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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Transient currents below and above the breakdown voltage have been studied for metal oxide (zinc oxide) varistors. Above the breakdown voltage the voltage overshoot phenomenon effectively lengthens the turn-on time making the turn-off time smaller than the effective turn-on time. Below the breakdown voltage, slow decaying currents following the capacitance-charging peak/discharging peak are found to show a power law temporal behavior, $1/t^n$ where n is very close to unity, over a time ranging from one microsecond to thousands of seconds after the beginning/end of the applied voltage pulse. Activation energies of these transient currents were found to be ~ 10 meV and ~ 160 meV. We have provided a theoretical explanation of this time dependence: tunneling from deep donors into the conduction band as the Fermi level is shifted down across the donor levels by the applied bias. A preliminary effort has been made to relate the cause of the voltage overshoot to the time needed for the depletion layer narrowing and hole creation.					
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Experimental and Theoretical Study of Transient Behavior of Varistors

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Statement of the problem studied

Zinc oxide varistors¹ are made of ceramic materials consisting of zinc oxide with a few percent of additive oxides, mostly bismuth or praseodymium oxide (varistor-forming ingredient) and transition metal oxides (performance-enhancing ingredients). The varistor shows a strongly nonlinear i - V characteristics, with a sudden transition from insulating to conducting state at the "breakdown" voltage. This sharp transition makes it an ideal device to protect electrical equipment against sudden voltage surge or electromagnetic pulse.

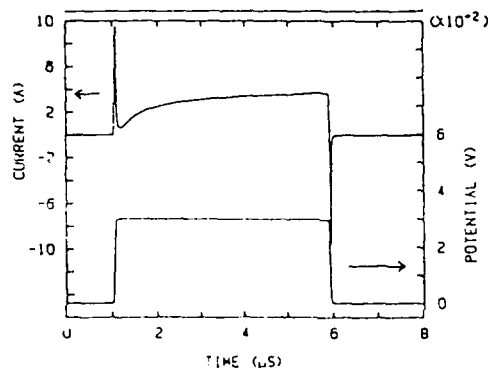


Figure 1

When a square voltage pulse of the amplitude greater than the breakdown voltage is applied, the varistor current shows a capacitance charging peak followed by a minimum before it rises to the steady state value as in Fig. 1. The current rise time is usually of the order of 1 μ s except at the applied voltage very close to the breakdown value; above a certain voltage for a given sample, the rise time remains constant and independent of the applied bias². This current minimum or voltage overshoot phenomenon is found for all ZnO varistors with highly nonlinear i - V characteristics. A few parts per million of indium removes the voltage overshoot but it also causes a drastic reduction of the nonlinearity³.

The voltage overshoot effectively increases the turn-on time. In order to design a varistor with a fast turn-on/turn-off time *and* high nonlinearity, a good understanding of microscopic mechanisms for the voltage overshoot and

high nonlinearity becomes essential. This grant supported a preliminary investigation of the varistor transient behaviors associated with turn-on and turn-off of the varistor.

Summary of the most important results

We have studied the temporal response of varistor devices fabricated by GE as well as Toshiba varistors. We have confirmed the time responses reported by F. Modine of Oak Ridge and further explored the initial fast decay region, Fig. 2. We find that after the initial exponential decay there is a power law behavior $i \propto t^{-n}$ where n is close to unity for the applied bias below the breakdown (threshold) voltage, very similar to the transient current following the removal of the bias voltage⁴.

