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The electrical properties and d.c. degradation characteristics of silver doped ZnO varistors

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$ZnO–Bi_2O_3$-based ceramic varistors containing up to 2500 p.p.m. Ag_2O were prepared by the mixed oxide route. The products were characterized in terms of current–voltage (*I–V*) behaviour, capacitance–voltage (*C–V*) behaviour and d.c. degradation behaviour. Additions of silver did not significantly affect ZnO grain growth or sintered density, but decreased the non-linearity exponent, α, and increased the breakdown voltage. Silver-doped specimens exhibited an unusual d.c. degradation behaviour, with the leakage current initially decreasing before reaching a stable value. For doping levels $\geq$ 500 p.p.m. Ag_2O, the change in breakdown voltage was positive for both forward and reverse directions. Silver doping appeared to increase the Schottky barrier height under conditions of continuous d.c. stress and improve the degradation behaviour. The optimum levels of Ag_2O addition were in the range 500–1000 p.p.m.

1. Introduction

Zinc oxide varistors are semiconducting ceramics which behave as highly non-ohmic resistors [1–6]. They are fabricated by the sintering of ZnO powders with small amounts of metal oxide additives, such as Bi_2O_3, CoO, MnO, and Sb_2O_3, etc. The current–voltage (*I–V*) characteristics of ZnO varistors can be expressed by an empirical equation [1–6]

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

where k is a constant and α is the non-linearity exponent. For commercial ZnO varistors, the α value is usually above 30. The excellent non-linear current–voltage (*I–V*) characteristics of ZnO varistors have resulted in their extensive application as surge-protection devices in electronic circuits and electric power systems [2–6].

In use, varistors are subjected to a continuous voltage which gives rise to a small leakage current. With time the varistor begins to degrade causing a gradual increase in the leakage current. This may eventually lead to thermal runaway and total destruction of the device. An understanding of the factors controlling degradation is, therefore, of considerable practical importance.

Several procedures have been found to improve the degradation characteristics of ZnO varistors. These include heat treatment [7], glass addition [8–10] and silver-doping [10]. For heat treatment, the sintered bodies of ZnO varistors are subjected to a temperature of approximately 600 °C for a time $\geq$ 30 min. This leads to an increase in the current stability of the varistors, but a decrease in the non-linearity exponent and an increase in the leakage current. Glass additions are usually made with a B–Si–Pb-based glass, which has to be prepared and powdered before use. Both glass additions and silver-doping can improve the degradation properties of ZnO varistors effectively. Amongst these procedures, silver-doping is both simple and convenient, but has not been studied in detail. In the present investigation, the effects of Ag_2O doping on the current–voltage (*I–V*) characteristics and the d.c. degradation behaviour of ZnO varistors of a typical commercial composition were examined.

2. Experimental procedure

A series of specimens containing different amounts of Ag_2O were prepared. The base composition was a typical commercial formulation containing a range of additives including Bi_2O_3, Sb_2O_3, Co_2O_3, Cr_2O_3, and MnO_2. All powders were reagent grade. The additives were first mixed in the required proportions, ball milled in propan-2-ol with zirconia grinding media for 6 h, and calcined at 600 °C for 30 min. They were then mixed with ZnO (11:89, weight ratio) and Ag_2O (0, 250, 500, 1000, 2500 p.p.m.). The procedures for the second mixing were the same as the first. After drying, the mixtures were pressed into discs and sintered in air at 1180 °C for 1 h. The sintered samples were then lapped to 13.5 mm diameter and 2 mm thick. Silver electrodes were applied to both faces of samples with silver paste (which was subsequently heated at 550 °C for 15 min).

The densities of the samples were determined by an Archimedes' method with samples being weighed in air and in iodoethane. Microstructures were studied by optical microscopy and scanning electron microscopy (Philips 505 with an energy dispersive X-ray analytical facility). The ZnO grain size was determined by a linear intercept method using scanning electron micrographs. The phases were determined by X-ray diffraction analysis using CuK_α radiation and a Philips diffractometer (PW1710) in conjunction with a horizontal goniometer.

