Study on the IGZO Ceramics Sintered at Different Temperatures

Chao Qi¹, Jingming Zhong², Jie Chen¹, Wen Luo², Benshuang Sun¹, Bingning Liu¹, Yongchun Shu¹, Jilin He¹

¹ Henan Province Industrial Technology Research Institute of Resources and Materials, Zhengzhou University, Zhengzhou 450001, China
² State Key Laboratory of Special Rare Metal Materials, Northwest Rare Metal Materials Research Institute, Shizuishan 753000, China

Jack113.gg@163.com (Jie Chen), zhongjm@cnmnc.com (Jingming Zhong).

Abstract. In this study, the IGZO target was synthesized through a pressureless oxygen atmosphere sintering technique, and the effects of sintering temperature on IGZO ceramic target were studied. The In₂O₃, Ga₂O₃ and ZnO powders in the mole ratio of 1:1:2 were selected as raw materials. The powders were mixed by ball milling, and then the granulation and pressing process were used in order to obtain the green compacts. Then the green compacts were sintered at different temperature under oxygen atmosphere. The microstructure characterizations and compositions of the IGZO ceramic targets were analyzed. The results indicated that the lower sintering temperature was beneficial for IGZO ceramics to form the regular polygonal grains. With the temperature increased, the densification of IGZO ceramics was highly activated, and the low porosity was obtained. The XRD results demonstrated that the single phase of InGaZnO₄ had been generated at 1100°C and no phase transformation occurred between 1300°C and 1500°C. However, the SEM results showed that the grain growth of IGZO target was very obvious at 1500°C. The IGZO ceramic had a highest relative density of 99.4% and optimal resistivity of 18 mΩ·cm at the sintering temperature of 1400°C.

1. Introduction

The continuous advances in display technologies have prompted considerable interest in flexible displays, electronics and transparent electrodes[1-2]. Moreover, the amorphous indium-gallium-zinc(α-IGZO) thin-films have received much attention in the field of thin film transistors (TFT), which is the indispensable device for making flat panel display [3]. Compared with the α-Si and LTPS (Low Temperature Poly-silicon) TFT (Thin Film Transistor), IGZO-TFT has two obvious advantages [4]. On the one hand, the leakage current of the IGZO transistor is much lower than LTPS or α-Si technology [5]. On the other hand, the IGZO can pass 20-50 times more electrical current than equivalent amorphous silicon TFT[6]. Therefore, it is necessary to study high performance IGZO ceramics for preparing IGZO thin films [7-8].

With the development of flat panel display industry, the development of IGZO target shows the following trends [9-11]: (1) Low resistivity: transparent conductive films with smaller resistivity are needed due to the high requirements on the driver device. Therefore, the resistivity of the IGZO targets should be as lower as possible. (2) High density (relative density > 99%): the low target density will
decrease the effective sputtering area, and then the sputtering speed will decrease. At the same time, the high density target can prolong the service life of target and reduce application cost. (3) Improved utilization rate: Improving target utilization rate has always been the direction from equipment manufacturers, users and target manufacturers. The design of magnetron sputtering magnets moving periodically from front and back, the improvement of sputtering parameters, and the development of tubular target greatly increased the utilization rate of the targets [12-13].

In order to prepare high performance IGZO films, it is necessary to study high performance IGZO targets as sputtering materials [14-15]. At first, in order to optimize the performances of sputtered films, the correlations between target performance and film properties must be thoroughly clarified [16]. For the oxide targets, these factors are critical to the performance of the target, such as, the activity of powders, sintered density, grain size and electrical properties of targets can obviously affect the sputtering process and the film properties. Meiet al. [17] investigated the effects of particle size and dispersion methods of In$_2$O$_3$-SnO$_2$ mixed powders on the properties of ITO ceramics, the study demonstrated that the dispersion of mechanical ball-mill methods for nanosized In$_2$O$_3$ and SnO$_2$ powders is beneficial to the densification and structural homogeneity, and the smaller the relative grain size, the more uniform the distribution of grain size. Furthermore, Han et al. [18]investigated the densification and grain growth of ZnO doped with Al during isothermal sintering between 1100 and 1400 °C. In this study, a mechanism of pore surface drag (pinning) on densification equivalent to the observed drag (pinning) of grain boundaries on grain growth was proposed. Ma et al. [19] fabricated ITO sputtering targets using In$_2$O$_3$-SnO$_2$ mixed powders and tin doped indium oxide powders, respectively. Meanwhile, the difference in microstructure and sintering mechanism, especially grain size distribution, grain morphology, major element distribution and sintering rate, were studied. Lee et al. [20] found that when the O$_2$ flow rate was zero, the results of a Hall measurement of a-IGZO films deposited from targets with higher Zn atomic ratio showed lower resistivity, higher carrier concentration, and lower mobility. Nevertheless, as the O$_2$ flow rate was more than 5 sccm, the result was opposite.

