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Structural Origin of Dimensional Effect in ZnO Varistors

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Abstract. The relations among breakdown field $E_{1\,\mathrm{mA/cm^2}}$ (electric field at 1 mA/cm^2), nonlinear coefficient α (measured via current-voltage, I-V, characteristics), and change in breakdown field ($\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$) (obtained via current impulse measurement), and thickness d of ZnO varistors were investigated. The *dimensional effect* refers to the variation in $E_{1\,\mathrm{mA/cm^2}}$, α, and $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$ with thickness of the samples. The dispersion of the ZnO grain size and the aspect ratio of the ZnO grains are used in characterizing the microstructure to represent the degree of heterogeneity of the grain size distribution and irregularity of the shape of the ZnO grains. The distribution of the ZnO grain size is statistically analyzed and found that the critical thickness d_c increases linearly with the dispersion of the ZnO grain size. The breakdown electric field can be empirically termed as $E_{1\,\mathrm{mA/cm^2}} \propto \exp(bd)$, where d is the thickness and b represents the transitional behavior for the curve of the $E_{1\,\mathrm{mA/cm^2}}$ versus d plot. Based on the inflecting response of this curve, b_1 represents the *small thickness domain* prior to the inflection and b_2 represents the *large thickness domain* in the post-inflection domain. It is observed that b_2 is directly proportional to aspect ratio of the ZnO grains. Also it is revealed from the analysis that b_1 increases with the increase in the critical electric field while b_2 decreases with the increase in the critical electric field. Based on these observations it is suggested that the dimensional effect of ZnO varistors originates from the distribution of the grain size and proven via experiments involving the measurements of $E_{1\,\mathrm{mA/cm^2}}$, α, and $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$. The dimensional effect is the macroscopic expression of population behavior of varistors that is consisting of the ZnO grains as well as the grain boundaries.

Keywords: ZnO ceramics, dimensional effect, breakdown field, varistors

1. Introduction

Zinc oxide (ZnO) varistors are multi-component polycrystalline semiconductors made from ZnO added with a large number of cationic oxides [1]. They have excellent nonlinear current-voltage (I-V) behavior possessing large withstanding capability against surge over-voltages. Thus, they are widely used for transient protection in electrical and electronic circuits.

Numerous articles exist in the literature in order to explain the nonlinear behavior of the I-V response. Levine [2] suggested that the multi-component polycrystalline semiconductors form double Schottky barriers across the grain boundaries, and these barriers lead to the nonlinearity of the ZnO composite hybrid. Morris [3] confirmed it via the Mott-Schottky plot and noted the extraneous frequency-dependent contribution attributing to the trapping effect across the grain boundaries. Later Mahan et al. [4] proposed that the large nonlinear coefficient in the breakdown region is attributed to the generation of the minority carriers potentially formed within the inversion layer in the Schottky barrier regions across the ZnO grains. This is a similar concept to that observed as the inversion layer in the MOS (metal oxide silicon/semiconductor) devices. This concept explains the increment in the terminal capacitance at low frequencies but does not conform to the response at high frequencies as verified via the Mott-Schottky plot of numerous well-formed commercial

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varistors [5]. Several studies indicate [6–10] that the holes are formed by impact ionization while the electron hole pairs are formed by energetic electrons surmounting these barriers. Many studies [6–9] of the microstructure strongly support the model noted above. Needless to say per today's available advanced technology that the commercial varistors possess maturity in processing having much higher performance characteristics and, thus, may be termed as the well-formed varistors.

By now, it is generally accepted that the breakdown voltage of each grain boundary is a constant. The breakdown field of ZnO varistor is the product of breakdown voltage of each grain boundary and the number of grain boundary per unit. According to this theory, if the same material system is adopted, the breakdown strength should have nothing to do with the thickness of samples. However, this result can not be made because the microstructure is not in an ideal state.

In an earlier study [11], the dimensional effect was noted for the variation of the breakdown field strength $E_{1\,\mathrm{mA/cm^2}}$ with the thickness of the samples. It was indicated that the dimensional effect of $E_{1\,\mathrm{mA\,cm^2}}$ is an intrinsic property of ZnO varistors. In this context it is relevant to mention that at $E_{1\,\mathrm{mAcm^2}}$ *conduction path channeling* occurs in a singular fashion via depression angle $\theta_{\mathrm{im}} \rightarrow 0^{\circ}$ obtained in the impedance plane formalism [12] when the *ac small signal* electrical data were used. The same phenomenon is described as the *current localization* [13]. Experimental evidence suggests that the well-formed varistors, in general, possess certain intrinsic properties under specific conditions. This is presumably due to the well-formed nature of the grain boundaries having a grain size distribution. For the laboratory varistor samples it is quite uncertain to probe into the intrinsic varistor properties in an identical manner as often these samples may not possess stable electrical behavior like those of the well-formed devices. Nevertheless, conduction path channeling or current localization can also be potentially extended to other polycrystalline semiconductors possessing grain boundary effects such as positive temperature coefficient of resistance (PTCR) ceramics and ceramic capacitors.

