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Thermionic, Tunnelling, and Polarization Currents in Zinc Oxide Varistors

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Abstract

We report an analysis of time, voltage, and temperature dependencies for ZnO varistors conductance. The conduction mechanisms proposed to interpret experiments include thermionic, tunnelling, and polarization currents. We analyse here the contributions of these mechanisms to conduction in order to identify their roles. We conclude that a tunnelling current shows the correct trends in the current-temperature curve. Also, capacitance measurements as a function of time and temperature are presented to discuss the influence of interface and deep bulk traps. © 1997 Elsevier Science Limited.

1 Introduction

Varistors are solid-state electronic devices made of sintered semiconductor powder. These devices act as variable resistors, with high resistance at low voltages and low resistance at high voltage. Zinc oxide varistors are made of semiconducting ZnO grains containing dissolved Co, Mn, and Cu and intergranular phases with Bi_2O_3 and Sb_2O_3. Varistors are insulators at low voltages but they become conductors at high voltages presenting highly nonlinear current-voltage characteristics curves. Varistors are used extensively for transient overvoltage suppression in electronic circuits and electrical power distribution system.[1,2]

The sintering process of these ceramics gives rise to a structure which consists of conductive ZnO grains surrounded by thin intergranular zones, resulting in a three-dimensional network. Despite the complexities of the actual material microstructure, with irregular grains forming series and parallel electrical paths, varistors have been described in a relatively simple way. Indeed, varistors have been successfully represented by a block model. In this model, cubic crystals of ZnO are kept apart from each other by insulating barriers.[3] Interestingly, the behaviour of the whole device is essentially determined by that of an isolated junction between two ZnO grains. From these results it has been concluded that the material electrical properties are governed by intergranular conduction.

The electrical characteristics of ZnO ceramic varistors have been interpreted as being due to the formation of potential barriers at the grain boundaries. Due to presence of intergrain states, the region near the junction is depleted of electrons. Since two opposite Schottky type barriers are then formed, this interpretation is called the double Schottky barrier model.[4] However, there is no consensus regarding the detailed mechanisms responsible for conduction. Several models have been proposed to explain the electrical properties, indicating that, for a correct quantitative description of the varistor behaviour, several additional mechanisms should be considered. Nonetheless, most researchers accept that at low voltages, at the prebreakdown region, the main mechanism responsible for conduction in polycrystalline ZnO consists in thermal excitation over the interface barrier.[5] A thermionic current, however, cannot account for experimental observations. Indeed, this has been noticed by Levinson, Philipp and Mahan who were compelled to postulate leakage paths acting in parallel with the Schottky barrier-controlled current flow.[6]

Although a double Schottky barrier model is widely accepted, some researchers consider grain boundaries of essentially zero width, while a non-negligible disordered layer at the grain boundaries is taken into account by others.[7] According to our results, the model having an intergranular layer describes better the electrical properties of ZnO varistors. This means that electrons stop and spend time in the interface during their passage through it. Electrons would transfer from the

