

## Crystal Phase Control for Metal Oxide Films Grown in Aqueous Solutions

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The crystal phase of metal oxide films grown in aqueous solutions was fundamentally determined by the pH value in aqueous solutions. Titanium dioxide ( $\text{TiO}_2$ ) films with rutile and anatase phases were directly grown on substrate surfaces in acidic aqueous solutions with titanyl sulfate ( $\text{TiOSO}_4$ ) at 60 °C. At a constant Ti concentration, the crystal phase of  $\text{TiO}_2$  changed from rutile to anatase with increasing the pH value in aqueous solution. The rutile and anatase phases were produced around their thermodynamic equilibrium conditions between Ti(IV) soluble species and the solid phases. We also yielded wurtzite zinc oxide ( $\text{ZnO}$ ) films using alkaline aqueous solutions with zinc sulfate ( $\text{ZnSO}_4$ ) and ammonium salts as complexing agents at 60 °C. A pH above 9.0 was the essential condition for the formation of wurtzite  $\text{ZnO}$  crystals in aqueous solutions. Wurtzite-type  $\text{ZnO}$  was produced by dehydration reaction of Zn(II) soluble species due to an increase in the chemical potential of  $\text{OH}^-$  under such strongly basic conditions. In these systems, the formation of the crystal phases was not affected by their deposition rate. Continuous  $\text{TiO}_2$  and  $\text{ZnO}$  films were achieved by preparing the suitable surfaces as nucleation sites and controlling the degree of supersaturation in aqueous solutions.

**Key words:** titanium dioxide, zinc oxide, thin film, low-temperature, aqueous solution

### 1. INTRODUCTION

Transition metal oxides are industrially important materials because of many attractive characteristics such as optical, electrical, catalytic, and magnetic properties and their thin films are widely applied in extensive fields. Recently, deposition techniques for thin films of metal oxides using aqueous solution systems under near ambient conditions have been developed [1]. Film formation is based on heterogeneous nucleation and subsequent crystal growth in an aqueous solution with a relatively low degree of supersaturation. The inspiration for the aqueous solution processing comes from biomineralization [2]. This low-temperature synthetic route is clean, economical, and versatile processing. Moreover, this deposition method having some advantages over prevalent dry and wet methods in technology is able to be an alternative for them.

Many works on low-temperature synthesis of metal oxide films by means of aqueous solution processing

have been reported [1]. However, most of the as-deposited films were metastable or amorphous phases. Therefore, post annealing at several hundreds degrees were required to obtain preferred crystalline oxide films, although the authors reported these synthetic routes as low-temperature processing. Furthermore, even if crystalline films were formed, the essence, including the mechanism and condition, for their formation was not sufficiently understood.

In this study, we attempted to deposit crystalline films of metal oxides, such as titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ), directly on substrate surfaces in aqueous solutions at near ambient conditions. Thin films of  $\text{TiO}_2$  with two valuable crystal phases, *i.e.*, rutile and anatase, and  $\text{ZnO}$  with many optical and electrical properties are technologically and industrially significant materials. We discussed the growth mechanisms and conditions for the crystalline films of metal oxides based on the thermodynamic study.

2. EXPERIMENTAL

2.1 Preparation of Precursor Solutions

For deposition of TiO<sub>2</sub> films, TiOSO<sub>4</sub>·xH<sub>2</sub>O (Nacalai Tesque, Inc., x<sub>av</sub>=4.6) was dissolved in aqueous solvents (pH −0.50–11.0) at concentrations of 0.001–0.1 M. The pH of the precursor solutions after 1 h stirring was adjusted in the range from −0.50 to 1.80.

For deposition of ZnO films, precursor solutions with 0.01 M ZnSO<sub>4</sub>·7H<sub>2</sub>O (Kanto Chemical) and a certain amount of NH<sub>4</sub>F (Junsei Chemical) as a complexing agent were prepared. NH<sub>4</sub>F was added at molar ratios to ZnSO<sub>4</sub> (R<sub>a</sub>) of 20–50. The pH of the precursor solutions was varied from 3.0 to 13.0 with HCl<sub>aq</sub> or NaOH<sub>aq</sub>.

The preparation methods of the precursor solutions for deposition of TiO<sub>2</sub> and ZnO films were mentioned elsewhere in detail [3,4].