In this study, further investigation of the dimensional effect of other parameters such as nonlinear coefficient α and change in the breakdown electric field ($\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$) in ZnO varistors is presented. The microstructure dependence of the dimensional effect is also explored in this study.

2. Experimental

Conventional ceramic processing technique was used in preparing varistor materials using small amounts of additives of Bi_2O_3, Sb_2O_3, $MnCO_3$ Cr_2O_3, NiO, Co_2O_3, SiO_2, B_2O_3, and Al_2O_3 to ZnO. These additives constitute about 5 mole% and ZnO constitutes about 95 mole%. Three types of samples were used to investigate the dimensional effect of the breakdown electric field $E_{1\,\mathrm{mA/cm^2}}$ and nonlinear coefficient α. The size of these samples is referred to as *diameter* × *length*. These samples are: (1) low breakdown field samples **L** with dimension 14.0 × 1.71 mm; (2) intermediate breakdown field sample **M** with dimension 7.42 × 0.705 mm; and (3) high breakdown field sample **H** with dimension 7.41 × 1.98 mm. The first type of the samples represents prototype device while the later two types of samples are the commercial devices. As noted earlier, commercial samples are reasonably well-formed varistors. Sample **L** includes $\mathbf{L_1}$ with a breakdown field of 33 V/mm and $\mathbf{L_2}$ with a breakdown field of 18 V/mm. To investigate the dimensional effect of change in breakdown electric field ($\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$), special samples were prepared in the laboratory with different thickness and a diameter of 7.41 mm, and coated with epoxy powder layer.

Larger sampling of all these devices (minimum 10 per type of device such as **L** or **M** or **H**) was used in the present investigation. Only three types of aforementioned devices are reported. Careful coarse grinding followed by fine lapping operation in the laboratory provided the choice of thickness of the samples. The electrode was applied using silver paste on the opposite faces of each sample having a specific area and then dried in the oven. The breakdown electric field, $E_{1\,\mathrm{mA/cm^2}}$, was determined by measuring the electric field applied to the device when the current density corresponded to 1 mA/cm^2.

For the microstructure studies the samples were polished and etched with the hydrofluoric acid solution, and then cleaned and dried. The microstructure was monitored using a scanning electron microscope (SEM: Hitachi S-2700). Since most of the grains exhibited non-spherical shape the distance in the horizontal direction was defined as the *horizontal distance* while the distance in the vertical direction was defined as the *vertical distance*. For every sample studied the number of grains included in the measurement exceeded 150 grains.

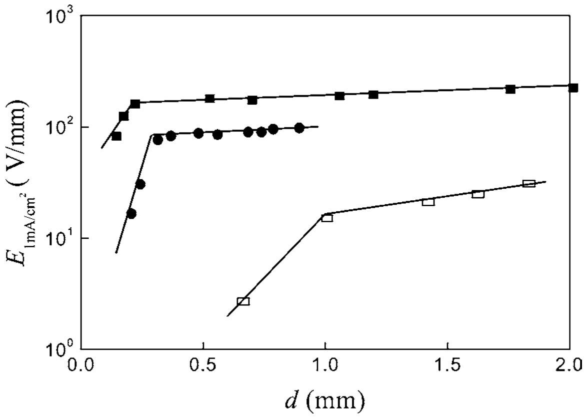

Fig. 1. The relation between the breakdown field, $E_{1\,\mathrm{mA/cm^2}}$, and the thickness d of various samples: □ —Sample $\mathbf{L_1}$, ● —Sample **M**, and ■ —Sample **H**.

