–TiO_2 mixed films. We also show that the composition of the films in the direction of film thickness can intentionally be controlled by varying the mixing conditions of the treatment solution. Gradient-type amorphous $Si_{1-x}Ti_xO_2$ films might be suitable for a variety of optical fiber applications and solar cells.[15,16]

In our LPD method, master solutions of the Ti and Si sources were separately prepared by dissolving ammonium hexafluorotitanate ($(NH_4)_2TiF_6$) in distilled water containing boric acid (H_3BO_3) (solution A) and ammonium silicafluoride acid ($(NH_4)_2SiF_6$) containing H_3BO_3 (solution B), respectively, in appropriate proportions.[17] Borosilicate glass and Au wire were used as substrates. For the deposition of gradient-type films of $Si_{1-x}Ti_xO_2$, the substrates were first immersed into solution A kept at 30 °C. After immersion for several hours (pre-treatment time), solution B was added to solution A, and the mixed solution was removed simultaneously in order to maintain the volume of the treatment solution at 500 ml. The addition and subtraction rates were controlled by a fixed flow console pump. The substrates with deposited films were then removed from the solution, washed with distilled water and dried at room temperature. Highly transparent films having sufficient mechanical strength were deposited on the substrates after appropriate reaction times. The microstructure and composition of the deposited films were identified by using a cross-sectional transmission electron microscope (TEM, JEOL JEM-2010) equipped with an X-ray microanalyzer (NORAN Instrument, Inc.). Thin cross sections for TEM observations were prepared by conventional microtome techniques for the samples deposited on Au wires.

In our previous study, a ligand-exchange hydrolysis reaction is suggested to proceed as follows:[7,14]

$$MF_x^{(x-2n)-} + nH_2O \rightleftharpoons MO_n + xF^- + 2nH^+ \qquad (1)$$

This reaction can be shifted to the right-hand side by adding boric acid, which reacts with F^- ions to form more stable complex ions:[18]

$$H_3BO_3 + 4HF \rightleftharpoons BF^{4-} + H_3O^+ + 2H_2O \qquad (2)$$

The addition of the boric acid leads to the consumption of F^- ions and accelerates the ligand-exchange reaction. Thus, thin films are slowly deposited homogeneously on the substrate. In the present study, since the concentration of the treatment solution is gradually varied as a function of time by addition of solution B into solution A, the film composition can be simultaneously changed under controlled conditions. As shown in Fig. 1, cross-sectional transmission electron microscopy of the deposited films confirms that a continuous film with a thickness of *ca.* 80 nm was formed on Au the substrate (sample

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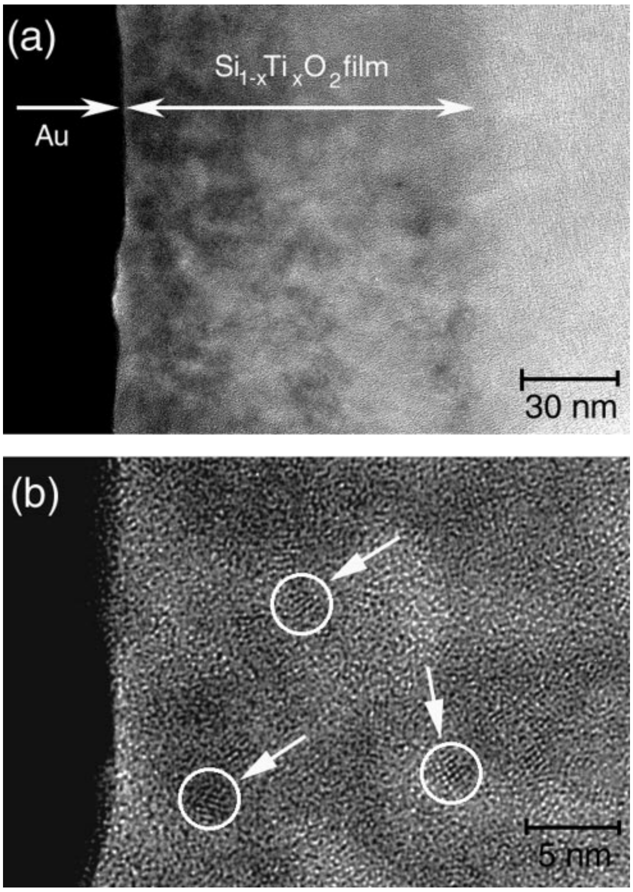

Fig. 1 (a) Cross-sectional TEM image of an $Si_{1-x}Ti_xO_2$ thin film (sample 1) deposited on Au substrates. (b) Enlarged image near the substrate. White circles indicate TiO_2 nanocrystals formed in the film.