The current–voltage ($I-V$) characteristics were determined at room temperature using a variable dc power supply (Branderburg 475R) with applied voltages up to 800 V (i.e. giving a field up to 4000 V/cm for the 2 mm thick specimens). The capacitance-voltage ($C-V$) evaluation was performed at room temperature with an LCR meter (Hewlett Packard 4275 A) at a frequency of 10 kHz with bias voltage in the 0-160 V range. Degradation tests were carried out at 115 ± 1°C for periods up to 22 hours using the dc supply. The applied voltage ratio was 0.85 $V_{1\mathrm{mA/cm}^2}$. The variation of leakage current with time was measured.

3. Results and discussion

Fig. 1 shows a typical scanning electron micrograph of an undoped (ZNR) sintered specimen. Three phases were found in all the specimens; they were ZnO grains, $Zn_7Sb_2O_{12}$ spinel and a bismuth-rich intergranular phase. No obvious phase change could be detected in the silver-doped samples. The average grain sizes and densities of specimens are shown in Fig. 2. It is clear that silver doping caused no significant change in the average grain size. This suggests that the silver-doping does not affect the ZnO grain growth. Consequently, sample densities did not vary significantly with silver-doping.

The current–voltage ($I-V$) characteristics of the undoped and silver-doped ZnO varistor samples are shown in Fig. 3. The $I-V$ behaviour deteriorated as the level of silver increased, especially from 1000–2500 p.p.m. From the $I-V$ curves, the non-linear exponents were determined according to the following equation (which is derived from Equation 1)

$$\alpha \simeq \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1} \tag{2}$$

where E_1 and E_2 are the electric fields when the current densities are J_1 and J_2, respectively. In the present investigation, J_1 and J_2 were 0.1 and 1 mA cm^{-2}, respectively. The α values and breakdown fields are shown in Fig. 4. It is clear that the α values exhibit little change when there are only small additions of silver (250 p.p.m. Ag_2O), but α decreases rapidly at higher silver levels. In contrast, the breakdown field shows the inverse relationship.

The time dependence of the leakage current for samples subjected to d.c. degradation is shown in Fig.

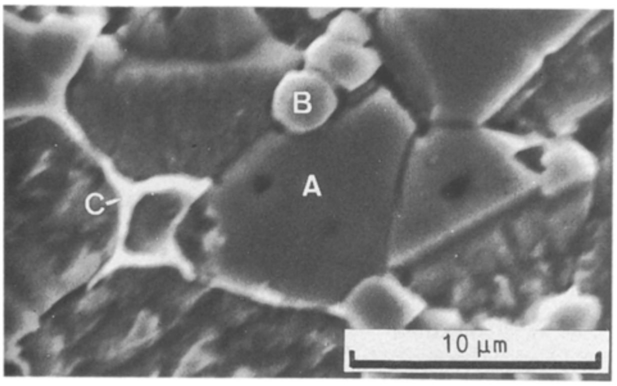

Figure 1 A typical scanning electron micrograph of a ZNR varistor. (a) ZnO grain, (b) $Zn_7Sb_2O_{12}$ spinel, (c) bismuth-rich intergranular phase.

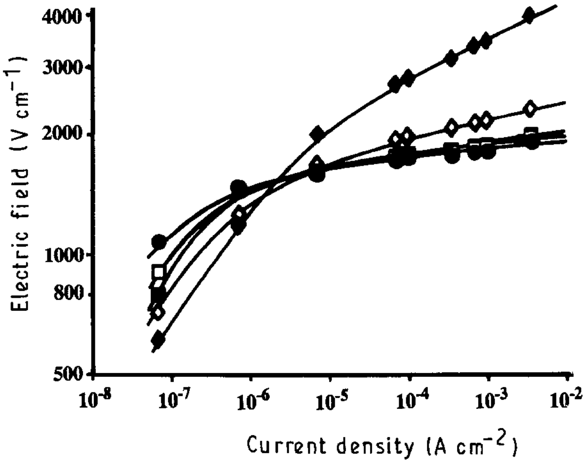

Figure 3 $I-V$ characteristics of the ZnO varistors as a function of silver content. (●) ZNR (□) ZNR + 250 p.p.m. Ag_2O, (■) ZNR + 500 p.p.m. Ag_2O, (◇) ZNR + 1000 p.p.m. Ag_2O, (◆) ZNR + 2500 p.p.m. Ag_2O.