Glass slides washed ultrasonically with diluted nitric acid and ethanol or acetone were used as substrates. The substrates were immersed into the precursor solutions based on Ti(IV) or Zn(II), and then maintained at 60 °C. After appropriate reaction time, the substrate deposited with TiO<sub>2</sub> or ZnO were withdrawn from the solutions, rinsed with purified water, and dried at room temperature.

3. RESULTS AND DISCUSSION

3.1 Deposition of TiO<sub>2</sub> Films

Figure 1 shows relationship between the experimental conditions and crystal phases of TiO<sub>2</sub> deposited on substrate surfaces.

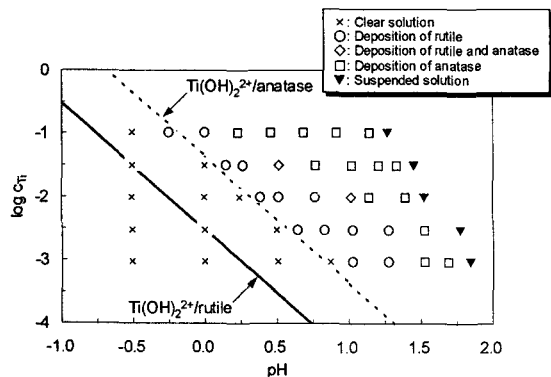


Fig. 1. A diagram for the experimental conditions and crystal phases deposited on the surface. The thermodynamic equilibria of Ti(OH)<sub>2</sub><sup>2+</sup>/rutile (solid line) and Ti(OH)<sub>2</sub><sup>2+</sup>/anatase (broken line) were also drawn [3,5].

Clear precursor solutions were stable at low pH values. Aqueous solutions suspended with insoluble TiOSO<sub>4</sub> were obtained at high pH values. In the intermediate pH range between them, crystalline TiO<sub>2</sub> was directly grown on substrate surfaces via heterogeneous nucleation. XRD analyses revealed that TiO<sub>2</sub> produced in this pH range was rutile or anatase phases. At a constant Ti concentration, moreover, rutile was deposited at lower pH and anatase was grown at higher pH within this pH range.

The boundaries drawn in the phase diagram denote the equilibrium between the TiO<sub>2</sub> solids and Ti(IV) soluble species in Ti(IV)–H<sub>2</sub>O system. The solid and broken lines represent the equilibria of Ti(OH)<sub>2</sub><sup>2+</sup>/rutile and Ti(OH)<sub>2</sub><sup>2+</sup>/anatase, respectively. Because Ti(IV) soluble species exists as a form of Ti(OH)<sub>2</sub><sup>2+</sup> at such high acidic conditions, these boundaries were estimated by the thermodynamic data of Lencka *et al.* [5] with the ideal solution approximation on the basis of the following equilibrium.

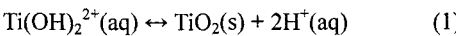


Fig. 1 shows that the calculated solid and broken lines lie parallel to the experimental boundaries between soluble species and rutile and between rutile and anatase. Assuming that the activity coefficients of Ti(OH)<sub>2</sub><sup>2+</sup> is equal to 0.10, these calculated boundaries overlap with the experimental boundaries. Accordingly, it is inferred that the rutile and anatase phases are produced under the conditions close to the thermodynamic equilibria between Ti(OH)<sub>2</sub><sup>2+</sup> and those solid phases, respectively.

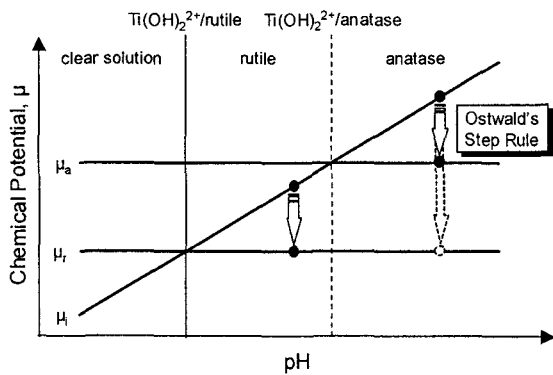


Fig. 2. Schematic diagram showing phase transformation from Ti(IV) soluble species to solid TiO<sub>2</sub> by means of the chemical potential.

