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Zinc Oxide Varistors for Lightning Arrester Service

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Electron Devices Division
Center for Electronics
and Electrical Engineering
National Bureau of Standards
Washington, DC 20234

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Zinc Oxide Varistors for Lightning Arrester Service

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Abstract - The application of zinc oxide (ZnO) varistors to high-power surge arresters for electrical transmission lines is considered, with particular attention to the special measurement problems posed by the application and by the unique properties of these varistors. The development of ZnO varistors and the present theory of ZnO varistor action are discussed. Consideration is given to the need for further elaboration of the theory.

Key Words: Electrical transmission; electrically conducting ceramics; lightning arresters; nonlinear resistors; semiconductors; surge arresters; varistors; voltage-variable resistors; zinc oxide.

1. Executive Summary and Recommendations

All of the companies engaged in development of lightning arresters using zinc oxide (ZnO) varistors were visited, and the technical literature was examined, to learn about the present state of knowledge of ZnO varistors and about the measurement problems that might exist. It is clear that significant problems of measurement and understanding for these varistors abound. Enough is known to make the application of ZnO varistors to surge arresters for transmission line service both likely and attractive. The characteristics of ZnO varistors are sufficiently more stable than those of silicon carbide (SiC) varistors that their use while continuously energized is possible, though much remains to be learned.

While a theory of the basic mechanisms of varistor operation has been developed, improved understanding is needed, especially of the relation between the microstructure, the energy levels arising from it, and the electrical properties. Explanations are needed for the changes in characteristics with time and stress, and what the related structural causes are. It is conceivable that the instabilities that are seen are not related to the varistor effect but to the presence of mobile ions or other charge-carriers, and that they can be better controlled. Without better basic understanding, the possibility of achieving this improved control is much reduced.

Electrical test facilities which were adequate for characterizing SiC varistors are not sufficiently precise for evaluation of ZnO varistors. The much-reduced leakage currents, greater degree of nonlinearity, and generally more stable electrical properties of ZnO all combine to require greater accuracy of measurement than heretofore. Varistors are charac-

terized at low power levels using dc, at intermediate levels using ac, and at high power with pulsed dc. The desired measurement accuracy of 0.1 percent can be achieved only with the greatest difficulty if at all. The precise measurement of highly distorted ac currents is not possible. Even consistency of measurement in the three power ranges mentioned is hard to obtain.

Because ZnO varistors are intended to operate while energized continuously, there is much greater concern about the stability of electrical characteristics than was the case with SiC. In the absence of any significant service history, the relationship between life test results in the factory and service life is unclear and unproven. The absence of a suitable model for the causes of electrical instability only sharpens this concern.

2. Introduction

A varistor is an electrical resistor whose resistance is not constant, but is a function of some externally imposed variable. The varistors to be described in the following report have a resistance which is strongly dependent on the applied voltage, or electric field. The sense of the change is such that the resistance drops with increasing voltage.

Devices of this kind have found wide use as voltage limiters for many applications. When the applied voltage rises, the resulting decrease in the resistance of the device causes the current through it to increase much more rapidly than Ohm's law would predict; the voltage drops in the source impedances in the circuit likewise increase, and the voltage rise at the varistor location is held to a lower value than would otherwise be the case. The energy of the voltage surge is dissipated as heat in the varistor and in other resistive parts of the circuit.

There are many types of devices which are useful for voltage limiting. They include Zener diodes, spark gaps, and varistors made from SiC or carbon blocks, as well as those made with ZnO. Table 1 is a listing of the advantages and problems associated with these devices. It should be recognized that each of these kinds of voltage limiters has particular areas of application for which it excels over the others. Table 1 should not be taken to mean that any one of these devices is superior for all applications.

For transmission line service, the standard product for surge limiting (called an "arrester") is an SiC varistor in series with a spark gap. The gap is needed because the varistor has only a limited variation in its resistance. It cannot meet the simultaneous requirements that its conducting resistance be low enough for effective voltage limiting and that its standby resistance be high enough that no significant heating of the varistor occurs. The varistor is only connected to the transmission line when a voltage surge has broken down the gap.

This device thus has two principal shortcomings. First, the gap must fire, which requires a substantial overvoltage; further, the limited re-

Table 1 - Voltage Surge Limiting Devices

Device Type	Relative Strengths	Limitations
Carbon Block	Very inexpensive.	Low impedance; characteristics vary with time and temperature; rarely used except in telephone service.
Selenium	Relatively good energy absorption rating.	Large; costly; limited temperature rise; significant leakage current.
Silicon Carbide	Inexpensive; can have large energy absorption rating.	High leakage current; limited resistance change with voltage; less stable than ZnO.
Spark gap	Can handle large currents; low leakage current.	Low impedance when arcing; difficult to interrupt; costly in small sizes; breakdown voltage sensitive to environment.
Zener diode	Very sharply defined onset of limiting; low dynamic resistance; stable characteristics.	Limited power dissipation; relatively expensive.
Zinc Oxide	Inexpensive; can have large energy absorption rating; large design range; very good α; temperature insensitive.	Leakage is temperature dependent; some change of characteristics under heavy surges.

sistance range of SiC does not allow the varistor to clamp the voltage as well as one would like. Both of these factors lead to the overall result that these arresters can only hold the maximum voltage during a surge to about 1.8 times nominal at best; twice nominal is common.

3. ZnO Varistors

Small ZnO varistors have been available for several years [1]. Electrically, they have the characteristic of two back-to-back Zener diodes. That is, they limit overvoltages equally in either polarity. Physically, the small devices look like ceramic disc capacitors. Structurally, the device is a ceramic body composed of a micro-crystalline ZnO major constituent with an intergranular phase composed of a number of other oxides. These other oxides are termed "additives" and may include oxides of boron, bismuth, arsenic, antimony, silicon, cobalt, titanium, manganese, chromium, etc.

Most varistors include four or more additives in mixes which are empirically arrived at and which are proprietary. While the mixture of materials is prepared by standard ceramic manufacturing techniques using "high purity" raw materials, by semiconductor standards these are dirty products. Impurity levels in the source materials range up to 0.1 percent. Yet the finished device is a semiconductor, and it can be characterized by some of the same methods which are used for silicon devices.

