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Improving the electrical properties of niobium-doped titania sputtering targets by sintering in oxygen-deficient atmospheres

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Abstract

Niobium-doped titania (TNO) film can be used as a transparent conductive oxide (TCO) film due to its excellent conductivity and visible transparency. The performances of TNO sputtering targets are thus critical issues in optimizing sputtered films. This study clarifies the influences of inert and reducing atmospheres on the microstructure, densification, crystal structure, and electrical properties of TNO sputtering targets. The results indicate that a sintering atmosphere of 90% Ar–10% H_2 can result in a lower sintered density, larger grain size, and lower resistivity than can an atmosphere of Ar, followed by one of air. Sintering in 90% Ar–10% H_2 or Ar obviously decreases the resistivity of TiO_2, from $> 10^8\ \Omega$ cm to $< 10^{-1}\ \Omega$ cm, and the TNO target, from $> 10^1\ \Omega$ cm to $< 10^{-1}\ \Omega$ cm. The resistivity of TNO target sintered at 1200 °C in 90% Ar–10% H_2 is as low as $1.8 \times 10^{-2}\ \Omega$ cm.

Keywords: A. Sintering; C. Electrical properties; Niobium-doped titania; Titanium dioxide; Reducing atmosphere

1. Introduction

TNO films, which are both highly transparent and conductive, can be used as transparent conductive oxide films [1–4]. Nb_2O_5 dopant significantly improves the electrical conductivity of TiO_2 films without apparently degrading their visible transmittance [1–3]. Magnetron sputtering is an ordinary method for the deposition of TCO films in industry due to its versatility [5,6]. Thus, the characteristics and performances of sputtering targets are important factors in optimizing sputtered films and cannot be neglected. In general, only radio-frequency (RF) power can be used for the sputtering of ceramic films because the resistivity of ceramic sputtering targets is quite high. However, various TCO films have been extensively produced by direct-current (DC) sputtering due to the low resistivities of TCO ceramic targets [4,5,7,8]. Ohsaki et al. [9] and Sato et al. [10] have also indicated that a TiO_{2-x} target with a resistivity about 0.3 Ω cm can be used to fabricate TiO_2 and TNO films, respectively, using DC sputtering. Thus, the resistivity of a ceramic target is a dominant criterion for DC sputtering.

Recently, the correlations between TCO targets and films and the processes and properties of aluminum-doped zinc oxide (AZO) and gallium-doped zinc oxide (GZO) ceramic targets have received much focus [7,8,11,12]. Several studies have found that the characteristics of sputtering targets affect both the film properties and the sputtering process [4,7,8,13,14]. Minami et al. [7] and Huang et al. [8] have demonstrated that an AZO ceramic target with a lower resistivity can be used to manufacture an AZO film with better electrical properties and uniformity. An AZO ceramic target with a lower resistivity can also increase the deposition rate and reduce the arcing phenomenon during sputtering [7].

Moreover, Yamada et al. [4] investigated the importance of the TNO sputtering target on the performances and process windows of TNO films. These authors demonstrated that it is very difficult to manufacture a TNO film with high electrical properties using reactive sputtering of a Ti:Nb metallic target. In contrast, both TiO_2:Nb and Ti_2O_3:Nb ceramic targets can be used to produce TNO films with outstanding electrical properties under a wide

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process window of oxygen pressure. Unfortunately, the process and the characteristics of the TNO target were not reported in that study [4]. Wu and Chen [15] recently investigated the sintering behaviors and electrical properties of TiO_2 and TNO (97 mol% TiO_2: 3 mol% Nb_2O_5) ceramic targets sintered in air. They found that 3 mol% Nb_2O_5 dopant greatly decreases the resistivity of a TiO_2 target from $> 10^8\ \Omega$ cm to $4.6 \times 10^1\ \Omega$ cm. However, a TNO film could not be produced by a TNO target with a resistivity of $4.6 \times 10^1\ \Omega$ cm using DC sputtering. The feasibility of DC sputtering and the performances of TCO films depend on the electrical properties of the TCO targets [4,7,8].

To further improve the electrical properties of TNO targets, a feasible approach is to modify the sintering atmosphere. Oxygen vacancies of TiO_2 can be created after annealing in various oxygen-deficient atmospheres [2,16–19]. Ar is an inert and oxygen-deficient atmosphere and is thus a practical atmosphere for improving the electrical properties of titania-based targets. Furthermore, Shin et al. [20] showed that the electronic conductance of TiO_2 particles can be increased by more than one order of magnitude by changing the annealing atmosphere from pure Ar to 95% Ar–5% H_2. Wang et al. [21] indicated that increasing the hydrogen concentration in Ar–H_2 gas mixture is obviously beneficial to the reduction degree of ilmenite. An Ar–H_2 atmosphere has been regarded as a reducing atmosphere for TiO_2 [17,20–22]. The objective of this study was thus to investigate the effects of sintering atmospheres on the sintering and particularly the electrical properties of TNO ceramic targets. The roles of inert (Ar) and reducing (90% Ar–10% H_2) atmospheres were evaluated and compared.

