The Effect of Microstructure Nonuniformity on the Electrical Characteristics of ZnO Varistors with Al_2O_3 doping

Se-Won Han* and Han-Goo Cho*

Abstract - The influence of microstructure nonuniformity on the electrical characteristics of ZnO varistors was analyzed with the added amount of Al_2O_3 dopants. Al_2O_3 doping can effectively inhibit grain growth. When Al_2O_3 content is in the range between 0-0.1%, the average grain size and the standard deviation decrease quickly and the grain growth is strongly inhibited. Therefore, it is possible to increase the microstructure uniformity by accurate addition of Al_2O_3 to the ZnO varistor. The breakdown voltage increases with the decrease of standard deviation. The greater the uniformity of the ZnO varistor means the higher the global breakdown voltage. The Al_2O_3 dopants having about 0-0.023 wt% content can effectively improve the voltage ratio, and the voltage ratio reaches a minimum value of 2.32 at an Al_2O_3 content of 0.005 wt%.

Keywords: ZnO Varistor, Al_2O_3 Doping, Microstructure Nonuniformity, Electrical Properties, Standard Deviation

1. Introduction

The ZnO varistor is an intrinsic semiconductor and its microstructure is nonuniform, that is, its grain size or grain boundaries are irregular. Wang, et al. [1] observed that the broad distribution of grain size has a substantial effect on the *I-V* characteristics of the device when they are analyzed by the averaging effect on the *I-V* characteristics of commercial ZnO varistors by a special electrode arrangement.

The oversized and undersized grains from both ends of the distribution have a very significant influence on the varistor characteristics. An oversized grain reduces the number of junctions in the serial connection and provides a lower voltage conducting path for the current. Early breakdown tends to lower the value of the nonlinearity coefficient, causing multiple breakdown peaks. As such, oversized grains are considered detrimental. Although the number of large grains is quite small, it only takes one of them to greatly degrade the *I-V* behavior of the device. In contrast, very small grains are also considered detrimental, because their existence causes an increase in the serial path junctions, and higher breakdown voltages are required. Small grains greatly reduce the availability of conducting paths in the designed breakdown voltage range. In this case, every single-junction in the serial path may have good varistor-like responses, but the group behaves like an inactive junction simply because a higher voltage is needed to research the breakdown region [2, 3]. Therefore, the wide distribution of grain sizes would increase the nonuniformity of global electrical characteristics of ZnO varistors. In order to obtain varistors with superior quality, a narrow grain size distribution is desirable.

Actual industrial compositions are multicomponent, containing a number of other metal oxide additives, such as Bi_2O_3, Co_3O_4, Cr_2O_3, MnO_2, Sb_2O_3, Al_2O_3, and Nb_2O_5. These oxide additions can affect the varistor characteristics in two ways: (1) directly, in an electrical sense, Bi_2O_3, which segregates at the ZnO grain boundaries and related to the nonlinearity of the *I-V* characteristics; (2) indirectly, by affecting the microstructural development of the ceramic body during firing. Bi_2O_3 locates at grain boundary and forms the electrical characteristics of the grain boundary. Sb_2O_3 in the ZnO varistor inhibits densification and grain growth initially by formation of a continuous polycrystalline layer of $ZnSb_2O_6$ [4]. To add dopants of Al_2O_3, and Ga_2O_3 into ZnO varistors, the control compositions can effectively improve the nonlinearity by delaying the onset of the voltage upturn [3, 4]. Though Al_2O_3 improves the characteristics in the high current region, excessive Al_2O_3 doping worsens the characteristics in the low current region [6, 10].

The quantitative analysis on the relation between the microstructure and the electrical characteristics remains to be resolved. In the present study, the influence of microstructure nonuniformity on the electrical characteristics of ZnO varistors was analyzed when Al_2O_3 dopants were added.

