Origin of varistor properties of tungsten trioxide (WO_3) ceramics*

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Abstract: To study the physical origin of the non-ohmic behavior of WO_3 ceramics, the effects of heat treatment in different atmospheres on WO_3 varistors were investigated. Experiments showed that there was a dependence of the nonlinear coefficient on thermal treatment under different atmospheres. Thermal treatments in argon and oxygen atmospheres at 900 ℃ proved this dependence, and indicated that the nonlinear coefficient got significantly lower when the samples were thermally treated under argon atmosphere. Subsequent exposure to oxygen atmosphere at the same temperature led to the restoration of electrical properties. The result shows that the physical origin of the non-ohmic behavior of WO_3 ceramics is oxygen on the grain surfaces adsorbed by intrinsic defects.

Key words: varistor; tungsten trioxide; thermal treatment; intrinsic defects
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1. Introduction

Varistors are nonlinear, voltage-dependent resistors whose value of resistance decreases with increasing voltage. Varistor ceramics have become important because of their highly nonlinear electrical properties that enable them to be used as reversible, solid-state switches with large-energy-handling capabilities. The earliest used varistors were SiC-based ceramic systems[1,2]. The ZnO varistors were first developed by Matsuoka and his research group at Matsushita Electric (Japan) in 1968. In the first decade after the invention, various additives to the ZnO varistors were discovered[3]; since then great strides have been made in applications and research on ZnO varistors[4–6]. In 1995, Pianaro *et al.*[7] first discovered a low-dose doped SnO_2 ceramic with good density and electrical nonlinearity. At the same time, a lot of research has been done on varistor systems based on TiO_2, $SrTiO_3$, $BaTiO_3$ and WO_3[8–10].

A set of theoretical models, based on ZnO, were put forward to explain the non-ohmic behavior of the varistors. In these theories, the grain-boundary barrier mode, proposed by Pike *et al.*, is consistent with the experimental results and has been widely accepted[11–15]. But there is still a lack of agreement on how to explain the physical origin of the non-ohmic behavior of the ceramics[16,17]. The non-ohmic behavior of most metal oxide varistor systems, as mentioned above, arises from doping, more concretely, results from the metal atoms segregated at the grain boundaries. These metal atoms, such as Pr and Dy in ZnO-based varistors or Mn in SnO_2-based varistors, facilitate the adsorption of oxygen on the grain surfaces[18,19]. Some authors[10,20] have reported studies on non-ohmic behavior of WO_3 ceramics, indicating that WO_3-based ceramics are potential varistor materials for low voltage applications.

It is clear that the doping method has some limitations for studying the origin of the varistor properties of WO_3 ceramics, due to the complicated structures caused by various additives, so a method without doping is needed. Recently, our group studied pure tungsten trioxide (WO_3) ceramics by using thermal treatment, and found that there is a dependence of nonlinear constant values on thermal treatment under different atmospheres. This approach is more conducive to further understanding the physical origin of the non-ohmic behavior of the ceramics.

2. Experiment

The samples were fabricated according to the conventional electroceramic process. The raw chemical in the present study was analytical grades of WO_3 (99%). After milling with agate balls for 3 h, the powder with binder addition (2% by weight polyvinyl alcohol binder) was pressed into pellets of 10 mm in diameter and 1.0–1.5 mm in thickness by a conventional molding method at a pressure of 10 MPa. The pressed disks were sintered in an electric furnace at 1100 °C for 2 h in air, and furnace cooled to room temperature. The samples were subjected to treatment in Ar (99.9%, under a flux of 20 cm^3/min) at 900 °C for 1 h and further treated in O_2 (99.9%, under flux of 20 cm^3/min) atmospheres at 900 °C for 1 h. To take the electrical measurements, gallium–indium eutecticum as electrode material was coated on both polished surfaces of samples.

The sample phase was observed by X-ray diffraction (XRD, 7602EA ALMELO) with CuKα radiation (λ = 0.15406 nm) at 40 kV. For microstructure characterization, the surfaces of the samples were analyzed by scanning electron microscopy (SEM, FEI QUANTA200). Current-tension measurements were taken using a high voltage measure unit (KEITHLEY 2410). Impedance measurements were taken using a frequency response analyzer (HP 4294A) at frequencies ranging from 40 Hz to 15 MHz, with an amplitude voltage of 0.5 V. The electrical nonlinear coefficient α was obtained by[21]:

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Table 1. Some electrical characteristic parameters of WO_3-based ceramics.

