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# Investigation of aluminum and gallium co-doped ZnO powders and their effects on the properties of targets

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ABSTRACT

Aluminum and gallium co-doped ZnO (AGZ) powders were synthesized by the chemical co-precipitation method with the same Al doping concentration (3 at%) and different Ga doping concentrations (0–0.5 at%). The microstructure, lattice distortion and surface morphology of AGZ powders were investigated because the properties of targets were related to corresponding powders. Both AZO and AGZ targets were prepared by molding and atmospheric pressure sintering. The microstructure, morphologies, electrical properties and densification of sintered targets were also studied. The measured results showed that the grain sizes of AGZ powders are smaller than AZO powder, the former has a larger specific area, and the distribution of AGZ particles are more homogeneous, which are good for preparation of a high-density target. Besides, the extent of ZnO lattice distortion exhibits a downward trend with the increase of the Ga doping concentration. The AGZ target with appropriate concentration of Ga (0.3 at%) has the lowest resistivity of $2.518 \times 10^{-3}\ \Omega$ cm and the highest relative density of 99.2%. In general, the moderate Al–Ga co-doping proportion leads to finer grain size, lower resistivity, higher Hall mobility and higher sintered density.



## 1. Introduction

Recently, transparent conductive oxide (TCO) materials have attracted attention due to their high optical transmittance ( > 80%) and low resistivity ($10^{-3}\ \Omega$ cm). They have been used extensively in liquid crystal displays, solar cells, and other optoelectronic devices as the transparent conductive electrode [1,2]. Currently the most developed TCO technology for practical applications is based on indium-tin-oxide (ITO). However, alternatives to ITO have been extensively developed because of the shortage and high cost of indium [3,4].

Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap of 3.37 eV at room temperature and doped ZnO is one of the most promising replacements for ITO [5–7]. When doped with III elements, such as B, Al, Ga or In, the electrical resistivity of ZnO decreases [8–10]. Al-doped ZnO (AZO) [11] and Ga-doped ZnO [4] are the most widely developed TCO materials for transparent electrode and infrared insulator application. Recently, the Al–Ga co-doped ZnO (AGZ) material has been studied and some improvements in properties have been proven. Agyeman et al. [12] reported that they successfully prepared aluminum and gallium co-doped zinc oxide (AGZ) films on glass substrates by RF magnetron sputtering under different substrate temperatures, and the pure ZnO target doped with $Al_2O_3$ (2 wt%) and $Ga_2O_3$ (1 wt%) was used as the target. There are several techniques, including chemical vapor deposition [13],

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sol–gel [14], pulsed laser deposition (PLD) [15] and magnetron sputtering [16] that can be used for the deposition of TCO films. Magnetron sputtering is a versatile method for its high deposition rate, low deposition temperature, feasibility for large-area deposition, and high quality of films [17]. Therefore, the sputtering targets have become the key materials required, as have the related powders, which are used for fabricating the targets. However, few studies have been carried out on Al–Ga co-doped ZnO materials.

In this study, AGZ powders with different Ga doped proportions were synthesized by the chemical co-precipitation method. For comparison, AZO powder with the same Al doped proportion was also produced in the same way. The effects of additional Al–Ga co-doping on the microstructure, lattice distortion and surface morphology of ZnO powders were investigated. Then, AZO and AGZ ceramic targets were prepared by sintering as-synthesized powders at 1450 °C for 2.5 h. The microstructure, morphologies, electrical properties and densification of these targets were also studied to illustrate the advantage of the AGZ target with the appropriate concentration doping of Al and Ga.

## 2. Experimental

Al-doped ZnO powder and Al–Ga co-doped ZnO powders were synthesized by the chemical co-precipitation method. Made by dissolving metal zinc, aluminum, gallium in nitric acid separately, $Zn(NO_3)_2$, $Al(NO_3)_3$ and $Ga(NO_3)_3$, together with $CO(NH_2)_2$ were used as starting materials, dopant and precipitator, respectively. All the three metals were 99.999% in purity, while nitric acid and $CO(NH_2)_2$ were analytic reagent and used without further purification. Moreover, the Al doping concentration was fixed at 3 at% for all samples, while Ga doping concentration varied from 0 to 0.5 at%.