The I-V characteristic of a ZnO varistor is shown in figure 1 for one polarity of applied voltage. In the nonlinear (breakdown) region, the current is given by the traditional empirical relation [2]

$$I = kV^{\alpha},$$

where α ranges typically from 25 to 60. At current densities of about 100 A/cm^2, the current begins to be limited by the series resistance of the ZnO grains, while at the other end of the characteristic, there is an excess current which has a strong temperature dependence [3].

An ideal varistor would have no series resistance region (maintain effective voltage limiting right up to its thermal limit), have minimal and stable leakage current, and a high nonlinear exponent α. Typical varistors can absorb up to 100 J/cm^3 before their thermal stability limit is reached and they must be allowed to cool.

The application of varistors of this type to high-voltage transmission lines is appealing because they should control transient overvoltages to a greater degree than presently available surge arresters can. It is intended that ZnO arresters should limit voltage surges to 1.5 times nominal. They should not need series gaps, so they must be able to stand being on line continuously without adverse effect for the normal 20-year service life of such hardware.

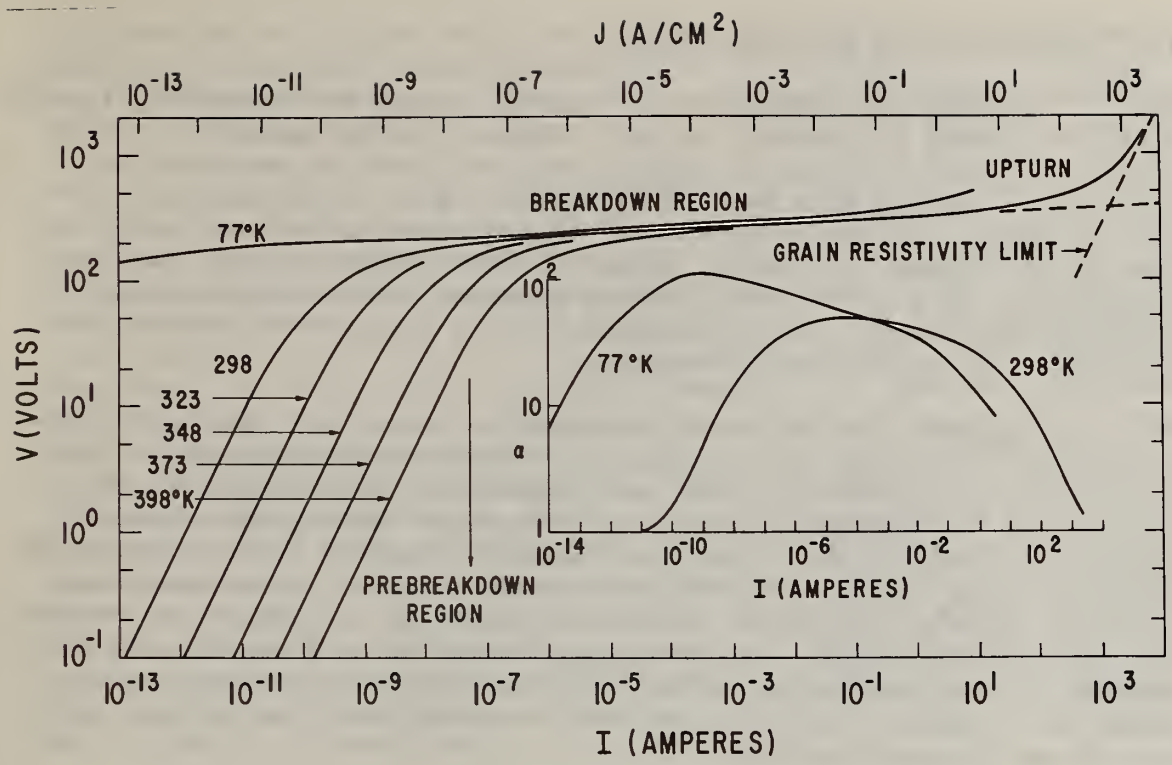

Figure 1. The current-voltage characteristics of a ZnO varistor at 77 K and for a small range of temperatures near 300 K. A simple extrapolation of the breakdown characteristic at 298 K is indicated by the dashed line. The grain resistivity limit is drawn for ρ = 3.2 $\Omega\cdot$cm. The coefficient of nonlinearity, $\alpha = d\ln I/d\ln V$ *versus* I, is shown in the inset [31].

4. Physical Properties of ZnO Varistors

The initial development of ZnO varistors was done in Japan [2-4]. Earlier Russian work on zinc oxide includes one reference to varistor action [5], but there seems to have been no further development of the topic; the Japanese work is apparently independent of the Russian [6]. Pure ZnO and ZnO ceramics with additions of beryllium oxide or magnesium oxide are linear resistors. Additions of oxides of calcium, strontium, or barium cause nonlinear resistive effects [4]. Varistor action is greatly enhanced with the addition of bismuth oxide (Bi_2O_3) [2] or cobalt oxide (Co_3O_4) [7]. The former is the more commonly used.

Understanding of the nonlinear resistance has been sought through studies of the microstructure [2,3,7-16] and of the electrical properties. The latter measurements cover the voltage drop across a single intergranular boundary [17-23]; the dielectric constant, and loss tangent, from 10^{-1} to 2 x 10^9 Hz [24-26]; and electrical responses to high pressures [27,28], light [29,30], and low temperatures [31,32]. Process variables have also been explored [33,34]. Efforts to describe the behavior of ZnO varistors in terms of accepted semiconductor theory have proceeded in parallel with the above measurements [2,17,19,21,31,35-44].

4.1 Microstructure and Composition

Detailed recipes for formulating the mix of oxides and processing it into varistors remain proprietary and will unquestionably remain so. It is likely that most of these are similar to that given by Matsuoka [3], which calls for 0.5 mol% each of Bi_2O_3, CoO, MnO, and Cr_2O_3; 1.0 mol% of Sb_2O_3; and the balance ZnO. This mixture is referred to by most later workers as typical. When fired at 1350°C for 1 h, this composition has an α of 50 and a voltage gradient of 135 V/mm. Unless otherwise specified, this formulation will be taken to be the one under discussion in the following sections.