For the preparation of IGZO ceramics, the In$_2$O$_3$, Ga$_2$O$_3$, and ZnO powders are the raw materials. Then, the ball milling, drying, forming and sintering technology were used for obtaining the final product of IGZO target. However, little research has been done on composition transformation and densification process of IGZO ceramics during sintering. In the sintering process of target material, the changes of microstructure and phase transformation are complicated. Therefore, it is necessary to study the sintering process of IGZO ceramics at different temperature for improving the properties of IGZO ceramics. In this study, the influences of sintering temperature on the sintering process, microstructures, and electrical properties of IGZO targets are clarified.

2. Experiments

2.1 Powder processing and forming
The In$_2$O$_3$, Ga$_2$O$_3$ and ZnO powders were mixed in the mole ratio of 1:1:2. The purity of the powders was 99.99%, and the median size of In$_2$O$_3$, Ga$_2$O$_3$ and ZnO were 40nm, 3μm and 0.2μm, respectively. The raw material powders with the above proportion were put in the zirconia ball mill. Water and organic dispersant were added to improve the ball milling effect of the slurry. And then the high energy planetary ball milling technology was used for ball milling process. The rotating speed of ball mill was 200r/min, and the ball milling time over 48 hours. In order to improve the cohesiveness of spray-dried powder, polyvinyl alcohol (PVA)0.8 wt% was added into the slurry and milled for one additional hour. During ball milling, the solid content of slurry was about 60%.

Then the previous slurry was spray-dried to improve the liquidity of mixed powders. Thus, the pressing properties of mixed powders can be improved. The drying temperature of slurry was 200°C and the feeding speed was about 5ml/min. Then, the spray dried powders were obtained and the size ranged from 10 to 30μm, which have good fluidity and filling property.
Then the spray-dried powders were pressed into the green compact disks. The green compacts of IGZO ceramics with 50mm diameter and 6mm height were obtained by using uniaxial dry-pressing (50MPa) and cold isostatic pressing (250MPa). The purpose of cold isostatic pressing was to improve the density and eliminate internal stress of green compacts. After cold isostatic pressing, the green compacts with 46mm diameter and 5.7mm height was obtained.

2.2 Sintering of IGZO ceramics
The green compacts were heated at 3°C /min to 750°C and held for 2 hours in air to remove the additive. Then, the green compacts were directly heated to 1100°C, 1300°C and 1500°C at 3°C /min, respectively, and held the temperature for 8 hours under oxygen atmosphere, then followed by furnace cooling. After the characterization of above samples, another green compact was sintered at 1400 °C, and other experimental conditions were the same.

2.3 Sample characterization
The density of IGZO target prepared at different sintering temperatures was measured by Archimedes’ method. The shrinkage rates of the IGZO ceramics in the sintering process were determined using a thermomechanical analyzer(PCY-1600, Xiang Yi instrument co, Ltd, China). In addition, the X-ray diffractometer (D8, Bruker, Karlsruhe, Germany) was used to confirm the crystal structures of IGZO ceramics. To understand the microscopic morphology of IGZO ceramics, the cross-section of sintered specimens were ground, polished, thermally etched at 1100 °C for one hour, and examined by a scanning electron microscope (SEM, Quanta 250 FEG, American).The average grain size of the sample was analyzed by Nano Measure. The fracture surfaces were observed to collect valuable information on the three-dimensional distribution of pores and grains in the material[21]. In addition, the effects of sintering temperature and corresponding microstructure on the resistivity of IGZO ceramics were studied by four-point probe method.

![Figure 1](image)

**Figure 1.** (a) the SEM images of the Ga2O3 raw powders, (b) the enlarged view of (a), (c) and IGZO spray-dried particle, (d) the enlarged view of (c).