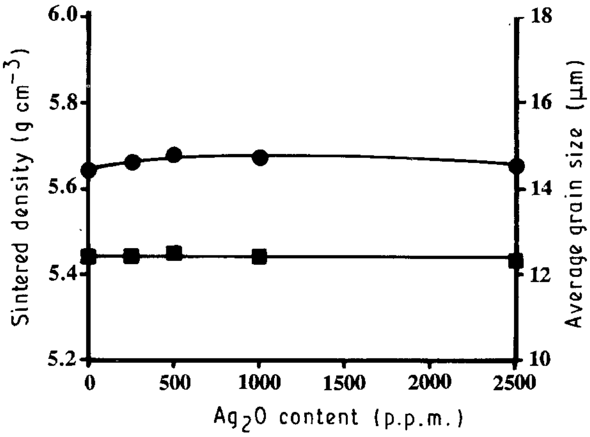

Figure 2 (●) Average grain size and (■) sintered density as a function of silver content for ZnO varistors.

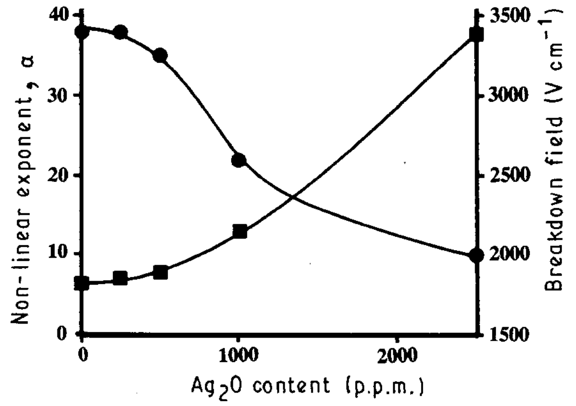

Figure 4 (●), Non-linear exponent, α and (■) breakdown field as a function of silver content for ZnO varistors.

5. It is interesting to note that although the initial values of I_{L0} (i.e. leakage current I_L at time zero) for silver-doped specimens are larger than that of ZNR, the I_L values for the doped specimens decrease with time, while those for ZNR increase with time. In general, I_L values for the silver-doped specimens decrease initially and approach an equilibrium value. The duration of the first stage depends on the amount of silver added: the greater the silver doping, the longer is the first stage.

Fig. 6 shows the relative changes of breakdown voltage ($V_{1\mathrm{mAcm}^{-2}}$) after d.c. degradation tests for 10 h.