2. Experiments

The ZnO varistors were prepared by well known and accepted manufacturer's procedures [6]. A series of varistors

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containing ingredients similar to those employed in commercial varistors were used, namely ZnO, 3wt%Bi_2O_3, 3.6wt%Sb_2O_3, 1.16wt%Co_2O_3, 0.88wt%NiO, 0.71wt% MnO_2, 0.93wt%Cr_2O_3 and 0-5wt%Al_2O_3. Al_2O_3 was used as a dopant in the amount of volume 0-5wt%. Sample A1 did not contain Al_2O_3, sample A2 had 0.005wt% Al_2O_3, sample A3: 0.02wt%, sample A4: 0.1wt%, sample A5: 0.5wt%, sample A6: 1.0wt%, and sample A7: 5.0%wt%, respectively. In order to study the single effect of Al_2O_3 addition, C series varistors with different prescriptions were prepared, which only contained ZnO, 3wt%Bi_2O_3, and 0-0.5wt%Al_2O_3. C1 did not contain Al_2O_3, sample C2 had 0.005wt% Al_2O_3, sample C3: 0.02wt%, sample C4: 0.1wt%, sample C5: 0.5wt%, sample C6: 1.0wt%, and sample C7: 5.0%wt%, respectively. Each ingredient was mixed by a wet milling method. The mixture was dried by spraying at 8,000rpm and then pressed into discs at a pressure of 600 kgf/cm^2. The pressed bodies were sintered at 1200°C for 2hrs in air and cooled to room temperature. Following lapping of both surfaces of the sintered bodies, silver paste electrodes were applied to both surfaces. The standard final samples were 15 mm in diameter and 1 mm in thickness.

The microstructures of the sintered samples were examined using a scanning electron microscope (SEM), and SEM photos were obtained for the analysis of microstructure nonuniformity. X-ray diffraction analyzer (Phillips PW 1830) was performed by Al-Kα target at a scanning speed of 1.5°/min to analyze the crystalline phase of the samples. The average intercept length was obtained over a large number of grains from a number of intercept lines at random directions, and the average intercept length was conversed into an average grain size.

The *J-E* characteristics of ZnO varistors were measured by a precise electrometer (Keithly 237) and the nonlinear exponent α was estimated between two desired magnitudes of current and corresponding voltages by the following equation from $J = KE^{\alpha}$:

$$\alpha = \ln(J_2 / J_1) / \ln(E_2 / E_1)\ , \qquad (1)$$

where K is a material constant and E_1 and E_2 are the electrical field strengths at current densities J_1 and J_2 (J_2>J_1).

3. Results and Discussion

3.1 Geometric Microstructure Characteristics

The SEM picture of a ZnO varistor sample (A3) with 0.02wt% Al_2O_3 amount is shown in Fig. 1. Here, the average intercept length and respective standard deviation of ZnO varistors were used as the average grain sizes $\overline{D}$ and standard deviations σ. This photo clearly illustrates that the grain shapes and grain sizes are quite dissimilar, and that nonuniformity exists in the microstructures of all ZnO varistor samples.

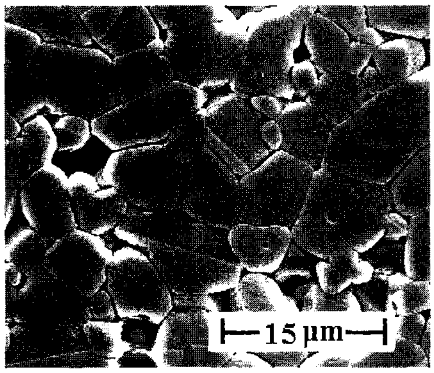

Fig. 1 The SEM picture of a ZnO varistor sample (A3) with 0.02 wt% Al_2O_3 amount.

The relations between the standard deviation and average grain size are shown in Fig. 2 and Fig. 3. The average grain size and the standard deviation of ZnO decrease with the increase of Al_2O_3 content. The relation curves of average grain size and standard deviation with Al_2O_3 content were close to linear in the semi-log coordinates, that is, the average grain size and the standard deviation exponentially decrease with the increase of Al_2O_3 content. When Al_2O_3 content is in the range of 0-0.1%, the average grain size and the standard deviation decrease quickly with the Al_2O_3 content, and the grain growth is strongly inhibited.

