The microstructure, mechanical and electrical properties of Niobium pentoxide-doped Titanium oxide ceramic targets

Qi Ling 1, TingTing Xu 1, LianZi Wu 1, Wei Peng 1, ZuoXiang Zhu 1, ShengHui Xie 1, HaiPeng Yang 1, JiHua Gao 1, Ling Gao 1 and HaiTao Yang 1*

1Key Laboratory of Functional Materials of Shenzhen, Shenzhen Engineering Laboratory for Advanced Technology of Ceramics, Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen, 518060, China

E-mail: *2151120221@email.szu.edu.cn, yanght63@szu.edu.cn

Abstract. Nb2O5 doped TiO 2 (NTO) ceramic targets were prepared by sintering in Ar at 1350 ℃ for 2 hours. The morphologies structures, densification behavior, mechanical and electrical properties of the sintered ceramic targets with different doping concentration were investigated. The results show that the Nb 2O5 content of increase from 0 wt% to 10 wt% not only enhance the densification but promote the grain growth. The morphologies, compositions, microstructure and chemical state were characterized by SEM and XRD. The relative density, grain size and resistivity of 7.5 wt% content sintered at 1350 ℃ in Ar were 94.5%, 13.76 μm, and 7.8×10−2 Ω·cm, respectively.

Keywords: NTO, ceramic targets, sinteing behaviour, transparent conductive films

1. Introduction

Transparent conducting oxide (TCO) thin films have been widely used in liquid crystal displays (LCD), organic light-emitting diodes (OLED) and thin film solar cells. Indium tin oxide(ITO) is currently the most popular commercially available TCO material due to its high transparency (>80%) and low resistivity (<10−3 Ω·cm). However, the alternatives to ITO have been extensively developed due to the shortage and high cost of indium. In recent years, worldwide interests have been attracted on TiO2-based materials which were thought to be most promising in replacing ITO because of its low electrical resistivity with good thermal and chemical stability as well as low cost and non-toxicity [1, 2]. As a wide band gap (Eg = 3.2 eV) semiconductor material, intrinsic TiO2 is highly transparent in the visible region, but relative poor in conductivity. In order to improve its conductivity, it is necessary to induce a proper amount of carriers into it in an adequate manner.

To optimize the performances of TCO films, most researchers have studied the influences of sputtering parameters on the properties of films, including the type of sputter power, sputter power, working pressure, base pressure, substrate temperature, atmosphere, film thickness and post annealing treatment. Unfortunately, only a few studies have attempted to clarify how the TCO target affects the sputtering process and the properties of various films. Many studies were focused on doping of Group III elements into the TiO2 film, such as B, Al, and Ga [3-13]. In these cases, the plus pentavalent cations of Group V elements Nb as the dopants would substitute the tetravalent Ti cations inside the
film, the extra electron is provided as free carrier. Therefore the resistivity was lowered by several orders comparing with pure TiO$_2$.

For a successful substitution with small lattice deformation, the dopant needs to have a similar radius to that of the host ion Ti (0.56 Å). Based on this consideration, the pentavalent elements of Nb(0.62 Å) have been widely studied as a dopant for fabricating high conductive TiO$_2$ films. Nb is especially being considered as the most promising candidate because its radius is very similar to that of Ti.

Few researches on pentavalent cation-doped TiO$_2$ have been published. The pentavalent cation can provide one free electron to contribute the conductivity as it substitutes Ti in TiO$_2$ films. Ti is a pentavalent cation and has a radius of 0.62Å, which is very close to that of Ti(0.56Å). Thus, it is suitable as a dopant to fabricate high conductive TiO$_2$ films. Adding Nb$_2$O$_5$ dopant to TiO$_2$ film greatly improve the electrical conductivity of the film without significant decrease its visible transmittance. Furubayashi et al. [1] reported the preparation of Nb-doped TiO$_2$ film with an electrical resistivity of 3.48×10$^{-3}$Ω·cm on single crystal substrate. Moreover, Nb-doped SrTiO$_3$ film is also highly conductive. Zhu et al. [14] fabricated a Nb-doped SrTiO$_3$ film with a resistivity of 3.6×10$^{-3}$Ω·cm. Ohsaki et al. [15] have indicated that a TiO$_{2-x}$ target with a resistivity about 0.3 Ω·cm can be used to fabricate TiO$_2$ and NTO films, respectively. Yamada et al. [16] demonstrated that it was very difficult to manufacture a NTO film with high electrical properties using reactive sputtering of a Ti:Nb metallic target.