When the ceramic body is either sectioned or broken and examined microscopically, it is seen to be composed of small crystals of ZnO in a matrix of other ingredients. The ZnO crystals range in size from about 3 to 50 μm on the average; the size is influenced both by the firing (sintering) conditions of time and temperature and by the composition of the mix. Some additives act to limit grain growth. It has been found that the voltage gradient is inversely related to the grain size because the voltage drop across each intergranular boundary is essentially independent of the formulation and of the processing conditions. Hence, there is a degree of control possible in establishing the voltage gradient of the finished varistor.

At first, it was thought that the intergranular matrix completely surrounded the ZnO grains, but later work has shown that this is not the case [9,11,15]. Ion scattering, Auger electron, and transmission electron microscopical analyses have all shown that over the larger part of the boundary between ZnO grains the thickness of the intergranular layer is at most 5 nm, if indeed there is such a layer at all. Only at three- and four-grain intersections (edges and corners) does the thickness of the intergranular matrix vary with the total amount of additives, and this matrix is electrically insulating.

In a ceramic with the composition given by Matsuoka, but with tin oxide substituted for the chromium oxide, Wong [12] has found the intergranular material to be composed of a spinel ($Zn(Zn_{4/3}Sb_{2/3})O_4$) doped with Co^{2+} and Mn^{2+} and of an oxygen-deficient pyrochlore ($Bi_2Zn_{4/3}Sb_{2/3}O_6$) similarly doped. The ZnO was found to be doped with Co^{2+}. The proportion of spinel increased with increasing firing temperature, and α decreased. The connection between these structural changes and electrical ones is not understood.

The electrical resistivity of the ZnO grains is in the vicinity of 1 Ω·cm, as measured by infrared reflectance [30], rf measurements [25], and pulsed high-current methods [25]. It does not seem to be strongly affected by composition or process variables and is always *n*-type. Whether these characteristics arise from doping with one of the additive ions (such as Co^{2+}) or from oxygen vacancies [45] is not known. Unusually strong accumulation layers (greater than 5×10^{13} electrons/cm^2) are produced on the surface of ZnO by adsorption of oxygen [46]. Since there is evidence that the intergranular boundary which is the site of

varistor action is also the site of adsorbed bismuth [11] in an unknown state of ionization or partial oxidation, it is tempting to speculate that varistor effects are in some way connected with chemisorbed material which induces a strong depletion layer in the surface regions of the ZnO.

Variations in the electrical properties of ZnO varistors are correlated with changes in the sintering conditions. From the very beginning, it has been observed that leakage currents and α are functions of both sintering temperature and the duration of firing [2-4], with α becoming very low with long firing times at high temperatures. Marked nonlinearity has been observed over a range of Bi concentrations of 60:1 [9]. Bismuth has been left out of the mix and later diffused in [3], and excellent varistors have resulted. Under reduced oxygen partial pressures during firing, the barriers disappear and the ceramic has a linear resistance [11]. Such observations, in the absence of any good understanding of how the physical arrangements of the different atomic species that are present affect the nonlinear resistance, have led to much empirical work to optimize the varistor for different applications. The kinds and proportions of additives, the preparation of the mix, and sintering conditions of time, temperature, atmosphere, and cooling rate [18] are all variables; there is a rich field of exploration for the applied alchemist.

4.2 Electrical Properties

The fact that ZnO varistors are polycrystalline bodies presents immediate difficulties in understanding their behavior. A number of parallel paths for current are available. Some of these paths traverse more grain boundaries than others; the number of boundaries has a statistical distribution. Thus, voltage measurements on the ceramic body are related to the voltage drop across the intergranular boundary somewhat indirectly.

Direct measurements of the intergranular voltage drop have been made [14,16,18,21-23,40]. The best value seems to be about 3.6 ± 0.2 V at 1 A/cm^2 at room temperature [40]. Careful probing measurements and observations by scanning electron microscopy with voltage contrast both support the belief that the voltage drop at all but the highest currents is confined to the neighborhood of the grain boundaries.* The temperature dependence of the voltage drop has not been measured on individual boundaries, since it is easier and just as accurate to measure it on a large specimen. The temperature coefficient is negative and is in the range of 2 to 5 x 10^{-4}/°C over a temperature range of -30 to 120°C [17,31,38]. Both the intergrain voltage and its temperature coefficient at a fixed value of current are essentially independent of composition and of the details of the fabrication process.

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*This conclusion is supported by work using photoexcited carriers in varistors both with and without cobalt, which changes the optical absorption behavior of the ZnO [29].

As figure 1 shows, α is not a constant for real varistors. This specimen has an α greater than 10 over a range of about 11 orders of magnitude of current at room temperature. At the low-current end of this range, the onset of pre-breakdown leakage current causes the decrease in α; as the temperature is decreased, the leakage current also drops, and high values of α are retained at lower levels of current. At high current, α is decreased because of the series resistance of the ZnO grains themselves. This resistance increases at low temperatures as carriers are frozen out. Apart from these effects of leakage current and series resistance, the magnitude of the nonlinearity coefficient is not much affected by temperature.

The leakage current has a more complex behavior. For temperatures of 0°C and higher, it has an exponential dependence on reciprocal temperature with an activation energy of 0.82 eV [38]. At lower temperatures, there is a marked change, with long-time-constant polarization currents being dominant. These currents have an activation energy of about 0.035 eV over the temperature range of -196 to 102°C [26,31]. Leakage currents increase with increasing ZnO carrier concentration [43] and have linear dependence on the applied voltage [31]. It has been possible to separate the polarization current component from the steady-state component and to show that the steady-state part has essentially the same activation energy down to temperatures at which it becomes too small ($<10^{-15}$ A) to be easily measured [26].

The current-voltage characteristic of a ZnO varistor can become displaced as a result of high-current surges having a dc component, or from long-time application of steady dc fields [31]. These effects have not been widely reported in the literature, so quantitative information is scarce. It is possible that these polarization effects are related to the low-level polarization currents described above. Several workers in the field have said privately that these effects relax with time or can be completely removed by annealing at elevated temperatures.

