Solid State Phenomena Vols. 99-100 (2004) pp 127-132
Online available since 2004/Jul/31 at www.scientific.net

doi:10.4028/www.scientific.net/SSP.99-100.127

Microstructure and Electrical Properties of Doped ZnO Varistor Nanomaterials

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Key words: ZnO varistor nanomaterial, microstructure, electrical properties

Abstract: A sol-gel method of preparation doped ZnO varistor nanomaterials is described, The influences of doped ZnO nanomaterials for varistor microstructure and electrical properties (nonlinear coefficient α, breakdown voltage V_{1mA}, dielectric constant ε, and dielectric loss $tan\ \delta$) are investigated. Compared with the conventional mixed oxide technique, varistor ceramic of prepared by nanometer materials showed a more homogeneous microstructure, smaller grain sizes, higher densities and excellent electrical properties.

Introduction

ZnO varistors exhibit highly nonlinear current-voltage characteristics [1], which enables them to be widely used as protection devices against voltage surges and voltage transients. The varistor effect takes place at the grain boundaries within the ceramic. A number of theories have been developed to explain these effects [2-4]. It is presumed that the electrical behaviour of varistors is the result of a network of grain boundaries with different electrical properties. The excellent properties would be achieved by very homogenous distribution of doping and a regular microstructure with each grain boundary following the non-ohm conduction mechanism. Commercial varistor precursor powders are usually produced by conventional ceramic technology using ZnO and others metal oxide additives as starting materials. This process is recognized as being unsuitable for achieving homogenous doping and microstructure. Several authors have published new methods for preparing varistor powders [5-7]. A sol-gel method [8] is also investigated in order to achieve high breakdown strength because of the small grain size.

The paper describes a new sol-gel method of processing doped ZnO nanometer powders for varistor application. These powders can be sintered at low temperature and give excellent electrical properties and homogenous microstructure compared to the conventional mixed-oxide-technique. In addition, the properties, the microstructure and electrical properties of the varistor ceramic are investigated thoroughly.

Experimental procedure

Preparation of sol-gel nanometer powders and conventional powders. Reagent-grade metal oxide, metal acetates, metal nitrates, citric acid, ethyleneglycol and triethanolamine were used. The

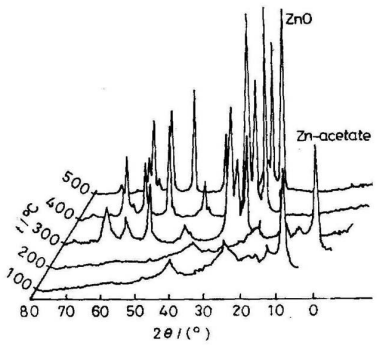
composition of the varistor samples were 95.74 mol% ZnO and 4.26 mol% Bi_2O_3、Co_2O_3、MnO_2、Al_2O_3、BaO and Sb_2O_3). Three solutions were prepared: Zn-acetate, Co-acetate and Mn-acetate are dissolved in ethyleneglycol at 140 °C. The other dopants (Bi-nitrate、Sb-nitrate、Al-nitrate and Ba-nitrate) were dissolved in an excess of triethanolamine at 140°C, and the two solutions were mixed together. Citric acid was dissolved in ethyleneglycol at 140 °C and this solution is then added, whilst stirring, to the metal acetate solution.

The mixture was maintained at 140 °C until acetic acid and water evolution ceased. On cooling to room temperature, the product was a clear viscous gel which was heated to 500 °C at 1 °C /min in flowing air to convert the metal salts to metal oxide. The highly friable resulting powders were ground. The gel powders are denoted as sample (S1).

Sample (S2), with the same composition as (S1), was prepared by the conventional technique. (S1) and（S2）powders, without any organic binder addition, were packed under a pressure of 2.5 MPA into disks (diameter of 7mm and thickness of 1mm) respectively. The sintering temperature was 850 °C for 1hr. During sintering the heating and the cooling rates were 400 °C/h. During investigations of microstructure homogeneity of varistor ceramics prepared by nanometer and micrometer powders respectively, (S1) was sintered at 1050 °C for 2h, and (S2) at 1200 °C for 2h.

Measurements

The properties of the synthesized nanometer powder (S1) were investigated by X-ray diffraction (XRD) and thermal analysis [thermo gravimetric analysis (TG), differential thermal analysis (DTA)] and the result are given in Fig.1 and Fig.2.