It is also widely known that high-quality targets are crucial for the production of high-quality thin films by sputtering. Most research works were focused on thin films and paid little attention to targets.

In this paper, the Nb doped TiO$_2$ (NTO) ceramic targets were prepared by sintering at 1350°C for 2 hours. The morphologies, structure, densification behavior, mechanical and electrical properties of the sintered ceramic targets with different doping concentration were investigated.

2. Experimental

The selected Nb$_2$O$_5$ doping concentration was 0wt%, 2.5wt%, 5wt%, 7.5wt% and 10wt% respectively. The selected compositions were mixed ball milled with deionized water. Ball mill for 48 hours with ZrO$_2$ milling balls in a commercial ball mill, the ball to powder ratio was 2:1. After drying, sieving and granulating, the powder mixtures were dry-pressed into bars in a steel die at 100 MPa.

The compacts were then sintered at 1350°C for 2 hours in Ar. The bulk density was measured using the Archimedean principle. Without being machined, the sintered bar specimens, 5 by 5 by 20 mm in size, were used for three-point bend strength measurements conducted with steel fixtures at a speed of 3 mm/min, with bottom spans of 15 mm. The Vickers hardness was measured hardness tester. The crystal structure, the fracture surface morphology were investigated via X-ray diffraction (XRD) analysis and scanning electron micro-scope (SEM), respectively.

The electrical resistivity of NTO targets was measured by a Physical Properties Measurement System (PPMS). The resistivity, mobility and carrier concentration of the ceramics targets were measured by Hall test while the sheet resistance was obtained through four-probe method.

3. Results and discussion

3.1. Electrical resistivity of NTO targets

Figure 1 shows the electrical resistivity of NTO targets sintered at 1350°C for 2 hours. The results indicated that the electrical resistivity of TiO$_2$ without any doping additives is over 10$^8$ Ω·cm. The electrical resistivity of NTO targets decreased rapidly to 7.8×10$^{-2}$ Ω·cm with the doping amount increased from 0 to 7.5 wt%. Because the Nb$^{5+}$ can provide one free electron to contribute the conductivity as they substitute the Ti$^{4+}$ in TiO$_2$ to form NTO solid solution.

We obtain the minimum electrical resistivity at the point of 7.5 wt% doping amount. The electrical resistivity increased to 8.74×10$^{-2}$ Ω·cm with further increasing total doping amount to 10 wt% due to
the formation of excessive Nb$^{5+}$ distributing over the grain boundaries which increases the electrons scattering centers and decreases the mobility of the electrons.

![Figure 1](image1.png)

**Figure 1.** The electrical resistivity of five NTO ceramics as a function of doping content.

### 3.2. Relative density of NTO targets

Figure 2 shows the relations of relative density versus Nb$_2$O$_5$ doping amount for the samples sintered at 1350°C for 2 hours. The theoretical density of NTO ceramic targets range from 4.23 g/cm$^3$ to 4.31 g/cm$^3$, because the theoretical densities of TiO$_2$ and Nb$_2$O$_5$ are 4.23 g/cm$^3$ (JCPDS 76-0318) and 4.98 g/cm$^3$ (JCPDS 30-0873), respectively. The relative density of TiO$_2$ without any doping additives is only about 89.6%. The relative density increased rapidly to 93% with the increase of doping amount from 0 to 2.5 wt%, and then the relative density increased slightly to 94%, the highest point, with increasing the doping amount to 5 wt%. The relative density varied slightly decrease from 94% to 92% with further increasing the doping amount to 10 wt%.

The results indicated that the porosities of NTO sintered at 1350°C were still high. Nb$_2$O$_5$ were not only effective carriers suppliers but also excellent sintering aids for TiO$_2$.

![Figure 2](image2.png)

**Figure 2.** the relative densities of NTO ceramics as a function of doping content.

### 3.3. grain size of NTO targets


It is well known that the characteristics of the sputtering targets directly affect the quality of the deposited thin films and the stability of the sputtering process [17-20]. In the process of sputtering, targets with high strength and hardness are required to withstand the bombardment of high energy particles. The appropriate size of the grains can get excellent film properties. The average grain sizes of NTO ceramics as a function of the content are shown in figure 3. For the samples sintered at 1350°C for 2 hours. The results demonstrate that the grain sizes of NTO ceramics increased from 6.4 to 22.79 μm, when the Nb₂O₅ content was increased from 0 to 10wt%. The findings on the microstructure and grain size show that increasing the Nb₂O₅ content from 5 to 10 wt% inhibited both the densification, however enhance the grain growth.

