THE SUMMARY OF Ph.D. DISSERTATION

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Title

A Study on Low-Temperature Synthesis of Metal Oxide Films via Aqueous Solution Route

Abstract

Transition metal oxides are industrially important materials because of many attractive characteristics and their thin films are widely applied in extensive fields. The thin oxide films with high quality and performance are indispensable for highly advanced modern technology. The fabrication techniques have been developed to satisfy such demands, while the environment has been damaged by their consumption and emission of energy. On the other hand, recently, soft solution processing (SSP), defined as environmentally friendly processing for materials syntheses with solutions, is suggested. Especially, an aqueous solution processing is a low-energy, clean, economical, and versatile processing. Many works on low-temperature synthesis of metal oxide films via the aqueous solution routes have been reported. In the previous studies, however, the thin films were metastable or amorphous phases. Thus, post annealing at several hundreds degrees were required in order to obtain preferred crystalline oxide films, although these works were reported as low-temperature syntheses. Even if crystalline films were formed, the essence, including the mechanism and condition, for their formation were not sufficiently understood. In this study, I deposit crystalline films of metal oxides, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), directly on substrate surfaces with aqueous solutions at near ambient condition and clarify their growth mechanisms and conditions on the basis of the thermodynamic study.

In chapter 1, I mention the backgrounds of this study, the energetic and technological features of aqueous solution processing, and the previous investigations for synthesis of metal oxide thin films by aqueous solution processing.

In chapter 2, I elucidate the classical theory of nucleation and growth for thin film formation in a vapor and aqueous system. I also discuss the behavior of cationic and anionic species in an aqueous solution, including hydrolysis, condensation, and complexation, on the basis of the principle of electronegativity equalization.

In chapter 3, I state the direct deposition of crystalline TiO_2 films by the aqueous solution processing and clarify the mechanism for the crystal phase control for TiO_2 films grown in aqueous solutions based on the thermodynamic study. The crystal phase of TiO_2 films was essentially determined by the initial pH value and the Ti concentration of the precursor solutions. The rutile and anatase phases were produced in the solutions around their thermodynamic equilibrium conditions between Ti(IV) ionic species and the solid phases. The morphology of the TiO_2 products was influenced by the reaction rate controlled with the properties of anions as a ligand for titanium cations. Continuous films of both rutile and anatase were successfully formed on a relatively hydrophobic surface.

In chapter 4, I describe the preparation of TiO_2 with periodic microstructures by templating as an example of application of the aqueous solution processing for TiO_2.

In chapter 5, I mention the direct deposition of wurtzite ZnO films by aqueous solution processing and discuss the significant conditions for the film growth. The crystal phases were fundamentally determined by the pH of the aqueous solution systems. Wurtzite ZnO was produced in a basic region of pH 9.0−13.0. Deposition on the surface of substrates via heterogeneous nucleation was achieved with a decrease in the deposition rate by changing the pH and the concentration of the complexing agents. The nucleation of the crystals was promoted by means of underlying thin layers derived from zinc acetate.

In chapter 6, finally, I state the nature of film growth of crystalline metal oxides in aqueous solutions at near ambient conditions on the basis of the above-mentioned results and discussion. I conclude that the formation of continuous thin films of crystalline metal oxides in aqueous solutions at a low temperature is achieved by (i) the condition producing crystal phases in aqueous solutions, (ii) the low deposition rate to inhibit deposition of metastable or amorphous phases and induce heterogeneous nucleation, and (iii) the proper surface for the heterogeneous nucleation.