Sample	α	E_b (V/mm)	ϕ_B (eV)	N_d ($10^{28}m^{-3}$)	N_s ($10^{18}m^{-2}$)	w(Å)
As-sintered	4.8	50.13	0.27	0.92	8.07	4.39
Argon atmosphere	1.0	0.24	–	–	–	–
Oxygen atmosphere	4.0	30.36	0.35	1.02	9.55	4.67

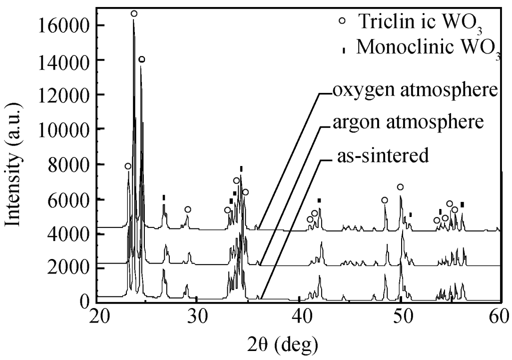

Fig. 1. XRD data obtained from the ceramic samples.

$$\alpha = \lg(I_2/I_1)/\lg(V_2/V_1), \quad (1)$$

where V_1 and V_2 are the voltages at currents I_1 and I_2, respectively. The field at a current of 10 mA/cm^2 was chosen as the breakdown field E_b. The values of the nonlinear coefficient and breakdown field are listed in Table 1.

The microstructure and electrical behavior were checked throughout the above mentioned procedures after each treatment.

3. Results and discussion

Figure 1 presents the X-ray data for the samples after each treatment. The results show that the samples are mixtures of triclinic and monoclinic phase WO_3. Besides the two phases, no additional phases were found in the samples when the varistors were thermally treated in argon and oxygen atmospheres. From the obtained X-ray data, it can also be observed that all the patterns are identical indicating that no crystal phase changes occur with the different annealing atmospheres at a constant temperature. Figure 2 shows SEM micrographs of different samples. The SEM images show that the grains are almost the same shape after heat treatment. It can be seen that the grains are basically spherical.

Figure 3 presents the current–voltage (I–V) characteristics of the samples heat treated in different atmospheres, while Table 1 gives some electrical parameters, such as α, E_b values. It can be seen that varistor action is observed in the sample. The current density increases sharply when it exceeds 10 mA/cm^2, so we can define the breakdown field as the electrical field corresponding to $I = 10\text{mA/cm}^2$. The as-sintered sample is nonlinear with a nonlinear coefficient α of 4.8 which is consistent with the value reported by Makarov *et al.*[10]; its nonlinearity disappears after heat treatment in argon atmosphere. However, repeating the thermal treatment in oxygen atmospheres make the nonlinear properties appear again. Because of heat treatment temperature and time restrictions in the experiment, the parameters failed to recover to their original values.

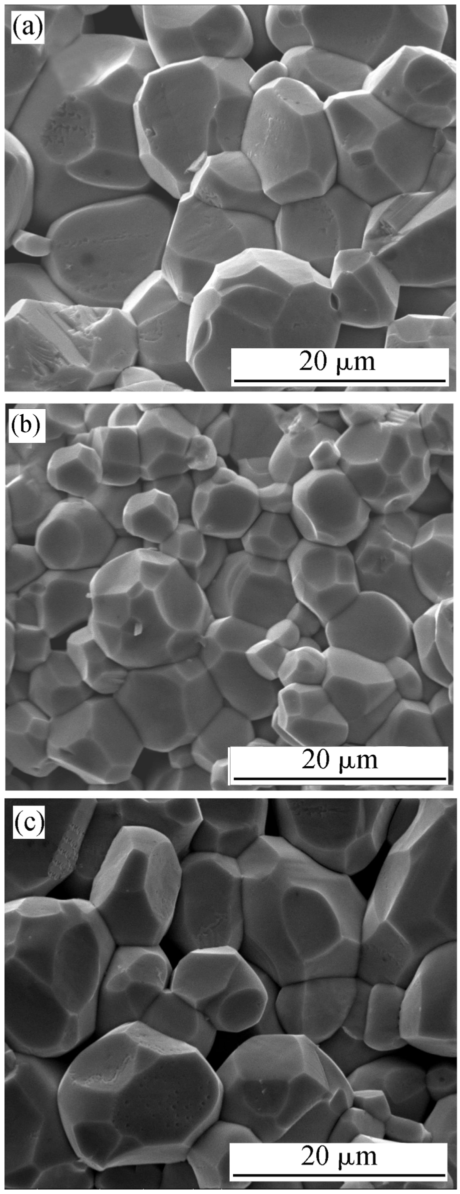

Fig. 2. SEM micrographs of WO_3 ceramics. (a) As-sintered. (b) Argon atmosphere. (c) Oxygen atmosphere.