![Figure 3](image)

**Figure 3.** the grain sizes of NTO ceramics as a function of doping content.

3.4. **Bending strength of NTO targets**

As shown in figure 4, The strength increased from 95.25 MPa to 83.38 MPa with increasing the doping amount from 0 to 2.5 wt%. The highest strength of 95.25 MPa was obtained at the doping amount of 0wt%, in other words, is pure TiO₂. The results indicated that Nb₂O₅ doping would lower the strength of TiO₂ and reduced the combination of TiO₂ ceramics targets. The strength decreased to 86.34 MPa within increasing doping amount to 10wt% due to the radius of Nb ion was larger than Ti ion radius, a large number of Ti ions were substituted in the high doping amount, which led to serious crystal lattice distortion and the decrease of binding force. The trend of the change of the bending strength was consistent with the relative density.

Strength is the most important property for targets, which has been neglected by many researchers and producers [21-26]. During sputtering process, the grains and particles with poor bonding strength may be hit off from the target, which contaminates the film being coated, and form new pores on the surface of the targets which deteriorates the quality of the film and shorten the lifetime of the target. High strength targets must be used for the production of large-area high-quality thin films.

![Figure 4](image)

**Figure 4.** the bending strength of NTO ceramics as a function of doping content.
3.5. The analysis of the XRD on NTO targets

Figure 5 is the XRD pattern of NTO targets with different Nb_2O_5 doping amount from 0 to 10wt% sintered at 1350°C for 2 hours. It is clear that the peaks of NTO targets are quite identical to the TiO_2 rutile standard patterns. The Nb_2O_5 peaks could not be found, which suggests that the Nb^{5+} has entered into the TiO_2 lattice structure to form a solid solution and provide free electrons to contribute the conductivity after sintering.

With the doping amount increased from 0 to 10wt%, the carrier concentration increased which leads to the electrical resistivity decreased rapidly from 10^8 Ω·cm to 7.8×10^{-2} Ω·cm. Meanwhile, as shown in figure 5. The doping amount reaches 10 wt% without appear the second phase. The second phase would increase the electrons scattering centers and decrease the mobility of the electrons. The results indicated that the solid solubility limit of Nb_2O_5 in TiO_2 was over 10 wt%. That is why the electrical resistivity increased to 12.14×10^{-2} Ω·cm with further increasing doping amount to 10wt% as shown in figure 1. The peak shift indicates the presence of internal stress inside the crystal. With the increase of the doping amount, the peak intensity of (110) lattice plane shows that Nb has a preferential growth effect on the crystal surface.

![Figure 5. XRD pattern of NTO targets sintered with different doping content.](image_url)

3.6. The fracture surfaces analysis on targets

Figure 6 shows SEM micrographs of fracture surfaces of the targets with Nb_2O_5 content from 0 to 10wt% sintered at 1350°C for 2h.

The TiO_2 target without any dopant shows a large amount of big pores due to its poor density. The fracture surface is simply and smooth. The targets with 5 wt% and 7.5 wt% doping amount show very few small pores, and the fracture surface is rough and complex that often means high strength by absorbing more fracture energy while low strength often leads to simple and smooth fracture surface.

The second phase have not been observed in the samples with the doping amount of 7.5 wt% and 10 wt%, which is corresponding to the results of XRD analysis.
4. Conclusions
The doping of Nb₂O₅ was very effective for the densification and the conductivity of TiO₂. The optimum doping amount was 7.5 wt.%. The sintered NTO targets with Nb₂O₅ content achieved an electrical resistivity of 7.8×10⁻² Ω·cm, a relative density of 94%, and a bending strength of 85.3 MPa.

The solid solubility limit of Nb₂O₅ in TiO₂ was over 10 wt.%. Doping amount of more than 7.5 wt.% in the sintered NTO targets is harmful to the density, and conductivity.

This kind of NTO ceramic target has a potential to be used as a high-quality sputtering target to deposit TiO₂-based transparent conductive films.

