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# Donor and acceptor doping of zinc oxide varistors

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**Abstract**

ZnO-based varistors containing 0–10 000 ppm Ga were prepared by the mixed oxide route. Disc-shaped samples were sintered in air at 1030 °C for 2 h. All products were of high density (>94% theoretical). Gallium addition led to a reduction in grain size from 12 $\mu$m to approximately 8 $\mu$m. From $I$–$V$ characteristics the non-linear coefficients ($\alpha$) were determined to be $\sim$38. The doped varistors exhibited donor-like behaviour for Ga contents up to 1500 ppm Ga and acceptor-like behaviour at higher levels. Above the 1500 ppm transition doping level, the leakage current density decreased and breakdown fields were consistently high.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Zinc oxide varistors [1] are polycrystalline ceramic devices with grossly non-linear current–voltage ($I$–$V$) characteristics, which allows them to be exploited in voltage surge suppression applications. Commercially, varistors are usually produced by a mixed oxide processing route. The final microstructures and electrical properties are strongly dependent on both processing method and chemical constituents.

The $I$–$V$ characteristics of ZnO varistors are characterized by three distinct regions (figure 1): the pre-breakdown region (a) under grain boundary control; the non-linear region (b); and the upturn region (c) controlled primarily by the impedance of the ZnO grains. Several groups of workers [2–7] have examined the effects of trivalent and monovalent additions upon the microstructural and electrical characteristics of varistors. It has been found that trivalent additions, e.g. $Ga^{3+}$, $Al^{3+}$, act as donors, increasing leakage currents and displacing the $I$–$V$ characteristic to higher current densities; i.e. the $I$–$V$ curve moves to the

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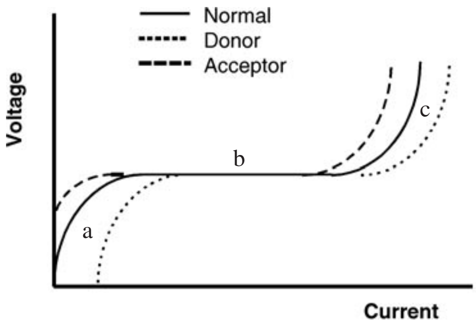


**Figure 1.** Effects of donor and acceptor doping on the $I$–$V$ characteristic of a zinc oxide varistor (after [5]).

right in figure 1, compared to that for undoped varistors. This is most clearly represented by displacement of regions (a) and (c) in figure 1. Conversely, monovalent additions, e.g. $K^+$, $Li^+$, $Na^+$, act as acceptors, decreasing leakage currents and displacing the $I$–$V$ curve to lower current densities (i.e. the $I$–$V$ curve moves to the left) compared to that for undoped varistors (figure 1).

Miyoshi *et al* [3] discussed the effects of donor (Al and Ga) and acceptor (Li) dopants on the $I$–$V$ characteristics of varistors. The addition of $Al^{3+}$ ions increased the leakage current in the pre-breakdown region, and decreased the resistivity in the upturn region. Similar effects were observed for $Ga^{3+}$ ions, but the inverse effects occurred when Li was added. Each set of results was interpreted in terms of the variation in carrier concentration. As expected, there was an increase in carrier concentration in the donor-doped samples, and a decrease in carrier concentration in the acceptor-doped samples. The reduction in carrier concentration upon Li doping was much greater than the increase recorded for Ga and Al doping at equivalent concentrations.

Carlson and Gupta [2] examined the improvement of non-linearity upon donor doping (apparent through a reduction of the gradient in the non-linear region (region (b), figure 1)). Since it is generally accepted that the upturn region is controlled by the composition of the grains, their approach was to reduce the resistivity of the ZnO grains. Carlson and Gupta found that small additions of Al or Ga caused a delay in the onset of the upturn region (region (c), figure 1). However, at higher levels of Al or Ga, the upturn region occurred at lower current densities. Only small amounts of Ga or Al were required to generate high non-linear coefficients ($\alpha$); in the low-current-density range larger amounts of the dopants were required to achieve the same $\alpha$-values as in the high-current-density range. Overall, they found that small additions of Al or Ga improved the high-current upturn characteristics and the non-linearity.