Impedance spectroscopy is a powerful technique for the characterization of grain boundaries in ceramic materials[22]. Complex impedance plots were carried out on the as-sintered sample and the sample treated in oxygen atmosphere (Fig. 4(a)), presenting a grain-boundary semicircle. This means that the grain boundaries are highly resistive regions. The spectra obtained on varistors thermally treated in argon atmosphere (Fig. 4(b)) are devoid of any grain-boundary semicircle. That is to say, the highly resistive grain-boundary layers disappear and the grain interior is the only contribution to the frequency

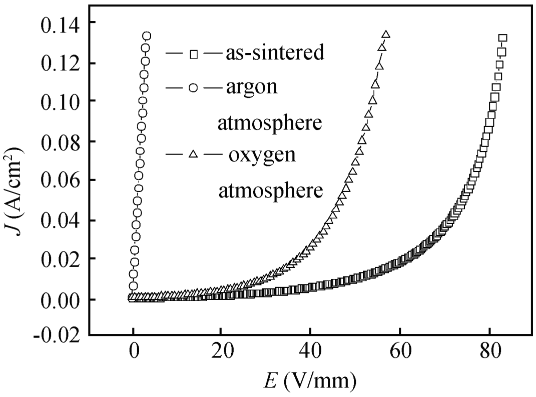

Fig. 3. Current–voltage characteristics of the WO_3 varistors.

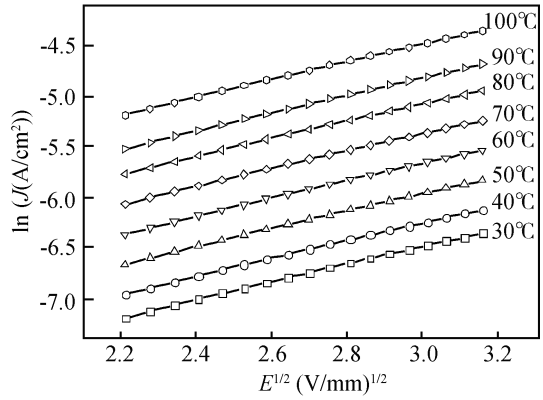

Fig. 5. ln J as a function of $E^{1/2}$ for the as-sintered sample.

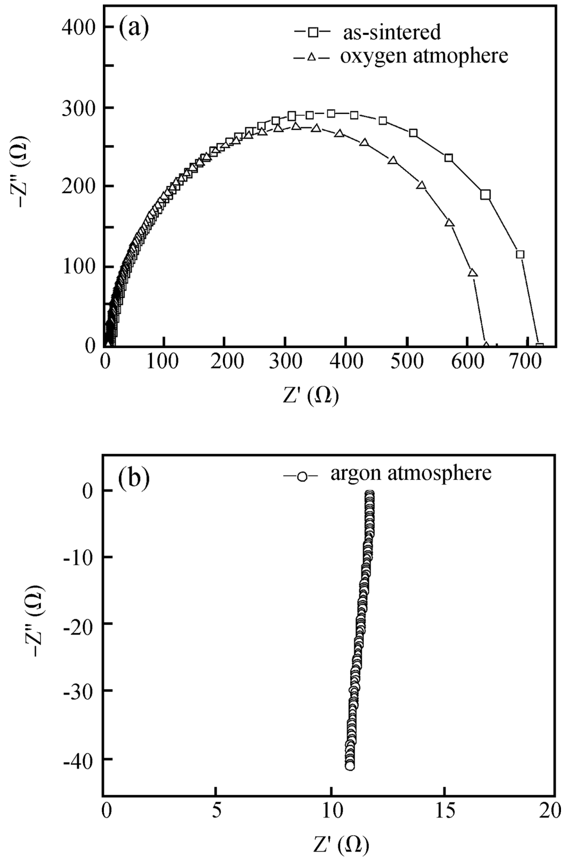

Fig. 4. Complex impedance plots of the WO_3 ceramics.