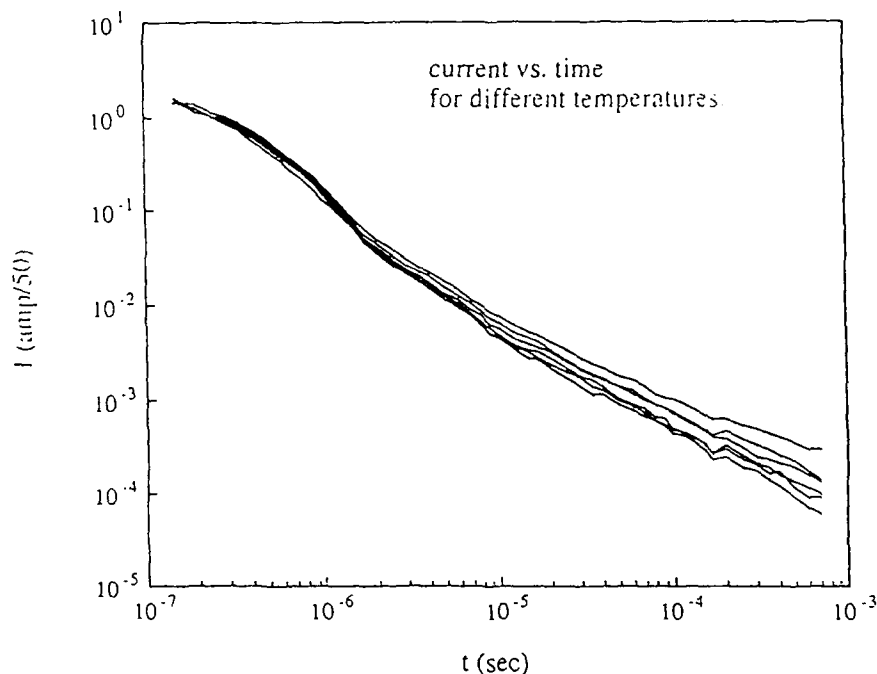


Figure 2

The temperature dependence of the transient current is small-- too small to be associated with charge carrier creation mechanisms. In stead of *one* activation energy reported in the past, a new analysis of the Modine's data yields *two* activation energies of ~ 10 meV and ~ 160 meV for the delayed transient current in the region from 10^{-1} second to 10^3 second. In the region immediately following the exponential decay, our own data show an activation energy of ~ 160 meV; the lower activation energy, ~ 10 meV, has not been seen

because we have not been able to carry out measurements at low temperatures where it is dominant over the higher activation energy. These activation energies are too small to be consistent with the slow decaying nature of this polarization current if they are associated with carrier creation processes; they must be associated with the carrier mobility. We have developed a theory which explains the slow decaying polarization current. We propose that this slow decaying polarization current is generated by the tunnelling into the conduction band of deep donors under the influence of the depletion layer potential energy provided by the shallow donors which ionize in a very short time, say a few nanoseconds, when the Fermi energy is shifted down across them. Since this is only a part of our theoretical program, we start with a general description of our view of the varistor mechanism.

Since existing theories do not provide satisfactory explanations for the long turn-on (the voltage overshoot) and short turn-off time, *and also* how some transition metal additives (performance ingredients) improve the varistor performance so drastically by increasing the nonlinearity, we have tried to develop a theory which provides explanations for them. The theory we are developing is based on the following observation:

1. The double Schottky barrier model of the grain boundary region is valid,
2. The performance ingredients such as Mn and Co introduce additional electron donor levels in the energy band gap,
3. There are shallow donors within a few kT of the conduction band edge,
4. Tunnelling as well as thermally activated electronic processes are involved, and
5. Hot electrons have short mean free path and consequently a short thermalization length.

We start with the double Schottky barrier models of Pike⁵; Mahan, Levinson and Philipp⁶; and Blatter and Greuter⁷, but recognize that the short mean free path, with accompanying energy loss, make the creation of holes in the valence band -- or impact ionization -- by the electrons in the conduction band unlikely

at the bias of approximately 3 eV if the width of the depletion layer remains as large as 1000 Å or greater. We estimate the mean free path as small as 10 Å, leading to the conclusion that at least 100 scattering events occur before the electron leaves the depletion layer. The electrons coming over the barrier may be assumed thermalized by the time they leave the depletion layer. We consider the possibility that the width of the depletion layer can decrease on the positively biased side as the deep donors ionize by tunneling into the conduction band and also by impact ionization by hot electrons. Although there are donors at various energy levels, we assume only two types of donors, shallow donors of density n_1 and deep ones of n_2 , in order to bring out the physics clearer.

