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Influence of different nano titania on microstructure and electrical properties of low voltage zinc oxide varistors

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Abstract A series of check experiments showed that ZnO varistors doped with TiO_2 of different particle sizes and dispersing states have different densities, porosities and grain morphologies, which relate to their electrical properties tightly. Compared with samples added with TiO_2 dopants of others types, the varistors added with nm-TiO_2 sol exhibit large density, low porosity, big granular size, low breakdown voltage gradient and small leakage current. Hence nm-TiO_2 sol dopant is the best grain growth enhancing additive for optimizing almost all the electrical parameters.

Keywords Porosity · Dispersing state · Electrical properties · Morphology · Voltage gradient

1 Introduction

ZnO varistors, which are ceramic semiconductor devices with highly nonlinear current/voltage characteristics, have been proved [1] to be of excellent properties in surge protection against transient overvoltage in electronic circuitry. They are produced by sintering ZnO powder together with small amount of other metal oxides such as Bi_2O_3, Sb_2O_3 and TiO_2.

The mechanism of conduction and the influence of additives in varistors have been investigated by many workers [2–5], nevertheless most of their results were drawn from varistor samples based on ZnO–Bi_2O_3–Sb_2O_3 system ceramic with high breakdown voltage. The studies of ZnO–Bi_2O_3–TiO_2 system based varistor with low breakdown voltage are still inadequate so far.

H. Suzuki and R.C. Bradt [6] attributed the low breakdown voltage to the large grain size in ZnO–Bi_2O_3–TiO_2 system ceramic compared with that of ZnO–Bi_2O_3–Sb_2O_3 system. They also suggested that TiO_2 enhances the growth of ZnO grains by replacement diffusion of Ti cations on the surface of grains.

In this paper, three types of TiO_2 additives-micron-sized (5–10 μm) TiO_2 powder, nano-sized (20 nm on average) TiO_2 powder and nano-sized TiO_2 sol (19 nm on average), were used in the experiment. The influence of TiO_2 of different particle sizes and dispersing states on low voltage varistors were systematically studied for complementing previous pertinent studies.

2 Experimental

For 2 h 98.3 mol% ZnO, 0.7 mol% Bi_2O_3 and 1.0 mol% TiO_2 were ball milled with zirconia balls and deionised water. The mixtures were then dried and pressed into discs of 17-mm and 2-mm thickness. The samples were sintered at 900, 1000, 1100, 1200 °C for 2 h, respectively.

For electrical measurements, the sintered samples were coated with conductive silver paint on both surfaces, then

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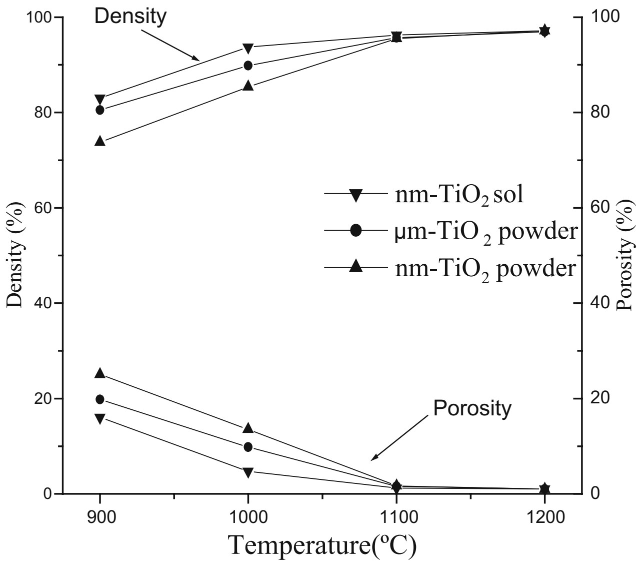


Fig. 1 Variation of density with sintering temperature

heat cured to provide ohmic contacts. *I–V* characteristics were determined using CJ1001 semiconductor testing device at room temperature. Rough polished by 400#–1200# grit SiC papers and Cr_2O_3 powders, samples were etched by acetic acid for 10 min for SEM analysis.

