PHYSICS OF ZINC-OXIDE CRYOVARISTORS IN HIGH POWER SWITCHING APPLICATIONS

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Abstract

High power switching converters, high current opening switches, and other pulse mode operating devices often store energy in unwanted forms such as voltage spikes or residual energy stored in an inductor or capacitor. Usually, these problems are solved by simple transient energy absorbing (transorb) devices like inductive-capacitive suppression networks, selinium thyrectors, or ceramic metal oxide varistors. Transorb devices either dissipate the excess energy as heat or return the energy to the circuit by resonance. Dissipative transorb devices must tolerate and rapidly remove the heat added when operating. Recent work at CeramPhysics and Ohio State University has shown that a new ceramic metal oxide varistor (ZnO cryovaristor) has a high thermal conductivity and enthalpy at liquid nitrogen temperatures (77 K), yet, unlike other varistor material, retains the characteristic back to back Zener diode I-V relationship at 80 K. Measurements show that the thermal conductivity of the new cryovaristor has a maximum value of 0.65 W/cm/K at 80 K and a value of 0.24 W/cm/K at 320 K. The enthalpy of ZnO ceramic was determined to be 1186 J/cm^3 at 80 K, with an upper adiabatic limit of 1215 J/cm^3. Computational analysis shows that a variable-range-hopping model can explain the small temperature dependence of the prebreakdown conductivity.

Introduction

Zinc-oxide varistors have been used as shunt overvoltage and series overcurrent protection devices because of their ability to absorb large energy transients. The ZnO varistor was developed in Japan in 1969[1] and has been available in the United States since 1972[2]. ZnO varistors are use commercially in applications ranging from silicon-controled rectifier (SCR) voltage suppressors to lighting arrestors for utility power systems. Some of the more exotic applications reported in the open literature include a high current pulse LRC circuit, where the R is a non-linear resistor (varistor)[3], and as a nuclear electromagnetic pulse (EMP) suppressor[4].

The ZnO varistor is simply a non-linear resistor produced by sintering ZnO and using additives such as Bi, Co, Pr, Mn pressed together to form a device which has an I-V curve similar to two back-to-back Zener diodes. The I-V relation of a varistor is given by the equation,

$$I = K V^{a} \tag{1}$$

where K = material constant
V = voltage rating
a = slope of the I-V curve defined by,

$$a = d(\ln(I))/d(\ln(V)) \tag{2}$$

The value of the I-V slope constant depends on material properties, but is typically 20 to 40 at room temperature.

The temperature dependence of the I-V curve for commercially available ZnO varistors was studied by Philipp and Levinson in 1977[5} and 1978[6]. The ZnO demonstrated a characteristic Zener diode behavior at 320 K, but also demonstrated a flatten I-V curve at 77 K. Philipp and Levinson concluded that a tunneling process best described the conduction process at breakdown. Gupta developed a new composite of ZnO ceramic varistor and proposed that a defect model could explain the nonlinear behavior of the new composite material. Gupta and Lawless in 1986[7] reported on the thermal properties of pure ZnO and the new composite ceramic ZnO varistor at cryogenic temperatures between 1.7-25 K. Gupta and Lawless concluded that the specific heat characteristics of varistor ZnO was the same as pure ZnO.

The electrical breakdown field strength of ZnO varistors can vary between 1 to 3 kV/cm, and current densities range from 10^{-4} to 10^{2} A/cm^{3} in the breakdown region. Usually a varistor is viewed as an N-type semiconductor with high resistivity boundaries separating the semiconducting ZnO grains. Estimates of the resistivities of the grains and the grain boundaries are about 1 and 10^{12} ohms-cm, respectively. The N-type ZnO grains deplete the boundary region of electrons, establishing a voltage drop across the grain boundary when an external voltage is applied. This barrier voltage of the order 2 to 4 V per grain boundary. The unusual electrical properties of the ZnO varistor arise from the barriers at the heavily doped grain boundaries. The cryogenic studies of Philipp and Levinson measured current densities of ZnO at 77 K as low as 10^{-13} A/cm^{2} in the breakdown regions, concluding essentially that no insulating prebreakdown region existed.

