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The Effect of Impulse Surge Current on Degradation in ZnO Varistors

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Abstract

J-E 특성, AC 임피던스 분석 그리고 주파수-전도 특성 등을 실험하여 임펄스 전류 서지가 ZnO 바리스터의 열화(degradation)에 미치는 영향을 고찰하였다. ZnO 바리스터 시편에 임펄스 전류(300 A/㎠, 8/20μs)를 인가시킨 결과, 입계(grain boundary) 특성을 나타내는 비선형계수 α와 $E_{0.01mA}$의 값은 크게 감소하였으나, 입자 특성을 나타내는 E_{100A}, E_{300A}의 값에는 큰 변화가 없었다. 이러한 열화 현상은 입계에 위치한 부성 전하 밀도, N_s의 감소에 의한 쇼트키 장벽의 변화에 기인한 것으로 나타났다. 임펄스 서지에 의해 열화된 ZnO 바리스터는 AC 임피던스 분석에서 현저한 non-Debye 특성을 보이며, 이는 병렬 RC 네트워크로 모델링한 Cole-Cole 완화 관계식으로 입계의 열화 특성을 잘 설명할 수 있었다. 주파수-전도도 관계를 검토한 결과 ZnO 바리스터는 호핑 전도(hopping conduction), $\sigma(\omega) \propto \omega^n$ 특성을 나타내며, 임펄스 서지가 인가된 이후 n 값이 감소하였다. 이는 임펄스 서지에 의해 입계 결함 상태(defect states)가 호핑 전도가 발생하기 쉽고 다중(multiple) 호핑에 의한 전도 메커니즘을 갖는 것으로 고찰되었다.

Key words : ZnO varistors, Degradation, Impulse current surge, AC impedance, Hopping, Cole-Cole

1. Introduction

The properties of the ZnO varistors are similar to a pair of back-to-back avalanche diodes but with markedly enhanced energy handling capability.[1)] Actually, it is due to their superior nonohmic electrical properties and better surge withstanding capability than other types of varistors devices that the ZnO varistors are extensively employed in protecting power and signal level electrical circuits against dangerous voltage surges. Therefore, the stability of ZnO varistors against impulse surges is recognized as one of the important subjects to be investigated.[1,2)]

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The investigation on the varistor degradation has received as much attention as the investigation on varistor conduction mechanism since the former in related to the life of the device, an important consideration for the customer. The degradation phenomena are studied under AC, DC and pulse electrical field. The mechanism suggested to account for the degradation are electron trapping, dipole orientation, ion migration and oxygen desorption. Among these works on ZnO varistors degradation, it is common sense that the degradation is a grain boundary phenomenon.[3,4)]

That the degradation is a phenomenon related with grain boundaries would be assessed by comparing the *J-E* curves of unstressed and stressed varistors. The major degradation occurs in the prebreakdown region with the upturn region remaining unaffected by stressing. Since the prebreakdown region is controlled by grain boundary, the degradation is concluded to be a grain boundary related phenomenon. Further evidences that the grain boundary is affected by stressing can be inferred from the increase in low frequency dielectric loss and from bias voltage dependence of capacitance.[5]

The barrier voltage of ZnO varistors can be electrically, chemically and thermally degraded due to applied stresses, leading to the reduction of a barrier height and consequently to the increase of a leakage current, which could be useless for surge arresters. The degradation of these barriers has been extensively studied, but the effects of high intensity current pulses on the degradation is not well known. By now, researches in degradation due to pulses has not been explained the whole phenomenon that is of fundamental importance for ZnO varistor technology.

In this paper, the effects of impulse current surge on the degradation of ZnO varistors is studied by means of *J-E* behaviors and the characteristics of AC impedance analysis, and the frequency conductivity relation. The complex plane analysis could be a useful method in characterizing the electrical nature of heterogeneous materials such as ZnO varistors. Applying this analytical technique to data for the AC response of the varistor samples, it is possible to estimate the principle relation between the degradation and the behavior of the grain boundaries of ZnO varistors.

2. Experimental Process

The varistor samples used in this work are prepared by conventional fabrication procedures.[15] Reagent-grade powders of ZnO, Bi_2O_3, Sb_2O_3, Co_2O_3, NiO, MnO_2, and Cr_2O_3 are used for preparation of samples. These oxides are pressed with a pressure of 600 kgf/㎠ into disks, and are placed in an alumina crucible sintered in static air at 1200 ℃ for 2hrs. The compositions of ZnO varistors for testing are given in Table 1. After lapping of both the surfaces of the sintered bodies, silver electrodes by using the plasma deposition method are applied to both surfaces. The standard final samples are circular disks of 15 ㎜ in diameter and 1 ㎜ in thickness.

