Materials Science in Semiconductor Processing 84 (2018) 17–23

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Preparation of high-density $InGaZnO_4$ target by the assistance of cold sintering

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ARTICLE INFO

Keywords:
$InGaZnO_4$
Precipitation method
Cold sintering process
Densification
Master sintering curve

ABSTRACT

In this study, near stoichiometric $InGaZnO_4$ (IGZO) nano-powders were synthesized by a multistep precipitation method with the ammonia solution used as precipitant at 10 °C. Then cold sintering process (CSP) was applied to benefit the green pellets. In the next step, the green pellets fabricated by CSP and dry pressing process (CP) were pressureless sintered (PLS) at 1200 °C or higher temperature for a scheduled time respectively. The in-situ high temperature optical dilatometric test, XRF, XRD and SEM were carried out and the sintering kinetics was analyzed based on the Master Sintering Curve (MSC) model. The results showed that the holding time for densification of CSP/PLS pellets was about 1 h at 1200 °C, just about 1/5 of CP/PLS ones. MSC model revealed that the sintering activation energy (Qa) of CSP/PLS and CP/PLS were 489.7 KJ /mol and 655.6 KJ /mol respectively. The highest relative density (99.30%) of all sintered pellets was achieved by CSP/PLS process and the optimal process parameters were CSP at 180 °C, 200 MPa and 10 min, and PLS at 1200 °C for 1 h. CSP/PLS effectively reduced the sintering temperature and holding time in comparison with the CP/PLS in this research and previous research.

1. Introduction

$InGaZnO_4$ is a n type conductive oxide with excellent optical transparency and high electron mobility [1]. In recent years, amorphous indium–gallium–zinc-oxide (IGZO) has been widely used as the channel material of thin-film transistors (TFT) in FPD [2–5]. IGZO films in industry are mainly fabricated by magnetron sputtering of the corresponding targets. As the quality of the IGZO target is vital to the properties of oxide films, several studies have been conducted to the preparation of $InGaZnO_4$ target in recent years [3,5,6]. In these researches, harsh conditions of experiment conditions such as high sintering temperature and long holding time are indispensable. However, longer sintering time and higher sintering temperature mean the increase of thermal energy. Thus, it is economical to decrease the sintering time or the sintering temperature.

Recently, Guo and his colleagues proposed the concept of Cold Sintering Process, which could produce dense ceramics at substantially reduced temperatures compared with the conventional solid-phase sintering method [7–12]. In their researches, ceramic powders were uniformly wetted with a small amount of water or volatile solution. When the powders were pressed with a given temperature and external pressure, the particle surface free energy was minimized and the ceramic solid particles were compacted in the process of dissolution precipitation. In this way, they had successfully demonstrated its feasibility to achieve relative density of 80–99% at incredibly low temperatures of 25–300 °C within a short time period of 1–60 min [7].

Also, sintering has long been recognized as a complicated process. Johnson and coworkers [13] developed the master sintering curve (MSC) method on the basis of combined stage sintering mode proposed by Hansen [14]. It was assumed that only one diffusion mechanism dominates in the sintering process, the MSC model was expressed by following equation [14–16]:

$$\frac{k}{\gamma\Omega D_0}\int_{\rho_0}^{\rho}\frac{(G(\rho))^n}{3\rho\Gamma(\rho)}d\rho=\int_0^t\frac{1}{T}\exp(-\frac{Q_a}{RT})dT \quad (1)$$

where γ is the surface energy, Ω is the atomic volume, k is the Boltzmann constant, T is the thermodynamic temperature and t is the time, G is the mean grain size, ρ is sample density, D_0 is the coefficient of diffusion process, Qa is the sintering activation energy, Γ is geometric factors which represents driving force for sintering. The parameter Θ represents the time-temperature profile of the sintering process and Θ_0 is the value of Θ at the point of inflection of the sintering curve.

In this model, the sintering parameters can be divided into two categories: time, temperature and parameters describing

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https://doi.org/10.1016/j.mssp.2018.04.030
Received 20 November 2017; Received in revised form 10 April 2018; Accepted 22 April 2018