Comparing these results from two system varistors led to the observation that the average grain size and standard deviation of C series varistors are about two times higher than those of A series varistors under conditions having the same Al_2O_3 content. Therefore, other additions, such as Sb_2O_3, Co_2O_3, NiO, MnO_2, and Cr_2O_3, will inhibit the grain growth. On the other hand, the average grain size of a sample in the C series ZnO varistors is higher than that of the sample inform the A series ZnO varistors under identical Al_2O_3 content conditions. It also indicates that the grain growth inhibition of the A series ZnO varistors is stronger than that in the C series.

It is commonly known that the standard deviation stands for the nonuniformity degree of the microstructure of ZnO varistors. The higher the standard deviation means the more nonuniform the microstructure of the ZnO varistor. As such, the uniformity on the microstructures of ZnO varistors is increased with an increase in Al_2O_3 content. Another important phenomena showing that the uniformity of microstructures are improved with the increase of Al_2O_3 content, is that the ratios between the maximum and minimum grain sizes, as well as between the maximum and average grain sizes decreases, as shown in Fig. 4. These results clearly indicate that Al_2O_3 added to the ZnO varistor can effectively inhibit the grain growth and improve its microstructure nonuniformity, therefore, by adding a suitable content of Al_2O_3 to the ZnO varistor, it is possible to increase the uniformity of the microstructure.

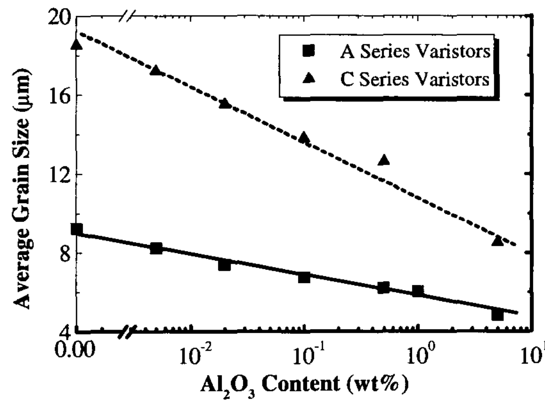

Fig. 2 The influence of Al_2O_3 content on average grain sizes.

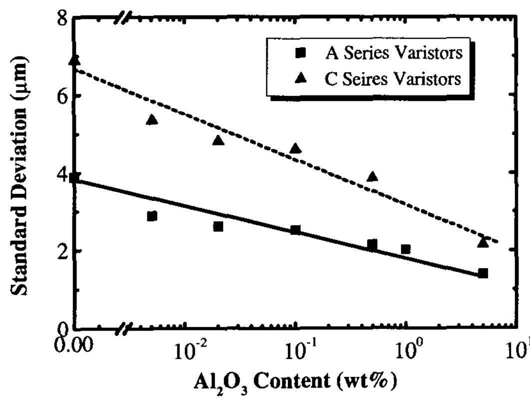

Fig. 3 The influence of Al_2O_3 content on standard deviations.

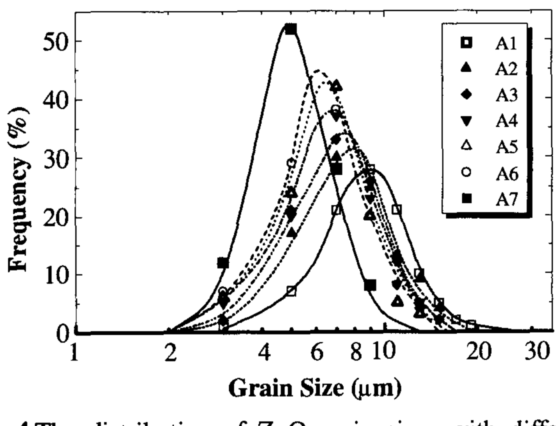

Fig. 4 The distribution of ZnO grain sizes with different Al_2O_3 contents.