Dielectric constant measurements were initially made to determine the thickness of the intergranular layer on the assumption that the layer was insulating and that it was the factor which determined the dielectric constant. More recent work, described above, has established that the intergranular layer is indeed insulating, but that it is not present in the current path between grains as a layer more than at most a few nanometers in thickness. Therefore, the layer whose capacitance is measured is a depletion layer.

The real part of the dielectric constant at room temperature and at a frequency of 10 Hz is about 1500 [24,26]. This implies a depletion layer of about 100-nm thickness. There is a gradual drop in dielectric constant as the frequency is increased to 10^5 Hz, followed by a sharper decrease of about 30 percent by the time that 10^6 Hz is reached. Above that frequency, there is no change up to 2×10^8 Hz, beyond which there is a sharp resonance. The dielectric constant peaks at a value above 1600 at 1.34×10^9 Hz, for the specimen studied [25].

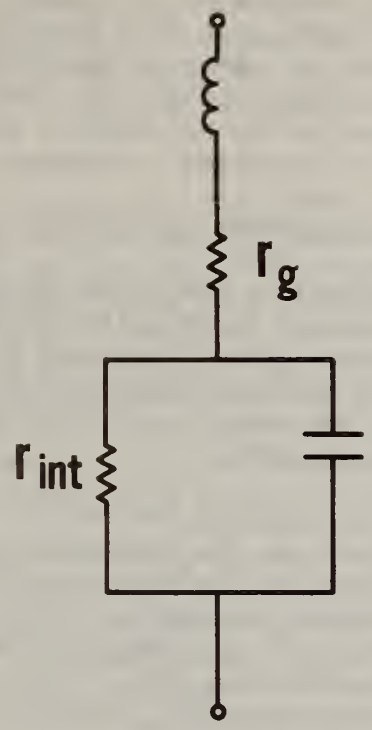

Figure 2. Equivalent circuit model for the behavior of the dielectric constant with frequency [25].

An equivalent circuit such as that in figure 2 has been used to model this behavior [25]. A pure capacitance is in parallel with a voltage-dependent resistor, r_{int}; in series with this combination is the ZnO grain resistance r_g and an inductance which is an intrinsic part of the ceramic body and not associated with the connecting leads. The observed resonance is the series resonance of the capacitance and the inductance. The parallel resistance has a frequency dependence which is almost 1/f at low temperatures (-196°C) and which has a small superimposed dispersion at higher temperatures.

At frequencies above 10^7 Hz, the parallel resistance is sufficiently low that the series resistance dominates. The ZnO grain resistivity deduced from this measurement agrees with that found by infrared reflectance [25,30] and is less than the value found by high-current pulse measurements. It is postulated that the added resistance in the latter case results from the fact that not all of the interface area between grains is equally available for passing current, but there is a spreading resistance component. If this is correct, then only about 10 percent of the physical contact area between grains is involved in the current path.

The dissipation factor is typically low, about 0.03 or less, except for one broad peak which rises to 0.1 at 2×10^5 Hz at room temperature. The frequency at which the peak occurs depends on temperature in a way consistent with an activation energy of 0.36 eV [24]. Levinson and

Philipp, whose work on the dielectric constant and dissipation factor is cited above, have concluded that this behavior is consistent with that of many other dielectrics. A number of these are cited in reference [24]; all of them possess a highly disordered structure. It is not clear whether the dissipation in the varistor is related to disorder in the depletion region or to an unrelated, different mechanism.

5. Models of Varistor Behavior

Most of the work described in the foregoing has been done to gather information which can be used to identify the mechanisms by which the nonlinear resistance arises. There have been a number of models proposed, but most of these have not been successful in explaining all of the experimental evidence. The most satisfactory theory at present is based on a double Schottky barrier model.

This model was first proposed by Levine [36], who was able to account for the observed dc capacitance, the departure of the current from a power law at low voltages, and for the magnitude of the nonlinear exponent and its modest temperature dependence. This approach has been further developed [39-44]; the most comprehensive treatment of the theory of ZnO varistors is given in reference [43]. This reference also contains a review of other, previously proposed, theories and shows why they have been found unsatisfactory or incomplete.

The model is based on well-understood semiconductor theory and explains the following properties without the use of *ad hoc* constants:

- the value of the intergrain breakdown voltage and its insensitivity to temperature and ZnO donor density changes,
- the current-voltage characteristic of a single intergranular barrier over 13 orders of magnitude in current density,*
- the value of the nonlinear exponent α, and the facts that the value is larger and that the peak value moves to lower current densities at low temperatures, and
- the variation of capacitance with voltage.

With regard to the last item, the theory predicts that as the breakdown region is reached, the capacitance should rise sharply. This had not been previously reported in the literature, probably because the measurement of capacitance in the presence of large currents is difficult. Such behavior in agreement with the predictions of the model has since been found [43,44].

The model has other features which can be tested experimentally. It gives quantitative relations between the leakage current and the donor

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*The "upturn" region at high current densities is not included in the model.

densities in the ZnO grains and similar relationships between α and the ZnO doping. The resistivity of the ZnO can be measured by at least two independent means, by infrared reflectance, and by microwave absorption, which have been shown to agree reasonably well. These relationships have not been reported in the literature, but the means to do such a study are available.

There are some important areas which the model does not address, nor was it intended to. It makes no statement regarding the structural details of the interface between the grains, which is assumed only to be thin and to have a high trap density. There is no theoretical understanding of the relationships between the electrical properties of the varistor and the structural details of the ceramic. One cannot predict the effect of a change in composition or processing on the electrical behavior in sufficient detail to be useful. Thus, any potential improvements in the characteristics of a varistor which are consistent with the predictions of the model (and thus likely) must still be obtained empirically.

This lack of understanding is of particular concern with regard to the leakage current. As will be seen later, leakage currents and their changes with time and electrical stress history are important in lightning arrester service. The present model tells little about the sources of the long-term polarization currents [26] and whether or not these are related to other observed polarization effects. One would like to know if these are the result of trapped charges or of ionic movements; the approaches to reducing these effects are likely to be different depending on their source.