3. Results and Discussion

3.1. *The Dimensional Effect of Breakdown Electric Field $E_{1\,\mathrm{mA/cm^2}}$*

The relation between the breakdown field $E_{1\,\mathrm{mA/cm^2}}$ and the thickness d of various samples are shown in Fig. 1 where it is seen that each curve is drifting toward the increasing breakdown electric field of the samples. However, there is a critical point corresponding to the thickness d for each of these curves referring to as the turning point. Each curve determines two parameters: (1) critical thickness d_c, and (2) critical (or transition) breakdown field, E_c. At the inflecting point for each curve where d is smaller than d_c, the logarithm of the breakdown field $E_{1\,\mathrm{mA/cm^2}}$ ($E_{1\,\mathrm{mA/cm^2}} < E_c$) increases linearly with an increase in d. However, beyond the inflecting point where d is greater than d_c, the thickness of the sample keeps increasing. The increment in the logarithm of $E_{1\,\mathrm{mA/cm^2}}$ ($E_{1\,\mathrm{mA/cm^2}} > E_c$) is too small in this domain making the entire curve highly nonlinear. Although device processing methods and the adjustment of the varistor recipe have significantly improved the performance characteristics of the resulting device during the past three decades, this observation is reasonable for most modern commercial devices. Nevertheless, such a behavior can be empirically represented as:

$$E_{1\,\mathrm{mA/cm^2}} \propto \exp(bd), \quad (1)$$

where the exponent b represents the transitional behavior for the entire curve. Let this exponent in the $d < d_c$ domain in Fig. 1 may be denoted as b_1 while in the $d > d_c$ domain this exponent may be denoted as b_2. The summary of the parameters b_1, b_2, d_c, and E_c for these varistors is provided in Table 1. It is obvious that the parameter b_2 decreases as E_c increases while b_1 increases as E_c increases except for the sample **H**. This is a repeated observation and such an effect is described as the *dimensional effect in ZnO varistors*.

Table 1. The values of the exponents b_1 and b_2, critical thickness d_c, and the transition breakdown electric field E_c of various types of ZnO varistors

Sample	b_1	b_2	d_c (mm)	E_c (V/mm)
H	9.4	0.21	0.19	185
M	18.6	0.31	0.28	110
$\mathbf{L_1}$	6.0	0.36	0.98	33
$\mathbf{L_2}$	2.4	0.43	1.34	18

In an earlier study [14] it has been reported that the *dimensional effect* is noticed for the as-sintered samples of variety thickness. This study was in addition to the variation of the sample thickness achieved by the grinding and lapping operations of the device. From continued extensive studies in conjunction with the present investigation it is reasonable to consider the *dimensional effect* as an intrinsic characteristic of the ZnO varistors. Again, b_1, b_2, d_c, and E_c are the determining parameters for the *dimensional effect* in these varistors.

3.2. *The Dimensional Effect of Nonlinear Coefficient α*

Figure 2 shows the relation between nonlinear coefficient α of sample **H** and the thickness d. It is clear that there exists a transition in the form of a sharp inflection point for both d_c and α similar to $E_{1\,\mathrm{mA/cm^2}}$. Thus, an empirical relation may be developed in an identical manner provided in Eq. (1):

$$\alpha \propto \exp(cd), \quad (2)$$

where exponent c represents the transitional behavior for the entire curve. Let this exponent in the $d < d_c$ domain in Fig. 1 may be denoted as c_1 while in the $d > d_c$ domain this exponent may be denoted as c_2. It was further observed that to some extent samples **M** and **L** show identical tendency as that of **H** in Fig. 2. However, at this time it is premature to draw a firm conclusion about the systematic range of the values for

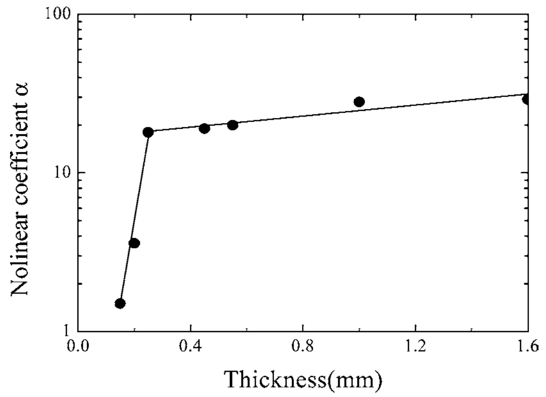

Fig. 2. The relation between the nonlinear coefficient α and the thickness d.

both c_1 and c_2. This is currently under evaluation to erect a reasonable model for ZnO varistors.