Cryovaristor Behavior

Recently, W. N. Lawless and C. F. Clark of CeramPhysics, Westerville, Ohio, and B. R. Patton and F. S. Kahn of Ohio State University, Columbus, Ohio performed experimental and theorectical work, sponsored by the U. S. Air Force, to measure and understand the electrical and thermal properties of ZnO varistors at cryogenic temperatures. The material they selected was the composite developed by T. K. Gupta.

CeramPhysics and Ohio State discovered the varistor material fabricated by Gupta displays a markedly different behavior at cryogenic temperatures compared to conventional varistors. The electrical properties reveal an extended switching plateau with a pre-breakdown region which is not activated and an I-V curve which shows only a small dependence on temperature in contrast with the findings of Philipp and Levinson. The resistivity in the pre-breakdown region increases as the temperature decreases. The specific heat of the cryovaristor has many degrees of freedom as compared to pure ZnO, while the thermal conductivity is boundary limited by the grain size at low temperatures. In addition the non-linear behavior of this varistor is independent of a magnetic field up to 100 kG.

Electrical Properties Of Cryovaristors

The cryovaristor, in the highly conductive region of the I-V curve, appears to perform near the percolation threshold for random three dimensional composite systems, that is, the interface material is on the verge of forming a connected network througout the material. In fact, the cryovaristor must be fabricated close to the percolation transistion in order that the unique properties may be created. The ZnO varistor is composed of three distinct regions: the interface region consisting of high resistivity oxides, the bulk ZnO grain, and the depletion region approximately 300 A thick on the surface of the ZnO grain.

The conductivity of the depletion region is extremely voltage dependent and the resistivity of the barrier changes from a high state at low voltage to a conductive state above breakdown voltage. In addition, the depletion region coats the ZnO material so that the components have a high correlation. A two-component composite was fabricated to mimic the behavior of the three-component composite at a simpler level. One experimental condition was at low voltage, low current when the conduction takes place only by leakage current through the interface material, in which case, the depletion barriers are well below their threshold voltage and act as insulators around the ZnO grains. The insulating barriers seperate the highly conductive ZnO grains, so that the composite conducts through the interface material as if the interface material were filled with voids instead of ZnO grains.

The non-linear I-V characteristic may be calculated using effective medium theory. When the voltage drop across the barrier between ZnO grains is below the breakdown threshold for conduction through the barrier, the concentration of ZnO is too low to permit percolation conduction through the ZnO grains. However, when the voltage is increased above threshold, the depletion region becomes conductive. The net effect is to essentially expand the size of the ZnO grains. Since the material is very close to the percolation threshold as a function the compositional fraction of ZnO, a small change in the effective fraction of the conductive material (ZnO) can have an enormous effect on the conductivity of the composite material.

The temperature dependance of the electrical properties of the cryovaristor deviates from the generally accepted model of varistors. Measurements show that the resistivity in the pre-breakdown region of the cryovaristor increases weakly as the temperature is decreased, which contrast with existing varistors that exponentially vary in resistivity with decreasing temperature.

The new theory proposes that cryovaristors differ from ordinary varistors in the electrical properties that arise from the ZnO grain boundaries. The electronic states in the grain boundary in ordinary varistors are considered localized states. The localized states arise either from the insulating interface material or from the material being below the percolation threshold, where the interface material consists of finite regions with limited conduction. Electrons in the grain boundaries of the cryovarsistor are able to move and the composite exists in a state just above the percolation threshold. Conduction in the prebreakdown region may take place entirely within the grain boundary region, hindering activation over a barrier, so that conduction is not exponentially activated. The grain boundary material has a characteristic ohmic conductance in the pre-breakdown region of the I-V curve.