This phenomenon can be elucidated using chemical potentials of soluble and solid species. The precursor solutions were stable against both deposition and precipitation in the low pH region below the boundary of  $\text{Ti}(\text{OH})_2^{2+}$ /rutile because of the lowest chemical potential of  $\text{Ti}(\text{OH})_2^{2+}$  ( $\mu_i$ ). At higher pH than the thermodynamic equilibrium of  $\text{Ti}(\text{OH})_2^{2+}$ /rutile,  $\mu_i$  slightly becomes larger than the chemical potential of the rutile phase ( $\mu_r$ ). When the pH is higher than the thermodynamic equilibrium of  $\text{Ti}(\text{OH})_2^{2+}$ /anatase, the chemical potential of anatase ( $\mu_a$ ) is lower than  $\mu_i$ . These chemical potentials have the order of their magnitude such as  $\mu_r < \mu_a < \mu_i$  in the pH region above the  $\text{Ti}(\text{OH})_2^{2+}$ /anatase boundary. In this case, it is expected that most labile  $\text{Ti}(\text{OH})_2^{2+}$  transforms into the rutile phase having the lowest chemical potential. However, according to Ostwald's step rule, a phase transforms into a state with the closest chemical potential. Thus, it is suggested that the metastable anatase phase is successfully created in the aqueous solutions under the relatively high pH conditions.

### 3.2 Deposition of ZnO Films

A diagram of solid phases deposited in aqueous solutions based on Zn(II) and  $\text{NH}_4\text{F}$  is shown in Fig. 3. The crystal phase of products was fundamentally influenced by pH of the precursor solutions.

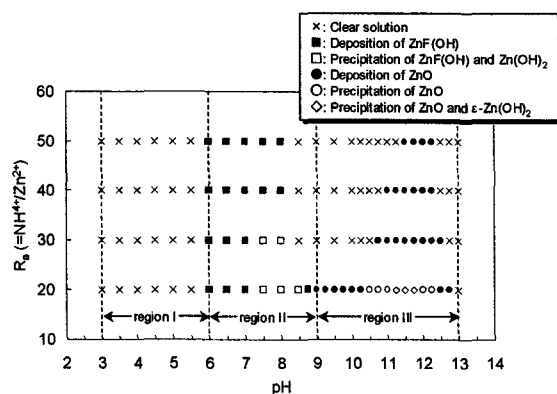


Fig. 3. A diagram for the crystal phases deposited in aqueous solutions and the mode of deposition (heterogeneous nucleation on substrate surfaces or homogeneous nucleation in bulk solutions) [4].

In region I (pH 3.0–6.0), the aqueous solutions showed neither deposition on substrate surfaces nor pre-

cipitation in bulk solutions. Deposits or precipitates of hydroxides such as  $\text{ZnF}(\text{OH})$  and  $\text{Zn}(\text{OH})_2$  was observed in region II (pH 6.0–9.0). Wurtzite-type ZnO was mainly produced in region III (pH 9.0–13.0).

Figure 4 shows phase stability diagrams for  $\text{ZnO-H}_2\text{O}$  and  $\text{Zn}(\text{OH})_2\text{-H}_2\text{O}$  systems. The broken lines denote the thermodynamic equilibria between Zn(II) soluble species and solid phases. These equilibrium boundaries were estimated on the basis of the equilibria between solid phases and soluble species using thermodynamic data [6]. The solid lines represent the solubility of the solid phases as a function of pH.

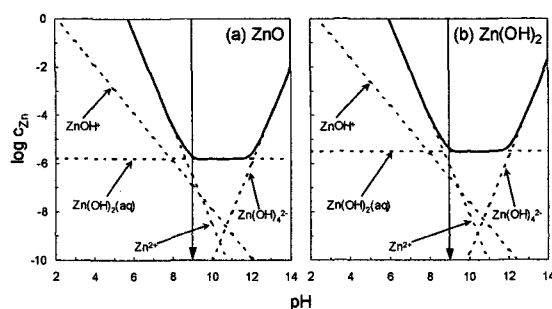
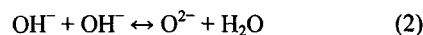


Fig. 4. Phase stability diagrams for  $\text{ZnO-H}_2\text{O}$  (a) and  $\text{Zn}(\text{OH})_2\text{-H}_2\text{O}$  (b) systems as a function of pH [4,6].