Subsequently, Gupta [4] examined in more detail the effects of Ga doping, using additions of 300, 750, and 1800 ppm. A transition from donor-type behaviour to acceptor-type behaviour was found between 750 and 1800 ppm Ga. The precise transition could not be determined, but the behaviour was analogous to that of Al, which had been noted previously by other workers [3]. In the case of Al doping, there was a change from donor-type to acceptor behaviour when the doping level increased from 2000 to 20 000 ppm. On the basis of ionic size, Gupta [4] predicted that the transition for Ga would be at a lower level than that of Al, because of the larger ionic radius of Ga. Gupta also concluded that the electron generation process at the grain boundary was independent of the donor type, but dependent on the valence state of the dopant.

Fan and Freer investigated the effects of doping with silver [6] and then the combination of silver and aluminium [7]. Varistors were first doped with Ag at 0–2500 ppm. Increasing the Ag doping level decreased the $\alpha$-value, but increased the breakdown voltage. An optimum doping level of 500–1000 ppm Ag was deduced; higher levels led to a degradation in the electrical properties. When the varistors were doped with Al there was an increase in the $\alpha$-value but a deterioration in the degradation behaviour. However, by doping with optimum amounts of Ag and Al, high $\alpha$-values and improved degradation characteristics were achieved. The improvement in electrical characteristics was related to the increase in donor density.

Whilst the overall effects of donor and acceptor additions to varistors are distinct and specific (figure 1), the behaviour of certain ions depends upon location and concentration. Should the dopant be grain or grain boundary specific, then the pre-breakdown and upturn regions can be displaced individually. Gupta [5] noted that sodium is grain boundary specific, acting as a donor at small concentrations, and as an acceptor at higher concentrations. Aluminium can be accommodated at both the grain and at the grain boundaries, and acts like sodium, in that at small concentrations it is a donor, and at higher concentrations it is an acceptor.

The work of Gupta [4] demonstrated that Ga can also act as a donor or acceptor. The aim of the present study was to examine the effects of Ga doping over a significantly wider concentration range, and attempt to define the boundary of the transition from donor to acceptor behaviour.

## 2. Experimental procedure

Zinc oxide varistors of nominal formulation 89 wt% ZnO, 5 wt% $Bi_2O_3$, 4 wt% $Sb_2O_3$, 1 wt% CoO, 0.5 wt% $Mn_3O_4$, 0.5 wt% $B_2O_3$ (the 'control' composition) were produced using a conventional mixed oxide processing route. The raw materials were vibration milled with zirconia media and propan-2-ol for 24 h. The mixture was filtered and evaporated to dryness at 100 °C for 24 h and then sieved through a 212 $\mu$m mesh screen. Powders were pressed using a single-action uniaxial die at 80 MPa, to produce 12 mm diameter discs, having green density of approximately 3000 kg $m^{-3}$. Samples were sintered in air at 1030 °C for 2 h with heating and cooling rates of 50 °C $h^{-1}$. Varistors doped with 1000, 1500, 2000, 3000, and 10 000 ppm gallium were also produced under the same conditions. Gallium was added in the form of $Ga_2O_3$ (99.99%) to the raw materials prior to milling.

Specimen densities were determined from weight and dimensional measurements. The phases present were determined by x-ray diffraction analysis (Cu K$\alpha$ radiation). Samples were ground and polished, down to 1 $\mu$m diamond paste, and etched (10% HCl for 5 s) prior to optical microscopy and scanning electron microscopy (SEM) (Philips 505, equipped with EDAX). Grain sizes were determined by the linear intercept method [8]. This involved drawing a series of parallel lines on micrographs of the samples; the total length of the lines (scaled for magnification) divided by the number of grain boundaries intercepted by the lines yielded the average grain size (once a correction factor had been applied to allow for the fact that not all grains shown in the micrographs had been sectioned through their centres).