Table 1. The composition of ZnO varistor samples in [wt%].

ZnO	Bi_2O_3	Sb_2O_3	Co_2O_3	NiO	MnO_2	Cr_2O_3
97	3.0	3.6	1.16	0.88	0.71	0.93

The microstructure of as-polished surfaces is examined with the SEM(scanning electron microscope, HITACHI S-2700). Fig. 1 is the typical SEM photo of ZnO varistor sample used in this experiment.

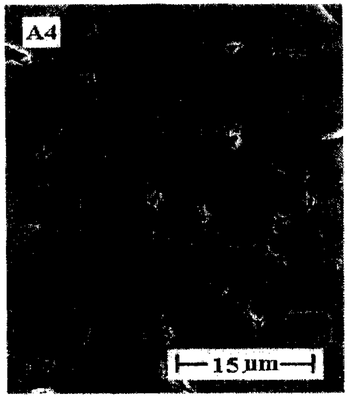

Fig. 1. The SEM photo of ZnO varistor sample.

The *J-E* behaviors of ZnO varistors are measured by using a electrometer(KEITHLY 237) and then, the nonlinear exponent α is calculated by the following equation, $J_1/J_2 = (E_1/E_2)^{\alpha}$. Where E_1 and E_2 are the electric field at the current density of J_1, J_2, respectively.

The AC impedance properties with frequency are measured in the frequency range of 10^{-4}Hz~10 ㎒ by using the impedance analyser (HEWLETT Packard, 4194A) and impedance measurement unit(ZAHNER IM6).

A impulse surge generator(801-Plus, Key Tek Co. MA) with a voltage and current combined surge wave is used in this study. As soon as this generator applied a voltage surge to the varistor samples, a surge current became available instantaneously. Then, surge current used in this test has the intensity of 300 A/㎠ and the width of 20μs and a rise time of 8μs. as schematically shown in Fig. 2. The degradation is estimated by measuring the reference electric field at 0.01 mA/㎠ ($E_{0.01mA}$), nonlinear coefficient(α) and leakage current(I_L) as a function of the number of applied pulses. Where, this intensity and the numbers of applied impulse current are controled by the estimation of limitation that is operating range without a fractural and punctual failures into ZnO varistors.

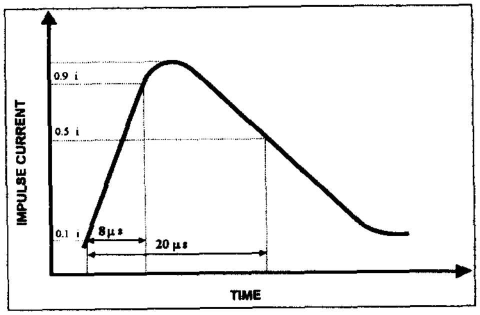

Fig. 2. The schematic representation of impulse current surge(8/20μs).

2. Results and Discussion

(1) Degradation by impulse current surge

The typical J-E curves with before and after applied impulse current of 300 A/㎠ and the width of 8/20μs are shown in Fig. 3.

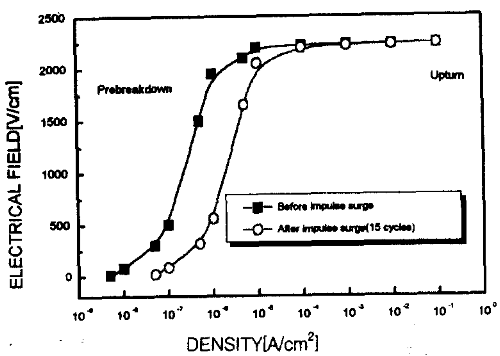

Fig. 3. The effect of impulse surge on the J-E characteristics of ZnO varistor samples.

It is observed in Fig. 3 that there is a gradual reduction of $E_{0.01mA}$ and decrease of α in prebreakdown region which has a relation with grain boundary in ZnO varistor.

The change of discharge voltages(E_{100A}, E_{300A}) at 100 and 300 A/㎠ with applied impulses numbers are shown in Table 2. This shows that there are a little variation of E_{100A} and E_{300A} which have a relation with ZnO grain, after applying impulse current surge.

