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Preparation and sintering of indium–gallium–zinc oxide ceramics with different zinc oxide contents

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ABSTRACT

Amorphous IGZO film has been extensively used as the channel layer of thin-film transistors. To investigate the IGZO sputtering targets, the effects of sintering temperatures on the sintering, microstructure, and electrical properties of IGZO ceramics with In_2O_3:Ga_2O_3:ZnO mole percentages of 1:1:1 (IGZO-111) and 1:1:2 (IGZO-112) were studied. In IGZO-111 ceramics, the In_2O_3 and $ZnGa_2O_4$ phases are completely replaced by $In_2Ga_2ZnO_7$ and $InGaZnO_4$ phases when the sintering temperature is increased from 1300 °C to 1400 °C. Moreover, the crystal structure of IGZO-112 ceramic is a single phase of $InGaZnO_4$, and no phase transformation occurs between 1200 °C and 1500 °C. The optimum relative densities of IGZO-111 and IGZO-112 ceramics are 99.8% and 99.0%, respectively. After 1500 °C sintering, the resistivities of IGZO-111 and IGZO-112 ceramics are 1.5×10^{-3} Ωcm and 2.5×10^{-3} Ωcm, respectively. The properties of IGZO ceramics are comparable to those of AZO and GZO ceramics reported in the literature.

1. Introduction

Amorphous indium–gallium–zinc-oxide (IGZO) film exhibits outstanding electrical performance and visible transparency, so it is widely used as the channel material of thin-film transistors [1–9]. Among the deposition techniques of thin films, magnetron sputtering is a dominant preparation method due mainly to its low coating temperature, high coating rate, good quality of the film, and high feasibility for large-area deposition [10–12]. The effects of various sputtering parameters, particularly the oxygen partial pressure, on the properties of IGZO films have been the focus of previous research [1–9]. Recently, several studies [13–21] have demonstrated that the characteristics of the sputtering targets for various oxide thin films play important roles on the preparation and the performances of sputtered films. Thus, in addition to the sputtering parameters, the sputtering target is an important factor in determining the properties of oxide films.

To optimize the performances of sputtered films, the correlations between target performance and film properties must be thoroughly clarified. The characteristics of the oxide targets, including the sintered density [13,14], microstructural uniformity [15], stoichiometry [17–19], and electrical properties [20,21], have been found to obviously affect both the sputtering process and the film properties. A tin-doped indium oxide (ITO) target with higher sintered density and more homogeneous SnO_2 distribution can suppress the arcing phenomenon and nodule generation during sputtering [14,15]. Furthermore, Minami et al. [20] found that using aluminum-doped zinc oxide (AZO) targets with lower resistivity can increase the deposition rate and lower the arcing counts.

In addition to the sputtering process, the properties of sputtering targets also affect the film performances significantly. Using an ITO target with a higher sintered density can result in a film with lower resistivity [13]. Neves et al. [17] found that a ZnO target produced with non-stoichiometric nanometer powder can generate a ZnO film with lower resistivity. Furthermore, Minami et al. [20] and Huang et al. [21] investigated the effects of the electrical properties of AZO targets on the performances of AZO films. These two studies clearly demonstrated that an AZO target with lower resistivity can result in a more uniform film having lower resistivity. In addition, Yamada et al. [18] demonstrated that using Ti_2O_3:Nb and TiO_2:Nb ceramic targets instead of a Ti:Nb metallic target further facilitates the production of a niobium-doped titanium oxide (TNO) film with excellent electrical properties under a wide process window of oxygen pressure.

On the other hand, radio-frequency (RF) power, whose coating rate is lower than that of direct-current (DC) power, is usually used for the sputtering of various oxide films due to the high intrinsic resistivities of oxide targets [6]. However, DC power has been

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widely applied to deposit various transparent conductive oxide (TCO) films because of the low resistivities of their targets [20–23]. Fang et al. [22] showed that an AZO target with a resistivity of 0.2 Ωcm can be used to manufacture an AZO film by DC sputtering. TNO and TiO_2 films can also be prepared by DC sputtering using TiO_{2-x} targets with resistivities of about 0.3 Ωcm [23,24]. Therefore, it is clear that the electrical properties of TCO targets affect the performances of the films, the stability of the sputtering process, and the feasibility of DC sputtering.

Given the importance of sputtering targets, the processes and properties of sputtering targets for TCO films have been extensively investigated, particularly those of AZO and gallium-doped zinc oxide (GZO) [20,21,25–37]. Unfortunately, the process and characteristics of IGZO targets have been studied relatively little [3,4]. These unresolved questions prevent IGZO films and their devices from being optimized. Lo and Hsieh [3] studied the fabrication of an IGZO (In_2O_3:Ga_2O_3:ZnO = 1:1:2 mol%) target and reported that the crystal structure and relative density of the target are a single $InGaZnO_4$ phase and 93%, respectively. Lee et al. [4] investigated the preparations of IGZO targets with atomic ratios (In:Ga:Zn) of 2:2:1, 1:1:1, and 1:1:2 and the correlations between the compositions and crystal structures of IGZO powders. For IGZO powders with an atomic ratio (In:Ga:Zn) of 2:2:1, the main In_2O_3 phase decreased and the $ZnGa_2O_4$ phase increased as the calcination temperature was increased from 730 °C to 1030 °C. When the atomic ratio of Zn is gradually increased, the amounts of $InGaZnO_4$ and $InGaZnO_6$ phases increase and those of In_2O_3 and $ZnGa_2O_4$ phases decrease. The above findings indicate the complexity of the microstructural changes during sintering of the IGZO powders. The objective of this study was thus to clarify the influences of sintering temperature (1200–1500 °C) on the sintering, microstructures, and electrical properties of IGZO targets with different ZnO contents.