It should be pointed out that the development of a complete theory of how ZnO varistors work and the details, at an atomic level, of how the structure of the ceramic is related to its function is a very difficult problem. The present model and its underlying theory are drawn extensively from work on much simpler structures and materials: the monocrystalline, high-purity elemental semiconductors such as silicon and germanium. The complications introduced by the polycrystalline nature of ZnO varistors are very great, and one cannot work with simpler structures because the nonlinear resistance is a property of the intergranular interface. One cannot expect to draw on the supply of knowledge derived from simpler materials indefinitely, since intergranular effects are not dealt with there.

One particularly important topic on which more theoretical and experimental knowledge is essential is the subject of interface states in the intergranular region. The present model, given this kind of information, could be developed further to give more accurate predictions of performance of varistors. If, in addition, the structural origins of these states were known, then the materials and process work needed to design varistors with improved properties would be more likely to produce the desired results than would be the case if only the present empirical methods were available.

6. Application of ZnO Varistors

The original applications envisioned for ZnO varistors were as surge arresters in low-energy circuits, particularly as protective devices for semiconductor components which are sensitive to overvoltages [1]. Presumably, this choice was made for the reasons that a large number of potential points of application already existed, the transition to solid-state circuits in many large-volume applications such as television was occurring, and the varistors could be made in volume and sorted out by their electrical properties later (much as transistors are). The latter is attractive for a product which is new and for which one is not sure of the degree of control of its characteristics at the time of manufacture.

At the same time, there was a growing awareness of the prevalence of voltage surges on low-voltage lines [47-49]. Residential data show a wide range of such surges, with one home experiencing a 2-kV, one-cycle surge on the average 0.4 times an hour on a nominal 120-V circuit. The surges originate in switching operations inside the home, out of control of the electric utility company, as well as from lightning and line switching on the utility's circuits. The energy content of these surges is not well known since the source impedance is not controlled, nor was it measured in these studies.

With the further development of the varistor and the improved understanding of its technology, a serious effort was begun to apply ZnO varistors to higher power circuits. There are several differences between this application and those mentioned earlier. Obviously, the surge energy levels are far greater. The varistor must be designed and made to meet a well-defined specification, and it will displace an existing product (SiC varistors).

One such design is described in the literature [50]. While this reference contains few specifics about the physical size and other mechanical features, there are many useful comparisons with SiC varistors and arresters made with them. Notwithstanding all of the problems described above, ZnO is a much better varistor material than SiC. The latter has an α which is an order of magnitude lower; a comparison of the I-V characteristics is given in figure 3. The leakage current of SiC is larger and less stable with time, temperature, and electrical stress. SiC has a temperature coefficient of resistance of -0.24%/°C, compared with -0.03%/°C for ZnO. At very high current densities, the voltage upturn for ZnO is much less than for SiC.

Because of these characteristics of SiC, arresters using this material must have a series spark gap. A SiC varistor which has a sufficiently low resistance to be an effective surge limiter has too low a resistance at nominal circuit voltages to be left on line continuously; the standby power dissipation is too great. The spark gap has a special design characteristic which causes it to have a current-limiting action. When an overvoltage surge occurs, the gap fires, and the varistor is connected to the circuit.

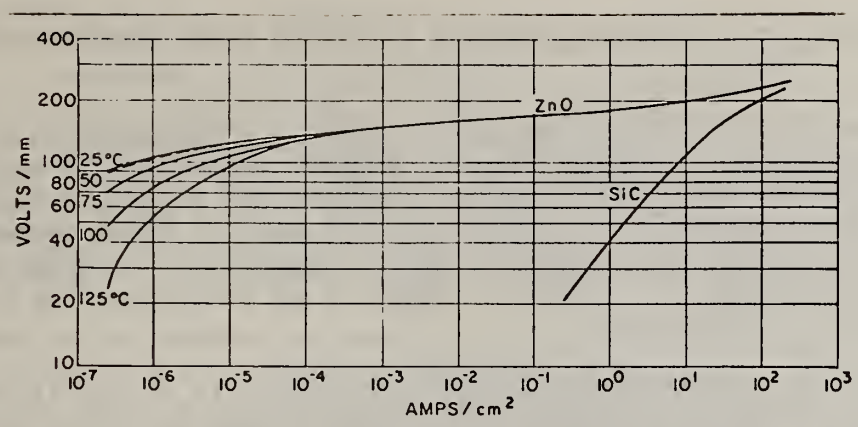

Figure 3. Normalized volt-ampere characteristic of zinc oxide and silicon carbide valve elements [50].

The current-limiting action of the gap does not develop until a few hundred microseconds have passed. During that time, the varistor draws too much current because the nonlinearity of SiC is insufficient and because the gap has not developed its current-limiting action. In cases where the source impedance of the circuit is particularly low (in the vicinity of capacitor banks, for example), the gap may not develop any current-limiting effect and can be damaged by the high current. The spark gap assembly has a number of components which make it costly, and it is sensitive to contamination which can change its sparkover voltage.

For these reasons, it would be desirable to have a surge arrester which did not require any spark gaps. In such an arrester, the varistor is connected to the circuit at all times and must be able to maintain its characteristics, especially in the leakage current region, over a long period without significant change. This is a very important difference; in spite of the large improvements in properties of ZnO varistors in comparison with SiC ones, it is not a trivial task to apply ZnO to this application. The work reported [50] is the result of over five years' effort, and at the time of its publication, only one field installation, of an experimental nature, was reported to have been made.

6.1 Measurement Problems in ZnO Varistor Technology

In the discussion which follows, much of the subject matter was learned in visits to the companies that are developing ZnO for surge arrester service. No association of a given topic or problem with a particular firm will be made. These subjects are not described in the literature, due to the fact that they are unsolved problems or are felt to have a proprietary aspect. The discussion will follow the general sequence for manufacture and evaluation of the varistor.

The raw materials, such as ZnO, Bi_2O_3, and the like, in laboratory work are usually of reagent grade. It is desirable to keep the uncontrolled variables to a minimum, and thus one tries to use the highest purity source materials. In production, cost is important. Lesser quality grades of materials cost less, and there is great economic value in

knowing what specific impurities are likely to cause problems and which are not.