response of the sample. However, the shape of the spectrum indicates the existence of inductive effects which are similar for the different samples[23]. It is clear that the grain boundary resistance is totally recovered after thermal treatment in oxygen atmosphere. Thus, the adsorption of oxygen in grain boundaries, which leads to the highly resistive surface layer, is the origin of the varistor property of WO_3 ceramics. As reported by Santos *et al.*[24] the atmosphere strongly affects the electrical properties, due to the oxidizing mechanism at the grain boundary.

In order to conduct further investigation on the grain boundaries of WO_3 varistors, an I–V test at temperatures ranging from 30 to 100 °C was made. Figure 5 shows the plot of ln$J$ versus $V^{1/2}$ at different temperatures for the as-sintered sample. A set of parallel straight lines are observed for the electric field and temperature range studied.

The results suggest that thermionic emission is the conduction mechanism in the WO_3-based varistor system. The model for the barrier at the grain boundaries is a Schottky-type. Similar behavior was observed in the samples after heat treatment in different atmospheres.

For a Schottky type of mechanism, the current density of a varistor is related to the electric field and temperature by[25]:

$$J = AT^2 \exp[(\beta E^{1/2} - \phi_B)/kT], \tag{2}$$

where A is Richardson's constant, k is Boltzmann's constant, Φ_B is the interface barrier height, and β is a constant related to the grain size and the barrier width. In the thermionic emission model, Eq. (2), the β constant is given by Eq. (3),

$$\beta = \sqrt{(1/nw)(2e^3/4\pi\varepsilon_0\varepsilon_r)}, \tag{3}$$

where n is the number of grains in series, w is the barrier width, e is the electron charge, ε_0 and ε_r are the vacuum and material dielectric constant ($\varepsilon_r = 230$)[26], respectively, and n is defined by

$$n = L/G, \tag{4}$$

where L is the sample height and G is the mean grain size determined from the scanning electron micrographs. By plotting ln$J$ versus $E^{1/2}$ in Eq. (2) a straight line is obtained where the slope is β/kT. Therefore the barrier voltage width w can be determined by Eq. (3). The plot of ln$J$ versus l/T of Eq. (2) is a straight line with a slope equal to $(\phi_B - \beta E^{1/2})/k$. By using β values, ϕ_B is determined. Both ϕ_B and w values were carried out in a temperature range of 30–100 °C in a DC biasing test. Donor density (N_d) and surface state density (N_S) can be derived from the equation $\phi_B = e^2 N_S^2 / 2\varepsilon_0\varepsilon_r N_d$ and $N_S = 2wN_d$.

These sets of parameters are listed in Table 1, which shows the reversible trends in the barrier height, the donor density, the surface state density and the barrier width of the varistor. It can be concluded that oxygen plays a key role in the formation of the Schottky-type barriers.

The composition on the grain surface of the as-sintered sample was determined using AES depth profile curves[27] by our group, The results show that its oxygen content decreased with increasing sputter depth, and the O/W ratio balanced at a depth of 2–3 nm. That is to say, the extra oxygen exists in grain surfaces (about 3–4 oxygen ion layers) in the state of adsorbed ions. Due to the multiple oxidation states, tungsten trioxide (WO_{3-x}) has different oxygen compositions with x ranging from 0 to 2 (+2, +3, +4, +5 and +6) of W[28]. It can release oxygen with the increase of ambient temperature and incorporate oxygen in the process of cooling. During the cooling process, the molecule oxygen may be adsorbed by grain surface defects, such as native oxygen vacancies and lattice mismatch. The adsorbed oxygen can easily capture electrons to become negatively charged ions. In this way, a double Schottky barrier makes the WO_3 exhibit non-ohmic behavior.

4. Conclusion

The effects of thermal treatment in argon and oxygen atmospheres on the structural and varistor properties of WO_3 ceramics have been investigated. It was found that the nonlinear coefficient first decreases and then increases when treated successively in argon and oxygen atmospheres, but no significant changes in phase or grain shape occur. The physical origin of the non-ohmic behavior of the WO_3 ceramics is oxygen on the grain surfaces adsorbed by intrinsic defects.