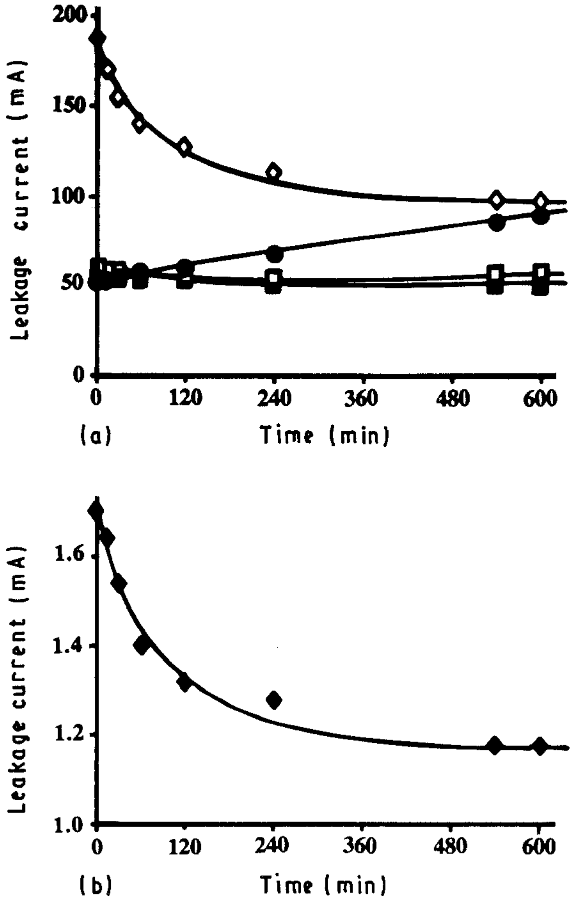

Figure 5 D.c. degradation behaviour of ZnO varistor samples subjected to 0.85 $V_{1\mathrm{mAcm}^{-2}}$ bias voltage at 115 °C. (●) ZNR, (□) ZNR + 250 p.p.m. Ag_2O, (■)ZNR + 500 p.p.m. Ag_2O, (◇) ZNR + 1000 p.p.m. Ag_2O, (◆) ZNR + 2500 p.p.m. Ag_2O.

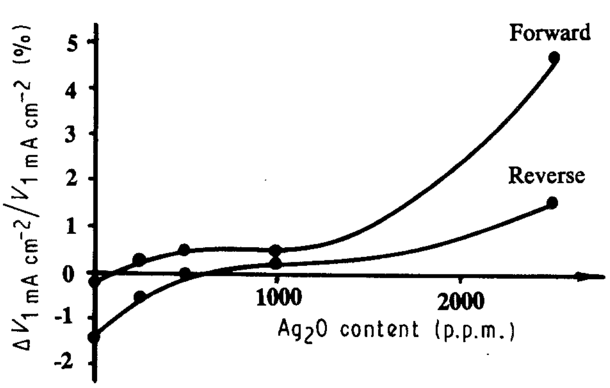

Figure 6 The percentage change of breakdown voltage for ZnO varistors under forward and reverse bias after d.c. degradation (at room temperature). (D.c. degradation conditions: 115 °C, 0.85$V_{1\mathrm{mAcm}^{-2}}$, 10 h.)

A particular feature is the difference in results for samples tested with forward and reverse bias. As the back-to-back Schottky barrier model [2, 3] is generally accepted for explaining the conduction mechanism of ZnO varistors, this difference could be interpreted in terms of the reverse bias barriers being subjected to most of the applied voltage under d.c. stress. It may be seen in Fig. 6, that the percentage change of breakdown voltage for undoped ZnO varistor is negative in both directions in accordance with earlier studies [6, 11]. The specimens doped with a very small amount of silver (250 p.p.m. Ag_2O) have a smaller negative change in the reverse direction and small positive change in the forward direction. Above 500 p.p.m. Ag_2O doping, the samples have positive changes in both directions with the rate increasing with silver content. It should be noted that between 500 and 1000 p.p.m. Ag_2O addition, not only is the change of breakdown voltage small, but also the difference between the changes for the two directions is a minimum. To understand the behaviour of the leakage current and breakdown voltage over longer time intervals, degradation tests were performed on ZNR and specimens doped with 1000 p.p.m. Ag_2O for periods up to 22 h. The results are shown in Fig. 7. It confirms that with increasing time the leakage current and breakdown voltage of the silver-doped specimens approached a stable value, but the degradation of the