The doping effect of Al_2O_3 additive affects the electrical characteristics of the ZnO varistors in two aspects: the first, changing the global electrical characteristics by changing the geometrical microstructure properties of ZnO varistors; the second, changing the electrical characteristics by the nonuniformity of the microstructures.

The geometrical properties of the microstructures of ZnO varistors are presented by the average grain size and its respective standard deviation. The relation between the breakdown voltage and the average grain size of A series varistors is shown in Fig. 5. The global breakdown voltage increases with the decrease of average grain size. The smaller the average grain size is within the identical ZnO varistors dimensions, the higher the maximum number of grain boundaries between the upper and lower electrodes, and the higher the breakdown voltage of the ZnO varistors.

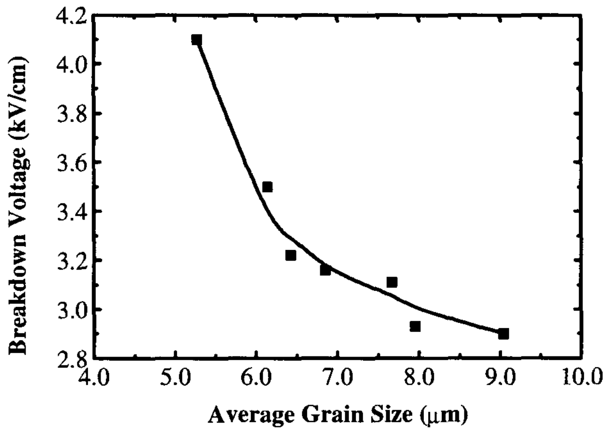

Fig. 5 The relation curve between the average grain size and the breakdown voltage (A series varistors).

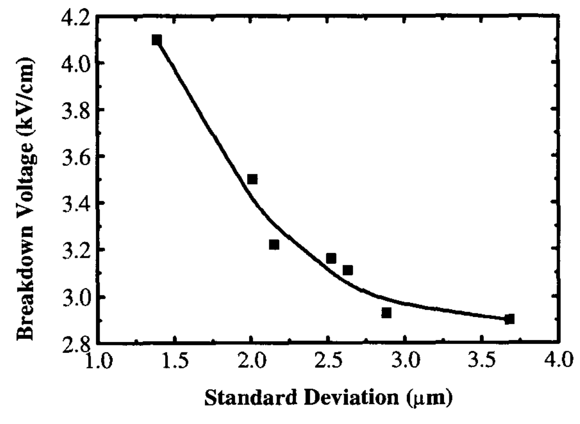

Fig. 6 Influence of microstructure nonuniformity on the breakdown voltage (A series ZnO varistors).

The standard deviation σ of grain sizes indicates the geometrical nonuniformity degree of the microstructure of ZnO varistors. The relation curve between the standard deviation of ZnO varistor samples with different Al_2O_3 contents and their breakdown voltage is shown in Fig. 6, which shows the influence of microstructure nonuniformity of ZnO varistors on the electrical characteristics in the high current region. We observed that breakdown voltage augments with the decline in standard deviation. The more uniform the ZnO varistor is equals the higher the global breakdown voltage.

Another important parameter of ZnO varistors is nonlinear coefficient, which indicates the electrical characteristic of ZnO varistors. The relation curves between the average grain size and the nonlinear coefficient, and between the standard deviation and the nonlinear coefficient are shown in Fig. 7 and Fig. 8, respectively. These graphs approximately show the linear relation between the nonlinear coefficient and the geometrical microstructure uniformity of ZnO varistors.

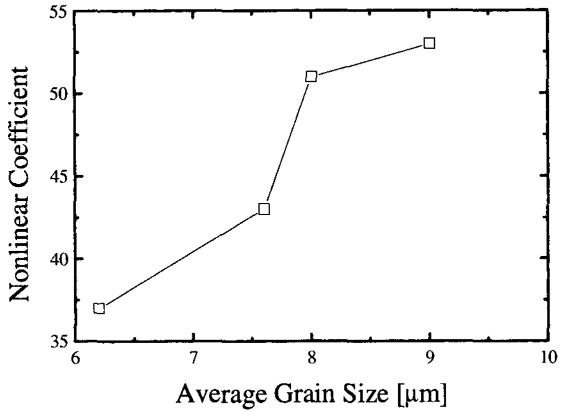

Fig. 7 The relationship between the average grain size and the nonlinear coefficient (A series varistors).