2. Experimental procedure

In_2O_3, Ga_2O_3, and ZnO powders with median sizes of 0.1 μm, 0.1 μm, and 0.4 μm, respectively, were used to produce the IGZO ceramic targets. IGZO ceramics with molar fractions (In_2O_3:Ga_2O_3:ZnO) of 1:1:1 and 1:1:2 were investigated because these two fractions are the predominant compositions of IGZO films [1–9]. In this study, these two IGZO ceramics were designated as IGZO-111 and IGZO-112. To prepare the IGZO ceramic slurry with a solid content of 25 vol%, a 0.5 wt% dispersant of ammonium polyacrylate was first added into distilled water. The In_2O_3, Ga_2O_3, and ZnO powders were added into the aqueous solution, and then the powder slurry was ball milled with ZrO_2 grinding balls for three hours. The ball to powder ratio (BPR) of ball milling was 3:1. Afterwards, a 0.5 wt% binder of polyacrylic emulsion was added into the slurry and the slurry was ball milled for one additional hour.

The previous slurry was subsequently spray-dried in 140 °C air using a spray dryer (L-8, Ohkawara Kakohki Co., Yokohama, Japan). The IGZO spray-dried granules were spherical and ranged in size from 10 to 40 μm. To prepare the green compact, the IGZO spray-dried granules were uniaxially compacted at a pressure of 150 MPa into disks of 12.5 mm diameter and 4.5 mm thickness. For binder removal, the green compacts were heated at 5 °C/min to 600 °C and held for 30 min in air. Afterwards, the specimens were directly heated at 10 °C/min to the sintering temperatures (1200 °C, 1300 °C, 1400 °C, and 1500 °C) and were sintered for three hours in air, followed by furnace cooling.

Archimedes' method was used to evaluate the sintered densities as a function of sintering temperature. A dilatometer (DIL 402C, NETZSCH, Selb, Germany) was used to identify the amount and rate of the dimensional change during heating and sintering. To understand the evaporation behavior during high temperature sintering, thermogravimetric analysis (TGA, STA 449 F3, NETZSCH, Selb, Germany) and weight loss after sintering were measured. The sintered specimens were then fractured and thermally etched at 1100 °C for one hour. The etched fracture surfaces were observed by a field-emission SEM (LEO-1530, Zeiss, Oberhochem, Germany). The fracture surfaces were observed to collect valuable information on the three-dimensional distribution of pores and grains in the material. To understand the distributions of different phases, the cross-section of sintered specimens were sampled, ground, polished, thermally etched at 1100 °C for one hour, and then examined

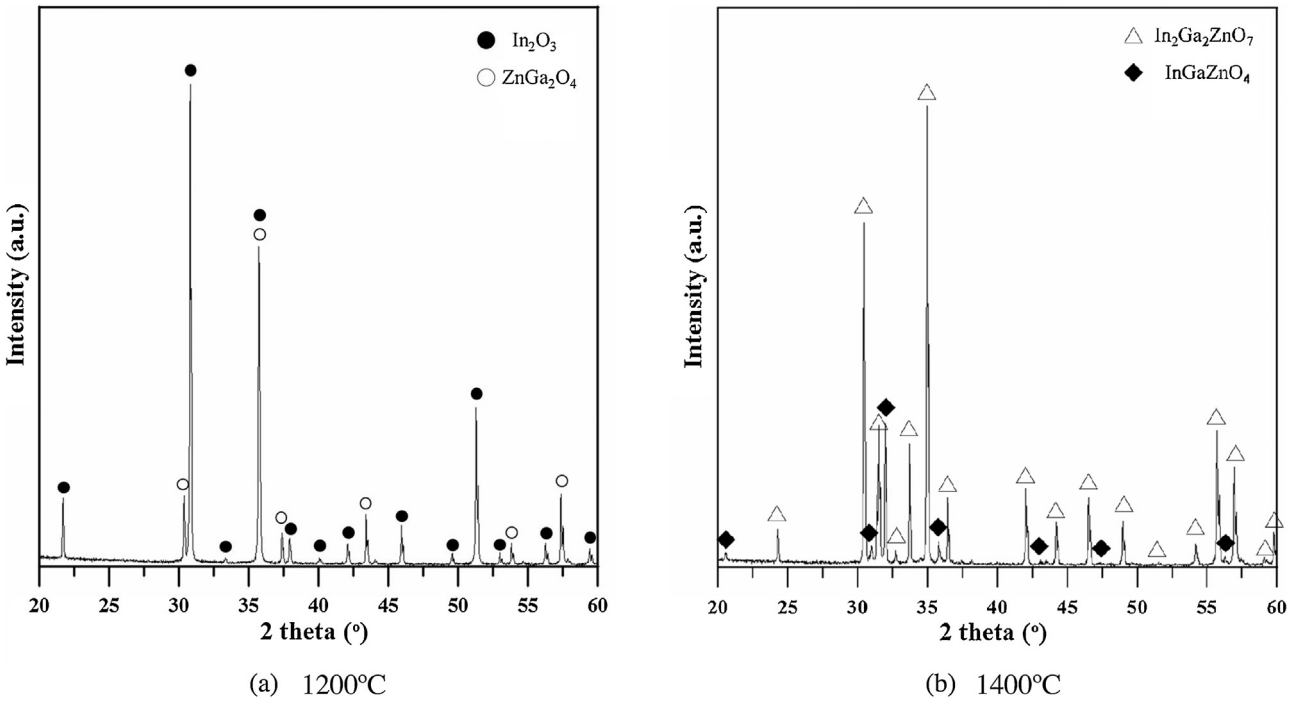

Fig. 1. X-ray diffraction patterns of IGZO-111 ceramics sintered at (a) 1200 °C and (b) 1400 °C.