ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Tin oxide-based ceramics of high density obtained by pressureless sintering

Eugene Medvedovski

Endurance Technologies Inc., #71, 4511 Glenmore Trail SE, Calgary, AB, Canada T2C 2R9

ARTICLE INFO

Keywords:
A. Sintering
B. Microstructure-final
C. Electrical properties
Tin oxide

ABSTRACT

Dense tin oxide-based ceramic semiconductors have a high potential as electrodes for aluminum production, glass industry, sputtering targets for transparent conducting thin films, varistors, and thermoelectrics due to their specific electrical properties, high corrosion resistance and ability to withstand high temperatures. The application of these ceramics is still limited because of the necessity to reach density of 99% of TD or greater and high electrical conductivity, and because of the manufacturing difficulties to produce components of different shapes and sizes with low cost. The paper reviews the results of the works conducted towards obtaining tin oxide-based ceramics with density up to 99.5+% of TD through low-temperature pressureless sintering. The selected sintering aids/dopants and firing conditions promoted both liquid phase sintering and electrical conductivity. The uniform microcrystalline structure is obtained.

1. Introduction

The growing interest and attention to tin oxide ceramics for a few last decades are related to their high potential as semiconductors and corrosion resistant materials, which can serve at elevated temperatures. These ceramics can be employed as electrodes for aluminum production and glass industry, e.g. as anodes in the Hall-Heroult electrolytic cell in aluminum production (for extraction of aluminum in the cryolite electrolyte to replace graphite anodes) or electrodes for electrical melting of lead glasses, as well as different igniters and heaters, crucibles, thermocouple protection and other components, where the material is subjected to harsh corrosive attacks at high temperatures achieving 1000 °C [1–7]. Another area of application of tin oxide ceramics is sputtering targets for the formation of transparent conductive oxide (TCO) thin films for optoelectronic devices and energy generation and conversion, e.g. for photovoltaic applications, electrochromic devices, touch panels, high temperature thermoelectrics and sensors and some other products [8–17]. In this case, in order to achieve high quality and performance of TCO films, as well as for a possibility to use DC magnetron sputtering systems employed in industry, the ceramics with density of greater than 98% of TD and high electrical conductivity are strongly required. Highly dense conductive ceramic targets provide low arcing during sputtering, thin film uniformity, and guarantee a long operational sputtering cycle. Tin oxide-based ceramics is currently manufactured for some kinds of varistors [18–24] where specific electrical properties are attained using specially selected dopants. Tin oxide-based ceramic varistors demonstrate lower susceptibility to degradation in service (e.g. at cycling and at high voltage) compared to ZnO-based varistors.

Tin oxide SnO_2 has a crystalline lattice similar to the tetragonal rutile structure with a high extent of covalent bonds [8,9,25]. However, when this ceramics is pure, it has a rather high electrical resistivity with ρ_v~$(0.5–1)10^{12}$ Ω cm, and the conductivity level is definitely not enough to serve as the electrode and, moreover, for DC magnetron sputtering industrially used for TCO film formation. In order to overcome this drawback, special dopants are used; they promote the electrical conductivity of the ceramics through the distortion of its crystalline lattice and related formation of defects, and affect carrier concentration. Pure tin oxide ceramics generally is not dense that also restricts its applicability due to not high enough corrosion resistance. So, until the present time, pure tin oxide ceramics have still limited application in the market because of lower sinterability and rather high electrical resistivity.

Poor sinterability of tin oxide ceramics is related to decomposition of SnO_2 at elevated temperatures with vaporization of the decomposition products. Thus, rather intensive vaporization occurs at temperatures over 1200 °C according to the reaction [26–29]:

$$SnO_{2\,(s)} \rightarrow SnO_{(g)} + 1/2O_{2(g)}$$

Because of this, the mass transport at the sintering process is related to the evaporation-condensation mechanism. As a result, it leads to only coarsening of tin oxide ceramics with very low densification. Thus, according to the studies of Varela et al. [29], firing of SnO_2 in argon or oxygen at 1000–1250 °C provided density of only 4.1 g/cm^3 that is below 60% of TD. Our firing experiments with pure SnO_2 ceramics conducted in air and in protective gaseous environments

E-mail addresses: eugenem@endurancetechnologies.com, emedvedovski@shaw.ca.

http://dx.doi.org/10.1016/j.ceramint.2017.03.185
Received 7 March 2017; Received in revised form 26 March 2017; Accepted 27 March 2017

confirm the literature data [2,27,28,30] indicated that the temperature increase up to 1550 °C resulted in densities of only ~60–62% of TD.

