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Abstract. Non-ohmic characteristics of ZnO varistors are obtained by diffusing Bi_2O_3 and/or Sb_2O_3 into a ZnO-based matrix. The varistors derived from metal oxide diffusion have a smaller non-linearity parameter, lower threshold field, larger dielectric constant and larger dissipation factor than conventionally processed varistors. The difference between these two types of varistors is discussed on the basis of the Schottky barrier model. The low threshold field thus obtained makes the metal oxide diffusion process a potential approach in fabricating low-voltage varistors.

1. Introduction

ZnO varistors are widely used for surge protection in electric power lines or electronic circuits because of their excellent non-ohmic electric-field–current-density ($E–J$) characteristics and surge-handling capability [1–3]. The typical ZnO varistor has three kinds of crystal phases, including ZnO phase as sintered grain, a Bi_2O_3-rich phase as an intergranular layer, and a spinel phase as a localised particle in the intergranular layer [4]. The non-ohmic property of ZnO varistors mainly results from the Bi_2O_3-rich intergranular layer.

In general, diffusion and mass transport are more rapid along grain boundaries, and the grain boundaries act as diffusion short circuits. It is proposed that the non-ohmic property of ZnO varistors can be obtained by diffusing oxides such as Bi_2O_3 and/or Sb_2O_3 into ZnO-based ceramics, as the oxide diffuses faster into the grain boundaries and reacts to form the intergranular layer, which is essential to the non-ohmic behaviour of the ZnO varistors. In this study, ZnO non-ohmic ceramics are fabricated through metal oxide diffusion. The authors investigate and discuss the $E–J$ characteristics and the dielectric behaviour of the metal-oxide-diffused (MOD) varistor and varistors fabricated by the conventional process (CP varistors).

2. Experimental procedure

For the MOD varistors the matrix materials used were ZnO–0.5 m/o Sb_2O_3 and ZnO–0.5 m/o (MnO_2, CoO, Cr_2O_3). Appropriate amounts of ZnO, Sb_2O_3, MnO_2, CoO and Cr_2O_3 were mixed thoroughly and pressed into pellets with 1.5 cm thickness and 2 cm diameter. The pellets were then sintered at 1400 °C for 1 h. The diffused oxides were prepared by pressing 1 g of Bi_2O_3 and/or Sb_2O_3 into a 1 cm diameter disc. The oxide disc was placed over the pellet matrix and sintered within a covered crucible at temperatures from 850 to 1350 °C for 1 h. After firing, samples were furnace-cooled and cut into four thin slices of equal thickness, designated as specimens 1, 2, 3 and 4, specimen 1 being the slice nearest to the diffused oxide and specimen 4 the one farthest away. Table 1 lists the sample compositions used in this study. In the designation of the samples,

Table 1. Sample composition employed in this study.