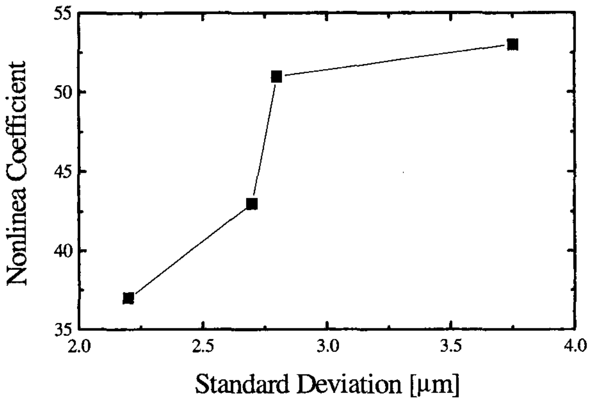

Fig. 8 Influence of microstructure nonuniformity on the nonlinear coefficient (A series ZnO varistors).

3.3 The Effect of Al_2O_3 Dopants on Voltage Ratio

The *J-E* characteristic of each sample was measured from 10^{-9} to 10^4 A/cm^2. Small current data were obtained by 60 Hz voltage and high current density data were acquired by a surge current generator with 100kA magnitude and 8/20 μs wave.

The effect of Al_2O_3 dopants is to influence the electrical characteristic of ZnO varistors, as shown in Fig. 9 (a). The onset of the voltage upturn delays into the high current region as described previously [7-9]. The dramatic effect of a small addition of Al_2O_3 at the onset of voltage upturn is clearly indicated with 0.005 and 0.02 wt% Al_2O_3. However with greater amounts of Al_2O_3 (about 0.5 wt%), the upturn occurs at a low current density.

On the other hand, we measured the voltage V_{1mA} of ZnO varistor samples with different Al_2O_3 contents under 1mA current and the respective voltage V_{10kA} under 10kA surge current with 8/20μs wave shape is listed in Table 1. In general the ratio between the voltage of the varistor under 10kA surge current and the respective voltage under 1mA DC is defined as "voltage ratio", and the relationship between voltage ratio and Al_2O_3 content is shown in Fig. 10. We observed that the Al_2O_3 dopants with about 0-0.023 wt% content can effectively improve the voltage ratio, and the voltage ratio reaches a minimum value of 2.32 at 0.005 wt% Al_2O_3 content. The voltage ratio can effectively present the protective property of the ZnO varistor. When the

