A COMPREHENSIBLE NEED OF ZINC OXIDE VARISTORS IN ELECTRONICS TECHNOLOGY

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**Abstract**

A range of varistors, in terms of break down voltage, is required to protect integrated circuits, automotive systems and other modern electronics against transient over-voltages. There is a progressing need for the development and advancement of rugged and reliable varistor capable and proficient of working in harsh and callous environment like automotive industry where greater than before use of electronics technology has led to improvements in equipment performance and presentation. There is a comprehensible need to combine triumphant and succesable models developed at different length scales into an integrated framework that can be used to drive new research and guide experimental efforts and device development. The review of ZnO varistor in particular and metal-oxide varistors (MOVs) in general is presented in this article.

**Keywords:** Automotive systems, metal-oxide varistors, Zinc oxide.

**BACKGROUND INFORMATION**

Varistors are electronic components that show nonlinear current-voltage behavior, and are used to protect circuits against voltage transient. The commonly known metal-oxide varistors (MOVs) are polycrystalline electronic ceramic devices. ZnO is one of the MOV's. The non-linear properties of ZnO varistors are characterized by an electrical resistance that decreases as the applied field increases. The non-linear properties may be characterized by a non-linear parameter n, given by

\[ I = cV^n \rightarrow (1) \]

where \( V \) is the voltage across the sample, \( I \) is the current flowing through the sample, \( c \) is a constant and \( n \) is a coefficient of non-linearity by

\[ n = d(\log I)/d(\log V) \rightarrow (2) \]

\( n \) may therefore be determined from the slope of a log \( I \) verses log \( V \) curve as shown in fig.1. This phenomenon was observed in bulk material, thick film, thin film, and heterojunction.
SOURCE OF CHARGE CARRIERS

ZnO is well known as n-type semiconductor with a wide bandgap of about 3.3eV, owing its conductivity to excess Zn atoms or to oxygen vacancies. The thin insulating grain boundaries are thought to constitute double Schottky barriers [Emtage 1977]. These Schottky barriers arise from the trapping of electrons and control the electrical characteristics of varistors. These trapped electrons are charge-compensated by positive shallow donors and donor-like traps located at the depletion regions of the grain boundaries [Cordaro et al. 1986]. The electron traps are majority carrier traps in ZnO varistors. Since the charge-trapping phenomena occur mainly in depletion regions of the grain boundaries they result in ac dispersion [Mahmood and Gould 1994]. Multiple trapping relaxations lead to a terminal capacitance. One of the relaxation processes in ZnO varistors is associated with the native/intrinsic defects within depletion regions of the grain boundaries [Cordaro et al. 1986, Alim et al. 1988, Sletson et al. 1988, Alim 1989]. Electrical conduction through the bulk devices is thought to take place between the ZnO grains [Bernasconi et al. 1976] and generally exhibits a power-law dependence of current on the applied voltage as shown in Fig. 1. There is disagreement concerning the particular conduction mechanisms involved, especially in view of the high values of the power-law exponent n observed experimentally [Mahmood 1994]. Levinson and Philipp [1975], and Mahmood [1993, 1994, 1995] have explained their results in terms of Schottky or Poole-Frenkel emission and of Fowler-Nordheim tunnelling. Matsuoka [1971] has concluded that the behaviour is due to space-charge-limited conductivity (SCLC),
while Lee et al. [1977] have stressed the importance of trapping levels situated below the Fermi level of the ZnO.

Bernasconi et al. [1976] concluded that none of the simple models could explain experimentally observed values of the power-law exponent greater than about 25, although consistent values were possible for tunnelling out of surface states and SCLC.

DC measurements on pure ZnO devices [Gould and Carter 1983] and on similar devices containing only Sn [Gould and Rahman 1981] have confirmed that in these simpler structures SCLC is apparent; however they showed only moderate values of $n$ in comparison to those for samples containing several additives.

