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Effect of indium- and gallium-doped ZnO fabricated through sol-gel processing on energy level variations

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ABSTRACT

Properties and energy levels of In-doped ZnO (IZO), Ga-doped ZnO (GZO), and In- and Ga-doped ZnO (IGZO) crystals, were investigated. Metal-doped ZnO with different dopants were prepared by sol-gel processing. Results showed that the lattice crystal of the doped ZnO was distorted and the average grain sizes of the crystals decreased. The resistivity and mobility of all doped samples decreased, but the carrier concentration increased in the presence of In and Ga. The energy levels of all crystals were varied depending on the dopants in ZnO. Although the conduction band energy (E_c) and valence band energy (E_v) of IZO apparently shifted to lower energy levels, the bandgap energy (E_g) varied little. The E_g of GZO was widened with respect to ZnO because its E_v was altered. The E_g of IGZO was widened because the E_c was significantly shifted by In and the E_v was mainly varied by Ga.

1. Introduction

Recently, metal oxide semiconductors, such as metal-doped ZnO, have been applied in many modern optoelectronic devices. Metal-doped ZnO materials, i.e. In-doped ZnO (IZO) [1–4], Ga-doped ZnO (GZO) [5–8], and In- and Ga-doped ZnO (IGZO) [9–12] have been successfully applied in sensors, photocatalysts, and thin film transistors (TFTs). To improve device performance, the properties of ZnO have been modified by adding dopants. For example, many studies have reported that using IGZO in TFT devices is associated with the advantages of high mobility, low energy dissipation, and low-temperature processing. Using IGZO in TFT devices can significantly improve the device stability and performance compared to the use of Si-based devices [9–11].

IZO, GZO, and IGZO materials are fabricated using various methods, such as sputtering [13–15], pulse laser deposition [5,11], and sol-gel synthesis [16–25]. Among these methods, sol-gel synthesis with hydrothermal processing is a simple and low-cost approach for fabricating IGZO. The effects of process factors, i.e. precursor concentrations, pH values, temperatures, and additives, on metal-doped ZnO material properties, i.e. crystallinity, grain size, and lattice structure of IGZO have been investigated. The ratio of In:Ga:Zn in IGZO has been found to be one of the main factors affecting the material properties of IGZO. Synthesized metal-doped ZnO samples have been prepared and fabricated for device production, such as sensors, and TFTs. In previous studies, sol-gel IGZO samples were fabricated in the TFT channel layer, and transistor performance was evaluated based on the properties of IGZO. The device performance for the IGZO-based TFT improved when IGZO was used with in TFT device.

The electrical and optical properties of the metal-doped ZnO materials are currently among the most important topics in studies because these materials exhibited unique optical and electrical properties when applied in optoelectronic devices. The electrical properties of the metal-doped ZnO have been modified to achieve stable and high electrical conductivity and mobility. The mobility of amorphous-IGZO (a-IGZO) was proposed to be higher than 10 cm/V s, which is significantly higher than that of a-Si (0.1 cm/V s) [9,11]. The stable electrical property of a-IGZO can enhance the device performance and operation. Moreover, the power dissipation for the IGZO-based TFT was lower than that of a-Si based TFT [9].

Energy band theory is a useful approach for explaining the electrical and optical properties of IGZO [9,26]. The bandgap energy (E_g) of IGZO has been found to be wider than that of ZnO, which is also attractive for the optoelectronic development. The change in E_g is attributable to the energy-level variations for the IGZO materials, which are influenced by the presence of In, Ga, or both. The energy bands of conduction band energy (E_c) and valence band energy (E_v) are critical energy states that affect material properties. The levels of these energy bands in IGZO vary because of the crystal structure distortion induced by the In and Ga-dopants in ZnO. The E_g of IGZO widens in the presence of In and Ga because of the energy level variations. In addition, the E_g shifts from a direct (ZnO) to indirect (IGZO) bandgap according to the E_c and E_v locations in the energy band structure [26]. The distribution of energy

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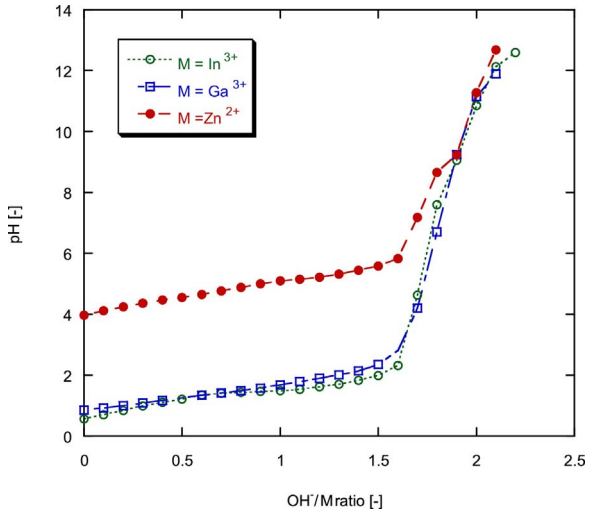

Fig. 1. Change of pH in the Zn, In, and Ga solutions with the addition of $NaOH_{(aq)}$.