For low-power electrical measurements the specimens were ground parallel (2400 grade SiC) and the thickness reduced to 2.0 mm. After ultrasonic cleaning, silver ink (Johnson-Matthey E1100) electrodes (10 mm diameter) were applied to both faces and dried at ~150 °C for 30 min. $I$–$V$ tests were undertaken for the current range 0.1 $\mu$A–5.0 mA. Data are reported in the conventional format of $E$ (electric field) versus $J$ (current density). Breakdown fields $E_b$ were determined from $E$–$J$ characteristics when the current density was 2 A $m^{-2}$.

To facilitate high-power electrical tests, the original electrodes were removed (using 6 $\mu$m diamond paste) and smaller 8 mm diameter (Hereaus conductive ink) electrodes screen printed to each side of the disc. These were fired at 890 °C and termination contact wires attached by conventional Pb–Sn solder. Specimens were encapsulated in epoxy resin. High-power

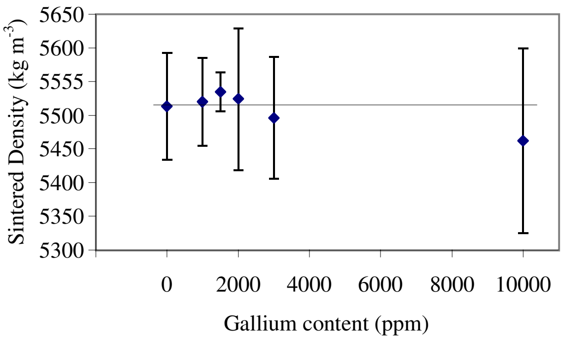


**Figure 2.** Densities of the control and gallium-doped varistors after sintering at 1030 °C.

investigations were carried out using the 8/20 $\mu$s wave pulse test over the range 0.2 mA–100 A. Non-linear coefficients ($\alpha$) were determined over the range of current density ($J$) 1–10 A m$^{-2}$, according to the equation

$$\alpha \simeq \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1} \tag{1}$$

where $E_1$ and $E_2$ are the electric fields across the sample when the current densities are $J_1$ and $J_2$ respectively.

After reducing specimen thickness to 1.0–1.3 mm, capacitance–voltage ($C$–$V$) characteristics were determined at a frequency of 10 kHz over the voltage range 0–200 V using an HP4275A in conjunction with a G&E dc Calibrator. Carrier density ($N$) and barrier height ($\phi$) are related to capacitance [9] via

$$\left\{\frac{1}{C_\mathrm{b}} - \frac{1}{2C_\mathrm{b0}}\right\}^2 = \frac{2}{q^2 N \varepsilon}\left(\phi - qV_\mathrm{g}\right) \tag{2}$$

where $C_\mathrm{b}$ is barrier capacitance per unit area, $C_\mathrm{b0}$ is the value of $C_\mathrm{b}$ at zero bias, $q$ is the electronic change, $\varepsilon$ is relative permittivity (8.5 for ZnO), and $V_\mathrm{g}$ is the voltage per grain.

## 3. Results

### *3.1. Physical properties and microstructure*

The densities of the sintered varistors are presented in figure 2; all the densities are high, typically above 94% theoretical, and there is no significant difference in sintered density as a function of gallium content. The results presented here are consistent with published data [6, 10–14]. Samples were not prepared with Ga contents in the range 3000–10 000 ppm because previous studies [3,5,7] of doping by trivalent ions showed no evidence of unusual (non-linear) changes in properties once the acceptor region (typically $\leqslant$2000 ppm) had been reached.