**DEVELOPMENT OF ZnO VARISTORS THEORY**

The theory of ZnO varistors has evolved along with the increasingly detailed experimental description [Levinson and Philipp 1976a, 1976b, Philipp and Levinson 1975, 1977, 1979]. The extreme nonlinearity in the current-voltage curves naturally led the early investigators to suggesting well-known nonlinear mechanisms, such as SCLC or electron tunnelling. Later experiments proved these first proposals untenable [Morris 1976]. After that a second generation of theories was proposed, with many different mechanisms suggested for the extreme nonlinearity [Levine 1975, Mahan et al 1979, Vanadammme and Brugman 1980]. All theories have used the single grain boundary to describe the nonlinear electrical behaviour. Experiments have shown that a single grain boundary has nonlinear electrical properties, and the overall network is thought to be multistage of the same nonlinear element. Bai and Tseng [1992] found the breakdown voltage of a single grain boundary that varied widely between 1.5 - 5 V with an average value of 3.3 V. Wakuja et al. [1991] have calculated the value of breakdown voltage to be 1.88 V. Suzuoki et al. [1987] found a value of 3.3 V in their work on ZnO/Bi$_2$O$_3$ interfaces used to model a single grain boundary. Bai and Tseng [1992] also investigated the influence of the cooling rate on the microstructure, the nonlinear parameter $n$, the breakdown voltage, the dielectric properties and the leakage current in ZnO varistors, and found that the morphology of the microstructure had different appearances under the effect of varying cooling rates. The nonlinear parameter and the breakdown voltage reached a maximum value for a cooling rate of 240°C h$^{-1}$ (4°C min$^{-1}$). As a result, varying the cooling rate may control the physical and electrical properties of the ZnO varistors.

**BULK ZnO-BASED VARISTORS**

Bulk ZnO-based varistors have been widely used since their original development in the early 1970s for the protection of electrical circuits against dangerous voltage levels, such as lightening surges, switching surges, electrostatic discharges and electromagnetic transients. Such devices are prepared by sintering and usually incorporate several different oxide additives such as Bi$_2$O$_3$, Sb$_2$O$_3$, CoO and MnO, of which Bi$_2$O$_3$ is probably the most important. It is well known that non-ohmic ZnO varistors are largely affected by the addition of metal oxides [Kusy and Kleinpenning 1983, Koumoto et al 1982], in which manganese and cobalt can enhance the non-linear coefficient of the varistor. However, the mechanisms of these effects, particularly on the electrical
properties, have not been clarified. Traps resulting from various valence states of additive oxides have not been thoroughly investigated, although the types of trap resulting from valence states of manganese and cobalt when employed in ZnO-based varistors containing Bi$_2$O$_3$, have been analyzed by Chen et al. [1991]. Alim [1993] studied some ac properties. The material microstructure has been shown to comprise grains of ZnO surrounded by a complex intergranular material [Matsuoka 1971, Levinson and Philipp 1975, Wong 1974, 1975], whose composition depends on the type and number of additives.

Silva et al. [2006] described in their short communication the effects of La$_2$O$_3$ on the properties of (Zn, Co, Ta) doped SnO$_2$ varistors. The samples with different La$_2$O$_3$ concentrations were sintered at 1400 °C for 2 h and their properties were characterized by XRD, SEM, I–V and impedance spectroscopy. The grain size was found to decrease from 13 μm to 9 μm with increasing La$_2$O$_3$ content. The addition of rare earth element leads to increase the nonlinear coefficient and the breakdown voltage. The enhancement was expected to arise from the possible segregation of lanthanide ion due to its larger ionic radius to the grain boundaries, thereby modifying its electrical characteristics. Furthermore, the dopants such as La may help in the adsorption of O’ to O” at the grain boundaries characteristics.

Sedky et al. [2007] studied the nonlinear I–V characteristics in doped ZnO based-ceramic varistor. They prepared two similar sets of Zn$_{1-x}$Fe$_x$O ceramic samples with various $x$ values (0.00< $x$<0.50) by two different heat treatments. The first set was quenched from sintering temperature down to room temperature, and the second was left in the furnace and slowly cooled to room temperature. These samples were examined by using X-ray diffraction patterns (XRD), scanning electron microscope (SEM) and DC electrical measurements. XRD data indicate that the replacement of Zn$^{2+}$ ion by Fe$^{3+}$ ion did not influence the Wurtzite structure of ZnO samples. The result of SEM showed that no secondary phases were formed at grain boundaries, supporting the XRD results. They concluded the average grain size decreased with increasing Fe content up to $x$=0.10, followed by an increase at $x$>0.30. With increasing Fe content, a nonlinear region, obtained from I–V characteristics, clearly appeared and was shifted to higher fields. The nonlinear coefficients increased by adding Fe up to $x$=0.30, followed by a decrease at $x$=0.50. The values of the barrier heights were increased with Fe up to $x$=0.10 and kept unchanged with further Fe content.