Acknowledgements
The research is supported by Shenzhen Innovation and Technology commission under Basic Research Project (Contract NO. JCYJ 2016 0422 1447 51573, JCYJ 2016 0422 1049 21235, JCYJ 2014 0418 1819 58489)

References
[1] Y Furubayashi, T Hitosugi, Y Yamamoto, K Inaba, G Kinoda, Y Hirose, T Shimada and T Hasegawa 2005 J. Appl. Phys. Lett. 86 252101

[2] Ming-Wei Wu and Yan-Chi Chen 2015 J. Am. Ceram. Soc. 98(1) 163–170

[3] S Y Kuo, W C Chen, C P Cheng, C C Kuo, S C Wang and W F Hsieh 2006 J. Cryst. Growth 287 78–84

[4] S Benramache, B Benhaoua and O Belahssen 2014 J. Optik. 125 5864–5868

[5] Ming-Wei Wu, Pang-Hsin Lai, Chia-Hong Hong and Fang-Cheng Chou 2014 J. Journal of the European Ceramic Society 34 3715–3722

[6] M Nisha, S Anusha, A Antony, R Manoj and M K Jayaraj 2005 J. Appl Surf Sci. 252 1430–1435

[7] Deuk Yong Lee, Ju-Hyun Park, Young-Hun Kim, Myung-Hyun Lee and Nam-Ihn Cho 2014 J. Current Applied Physics 14 421–427

[8] J M Lin, Y Z Zhang, Z Z Ye, X Q Gu, X H Pan, Y F Yang, J G Lu, H P He and B B Zhao 2009 J. Appl Surf Sci. 255 6460–6463

[9] Jinning Liu, Xiaoru Zhao, Libing Duan, Mengmeng Cao, Huinan Sun, Jifeng Shao and Shuai Chen 2011 J. Appl Surf Sci. 257 10156–10160

[10] J Lee, K N Hui, K S Hui, Y R Cho and H H Chun 2014 J. Appl Surf Sci. 293 55–61

[11] A Shah, Arshad Mahmood, Uzma Aziz, Rashad Rashid, Qaiser Raza and Zahid Ali 2016 J. Materials Chemistry and Physics 1–7

[12] Chang-Feng Yua, Shih-Jye Sunb and Jian-Ming Chen 2014 J. Applied Surface Science 292 773–776

[13] T Potlog, P Dumitriua, M Dobromir, A Manole and D Luca 2015 J. Materials and Design. 85 558–563

[14] Y L Zhu, X L Ma, D X Li, H B Lu, Z H Chen and G Z Yang 2005 J. Acta Mater. 53 1277–1284

[15] Linhui Gan, Congcong Wu, Yuan Tan, Bo Chi, Jian Pu and Li Jian 2014 J. Journal of Alloys and Compounds 585 729–733

[16] H Ohsaki, Y Tachibana, A Mitsui, T Kamiyama and Y Hayashi 2001 J. Thin Solid Films 392 169–173

[17] N Yamada, T Hitosugi, J Kasai, N L H Hoang, S Nakao, Y Hirose, T Shimada and T Hasegawa 2010 J. Thin Solid Films 518 3101–3104

[18] J Liu, W J Zhang, D Y Song, Q Ma, L Zhang, H Zhang, X B Ma and H Y Song 2014 J. Mat Sci. Semicon Proc. 27 1–11

[19] C S Wu, B T Lin and R Y Yang 2011 J. Thin Solid Films 519 5106–5109

[20] Chaojun Wang, Jian Li and Joonghoe Dho 2014 J. Materials Science and Engineering. B 182 1–5

[21] Liu Lu, Meilan Guo, S Thornley, Xiaoping Han, Junhua Hu, M J Thwaites and Guosheng Shao 2016 J. Solar Energy Materials & Solar Cells. 149 310–319

[22] T Potlog, M Dobromir, D Luca, P Onufrijevs, A Medvids and A Shamardin 2016 J. Current Applied Physics 16 826–829

[23] S K Mukherjee, H W Becker, A P Cadiz Bedini, A Nebatti, C Notthoff, D Rogalla, S Schipporeit, A Soleimani-Esfahani and D Mergel 2014 J. Thin Solid Films 568 94–101

[24] Alireza Sasani, Ardeshir Baktash, Kavoos Mirabbaszadeh and Bahram Khoshnevisan 2016 J. Applied Surface Science 384 298–303

[25] Naoomi Yamada, Taro Hitosugi, Ngoc Lam Huong Hoang, Yutaka Furubayashi, Yasushi Hirose, Seiji Konuma, Toshihiro Shimada and Tetsuya Hasegawa 2008 J. Thin Solid Films 516 5754–5757

[26] Guangmiao Wan, Shenwei Wang, Xinwu Zhang, Miaoling Huang, Yanwei Zhang, Wubiao Duan and Lixin Yi 2015 J. Applied Surface Science 357 622–625