To this end, most companies are using analytical methods such as emission spectrography, atomic absorption, and similar techniques to analyze the input materials. One then tries to correlate the results with the properties of the varistor. The sensitivity of most of these methods is in the neighborhood of one part per million, depending to a great extent on the specific element in question. There is no assurance that this level of detection is sufficient.

Furthermore, to calibrate the analytical method, it is usually necessary to prepare a reference standard of the matrix material, such as ZnO, with known amounts of the probable impurities. A sample of this standard is analyzed at the same time or just before the unknown specimen is tested, and a comparison of the results allows removal of most sources of error. Unless they have been made in-house, standards are not available for this calibration. Accurate assay of the standard requires evaluation by an independent means with a greater detection sensitivity than the method that is normally used for analysis. Such a means is not usually at hand, or it would be used for the evaluation of the specimen. That fact, and the considerable time and skill required for preparing and assaying of standards, usually means that routine analyses of the materials used to make varistors are not done with great accuracy.

Undesired, and usually uncontrolled, impurities can enter the process from any of the raw materials, during ball-milling and other blending operations, and from solvents or binder fluids used in preparing pressed bodies for firing in the kiln. An approach to control of these impurities by purely analytical methods is both time-consuming and troubled by the inaccuracies mentioned above. Most firms instead use a comparative method of control, in which a supply of known good materials (as determined empirically) is set aside to be used as controls in the evaluation of newly acquired supplies. The new material can thus be qualified for use if it produces varistors as good as those made from the known control material.

Little new information is learned from this way of operating. With care, one can be protected from serious yield losses if a lot of raw material is not suitable because this method of testing will usually uncover that fact early. The specific reason why a bad lot is bad is not learned, and the opportunity to improve the capabilities of the suppliers of raw materials in producing better materials is lost.

There have been cases involving additives in which all of the additive materials independently passed such a comparative qualification test but in combination did not produce good varistors. Each of these instances was eventually found to involve a pair of the additive materials. Either member would qualify singly, but they would fail in combination. The real cause for this problem, in terms of kinds and amounts of undesired impurities or in any other sense, is not known.

Another problem with the empirical approach to control is related to the decision of what is "good" when the varistors are evaluated. Not all problems in varistors show up immediately, but they appear after some time on life test. In practice, there is only a limited time for life testing when materials acceptance questions must be answered. If material is to be rejected, only a limited time is available before the vendor will refuse to accept its return for credit; decisions must be made sooner than that, whether or not life testing has provided the information needed to make the decision to accept or reject the material.

In one way, it is possible to combine the empirical and analytical approaches to control to yield some objective information. If a lot of material fails, it can be analyzed in comparison with the control material. An absolute calibration may be lacking, but at least some relative, semiquantitative information is obtained about the impurities present in the two specimens.

After the varistor has been fired in a kiln and transformed into a ceramic, evaluations are mostly electrical. However, measurements of grain size and other gross structural features are done with both optical and scanning electron microscopy, and samples are scanned ultrasonically for the presence of cracks or voids, which will affect the electrical and thermal properties of the varistor. There do not seem to be any serious measurement problems in these nonelectrical areas.

There are, however, difficulties with the electrical measurements. Most companies measure leakage currents by dc methods. The currents are small enough that no heating of any consequence occurs during the test, an important consideration in this current range because of the strong temperature dependence of the leakage. Pulsed dc methods are used up to the maximum currents of 10 kA or so. Some firms use sine-wave ac tests at the lower end of the nonlinear range. Most* do life tests under ac excitation.

Because of the very wide range of currents which must be measured, from microamperes to kiloamperes, and because of the corresponding range of power required from the test equipment, no single piece of equipment can be used over the whole range. This is further complicated by the fact that the tests use ac, dc, and pulse methods. Consistency of calibration is a problem, with most firms trying to achieve 0.1-percent accuracy. This is felt to be needed because the value of the nonlinear exponent is a sensitive measure of certain processing parameters. High accuracy is required in the voltage measurements to allow the exponent to be calculated with useful precision.

Correlation of measurements over the whole voltage range, using the various excitation methods mentioned above, is made more difficult by the

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*Possibly all do, but confirmation of this is lacking from one company.

fact that the varistors do not respond in the same way to dc as they do to ac. Polarization currents which are apparent in dc tests but which have time constants of the order of and longer than a half-period of the 60 Hz ac (8.3 ms) do not show up in ac measurements. Furthermore, in ac measurements most of the current at low levels is capacitive; the in-phase (dissipative) component is small and difficult to measure accurately. This is just the current component which relates to the dc leakage measurements. In ac tests at higher levels, the current has a marked peak at the crest of the voltage. This distorted current waveform can have a crest factor which is larger than the rating of rms-to-dc converters used in the measurement and which leads to measurement errors of unknown amounts.

Measurements of 0.1-percent accuracy cannot be done oscillographically. Digital instruments are required. These instruments respond to transients and there is concern that correct steady-state measurements are not obtained. Most digital voltmeters have a sample-and-hold circuit at the input which follows the signal until the measurement command is received. At that time, the value of the signal is held and measured. If the value which is held is a transient one, the measurement will be in error. Transients are particularly troublesome when pulse measurements are being made, because at high currents very large rates of change exist and appreciable voltages are developed across small inductances.

High-power measurements are usually made with an 8 by 20 wave, that is, one with a rise time of 8 μs and which decays to half of the peak value in 20 μs. In a linear resistor, a 10-kA pulse of this form would have a rate of rise of about 1.25×10^3 A/μs, but in such nonlinear resistors as ZnO varistors, the application of an 8 by 20 voltage pulse of appropriate magnitude to develop 10 kA of current results in rates of current rise much larger than that. This exacerbates the transient problem.

Some workers have tried using filters to avoid having the measurement instruments respond to transients, but there is concern that the filters may introduce other errors. There is no industry standard which deals with this problem.

Other difficulties exist in connection with life testing. The application of ZnO to high-power transmission lines is new and differs significantly from previous practice. To gain acceptance by the electric utilities, manufacturers of arresters using ZnO must be able to give assurance that the product will serve reliably for 20 years or more. Accelerated life tests are necessary, since 20 years are not available for testing.

