



Gallium-doped zinc oxide targets fabricated by sintering: Impact of target quality on sputtered thin film properties



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ABSTRACT

This research reports the sintering mechanism of Ga doped ZnO (GZO) ceramic targets. The GZO powders with different Ga doping concentrations were synthesized by chemical co-precipitation method and compacted to form green compacts. The green compacts underwent a normal sintering process under different temperatures. Then a series of GZO targets sintered at 1300 °C were used for depositing thin films by DC magnetron sputtering method. The influences of sintering temperature and doping concentration on the densification, structural and electrical properties of GZO targets were investigated. Results showed that Ga doping effectively promoted the qualities of GZO targets. When sintering temperature surpassed 1300 °C, the relative densities for all the targets were higher than 97%. The lowest resistivity of $2.25 \times 10^{-3} \Omega \text{ cm}$ was attained on the 0.5 at% Ga doped ZnO sintered at 1300 °C. In addition, the performances of GZO thin films were greatly influenced by the qualities of their sputtering targets.

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1. Introduction

Zinc oxide (ZnO) is a direct wide band gap ($E_g=3.37 \text{ eV}$) semiconductor possessing excellent electrical conductivity and optical properties (transparency in the visible). ZnO-based thin films are suitable for the fabrication of transparent conductive oxide (TCO) layer [1–6]. They are also appropriate candidates for substituting Indium-Tin Oxide (ITO) by virtue of low manufacture cost and non-toxicity. ZnO-based materials have been widely applied as transparent conductive electrodes on many kinds of optoelectronic and photovoltaic devices, such as light-emitting diodes (LEDs), laser diodes (LDs) and solar cells [7–10]. In

recent years, worldwide interests have been attracted on ZnO-based materials because various chemical elements are able to be doped into ZnO for modifying or enhancing properties. Among these, gallium (Ga) is a typical element for n-type doping. The ionic and covalent radii of Ga atom are 0.62 Å and 1.26 Å, respectively, approximate to those of Zn atom (0.74 Å and 1.34 Å), so the discrepancy between the covalent bond lengths of Ga–O (1.92 Å) and Zn–O (1.97 Å) is extremely small. As a result, significant structural deformation would not occur in GZO. In addition, Ga atom is relatively inactive in oxidizing atmosphere [11]. These distinct advantages make GZO a promising TCO material.

One of the most efficient ways of preparing GZO thin films is magnetron sputtering, which has distinct advantage in rapid deposition and production of large-scaled thin film, and also has potential to be applied for room

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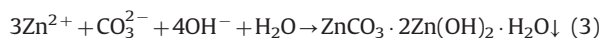
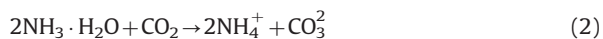
temperature process [12]. Similar as Al doped ZnO (AZO) thin films, GZO thin films are commonly prepared by sputtering ZnO and Ga₂O₃ targets simultaneously. However, this co-sputtering process is rather difficult to be controlled. So it is better to develop the Ga doped ZnO targets, and the sintering mechanism of GZO ceramic should be comprehensively investigated as the quality of thin films greatly depend on the properties of sputtering targets [13–14]. Until now, many studies have been reported about the sintering mechanism of AZO ceramic [15–17], but there are still seldom papers concerning the sintering mechanism of GZO ceramic.

In this article the sintering mechanism of GZO ceramic target was reported for the first time. We analyzed the influences of Ga doping concentration and sintering temperature on the properties of GZO ceramic in detail. In our study, GZO powders with different Ga/Zn atomic ratios were synthesized by a chemical co-precipitation method and compacted to green compacts, subsequently the green compacts underwent a sintering process. Various characterizations were carried out on the densification as well as the structural and electrical properties of sintered GZO targets. In order to verify the correlations between target and thin film, we employed the densest sintered targets with different Ga concentrations to sputter thin films. The optical and electrical properties of thin films were further investigated.

2. Experimental details

2.1. Production of powder and ceramic target

In this research, our study focused on the influences of two parameters: sintering temperature and doping concentration. The GZO ceramic targets were produced through powder metallurgy method, the whole process consists of four steps: (1) Co-precipitation method was adopted to prepare GZO powders. With the aim at obtaining highly pure metal nitrate solutions, 99.999% pure metal Zinc and Gallium (supplied by General Research Institution For NONFERROUS METALS, China) were dissolved into nitric acid, respectively. Then the two kinds of solutions were mixed together according to the Ga/Ga+Zn ratios ranging from 0.2 at% to 3 at%. Thereafter, carbamide (99% in purity) was continually added into the solutions until the pH value achieved about 8, which is the most suitable value for the generation of precipitations. The chemical equations of the process are given



(2) After reactions, precipitated precursors containing $\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and $\text{Ga}(\text{OH})_3$ were dried at 110 °C and grounded into powders. About 2 wt% adhesive

polyvinyl alcohol (PVA, 97% in purity, about 77087.5 ± 2202.5 in average molecular weight) was dissolved into de-ionized water at 90 °C and mixed with the powders completely. Then the powders were roasted in a muffle furnace at 450 °C for 3 h. (3) The roasted powders were put into Φ60 mm mold and contacted to form green compacts by a tablet-pressing machine. For the compressing process, the two key parameters: pressure and compressing time, were set to 4 MPa and 5 min, respectively. The relative densities of green compacts were about 61–63%. (4) Lastly, considering that the normal sintering method has advantages in the production of large-scaled and low-cost targets, all the green compacts were put in a resistance furnace for normal sintering. The whole temperature-increasing process was divided into three steps. The terminated temperatures of the first two steps were 750 °C, 900 °C, respectively. When one step ended, the terminated temperature was maintained for 1 h, and the temperature rising rate was constantly hold at 3 °C/min. For the last step, when the terminated temperatures reached 1100–1500 °C, the GZO targets were sintered for 2 h. Afterwards the samples were kept in furnace for cooling at the rate of 5 °C/min.

2.2. Thin film deposition

A series of sintered GZO targets were employed to prepare thin films by DC magnetron sputtering method. All the sputtering experiments were carried out in a single vacuum chamber which was evacuated to 1.2×10^{-6} Torr before deposition. The quartz glasses and silicon chips were chosen as substrates. Before deposition, the quartz glasses were dipped in the mixture of H₂SO₄ and H₂O₂ solutions (1:1 in volume), while the silicon chips were cleaned using RCA method. The sputtering DC power, Argon gas flow, oxygen flow and sputtering pressure were fixed at 300 W, 70 sccm, 0.5 sccm and 3.8×10^{-3} Torr, respectively. The deposition time and substrate temperature for all the thin films were 10 min and room temperature, respectively.

2.3. Characterization methods

The X-ray diffraction (XRD) was used to study the structural properties by an X-ray diffractometer (DMAX-III B type XRD, Cu Kα radiation Cu, Kα, λ=0.15418 nm) in the range of 20–70°. The morphologies of powders were investigated using a transmission electron microscopy (TEM) JEOL2100 which runs at 200 kV. The micro-morphologies of thin films and etched targets were observed using a scanning electron microscopy (SEM) NOVA NANOSEM200. The densities of GZO targets were tested by a BSA224S-CW balance and the thicknesses of GZO thin films were measured by a Dektak 6M step profiler. The electrical properties were evaluated based on resistivity ρ, mobility μ and carrier concentration n. Carrier concentration were measured by Hall test while resistivity were obtain through 4-probe method, and mobility was calculated by the formula: $en\mu\rho=1$. The optical transmittance and reflection spectra were obtained

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