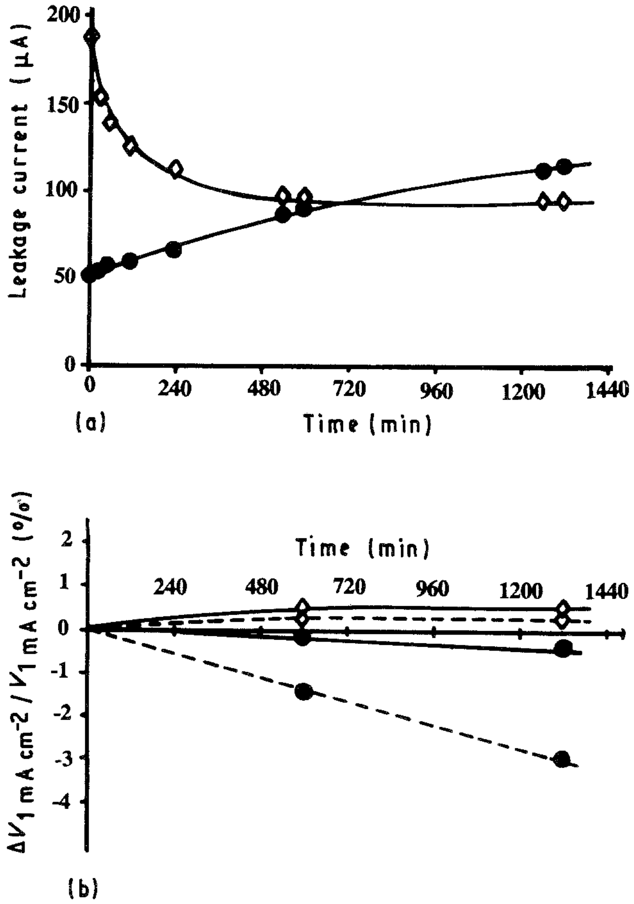

Figure 7 D.c. degradation behaviour of ZnO varistor samples subjected to d.c. stress for extended times. (a) Leakage current as a function of time (115 °C). (b) Percentage change of breakdown voltage as a function of degradation time (at room temperature) (●) ZNR, (◇) ZNR + 1000 p.p.m. Ag_2O.

ZNR samples became enhanced with time. From these results, it appears that the optimum amount of silver addition is of the order of 500–1000 p.p.m. (in Ag_2O). Over this range, the non-linear exponent of the doped specimens was 35–22. Under d.c. stress, the change of breakdown voltage was small and positive in both forward and reverse directions. For smaller amounts of silver doping, the effects on degradation behaviour were subtle, and at higher than optimum levels of doping the electrical characteristics deteriorated.

As Schottky barriers play a key role in the conduction processes, the difference between the electrical characteristics of the doped and undoped samples may mean that their barriers are different. The difference between the barriers can be described in terms of the parameters of the barriers. To estimate these, capacitance–voltage (C–V) measurements were carried out. According to the Schottky barrier model, the C–V relation can be given [12] by

$$\left(\frac{1}{C}-\frac{1}{2C_0}\right)^2 = \frac{2}{q^2\varepsilon_s N_d}(\phi + qV_g) \qquad (3)$$

where C is the barrier capacitance per unit area, C_o is the capacitance at zero bias, ϕ is the barrier height, q is the electronic charge, ε_s is the dielectric constant of ZnO (7.52×10^{-13} F cm^{-1}) [13]. N_d is the donor density in the grains and V_g is the applied voltage per grain boundary. Fig. 8 shows $(1/C - 1/2C_o)^2$ as a function of V_g for samples containing different additions of silver. The donor density, N_d and barrier height, ϕ, can be determined from the slope and intercept of the C–V line, respectively. Once ϕ and N_d are known, the width of the depletion layer, L, can be obtained from following equation [13]

$$L = \left(\frac{2\phi\varepsilon_s}{qN_d}\right)^{\frac{1}{2}} \qquad (4)$$

The calculated values of N_d, ϕ, and L as function of silver content are shown in Fig. 9. The data for the barrier voltage, V_B (i.e. the breakdown voltage per grain boundary), are plotted in Fig. 9d (deduced by combining results for the breakdown field, Fig. 4, with the average grain sizes, Fig. 2). It may be seen in Fig. 9, that silver doping appears to have a significant effect on the barrier parameters. The donor density is directly related to the dopant level with N_d decreasing almost linearly with increasing silver content. As the monovalent silver can act as an acceptor, this result is understandable. Furthermore, the decrease in donor density is accompanied by an increase in barrier voltage, barrier height and the width of the depletion layer.

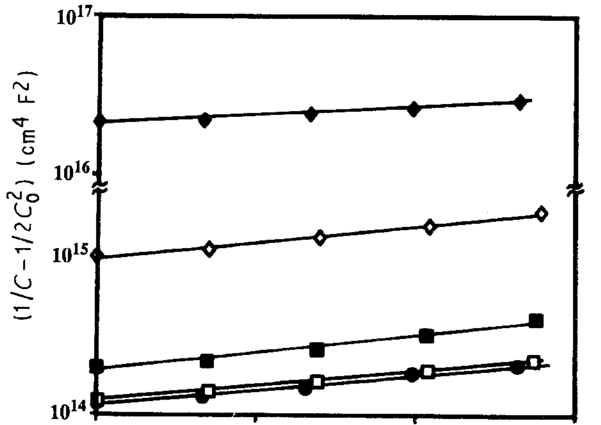

Figure 8 C–V characteristics of ZnO varistor samples. (●) ZNR, (□) ZNR + 250 p.p.m. Ag_2O, (■) ZNR + 500 p.p.m. Ag_2O, (◇) ZNR + 1000 p.p.m. Ag_2O, (◆) ZNR + 2500 p.p.m. Ag_2O.

