JOURNAL OF MATERIALS SCIENCE **39** (2004) 4373–4374 LETTERS

Nonlinear electrical behaviour of the WO_3-based system

G. Z. ZANG, J. F. WANG, H. C. CHEN, W. B. SU, C. M. WANG, P. QI
School of Physics and Microelectronics, Shandong University, Jinan 250100, People's Republic of China
E-mail: zanggouxhong@sina.com

Varistors can limit high transient voltage surges and can repeatedly endure such surges without being destroyed, therefore they are usually used to protect electronic circuits from voltage pulse shocks. The most important property of a varistor is its nonlinear voltage–current characteristic. This can be expressed by the equation $I = KV^{\alpha}$, where α is the coefficient of non-linearity, the essential parameter to scale the nonlinearity.

Commercial varistors used in protection systems are based on SiC or ZnO. Varistors based on SiC have low coefficients (of non-linearity) [1]. ZnO varistors exhibit high coefficients (of nonlinearity), but the degradation problem of ZnO varistors has not been resolved [2, 3]. While efforts to improve the temperature stability of ZnO varistors are being made, the search for new varistor materials is ongoing. In 1995, Pianaro found a new varistor material, (Co, Nb)-doped SnO_2, which is single phase with the rutile structure [1]. In 1999, Kim *et al.* found a one-step-air-fired $SrTiO_3$-based ceramic which had varistor characteristics [4]. In 2000, Wang found that only one oxide (Sb_2O_3)-doped TiO_2 ceramics shows varistor behavior [5]. Following Wang, in 2002, Su found another TiO_2 varistor, doped with only one oxide (WO_3) [6].

In this letter, the processing of a new WO_3-based varistor system, $WO_3{\cdot}Na_2CO_3{\cdot}CuO/CdO/Bi_2O_3/Sb_2O_3$, as well as its nonlinear properties (electrical field as a function of current density) and dielectric properties are described.

The raw chemicals used in this study were analytical grades of WO_3 (99%), Na_2CO_3 (99.8%), CuO (98%), CdO (99%), Bi_2O_3 (99%), Sb_2O_3 (99.9%) and obtained from Shanghai Chemical Company. The composites investigated in the present work contain a molar ratio of $WO_3{:}Na_2CO_3{:}X = 96.5{:}0.5{:}3$, where $X =$ CuO, CdO and $WO_3{:}Na_2CO_3{:}Y = 98{:}0.5{:}1.5$, where $Y = Bi_2O_3, Sb_2O_3$. Varistors were obtained by conventional ceramic processing. The mixed raw chemicals were milled in nylon pot for 15 h with ZrO_2 balls and some distilled water, dried, mixed with 0.5 wt% PVA binder and pressed into disks 15 mm in diameter and 1.5 mm in thickness at 180 MPa. After burning out the PVA binder at 650 °C, the disks were sintered in air at 1000 °C for 60 min and then slowly cooled to room temperature. During sintering, compacts were surrounded with powders of matching compositions and covered with crucibles to reduce evaporation. The frequency dependence of the relative dielectric constant and complex impedance spectra were obtained using an impedance analyzer (Agilent 4294A). For electrical characterization of current density as a function of applied electrical field, a semiconductor I–V grapher (QT2) was used. The coefficient of non-linearity α was obtained from

$$\alpha = \frac{\log(J_2/J_1)}{\log(V_2/V_1)} \tag{1}$$

where V_2 and V_1 are the voltages at the current densities $J_2 = 10\ \text{mA/cm}^2$ and $J_1 = 1\ \text{mA/cm}^2$, respectively.

Current density as a function of electrical field curves measured at room temperature for WO_3-based ceramics is shown in Fig. 1. A high degree of non-linearity was observed for all the samples and the sample doped with 1.5 mol% Sb_2O_3 has the best nonlinear electrical behavior ($\alpha = 4.1$) and the lowest breakdown electrical field (field at current 1 mA) of 4.1 V/mm.

