Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 34 (2014) 3715–3722

www.elsevier.com/locate/jeurceramsoc

The sintering behavior, microstructure, and electrical properties of gallium-doped zinc oxide ceramic targets

Ming-Wei Wu [a,*], Pang-Hsin Lai [a], Chia-Hong Hong [b], Fang-Cheng Chou [c]

[a] Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei 10608, Taiwan, ROC
[b] Department of Materials Science and Engineering, National Formosa University, Huwei, Yunlin 63201, Taiwan, ROC
[c] Center for Condensed Matter and Science, National Taiwan University, Taipei 10617, Taiwan, ROC

Received 9 April 2014; received in revised form 5 May 2014; accepted 6 May 2014
Available online 28 May 2014

Abstract

The properties of sputtering targets have recently been found to affect the performances of sputtered films and the sputtering process. To develop high-quality GZO ceramic targets, the influences of Ga_2O_3 content and sintering temperature on the sintering behavior, microstructure, and electrical properties of GZO ceramic targets were studied.

The results showed that the increase in Ga_2O_3 content from 3 wt% (GZO-3Ga) and 5 wt% (GZO-5Ga) not only inhibited the densification but retarded grain growth. During sintering, $ZnGa_2O_4$ phase formed before 800 °C, and $Zn_9Ga_2O_{12}$ phase was found after sintering at 1000 °C. Moreover, after sintering at 1200 °C, the number of $Zn_9Ga_2O_{12}$ precipitates increased at the expense of $ZnGa_2O_4$ and $ZnGa_2O_4$ disappearing completely. The relative density, grain size, and resistivity of GZO-3Ga sintered at 1400 °C in air were 99.3%, 3.3 μm, and 2.8×10^{-3} Ω cm, respectively. These properties of GZO ceramics are comparable to properties reported in the literature for AZO sintered in air.

Keywords: GZO; Sintering; Microstructure-final; Electrical properties; Sputtering target

1. Introduction

Transparent conductive oxide (TCO) films have been extensively used as the transparent conductive electrode in the optoelectronic and related fields, in applications such as liquid crystal displays, solar cells, and touch panels. To date, tin-doped indium oxide (ITO) film is the predominant TCO film due to its low resistivity (<10^{-3} Ω cm) and high visible transmittance (>80%).[1,2] However, efforts to develop alternatives to ITO have been intense because the cost of ITO film is relatively high. Currently, gallium-doped zinc oxide (GZO) and aluminum-doped zinc oxide (AZO) films are regarded as potential TCO materials due to their versatility.[3–13] TCO films can be produced by magnetron sputtering, a multi-functional and versatile method, because of its high deposition rate, feasibility of large-area coating, low deposition temperature, and high quality of the film.[11–13] A key material in the production of TCO film is the sputtering target.

To optimize the performances of TCO films, most researchers have studied the influences of sputtering parameters on the properties of films, including the type of sputter power,[7,13] sputter power,[5,12] working pressure,[5] base pressure,[10] substrate temperature,[4–8,11] atmosphere,[12] film thickness,[3] and post annealing treatment.[7,9] Unfortunately, only a few studies have attempted to clarify how the TCO target affects the sputtering process and the properties of various films.[14–18] Moreover, the correlations between target performance and film properties, and the information about the properties and processes of sputtering targets, have not been well established. These underlying issues inhibit attempts to optimize sputtered films.

Recently, the importance of the sputtering target has been gradually revealed. The sintered density,[18] grain size,[19] electrical properties,[14,15] stoichiometry,[16,20,21] and microstructural uniformity[17] of the sputtering targets are now known to affect

* Corresponding author. Tel.: +886 2 2771 2171 ext. 2721; fax: +886 2 27317185.
E-mail addresses: mwwu@ntut.edu.tw, r91527045@ntu.edu.tw (M.-W. Wu).

http://dx.doi.org/10.1016/j.jeurceramsoc.2014.05.022
0955-2219/

significantly not only the properties of various thin films but also the sputtering process. Minami et al.[14] studied the influences of the electrical properties of nine commercial AZO targets on the properties of AZO films and indicated that a target with lower resistivity can be used to achieve a higher deposition rate, lower arcing counts, and a more uniform film having lower resistivity. Huang et al.[15] investigated the effects of sintering parameters on the characteristics of AZO targets and sputtered films. They also showed that an AZO target with lower resistivity can be used to produce films with better electrical properties and uniformity. These two studies clearly indicated that the electrical properties of AZO targets play an important role in determining film performance.

Moreover, several works have investigated the fabrications and properties of the various sputtering targets, particularly those of AZO ceramic targets.[15,22–33] Unfortunately, the studies concerning GZO ceramic targets have been rare. Liu et al.[34] investigated the effects of Ga_2O_3 content (0–3 wt%) on the properties of GZO ceramic targets. Wiff et al.[35] and Jung et al.[36] concentrated their studies on the Hall mobilities and thermoelectric properties of GZO ceramics, respectively. Before the correlations between GZO targets and films are identified, the process and characteristics of the GZO target must first be examined. The purpose of this study was thus to investigate the influences of Ga_2O_3 content (3 and 5 wt%) and sintering temperature (1200–1500 °C) on the sintering behavior, microstructure, and electrical properties of GZO ceramic targets.