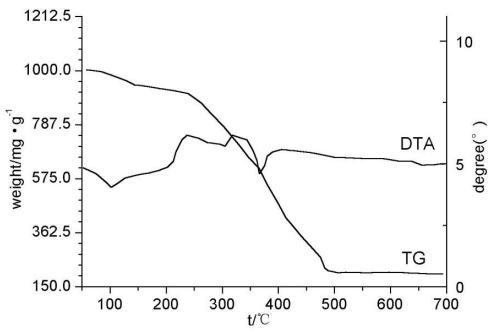


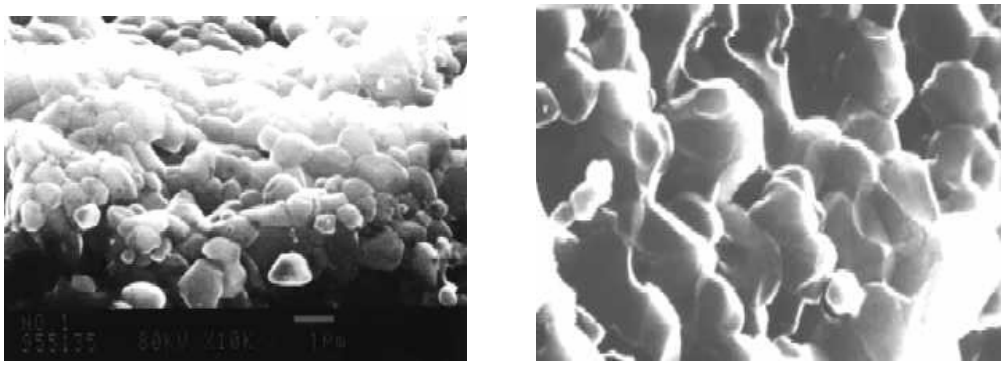
Fig.1. XRD of gel calcinations from 100℃ to 500℃ **Fig.2. DTA/TG of gel from 30℃ to 700℃**

Fig 3 gives TEM micrographs of nanometer powders (S1) and micrometer powders (S2).

Fig.3. (a) TEM of sol-gel nanometer powders Average particle size 20nm

Fig.3. (b) TEM of conventional powders average particle size 600nm

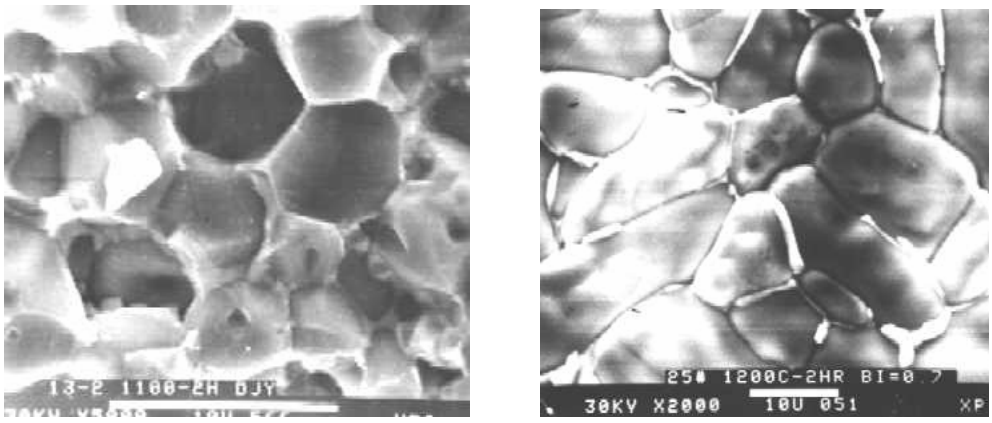
The SEM micrographs of (S1) and (S2) sintered at 850℃ are shown in Fig.4.



(a) (b)

Fig.4 SEM micrographs of (S1) and (S2) sintering at 850℃ 1h.
(a) average grain size of (S1) is 0.6μm. (b) average grain size of (S2) is 2μm.

Fig.5 and Fig.6. shows TEM and SEM micrographs of grain-boundary and grains of (S1) and (S2).