Optical micrographs of the control and gallium-doped varistors are presented in figure 3. X-ray diffraction analyses and detailed SEM studies confirmed that three main phases are present: ZnO grains, a Bi-rich intergranular network which is particularly apparent at triple grain junctions, and a spinel phase, located mainly at grain boundaries and occasionally within the ZnO grains. It is clear that the grain size varies with the Ga content of the varistor (figures 3 and 4). In gallium-free varistors, the grain size is approximately 12 $\mu$m. The addition of gallium inhibits grain growth; for 1000 ppm Ga the grain size is only 7.2 $\mu$m. However, as the amount of gallium increases (1000–10 000 ppm) the grain size slowly increases. Nevertheless,

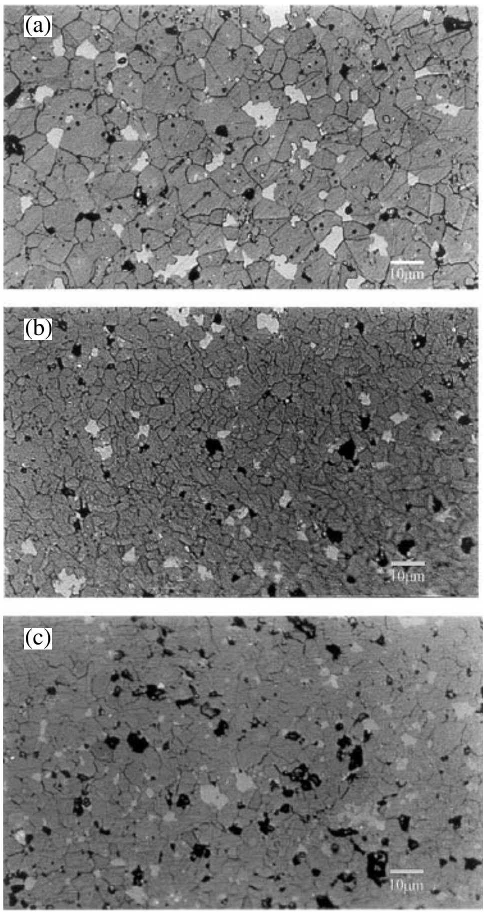


**Figure 3.** Optical micrographs of varistors sintered at 1030 °C: (a) gallium-free specimen (control); (b) specimen containing 1000 ppm Ga; (c) specimen containing 1500 ppm Ga.

at 10 000 ppm Ga, the grain size is still significantly smaller (9 $\mu$m) than that in the Ga-free varistors (12 $\mu$m). There are no directly equivalent published data for Ga doping for comparison. For Al-doped varistors (aluminium has similar charge and ionic radius to Ga), Carlson and Gupta [2] noted that Al additions led to a decrease in grain size from 15.4 $\mu$m (0% Al) to 7 $\mu$m (1% Al). For varistors of different composition, Fan and Freer [14] reported a similar decrease in grain size upon the addition of aluminium (from 14.4 to 8.1 $\mu$m).

## 4. Electrical properties

The $I$–$V$ characteristics are presented in figure 5. Over the current-density range of approximately 1–100 A m$^{-2}$ the data collected in the low- and high-power regions overlap; the two sets of data are consistent and are represented by a single set of data points. It is noted that the combined $E$–$J$ results for the control varistors (0 ppm gallium) represent only the central 'non-linear' portion of the $I$–$V$ characteristic (region (b) in figure 1). The dotted continuation to the data for the control varistors indicates where the pre-breakdown (region (a) in figure 1) is expected to occur. Small additions of gallium (1000 ppm) modified the $I$–$V$ characteristics by displacing the $I$–$V$ curve to a higher electric field (i.e. the curve moves upwards) and to higher