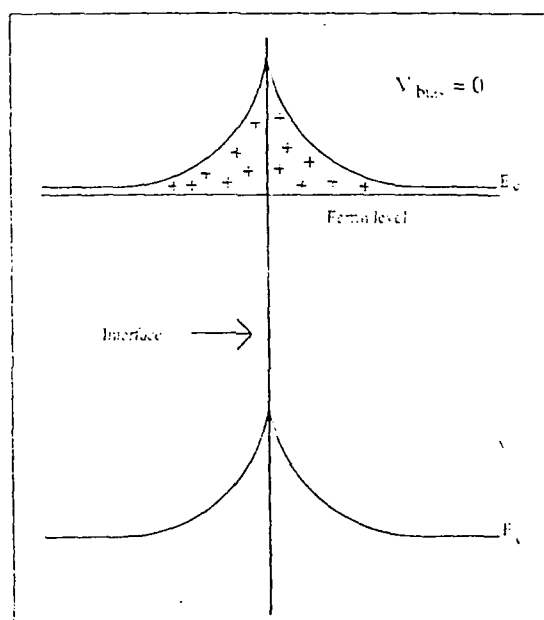


Figure 3

With zero bias, all donors above the Fermi level are ionized as illustrated in Figure 3. When a bias V is applied, the Fermi level on the positive biased side is lowered while that of the negative side is raised. Soon after the bias is applied, some conduction electrons move into the depletion layer on the negative side and neutralize some ionized donors while the shallow donors on the positive side which are now above the Fermi level become ionized in a time of τ_1 while the deep donors will take a longer time τ_2 to ionize. Soon after, that is, τ_1 after the bias is applied, the conduction band edge in the depletion

layer (the electron potential energy curve) consists of two parts: the sum of the parabolic curve due to n_1 and the other parabola due to n_2 as given by Eq. 2.

$$V(x) - V_R = \begin{cases} (e^2 n_1 / 2\epsilon) (x - x_{R0})^2 & \text{for } x_{R0} \leq x \leq x_R \\ (e^2 n_1 / 2\epsilon) (x - x_R)^2 + (e^2 n_2 / 2\epsilon) (x - x_{R20})^2 & \text{for } 0 \leq x \leq x_{R20} \end{cases} \quad (2)$$

where V_R is the barrier height and x_{R20} is the width at zero bias of the ionized deep donor distribution, for the positive side.

All the *shallow* donors above the positive side Fermi level are ionized to provide a wide parabola while only ionized *deep* donors are those which were ionized at zero bias and provide a parabola of the zero bias width, Eq. 3.

$$x_{R0} = [2\epsilon V_B / e^2 (n_1 + n_2)]^{1/2} \quad (3)$$

where V_B is the barrier height at zero bias.

After τ_2 the deep donors above the positive side Fermi level would have been ionized, resulting in the narrowing of the depletion layer as indicated in Figure 4. If n_2 were much larger than n_1 , the narrowing would be drastic and tunneling from the grain boundary may become feasible.