1). Its selected area electron diffraction pattern showed a diffuse halo indicating the amorphous structure (not shown here). A slight contrast difference in the direction of the deposited film is seen in the images. High-resolution observation revealed that the lattice fringes due to the nanocrystalline TiO_2 phase (*ca.* 2 nm in size) sometimes appeared near the substrate (Fig. 1b) but the amorphous nature of the film was mostly observed throughout the entire film. The difference in the composition of the film in the direction of the film thickness was discriminated by X-ray microanalysis using a 5 nm electron probe. In Fig. 2(a), the molar fractions of Si and Ti, determined by quantitative analysis, are plotted as a function of the direction of film thickness. The Ti fraction gradually decreases from 0.2 to 0 over the range 0–80 nm in a fashion that parallels the corresponding increase in the Si fraction from 0.8 to 1. In Fig. 2(b) (sample 2), a different composition profile (Si fraction from 0 to 1 in the direction of thickness) is clearly observed for the film deposited under different pre-treatment time and flow rate.[19] The total elemental composition of both samples 1 and 2 was MO_2 (M = Si, Ti) as confirmed by X-ray microanalysis, and no indication of the existence of boron and fluorine was observed. The pre-treatment time is related to the induction period that is denoted as the period for which the boric acid preferentially reacts with free F^- ions at the initial stage of the reaction (typically several hours), because metal-fluoro complex ions partially hydrolyse and release F^- ions.[20] In the present study, therefore, the gradient film is obtained, of which the Ti content is much higher close to the substrate for longer pre-treatment times (Fig. 2(b)). The changes in the flow rate directly lead to a time dependent change in the concentration of Ti and Si species in the treatment solution during film deposition. As a consequence, the composition gradient of the film in the direction of the film thickness can be controllable over a wide range, with no post-annealing process as is the case with other conventional preparation techniques for FGMs.

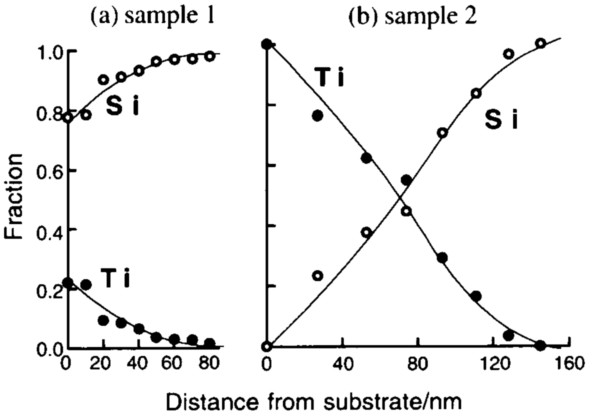

Fig. 2 Plots of Si and Ti molar fraction in the deposited films as a function of the direction of film thickness for samples 1 and 2, prepared under different reaction conditions. The solid lines are the guide to the eyes. Details of the reaction conditions are given in ref. 19.

In conclusion, the present boric acid-promoted simultaneous hydrolysis of $(NH_4)_2TiF_6$ and $(NH_4)_2SiF_6$ under controlled reaction conditions enables us to form compositionally modulated structures in $Si_{1-x}Ti_xO_2$ glassy films. This procedure provides a direct fabrication of gradient-type thin films of which the composition and gradation of the film are highly controllable in the direction of film thickness, and consequently the optoelectronic properties of the films can be well modified on the nanometer scale. Such direct modification of film microstructure based on the concept of FGMs may be a useful method for the fabrication of modified electrodes, optical filters and solid state solar cells. The present technique may be extended to prepare other gradient-type metal oxide or oxyhydroxide thin films including TiO_2–VO_2, VO_2–SiO_2 and TiO_2–FeOOH; attempts at this are currently under way and the results will be presented in a forthcoming article.

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