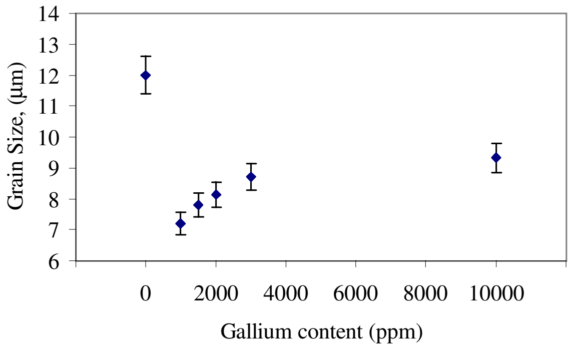


**Figure 4.** Grain sizes of the control and gallium-doped varistors sintered at 1030 °C.

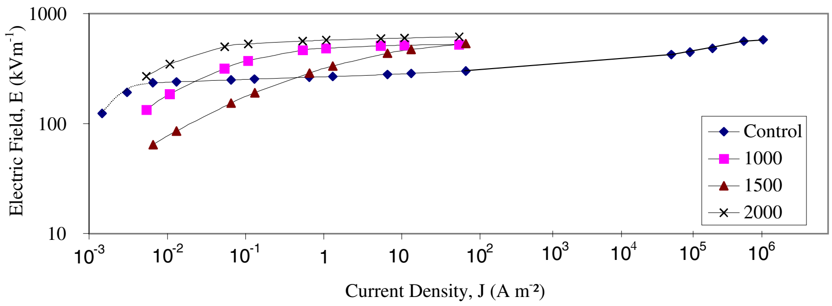


**Figure 5.** $I$–$V$ characteristics of the control and gallium-doped varistors sintered at 1030 °C. The dotted continuation on the curve for the control sample indicates that the pre-breakdown region is expected to occur at much lower current densities than for the doped samples.

current density (i.e. the non-linear region, (b) in figure 1, moves to the right). The same displacement of the $I$–$V$ curve continued when the dopant level was increased to 1500 ppm. In contrast, when the gallium content was raised to 2000 ppm the $I$–$V$ curve was displaced to lower current densities (i.e. a transition from the pre-breakdown to the non-linear region (a) → (b) (figure 1) occurs at lower current density), indicating a reduction in the leakage current and a transition from donor to acceptor behaviour (see figure 1). The latter behaviour was expected on the basis of the earlier studies of Carlson and Gupta [2], Gupta [4], and Fan and Freer [14]. Analysis of the $I$–$V$ characteristics enabled leakage current and breakdown field data to be determined; the results are presented later in this section (figures 6 and 7). In general the gallium-doped varistors are characterized by higher breakdown fields, and higher leakage currents.

Gallium additions are known to affect both the grain and grain boundary regions, and therefore should modify the pre-breakdown and upturn regions. The former was confirmed in the low-power region with the transition ((a) → (b) figure 1) in the $I$–$V$ curve being displaced to higher current densities (i.e. to the right), indicating donor behaviour. The anticipated displacement of the upturn region to lower current densities (upon Ga doping) could not be formally assessed as the high-power data did not extend into the upturn region (figure 5).

From the $I$–$V$ characteristics (figure 5), leakage current densities were determined (figure 6). As the gallium content increased from 1000 to 1500 ppm, the leakage current density increased significantly. This is consistent with donor-type behaviour caused by the substitution of gallium on zinc lattice sites, as described by equation (3):

$$\tfrac{1}{2}Ga_2O_3 \xrightarrow{ZnO} Ga_{Zn} + O_o + \tfrac{1}{4}O_2(g) + e'. \qquad (3)$$