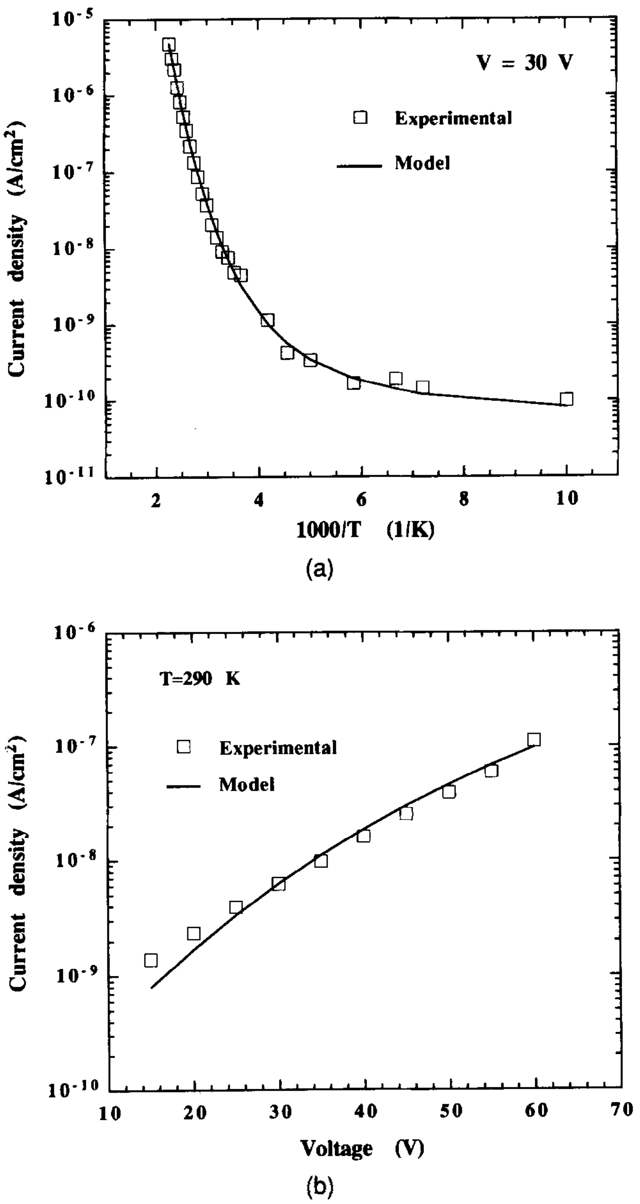


Fig. 1. (a) Current density versus temperature curve; (b) current density versus voltage curve.

grain to the interface and then to the next grain in separate processes.[1,8] On the other hand, Modine *et al.* have reported the time, voltage, and temperature dependencies of transient polarization currents.[9] They established that at room temperature and low voltages about 1000 seconds are required for the polarization currents to become negligible in comparison to the steady-state conduction. The polarization currents would be predominant for much longer times at low temperatures because the thermally activated steady-state conduction is greatly diminished.

In this work we report an analysis of time, voltage, and temperature dependencies for ZnO varistors conductance. The discussed conduction mechanisms to interpret experiments include thermionic, tunnelling, and polarization currents. We analyse here the contributions of these mechanisms to conduction in order to identify their roles. Also, capacitance measurements as a function of frequency and temperature are presented to explore the influence of possible interface traps.

2 Experimental Procedure

Experimental measurements were made on commercial varistors Zenamic Z151 9F. Since features for varistors of the same type present varying characteristics, the same varistor was used for a complete set of measurements. Currents were measured with a Keithley 614 electrometer and a Phitronics power supply (0–60 V, 0–1·5 A). Capacitance measurements were carried out with a Hewlett Packard model 4184A impedance analyser in the range 10 kHz–1 MHz. Measurements were made in the range 100–453 K. Low temperatures were achieved with liquid air whereas a furnace was used for heating.

3 Results and Discussion

In Fig. 1 we present the current density dependence with temperature in the range 100–453 K for an applied voltage of 30 V. When using the thermionic emission model, the current density takes the form (for eV >> kT)

$$J = AT^2 \exp(-\phi/kT), \qquad (1)$$

where A is the Richardson constant, ϕ the barrier height, and k the Boltzmann constant. According to this model, changes in slope represent different activation energies, which directly represent a change in the barrier height. Indeed, from Fig. 1(a) three barrier heights could be proposed: ϕ_1 = 0·57 eV for $T > 370$ K, ϕ_2 = 0·17 eV for 240 K $< T <$ 370 K, and ϕ_3 = 0·006 eV for $T < 240$ K, values which are in the order of those found in the literature.[10]

Now we will introduce a model with tunnelling current through a potential barrier with a non-negligible intergranular layer. Conduction is then governed by a forward-biased Schottky diode, a thin insulator with traps, and a reverse-biased Schottky diode. Since the reverse-biased Schottky diode plays the dominant role in the series connection of back-to-back rectifying barriers, the conduction process in the forward-biased Schottky diode then has no strong effect on the V-I curves of non-ohmic ZnO ceramics. Then, we consider a reverse Schottky diode with an exponential donor concentration.

$$N(x) = N_b + N_s \exp(-x/d), \qquad (2)$$

where N_b is the bulk donor concentration, $N_b + N_s$ the grain boundary donor concentration, and d a

Table 1. Current densities (A/cm^2) at several times at 100 K

Time	*Case (a)*	*Case (b)*
20 s	—	$3{\cdot}35 \times 10^{-10}$
1 h	$3{\cdot}37 \times 10^{-10}$	$3{\cdot}0 \times 10^{-10}$
5 h	$3{\cdot}37 \times 10^{-10}$	$3{\cdot}12 \times 10^{-10}$

parameter. In this model the total current density is given by a thermionic current and a tunnelling current. Although a Fermi–Dirac distribution gives enough accuracy according to our needs, the results reported here were obtained using the supply function proposed by Fonash.[11] Experimental current density-temperature and current density-voltage data could be fitted with $N_b = 3 \times 10^{17}$ cm^{-3}, $N_s = 1{\cdot}8 \times 10^{19}$ cm^{-3}, $\phi = 1{\cdot}54$ eV, and $d = 75$ Å (see Fig. 1(a) and (b)). The main error sources for this model are the non-inclusion of the forward-biased diode and the adopted profile for the donor concentration.

