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New $ZnSnO_3$-based varistor system

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

Semiconducting ceramics are widely used in electrical industries involving mobile communications, computers, signal processing, power transport, and control systems, because of their unique and useful electrical characteristics [1]. Varistors which are generally used to protect electronic circuits from voltage shock can sense and limit high transient voltage surges and can repeatedly endure such surges without being destroyed. The most important property of a varistor is its nonlinear voltage–current characteristic. It can be expressed by the equation $I = KV^{\alpha}$. The α coefficient gives the degree of nonlinearity and the constant K depends on the microstructure and is related to the electrical resistivity of the material.

Commercial varistors used in protection systems are based on SiC or on ZnO. Varistors based on SiC have low nonlinearity coefficients [2–4] and ZnO varistors exhibit high nonlinear coefficients, but the degradation problem of ZnO varistors has not been resolved [5–7]. Therefore, the efforts to find new varistor materials have been ongoing. In 1983, N. Yumaka, M. Masuyama found that $SrTiO_3$-based ceramics made by a two-step process had varistor characteristics [8]. In 1995, S. A. Pianaro found a new varistor material [4], (Co,Nb)-doped SnO_2, which has only a single phase, rutile structure. In 2000, J. F. Wang found one oxide (Sb_2O_3)-doped TiO_2 ceramic to have varistor behavior [9]. Following Wang, W. B. Su found, in 2002, another TiO_2 varistor doped with only one oxide (WO_3) [10].

In this work, we found a new varistor material, (Nb,Si)-doped $ZnSnO_3$, and investigated the effects of SiO_2 on the properties of the (Nb,Si)-doped $ZnSnO_3$ varistor.

The materials used were analytical grades of SnO_2 (99.5%), Nb_2O_5 (99.5%), ZnO (99.5%), and SiO_2 (90.0%). The compositions were $SnO_2 + ZnO + 0.2\%Nb_2O_5 + x\%SiO_2$ in molar terms, where $x = 0, 0.25, 0.4, 0.5, 1.0$. The varistors were prepared by conventional ceramic processing. The mixed raw chemicals were milled in a nylon kettle with ZrO_2 balls and some distilled water, dried, mixed with 0.6% weight of PVA binder and pressed into disks 15 mm in diameter and 1.5 mm in thickness at 160 MPa. The disks were sintered at 1427 °C for an hour and cooled to room temperature after burning out the PVA binder at 650 °C. To measure the electrical properties, silver electrodes were made on both surfaces of the sintered disks. For microstructure characterization, the surfaces of the samples were observed by scanning electron microscopy (SEM) and the phases were analyzed by X-ray diffraction (XRD). For electrical characterization of current density versus applied electrical field, an I–V grapher (QT2) was used. The complex impedance dependent on frequency is measured using an Agilent 4294A impedance analyzer.

According to the XRD analysis (Fig. 1), no apparent second phase was observed and SnO_2 and ZnO should be synthesized according to the following reaction [11]:

$$ZnO + SnO_2 \xrightarrow{1427\,^{\circ}C} ZnSnO_3 \tag{1}$$

The electrical nonlinear characteristics of the samples are shown in Figs 2 and 3. The nonlinear coefficients α which are shown in Table I are calculated by the following equation [4, 11]:

$$\alpha = \frac{\log(I_2/I_1)}{\log(V_2/V_1)} \tag{2}$$

where V_1 and V_2 are the voltages at currents I_1 and I_2, respectively. It is found obviously from Figs 2 and 3 that the breakdown electrical field E_b of the varistor without SiO_2 is much higher than that of the varistors with different contents of SiO_2 dopant.

The microstructure of the samples doped without SiO_2 and with 0.4 mol% SiO_2 is shown in Figs 4 and 5. One can find some flaws on the surface of the sample without SiO_2. The flaws might be produced by the internal uneven stresses caused by cooling.

Potential barrier height of the grain boundaries is measured according to the following equation [13, 14]:

$$J_S = AT^2 \exp\left[\frac{\beta\sqrt{E} - \phi_B}{k_B T}\right] \tag{3}$$

where A is the Richardson constant, k_B is the Boltzman constant, ϕ_B is the barrier height, E is the electrical field, and β is a constant determined by the relation

$$\beta = \sqrt{\frac{1}{n\omega}\left(\frac{2e^3}{4\pi\varepsilon_r\varepsilon_0}\right)} \tag{4}$$

where n is the grain number per unit length, ω is the barrier width, e is the electron charge, and ε_r is the relative permittivity. J and E of some of the samples were measured at different temperatures. The value of ϕ_B of the varistor without SiO_2 is much higher than that of the varistors with different contents of SiO_2 dopant as shown in Table I.