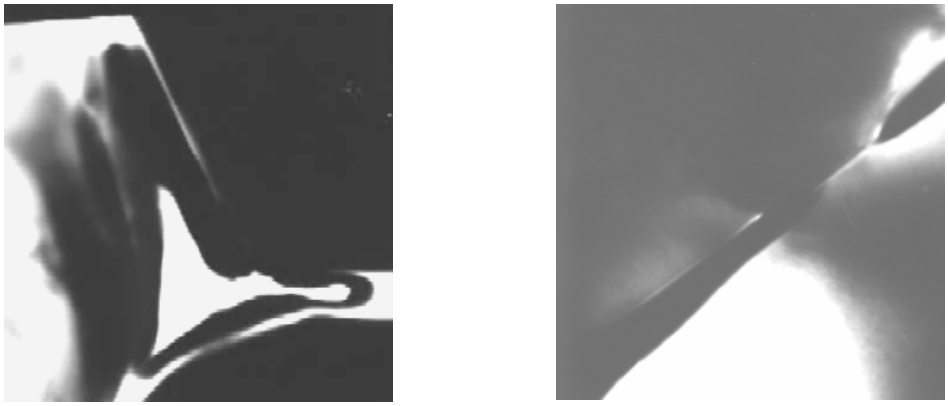


(a) (b)

Fig.5 SEM micrographs of (S1) sintering at 1100℃ 2h and (S2) sintering at 1200℃ 2h
(a) average grain size of (S1) is 3-4μm. (b) average grain size of (S2) is 8-10μm.

(a) (b)

(a) triangle shape grain boundary (S1) . (b) grain boundary between two grains(S1).



(c) (d)

(c) triangle shape grain boundary(S2) (d) grain boundary between two grains (S2).

Fig.6 TEM micrographs of (S1) and (S2) triangle shape grain boundary and grain boundary between two grains.

The voltage-current (V-I) characteristic of non-ohm ZnO varistors is expressed by:

$$I=CV^{\alpha} \qquad (1)$$

where V is the voltage across the sample; I is the current flowing though the sample; C is a constant, and α is a coefficient of nonlinearity that also is defined as:

$$\alpha = \mathrm{d}(\log I) / \mathrm{d}(\log V) \qquad (2)$$

The voltage-current (V-I) characteristics are measured by using a MY-4C varistor testing are shown in Table1.The frequency dependence of the dielectric constant ε and dielectric loss tan δ were measured in the frequency range from 100HZ to 10MHZ by means of an HP4194A impedance analyzer and are shown in Figs.7 and 8.

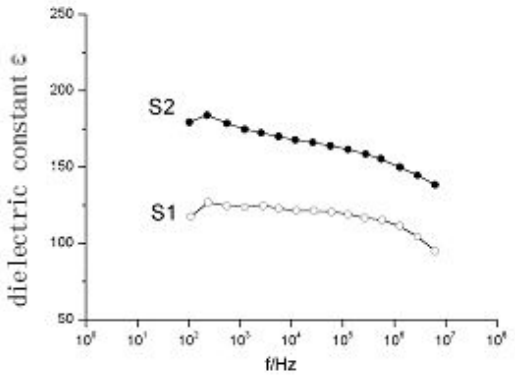


Fig.7 Variation of the dielectric constant ε of (S1) and (S2) with frequency

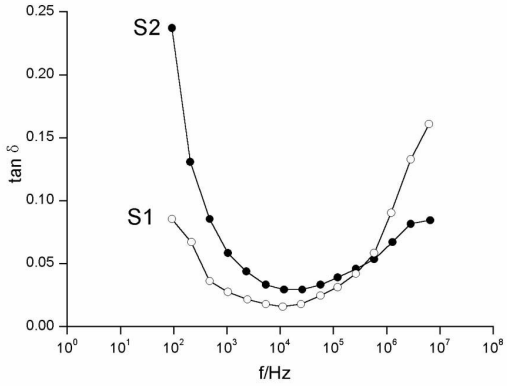


Fig.8 Variation of the dielectric loss tan δ of (S1) and (S2) with frequency

3. Results and Discussion

3.1 Powder analysis

The XRD of the dried gel calcinations from 100 °C to 500 °C is shown in Fig.1. The Zn-acetate dissolved in ZnO began at 200°C and all organics were removed at 500 °C. The DTA/TG analysis of the dried gel is shown in Fig.2. The weight lost of dried gel began at 200 °C and was completed at 500 °C. The remaining powder had only 16~18% of the initial weight. XRD and DTA/TG, was used for the dried gel powders heated at 500 °C in air for 2h. The TEM of the (S1) powders and (S2) powders are shown in Fig.3. Fig3. (a) gives nanometer powders prepared by sol-gel method, the average particle size is 20nm; Fig.3 (b) is conventional powders prepared by ball-milling, the average particle size being 600nm.