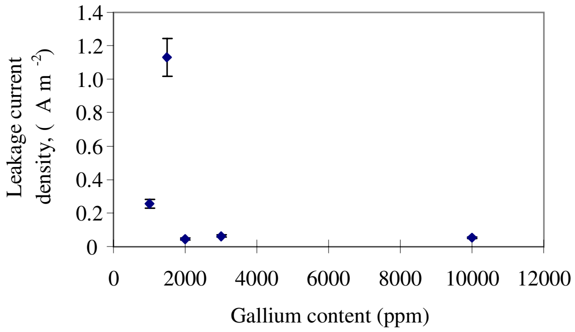


**Figure 6.** Leakage current densities of gallium-doped varistors sintered at 1030°C.

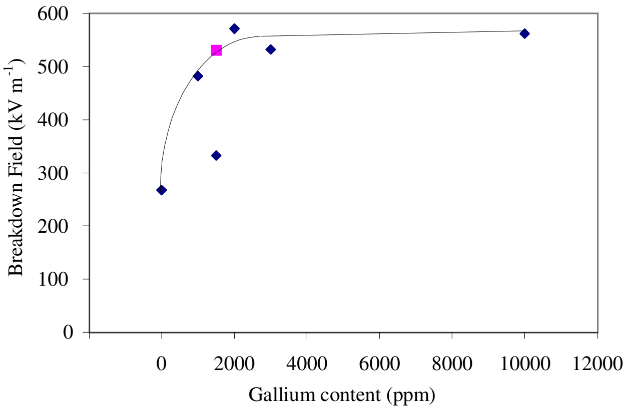


**Figure 7.** Breakdown field for varistors as a function of gallium content: (♦) $E_b$ determined at a current density of 2 A m$^{-2}$; (■) the $E_b$-value determined within the breakdown region for the 1500 ppm gallium specimen (see the text).

Substitution of $Ga^{3+}$ ions onto a zinc lattice site results in an increase in carrier concentration. This increases the leakage current by decreasing the resistivity of the grain boundary.

The subsequent increase of gallium doping to 2000 ppm and higher caused the leakage current density to decrease and remain low. On the basis of the work of Gupta [5] it is inferred that the net increase in grain boundary resistivity, accompanying the transition to acceptor-type behaviour for the Ga, may occur as Ga ions begin to occupy sites normally occupied by zinc interstitial ions, i.e.

$$\tfrac{1}{2}\mathrm{Ga_2O_3} \rightarrow \mathrm{Ga}_\mathrm{i}' + \mathrm{h} + \tfrac{3}{4}\mathrm{O_2(g)}. \tag{4}$$

The effective breakdown fields (at $J \sim 2$ A m$^{-2}$) were determined from the $E$–$J$ characteristics (figure 5); $E_b$-results are presented in figure 7. For gallium-free varistors the breakdown field ($E_b$) is approximately $2.7 \times 10^5$ V m$^{-1}$. Addition of gallium to the varistors increases the breakdown field to a maximum value of approximately $5.5 \times 10^5$ V m$^{-1}$. As breakdown voltage is directly related to grain size, a decrease in the grain size effectively increases the breakdown voltage due to the increase in the number of grain boundaries per unit thickness. This trend is broadly in accordance with the variation of grain size with doping (figure 4) and is in good agreement with the work of Carlson and Gupta [2]. It should be noted that it was necessary to determine the breakdown field, for the samples doped with 1500 ppm Ga, at a higher current density than normal; at $J = 2$ A m$^{-2}$ the $E$–$J$ characteristic for this sample was

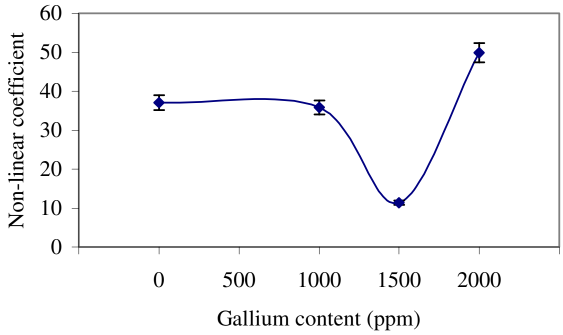


**Figure 8.** Non-linear coefficients ($\alpha$) for varistors as a function of gallium content; the ($\alpha$)-value for the 1500 ppm gallium specimen was determined over the current-density range 1.0–50 A $m^{-2}$ (see the text for details).

still within the pre-breakdown region (see figures 1 and 5) and as such yielded an anomalously low $I_L$-value of $3.2 \times 10^5$ V $m^{-1}$ (figure 7) which is an artifact of the analysis. The $E_b$-value (for the 1500 ppm Ga sample) was therefore determined in the non-linear region, and the datum follows the trend for all the other samples (figure 7).