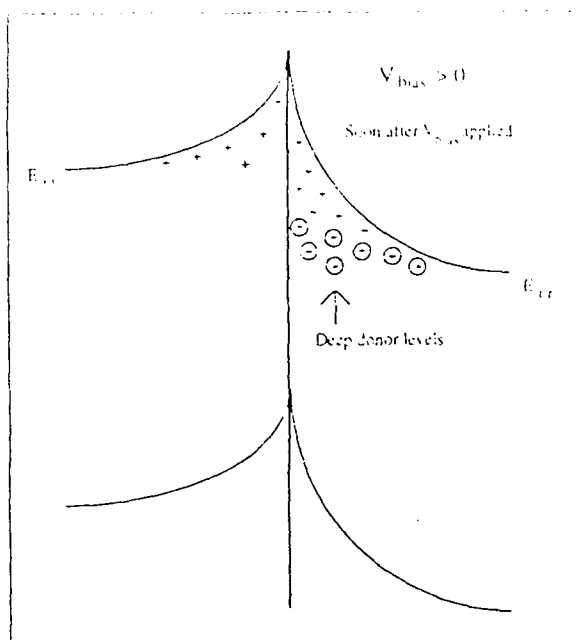


Figure 4a

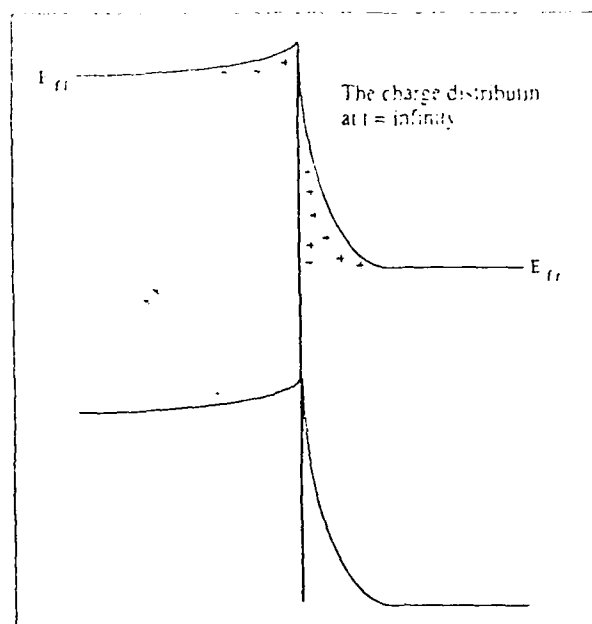


Figure 4b

As the bias is increased, some electrons coming over the barrier and across the grain boundary may have enough energy to excite a valence band electron to the conduction band creating a hole. This could happen for the bias comparable to the band gap only if the depletion layer width is small enough so that the electron does not lose significant fraction of its energy before it leaves the depletion layer. The value for n_1 is often equated to the estimated carrier density of 10^{17} cm^{-3} . If the value of n_2 is 10^{20} cm^{-3} , the depletion layer width would shrink, in τ_2 , to $1/\sqrt{1000} \approx 1/32$ of the width at τ_1 . A $1000 \text{ \AA}$ wide depletion layer would shrink to a $31 \text{ \AA}$ wide thin layer, making it feasible for an electron move across the layer without losing more than a fraction of its energy and thus making hole creation possible when the barrier height on the positive side is slightly larger than the band gap. The value of 10^{20} cm^{-3} for n_2 is not unreasonable large since a few percent of transition metal oxides are added to improve the varistor performance. This mechanism can provide explanations to (i) why the turn-on voltage per grain boundary (the breakdown voltage) seems to be independent of the additives, (ii) why the

metal oxide varistor with high nonlinearity coefficient has a voltage overshoot lasting microseconds, and (iii) why the displacement current peak is followed by a very small transient current which decays over a long time if the bias is less than the turn-on voltage and also when the applied bias is turned off.

As stated previously a slow-decaying transient current follow the removal of the bias and also follow the displacement current peak for the bias less than the breakdown (turn-on) voltage. This transient current has been found, by Modine and us, to have a power law time dependence $i \propto 1/t^n$ from a few microseconds to thousands of seconds, with the value of n close to unity. The power law time dependence can be explained if we assume that the charge carriers are generated by the tunnelling into the conduction band of the deep donor electrons which are now metastable since the Fermi level shifted down across their energy levels. As discussed above, the deep donors, after τ_1 , are under the influence of the parabolic potential provided by the ionized shallow donors. We approximate the potential barrier by a triangle (constant potential gradient approximation) as shown in Fig. 7 and Eq. 4.

$$V(\xi) - E = [E_d/(x_2 - x)] (x_2 - \xi) \quad (4)$$

for the trap at x . $E_d = V(x) - E$ is the trap depth measured from the conduction band edge at x . The WKB approximation yields

$$\tau \propto \exp \{ [(2mE_d/h^2)^{1/2}(-4\epsilon E_d/3e^2 n_1 x)] \} \quad (5)$$

where x takes negative values because of our choice of the zero. An interesting consequence of this formula is: *the life-time of the trap is greater for those farther inside the bulk, i.e. for smaller (-x)*. This dependence of the life-time on x does produce the power law time dependence of the slow-decaying transient current in a time range.

We may assume the current to be proportional to the rate of carrier creation or carrier injection from the depletion layer to the bulk. Then

$$i(t) \propto \int_{\tau_b}^{\infty} \frac{n_2}{\tau} e^{-t/\tau} \frac{dx}{d\tau} d\tau \quad (6)$$

where τ_b is the life-time at $x = x_b$, adjacent to the grain boundary.

From Eq. 5, we derive

$$\frac{dx}{d\tau} = \frac{\tau_b}{A} \frac{1}{\left[\frac{1}{x_b} - \frac{1}{A} \ln \frac{\tau}{\tau_b} \right]^2} \frac{1}{\tau} \propto \frac{1}{\tau} \quad (7)$$

where A is a constant independent of τ ; the weak τ -dependence in the brackets is neglected. Substituting Eq. 7 into Eq. 6 yields

$$i(t) \propto \int_{\tau_b}^{\infty} \frac{1}{\tau} e^{-t/\tau} \frac{1}{\tau} d\tau = \frac{1}{t} (1 - e^{-t/\tau_b}) \approx \frac{1}{t} \quad \text{for } t \gg \tau_b \quad (8)$$

A slightly different formulation is given in our paper ⁴ to be published in *Advances in ceramics*.

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Publications resulting from this grant

F. A. Modine, R. W. Wheeler, S. Choi, L. B. Bergman, and M. Silver, *Advances in Ceramics* (in press)

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