3.2 Microstructure analysis

The conventional sintering temperature for ZnO varistor ceramics is from 1200 to 1300 °C. Nanometer powders have higher activity and larger surface area compared to conventional micrometer powders, so they can be sintered at lower temperature. The SEM micrographs of (S1) and (S2) sintered at 850 °C for 1h are shown in Fig.4 (a) and (b). The average grain size of (S1) is approximately 0.6 μ m, (S2) is approximately 2 μ m. Fig4. (b) shows that (S2) has non-mature grains at 850 °C. The SEM micrographs of (S1) sintered at 1100 °C for 2h. and (S2) sintered at 1200 °C for 2h are shown in Fig.5(a) and (b). Fig5. (a), shows a homogenous and close microstructure, with average grain size of 3-4 μ m , and shape similar to hexagonal. In Fig.5 (b), for powders sintered at 1200 °C a non-homogenous microstructure of irregular shape and average grain size 8-10 μ m is observed. The TEM micrographs of (S1) and (S2) triangle shape grain boundary and the grain boundary between two grains are shown in Figs.6 (a) and (b) and Figs.6 (c) and (d) respectively. The triangle shape grain boundary and grain boundary between two grains of (S1) are close and clean and that of (S2) are spread out and spacious.

3.3 Electrical properties

Table 1 shows the nonlinear I-V properties of (S1) and (S2) varistor ceramics sintered at 850℃ for 1h. V_{1mA} means breakdown voltage; I_l means leakage current, and α means nonlinear coefficient.

sample	Sintering temperature	V_{1mA} (V)/mm	I_l (μA)	α
(S1)	850℃	1546	3.1	60
(S2)	850℃	976	6.7	24

Table 1. Nonlinear I-V properties of (S1) and (S2)

(S1) has a higher breakdown voltage 1545V/mm, smaller leakage current 3.1μA, and larger nonlinear coefficient, 60, than (S2). The excellent nonlinear I-V properties of (S1) comes from the homogenous microstructure and smaller grain size. That is the reason to use nanometer powders as initial materials. The variation of the room-temperature dielectric constant of (S1) and (S2) with frequency is shown in Fig.7. The dielectric constant ε of (S1) and (S2) decreases continuously with frequency increase in the range 100 HZ to 10 MHZ. (S2) shows a higher dielectric constant than (S1) due to its larger grain size than (S1). Fig.8 shows the variation of the dielectric loss tan δ of (S1) and (S2) in the frequency range 100 HZ to 10 MHZ. It is observed that tan δ of (S1) is lower at low frequency range than (S2) due to the more homogenous microstructure and clear grain boundaries than (S2). At higher frequencies the dielectric loss tan δ of (S1) is larger than that of (S2), because (S1) has more grain boundary per unit thickness than (S2). The grain boundary effect on dielectric loss at higher frequency becomes more obvious than at the lower frequency range.

4. Conclusion

The microstructure and electrical properties of doped ZnO varistor ceramic are affected by the initial powders. Nanometer powders used as precursors for varistor ceramic give a more homogenous microstructure and better electrical properties than the use of conventional micrometer The properties of varistor ceramics using nanometer powders as precursors are as follows:

1. Doped ZnO nanometer powders can be prepared by the sol-gel method. Dried gel calcinations at 500°C for 2h can get 20 nm doped ZnO nanometer powders.
2. Doped ZnO nanometer powders sintered at 850℃ produce a 0.6μm average grain size.
3. Compared to micrometer initial powders, nanometer powders produce a more homogenous, smaller and regular grain size, and a cleaner and closer grain boundary microstructure.
4. Varistor ceramics prepared from nanometer powders have a higher breakdown voltage, smaller leakage current, larger nonlinear coefficient, smaller dielectric constant and dielectric loss than conventionally produced varistors, due to their homogenous microstructure and small grain size.

Acknowledgments

This work was supported by the National High Technical “863” Foundation, P. R. China.

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