The weak increase in resistivity with decreasing temperature in the grain boundary material is best explained by Mott's variable-range hopping theory. According to Mott's theory, disorder produces random energy level sites on non-extended states and electrons contribute to conduction by hopping from site to site. An electron can hop to another site by tunneling to the energy level of that site, with the tunneling probability depending on the overlap of the wave functions belonging to the two sites and decreasing exponentially as the distance between sites, r, increases. A hop has to satisfy energy conservation, thus an electron can only hop to another site if the energy difference between two sites is within the thermal energy an electron can acquire. The probability of finding an energetically favorable state increases if the electron can sample many states and thus increases as r increases. The value of conductivity can be found by maximizing the hopping probability with respect to r and solving for the conductivity.

The conductivity is given by,

$$\sigma/\sigma_0 = \exp[-(T_0/T)^{1/4}] \quad (3)$$

where σ = conductivity

T = temperature

σ_0 and T_0 are material constants

The values of σ_0 determined from experimental data is given by σ_0 = 2.697×10^{-9}/ohm-cm at T_0 = 1.57 K.

Thermal Properties Of Cryovaristors

The specific heat data reported by CeramPhysics on the cryovaristor indicate the Debye temperature is Θ = 400 K as T -> 0 and increases to Θ = 540 K at T = 300 K. The specific heat below 10 K and above 100 K is dominated by defect modes. The density of modes at 100 K is about $6\times10^{23}/cm^{-3}$ and the energy of defect formation is 0.12 eV. By contrast, below 10 K, the dominant modes have densities of $10^{18}/cm^3$ and energies of defect formation between 0.7 to 3.5 meV. Over the entire range 1.7 to 300 K, the specific heat is understandable in terms of simple phonon models such as those of Debye and Schottky, where the specific heat (C) is given by,

$$C = C_D + (n_0 E^2 / kT^2)\ e^{-E/kT} \quad (4)$$

where E = energy of defect formation

k = Boltzmans constant

T = temperature

C_D = Debye contribution

and n_0 is a constant in the Boltzman relationship,

$$n = n_0\ e^{-E/kT} \quad (5)$$

where n is the number of defects in the cryovaristor.

Thermal conductivity measurements were made between 1.7 to 320 K. The thermal conductivity had a maximum value of 0.65 W/cm/K at 80 K, and a value of 0.24 W/cm/K at 320 K. The thermal conductivity behavior is similar to that in ionic crystals such as alkalai halides, in which the thermal conductivity of the low temperature boundary-limited scattering region dominates the thermal conductivity of the high temperature constant specific heat region.

Energy Absorption by a Cryovaristor

The observed temperature independence of the I-V characteristic of the cryovaristor opens the possibility of energy absorption at cryogenic temperatures rather than at ambient temperatures. The enthalpy calculated for the absolute adiabatic upper bound of energy absorbed at absolute zero is 1215 J/cm^3. The enthalpy of the cryovaristor is 1186 J/cm^3 at 77 K (liquid nitrogen), and the ambient case is about 612 J/cm^3. The data was calculated on a volumetric basis using a mass density of 5.47 g/cm^3. A comparison between the energy absorbing capacity of a cryovaristor and a capacitor would demonstrate the importance of the cryovaristor enthalpy measurements. Starting from the energy equation of a capacitor,

$$E = 1/2CV^2 \tag{6}$$

the equivalent Farads/cm^3 is given by

$$C_v = 2E_v/V^2 \tag{7}$$

where C_v = Farads/cm^3
E_v = Joules/cm^3

If the voltage were 150 V, which represents a nominal value, the equivalent Farads/cm^3 for 1186 J/cm^3 is 105,422 uF/cm^3, a very large value compared to an advanced filter capacitor with a rating of 0.16 uF/cm^3 recently proposed to the Air Force[8].

Conclusion

In conclusion, the proper interpretation of the prebreakdown conduction is variable range hopping in the interface material. Understanding the nature of the grain boundary region is important in determining the unique and useful electrical properties of ZnO cryvaristors. Determining whether the grain boundary material is amorphous or crystalline is important in understanding the material properties. CeramPhysics and Penn State University are currently investigating the amorphous versus crystalline question.

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