The non-linear coefficients ($\alpha$) were determined from the $I$–$V$ characteristics (figure 5) over the current-density range 1–10 A $m^{-2}$. The results are presented in figure 8. The control samples and varistors doped with 1000 ppm Ga exhibited $\alpha$-values of $\sim$38, which is typical for a commercial varistor. Increasing the gallium content to 1500 ppm yielded an apparent $\alpha$-value of $\sim$5, when determined at 1–10 A $m^{-2}$ (which corresponds to the pre-breakdown region for this sample). The $\alpha$-value only increased to 12 (figure 8) when determined over the range 1–50 A $m^{-2}$, which is still not fully within the breakdown (non-linear) region. The addition of 1500 ppm gallium, as stated earlier, resulted in donor-like behaviour, effectively displacing the pre-breakdown and non-linear regions of the $I$–$V$ characteristic to higher current densities (i.e. to the right). Donor doping of the grain boundary led to net decrease in the resistivity. As a result there was a smaller difference in resistivity between the grain and grain boundary, and thus a smaller $\alpha$-value.

Higher doping levels (from 2000 to 10 000 ppm Ga) produced $\alpha$-values in the range 50 down to 30, with a general downward trend as the doping level increased (data not shown graphically). Within the higher-doping (acceptor) region, the general decrease in non-linear coefficients is consistent with a decrease in the resistivity of the grain, as noted by Gupta [5] for Al doping of varistors. For example at 20 000 ppm Al, Gupta obtained an $\alpha$-value of 19.

The $C$–$V$ characteristics of selected varistors are presented in figure 9. The capacitance decreased with increasing voltage for all varistors. This is to be expected as a result of the deformation of the Schottky barriers upon application of the applied voltage (as noted by other authors [8, 9, 14–16]). When the data are recast into barrier capacitance format (equation (2)), there is a steady increase in $(1/C_b - 1/2C_{b0})^2$ with increasing applied voltage (figure 10). The data for samples containing 1000 and 1250 ppm Ga (donor doping) are very similar, but at 1500 ppm Ga (approaching the transition to acceptor doping) there is an increase in effective barrier capacitance. This mirrors the results for $(1/C_b - 1/2C_{b0})^2$ reported by Miyoshi *et al* [3] for the transition from donor doping (Ga doping at $\leqslant$1000 ppm) to acceptor doping (Li additions of $\leqslant$200 ppm).

Carrier densities (i.e. donor densities for Ga $\leqslant$1500 ppm) determined via equation (2) and figure 10 are typically 8–12 $\times 10^{23}$ $m^{-3}$. The donor density at 1000 ppm Ga is almost identical to that reported by Miyoshi *et al* [3] for experiments with similar samples and also