The results of Fig. 3, 4 and Table 2 indicate that the current impulses modify a barrier, that is, the Schottky barrier localized at grain boundary leading to the degradation, but with negligible

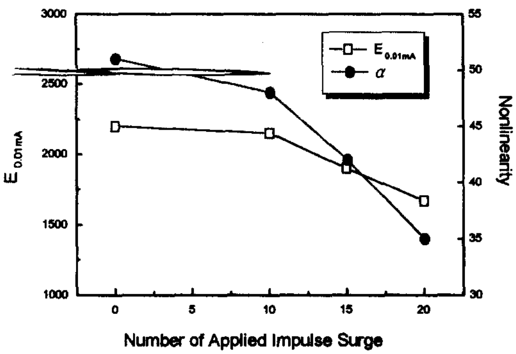

Fig. 4. The variation of $E_{0.01mA}$ and α with cycles of applied impulse surge(300 A/㎠, 8/20μs).

Table 2. The variation of E_{100} and E_{300} with before and after cycles of applied the impulse surge (300 A/㎠, 8/20μs).

	Before applied surge	After 10 applied surge	After 20 applied surge
E_{100A} [V/cm]	2150	2270	2357
E_{300A} [V/cm]	2240	2310	2400

modification in the electrical properties of ZnO grains.

The conduction mechanism through Schottky barriers could be due to thermionic emission from the ZnO grain conduction band to the isolating film conduction band. According to this model the current density J and electric field E are related by[6)]

$$J=J_o\ exp[-(\psi-\beta E^{1/2})/kT], \qquad (1)$$

where, J_o is a constant, ψ is the barrier voltage height(eV), β is a constant related to the barrier voltage width W, k is the Boltzman constant, and T is the absolute temperature(K).
In the thermionic emission model, Eq.(1), the β constant is given by

$$\beta=[(1/nW)(2e^3/4\pi\,\varepsilon_o\varepsilon_r)]^{1/2}, \qquad (2)$$

where, n is the number of ZnO grains in series in a sample of width L(㎝), W is the barrier width (㎚), e is the electron charge, and ε_o and ε_r are the electric permittivities of the vacuum and material, respectively. Defining G as the average ZnO grain sizes, n is (L/G). G values were determined by SEM photos using the line intercept method. And more detail method to determine ψ and W has indicated in previous study.[7)]

According to the proposed model of Gupta[4], in which the barrier voltage of Schottky type is due to formation of an atomic defect at the ZnO grain boundary and the negative charge states in the grain boundary are compensated by positive charges at depletion layer, a barrier model is proposed in which

$$\psi=(e^2N_s^2)/(2\varepsilon N_d), \qquad (3)$$

where, N_s is the surface state density with negative charges and N_d is the donor density with positive charges.

It is seen that the relative modification in N_s and N_d can explain the variation in ψ. The reduction of ψ can be promoted either by increasing N_d or decreasing N_s. N_s is related to N_d through the following equation

$$N_s=2N_d\cdot W. \qquad (4)$$

To verify the effect of current pulses on the barrier, ψ and N_d were calculated before and after application of impulse cycles in Fig. 5. The value of ψ with the increase of applied impulses decrease. These results show that ψ is deformed by current impulses, leading to degradation of the ZnO varistor. From this fact it appears that the deformation of Schottky barrier is changed by the barrier width and the barrier height.

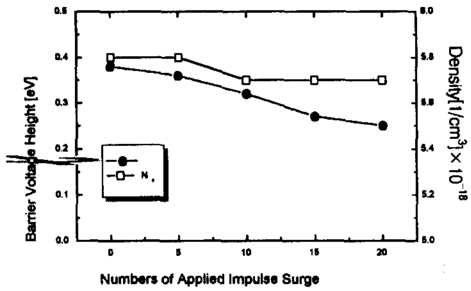

Fig.5. The variation of ψ and N_d with the number of applied impulse surge(300A/㎠, 8/20㎲).

But it is seen in Fig. 5 that N_d does not change significantly with the current pulse degradation. Thus the phenomena of degradation promoted by current impulses are due to the decrease of N_s, i.e. the decrease in negative charges located at the ZnO grain boundary, which can be either zinc vacancies or adsorbed oxygen.[8)]

The cations in the Schottky barrier depletion regions are believed to be the interstitial zinc ions because the diffusion velocity of interstitial zinc ions is several orders larger than that of the other ions, such as V_o, Bi_{Zn} and Sb_{Zn}. Furthermore, the driving force for the ion migration is believed to be furnished by the modification in the electrochemical potential which is induced by the surge.