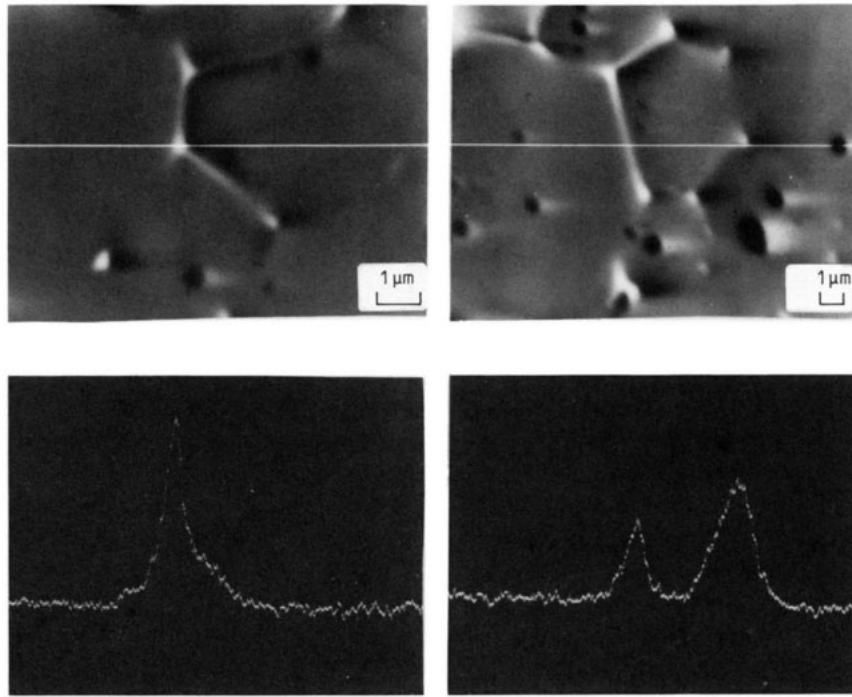| Matrix	Oxide diffused	Annealing condition	Sample designation
ZnO–0.5 m/o Sb_2O_3	Bi_2O_3	950 °C, 1 h	BZS1
		1250 °C, 1 h	BZS2
		1350 °C, 1 h	BZS3
ZnO–0.5 m/o (MnO_2, CoO, Cr_2O_3)	Sb_2O_3	1350 °C, 1 h	SZD
	Bi_2O_3	1350 °C, 1 h	BZD
	$Sb_2O_3–Bi_2O_3$	1350 °C, 1 h	SBZD

Figure 1. An x-ray line profile of the element Bi.

S, Z, B and D stand for Sb_2O_3, ZnO, Bi_2O_3 and 0.5 m/o (MnO_2, CoO, Cr_2O_3), respectively.

The elemental distribution of ZnO-based ceramics was analysed with an electron microprobe (JEOL JCXA-733). The E–J characteristic was measured with a curve tracer (Tektronix type 576). The non-ohmic parameter α was calculated from the E–J curve of the varistor as follows:

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)} \qquad (1)$$

where J_1 and J_2 are current densities in A cm^{-2}, and E_2 and E_1 are the fields at J_2 and J_1 respectively. The dielectric properties of the varistors were measured with two LCR meters (HP4274A and HP4275A) in the frequency range 100 Hz–1 MHz.

3. Results and discussion

The x-ray line profile of the element Bi is shown in figure 1. It is apparent that Bi is enriched at the multigrain junction and grain boundary, which is the result from the short-circuit grain boundary diffusion.

Figures 2 and 3 show the position dependence of the non-ohmic parameter α along the diffusion direction for samples with the ZnO–0.5 m/o Sb_2O_3 matrix and with ZnO–0.5 m/o (MnO_2, CoO, Cr_2O_3) matrix, respectively. For samples diffused with Bi_2O_3, α decreases along the diffusion direction. The smaller the Bi_2O_3 content, the lower the α value. The SBZD system exhibits the largest value of α in this study. This is attributed to the presence of the transition metal oxides, CoO and MnO_2, which make the traps and surface states [1, 5]. The α values for the SBZD system
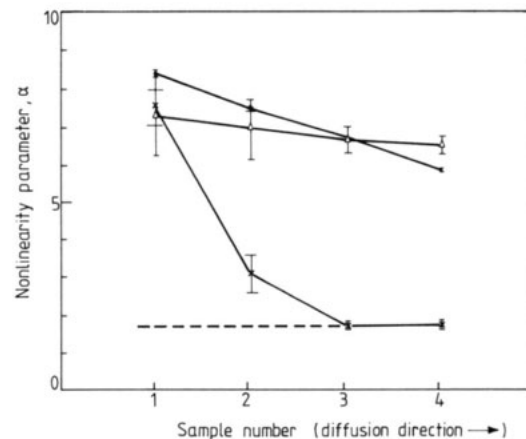

Figure 2. Position dependence of the nonlinearity parameter α along the diffusion direction of sample BZS: ––– ZnO–0.5 m/o Sb_2O_3 matrix; —×— BZS1; —△— BZS2; —●— BZS3.

are about $\frac{1}{3}$–$\frac{1}{2}$ of that for the CP varistors with composition 97 m/o ZnO–1.0 m/o Sb_2O_3–0.5 m/o (CoO, MnO_2, Bi_2O_3, Cr_2O_3) [6, 7].