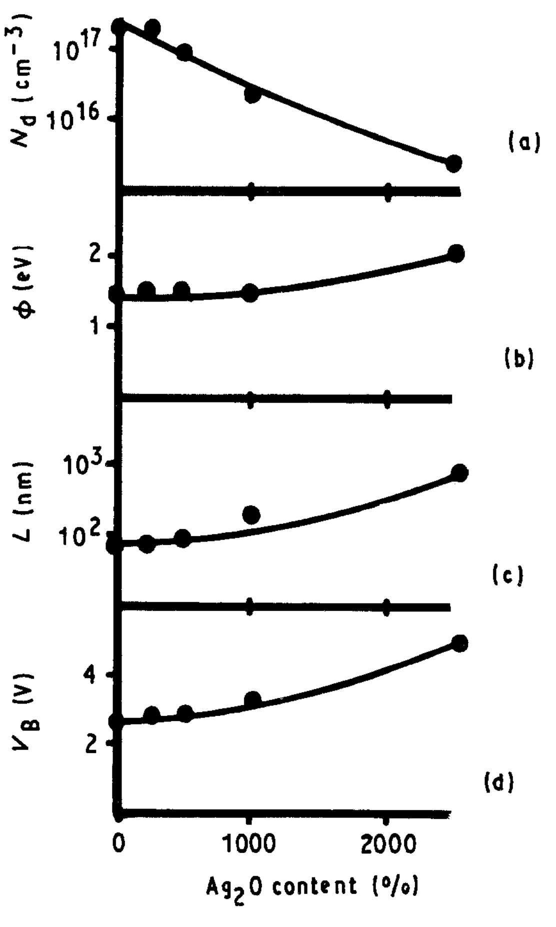

Figure 9 Barrier parameters as a function of silver content for ZnO varistors. (a) Donor density, N_d; (b) barrier height, ϕ; (c) width of depletion layer, L; (d) barrier voltage, V_B.

This study indicates that the use of silver doping decreases the non-linearity of ZnO varistors, but it also changes the degradation characteristics. It has been accepted that the degradation phenomena of ZnO varistors is attributed to the lowering of barrier height under continuous electrical stress [14, 15]. Therefore, the leakage current increases with time and the change of breakdown voltage is negative. However, the present experimental results suggest that silver doping causes an effect which is opposite to the usual degradation behaviour. The decreasing leakage current and the positive change of breakdown voltage indicate that silver doping enhances the barrier height instead of lowering it under electrical stress. This could be particularly valuable for reducing the degradation process.

4. Conclusions

1. The addition of silver to a ZnO–Bi_2O_3-based varistor formulation did not affect the average grain

size and sintered density significantly, but it decreased the non-linearity exponent and increased the breakdown voltage.

2. The degradation behaviour of silver-doped varistors were different from the usual degradation characteristics for ZnO varistors under d.c. stress. In the doped sample the leakage current initially decreased with time and then approached a stable value. The changes in breakdown voltage were different in the forward and reverse directions, becoming positive in both directions (at Ag_2O levels > 500 p.p.m.) instead of the usual negative values in silver free ZnO varistors. This suggests that silver doping enhances the barrier height under continuous electrical stress.

3. The modified electrical characteristics are closely related to the decreased donor density, increased depletion layer width and enhanced barrier height as result of silver doping.

4. The optimum amount of silver addition appears to be in the range 500–1000 p.p.m. (Ag_2O). With lower levels, the effect of silver doping on electrical behaviour was subtle. At higher doping levels the electrical characteristics deteriorated.

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