3.3. The Dimensional Effect of Change in Breakdown Electric Field $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$

Figure 3 shows the relation between change in breakdown electric field due to impulse current $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$ and the thickness d. This is similar to the dimensional effect of $E_{1\,\mathrm{mA/cm^2}}$ depicted Fig. 1. The dimensionless quantity $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$ decreases sharply with the increase of d. It remains the same of a value of about 0.46 for the thickness $d \geq 1.8$ mm. Thus, Fig. 3 indicates two finite

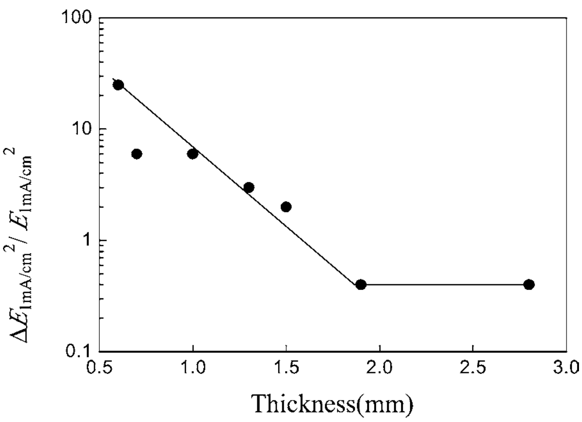

Fig. 3. The relation between $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$ and the thickness d.

regions: Region I ($d \leq 1.8$ mm) of sharp change and Region II ($d \geq 2.0$ mm) constant dimensionless quantity. Overall the response in Fig. 3 may be expressed in the same way as in Eq. (1). It can be concluded from Fig. 3 that the critical thickness ($d = d_c = 1.8$ mm) for $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$ is larger than that of $E_{1\,\mathrm{mA/cm^2}}$ and α ($d = 0.2$ mm), which show the stronger dependence of $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$ on the thickness d. This behavior is under evaluation for establishing empirical response.

3.4. Microstructure Dependence of the Dimensional Effect

The micrographs obtained via scanning electron microscopy (SEM) of three samples (**H**, **M**, $\mathbf{L_1}$) described above are depicted in Fig. 4. Sample **H** indicates well-formed microstructure via repetitively ordered shape of the identical grains having much less porosity. The grains in the sample **M** are slightly elongated and dispersed containing identical degree of porosity with respect to the sample **H**. The grains in the sample $\mathbf{L_1}$ are slightly skewed in shape possessing non-uniform size distribution having a little more porosity when compared to the samples **H** and **M**. This enhanced level of porosity is no way detrimental to the resulting performance of the device as the variation is estimated to be too small from the microstructural evaluation.

From the SEM micrographs, the horizontal and vertical distances of minimum 170 grains were measured for every sample. It can be seen that the horizontal and vertical distance of grains are randomly distributed in the microstructure. The aspect ratio (defined as the ratio of long diameter and short diameter for a single grain which is regarded as an ellipse in this paper) of the ZnO grains was also calculated. An extra kind of sample with a breakdown field of 18 V/mm was investigated. The corresponding values of b_1, b_2, d_c are 2.4, 0.43, and 1.34 mm, respectively. Figure 5 shows the linear relation between the critical thickness d_c and the dispersive ratio. The dispersive ratio is defined as the ratio of standard deviation of the grain length and average value of the grain length. A similar investigation indicates that d_c also depends linearly on the *dispersive ratio* along the shorter diameter of the ZnO grains. Such information provides a concept of critical thickness d_c that is related to the *dispersive ratio* of the ZnO grain size.