Figure 4 shows the E–J characteristics of the SBZD samples. The leakage currents of SBZD-2 and SBZD-3 are smaller than that of SBZD-1. The threshold fields are 45, 55 and 60 V mm^{-1} for SBZD-3, SBZD-2, and SBZD-1 respectively. The dieletric constants are 7500 for SBZD-2 and SBZD-3, and 5000 for SBZD-1, as shown in figure 5. The dissipation factors of samples SBZD-2 and SBZD-3 are larger than that of SBZD-1, as indicated in figure 6. The larger dielectric constant and dissipation factor are attributed to the smaller amount of the diffused Bi_2O_3 [8].

The threshold field and dielectric constant of a CP varistor are 800 and 700 V mm^{-1} respectively [7]. According to the barrier model of the ZnO varistors
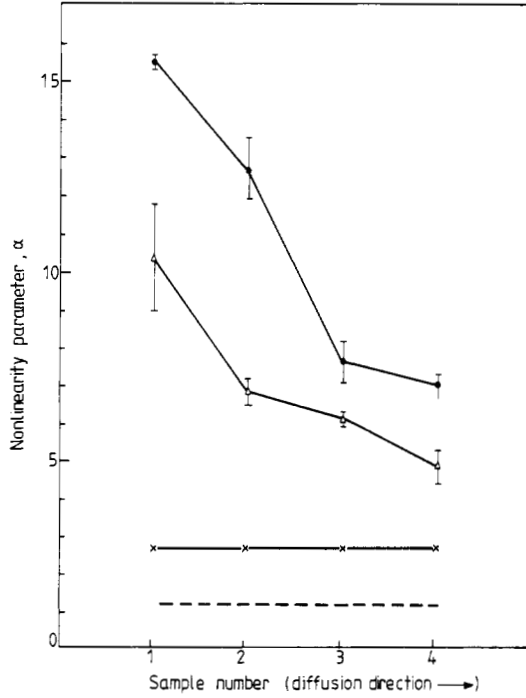
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Figure 3. Position dependence of nonlinearity parameter α along diffusion direction of samples with ZnO–0.5 m/o (MnO_2, CoO, Cr_2O_3) matrix: —×— SZD; —△— BZD; —●— SBZD.
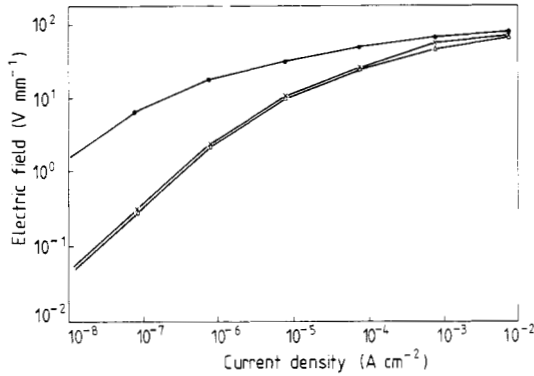

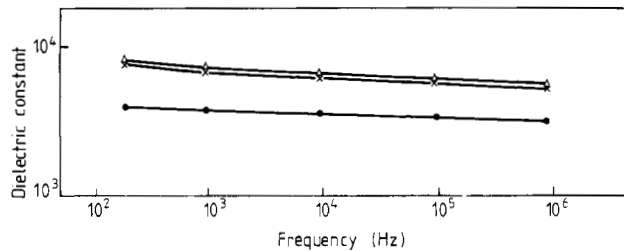**Figure 4.** *E–J* characteristics of SBZD samples: —●— SBZD-1; —×— SBZD-2; —△— SBZD-3.

Figure 5. Frequency dependence of dielectric constant of SBZD samples. Symbols as in figure 4.