Different oxides can be used for the promotion of electrical conductivity; they include oxides of transition metals, such as Sb_2O_3, Nb_2O_5, TiO_2, ZnO, Bi_2O_3, MnO_2, CoO, ZrO_2 and some others [6,8,9,13–16,20,23,31–40]. It is dealt with either by increasing the concentration of defects in the crystalline lattice or by the formation of additional energy states within the band gap. The electrical conductivity increase occurs through the reactions, like these:

$$2Sb_2O_3\ (SnO_2) \rightarrow 4Sb_{Sn}^{\bullet} + V'' + 10O_o^x$$

$$Sb_2O_3\ (SnO_2) + V_o^{\bullet\bullet} \rightarrow 2Sb_{Sn}'' + 2e^- + 3O_o^x$$

$$2Nb_2O_3\ (SnO_2) \rightarrow 4Nb_{Sn}^{\bullet} + V'''' + 10O_o^x$$

$$CoO\ (SnO_2) \rightarrow Co_{Sn}'' + V_o^{\bullet\bullet} + O_o^x$$

$$MnO\ (SnO_2) \rightarrow Mn_{Sn}'' + V_o^{\bullet\bullet} + O_o^x$$

In these high-temperature reactions, there takes place a substitution of the tetravalent Sn atoms by the atoms of the dopants providing conductivity increase through altering of carrier concentration. One of the most prospective dopants for electrical conductivity is Sb_2O_3, which provides an increase in electrical conductivity of SnO_2 ceramics in several times [8,9,14,15,31,32,39]. Doped SnO_2 has a wide band gap (3.5 eV or greater). The schematic of the band gap of doped SnO_2 is shown on Fig. 1.

An addition of these and similar oxides acts as electrons donors or ions vacancies in the SnO_2 crystalline structure promoting electrical conductivity depending on the type of dopants making SnO_2 ceramics as *n*- or *n-p*- type semiconductors. The doping with metals with charges greater than Sn can act as electron donors or result in formation of cation vacancies, while the doping with metals with charges lower than Sn can result in electron acceptor defects or oxygen vacancies [7,18,41]. Sb-ions act as the electron donors being added to SnO_2. The doping oxides should not create the formation of the additional phases, i.e. single-phase SnO_2 ceramics should be maintained. However, an addition of the mentioned oxides provides only a mediocre level of sinterability of tin oxide ceramics that is not enough for their service or application properties. One of the best dopant in terms of electrical conductivity Sb_2O_3 does not improve sinterability of tin oxide ceramics, and the ceramics with the compositions of SnO_2-(3–10%)Sb_2O_3 fired in the wide range of temperatures (1200–1500 °C) have a density level of only 60–65% of TD. As mentioned above, it is dealt with vaporization of SnO at elevated temperatures.