3. Results and discussion

3.1 Powder treatment
The morphology of the Ga2O3 powders and IGZO spray-dried powders were observed using SEM as shown in Figure 1. It is obvious that the particle size distribution of Ga2O3 was uneven, and the particle size was quite different from that of other raw material powders (In2O3, ZnO) (Figure 2). The
average particle size of raw Ga$_2$O$_3$ powders was about 3μm, and the Ga$_2$O$_3$ powders showed the porous rod-like structure. After wet grinding with ZrO$_2$ grinding balls for more than 48 hours, the rod-like particles of Ga$_2$O$_3$ was broken into small granules, and the median size of Ga$_2$O$_3$ powder was decreased to 0.4 μm. The results showed that ball milling can effectively decrease the primary particle size of raw powders and improve the sintering activity of powder[22].

The ball milled IGZO slurry mixture was used for granulation. Figure1(c) shows the spray-dried powders, it can be seen that granulated particles were individually spherical, which would be helpful to the fluidization of powders.

![Figure 2](image1.png)

**Figure 2.** (a) the TEM images of the In$_2$O$_3$ powders, (b) the ZnO powders.

![Figure 3](image2.png)

**Figure 3.** X-ray diffraction patterns of IGZO ceramics sintered at different temperature.

### 3.2 Phase evolution and thermal analysis of the IGZO ceramics

The crystal structures of IGZO ceramics are shown in Figure 3. According to the XRD patterns, it can be seen that both the samples sintered at 1300 °C and 1500 °C were single InGaZnO$_4$ phase, and no phase transformation occurred between the 1300 °C and 1500 °C during the sintering process, but there were residual In$_2$O$_3$ phase at 1100 °C. This result showed that the reaction was completed between 1100 °C and 1300 °C. According to the XRD patterns of IGZO ceramics in Figure 3, it can be concluded that the phase structures were indexed to the InGaZnO$_4$ (ICDD card 70–3625) with lattice parameters as $a = b = 3.299$ Å and $c = 26.101$ Å and the In$_2$O$_3$ (ICDD card 06–0416) with lattice parameters as $a = b = c = 10.118$ Å.

In order to further study the sintering behavior of IGZO ceramics, the densification process of the IGZO green compact was analyzed using a thermomechanical analyzer. First, the bar-shaped green compacts were fabricated by above-mentioned forming process. The sample was heated at 3 °C/min
to 1500 °C in air. The dates of sample size varying with temperature during heating were recorded, and the results were shown in Figure 3. It could be observed that there was a slight expansion at the beginning in this shrinkage curve, which could be attributed to the difference in volume between the original reactants (In₂O₃, Ga₂O₃, and ZnO) and the final products (InGaZnO₄) during the heating period [21]. Again, this can also be observed that the expansion rate was higher than shrinkage rate at the beginning. With increasing temperature, the densification was occurred, and the shrinkage of the sample exceeded its expansion. It is obvious that the ceramic sample began to shrink when the temperature reached to 742 °C. With the increasing temperature, the sample shrank continuously. The linear shrinkage of the sample reached 15.6% when the temperature was 1321 °C. However, the linear shrinkage of the sample kept stable and did not obviously change as further increase in temperature. When the temperature increased to 1500 °C, the linear shrinkage of the IGZO ceramics was 15.67%. Therefore, it can be concluded that the main densification of the sample was finished when the temperature was 1321 °C. In addition, it can be seen from Figure 4 that the densification was activated when the range of sintering temperature was 882 °C to 1321 °C. In this temperature range, the maximum shrinkage rate of the IGZO ceramic sample was 0.632 %/min when the temperature was 1230 °C. Then the shrinkage rate decreased gradually with further increasing temperature.

![Figure 4](image1.png)

**Figure 4.** Shrinkage and shrinkage rate of the IGZO ceramics as increasing temperature.

![Figure 5](image2.png)

**Figure 5.** Micrographs of fracture surface of the IGZO ceramics sintered at 1100 °C (a), 1300 °C (b), 1400 °C (c) and 1500 °C (d).
3.3 **Microstructure and grain size of the IGZO ceramics**

Figure 5 shows the microstructures of fracture surface of the IGZO ceramics sintered at different temperature. It can be found that the sample mainly consisted of many powders after sintering at 1100 °C, the bond between the grains was not completed, and the degree of densification was low.

According to the result of X-ray diffraction in Figure 3 and shrinkage of IGZO ceramics in Figure 4, it can be concluded that the reaction of green body was uncompleted and the densification process has not completed yet. It’s obvious that the grain combination was closer as increasing temperature, and pores on the fractured surfaces of the specimen was decreased. It can be indicated that the densification of IGZO ceramics improved as the increasing sintering temperature. However, the grain size of IGZO ceramic was rapidly increased when the sintering temperature was increased to 1500 °C. In addition, it also can be found that the fracture mode of the sample changed from transgranular fracture at 1300-1400 °C to intergranular fracture at 1500 °C.