Some researchers have suggested that polarization currents are important at low temperatures.[9] A possible origin of the polarization currents is electron hopping among randomly distributed traps. Then, accurate steady-state current versus voltage or capacitance versus voltage curves can only be measured when sufficient time is allowed to neglect the polarization currents. This would be particularly crucial when measurements are made at low voltages and low temperatures. To investigate this possible contribution we measured the current as a function of time at 100 K, see Table 1. In this table we compare two experimentally different conditions. First, we applied 30 V at room temperature and then cooled down the sample to 100 K (case a). Second, we cooled down the sample and then applied the voltage (case b). It is important to point out that before performing the second experiment the sample was left under short-circuit at room temperature for 16 h. Interestingly, a similar steady-state current was measured in both experiments and just a couple of minutes were needed to have a stable current in the second experiment with non-relevant changes after some seconds. From these results we can conclude that in our ZnO varistors polarization currents are not important, since appreciable changes in the current as a function of time are not observed.

Researchers have tried to determine barrier heights from capacitance versus applied voltage (C–V) curves by considering a system of two symmetric Schottky diodes with a highly conductive intergranular layer.[12] By considering a model in which the applied voltage mostly drops in the reverse-biased diode, the C–V relation takes the form

$$(1/C\text{-}1/2C_0)^2 = 2\, n^2/(q\epsilon_s N A^2)\,(\phi + V/n) \qquad (3)$$

with

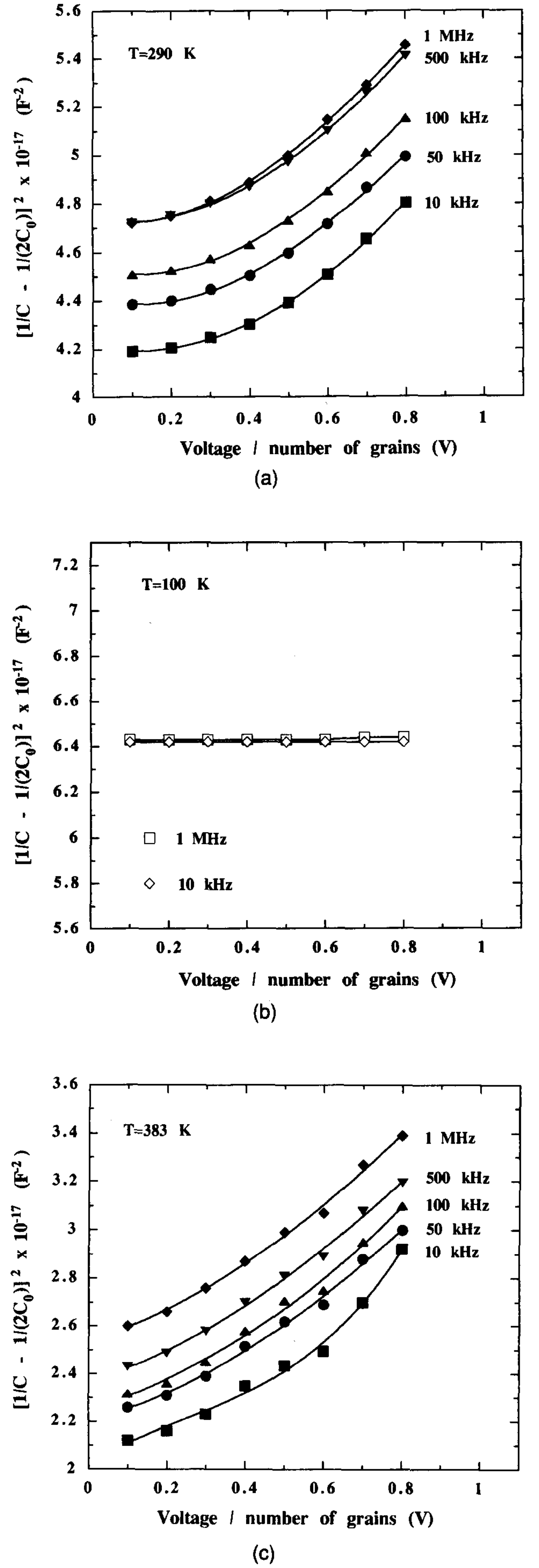
$$1/C_0 = 2\,[2\phi n^2/(q\epsilon_s N A^2)]^{1/2}, \qquad (4)$$

where N is the constant donor concentration, q the electron charge, n the number of grains, A the area and ϵ_s the dielectric constant of ZnO. According to this method, by measuring the capacitance as a function of voltage, N and ϕ can be determined from the slope of the line and the intercept on the voltage axis. Note that in eqns (3) and (4) the donor concentration is assumed to be constant. As we will discuss, varistors present unusual AC properties which need to be described by a comprehensive model.