[9], the conduction mechanism at breakdown is consistent with a Fowler–Nordheim tunnelling process with an *E–J* relation given by

$$J \propto \exp(-\gamma/E) \tag{2}$$

where $\gamma = 6.8 \times 10^7 [E_i(\text{eV})]^{3/2}$. In the breakdown
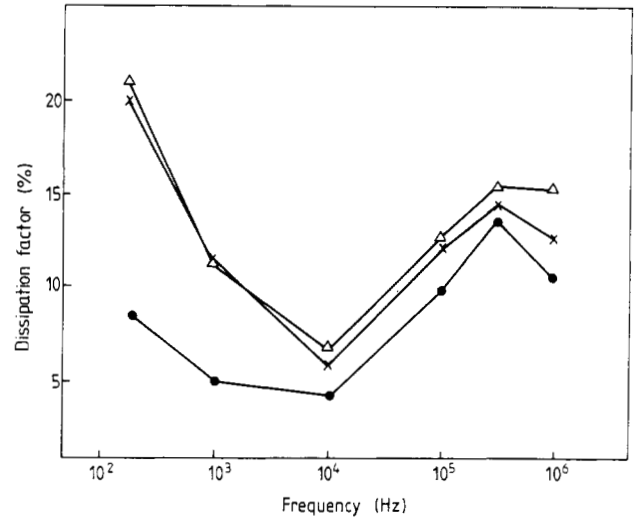

Figure 6. Frequency dependence of dissipation factor of SBZD samples. Symbols as in figure 4.

region, $E_1 \simeq E_2$. From equation (1), one obtains

$$\log(J_2/J_1) \approx (1 - E_1/E_2). \tag{3}$$

Also, from equation (2)

$$\log(J_2/J_1) \approx \gamma/E_1(1 - E_1/E_2) \tag{4}$$

and

$$\alpha = \gamma/E_1 \tag{5}$$

where E_1 is the actual field in the intergranular boundary.

The varistor microstructure can be simplified by a block model in which the device consists of ZnO cubes of side *d* separated from each other by an insulating layer of thickness *t*. For a plane-parallel capacitor configuration, one has

$$\frac{d}{t} = \frac{k_{\text{obs}}}{k_{\text{int}}} \frac{A}{A_{\text{int}}} \tag{6}$$

and

$$E_1 = E_t \times (d/t) \tag{7}$$

where k_{obs} and k_{int} are the observed dielectric constant and the dielectric constant of the intergranular layer, respectively. *A* is the electrode area, and A_{int} is the average area of close approach between the ZnO grains. Assume that the geometric factor A/A_{int} is approximately equal for the CP varistor and MOD varistor. Then

$$(d/t)_{\text{MOD}} \approx \frac{7500}{700} (d/t)_{\text{CP}}. \tag{8}$$

Combining equations (7) and (8), one has

$$E_{1,\text{MOD}} \approx 3E_{1,\text{CP}}.$$

From equation (5) one finds $\alpha_{\text{MOD}} \approx \frac{1}{3}\alpha_{\text{CP}}$. Thus, the conduction mechanism of the MOD varistors is consistent with what the barrier model predicts.

One advantage of the MOD varistor is its low

threshold field. The threshold fields of the MOD varistors are smaller than $1/10$ of that of the CP varistors. Hence, the metal oxide diffusion method is one alternative in manufacturing low-voltage ZnO varistors.

4. Conclusions

(i) ZnO varistors can be fabricated by diffusion of metal oxides into a ZnO-based matrix. The fast diffusion rate along the grain boundaries leads to the formation of the Bi_2O_3-rich intergranular layer in the varistor microstructure.

(ii) The electrical behaviour of metal-oxide-diffused varistor can be explained with a Schottky barrier model.

(iii) The metal-oxide-diffused varistor has a smaller threshold field than the conventionally processed one.

Hence, this diffusion method can be applied in fabricating low-voltage varistors.

References

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