3 Results and discussion

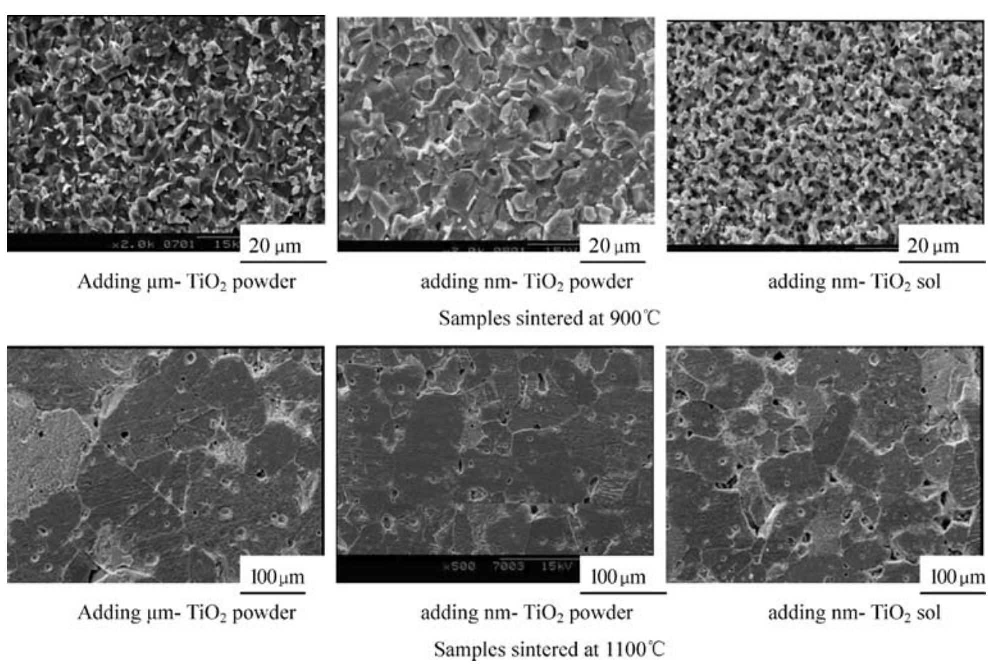
3.1 Microstructure

The curves of density and porosity are showed in Fig. 1. As shown, the difference in dispersing states of TiO_2 powders results in difference in density and porosity of samples. Below 1100 °C, the samples containing nm-TiO_2 sol exhibited the largest density and the lowest porosity. At the same temperature, the samples with nm-TiO_2 powder exhibited the lowest density, even lower than the samples with μm-TiO_2 powder apparently. From curves of porosity, the highest porosity of samples with nm-TiO_2 powder means a considerable amount of pores occurred while nm-TiO_2 powder agglomeration shrinking.

As SEM photos shown (see Fig. 2), the comparison of diameter of grains in each sample (measured by Mendelson method [7], as described in Fig. 3) shows that samples with nm-TiO_2 powder had smaller grains than samples with nm-TiO_2 sol. It should be noted that at 900 °C, different from other two samples, the grains of samples added nm-TiO_2 sol combined together without clear grain boundaries. Such phenomenon only occur in binary ZnO–TiO_2 system without Bi_2O_3, for Bi congregates at the grain boundary, separating the grains and forms Bi-rich grain boundaries [8].

Existing in forms of monodispersing nm-particles, nm-TiO_2 sol with large specific area and high mobility of surface atoms promotes grain rearrangement and mass transfer among grains, accelerates pyknosis of ceramics as well as lowers down porosity and enhances grain growth to the best advantage; different from nm-TiO_2 sol, nm-TiO_2 powder exists in forms of agglomerates with thermodynamic instability, whose size is even larger than μm- TiO_2 powder. The aggregating particles tend to shrink at initial sintering stage with lots of micro pores formed, resulting in inadequate grain rearrangement and mass transfer among grains, which is confirmed to be the reason why samples with nm-TiO_2 powder exhibit the highest