The only feasible acceleration factor is temperature. Electrical overstress is not feasible, since the current increases so rapidly with voltage; if this approach were tried, the temperature would increase markedly as well, and one would have the difficult problem of separating the effects of the thermal and the electrical acceleration factors from one another. ZnO varistors have been observed to develop asymmetrical electrical characteristics with prolonged dc stress or after large surges, with the effects being reversible after annealing at moderate tempera-

tures. There is some concern that life testing at elevated temperatures may not be entirely representative of service applications on a compressed time scale, and that some annealing of possible instabilities or of changes in characteristics may occur during the test.

This question is reminiscent of those raised in the early days of the application of high-power silicon devices to similar service. There is only one way in which such issues can be resolved without question. A history of performance must be developed which can be compared with the results of accelerated tests to show to what degree the latter can be depended upon as indicators of service life. Carefully chosen pilot installations, with extra instrumentation to record the events which occur as a function of time, and a conservative design approach to minimize the adverse effects which can result from inexperience, are helpful in gaining the needed experience without undue risk. This question will not be solved overnight.

There has been some difficulty encountered in obtaining stable, low-impedance ac sources for life testing. The source must be well regulated and have few, if any, voltage surges. One firm has observed discontinuous changes in the characteristics of varistors on life test when the test is interrupted either accidentally or purposely. The cause of the changes is not known.

Moreover, there are no generally accepted definitions for "stability" of ZnO varistors, no established levels of performance with regard to stability, and no real understanding of the causes for lack of stability. If a varistor exhibits a change in characteristics in one hour, it is regarded as unstable, yet one firm wishes for a test that would tell in a few seconds whether a varistor is stable or not. Work is needed to develop suitable criteria and tests for stability beyond the requirements of any one company. Both manufacturers and users of varistors need to be involved in that work.

Another concept in need of definition and understanding is that of wear-out. Small varistors are rated to absorb given amounts of energy and remain within their guaranteed specifications. The amount of energy is not a constant, but depends on the magnitude of the largest surges which are applied. It is not clear how this characteristic will be defined and specified for larger varistors. The mechanism of wear-out is not understood, nor whether it is related to polarization characteristics. It has also been observed that when a varistor is first energized on ac, the current is higher for the first few cycles and then settles to a value about half of the original one. This effect and its relation to those just mentioned is not understood.

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8. REFERENCES

1. Harnden, J. D., Jr., Martzloff, F. D., Morris, W. G., and Golden, F. G., Metal-Oxide Varistor: A New Way to Suppress Transients, *Electronics* 45 (21), 91-95 (1972).

2. Matsuoka, M., Masuyama, T., and Iida, Y., Nonlinear Electrical Properties of Zinc Oxide Ceramics, *J. Jap. Soc. Appl. Phys.* 39 (suppl.), 94-101 (1970).

3. Matsuoka, M., Nonohmic Properties of Zinc Oxide Ceramics, *Jap. J. Appl. Phys.* 10, 736-746 (1971).

4. Matusoka, M., Masuyama, T., and Iida, Y., Voltage Nonlinearity of Zinc Oxide Ceramics Doped with Alkali Earth Metal Oxide, *Jap. J. Appl. Phys.* 8, 1275-1276 (1969).

5. Kosman, M. S., and Pettsol'd, E. G., Possibility of Preparing Symmetrical Varistors from Zinc Oxide Containing an Addition of Bismuth Oxide, *Uch. Zap. Leningr. Gos. Ped. Inst. im. A. I. Gertsen* 207, 191-197 (1961).

6. Morris, W. G., private communication.

7. Mukae, K., Tsuda, K., and Nagasawa, I., Non-Ohmic Properties of ZnO-Rare Earth Metal Oxide-Co_3O_4 Ceramics, *Jap. J. Appl. Phys.* 16, 1361-1368 (1977).

8. Morris, W. G., Electrical Properties of ZnO-Bi_2O_3 Ceramics, *J. Am. Ceram. Soc.* 56, 360-364 (1973).

9. Morris, W. G., and Cahn, J. W., Adsorption and Microphases at Grain Boundaries in Non-Ohmic Zinc Oxide Ceramics Containing Bismuth Oxide, *Grain Boundaries in Engineering Materials*, J. L. Walter, J. H. Westbrook, and D. A. Woodford, Eds., Proc. 4th Bolton Landing Conf.,

Lake George, New York, June 9-12, 1974 (Claitor's Publishing Division, Baton Rouge, La.), pp. 223-233.

10. Wong, J., Nature of Intergranular Phase in Nonohmic ZnO Ceramics Containing 0.5 Mol% Bi_2O_3, *J. Am. Ceram. Soc.* 57, 357-359 (1974).

11. Morris, W. G., Physical Properties of the Electrical Barriers in Varistors, *J. Vac. Sci. Technol.* 13, 926-931 (1976).

12. Wong, J., Microstructure and Phase Transformation in a Highly Non-Ohmic Metal Oxide Varistor Ceramic, *J. Appl. Phys.* 46, 1653-1659 (1975).

13. Wong, J., Rao, P., and Koch, E. F., Nature of an Intergranular Thin-Film Phase in a Highly Non-Ohmic Metal Oxide Varistor, *J. Appl. Phys.* 46, 1827-1830 (1975).

14. Wong, J., Barrier Voltage Measurement in Metal Oxide Varistors, *J. Appl. Phys.* 47, 4971-4974 (1976).

15. Clarke, D. R., The Microstructural Location of the Intergranular Metal-Oxide Phase in Zinc Oxide Varistor, *J. Appl. Phys.* 49, 2407-2411 (1978).

16. Krivanek, O. L., Williams, P., and Lin, Y.-C., Direct Observation of Voltage Barriers in ZnO Varistors, *Appl. Phys. Letters* 34, 805-806 (1979).

17. Levinson, L. M., and Philipp, H. R., Metal Oxide Varistor — A Multijunction Thin-Film Device, *Appl. Phys. Letters* 24, 75-76 (1974).

18. Einzinger, R., Mikrokontakt-Messungen an ZnO-Varistoren, *Ber. Dt. Keram. Ges.* 52, 244-246 (1975).

19. Einzinger, R., Metal Oxide Varistor Action — A Homojunction Breakdown Mechanism, *Appl. Surface Sci.* 1, 329-340 (1978).