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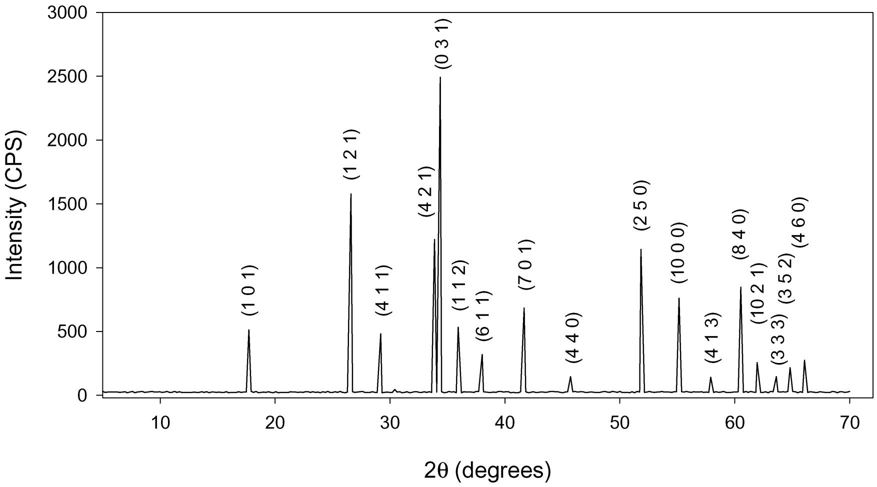

Figure 1 X-ray diffraction pictures for a sample doped with 0.4 mol% SiO_2.

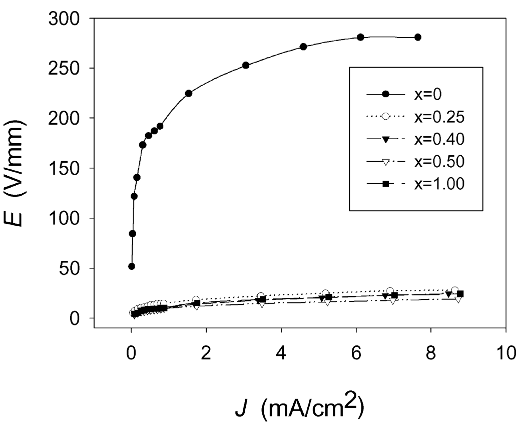

Figure 2 Electrical field applied vs. current density for samples with different SiO_2 contents.

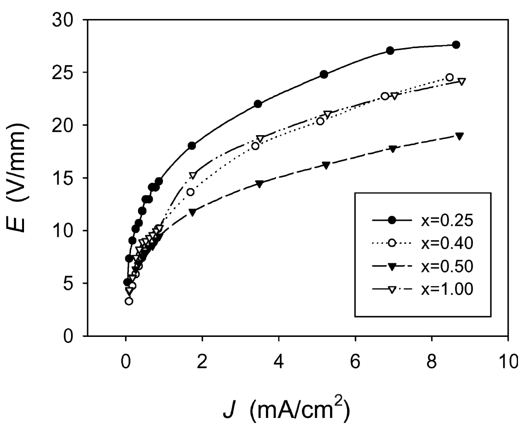

Figure 3 Electrical field applied vs. current density for samples with different SiO_2 contents.

Figs 6 and 7 show the complex impedance spectra of the varistors without SiO_2 and with 0.4 mol% SiO_2. It is found clearly that the resistance of the former is much higher than that of the latter at low frequency (40 Hz) and high frequency (15 MHz), respectively. This indicates that SiO_2 may have increased the electronic conductivity of the $ZnSnO_3$ grains and grain boundaries since the polycrystalline ceramic is often considered as a large number of capacitors in series [15]. So the addition of SiO_2 may lead to the following reactions:

$$SiO_2 \longrightarrow Si_i^{4+} + 4e^- + O_2 \quad (5)$$

$$SiO_2 \stackrel{ZnSnO_3}{\longrightarrow} Si_{Zn}^{2+} + 2e^- + O_O^\times + \frac{1}{2}O_2 \quad (6)$$

$$SiO_2 \stackrel{ZnSnO_3}{\longrightarrow} Si_{Sn}^\times + 2O_O^\times \quad (7)$$

The addition of Nb_2O_5 to the $ZnSnO_3$-based varistors may lead to the following reactions:

$$Nb_2O_5 \stackrel{ZnSnO_3}{\longrightarrow} 2Nb_{Zn}^{3+} + 6e^- + 2O_O^\times + \frac{3}{2}O_2 \quad (8)$$

$$Nb_2O_5 \stackrel{ZnSnO_3}{\longrightarrow} 2Nb_{Sn}^{+} + 2e^- + 4O_O^\times + \frac{1}{2}O_2 \quad (9)$$

The Si_i^{4+} located at the interstitial of $ZnSnO_3$ lattice and the e^- originated in the above reaction will increase the electrical conductivity of the varistors. The higher electronic conductivity and lower potential barrier height of the varistors doped with SiO_2 may be the main reason for their lower breakdown electrical field than that of the varistor without SiO_2. Some of the e^- originated in Equations 5, 6, 8, and 9 will be captured by the oxygen partly absorbed at $ZnSnO_3$ grain boundaries.