Fig. 2 Comparative SEM of polished sections of ternary system samples



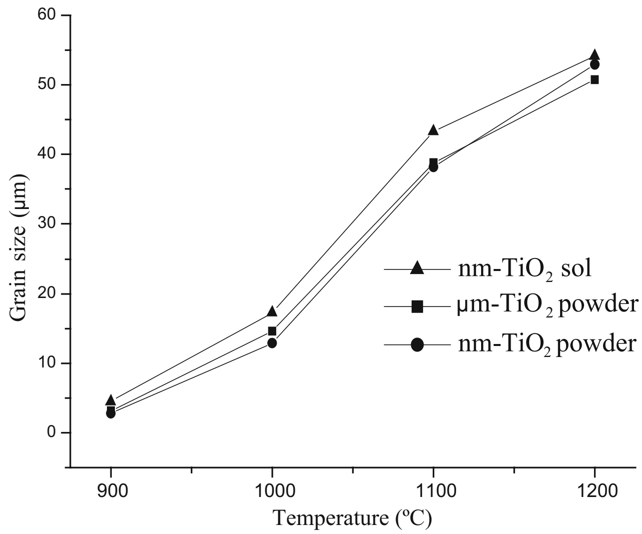


Fig. 3 Variation of grain size with sintering temperature

porosity and small grain sizes at low sintering temperature. Although μm-TiO_2 powder didn't aggregate during sintering, its size was much larger than that of nm-TiO_2 sol, which more or less restricted the effect of TiO_2 on ZnO grain growth and mass transfer. Thus, at 1200 °C, samples added with μm- TiO_2 powder exhibit the smallest grain size.

At 900 °C, as the Eq. 1 described [9],

$$TiO_2 + 6Bi_2O_3 \rightarrow Bi_{12}TiO_{20} \tag{1}$$

the reaction between TiO_2 and Bi_2O_3 resulted in lack of Bi_2O_3 liquid phases, which can form Bi-rich boundary. From that, lack of grain boundary in samples added nm-TiO_2 sol can be attribute to high reactivity of nm-TiO_2 sol.

3.2 Electrical properties

The most important electrical properties are breakdown voltage gradient (U_b), nonlinear coefficient (α) and leakage current (I_L). To low voltage varistor, U_b and I_L should be low. As described in Fig. 4, it's found that samples with nm-TiO_2 sol have the lowest U_b, α and I_L.

The relationship between U_b (V/mm), average grain diameter d_0 (μm) and breakdown voltage V_g (V) is given by:

$$U_b = (1000/d_0 - 1)V_g \approx 1000V_g/d_0 \tag{2}$$

According to this equation, the largest grains in samples with nm-TiO_2 sol result in the lowest U_b directly. Variation of