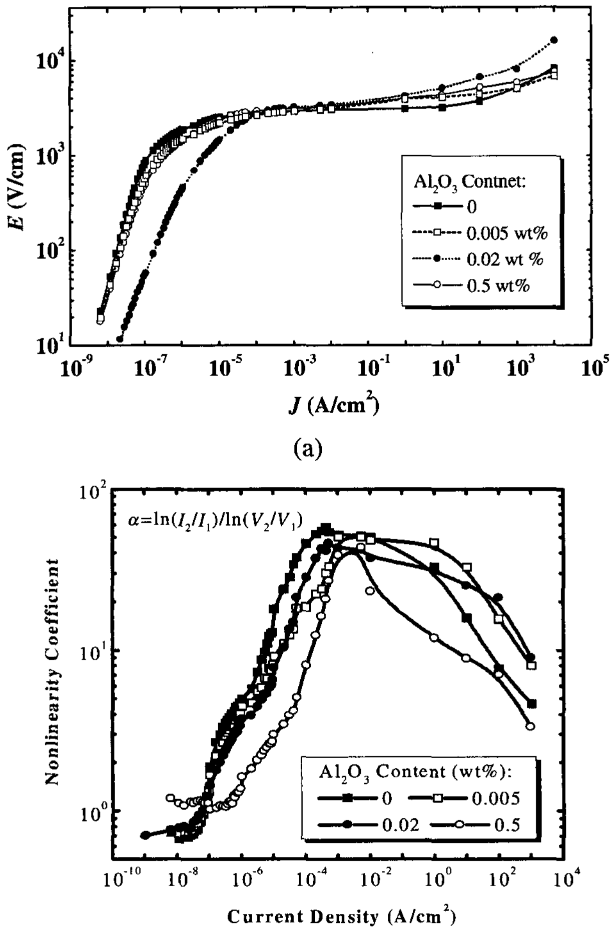

Fig. 9 (a) *J-E* and (b) *α-J* characteristics of A series ZnO varistor samples with different Al_2O_3.

voltage ratio is low, then the overvoltage is suppressed to a low level. This indicates that the ZnO varistor is used to protect the power system and the electronic system, and that the protective effect is superior. So, the ZnO varistor shows the best electrical characteristic when the amount of Al_2O_3 additive is 0.005 wt% as per our A series samples. The α-J characteristics of A series ZnO varistor samples with different Al_2O_3 amounts are illustrated in Fig. 10(b). It was observed that the ZnO varistor with 0.005 wt% Al_2O_3 content shows the best α-J characteristic above the breakdown region, maintaining the high nonlinearity coefficient in a the high current region, resulting in a wider current. So, Al_2O_3 dopants of suitable amount can effectively improve the nonlinearity coefficient in high current regions.

Table 1 The voltage ratio under different Al_2O_3 contents.

Al_2O_3 (wt%)	Voltage V_{1mA} (kV/cm)	Voltage V_{10kA} (kV/cm)	Voltage Ratio V_{10kA}/V_{1mA}
0	2.90	8.20	2.83
0.005	2.93	6.80	2.32
0.02	3.11	7.50	2.41
0.1	3.16	11.38	3.60
0.5	3.22	16.00	4.97
1.0	3.50	21.70	6.20
5.0	4.10	34.85	8.50

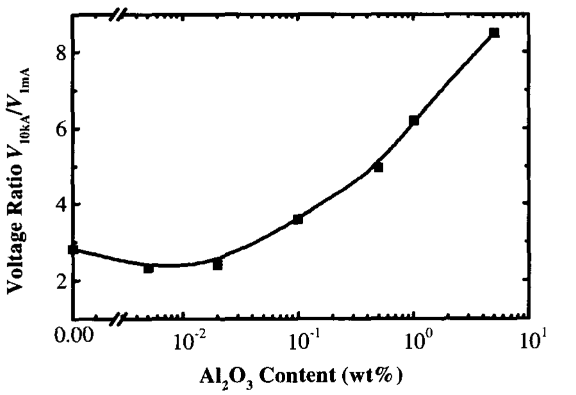

Fig. 10 The influence of Al_2O_3 dopants on voltage ratio.

The apparent effect to improve the onset of the voltage upturn in high current regions at about 0.005 wt.% Al_2O_3 is not understood at present, although we think that perhaps it is related to the optimum level of doping and the sintering process. Carlson, et al. [9] used the defect model proposed for pure ZnO crystal to explain this phenomenon. The defect model assumes that the predominant defect responsible for electrical conduction in ZnO is the interstitial Zn_i, which can be ionized as:

$$Zn_{(g)} = Zn_i = Zn_i^+ + e^- , \quad (2)$$

where e is the electronic charge. These interstitial cations occupy a shallow donar level (at about 0.05 eV) close to the conduction band and are completely ionized to Zn_i^+ ions and electrons. Then, the interstitial Zn_i^+ ions are produced in a concentration equal to the concentration of electrons:

$$[Zn_i^+] = [e^-] = n , \quad (3)$$

The conductivity σ can be presented as:

$$\sigma = ne\mu , \quad (4)$$

When Al_2O_3 is added into ZnO, the Al atom tends to dissolve as $Al^{3+} + 3e^-$. When an Al atom substitutes on a Zn site, then a trivalent Al^{3+} ion will replace a divalent Zn^{2+} ion leaving net electron to the conduction band according to the reaction:

$$\tfrac{1}{2}Al_2O_3 = Al_{Zn}^+ + e^- + ZnO + \tfrac{1}{4}O_2(g) , \quad (5)$$

This will give a net increase in the electron concentration n thus increasing the electrical conductivityσ. In spite of the complicated chemistry of the ZnO grain, the conductivity measurement shows an increase in grain conductivity with Al_2O_3 up to a certain concentration. This is compliance with the defect model proposed for pure ZnO [10].

At microwave frequency, the measured resistance and resistivity can be regarded as the grain resistance and resistivity. The grain resistivity of ZnO varistor samples with different Al_2O_3 contents was measured in the frequency range between 1-5GHz as shown in Fig. 11. The resistivity decreases with increasing Al_2O_3 contents, and the resistivity has a minimum value at about 0.005 wt.% Al_2O_3 content. The high resistivity at high Al_2O_3 concentrations may be explained as the formation of deep level traps. The apparent minimum value at about 0.005 wt.% Al_2O_3 content is explained by the fact that it may represent the optimum level of doping, which leads to improvements in the high current nonlinearity.

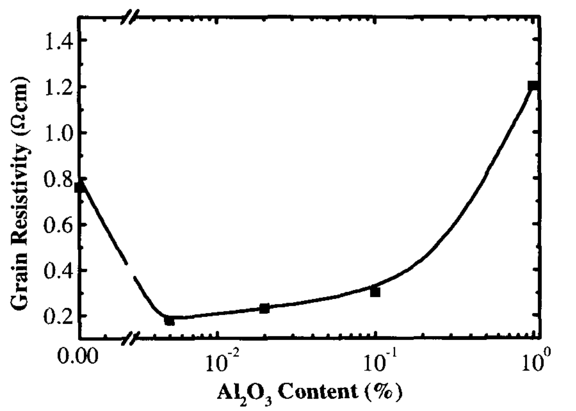

Fig. 11 The relationship between grain resistivity and Al_2O_3 content.

4. Conclusion

The uniformity of the microstructures of ZnO varistors is increased with the amplification of Al_2O_3 content. It was shown that Al_2O_3 added to the ZnO varistor can effectively inhibit the grain growth and improve the nonuniformity of its microstructure. Therefore, it is possible to increase the uniformity of microstructure by the appropriate addition of Al_2O_3 to the ZnO varistor.

The global breakdown voltage increases with the decrease of average margin size. The smaller the average size is in the same dimension as the ZnO varistor, the higher the maximum number of grain boundaries between upper and lower electrodes, and the higher the voltage of the ZnO varistor. The standard deviation of grain size refers to the geometrical nonuniformity degree of the microstructure of ZnO varistors, and the breakdown voltage increases with the decrease of standard deviation. It was clearly indicated that the more uniform the ZnO varistor is, the higher the global breakdown voltage.

The Al_2O_3 dopants with approximately 0-0.023 wt% content can effectively improve the voltage ratio, and the voltage ratio reaches a minimum value of 2.32 at 0.005 wt% Al_2O_3 content. The voltage ratio can effectively present the protective property of the ZnO varistor. The ZnO varistor with 0.005 wt% Al_2O_3 content has the best α-J characteristic above the breakdown region, which maintains the high nonlinearity coefficient in the high current region, resulting in a wider current region. As such, the Al_2O_3 dopant of suitable amount can effectively improve the nonlinearity coefficient in a high current region.

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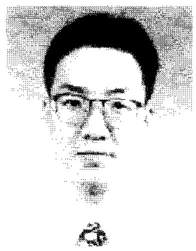

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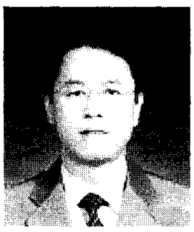

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