Figure 6 represents a near linear relationship be-

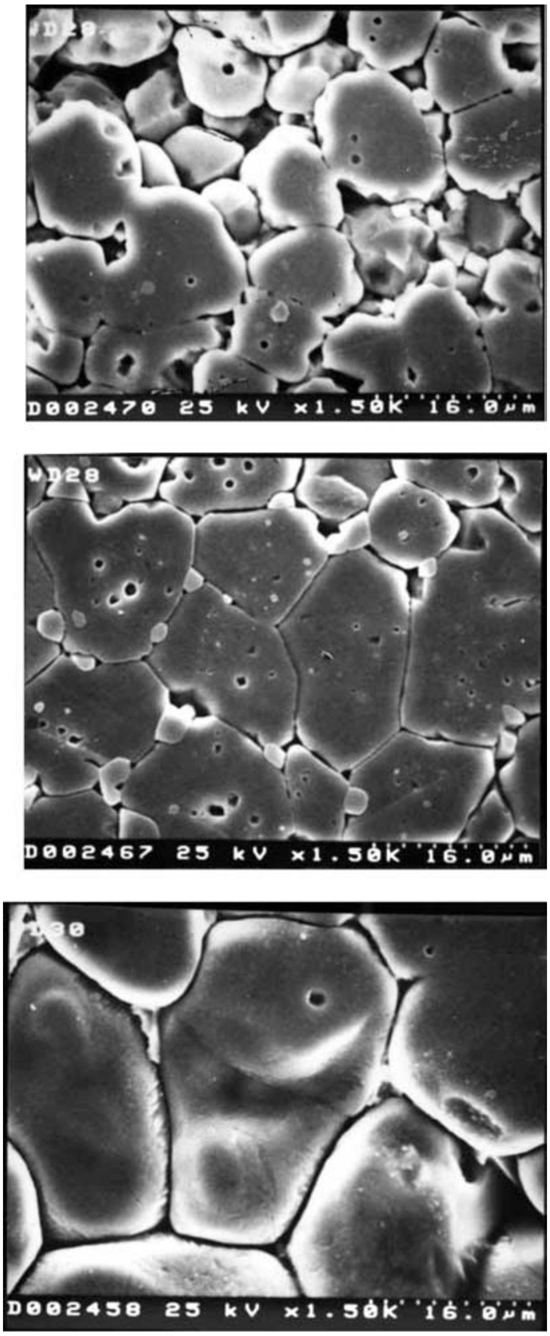

Fig. 4. Scanning electron micrographs of the three samples: **H**, **M**, and $\mathbf{L_1}$.

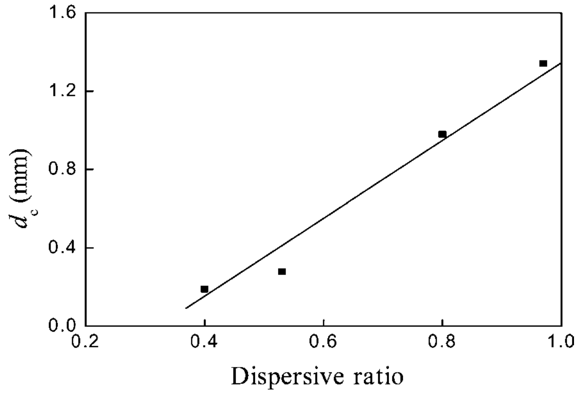

Fig. 5. The linear relation between the critical thickness, d_c, and the dispersive ratio.

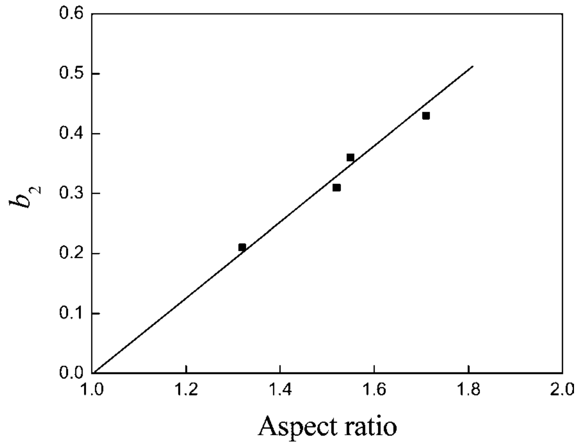

Fig. 6. The relation between b_2 and the average aspect ratio.

tween the exponent b_2 and the average aspect ratio of the ZnO grains. It appears that b_2 increases with an increase of average aspect ratio. This indicates that the thickness dependence is enhanced as the grain shape transforms from the regular nearly ordered or uniform (or near homogeneous) shape to the skewed or non-uniform (or inhomogeneous) shape. It is worth noting that Figs. 5 and 6 are repeated for all samples (**H**, **M**, $\mathbf{L_1}$, and $\mathbf{L_2}$) although three microstructures are shown in Fig. 4. This is due to identical microstructures of both $\mathbf{L_1}$ and $\mathbf{L_2}$. It is understood that the dimensional effect originates from the change in the deviation in the breakdown electric field with thickness d. It can be further proposed that the dimensional effect is a macroscopic expression of population behavior of varistor units or blocks or individual devices that consists of a distribution of ZnO grains and grain boundaries.

4. Conclusions

The relations between the breakdown electric field $E_{1\,\mathrm{mA/cm^2}}$ or nonlinear coefficient α or change in the breakdown electric field due to the current impulse $\Delta E_{1\,\mathrm{mA/cm^2}}/E_{1\,\mathrm{mA/cm^2}}$ and thickness d of the ZnO varistors show dimensional effect. The critical thickness d_c, transition breakdown electric field E_c, and parameters b_1 and b_2 can be suggested to be the characteristics of the dimensional effect. Under the same context the parameters c_1, and c_2 also represent the effect of the dimensional effect. It is strongly suggested that the dimensional effect originates from the degree of the heterogeneity of the ZnO grain size distribution and irregularity of the ZnO grain shape. The critical thickness d_c increases linearly with a visible dispersion of ZnO grain size, and parameter b_2 is directly proportional to average aspect ratio.

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