The electrical conductivities at room temperature were measured and its values were found to be decreasing with increasing Fe content, as compared to those of an undoped ZnO sample. They discussed their results in terms of point defects and intrinsic donors, which were the consequent of Fe doping in the ZnO ceramic system.

**THICK FILM VARISTORS**

Tohver et al. [2002] fabricated thick-film ZnO varistor. They developed Zinc oxide-based pastes with tailored rheological properties for direct-write fabrication of thick-film varistor elements in highly integrated, multifunctional electroceramic devices. Square and rectangular elements were patterned on dense alumina substrates and sintered at varying temperatures between 800° and 1250°C. Varistor elements fired at 900°C exhibited nonlinearity coefficients (n= 30) that were equivalent to high-density varistors formed by cold isostatic pressing.
ZnO-ZnO SINGLE-CONTACT VARISTORS
Nakamura et al. [1999] studied a couple of zinc oxide (ZnO) single crystals with single boundaries (ZnO-ZnO single-contacts) fabricated by the traditional vapour reaction method and their electrical properties were characterized. The ZnO-ZnO single-contacts obtained shown nonlinear current-voltage (I-V) characteristics without varistor-forming constituents. Some of the ZnO-ZnO single-contacts show pronounced nonlinear I-V characteristics with negative resistance. The I-V characteristics of the ZnO-ZnO single-contacts were apparently similar to those of ZnO varistors; however, there were marked differences in the electric structure of the boundaries between the ZnO-ZnO single-contacts and ZnO varistors. The capacitance-voltage (C-V) relations of the ZnO-ZnO single-contacts were quite different from that of ZnO varistors and no evidence for the formation of double Schottky barriers at the boundary region were found. A very slow response to current stress was considered a feature of ZnO-ZnO single-contacts and it was suggested that any thermal processes including Joule heat would modify the carrier transport efficiency through the boundaries.

MICROMODELS OF ZnO VARISTORS
Wang et al. [1995] studied the morphology of ZnO varistors made with seed grains. They found two kinds of combination of ZnO grains and put forward two different micromodels of ZnO varistors. The relation between the mean diameter of the ZnO grains and the proportion of seed grains was deduced from the proposed micromodels. One micromodel considers large ZnO grains embedded into small ZnO grains. The second micromodel considers only large ZnO grains. ZnO seed grains were derived from ZnO containing BaO sintered bodies Wang et al. [1994]. The seed grains selected were from 60 to 140 μm in diameter. The proportions of seed grains used were 0, 1, 8, 15, 25, and 40wt%. The seed grains were mixed with the base powder by sieving using a reciprocal particle-formalizing machine. Two different base powders were derived from the Sb system and the Ti system.

HETEROJUNCTION THIN FILM ZnO VARISTORS
Eda et al. [1982] and Mahmood [1994] studied the electrical properties of ZnO/\( \text{Bi}_2\text{O}_3 \) metal oxide thin film heterojunction prepared by sputtering. The junction showed highly non-ohmic properties. The thickness of the \( \text{Bi}_2\text{O}_3 \) and metal oxides were 1.1μm. The voltage-current characteristics and the dielectric properties were functions of the \( \text{Bi}_2\text{O}_3 /\text{metal oxide thin film thickness} \). The heterojunction showed similar dielectric properties to those observed in ZnO varistors. As the film thickness increased, the capacitance decreased, especially above 100 kHz. The inverse of the square of capacitance increased proportionally with the bias voltage when the ZnO substrate was positively biased. This behaviour confirmed the presence of a Schottky type barrier at the junction in the ZnO substrate. When the ZnO substrate was negatively biased, the capacitance increased. A grain boundary microstructure has been proposed as shown in Fig.2, which consists of three types of grain boundaries. The first is a grain boundary having a thick (~1μm) \( \text{Bi}_2\text{O}_3 \)-rich intergranular layer (region A) [Matsuoka 1971], the second is a grain boundary of a thin 10-100 nm \( \text{Bi}_2\text{O}_3 \)-rich intergranular layer (region B) (Inada 1978) and the third is a grain boundary not having a distinct \( \text{Bi}_2\text{O}_3 \)-rich intergranular layer (region C) [Kingery et al. 1979,
Clarke 1979]. However the latter has Bi-enriched regions along the grain boundary.