One of the possible routes to increase density of tin oxide based ceramics is the use of pressure-assisting sintering. Thus, hot pressing or spark plasma sintering (SPS) or field-activated sintering technique (FAST), which are actively used during last years providing significantly faster process than hot pressing, can be employed [30,42–51]. However, according to the literature data, the densification of the SnO_2, SnO_2-Sb_2O_3 and related SnO_2-based ceramics was reached only 90–97% of TD [30,44,46–51] that can be hardly accepted for many industrial applications yet. However, after firing in these considered conditions, even if rather high densification is obtained, uniformity of the ceramics would not be high enough because of decomposition and partial vaporization of SnO_2, when the surface and the middle of the ceramics would have some compositional and structural differences. The achievement of ~99% of TD using SPS has been recently reported, especially when sintering temperature was reduced to below 1000 °C, but only for the formation of small and simple shapes (pellets or tablets) [45]. The electrical conductivity reported for these ceramics was on the level of 10^{-1}–10^2 Ω cm. Due to the use of graphite dies for pressure-assisting consolidation, sufficient amounts of carbon were detected in the ceramic samples; however, it is not suitable for some applications. The decrease of electrical resistivity of the ceramics obtained by SPS, as well as the decreased carbon contents, can be attained by the long time high-temperature post-annealing, but that reduces the process efficiency. Thus, Chen et al. [52] could decrease electrical resistivity of tin oxide-based ceramic pellets from ~6.5×10^{-1} to ~5.7×10^{-3} Ω cm using post-annealing at 800 °C for 100 h. However, even after annealing, the residual C is still detected in the ceramics [52]. It has to be noted that, because of diffusion of C from the graphite die, the C distribution in the ceramics is uneven, and this unevenness depends on the size of producing components. In addition, the pressure-assisting sintering methods, despite fast process, have a serious limitation in terms of a possibility to produce components of different shapes and sizes, e.g. for electrodes for high temperature furnaces and heating devices with tubular and some other configurations, sputtering targets of large sizes and with rotary design, which are required in industry.

Another possibility to achieve high-density tin oxide based ceramics is the use of sintering aids promoting densification through liquid-phase sintering. In this case, different forming methods (e.g. pressing, casting, injection molding, extrusion) and a variety of commercial furnaces, which are significantly less expensive than hot presses or SPS equipment, can be employed to produce components of different sizes and shapes with multiple quantities. However, the sintering aids should be carefully selected, and their amounts should be minimized to avoid the formation of a second phase and/or rather large volume of a glassy phase, which may reduce electrical conductivity of the ceramics. Different sintering aids, such as oxides ZnO, MnO_2, Nb_2O_5, CuO, Cr_2O_3, TiO_2, Al_2O_3, CoO, V_2O_5 and some others, and their combinations have been tested [7,18–20,27,31–35,53–64]. The additives, which improve densification through liquid phase sintering and with formation of solid solutions, tend to segregate at the grain boundaries and affect the microstructure. In many cases, this inhibits the grain growth. Majority of the studies are related to the firing at rather high temperatures (up to 1500 °C) in air. As the prospective firing option, microwave furnace can be utilized. Thus, the authors reached the density up to 95% of TD using the microwave firing and a combination of oxides ZnO+Nb_2O_5+Al_2O_3 as sintering aids [7]. According to the published data, the addition of CuO may be considered as one of the highest potential. However, a negative impact of vaporization of SnO at elevated temperatures, which leads to poor sinterability of the ceramics, has to be overcome. This is the problem for different methods of sintering of SnO_2-based ceramics, e.g. pressureless and pressure-assisted. According to the published data [7,17,32,33,36,41,42,51,60], electrical resistivity of these SnO_2-based ceramics is on the level of 0.1 – 5.10^5 Ω cm that is rather high. If there are some (but very limited) data related to the influence of atmosphere on sintering of tin oxide ceramics [29], there is no information about the influence of firing atmosphere on electrical properties of these ceramics.

The present paper reviews and summarizes the results of the works focused on processing of the tin oxide based ceramics with high density (99% of TD or even higher) with a high level of electrical conductivity when the components of different shapes and sizes could be manufactured. Considering sintering options, the use of rather expensive hot pressing or other pressure-assisted firing technologies with manufac-

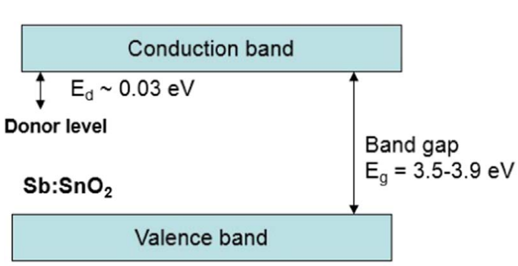

Fig. 1. Schematic of the band gap of doped SnO_2.