Fig. 2 shows the frequency dependence of the dielectric properties of the WO_3-based ceramics, which have very high dielectric constants of about 10^4–10^5. The relative dielectric constants of the varistors are found to decrease significantly with increase in frequency from 40 Hz to about 10 KHz, while, in the higher frequency range of 10 k–15 MHz, the dielectric constants of the ceramics were almost unchanged, which is very useful for application in the high frequency region. According to theoretical analysis [7], the relative dielectric constant is expected to change rapidly near the relaxation frequency, which means the relaxation frequencies of the varistors are lower than 100 Hz. The complex impedance data were measured at 32 °C in the range 40 Hz to 15 MHz. From the impedence data cole-cole diagrams were drawn as shown in Fig. 3 and it can be seen that the samples doped with CdO and Bi_2O_3 has the largest and lowest resistivity, respectively, at high frequency. The lowest breakdown electrical field may be related to the lowest resistivity of WO_3 grain boundaries in the sample doped with Bi_2O_3.

In 1985, Gupta and Carlson developed a grain boundary defect model for ZnO varistors [8]. By analogy to the model for ZnO, Wang *et al.* proposed a model for TiO_2 and SnO_2 varistors [5, 9]. All the models and studies for varistors indicate that a dopant with higher valency than the host cation is necessary to decrease the resistivity of varistor ceramics. However, the WO_3-based ceramics exhibit nonlinear electrical behavior without a donor dopant. Sahle *et al.* reported that even a very slight decrease of oxygen content in WO_3 could give rise to an increase in the electrical conductivity [10]. Wang *et al.* reported that pure WO_3 and WO_3-MnO_2 ceramics exhibited slight nonohmic behavior and the presence of Bi_2O_3 was useless for nonlinearity

0022–2461

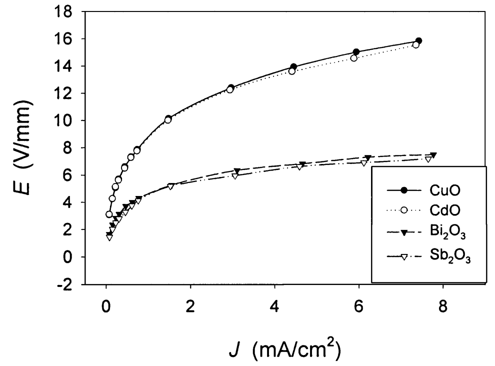

Figure 1 Applied electric field as a function of current density for the WO_3-based varistors.

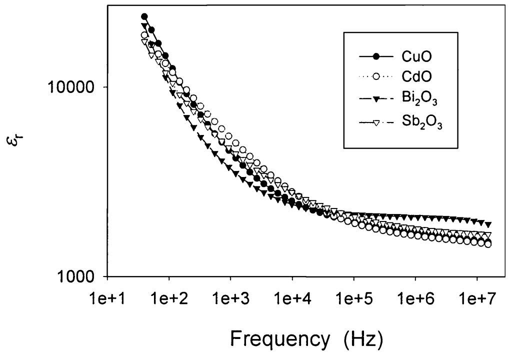

Figure 2 Relative dielectric constants as a function of frequency for WO_3-based varistors.

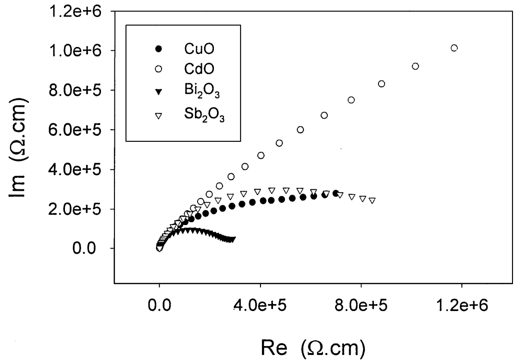

Figure 3 Complex impedance spectra of the samples.