The basic concept of the defects model is that the depletion layer comprising the barrier consists of two components ; a stable component consisting of spatially fixed, positively charged ions and a metastable component consisting of mobile, positively charged zinc interstitials.[4,8] The former ions are the trivalent substitutional ions, the so called donor ions, D_{zn}(D is bismuth, antimony, etc,), and the native oxygen vacancies V_o' and V_o'' whereas the latter ions are the singly and doubly charged native zinc interstitials Zn_i' and Zn_i''. These positively charged donors extend from both sides of the grain boundary into the adjacent grains and are compensated by a layer of negatively charged acceptors at the grain boundary interface, comprised primarily of native zinc vacancies, V_{zn}' and V_{zn}''. The oxygen interstitials, O_i' and O_i'' are not considered as major defect types in ZnO.

For electrical neutrality, the negative charges on the grain boundary are balanced on both sides by positive charges in the depletion layers in the adjacent grains. The important feature about the charges in the depletion layer is that the spatial locations of these positive ions are different : the substituted ions and vacancies are located on the lattice sites, whereas the zinc interstitials are located on the interstitial sites in the ZnO(wurtzite) structure. As a result, the zinc interstitials can rapidly migrate within the structure via these interstitial sites, whereas the host lattice ions or the ions substituted on the host lattice sites must move via adjacent vacancies which are fixed by the thermodynamics.

In developing the defect model for varistor degradation, it is first important to identify the driving force for ion migration. It is assumed that the varistor in energized during applying impulse surge which provides the necessary driving force for the migration of positively charged interstitials toward the negatively charged grain boundary interface i.e. at the interface, these charged defects are converted to neutral defects due to chemical reaction between defects.

Of the two neutral defects, V_{zn} disappears in the grain boundary sink, leaving a Zn_i at the grain boundary. As the number of applied impulse surge increases, the neutral Zn_i keeps accumulating at the interface because of continuous depletion of the opposite charges from adjacent reservoirs of positive and negative charges. This loss of charges causes the barrier voltage and barrier height to reduce as shown schematically in Fig. 5.

If the zinc interstitials in the depletion layer comprising the metastable component of the barrier are responsible for the instability of the device, it follows that the removal of the metastable components can restore stability. In theory, the metastable component can be removed thermally or chemically. Both were achieved in practice.

(2) AC Impedance Analysis

The impedance analysis is utilized for studying the electrical properties of the degraded ZnO varistors. The AC response in the Z plane for ZnO varistor samples degraded as a result of applied impulse surge is illustrated in Fig. 6.

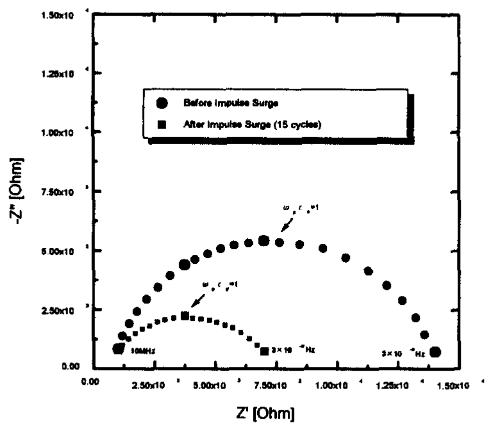

Fig. 6. The impedance spectra for the ZnO varistor samples before and after applied degradation.

The possible reasons accounting for the observed non-zero depression angle are summarized as nonuniformity in defect states from junction to junction, nonuniformity in defect levels within each junction, and a combination of the above two processes.[9] Furthermore, a recent investigation on different single grain junctions within an ZnO varistor reveals that all junctions are not identical.[10] Then the Cole-Cole empirical relation for the observed relaxation is given by

$$Z=Z'-jZ''=R_{ZnO}+[R_{DC}/1+(j\omega\cdot\tau)^{(1-h)}] \qquad (5)$$

where, $h(0\leq h\leq 1)$ is the depression angle($\theta=h\pi/2$) parameter indicating broadness of the frequency dependency of the imaginary component (i.e., average relaxation time due to the reactive term), $\omega(=2\pi f)$ is the angular frequency, $j=\sqrt{-1}$, and $(\omega_p\cdot\tau_p)=1$.