2. Experimental procedure

TiO_2 (CR-EL, Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) and Nb_2O_5 (Niobium Pentoxide, Maido corporation, Kobe, Japan) powders were used to produce TNO–3Nb (97 mol% TiO_2: 3 mol% Nb_2O_5) targets. The primary sizes of the TiO_2 and Nb_2O_5 powders were 0.2 μm and 0.8 μm, respectively. The Nb_2O_5 powder was further refined to 0.2 μm by ball milling for 48 h in a commercial ball mill (MUBM-340, Sun-Great Technology Co., Taiwan, ROC). To prepare the TNO–3Nb ceramic slurries, a 0.2 wt% dispersant of ammonium polyacrylate (Darvan-821A, R.T. Vanderbiltt, CT, USA) and a 0.5 wt% binder of polyacrylic emulsion (Duramax B-1000, Rohm and Haas, PA, USA) were added into the slurries. The amounts of the dispersant and the binder were weighted according to the weight of the dry powder. The detailed procedures of slurry preparation were described in a previous study [15]. The as-prepared slurries were spray-dried with a spray dryer (L-8, Ohkawara Kakohki Co., Yokohama, Japan). The spray-dried granules were uniaxially compacted at a pressure of 75 MPa into green compact disks with a diameter of 12.5 mm and a thickness of 6 mm. The green densities of the TNO–3Nb targets were 59.2%. The theoretical density of a TNO–3Nb target was regarded as 4.29 g/cm^3 in this study because the theoretical densities of TiO_2 and Nb_2O_5 are 4.23 g/cm^3 (JCPDS 76-0318) and 4.98 g/cm^3 (JCPDS 30-0873), respectively.

The green compacts were subsequently heated at 5 °C/min to 600 °C for 30 min to remove the organic additives. After debinding, the compacts were immediately heated at 10 °C/min to the sintering temperatures (900, 1000, 1100, and 1200 °C) and then held for three hours in Ar or 90% Ar–10% H_2, followed by furnace cooling. To identify the role of the sintering atmosphere on the densification and various properties, targets sintered in air were also examined. The sintered densities of the targets were measured using the Archimedes' method. The microstructures were observed under a scanning electron microscope (SEM, JSM-6360, JEOL, Tokyo, Japan), and quantitative metallography was used to estimate the average grain sizes [23]. An X-ray diffractometer (XRD, D8, Bruker, Karlsruhe, Germany) with Cu Kα radiation was used to examine the crystal structure. A high-resolution transmission electron microscope (HRTEM, Tecnai G2 F20, FEI Co., Hillsboro, OR, USA) was also used to identify if there was any Nb-containing second phase. To analyze the electrical properties as a function of sintering atmosphere and temperature, the resistivities at room temperature were determined by a source meter (2400, Keithely Instruments Inc., Cleveland, OH, USA) using the four-point probe method. Moreover, TO (pure TiO_2) and TNO–1.5Nb (98.5 mol% TiO_2: 1.5 mol% Nb_2O_5) targets were produced for comparison to identify the effects of Nb_2O_5 content on the resistivities of targets sintered in various atmospheres.

3. Results and discussion

The microstructures of TNO targets sintered at 1200 °C in air, Ar, and Ar–H_2 are shown in Fig. 1. The TNO target sintered in air exhibited better densification than that sintered in Ar, followed by that sintered in Ar–H_2. There were no pores in the TNO target sintered in air. Fig. 2 shows the sintered densities of TNO targets sintered in various sintering atmospheres. The results indicated that the sintered densities were much improved by increasing the sintering temperature from 900 °C to 1100 °C, irrespective of the sintering atmosphere. The sintered densities were further increased by sintering at 1200 °C. The relative densities of TNO–3Nb sintered at 1200 °C in air, Ar, and Ar–H_2 were 100%, 99.4%, and 98.3%, respectively. Moreover, the average grain sizes of TNO targets sintered at 1200 °C in air, Ar, and Ar–H_2 were 3.0 μm, 5.8 μm, and 7.3 μm, respectively.

These above findings demonstrate that a more reductive atmosphere resulted in a lower sintered density and a larger grain size in TNO–3Nb targets. In contrast, a more reductive atmosphere resulted in both a higher sintered density and a larger grain size for TiO_2 and TiN ceramics [24,25]. This phenomenon can be attributed to the fact that a reducing atmosphere can help generate oxygen or nitrogen vacancies and thus facilitate diffusion, densification, and grain growth. However, for TNO–3Nb targets, the reducing atmosphere simultaneously decreased the sintered density and increased the grain size. This finding could be the result of more oxygen vacancies being generated by the reducing atmosphere, leading to not only a higher diffusion rate but also a higher grain growth rate. The large grain size impaired the sintering