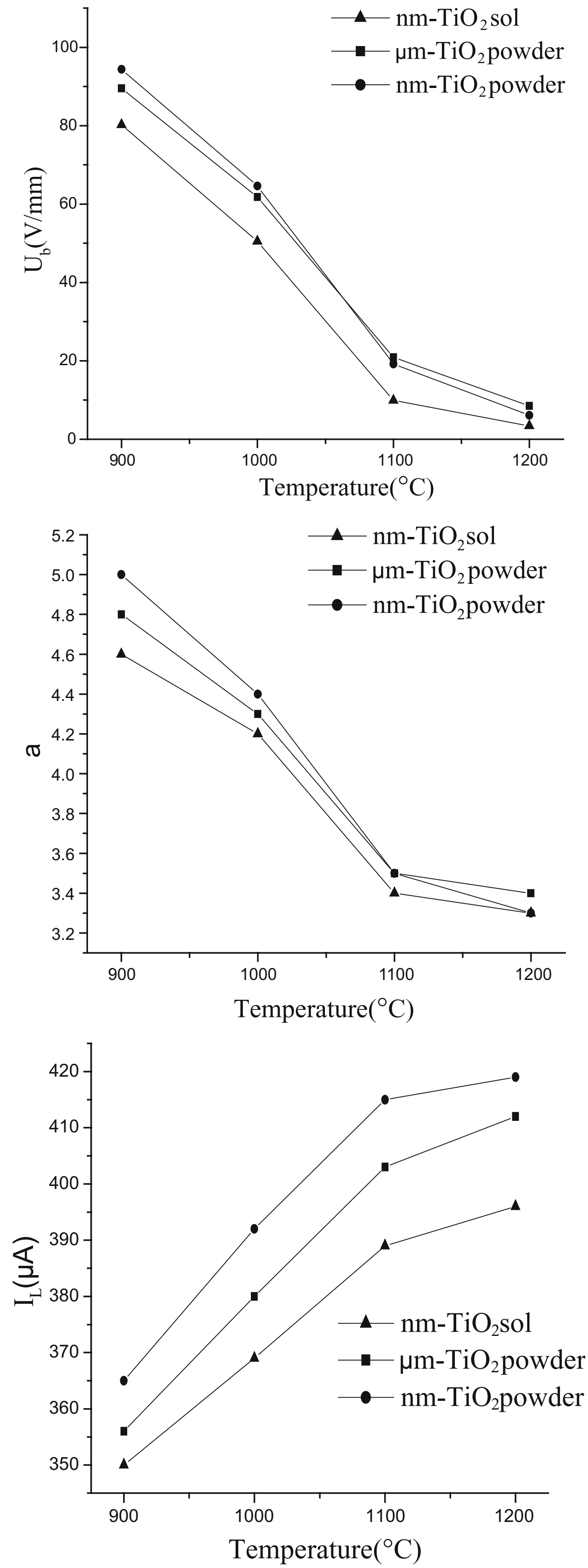


Fig. 4 Variation of electric properties data (U_b, α, I_L) of ternary system samples ($ZnO–Bi_2O_3–TiO_2$)

U_b is opposite to variation of grain size in combination with Figs. 3 and 4. It can be concluded that nm-TiO_2 sol can lower down breakdown voltage largely (even lower than 3.2V/mm).

In terms of hole induced tunneling theory [10], α results from the tunneling of the boundary barrier and deceases with increasing donor concentration. As previous papers [6] mentioned, replacement diffusion of Ti cations into the lattice sites of Zn cations gives rise to donor concentration. High reactivity of nm-TiO_2 sol provides a considerable contribution to donor concentration. Therefore, α of samples with nm-TiO_2 sol is the lowest, but not much lower than the other two samples.

The current/voltage characteristic of varistors is often empirically described by Power-Law Relation [11],

$$I = (U/C)^{\alpha} \quad (3)$$

where U is the on-load voltage, C is material constant. From this equation, in the condition of $U<C$, α is in inverse proportion to I_L. But there is an exception in samples with nm-TiO_2 sol that both α and I_L are the lowest, which is in apparent contradiction to Power-Law Relation. While loading DC voltage on the varistor, leakage current I_L is following grain–boundary–grain path mainly, whose value is determined by conductivity of Bi-rich skeleton. From microstructure analysis above, the Bi-rich grain boundaries are very lack in samples added with nm-TiO_2 sol, which result in lack of path for leakage current. Thus, leakage current is the lowest exceptionally.

4 Conclusion

The low voltage varistors added with nm-TiO_2 sol exhibits large density, low porosity, big granular size, low breakdown voltage gradient and small leakage current, hence nm-TiO_2 sol dopant is the best grain growth enhancing additive for optimizing almost all the electrical parameters of low voltage ZnO varistors, except nonlinear coefficient α, which can be improved by other ways.

Nm-TiO_2 powder exists in forms of agglomerates, whose size is even larger than μm-TiO_2 powder. As a result, nano-effect of nm-TiO_2 powder cannot bring into play fully as nm-TiO_2 sol.

The size of μm-TiO_2 powder is much larger than that of nm-TiO_2, which more or less restricted the effect of TiO_2 on ZnO grain growth and mass transfer. Thus, doping effect of μm-TiO_2 is not so well as nm-TiO_2.

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