The high frequency AC complex plane response bunched in a very small segment of this semicircle yield a very small intercept on its left side. This small intercept is reasoned to be associated with the resistance of the ZnO grains. The right intercept of the semicircle corresponds to a very good approximation for the DC leakage resistance R_{DC} of the ZnO varistor, if the left intercept of the semicircle in the impedance plane is negligible. But in Fig. 6 the left intercept of the semicircle is shifted toward slightly greater values, it is known due to stray inductive effects.[9] Therefore, because the observed parameters follow the relationship $\tau_p=R_{DC}\cdot C_{DC}$, the time constant τ_p derived from the peak frequency $\omega_p(\omega_p\cdot\tau_p=1)$ of the impedance graph allows an evaluation of the total capacitance C_{DC}, the total polarization within the ZnO varistors. A summary of the measured parameters, derived from the impedance graphs in Fig. 6, is given in Table 3.

The time constant τ_p decreases due to the applied impulse current of 300 A/㎠, 8/20㎲, as indicated in Table 3, because the diffusion

Table 3. The impedance plane parameters of the ZnO varistor samples with cycles of applied impulse current surges.

n	ω_p(㎑)	τ_p(㎲)	R_{DC}(kΩ)	C_{DC}(nF)	θ(degree)
0	11.5	87.0	13.5	6.44	15
10	23.0	43.4	11.2	3.87	17
15	130.7	7.6	6.4	1.18	25
20	270.5	3.7	2.1	1.17	31

potential of Schottky barriers, which is in the neighborhood of the grain boundaries, tends to decrease with applied impulse current. This occurs as a result of the shift of the Fermi level towards the middle of the forbidden gap.

According to results of Al Alim *et. al.*[10], the relaxation time is proportional to the donor density N_d and the depletion width W, but is inversely the density of electrons traped in the boundary states N_s. It is means that the decrease of the relaxation time with applied surges is mainly due to the decrease of the barrier height and the depletion width in this work, since the donor density and the density of electrons traped in the boundary states is not predominantly changed with applied surges.

The resistance of the ZnO varistor sample, which is contributed by the grain boundries, also decreases as the cycle of impulse surge increases. The ratios of the DC conductivity at the applied number 10, 15, and 20 of impulse surge are 1.2, 2.1, and 6.4, respectively. The ratios of the AC conductivity(measured at 500Hz) at the applied number 10, 15, and 20 of impulse surge are 1.2, 4.5, and 16.4, respectively. Thus, the AC conductivity increases somewhat fast with the cycle of applied impulse currents. This can be explained as it is reasonable that the conduction carriers will have more difficulty passing through the grain boundaries as the surge cycle increases.

The finite depression angle of the impedance spectra indicates that a considerable degree of nonuniformity exists in the capacitance term.[11] Furthermore, the net polarization represents both the trapping and barrier layer capacitances, originating from the junctions within the sample. This sample experiences a Schottky barrier at every junction, resulting in a fluctuation due to inhomogeneity in defects. However, the fluctuation in a Schottky barrier, as Mahan[12] pointed out, has no influence upon an measurement of capacitance. Therefore, this Z plot indicates that the net relaxation reactance in nonuniform, and authenticated via the presence of a finite depression angle.

The depression angle θ observed in the impedance plane is related to the degree of uniformity of the grain boundaries. In other words, the depression angles θ is related to the extent of the screening which shields the conduction carriers from following the changes of polarization brought about by an alternating electric field.[9,12,16]

This assumes that screening reduces the effective density of conduction carriers to a fraction of their unscreened value. The larger the screened charge, the larger the depression angle θ. Thus, θ increases as the cycle of applied impulse surge current increases because a larger number of carriers, which are created from ZnO grains, flow into the grain boundaries when the cycle of applied impulse surge current increases. Since the conduction carriers in the grain boundaries are moving by discontinuous hopping, their movement cannot be followed by an immediate readjustment of the others, so that initially each hop involves only the unscreened charge followed by a relatively slow adjustment of the screening to the new site.