Firstly, $Zn(NO_3)_2$, $Al(NO_3)_3$, $Ga(NO_3)_3$ and $CO(NH_2)_2$ were separately dissolved in de-ionized water. Then, appropriate amounts of $Al(NO_3)_3$ and $Ga(NO_3)_3$ solutions were added into the $Zn(NO_3)_2$ solution to obtain the desired Al-doping or Al–Ga co-doping concentration. Finally, a $CO(NH_2)_2$ solution was slowly added into the mixture solutions. The solutions were continually stirred at 100 °C for three hours to yield precipitates. The PH value of the buffer solutions were maintained as 8 for better precipitation reaction. The white precipitates were repeatedly filtered and washed with de-ionized water and dried in a drying oven at 110 °C for 24 h. AZO and AGZ powders were obtained after the precipitates were annealed at 500 °C for 2.5 h. The adhesive polyvinyl alcohol (PVA) was dissolved into de-ionized water at 90 °C, and then mixed with AZO powder or AGZ powders with a concentration of 2 wt% until saturated. Then, the solutions were dried at 110 °C for 24 h again and ground into powders. The powders were put into the mold of ⌀10 mm and compacted under 4 MPa to the pre-targets. In order to obtain the high-quality ceramic targets, the obtained green compacts were sintered at 1450 °C for 2.5 h. For simplicity, as-prepared samples with Ga concentration of 0, 0.1 at%, 0.2 at%, 0.3 at%, 0.4 at% and 0.5 at% were named AZO, AGZ1, AGZ2, AGZ3, AGZ4 and AGZ5, respectively.

All powders and targets were analyzed using a X-ray diffractometer (Shimadu XRD-6000, Japan) with a Cu-Kα ($\lambda$=0.15406 nm) radiation source. The average grain sizes were calculated by the Scherrer formula. The fracture morphology and particle size of powders were examined by a scanning electron microscope (SEM, JSM-7500F) and transmission electron microscopy (TEM,JEOL JEM-2100), while the morphology and compositional analysis of targets were studied by a focused ion beam (FIB)-scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). The powders for TEM measurements were prepared by depositing a drop of nanocrystals ethanol solution onto carbon-coated copper grids. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 spectrometer using an Al-Kα X-ray as the excitation source. The density was measured by BSA224S-CW balance and the resistivity was investigated by a Hall test from Institute of Semiconductors, Chinese Academy of Sciences.

## 3. Results and discussion

### 3.1. Properties of AZO and AGZ powders

Fig. 1(a) shows the X-ray diffraction patterns of prepared AZO and AGZ powders. All diffraction peaks, which

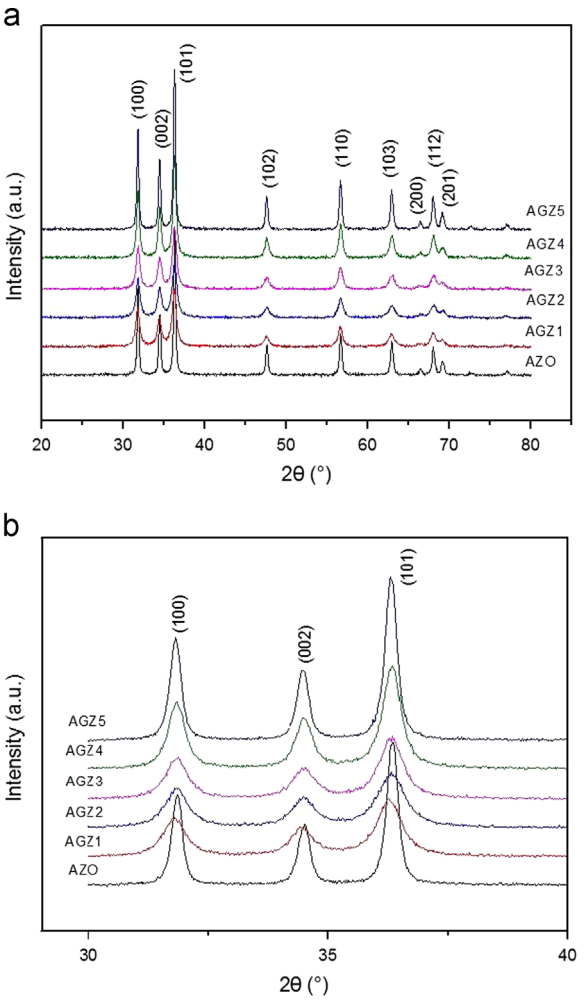


**Fig. 1.** (a) X-ray diffraction patterns of AZO and AGZ powders and (b) enlarge figure of XRD patterns.