in the WO_3-MnO_2-Na_2CO_3 system. However, the sample doped with Bi_2O_3 shows better nonlinearity than that of WO_3-MnO_2-Na_2CO_3-Bi_2O_3 system reported by Wang *et al.* [11] and Bi_2O_3 is essential for WO_3-based varistors according to the following reaction [1]:

$$Bi_2O_3 \xrightarrow{WO_3} 2Bi_W^{3-} + 3V_O^{2+} + xO_O + \frac{3-x}{2}O_2 \quad (2)$$

The substitution of W atoms by Bi leads to the formation of oxygen vacancies and can explain the better nonlinearity if one considers that vacancies are rate controlling in ion diffusion since the ion diffusion will lead to a more homogeneous microstructure. The dopant of Na_2CO_3 may lead to the following reaction at high temperature:

$$Na_2O \xrightarrow{WO_3} 2Na_W^{5-} + 5V_O^{2+} + xO_O + \frac{1-x}{2}O_2 \quad (3)$$

Oxygen in the above equations will be partly absorbed at WO_3 grain boundaries and the absorbed oxygen will capture electrons from negatively charged defects to become negatively charged O^- or O^{2-} [2, 12, 13].

The varistor behaviour of WO_3 materials can be explained by the introduction of defects in the crystal lattices that are responsible for the formation of Schottky type potential barriers at grain boundaries. By analogy to the atomic defect model proposed by Gupta [8], for ZnO varistor, the potential barrier is formed by intrinsic defects of WO_3, extrinsic defects created by solid substitution of dopants, and negative charges, O^- and O^{2-} at the interface. These defects create depletion layers at grain boundaries leading to the formation of a voltage barrier for the electronic transport. This transport occurs by tunneling and is responsible for the nonlinear behaviour of current density as a function of applied electric field [14].

In conclusion, WO_3-based ceramics, $WO_3 \cdot Na_2CO_3 \cdot CuO/CdO/Bi_2O_3/Sb_2O_3$, were found to exhibit nonlinear current–voltage characteristics. They are characterized by low breakdown voltage, and are therefore, potential materials for low voltage varistors.

Acknowledgment

The support of the National Natural Science Foundation of China (Grant No. 50072013) is gratefully acknowledged.

References

1. S. A. PIANARO, P. R. BUENO, E. LONGO, *et al.*, *J. Mater. Sci. Lett.* **14** (1995) 692.
2. E. R. LEITE, J. A. VARELA and E. LONGO, *J. Mater. Sci.* **27** (1992) 5325.
3. L. M. LEVISON and H. R. PHILIPP, *J. Appl. Phys.* **46** (1975) 1332.
4. S. H. KIM, H. W. SEON and H. K. KIM, *Mater. Sci. Eng.* B **60** (1999) 12.
5. J. F. WANG and H. C. CHEN, *Chin. Phys. Lett.* **17** (2000) 530.
6. W. B. SU, J. F. WANG and H. C. CHEN, *J. Appl. Phys.* **92** (2002) 4779.
7. J. M. WU and C. J. CHEN, *J. Mater. Sci.* **23** (1988) 4157.
8. T. K. GUPTA and W. G. CARLSON, *ibid.* **20** (1985) 3487.
9. Y. J. WANG, J. F. WANG and C. P. LI, *et al.*, *J. Mater. Sci. Lett.* **20** (2001) 19.
10. W. SAHLE and M. NYGREN, *J. Solid. St. Chem.* **48** (1983) 154.
11. Y. WANG, Z. ABURAS and K. L. YAO, *et al.*, *Mater. Chem. & Phys.* **58** (1999) 51.
12. P. R. BUENO, S. A. PIANARO, E. C. PERERIA, *et al.*, *J. Appl. Phys.* **84** (1998) 3700.
13. E. R. LEITE, A. M. NASCIMENTO and P. R. BUENO, *J. Mater. Sci.: Mater. Electr.* **10** (1999) 321.
14. H. R. PHILLIPP and L. M. LEVINSON, *J. Appl. Phys.* **46** (1975) 3206.

Received 11 September
and accepted 30 December 2003