Suzuoki et al. [1987, 1989] and Mahmood [1994, 1995] investigated the behaviour of rf sputtered ZnO/ Bi$_2$O$_3$ heterojunction structures and showed that such junctions exhibit typical varistor behaviour. They studied the junctions as a model of a single grain boundary in a ZnO varistor, because in actual varistors the grain boundaries are connected in a complex manner, both in series and parallel. It is therefore difficult to understand the characteristics of a single grain boundary by measuring the overall electrical properties. They suggested that the current in an actual ZnO varistor is governed by the reverse-bias interface and the forward-bias interface acts as an electron injector into the intergranular layer. This system can in principle be used as a thin film varistor and also as a humidity sensor because of its high non-linearity coefficient (60 - 100), and high sensitivity and fast response to humidity. The low-voltage varistor for electronics has the potential advantage of being directly fabricated in an integrated circuit for direct on-chip circuit protection.

**TEMPERATURE EFFECT ON ZnO VARISTORS**

Prisching and Pecina [2000] examined the temperature behaviour of ZnO varistor discs before and after post sintering heat treatment. A criterion was found that
predominantly determine the thermal behaviour of a ZnO varistor disc. In addition, it was found that a post sintering heat treatment could change the temperature behaviour. The majority of the tempered samples were in agreement with established models. However, one varistor disc, consisting of a commercial varistor mixture, appeared to be deviant. The tempered samples of this mixture showed an improved thermal behaviour, i.e., a significantly lower increase of the leakage current with increasing temperature.

Olorunyolemi et al. [2002] measured thermal conductivity of ZnO with different particle sizes (micrometer, submicrometer, and nanometer) using the laser flash technique. A model for interparticle neck growth was developed based on mass transfer to the neck region of a powder as a result of known temperature. By combining this model with a three-dimensional numerical code, the thermal conductivity of ZnO was calculated. Excellent agreement between the theoretical calculation and experimental data was claimed.

ELECTRODE EFFECT ON ZnO VARISTOR

Lavrov et al. [2004] investigated the electrode’s effect on ZnO varistor characteristics. They created silver electrodes by silver baking and copper electrodes obtained by electrodeposition of copper. The current–voltage characteristics of zinc oxide-based ceramics were investigated. For ZnO varistors with copper electrodes the leakage current in 3–4 times was less than for varistors with silver electrodes. It was attributed to thermal influence on ceramics at creation of silver electrodes. The transition layer between ceramics and the copper electrode, that had a negative influence on current–voltage characteristic at region of high electric current was not detected. The tearing strength for copper electrode was \((8.21\pm3.03) \times 10^6 \text{ N m}^{-2}\) and was close to similar magnitude for a silver electrode.

DEGRADATION AND AGING OF VARISTORS

Interesting features of ZnO varistors are the related phenomena of degradation and transient currents. Degradation occurs when the varistor is operated continuously with a large breakdown. The current-voltage characteristics change with time, and become asymmetric with regard to the direction of the original breakdown current. The degradation continuously occurs over periods of many hours [Eda et al. 1980]. The transient phenomena occur when a constant voltage pulse is applied to the varistor, and the final steady-state is approached very slowly in time [Philipp and Levinson 1975, 1977, 1979, Eda et al. 1980]. The initial response is faster than a microsecond, but the final approach to steady state can take much longer. It was suggested by several groups [Philipp and Levinson 1975, 1977, 1979, Eda et al. 1980] that both the degradation and transient phenomena are caused by the diffusion of ions within the depletion region. However, so far no theoretical models have been proposed for these phenomena.