References

[1] Frosch C J. Improved silicon carbide varistors. Bell Lab Rec, 1954, 32: 336

[2] Dienel H F. Silicon carbide varistors. Bell Lab Rec, 1956, 34: 407

[3] Eda K. Zinc oxide varistors. Electrical Insulation Magazine, 1989, 5: 28

[4] Zang G Z, Wang J F, Chen H C, et al. Efect of Na on the electrical properties of ZnO based varistors. Electron Compon & Mater, 2009, 22: 17

[5] Matsuoka M, Masuyama T, Iida Y. Voltage nonlinearity of zinc oxide ceramics doped with alkali earth metal oxide. Jpn J Appl Phys, 1969, 8: 1275

[6] Chen H C, Wang J F, Zang G Z, et al. Electrical properties of (Nb, Mg, A1)-doped ZnO based varistor. Electron Compon Mater, 2004, 23: 27

[7] Pianaro S A, Bueno P R, Longo E. A new SnO_2-based varistor system. J Mater Sci Lett, 1995, 14: 692

[8] Matsuoka M. Nonohmic properties of zinc oxide ceramics. Jpn J Appl Phys, 1971, 10: 736

[9] Selim F A, Gupta T K, Hower P L, et al. Low voltage ZnO varistor: device process and defect model. J Appl Phys, 1980, 51: 765

[10] Makarov V, Trontelj M. Novel varistor material based on tungsten oxide. J Mater Sci Lett, 1994, 13: 937

[11] Mahan G D, Levinson L M, Philipp H R, et al. Theory of conduction in ZnO-varistors. J Appl Phys, 1979, 50: 2799

[12] Pike G E, Leamy H J, Seager C H. Electronic properties of ZnO varistors. Amsterdam: North-Holland, 1982

[13] Bernasconi J, Knecht H P, Knecht B, et al. Investigation of various models for metal oxide varistors. J Electron Mater, 1976, 5: 473

[14] Bernasconi J, Strässler S, Knecht B. Zinc oxide based varistors: a possible mechanism. Solid State Commun, 1977, 21: 867

[15] Einzinger R. Metal oxide varistor action-a homojunction breakdown mechanism. Appl Surf Sci, 1978, 1: 329

[16] Zhao M, Wang W M, Zhang C S, et al. Present development of low-voltage ZnO varistor ceramics. J Mater Sci Eng, 2005, 23: 915

[17] Magnusson K O, Wiklund S. Interface formation of Bi on ceramic ZnO: a simple model varistor grain boundary. J Appl Phys, 1994, 76: 7405

[18] Nahm C W. Effect of sintering time on varistor properties of Dy_2O_3-doped ZnO-Pr_6O_{11}-based ceramics. Mater Lett, 2004, 58: 3297

[19] Orlandi M O, Bomio M R D, Longo E. Nonohmic behavior of sno-mno polycrystalline ceramics. II. analysis of admittance and dielectric spectroscopy. J Appl Phys, 2004, 96: 3811

[20] Clarke D R. Varistor ceramics. J Am Ceram Soc, 1999, 82: 485

[21] Gupta T K. Application of zinc oxide varistors. J Am Ceram Soc, 1990, 73: 1817

[22] Verges M A, West A R. Impedance and modulus spectroscopy of ZnO varostors. J Electroceram, 1997, 1: 125

[23] Smith A, Baumard J F, Abélard P, et al. Ac impedance measurements and V–I characteristics for Co-, Mn-, or Bi-doped ZnO. J Appl Phys, 1989, 65: 5119

[24] Santos M R C, Bueno P R, Longo E, et al. Effect of oxidizing and reducing atmosphere on the electrical properties of dense SnO_2-based varistors. J Eur Ceram Soc, 2001, 21: 161

[25] Pianaro S A, Bueno P R, Olivi P. Effect of Bi_2O_3 addition on the microstructure and electrical properties of the $SnO_2{\cdot}CoO{\cdot}Nb_2O_5$ varistor system. J Mater Sci Lett, 1997, 16: 634

[26] Salje E. Lattice dynamics of WO_3. Acta Crystallographica Section A, 1975, 31: 360

[27] Hua Z Q, Zhao H W, Li T Y, et al. The origin of varistor property of WO_3 ceramic. (To be published)

[28] Shen P W, Che Y X. Inorganic chemistry series eight. Beijing: Science Press, 1998