Journal of the European Ceramic Society xxx (2017) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Effect of thermal treatment on TiO_2 varistor properties in different atmospheres

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ARTICLE INFO

Article history:
Received 24 November 2016
Received in revised form 1 April 2017
Accepted 7 April 2017
Available online xxx

Keywords:
TiO_2 varistor
Oxygen partial pressure
Phase
Microstructure
Resistance
Dielectric property
Impedance
I–V curve

ABSTRACT

TiO_2 is a typical nonstoichiometric compound and defects such as oxygen vacancies in TiO_2 grains and at TiO_2 grain boundaries are very sensitive to the oxygen partial pressure in the environment. In this paper, commercial TiO_2 doped with Nb_2O_5 and Bi_2O_3 was used as the raw material to prepare TiO_2 varistors. The samples were thermally treated in three kinds of atmospheres: H_2, vacuum, and O_2 at 600 °C. In the two low oxygen partial pressure atmospheres of vacuum and H_2, due to the volatilization of lattice oxygen in TiO_2, the oxygen vacancy concentration and the number of semiconducting grains increase, while the height and width of the potential barrier and the varistor voltage decrease. After the oxygen atmosphere thermal treatment, the acceptor state density and the height and width of the potential barriers increase, the conductivity decreases, and the varistor voltage improves significantly as a result of oxygen accumulation at grain boundaries.

1. Introduction

Varistors are widely utilized for overvoltage protection and voltage stabilization because of their excellent nonlinear characteristics. Among them, ZnO varistor is the most widely used due to its relatively large nonlinear coefficient. However, its breakdown voltage is too high to be applied in low voltage integrated circuits as semiconductor components [1].

In recent years, TiO_2 varistor has become popular with its low breakdown voltage and multifunctional characteristics [2,3]. TiO_2 is a polycrystalline ceramic material and its electrical properties are closely related to the potential barrier at the grain boundaries [4–6]. At present most studies are focused on donor (Nb^{5+}, Ta^{5+}) or acceptor (Cr^{3+}, Sr^{2+}) doping in TiO_2 in order to further lower the breakdown voltage [7–9]. For example, Sousa [10] et al. prepared the varistor by doping TiO_2 with Ta_2O_5, Cr_2O_3, and MnO_2 oxides, the nonlinear coefficient was 8.23 and the varistor voltage was 34 V/cm. Luo [11] et al. studied (Ca, Si, Ta)-TiO_2 system and found 0.8 mol% Ta_2O_5 doping could significantly reduce the varistor voltage to 14.7 V/mm. High valence state Ta^{5+} replaced Ti^{4+} and occupied the Ti^{4+} lattice sites, thus releasing free electrons to promote grain conductivity and reducing the varistor voltage of TiO_2.

In addition to utilizing the valence difference of cations, processing atmosphere is another way to tune the grain conductivity and grain boundary characteristics. For example, Ponce [12] et al. found that the electrical conductivity of $CaCu_3Ti_4O_{12}$ (CCTO) n-type gas sensing film increased significantly after thermal treatment in CO and vacuum atmospheres. Fu [4] et al. treated ZnO varistor in an oxidizing atmosphere after sintering in reducing atmosphere, enabling the nonlinear coefficient of the material to increase substantially. In addition, TiO_2 is a typical nonstoichiometric compound, the oxygen vacancies in the grains are very sensitive to the oxygen partial pressure in the environment, and the grain boundary is sensitive to the oxygen concentration as the diffusion path for the oxygen species. Sousa [13] treated (Ti,Sn)O_2-based varistor in an oxidizing environment and obtained better varistor responses and nonlinear coefficient. Penneweiss and Hoffmann [14] doped Al in TiO_2 and used freezing to retain high-temperature defects and thus prepared TiO_2 low voltage varistor. The change in oxygen concentration at the grain boundaries can directly impact the acceptor defect density and the width and height of the grain boundary potential barrier, thus affecting the electrical properties of TiO_2 varistors [15,16].

