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# Advanced indium-tin oxide ceramics for sputtering targets

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**Abstract**

Indium-tin oxide (ITO) ceramic sputtering targets are widely used in formation of electrically conductive transparent thin films for electrodes in flat panel displays, solar cells, antistatic films and others, and which are commonly produced by a conventional dc magnetron sputtering process. The ceramic targets should be of high purity with a uniform microcrystalline structure and should possess high density and high electrical conductivity. In the present work, the challenges of the ceramic composition (e.g. the ratio of $In_2O_3$ and $SnO_2$) and manufacturing are considered; they include the use of high quality starting materials, particularly $In_2O_3$ powders with respect to purity, morphology and sinterability, manufacturing routes and sintering process. Positive experience in the development and manufacturing of ITO ceramic planar sputtering targets using in-house prepared $In_2O_3$ powders is reported. ITO ceramic tiles with areas up to 1500–1700 $cm^2$ and densities of 99+% of TD are manufactured. Physical properties of the ITO ceramics and sputtered films have been studied.


*Keywords:* A. Sintering; C. Electrical conductivity; Indium-tin oxide; Sputtering target

## 1. Introduction

Highly electrically conductive and transparent thin films are widely used as electrode layers in optoelectronic devices, such as in flat panel displays (FPD), e.g. liquid crystal displays (LCD), organic light-emitting diodes (OLED) and some others, solar cells, touch panels, electrochromic devices and antistatic conductive films [1–10]. The films are commonly produced by conventional dc magnetron sputtering on glass or polymer substrates, requiring a fine-tuned deposition process and high-quality sputtering targets. One of the most reliable and suitable materials, among different transparent conductive oxides (TCO), for sputtering targets is indium-tin oxide (ITO) ceramics. These ceramics are formed by the doping of some amounts of tin oxide to indium oxide, that results in modification (distortion) of crystalline lattice of indium oxide and in enhance its electrical conductivity. The ceramics should be of high purity with a uniform microcrystalline structure. They should possess high density (99+% of TD) to maximize the useful life of the targets and high electrical conductivity, and their use in sputtering system should provide a formation of crystalline or amorphous electrically conductive transparent films without structural defects. Due to the present need in large area optoelectronic devices with high-quality films, the ceramic targets are desirable to be as large as possible, i.e. dense monolithic tiles with areas up to 1500–1700 $cm^2$, which are used for assembling large-sized sputtering targets, are required. The manufacturing of these large-sized fully dense products is quite challenging for commercial ceramic processing.

Required electrical conductivity and transparency of ITO films are defined by compositional and structural features of the ceramics and by sputtering process parameters. Regarding ceramics, the structure of the crystalline lattice of $In_2O_3$ modified by the dopant and oxygen deficiency in the lattice have a high importance, i.e. the content of $SnO_2$, substitution of $In^{3+}$ by $Sn^{4+}$ in the cation sites (that results in the donation of free electrons to the lattice and provides n-type conductivity) and densification of ceramics are among crucial factors [8–10]. Due to the lattice defects caused by interstitial atoms or vacancies and oxygen deficiency, it is not straight forward to define theoretical density of ITO ceramics. For example, it is considered as 7.13–7.16 g/$cm^3$ for the ITO 90/10 ceramic compositions.

The quality of dc magnetron sputtered thin films is generally superior when the ceramic targets have higher density; also

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higher density targets enhance deposition rate [4]. Dense ceramic targets have higher resistance against sputtering erosion and nodules formation. In particular, nodules (''black spots''), which may be considered as indium sub-oxide, occur during the sputtering on the periphery of erosion race track of targets and tends to cause electrical arcing; they deteriorate properties of the films and should be periodically removed during processing. The nature of the nodules formation is complex, and its mechanism has not yet been completely understood [5–7]. However, based on the experimental results, the authors [4] noted that high ceramic target purity is not the major condition to attain the films with lower resistivity, i.e. ultrahigh purity grade targets would be only a small advantage of the film quality. Sputtering parameters may have a greater influence on the film quality [7].

One of the most widely used ITO compositions is 90/10 ITO, i.e. with an approximate wt.% ratio of 90/10 between $In_2O_3$ and $SnO_2$; this ceramic composition provides high-quality conductive and transparent films required for the optoelectronic applications. However, some other ITO compositions, such as 98/2, 97/3, 95/5, 80/20, can also be used in similar and other electronics devices.

