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Improving the densification of indium tin oxide targets via secondary cold isostatic pressing and oxygen exchange treatments

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ABSTRACT

Traditional preparation technology is difficult to achieve near full densified indium tin oxide targets with thickness more than 10 mm. By introducing an anti-densification sintering model into studying the densification behavior of In_2O_3-SnO_2 mixed powders, we proposed secondary cold isostatic pressing and oxygen exchange treatments to improve the densification of the targets by experiment. It is found that the application of secondary cold isostatic pressing and oxygen exchange treatments can increase the densification of targets and reduce the number and size of pores in sintered bodies effectively. Besides, two mechanism models were introduced to reveal the underlying causes.

The development of flat panel display industry has progressed in short order during the last few decades [1] and a large number of ITO materials could be needed. Due to the high electrical conductivity and high transparency to visible light, as the key transparent electrodes, ITO films are essential for various optoelectronic devices, such as liquid crystal displays (LCD), organic light emitting diodes (OLED), touch panels (TP), thin film solar cells, antistatic conductive films and automotive applications, et al. [2–5].

Since the great influence of the densification of ITO targets on the properties of ITO films and the sputtering behavior of ITO targets [3], it is very necessary to sinter ITO materials with the density to near the level of theoretical density (7.155 g/cm^3). Besides, ITO targets should be dense to avoid the formations of nodules [6]. However, it is all known that ITO targets are hardly densified materials [3, 7, 8]. Normal preparation process consists of three segments: powder preparation, formation and sintering [9], which can affect the characteristics of ITO targets. Hence, various efforts in optimizing these processes are carried out to enhance the density of ITO targets, including: refining the particle size [10] and improving the dispersion of nanopowders [10], adding the sintering additives [11], an oxygen pressure applied sintering [12], increasing the sintering temperature [13], climbing rate [13], dwelling time [13] and oxygen flow [14]. Generally speaking, ITO materials required by the high generation LCD panel factory are spliced together. Recently, because the both ends of the splicing targets are at the high-density area of the sputtering magnetic field, ITO targets with the thickness more than 9 mm are been preferred to the thin ITO targets due to the prolonged life time during sputtering [15]. Thus, the thickness of ITO targets is at least 10 mm due to the need of machining. At present, most commercial ITO targets have been prepared from In_2O_3-SnO_2 mixed powders in an oxygen atmosphere after die molding, cold isostatic pressing and dewaxing [2, 9]. However, in reality, this method is difficult to achieve near full densified ITO targets with the thickness more than 10 mm. The aim of this study is to provide a new method to achieve the dense ITO targets with the thickness more than 10 mm, such as secondary CIP and oxygen exchange treatments. However, theoretical understanding and experimental verification on the effects of secondary cold isostatic pressing (CIP) and oxygen (O_2) exchange treatments on the densification behavior of In_2O_3-SnO_2 mixed powders have not been carried out.

In our study, 90 wt% In_2O_3 and 10 wt% SnO_2 powders with a purity of 99.99%, which were provided by Zhuzhou Smelter Group Co., Ltd., were used as the starting materials to fabricate ITO targets. The mean primary particle sizes of In_2O_3 and SnO_2 powders estimated by using a scanning electron microscope (SEM) (Fig.1(a & b)) are about 100–150 nm. In order to achieve In_2O_3-SnO_2 mixed powders with good dispersibility and good liquidity, These raw powders containing 0.4 wt% dispersants and 1.0 wt% binders (the amounts of dispersants and binders are based on the weight of the powders) were granulated by spray method after continuous grinding process for 16 h with zirconia balls and pure water. The phase compositions of In_2O_3-SnO_2 mixed powders shown in Fig. 1(c) were observed by using an X-ray diffraction (XRD), which indicates that the mixed powders are consist of In_2O_3 and SnO_2 powders and have occurred no phase transformation.

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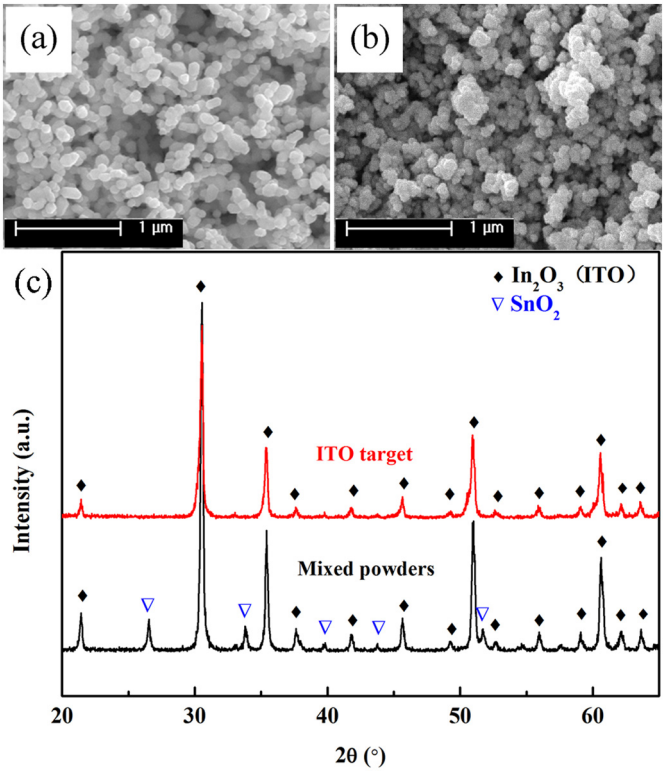

Fig. 1. SEM images of In_2O_3 (a), SnO_2 (b) powders and X-ray diffraction patterns (c) of In_2O_3-SnO_2 mixed powders and ITO targets.

