Controlled crystallization of TiO_2 and ZnO from aqueous solutions: effects of soluble organics

Yanfeng Gao,[1)] Won Seon Seo,[2)] Masayuki Nagai,[1)] Kunihito Koumoto[3)]

1) Advanced Research Laboratories, Musashi Institute of Technology, Tokyo 158-0082, Japan;

2) Advanced Materials Analysis & Evaluation Center, Korea Institute of Ceramic Engineering & Technology, Seoul, Republic of Korea;

3) Department of Applied Chemistry, Nagoya University, Nagoya 464-8603, Japan.

Email: yfgao@sc.musashi-tech.ac.jp

Synthesis of ceramics from an aqueous solution by partially mimicking the biomineralization process is a promising approach for the growth at low temperatures through an environmentally friendly manner, while it usually produces slightly crystallized or amorphous precipitates. Crystalline ceramic powders and films with a precise control of polymorphs, crystalline orientations, sizes and morphologies are of technical importance to achieve a wide range of functions. Investigations into the biomineralization mechanisms provide valuable considerations on the direct synthesis and crystalline control of ceramic oxides in solutions. In this presentation, we will introduce our efforts for the study of crystallization engineering of TiO_2 films that were commonly precipitated only as amorphous forms in the similar solutions. The work was also extended to develop reproducibly unique ZnO nanostructures from solutions in the presence of dissoluble organic additives.

In the first example, we have fabricated a rutile TiO_2 film from a peroxotitanate aqueous solution by kinetically controlling the nucleation and growth. A highly transparent, crack-free film about 2 μm in thickness with specific crystalline orientations along (101) and (002) diffraction planes was successfully deposited on a SnO_2: F (FTO)-covered glass substrate that was soaked for a long period of time in a peroxotitanate aqueous solution with a low concentration with respect to Ti(IV), and a low pH, but without any other additives. TEM images confirmed the column-shaped growth along the direction perpendicular to the substrate surface. Time-dependent experiments showed transformation from amorphous state to crystalline state with the deposition proceeding, suggesting that a kinetically-controlled, dissolution-recrystallization mechanism may operate in this process.

In the second example, we investigated the treatment of substrates in the solution analogous to the above one, but in the presence of a small amount of soluble polymers. The deposition rate was significantly lowered compared to that in the absence of organic molecules. Interestingly, XRD results showed that the deposits are anatase TiO_2 without obviously crystallographic orientations. The existence of about 30% residue of carbon was also confirmed, suggesting the formation of anatase/polymer hybrid composites. It seems that the polymer stabilized the metastable anatase phase probably by controlling the surface energies.

In the third example, we have been investigating how the solution conditions affect the crystalline control and morphology evolution of ZnO films for the application to dye-sensitized solar cells. A two-step process was realized to synthesize ZnO crystals and purposely arrange them into specific nanostructures, especially nanowire arrays with controllable diameter, length, and number of densities of nanowires. Firstly, we electrodeposited a thin ZnO layer onto a TCO (transparent conductive oxide) – covered glass. This layer was used as seed crystals to induce the growth of ZnO from aqueous solutions. Secondly, the pre-treated substrate was immersed in a solution containing Zn(II) and dissoluble organic molecules. Well aligned ZnO nanowires with a thickness over 15 μm were overgrown on the seed layer. This ZnO film shows a large aspect ratio up to 100 and a number density above 4×10^{12} m^2, implying that the film has a large surface area and may be appropriate to be integrated into solar cells.

References:

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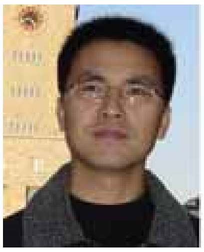
Biographical Sketch



Dr. Y.-F. Gao was born in January 2, 1970 in a small village of Xi'An, Shaanxi Province, China. He studied ceramics at Shaanxi University of Science and Technology, where he got his B. Eng. and M. Eng., and worked as a Research Associate and assistant professor from 1994 to 2001. In 1999, he studied at Kochi University of Japan with Professor K. Yanagisawa for 1 year. In 2001, he started his doctoral study at Nagoya University with Professor Koumoto, working on biomineralization-inspired processing of ceramic films. After he obtained his PhD in 2004, he still continued the related research as a postdoctoral fellow for 1 year before he moved to Musashi Institute of Technology to be an Assistant Professor. His current research interest is controlled crystallization and morphology control of functional ceramic films and their applications to green energy and photocatalysts. Dr. Gao can be reached by email at yfgao@sc.musashi-tech.ac.jp or gaoyf@hotmail.com.