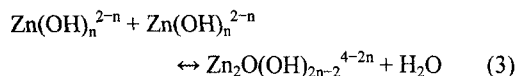
These phase diagrams indicate that the dependence of the solubility of ZnO on pH is almost the same as that of  $\text{Zn}(\text{OH})_2$ . Unlike above-mentioned  $\text{Ti}(\text{IV})\text{-H}_2\text{O}$  system, there is no evident relationship between the experimental results and thermodynamic studies. In the present study, however, the crystal phase of products changed at pH 9.0, i.e., hydroxides were formed at pH 6.0–9.0 (region II), while oxide was obtained at pH 9.0–13.0 (region III).

According to Fig. 4, in aqueous solutions at pH > 9.0 (indicated with arrows), Zn(II) soluble species are dominated by hydroxyl complexes such as  $\text{Zn}(\text{OH})_2(\text{aq})$  and  $\text{Zn}(\text{OH})_4^{2-}$  [6]. Under the strongly basic conditions, the equilibrium on Eq. (2) is inferred to move toward the right because of an increase in the chemical potential of  $\text{OH}^-$  in an aqueous system with increasing pH.



Thus, during the transformation of these hydroxyl complexes as precursors into the solid phases, the dehydra-

tion reaction depicted conveniently with Eq. (2) produced Zn–O–Zn bonds as follows:



where  $n = 2$  or  $4$ . Further dehydration between  $\text{OH}^-$  on the growing interface of crystals and  $\text{OH}^-$  ligands of hydroxyl complexes gradually constructed the wurtzite structure. As a consequence, we concluded that a pH above 9.0, where the concentration of the precursors and the chemical potential of  $\text{OH}^-$  increase with increasing pH, is an essential condition for the formation of wurtzite ZnO.

Li *et al.* [7] suggested hypothesis that the crystal lattice of ZnO was constructed by stacking  $\text{Zn(OH)}_4^{2-}$  as a growth unit through a dehydration reaction, although no effect of pH on this growth mechanism was mentioned. Hence, this hypothesis stands by our suggestion about the strategy of ZnO formation in the aqueous media.

#### 4. SUMMARY

In this study, we directly prepared thin films of crystalline metal oxides, such as rutile and anatase  $\text{TiO}_2$  and ZnO, on substrates using aqueous solutions under the near ambient conditions. We discussed the mechanisms and conditions for their growth in aqueous solutions at a low temperature with the thermodynamics-based study.

Crystalline  $\text{TiO}_2$  films were grown on a substrate via heterogeneous nucleation in acidic aqueous solutions of Ti(IV) at near room temperature. The crystal phase of  $\text{TiO}_2$  films was fundamentally determined by the pH and Ti(IV) concentration of the precursor solutions. The rutile and anatase phases were produced around their thermodynamic equilibrium conditions between the solid phases and soluble species.

We also obtained wurtzite ZnO films directly on substrate surfaces with basic aqueous solutions of Zn(II) at a low temperature. We found that a pH above 9.0 was necessary for the formation of wurtzite ZnO in this aqueous solution system. Wurtzite structure of ZnO was created via dehydration reaction between hydroxyl complexes as precursors. The dehydration was caused by an increase in the chemical potential of  $\text{OH}^-$  under such

strongly basic conditions.

As described above, in the previously reports on deposition techniques with aqueous solutions, most of the as-prepared films were metastable or amorphous phases. Therefore, heat treatments to obtain preferred crystalline thin oxide films were indispensable, although they reported these synthetic routes as low-temperature processing. This is because the heterogeneous nucleation of solid phases on surfaces has mainly been emphasized and the condition producing crystal phases has not been argued. However, this study revealed that the investigation of the environment where crystal phases are created is important as well as the promotion of heterogeneous nucleation.

Phase stability in an aqueous system is governed by the chemical potentials of crystalline solid phases and soluble species depending on pH and species concentrations of the aqueous solution. Thus, we conclude that the control over the chemical potentials with these parameters is required in order to create a desired crystalline oxide phase by aqueous solution processing.

#### ACKNOWLEDGEMENT

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