The morphologies of polished surfaces of IGZO ceramics sintered at different temperature are shown in Figure 6. Due to the state of IGZO ceramics was loose powder after sintering at 1100 °C (Figure5a), and the complete grains were not formed, so the polished SEM morphology sintered at 1100 °C was not shown in Figure 5. It has been found that there were still obvious porous in the ceramics after sintering at 1100°C, and in a state of loose powder stacked together (Figure5a). However, the pores in the ceramic were significantly reduced after sintering at 1300°C. And the amount of pores decreased as the sintering temperature increased. It’s obvious that the amount of pores in ceramics sintered at 1400°C and 1500°C were lower than that sintered at 1300°C. Besides, some cracks existed in the gap between grains when the sintering temperature was 1300°C. When the temperature increased to 1400 °C, there were almost no cracks. However, with the further increase of sintering temperature, the cracks existed in the grain interior when the sintering temperature was 1500°C. And the excessive sintering temperature would be harmful to the properties of ceramics. At the same time, it can be concluded that the IGZO ceramics had high density and the densification was most completed after sintering at 1400°C. In addition, the grain size of ceramics was related to sintering temperature.

![Figure 6. SEM micrographs of polished surfaces of the IGZO ceramics sintered at 1300°C (a), 1400°C (b) and 1500°C (c).](image)

Moreover, the sintering temperature significantly affected the grain size of IGZO ceramics. The average grain size of IGZO ceramics as a function of sintering temperature was shown in Figure 7. It is obvious that the grain size increased with the increase of sintering temperature. When the temperature increased from 1300°C to 1400°C, the average grain size of IGZO ceramics increased from 7.06μm to
9.28\mu m. But when the temperature increased to 1500°C, the average grain size rapidly increased to 42.09\mu m. It is possible that the exist of pores and cracks inhibited the grain growth when the temperature was relatively low. The densification degree of ceramics increased with increasing temperature, the amount of pores and cracks decreased, and the grain size increased more easily as temperature. But too high temperature tends to cause excessive grain size and lead to a negative effect on the properties of ceramics.

![Figure 7](image)

**Figure 7.** Average grain size of IGZO ceramics as a function of sintering temperature.

![Figure 8](image)

**Figure 8.** Sintered density and relative density of IGZO ceramics as functions of sintering temperature.

3.4 Densification process of the IGZO ceramics

Figure 8 shows the sintered density and relative density of IGZO ceramics as functions of sintering temperature. It can be found that the sintered density of IGZO ceramics increased rapidly from 3.907 g/cm³ to 6.281 g/cm³ when the sintering temperature increased from 1100°C to 1300°C. And there was a highest density of 6.323 g/cm³ at 1400°C. However, the sintered density was slightly reduced when the temperature increased to 1500°C. This result was consistent with the previous microstructure of IGZO ceramics (Figure 5 and 6). The theoretical density of InGaZnO₄ was 6.355 g/cm³ (JCPDS 70-
Thus, the relative densities can be calculated as the sintered densities divided by the theoretical densities [23]. The result of relative densities showed the changes of porosity in the process of sintering. With the sintering temperature increased from 1100°C to 1300°C, the relative density of IGZO ceramics increased from 61.5% to 98.8%. It is indicated that the densification process mainly taken place at this temperature range, which was consistent with the results of microstructure and shrinkage curve of the IGZO ceramics [24]. The relative densities increased to maximum at 1400°C and then decreased at 1500°C. The maximum value was 99.4% when the sintering temperature was 1400°C.

3.5 Electrical properties of the IGZO ceramics

In order to study the effect of sintering temperature on the electrical properties of IGZO ceramics, the resistivity of IGZO ceramics sintered at different temperature were measured by four-point probe method. It should be noted that the resistivities of ceramics sintered at 1100°C and 1200°C were too high to be measured, because they exceed the measured range of the instrument. It can be found that the resistivity of IGZO ceramic sintered at 1300°C was 28 mΩ·cm. The resistivities of IGZO ceramics were respectively 18 mΩ·cm and 31 mΩ·cm, when the sintering temperature increased from 1400°C to 1500°C. It has been reported that the IGZO ceramics with high conductive, can be used as sputtering target, which was suitable for the preparation of high performance IGZO thin films by magnetron sputtering[25-28]. It is well known that the electrical properties of ceramics were related to its microstructure and relative density. Therefore, it can be found that, the grain size of 9.28 μm and the relative density of 99.4% in the IGZO ceramics when the sintering temperature was 1400°C, had the optimal electrical property of IGZO ceramics in this study.