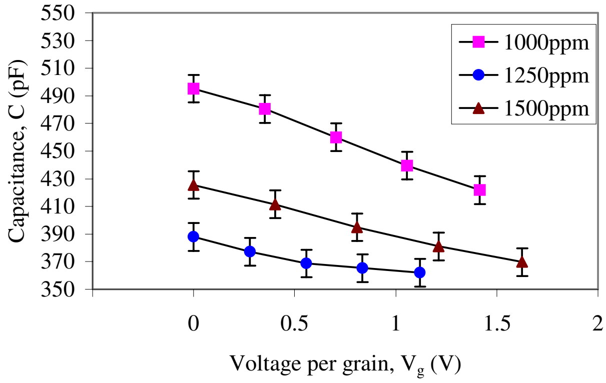


**Figure 9.** Capacitance–voltage characteristics at 10 kHz for gallium-doped varistors sintered at 1030 °C.

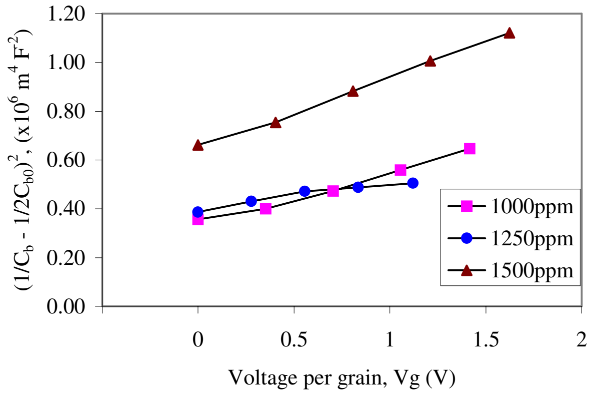


**Figure 10.** Barrier capacitance $(1/C_b - 1/2C_{b0})^2$ as a function of average voltage per grain for gallium-doped varistors.

for samples prepared with 500 ppm Al by Fan and Freer [14]. Thus donor doping at less than 1200 ppm with the trivalent ions Ga and Al leads to very similar behaviour in varistors. In the case of Ga, the transition from donor to acceptor behaviour appears to occur between 1500 and 2000 ppm. Gupta [5] was able to show that in Al-doped varistors ($\leqslant$1000 ppm) the electron concentration in the grain boundary is about nine orders of magnitude lower than that in the interior of the grain. He suggested that by analogy with Al, it should be possible to accommodate significantly more Ga in the grain boundaries than the grain, because of the more open and disordered structure of the grain boundary.

On extending the range of doping level to 10 000 ppm Ga, there is clear evidence of the transition from donor doping to acceptor doping. Beyond the transition (1500–2000 ppm Ga) there is a steady decrease in the non-linear coefficient, whilst leakage currents and breakdown fields show little variation. It would be of interest to confirm the location of Ga under donor and acceptor conditions to corroborate the various defect models and reaction mechanisms that have been proposed.

## 5. Conclusions

The densities of all the varistors were high (>94% theoretical). There was no significant change in density with increasing gallium content.

The microstructures consisted of three phases: ZnO grains, a Bi-rich intergranular network, and spinel particles dispersed within the intergranular layer and occasionally within the ZnO grains.

The grain size of the gallium-free varistors is approximately 12 $\mu$m. Small additions of Ga (1000 ppm) inhibited grain growth; larger additions (1500–10 000 ppm) led to a slight increase in the grain size. Nevertheless, for varistors containing 10 000 ppm, the grain size ($\sim$9 $\mu$m) is still significantly smaller than that for the gallium-free varistors.

The $I$–$V$ characteristics for gallium-doped varistors (determined from low-power $I$–$V$ tests) were displaced to higher current densities upon doping with gallium up to 1500 ppm, reflecting donor behaviour. Greater additions of gallium caused the $I$–$V$ characteristics to be displaced to lower densities, reflecting acceptor behaviour. Non-linear coefficients in specimens doped with Ga were typically 38.

The presence of gallium increased the leakage current; $I_L$ exhibited a maximum value in specimens containing 1500 ppm Ga. Greater additions of gallium led to a reduction in the leakage current.

The breakdown fields of gallium-containing varistors are higher than those of the gallium-free varistors, as a result of the change in grain size.

The $C$–$V$ data indicate donor densities of $\sim 10^{24}$ m$^{-3}$ in samples containing 1000–1250 ppm Ga.

From the combined electrical characteristics it is concluded that the transition between donor- and acceptor-like behaviour occurs for additions of Ga between 1500 and 2000 ppm.

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