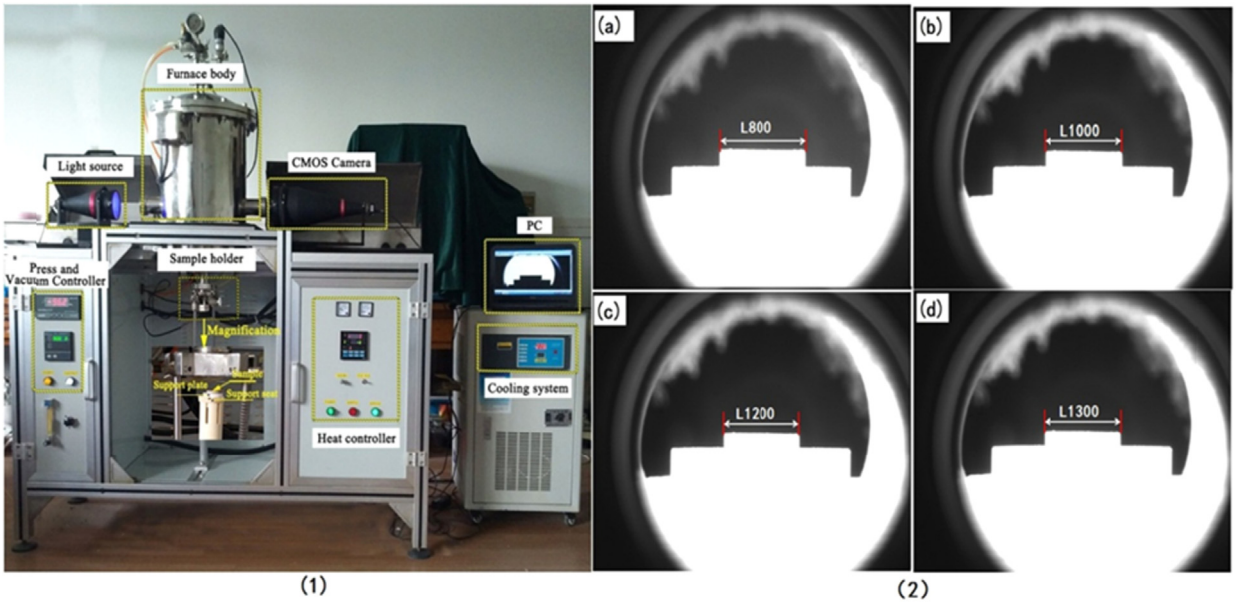

Fig. 1. (1) Photograph of the homemade in-situ high temperature optical dilatometer; (2) the image of the pellet sintered at different temperatures (a) 800 °C; (b) 1000 °C; (c) 1200 °C; (d) 1300 °C.

microstructural evolution. The right side of Eq. (1) is usually assigned as:

$$\Theta(t,\ T(t)) \equiv \int_0^t \frac{1}{T}\exp(-\frac{Q_a}{RT})dT \tag{2}$$

According to MSC formulation, the relationship between the density ρ and Θ can be described by following function:

$$\rho = \rho_0 + \frac{a}{[1+\exp(-\frac{\log(\Theta)-\log(\Theta_0)}{b})]^c} \tag{3}$$

MSC provides a simple way to predict the final sintering density. Teng [17] proposed the computer program which imported the experimental data of density, time and temperature into MSC model to calculate the sintering activation energy Qa. The accuracy of this model has been proved by many researches [15,17,18].

This study aimed to achieve high-density $InGaZnO_4$ target with lower sintering temperature and shorter sintering time. In this research, IGZO precursor powder was synthesized by a multistep precipitation method. Then CSP was used to benefit the green pellets. At the same time, the calcined precursor powders were dry pressed (CPed) at room temperature without adding water and any binder. Then the two kinds of pellets were pressureless sintered (PLSed) to compare the sintering behavior. In-situ high temperature optical dilatometer, MSC model and Teng's software [17] were applied to describe the whole sintering process and calculated Qa for the two methods.

2. Experimental section

2.1. Preparation of IGZO precursor powders

All the chemical reagents were analytical grade without further purification. 0.15 mol In_2O_3, 0.15 mol Ga_2O_3 and 0.3 mol ZnO were dissolved with nitric acid (HNO_3, 65%) in the hot water bath to prepare the $In(NO_3)_3$, $Ga(NO_3)_3$ and $Zn(NO_3)_2$ solution, respectively. Then $Ga(NO_3)_3$, $In(NO_3)_3$, and $Zn(NO_3)_2$ solution were diluted to 0.3 mol/L and successively dropped into the reaction vessel by peristaltic pump, the ammonia solution was added into the vessel at the same time. In the process, reaction pH values of Ga^{3+}, In^{3+}, Zn^{2+} were kept at 4.2, 4.8 and 8.15 respectively by adjusting the rate of ammonia solution droplets. The reaction temperature was kept at 10 °C in the whole precipitation process. Then the obtained precipitate was washed repeatedly with distilled water, followed by spray drying and calcination at 600 °C for 1 h.

2.2. Preparation of IGZO pellets

The precursor powders were mixed with ammonia solution of 15 wt % with the PH value of 10.5. After powders were pressed at different pressures of 100, 200, 280, 350 MPa for 10 min at different temperatures (25, 77, 126, 180 °C), the pellets were kept at 200 °C overnight in the oven to eliminate residual solution. The obtained pellets were heated up to 1200 °C for 1 h at the heating rate of 5 °C/min. In the next step, the CSP pellets which obtained the highest density were chosen to be heated to 1400 °C at heating rates of 2 °C/min, 3 °C/min and 5 °C/min respectively to construct master sintering curve. To make a comparison, green pellets using the same precursor powder were CPed under the same pressure at room temperature, then the pellets were PLSed in the same way as the CSP pellets.

2.3. Characterization

X-ray fluorescence diffraction (Panalytical, Holland) was carried out to identify the chemical composition of the IGZO precursor powder. The phase composition of the pellets were analyzed by X-ray diffraction (Shimadzu, Japan) equipped with a Cu Kα radiation source (λ = 1.5418 Å) at a scan rate of 10 °/min (2θ from 10° to 80°). The sintering processes of pellets were observed by a home-made in-situ high temperature optical dilatometer [19]. Fig. 1 shows the photograph of homemade in-situ high temperature optical dilatometer (Accuracy of 0.001 mm). Densities of the green bodies and ceramic samples sintered below 1300 °C were calculated from their dimensions and weights, the size of in-situ target images were measured by Image-Pro Plus 6.0 and the accuracy was 0.001 mm. The densities of the ceramic targets sintered at 1300 °C were measured by using Archimedes' method in distilled water by Mechanical Balance (Accuracy of 0.1 mg, Shanghai, China). The fracture morphology of the samples was analyzed by field-emission scanning electron microscopy (FEI 200, Holland Sirion, Japan JSM-7600F, 10 kV). The pore size distribution was examined by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption (V-sorb X800 series, App one technology, Beijing,China).