The development and characterization of ITO and some other $In_2O_3$-based ceramics are under ongoing consideration of the ceramic manufacturers and the TCO users [1–10]. Despite the numerous studies, it is not enough data for the ceramics produced on the commercial basis. In the present work, the challenges of the ceramic composition and manufacturing of ITO sputtering targets are considered; they include the use of high-quality starting materials, especially $In_2O_3$ powders with respect to purity, morphology and sinterability, manufacturing routes and sintering process. A positive experience in the development and manufacturing of ITO ceramic planar sputtering targets using in-house prepared $In_2O_3$ powders has been achieved by Umicore Indium Products (UIP). ITO ceramic tiles with areas up to 1200–1700 $cm^2$ (with a variety of dimensions) and densities of 99+% of TD are currently manufactured. Properties of the ITO ceramics manufactured in the industrial conditions and the films obtained from these ceramics deposited by dc magnetron sputtering are reported.

## 2. Experimental

### 2.1. Starting materials and manufacturing

High purity commercially produced $In_2O_3$ and $SnO_2$ powders are used as the main starting materials for production of ITO ceramics. The $In_2O_3$ powders are manufactured by UIP using a proprietary process from pure indium via its acidation with subsequent neutralization and precipitation of $In(OH)_3$. Then the prepared $In(OH)_3$ is calcined at a proper temperature. Usually hydrochloric acid is used for acidation, and the $In_2O_3$ powders prepared via this route are denoted as type II. Each lot of starting In and prepared $In(OH)_3$ and $In_2O_3$ powders are qualified by chemical analyses and powder characterization. Properties of the processed powders are summarized in Table 1, and their typical particle size distributions are performed in Fig. 1. The $In_2O_3$ powders have cubic shape, and they are generally aggregated (Fig. 2). Properties of $SnO_2$ powders manufactured by other suppliers are also summarized in Table 1.

Starting materials are mixed and milled using a ball milling process based on the specially designed procedure. Water-based ceramic slurries (employing specially selected dispersing and binding agents) with workable viscosities and specific gravities are used for slip casting process. Depending on the size of the manufacturing bodies, casting is conducted at specific parameters, which have to be selected for each case. After gentle drying and dry state cutting (if required), ''green'' bodies are fired in the high-temperature electric kilns using specially designed kiln loading and firing conditions. The optimized firing cycle (firing temperature is below 1600 °C) and firing conditions provide practically full densification (up to 99.5% of TD). Then fired tiles are cut and ground with diamond tooling in order to provide precise dimensions, flatness and surface quality, which are required for the back face metallization, bonding and magnetron sputtering processes. For example, roughness of the ceramics $R_a$ is attained to be not greater than 0.45 μm. It should be noted that a multi-step process control during powder preparation and ceramic manufacturing is maintained that provides high-purity and high-quality ceramic targets.

### 2.2. Sputtering

ITO films were deposited from ITO ceramic targets with dimensions of 381 mm × 127 mm × 6 mm cut from actually producing tiles onto glass substrates Corning No. 1737F using an industrial vertical planar dc magnetron sputtering system (LLS EVO II). The base pressure in the process module was below $5 \times 10^{-5}$ Pa. Typically a power density of 3.1 W/$cm^2$ was applied during the sputtering runs. The sputtering pressure was in the range of 0.3–0.6 Pa that could be adjusted using a

Table 1
Properties of starting powders for ITO ceramics

| Material | Purity (%) | Particle size distribution (μm) | | | Specific surface (BET) ($m^2$/g) |
|---|---|---|---|---|---|
| | | $d_{10}$ | $d_{50}$ | $d_{90}$ | |
| $In(OH)_3$ | 99.99 | 1–3 | 7–12 | 15–20 | 8–12 |
| $In_2O_3$, type II | 99.99 | 0.8–0.9 | 3-5 | 7-8 | 0.7–1.0 |
| $In_2O_3$, type IIB | 99.99 | 0.05–0.1 | 0.4–1.3 | 1–2 | 13–18 |
| $SnO_2$ | 99.9 | 0.1–0.2 | 0.3–0.9 | 2–3 | 4–9 |
| ITO slip | – | 0.1–0.2 | 0.4–0.6 | 1.5–2.5 | 5–7 |