For the traditional preparation technology of ITO target, the In_2O_3-SnO_2 mixed powders were poured into a high-strength steel die and pressed into a cold-pressed billet under a compaction pressure of 450 Kg/cm^2. In order to distinguish the relationship between the densification and the size of targets, molds of two sizes are used to form the ITO green bodies: one is the high-strength steel die with 30 mm in diameter, which is usually used in the literature; and the other is the high-strength steel die with 340 mm × 280 mm, which can meet the needs of industrial sputtering process. Prior to dewaxing, the green bodies with 56%–58% relative density were obtained by cold isostatic pressing (CIP) at a pressure of 250 MPa. ITO samples were dewaxed at 600 °C for 2 h in air, and then sintered at 1550 °C for 5 h in pure oxygen. After sintering, the phase composition of ITO target is shown in Fig.1(c), indicating that the target has the single phase of cube In_2O_3 due to no other phases appearing in the XRD diffraction peaks.

As we all known, the molding of commercial ITO products is carried out in the atmosphere, so it is inevitable to bring nitrogen (N_2) into the pores in ITO green bodies. Besides, there are other gases inside the pores in ITO green bodies after dewaxing, such as CO_2, CO, NO_2, etc. During the sintering process of In_2O_3-SnO_2 mixed powders, the closed pores are hard to be eliminated because the solubility of these gases in the ITO grains is negligible. So an anti-densification sintering model (Eq. (1)) [16] is utilized in the study to investigate the anti-densification influence of the gas inside the closed pores on the sintering behavior of In_2O_3-SnO_2 mixed powders.

$$\frac{dr}{dt} = -K(r)\left[\frac{2\gamma}{r} - P_g(T) + P_e\right] \tag{1}$$

where r is the radius of the closed pores, $K(r)$ is a function relating to the radius of the pores, $P_g(T)$ is the gas pressure inside the closed pores, P_e is the external pressure, $\frac{2\gamma}{r}$ is the intrinsic Laplace stress causing the shrinkage of pores. In this study, the influence of P_e can be ignored due to the press-less sintering process of ITO targets, so Eq.(1) can be re-written as:

$$\frac{dr}{dt} = -K(r)\left[\frac{2\gamma}{r} - P_g(T)\right] \tag{2}$$

According to Eq. (2), the shrinking or expanding of pores can be primarily determined by the gas pressure ($P_g(T)$) inside the closed pores and intrinsic Laplace stress ($\frac{2\gamma}{r}$) causing the shrinkage of pores.

When $\frac{2\gamma}{r} = P_g(T)$, then $\frac{dr}{dt} = 0$, indicating that no change occurs in the pores.

When $\frac{2\gamma}{r} > P_g(T)$, then $\frac{dr}{dt} < 0$, indicating that the shrinkage takes place in the pores.

When $\frac{2\gamma}{r} < P_g(T)$, then $\frac{dr}{dt} > 0$, indicating that the anti-densification occurs in the sintering process of In_2O_3-SnO_2 mixed powders.

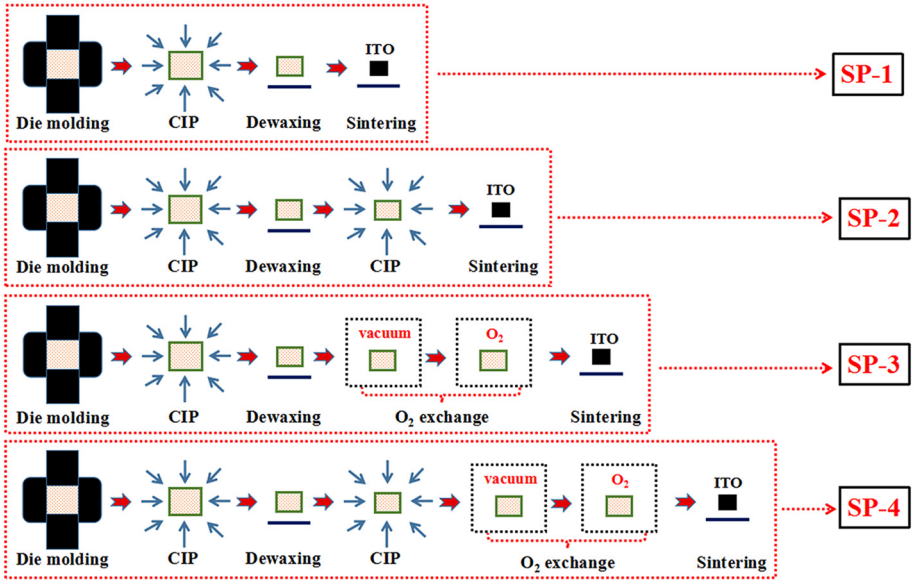

Fig. 2. Schematic diagram of special preparing processes of ITO targets.