Castro and Aldao [1996] investigated the degradation of ZnO-based varistors and found that it was attributed to ion migration in the depletion layers at intergrains. They found that ion migration could change the dopant profile and then the barriers’ shape. They also emphasized to distinguish two processes, permanent degradation and reversible degradation to account for the observed experimental results.
Chen and Chan [2002] examined water-induced degradation in ZnO-based ceramic varistors. A comparison experiment was conducted in which some varistors were immersed in a 0.05M NaOH solution for some time while other varistors were placed in a 0.05M NaOH solution to evolve hydrogen on their silver electrode by electrolysis of water. No degradation occurred to those samples that were immersed in the NaOH solution; the leakage currents increased and the switch voltage remained unchanged in the samples treated by electrolysis of water. These results indicated that the degradation resulted from the reduction reaction of hydrogen atoms generated by electrolysis of water rather than the permeation of water into the ceramics. It was proposed that the reduction reaction of hydrogen atoms generated by electrolysis of water might be an important origin for the degradation in ZnO varistors.

Wang et al. [2007] also investigated humidity-induced degradation in low voltage ZnO varistors. An experiment was conducted in which some varistors were put in humid condition with fixed relative humidity of 100% at 25 °C for a certain period of time. After the treatment, the samples showed serious degradation as their breakdown voltage decreased and their leakage current increased significantly. It was proposed that the diffusion and reaction of H⁺ generated by dissociation of water at the surface of ceramics induced the degradation due to humidity. When the degraded low voltage ZnO varistors were subject to continuous operating voltage for 120 h, thermal runaway did not occur in service, and the voltage–current characteristics of these degraded samples could be restored by polishing the surface of varistors. The experimental results indicated that the diffusion and reaction of H⁺ was confined to a surface layer of ceramic varistors. Wang et al. [2006] investigated the nonlinear electrical characteristics and stability against AC accelerated aging stress of Al-doped low voltage ZnO varistors as a function of Al content. The varistors with Al exhibited a high nonlinear coefficient above 30, compared with that without Al. The varistors with 200 ppm Al³⁺ exhibited a highest nonlinearity, with a nonlinear coefficient of 42.9 and a leakage current of 9.5 μA. But the varistor without Al showed high stability, in which the variation rate of varistor voltage, of nonlinear coefficient and of leakage current are −4.1, −4.3 and +20.7%, respectively, under AC accelerated aging stress (1.0 V, 1 mA per 125 °C for 24 h).

Lee and Kang [2006] presented the effect of multiple impulse voltages on the electrical and physical properties of a zinc oxide (ZnO) varistor. They designed and fabricated the multiple combination wave generators that produced multiple impulse voltages to investigate the dynamic characteristics of a ZnO varistor. The generator produced quintuple 1.2/50 μs impulse voltages of 100 kV and quintuple 8/20 μs impulse currents of 12 kA. Applying these voltages and currents, the electrical and physical properties of the ZnO varistor were evaluated. The multiple impulse failures of a ZnO varistor were mainly caused by the surface flashover. When multiple impulse voltages were injected, the charge enhancement near the joined edges of a ZnO varistor and metal electrodes played a decisive role on the surface flashover or breakdown initiation and developments. It was also observed that the residual voltage and quiescent current of the ZnO varistor were changed markedly after the injection of the quintuple 8/20 μs impulse currents of 10 kA.
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SUMMARY

A lot of work has been done to explore and to look at the properties of ZnO material from bulk to nano scale with pure and doping of different species. But still more work is required to accomplish the theoretical and experimental task. There is still a wide gap between the theoretical and experimental perceptive and understanding of the material concerning to varistor in particular. There is need to do work on it in a systematic and efficient way in order to pull off the task to get optimal benefit of the versatile material.

In order to abridge and reduce the gap, a research group comprises senior scientists of BZU Multan, QAU of Islamabad, and GCS Multan, has been established with collaboration of “MIAN ENGINEERS”.

References