2. Experimental procedure

In the literature, the compositions of GZO films[3,4,6–9] range from 3 to 5.56 wt%. Thus, the compositions of GZO ceramic targets (ZnO:Ga_2O_3) investigated in this study were 97:3 and 95:5 (wt%). The designations of these two GZO ceramics were GZO-3Ga and GZO-5Ga. ZnO and Ga_2O_3 powders with median particle sizes of 0.4 and 0.1 μm, respectively, were used in this study. A commercial ammonium polyacrylate of 0.2 wt% and a polyacrylic emulsion of 0.5 wt% were used as the dispersant and binder, respectively. The concentrations of the dispersant and the binder were based on the weight of the dry powder. To prepare GZO powder slurry, the dispersant of 0.2 wt% (2 g) was first added into distilled water (416 g), and the ZnO (970 g for GZO-3Ga; 950 g for GZO-5Ga) and Ga_2O_3 (30 g for GZO-3Ga; 50 g for GZO-5Ga) powders were subsequently added into the aqueous solution. The solid contents of these two GZO slurries were 30 vol%, which corresponded to 70.6 wt%. The slurry was ball milled with 2 mm-diameter ZrO_2 grinding balls for 3 h by a commercial ball mill (MUBM-340, Sun-Great Technology Co., Taiwan, ROC) with a rotation speed of 300 rpm. The ball to powder ratio (BPR) was only 3:1 because the role of the ZrO_2 grinding balls was not to refine the particle size of the ZnO and Ga_2O_3 powders but to help homogenize the ZnO and Ga_2O_3 powders in the slurry. Afterwards, the binder (5 g) was added into the slurry and the slurry was then ball milled for one extra hour.

The as-milled slurry was then spray-dried in hot air using a spray dryer (L-8, Ohkawara Kakohki Co., Yokohama, Japan). The inlet and outlet temperatures for spray drying were 140 and 90 °C, respectively. The sizes of GZO spray-dried granules ranged from 20 to 40 μm. The GZO granules (2.3 g) were compacted by dry pressing at a pressure of 150 MPa into green compact disks that were 13 mm in diameter and 5 mm thick. The green densities of GZO-3Ga and GZO-5Ga compacts were 3.43 and 3.44 g/cm^3, respectively. The green compacts were heated at 5 °C/min to 600 °C and held for 30 minutes to remove the organic additives. After 600 °C debinding, the densities of GZO-3Ga and GZO-5Ga ceramics were 3.48 and 3.50 g/cm^3, respectively. The debound specimens were then heated at 10 °C/min to the sintering temperatures (1200, 1300, 1400, and 1500 °C) for 3 h of sintering, followed by furnace cooling. The atmospheres for debinding and sintering were both air. The sintered densities of the specimens sintered at various temperatures were measured using Archimedes' method in distilled water. The weight loss after sintering was recorded to understand the evaporation phenomenon at different sintering temperatures. The influences of Ga_2O_3 concentration and sintering temperature on weight loss were also further evaluated using thermogravimetric analysis (TGA, STA 449 F3, NETZSCH, Selb, Germany). The TGA specimens were heated at 10 °C/min to 1500 °C for 1 h of sintering in air.

For microstructure examination, the specimens were ground, polished, and then thermally etched at 1050 °C for 1 h. The etched specimens were examined under field-emission SEM (LEO-1530, Zeiss, Oberhochem, Germany), and the average grain sizes were calculated according to quantitative metallography.[37] The crystal structure of the GZO ceramics were examined by X-ray diffractometer (D8, Brüker, Karlsruhe, Germany) with Cu Kα radiation. An electron probe microanalyzer (EPMA, JXA-8200SX, JEOL, Tokyo, Japan) was also used to determine the elemental distributions of Ga and Zn in the GZO ceramics. To clarify the effects of the Ga_2O_3 content and sintering temperature on the resistivity of GZO ceramics, the specimens sintered at various temperatures were analyzed at room temperature by four-point probe method using a source meter (2400, Keithely Instruments Inc., Cleveland, OH).

3. Results and discussion

3.1. Microstructure and grain size

Figs. 1 and 2 show the microstructures of GZO-3Ga and GZO-5Ga ceramics that were sintered at various temperatures, respectively. The result indicates that the densification of GZO-3Ga was obvious after sintering at 1300 °C. In contrast, the porosity of GZO-5Ga was still quite high, even after sintering at 1400 °C. The average grain sizes of two GZO ceramics as a function of the sintering temperatures are shown in Fig. 3. The results demonstrate that the grain sizes of GZO-3Ga and GZO-5Ga ceramics increased from 0.6 to 8.4 μm and from 0.5 to 3.1 μm, respectively, when the sintering temperature was increased from 1200 to 1500 °C. The findings on the microstructure and grain size show that increasing the Ga_2O_3 content from 3 to 5 wt% inhibited both the densification and the grain growth. Moreover, the small amounts of precipitates were mostly located