(3) The hopping conduction

Fig. 7 shows the variation of the conductivity $\sigma(\omega)$ with frequency for varistor samples for before and after appling of impulse surge of 300 A/㎠, 8×20㎲. In the case of sample without applying impulse surge, conductivity $\sigma(\omega)$ is almost constant in the region of low frequencies. After the flat region, there follows a region in which conductivity is a monotonously increasing function of frequency, ω, with the empirical relation

$$\sigma(\omega) \propto \omega^n \tag{6}$$

where, n is a constant. This relation implies that the hopping conduction observed by some researchers for other devices could also occur in the ZnO varistors.[12)]

The constant region disappears in the case of sample surged by the impulse current. The frequency independence behavior in low frequency region can be attributed to the motion of free band-like electrons.[13)] It is well known that the band-like conduction is governed by two factors,

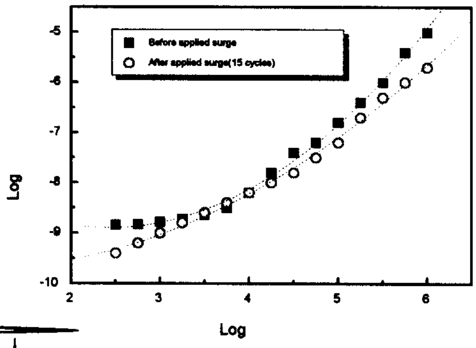

Fig. 7. The variation of the conductivity $\sigma(\omega)$ with frequency for varistor samples for before and after impulse surge(300A/㎠, 8×20㎲).

one is the DC loss term in which electrons of the shallow impurities directly flow over the grain boundary barriers, and the other is contributed that the electrons which come from the charge traps at the grain boundaries. For the charge traps, it is proposed that the electrons at the defect states, such as V_{zn}', Zn_i, conduct a current in the conduction band when they are thermally activated. However, as the applied frequency increases, the conductive path is dominated by hopping of electron between the defect states.

And Fig. 7 reveals that the value of n decreases as a result of applied impulse current surges. The lower n implies that the defect states are easier to hop from, since the decrease of n could be regarded as an indication of an increase in trapped electron hopping at the defect states.

Additionally, Pollak, *et. al.*[14)] has demonstrated that the relation $\sigma(\omega) \propto \omega^n$ would be observed if hopping takes place within a random distribution of localized states, and that the value of n is lower for multiple hops, while the value of n is higher for single hops. Therefore, we suggest that the multiple hops could be occurred more frequently after the impulse test. Such a phenomenon could be interpreted by the fact that the energy depth of the defect states becomes more shallow after applying impulse surge, as discussed above.

The interface layer in a highly nonohmic ZnO varistors was found to be amorphous, in a detailed examination by transmission electron microscopy(TEM) and selected area diffraction.[14]

In general, the frequency dependence of conductivity in crystalline solids could not be found in the condition of room temperature and low frequency, so such result suggests that the conductivity happened in the interface layer with the amorphous structure.

4. Conclusions

The degradation phenomena of the ZnO varistors caused by the impulse current surge is studied by means of *J-E* behaviors, the characteristics of AC impedance analysis, and the frequency conduction relation. Experimental results indicate that the electrical properties of the ZnO varistors are affected by the impulse surge. After examining its effects the following conclusions can be made on the basis of above discussions.

The results of *J-E* characteristics indicate that the impulse current surge modify a barrier, that is, the Schottky barrier localized at grain boundary leading to the degradation, but with negligible modification in the electrical properties of ZnO grains. The width and heigyt of th Schottky barrier by the impulse current surge in the ZnO varistors is changed, and the degradation phenomena promoted by impulse currents are due to the decrease of N_s, i.e. the decrease in negative charges located at the ZnO grain boundaries.

The ZnO varistors remarkably reveals a non-Debye characteristics(Cole-Cole relaxation) that can be modeled by a parallel RC circuit to simulate the behavior of the grain boundaries. The AC conductivity increases fast with the cycle of applied impulse currents. This can be explained as it is reasonable that the conduction carriers will have more difficulty passing through the grain boundaries as the surge cycle increases. The depression angle θ observed in the impedance plane is related to the degree of uniformity of the grain boundaries. In other words, the depression angles θ is related to the extent of the screening which shields the conduction carriers from following the changes of polarization brought about by an alternating electric field.

The hopping conduction, $\sigma(\omega) \propto \omega^n$ observes in our ZnO varistor samples, it appears that the multiple hops occur more frequently after the impulse current surge, due to the energy depth of the defect states being reduced as the number of applied surges increased. From the frequency dependence of conductivity, it suggests that the conductive mechanism in our ZnO varistor samples has a relation with the interface layer with the amorphous structure.

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