

Preparation and Luminescence Property of Transparent Eu³⁺/ZrO₂ Thin Films by the Liquid Phase Deposition (LPD) Method

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ZrO₂ (Zirconium dioxide) has three major polymorphs: monoclinic ZrO₂ is based on 7-coordinate Zr⁴⁺ ions, but it transforms to a tetragonal polymorph around 1170 °C. Phase transition from tetragonal to cubic phase is observed at *ca.* 2300 °C. The stabilization of tetragonal or cubic phase at room temperature has been achieved by reducing the grain size to the nanometer regime, or by doping with di-, or trivalent ions such as Ca²⁺ and rare-earth ions.

ZrO₂ stabilized by doping rare-earth have attracted great attention as potential materials in various application fields such as catalysis, transformation-toughened materials, solid oxide fuel cells (SOFCs), oxygen sensors and optics. For example, t-ZrO₂ is the most effective catalyst among many oxide used in the hydrogenation of aromatic carboxylic acid to the corresponding aldehydes, as well as in the isomerization of alkenes. On the other hands, c-ZrO₂ is promising electrolytes of SOFCs due to their high ionic conductivities at high temperatures. For many of these applications, rare-earth doped stabilized ZrO₂ thin films are strongly required so as to obtain the desirable properties.

In general, these multi-component zirconium dioxide thin films were prepared by some dry process such as CVD, sputtering and ion implanting techniques, and some wet process such as sol-gel method. Among those methods, solution-based synthesis has proved to be very powerful in synthesis of thin films from the viewpoint of the simplicity, cost and environmental emission.

In our recent work, we have reported a novel aqueous solution process to fabricate various kinds of metal oxide thin films by using ligand-exchange hydrolysis of metal-fluoro complex and the F⁻ consumption reaction with boric acid or aluminum metal (liquid phase deposition process, LPD). As this method relies on the chemical equilibrium reaction between metal-fluoro complex and metal oxide in aqueous solution which is a typical homogeneous mixing system, homogeneous and/or composite thin films can be readily deposited on various kinds of substrates with large surface areas and complex surface morphologies. In our previous work, we have prepared various metal oxide thin films by the method [1,2]. In this paper, we report that this method can be extended to the preparation of Eu³⁺ ion-doped ZrO₂ thin films. Rare earth ions readily react with F⁻ ions and to form LnF₃ precipitates (*Ln*: rare earth metal) in aqueous solution. The stabilization of Eu³⁺ ion can be achieved by masking with diethylenetriaminepentacetic acid (DTPA) to prevent from the formation of

insoluble EuF₃ in the LPD solution.

The as-deposited film consists of densely-packed small particles of approximately several tens of nanometer in diameter. These particle sizes increase with the increase of annealing temperature. Eu/Zr ratios in the deposited films increased with the increase of the initial concentration of Eu³⁺-DTPA complex in the reaction solution, and it indicates that the composition of the films can be controlled by varying the initial concentration of Eu³⁺-DTPA complex in the reaction solution. Fig. 1 shows photoluminescence spectra of the deposited Eu-doped ZrO₂ film after annealed at 900 °C for 1 hour. Xenon lamp was used as the excitation source. The characteristic peaks due to ⁵D₀ → ⁷F_j (*j* = 1~3) transition of Eu have been clearly observed. The fluorescence intensity of the film excited with 250 nm line is higher than that of the film excited with 396 nm line. The broad excitation band around 240 nm was observed due to a charge transfer in the host lattice, and the CT band plays an important role for strong emission of the deposited film.

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Reference

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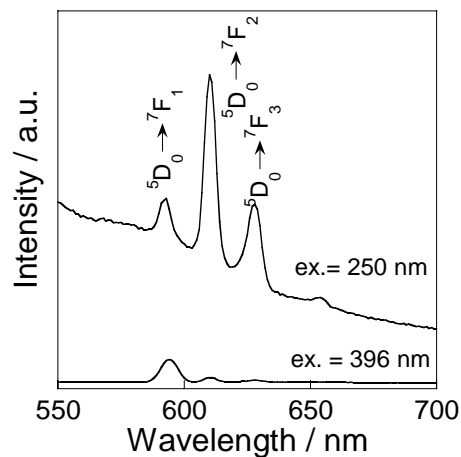


Figure 1 Photoluminescence spectra of the Eu³⁺/ZrO₂ thin film excited at 250 nm and 396 nm.