In this study, we doped commercial TiO_2 with Nb_2O_5 and Bi_2O_3 to prepare TiO_2 varistors. After sintering, we thermally treated the samples at 600 °C in H_2, vacuum, and oxygen atmospheres. TiO_2

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.021
0955-2219/

grain and grain boundary compositions were examined with X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). By comparing breakdown voltage, nonlinear coefficient, leakage current, and dielectric properties, the effect of thermal treatment atmosphere on TiO_2 varistor internal defects and grain boundary properties were discussed.

2. Experimental procedures

A TiO_2 powder of 250 nm particle size (Degussa AG)was used as the raw material. TiO_2 varistors with dopants were fabricated from the following powders: TiO_2 (AR, 99.5%, 99.5 mol%), Nb_2O_5 (AR, 99.99%, 0.2 mol%), and Bi_2O_3 (AR, 99.99%, 0.3 mol%). The powders were mixed with zirconium balls and ethanol with the ratio of 1:1:1.5, and ball-milled for 10 h. The slurry was then placed in a drying cabinet at 70 °C for 12 h to ensure that the powders were dry. After that the powders were ground in a mortar with 5% PVA solution. The powders were then pressed into green disks with a diameter of 12 mm and a thickness of 1.5 mm, which were kept at 600 °C for 2 h in air to remove the binder. All the samples were sintered in air at 1400 °C for 4 h. The sample almost completely transformed into rutile TiO_2 at 1400 °C, with the theoretical density of 4.25 g/cm^3. The density of the sintered samples was measured to be 3.63 g/cm^3. The relative density (d) was calculated to be 0.854. Three samples were chosen for each atmosphere treatment. The samples that were polished and thermally treated at 1300 °Cfor 30 min were used for the SEM analysis. Finally, different samples were respectively heat-treated at 5 °C/min heating rate to 600 °C for 3 h in hydrogen (10^{-2} Pa), vacuum (10^{-4} Pa), and oxygen (10^{-2} Pa).

The phase compositions and crystal structures were studied by XRD (Brucker D8), the morphology was observed by SEM (Philip ESEM x30), and the compositions were measured by EDS. For the electric measurements, the surfaces were polished and silver electro contacts were covered on both surfaces of the samples. Varistor voltage and nonlinear coefficient were measured by a DC varistor parameter instrument (CJ1001, Changzhou Chuangjie Lighting Protection Co., Ltd.). Each data point was obtained using three samples, and three different positions were selected on each sample for the testing. Relative dielectric constant and dielectric loss were determined using an original automatic analyzer (TH2818). Impedance measurements were performed by Aglient 4294A with a frequency ranging of 40 Hz–100 MHz. The I–V curves of the samples were measured by a VersLab system with four lead wires.

3. Results and discussion

3.1. Phase composition and microstructure

Fig. 1 shows the XRD spectra of the TiO_2 samples sintered at 1400 °C. The main crystal phase of the samples is rutile (JCPDS card number: 21-1276) after sintering. In addition, there are three small peaks at 33.19°, 47.25°, and 58.49°, which are the diffraction peaks of Bi_2O_3 (JCPDS card number: 52-1007) and indicate that the samples sintered at 1400 °C have a small amount of Bi_2O_3 precipitation.

Fig. 2 shows the SEM images of the TiO_2 samples after sintering at 1400 °C. Fig. 2(a) shows that the grain size is 5–18 μm after sintering, which is much larger than 250 nm of the TiO_2 particles in the green samples.