Although the above method has been regularly used, determined parameters appear depending on the frequency used (see Fig. 2(a)). For room temperature, using a frequency of 10 kHz, $\phi = 2{\cdot}26$ eV and $N = 4{\cdot}15 \times 10^{17}$ cm^{-3}, while, for 500 kHz–1 MHz, $\phi = 2{\cdot}76$ eV and $N = 3{\cdot}77 \times 10^{17}$ cm^{-3}. For $T = 100$ K, changes in $(1/C\text{–}1/2C_0)^2$ versus voltage are very small and the curves at different frequencies are overlapping (Fig. 2(b)). For $T = 383$ K, on the other hand, the curves appear separated in the whole range 10 kHz–1 MHz (Fig. 2(c)). These variations can be due to charge trapping in the interlayers and in bulk deep traps.[13] Then, this method can lead to a falsification of parameters since the determined values for the barrier height and the donor concentration are functions of temperature and frequency. However, for low frequencies and high temperatures (before degradation), parameters obtained with this method show values with a tendency to those obtained from current measurements.

Results of Fig. 2 have no physical meaning according to eqns (3) and (4) but they can be qualitatively explained by invoking some well-known phenomena. The constancy of the capacitance with the applied voltage at low temperatures can be interpreted as the result of a constant interface charge.[14] At higher temperatures, on the other hand, interface states can reach their steady-state charge in the time frame of our measurements, the capacitance becomes a function of the applied voltage, and then eqn (3) could be applied. The observed dependency with the frequency used can be attributed to the presence of deep bulk traps which respond according to their capture and emission ability. Thus, observed results are consistent with an increase of resonance frequency with temperature.

In order to clarify the effects of traps and interface states on the conductance, we measured the



(a)

(b)

(c)

Fig. 2. (a) Capacitance versus voltage at room temperature; (b) capacitance versus voltage at 100 K; (c) Capacitance versus voltage at 383 K.

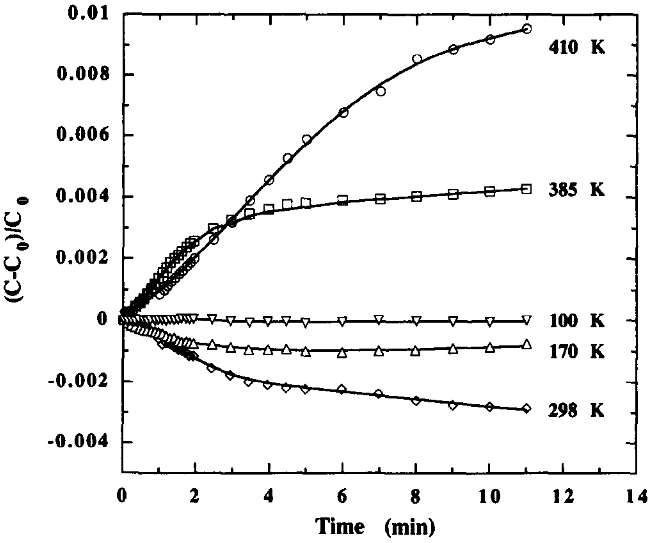


Fig. 3. Change in the capacitance versus time at several temperatures at 500 kHz. Here, C_0 refers to the initial capacitance.

capacitance versus time for different temperatures (100–410 K) at 500 kHz. From Fig. 3 it is evident that at very low temperatures the capacitance does not change with time. This result can be interpreted as a consequence of the interface charge constancy. In fact, results of Figs 2 and 3 show a constant capacitance, consistent with a double-depletion-layer model with a fixed interface charge.

For temperatures up to 360 K, we found that the capacitance decreases with time. This result corresponds to the usual findings at room temperature in which the capacitance is a slowly decreasing function of the applied voltage due to the existence of interface states. For even higher temperatures (360 K < T < 400 K), the capacitance is observed to increase with time. In this temperature range, deep bulk traps can respond to the applied voltage in the time frame of our measurements. Thus, as a consequence of the applied voltage, the sample capacitance increases due to the activation of a higher number of traps in the depletion region.

Finally, for temperatures higher than 400 K, the increase in the capacitance with time can be related to a degradation process involving a distortion of the Schottky barriers at intergrains.[15] Indeed, a change in the donor concentration profile would directly affect the conductivity and capacity of the sample.

4 Conclusions

The main conclusions are the following.

1. The observed J-T curve can be understood as the resulting current density corresponding

to a Schottky diode in reverse with a variable donor concentration. Tunnelling current produces the observed slope changes at the correct temperature in a J-T curve. Polarization currents are not important in our ZnO varistors.

2. Changes in capacitance with time at several temperatures can be related to the presence of interface states and the resonance of deep bulk traps. These traps may cause error in the determination of the barrier height associated with the interface and donor concentration from capacitance-voltage measurements.
3. For temperatures above 400 K, the increase of the measured capacitance with time can be an indication of a degradation processes involving a distortion of Schottky barriers. Low temperatures results, in which the capacitance is not a function of the applied voltage, can be interpreted as a consequence of charge transfer restrictions.

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