20. Lou, L. F., Electrical Properties of ZnO-Bi_2O_3 Junction, *153rd Meeting of the Electrochemical Society, Extended Abstracts* 78-1, Seattle, Washington, May 21-26, 1978, pp. 308-309.

21. Mahan, G. D., Levinson, L. M., and Philipp, H. R., Single Grain Junction Studies of ZnO Varistors — Theory and Experiment, *Appl. Phys. Letters* 33, 830-832 (1978).

22. van Kemenade, J. T. C., and Eynthoven, R. K., Direct Determination of Barrier Voltage in ZnO Varistors, *Ber. Dt. Keram. Ges.* 55, 330 (1978).

23. van Kemenade, J. T. C., and Eijnthoven, R. K., Direct Determination of Barrier Voltage in ZnO Varistors, *J. Appl. Phys.* 50, 938-941 (1979).

24. Levinson, L. M., and Philipp, H. R., ac Properties of Metal-Oxide Varistors, *J. Appl. Phys.* 47, 1117-1122 (1976).

25. Levinson, L. M., and Philipp, H. R., High-Frequency and High-Current Studies of Metal Oxide Varistors, *J. Appl. Phys.* 47, 3116-3121 (1976).

26. Philipp, H. R., and Levinson, L. M., Long-time Polarization Currents in Metal-Oxide Varistors, *J. Appl. Phys.* 47, 3177-3181 (1976).

27. Wong, J., and Bundy, F. P., Pressure Effects on Metal Oxide Varistors, *Appl. Phys. Letters* 29, 49-50 (1976).

28. Gupta, T. K., Mathur, M. P., and Carlson, W. G., Effect of Externally Applied Pressure on Zinc Oxide Varistors, *J. Electron. Mat.* 6, 483-497 (1977).

29. Philipp, H. R., and Levinson, L. M., Tunneling of Photoexcited Carriers in Metal Oxide Varistors, *J. Appl. Phys.* 46, 3206-3207 (1975).

30. Philipp, H. R., and Levinson, L. M., Optical Method for Determining the Grain Resistivity in ZnO-Based Ceramic Varistors, *J. Appl. Phys.* 47, 1112-1116 (1976).

31. Philipp, H. R., and Levinson, L. M., Low-Temperature Electrical Studies on Metal-Oxide Varistors — A Clue to Conduction Mechanisms, *J. Appl. Phys.* 48, 1621-1627 (1977).

32. Levinson, L. M., and Philipp, H. R., Behaviour of ZnO Varistors at Low Temperature, *Ber. Dt. Keram. Ges.* 55, 331 (1978).

33. van Kemenade, J. T. C., and Eijnthoven, R. K., Sintern von ZnO für spannungsabhängige Widerstände, *Ber. Dt. Keram. Ges.* 52, 243 (1975).

34. Einzinger, R., Dotierungseffekte in Metalloxid-Varistoren, *Ber. Dt. Keram. Ges.* 55, 329 (1978).

35. Klein, H. P., and Strässler, S., Ein einfaches Modell fur einen Zinkoxid-Varistor, *Ber. Dt. Keram. Ges.* 52, 243 (1975).

36. Levine, J. D., Theory of Varistor Electronic Properties, *CRC Critical Rev. Solid State Phys.* 5, 597-608 (1975).

37. Levinson, L. M., and Philipp, H. R., Conduction Mechanisms in Metal Oxide Varistors, *J. Solid State Chem.* 12, 292 (1975).

38. Levinson, L. M., and Philipp, H. R., The Physics of Metal Oxide Varistors, *J. Appl. Phys.* 46, 1332-1341 (1975).

39. Bernasconi, J., Strässler, S., Knecht, B., Klein, H. P., and Menth, A., Zinc Oxide Based Varistors: A Possible Mechanism, *Solid State Commun.* 21, 867-870 (1977).

40. Bernasconi, J., Klein, H. P., Knecht, B., and Strässler, S., Investigation of Various Models for Metal Oxide Varistors. *J. Electron. Mat.* 5, 473-495 (1976).

41. Emtage, P. R., The Physics of Zinc Oxide Varistors, *J. Appl. Phys.* 48, 4372-4384 (1977).

42. Knecht, B., and Klein, H.-P., Preparation and Properties of ZnO Varistors, *Ber. Dt. Keram. Ges.* 55, 326-328 (1978).

43. Mahan, G. D., Levinson, L. M., and Philipp, H. R., Theory of Conduction in ZnO Varistors, *J. Appl. Phys.* 50, 2799-2812 (1979).

44. Hower, P. L., and Gupta, T. K., A Barrier Model for ZnO Varistors, *J. Appl. Phys.* 50, 4847-4855 (1979).

45. Hausmann, A., and Utsch, B., Sauerstofflücken als Donatoren in Zinkoxid, *Z. Phys.* B21, 217-220 (1975).

46. Eger, D., Goldstein, Y., and Many, A., Oxygen Chemisorption and Photodesorption Processes on ZnO Surfaces, *RCA Rev.* 36, 508-530 (1975).

47. Levinson, L. M., and Philipp, H. R., ZnO Varistors for Transient Protection, *IEEE Trans. Parts, Hybrids, and Packaging* PHP-13, 338-343 (1977).

49. Martzloff, F. D., and Hahn, G. J., Surge Voltages in Residential and Industrial Power Circuits, *IEEE Trans. Power App. Sys.* PAS-89, 1049-1056 (1970).

49. Anon., Bibliography on Surge Voltages in AC Power Circuits Rated 600 Volts and Less, *IEEE Trans. Power App. Sys.* PAS-89, 1056-1061 (1970).

50. Sakshaug, E. C., Kresge, J. S., and Miske, S. A., Jr., A New Concept in Station Arrester Design, *IEEE Trans. Power App. Sys.* PAS-96, 647-656 (1977).

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The application of zinc oxide (ZnO) varistors to high-power surge arresters for electrical transmission lines is considered, with particular attention to the special measurement problems posed by the application and by the unique properties of these varistors. The development of ZnO varistors and the present theory of ZnO varistor action are discussed. Consideration is given to the need for further elaboration of the theory.

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