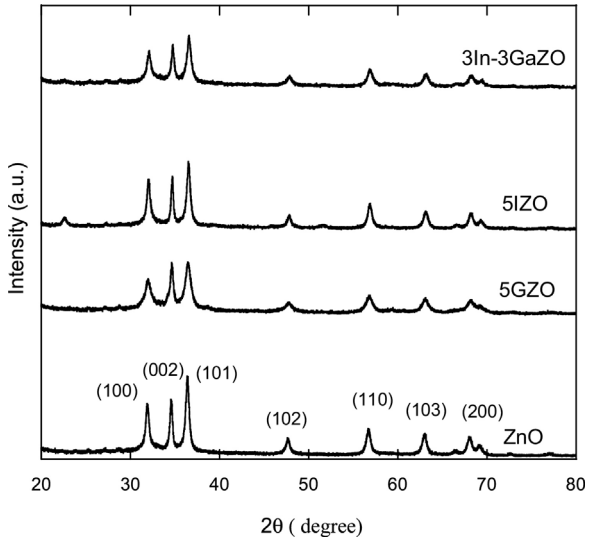

Fig. 2. X-ray diffraction patterns of the ZnO, IZO, GZO and IGZO samples.

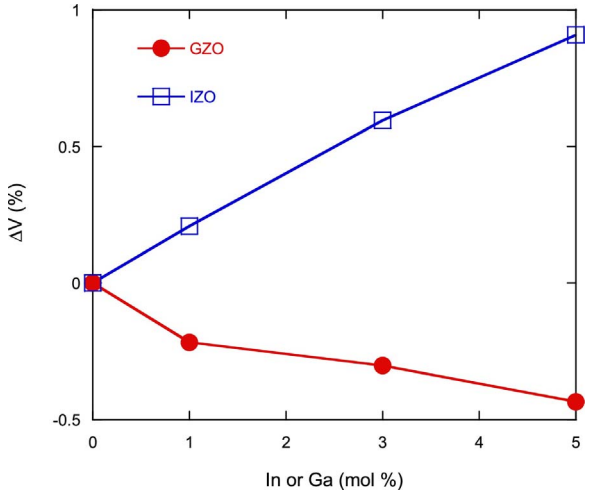

Fig. 3. Lattice volume variation (ΔV) of the metal-doped ZnO samples fabricated by different dopant compositions.

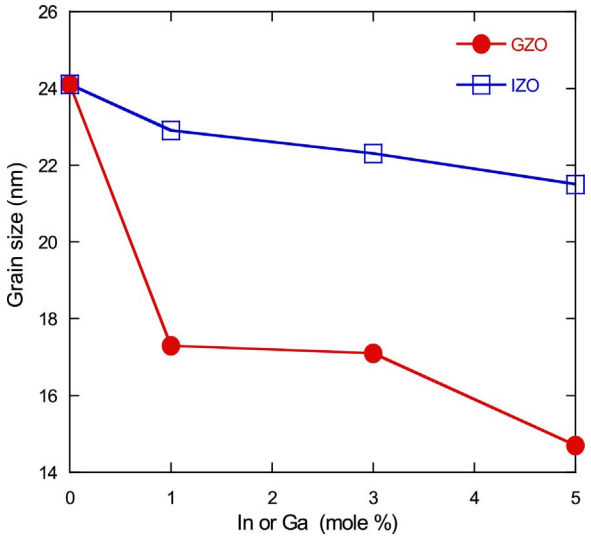

Fig. 4. Grain size of the metal-doped ZnO crystal samples fabricated by different dopant compositions.

bands can also influence the change of electrical properties of IGZO. Oxygen vacancies in ZnO with or without doping have been proposed to be one of the most significant factors affecting its electrical properties. Defect energy levels caused by oxygen defects, such as shallow donor, deep defect, and tail state energy levels, located between E_c and E_v in the band structure, have been studied to investigate the influence of IGZO on its optoelectronic applications. The distribution of E_c and E_v can be determined by first-principle calculations on the basis of density function theory [9,26]. To determine the E_c and E_v variations in the properties of IGZO must be evaluated to understand the effect of the dopants on the IGZO properties. However, few studies have experimentally determined E_c and E_v of IGZO to investigate the energy-level variations in the presence of In and Ga.

The present study evaluated the properties and energy levels of IZO, GZO, and IGZO crystals, fabricated through sol-gel synthesis at 60 °C. The metal-doped ZnO with different dopant compositions were prepared to estimate the effect of the dopants on the properties of ZnO. The material, optical, and electrical properties of the metal-doped ZnO samples were characterized. The energy levels of the doped ZnO samples with different dopant compositions were determined through current-potential (C-V) analysis. Variations of the E_c, E_v, E_F and E_g of the metal-doped ZnO samples were determined in the presence of the dopants. The effect of the dopants on the energy-level variations in IZO, GZO, and IGZO crystals was analyzed and discussed in this work.

2. Experimental method

Sol-gel IZO, GZO, and IGZO particles were fabricated. First, a 0.1 M $Zn(OH)_2$ solution was prepared by mixing 0.1 M $Zn(CH_3COO)_2$, and adding 1 M NaOH to adjust the pH value of the solution to 6.5 at room temperature. Moreover, 0.1 M $In(OH)_3$ and 0.1 M $Ga(OH)_3$ solutions were prepared by respectively mixing 0.1 M $In(CH_3COO)_3$ and $Ga(CH_3COO)_3$ and by adding 1 M NaOH to adjust the pH value of the solutions to 6.5 at room temperature. Various compositions of In, Ga or In and Ga ion with Zn ion solutions (1–5 mol%) were prepared by adding different amounts of 0.1 M $In(OH)_3$, 0.1 M $Ga(OH)_3$, or both, respectively, to a 0.1 M $Zn(OH)_2$ solution, and the mixture was thoroughly stirred at room temperature for 5 min. All chemicals were obtained from J.T. Baker Chemical Company. The pH values of the solutions were increased to 10 by adding 1 M NaOH. The based solutions were heated at 60 °C for 1 h to faciliate the sol-gel reaction. After processing, the powder solution was further analyzed. The IZO, GZO, and IGZO powders were obtained by centrifuging the colloidal particle