4. Conclusions

In this study, the influences of sintering temperature on the densities, microstructure, and electrical properties of IGZO ceramics were studied. The main results are given as follows:
1. The particle size of raw material powders was effectively decreased by improving the ball milling process.
2. The main densification process occurred when the temperature range was 882 °C to 1321 °C. The shrinkage rate of IGZO ceramic reached the maximum at 1230 °C. The linear shrinkage of the sample reached 15.6% when the temperature was 1321 °C. In addition, the compositions of ceramics were single InGaZnO₄ phase and no phase transformation occurred between the 1300 °C and 1500 °C
3. The IGZO ceramics had a highest density of 99.4% at the sintering temperature of 1400 °C. The grain size of IGZO ceramics increased as increasing sintering temperature. When the sintering temperature was 1400 °C, the IGZO ceramic had an optimal electrical property in this study.

Acknowledgements

This work was supported by the State Key Laboratory of Special Rare Metal Materials (Contract No. SKL2016K001), Northwest Rare Metal Materials Research Institute. Project funded by China Postdoctoral Science Foundation (2018M632797) and Science and Technology Project of Henan Province (Grant NO. 192102210014).

References

[1] Kumomi H, Nomura K, Kamiya T and Hosono H 2008 Thin Solid Films 516 1516
[2] Yao J, Gong L, Xie L and Zhang S 2013 Thin Solid Films 527 21
[3] Ohta H, Nomura K, Orita M, Hirano M and Hosono H 2003 Advanced Functional Materials 13 139
[4] Lo C C and Hsieh T E 2012 Ceramics International 38 3977
[5] Su H and Johnson D L 1996 Journal of the American Ceramic Society 79 3211
[6] Yao C et al. 2007 Chinese Journal of Semiconductors 28 883
[7] Neves N et al. 2012 Journal of the American Ceramic Society 95 204
[8] Utsumi K, Matsuana O and Takahata T 1998 Thin Solid Films 334 30
[9] HultaKer A and Niklasson G A 1999 MRS Proceedings 581 491
[10] Huang H et al. 2010 Thin Solid Films 518 6071
[11] Tsay C Y and Huang T T 2013 Materials Chemistry and Physics 140 365
[12] Murat A, Adler A U, Mason T O and Medvedeva J E 2013 Journal of the American Chemical Society 135 5685
[13] Nomura K, Ohta H, Hirano M, Kamiya T, Uruga T and Hosono H 2007 Bulletin of University of Osaka Prefecture 8 3
[14] Chung C Y, Zhu B, Ast D G, Greene R G and Thompson M O 2015 Applied Physics Letters 106 15
[15] Cebulla R, Wendt R and Ellmer K 1998 Journal of Applied Physics 83 1087
[16] Jeong J A and Kim H K 2011 Thin Solid Films 519 3276
[17] Mei F, Yuan T, Li R, Zhou L and Qin K 2018 International Journal of Applied Ceramic Technology 15 89-100
[18] Han J, Mantas P Q and Senos A M R 2001 Journal of Materials Research 16 459
[19] Xiaobo M, WeiJia Z, Dongxin W, Benshuang S and Jingming Z 2015 Rare Metal Materials and Engineering 44 2937
[20] Lee Y S, Dai Z M, Lin C I and Lin H C 2012 Ceramics International. 38 0-0
[21] Mingwei W, ShihSien C, Weiming C and Hungshang H 2015 Journal of the European Ceramic Society 35 3893
[22] Wu M C, Hsiao K C and Lu H C 2015 Materials Chemistry and Physics 162 386
[23] Liu J A, Li C H, Shan J J, Wu J M, Gui R F and Shi Y S 2018 Materials Science in Semiconductor Processing 84 17
[24] Wu M W, Lai P H, Hong C H and Chou F C 2014 Journal of the European Ceramic Society 34 3715
[25] Suresh A, Gollakota P, Wellenius P, Dhawan A and Muth J F 2008 Thin Solid Films 516 1326
[26] Hsu C M, Tzou W C, Yang C F and Liou Y J 2015 Materials 8 2769
[27] Park J H, Jung H K, Kim S, Lee S, Kim D M and Kim D H 2011 IEEE Transactions on Electron Devices 58 2796
[28] Nguyen Tran et al. 2016 ACS Applied Materials & Interfaces acesami. 6b10591.