Fig. 2(b) shows that after the sample has been polished and subjected to hot corrosion at 1300 °C for 30 min, the boundaries between the grains are clear and connected. Pores uniformly distribute among the grains; the pore size is far smaller than the grain size; and the pore volume is relatively small. Fig. 2(b) also shows that the rutile grains are well developed, small grains distribute near the grain boundaries between large grains. The insert

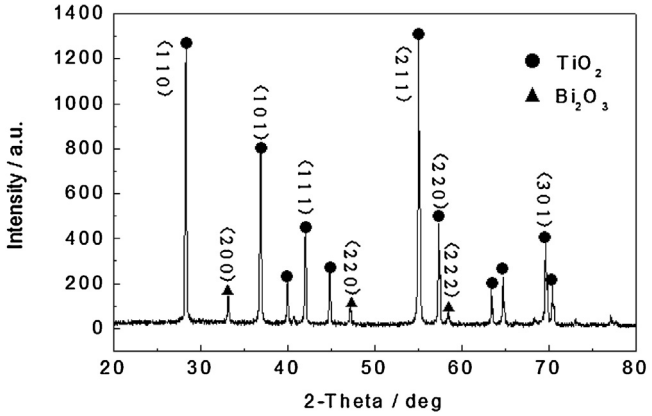

Fig. 1. XRD patterns of sintered TiO_2 samples.

of Fig. 2(b) in the upper right corner is the segregation at the grain boundary between two rutile grains; the grain boundary thickness is about 100 nm. White spots can be observed at the grain boundary; the size is 10–20 nm and the space is 50–100 nm. To obtain the compositions of the nanosized phase at the grain boundary, EDS spot analysis was carried out. The EDS results on a square area of 1 μm side length in Fig. 2(b) show that the elemental content of Bi reaches 58.12 wt%; and small amounts of oxygen and titanium elements as well as a trace amount of Nb element exist, indicating that the main composition of the white spots is Bi_2O_3. This result is consistent with that of Fig. 1.

The presence of a glassy phase at the grain boundaries of TiO_2 varistors can be understood as follows. The melting point of Bi_2O_3 is 824 °C, which is far lower than that of TiO_2 (1850 °C). During sintering to 1400 °C, Bi_2O_3 melts into a liquid phase to surround TiO_2 and Nb_2O_5 particles. When the sintering temperature reaches 1400 °C, chemical reactions among Bi_2O_3, TiO_2, and Nb_2O_5 lead to the formation of a certain amount of eutectic liquid. The liquid phase formed at high temperatures accelerates the densification process and promotes the growth of the TiO_2 grains [17]. The grain boundaries between the TiO_2 grains are filled with a melting thin layer of uniform thickness. During the cooling process, Bi_2O_3 precipitates from the liquid phase to form a secondary phase [10,18]. An amorphous grain boundary layer forms with high resistance, which contributes to the voltage-sensitive effect as to be discussed later.

From a different perspective, grain boundary is the main path of reoxidation for the TiO_2 sample [19,20]. During this process, grain boundaries absorb a large amount of oxygen. Due to the presence of the Bi_2O_3 precipitate in the reoxidation process, the grain boundaries are separated by the Bi-rich phase, which directly affects the diffusion of oxygen; oxygen-rich Bi_2O_3 phase can effectively migrate along the grain boundary during the oxidation process [4].

With the incorporation of Nb_2O_5, Nb^{5+} can easily dissolve into the TiO_2 lattice because of its small size. As a donor dopant, Nb^{5+} will replace part of Ti^{4+} and form a solid solution in TiO_2, promoting the semi-conductivity of the TiO_2 grains [21–23]. Nb_2O_5 presence at the TiO_2 grain boundaries can increase the interface state density, grain boundary layer resistance, and the height of the grain boundary barrier [9,24]. As a result, grain boundary potential barrier increases to impact the electrical behaviors of the TiO_2 varistors.

3.2. Influence of atmosphere on TiO_2 varistor resistance

Table 1 shows the Ti and O contents of the TiO_2 samples at the grain boundary and on the grain surface after the 600 °C thermal treatment in different atmospheres. The Ti/O ratios at the grain

Please cite this article in press as: J. Zhao, et al., Effect of thermal treatment on TiO_2 varistor properties in different atmospheres, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.021