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## Abstract

## 論文内容の要旨 (博士)

Title of Thesis 博士学位論文名	Study on Electrochemical Preparation of Oxide Semiconductor Films (酸化半導体膜の電気化学形成に関する研究)
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(Approx. 800 words)

(要旨 1,200 字程度)

Metal oxide films have been utilized in electronics and chemical industries due to their electrical, optical, piezoelectrical, and magnetic characteristics. The oxides have been also used as host materials for transparent conductive layers, electronic parts such as thin film transistors and capacitors and photocatalysts. Especially, oxide semiconductor layers with wide bandgap energy over 2 eV have attracted increasing attention as materials to open new door for ultraviolet light-emitting diode (LED), spintronics, and multi ferroic materials with controlled physical characteristics.

Oxide semiconductor films have been prepared using gas-phase deposition processes and solution chemical processes. Gas-phase deposition processes have several advantages like the ability to control thickness and form high purity semiconductors, with disadvantages of expensive apparatus, the need of facility for gasses and high vacuum, resulting in large amount of energy consumption and CO<sub>2</sub> emission. Solution chemical processes have several advantages over the gas-phase deposition processes in the equipment, facilities, and fabrication costs, and electrochemical processes have been employed to prepare precursors of Cu(In,Ga)Se<sub>2</sub> (CIGS) and Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) compounds for photovoltaic applications on the industry scale.

The wide bandgap oxide semiconductor films were applied to optical devices, and it is well known that their compositions, structures and chemical states influence their optical properties. However, electrochemical preparation for oxide semiconductor films applied to optical devices has some problems. It is well known that mixing other materials to an oxide semiconductor changes its optical properties and electrical properties, but almost no example of a mixed-oxide film is reported. Moreover, valence values of metal elements in oxide were uncontrollable because of the existence of mixed valence elements and impurities, and this led to the uncontrollability of optical properties and electrical properties of oxide semiconductor. These problems can be solved by designing the processes with thermodynamic calculation. In this thesis, I show resolving these problems using electrochemical preparation of oxide

films based on thermodynamic calculation with some examples, and I demonstrate a novel device fabricated by electrochemical preparation overcoming weaknesses of existing device, in order to show the possibility for industrial applications.

First, Zn-Ce-O films, mixed oxide films, were prepared on an electrodeposited Ag layer in an aqueous solution containing a zinc nitrate hydrate and cerium nitrate hydrate based on thermodynamic calculation. Theory of deposition for mixed-oxide films was discussed from a critical pH perspective relative to ion species and oxides. The concentrations of metal ions in the Zn-Ce-O films were depending on ions concentration of Zn and Ce in the solution. The Ce content in the films changed from 0 to 43 mol% depending on the Ce concentration in solutions. Zn-Ce-O films were identified as a wurtzite ZnO containing Ce (Ce:ZnO) at 5 mol% Ce and mixtures of Ce:ZnO and CeO<sub>2</sub> containing Zn(Zn:CeO<sub>2</sub>) at 20-43 mol% Ce. The bandgap energy of Zn-Ce-O films have changed from 3.4 eV to 2.9 eV depending on the Ce content.

Secondly, I demonstrated preparation of tungsten oxide hydrate films of WO<sub>3</sub>·H<sub>2</sub>O and WO<sub>3</sub>·(H<sub>2</sub>O)<sub>0.33</sub> with a controlled valence value of the metal element in the oxides using electrochemical preparation based on thermodynamic calculation. The valence state of obtained tungsten oxide hydrate films was only +6, and this film was proved to have high chemical uniformity. Tungsten oxide hydrate films of WO<sub>3</sub>·H<sub>2</sub>O and WO<sub>3</sub>·(H<sub>2</sub>O)<sub>0.33</sub> were prepared on conductive glass substrates by anodic deposition in aqueous solutions containing 0.01–0.5 mol/L WO<sub>4</sub><sup>2-</sup>. The large square-shaped WO<sub>3</sub>·H<sub>2</sub>O obtained in the 0.01–0.09 mol/L WO<sub>4</sub><sup>2-</sup> solutions possessed a bandgap energy of approximately 2.5 eV, and granular-WO<sub>3</sub>·(H<sub>2</sub>O)<sub>0.33</sub> films obtained in the 0.05–0.5 mol/L WO<sub>4</sub><sup>2-</sup> solutions showed 3.3 eV in bandgap energy.

Thirdly, on the basis of thermodynamic calculations, I tried to form SnO<sub>2</sub> films having uniformity in valence. Sn(O,OH), mixture of SnO<sub>2</sub> and Sn(OH)<sub>4</sub>, having unified valence of +4 was prepared by electrodeposition designed using thermodynamic calculations. Obtained Sn(O,OH) completely covered the substrates, and had smooth surfaces and structures with tetragonal fine crystals.

Finally, I fabricated the WO<sub>3</sub>·(H<sub>2</sub>O)<sub>0.33</sub>/Sn(O,OH) bilayer structure for all-solid-state electrochromic device by anodic electrodeposition on the FTO substrate. The WO<sub>3</sub>·(H<sub>2</sub>O)<sub>0.33</sub>/Sn(O,OH) bilayer device showed electrochromism; this was an evident demonstration of a novel and low-costly all-solid-state electrochromic device.

I resolved the problems of existing electrodeposition for wide band gap oxide semiconductor by electrochemical preparation based on thermodynamic calculation. The results demonstrated here will strongly contribute to the improvement of the preparation process of oxide semiconductors and their devices.