The varistor behavior of $ZnSnO_3$ can be explained by the introduction of defects in the crystal lattice that are responsible for the formation of Schottky-type potential barriers at the grain boundaries. By analogy to the atomic defect model proposed by Gupta [16] for the ZnO varistor, the potential barrier is formed by

TABLE I Characteristics of the samples doped with different contents of SiO_2

SiO_2 (mol%)	α	Density (g/cm^3)	E_b (V/mm)	ϕ_B (eV)
0	6.0	5.28	198	0.84
0.25	3.6	6.28	14.6	0.74
0.40	2.0	6.01	10.2	0.78
0.50	3.3	6.28	7.9	0.72
1.00	2.7	6.18	11.8	0.73

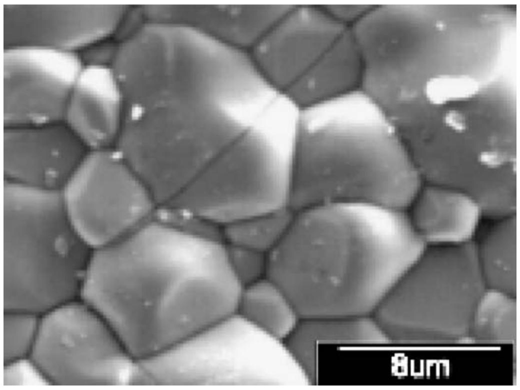

Figure 4 SEM photomicrographs of a sample doped without SiO_2.

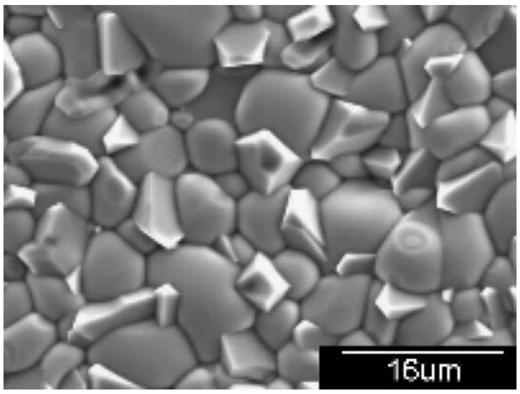

Figure 5 SEM photomicrographs of a sample doped with 0.4 mol% SiO_2.

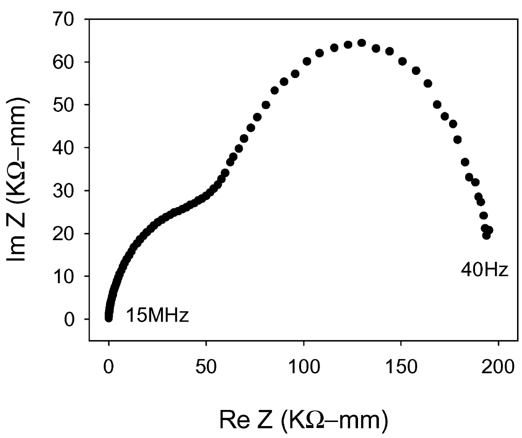

Figure 6 Complex impedance spectra of a sample doped without SiO_2.

intrinsic defects of $ZnSnO_3$, extrinsic defects created by solid substitution of dopants, and negative charges at the interface corresponding to vacancies of tin and zinc atoms. 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

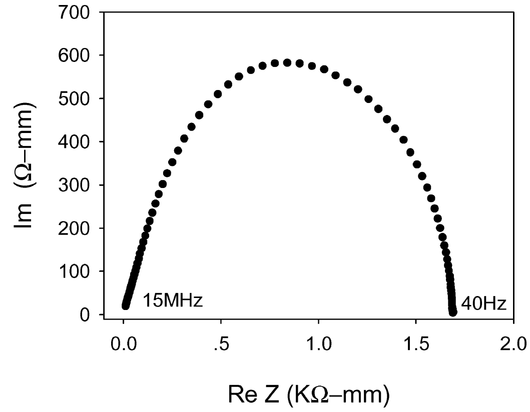

Figure 7 Complex impedance spectra of a sample doped with 0.4 mol% SiO_2.

behavior of current density versus applied electric field [17].

The values of the nonlinear coefficients α of the varistors obtained in this study are low. Efforts to further improve the nonlinear coefficient α are in progress.

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