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ZnO 바리스터에서 입계의 전기적 불평등성에 관한 연구

NONUNIFORMITY OF GRAIN BOUNDARIES IN ZnO VARISTORS

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Abstract

The nonuniformity of electrical characteristics of grain boundaries in ZnO varistors were systematically analyzed. The high nonuniformity exist in barrier voltages and nonlinearity coefficients among different grain boundaries. The barrier voltages have normal distributions, only a few grain boundaries were electrically active, and the grain boundaries can be simply classified into good, bad, and ohmic ones according to the electrical characteristics of grain boundaries. The average barrier voltage is equal to 3.3 V by direct method, but it is only 2.3 V by indirect method. There is a high difference between the barrier voltages by direct and indirect measurement methods. The Al_2O_3 dopants affect the electrical characteristics of grain boundaries by changing the electron status in grain boundary and intragrain.

1. Introduction

ZnO varistors are complicated networks of ZnO grains and grain-boundaries in parallel and in series. The electrical characteristics of ZnO varistors are synthetical responses of different single grain-boundaries. Many researchers [1-11] had measured the electrical characteristics of single grain-boundaries by different methods. From the experimental results, differences of electrical characteristics among different single grain-boundaries, and differences between the results of single grain-boundaries and that of the global ZnO varistors can be found. That is to say, the electrical properties of different single junctions are not identical. Many researchers had developed different kinds of techniques to study the single grain [1-11]. These single-junction *I-V* characteristics showed that there is a distribution of the breakdown behavior depended on the microstructures [6, 7, 10]. When these single-junction are put together to form a bulk device, the electrical properties of each individual junction will contribute to the overall signal. It is very important to understand the influence of the junction network on the device properties [12]. So, analyzing the nonuniformities of electrical characteristics of single grain-boundaries is useful to understand the global electrical characteristics of ZnO varistors.

In order to research the electrical characteristics of grain boundaries, suitable measuring method should be used. In our knowledge, five different methods [1-11] are used to determine the characteristics of single grain junctions. All these methods consists of contacting two adjacent grains by small and narrow electrodes and measuring the *I-V* characteristics of these grains.

Up to now, in our knowledge, the systematic analysis on the nonuniformity of ZnO varistors can not be found in literature. The purpose of this paper is to discuss the nonuniformity of electrical characteristics of grain boundaries inside ZnO varistors by our research results and provided measured data in literature.

2. Nonuniformity of Barrier Voltages of Grain Boundaries in ZnO Varistors

One of the important parameters in the physical models of ZnO varistors explaining the transition phenomena from the low-current region to the high-current region is the value of the barrier voltage, which means the breakdown voltage per grain boundary barrier and has been typically determined by two methods. The first indirect one [2, 14, 15], sometimes called as calculation method, derives this breakdown voltage from the experimental observation that the voltage at a constant current is inversely proportional to the grain size. Diving this voltage by the average number of grains between the electrodes yields a calculated barrier voltage. In general, it is very difficult to obtain a homogeneous microstructure in a practical ceramic body, and therefore, it is not possible that all grain sizes are the same, but rather the microstructure has a distribution of different grain sizes. The second method is a direct one [2-5], which consists of contacting two adjacent grains by small and narrow electrodes and measuring the *I-V* characteristics of these grains described above.

In the bulk *I-V* measurements, varistor breakdown voltage is usually defined as the voltage at a certain current density, typically 1μA [2-4], and 1mA/cm² [1-17]. This requires an estimation of the junction area which is difficult to be known, and may introduce error into the measurement. To eliminate the estimation of junction area, Tao *et al.* [6] and Olsson *et al.* [18] presented another method to determine the breakdown voltage. The definition of varistor breakdown voltage, V_B, is the voltage where α researches a maximum.

Several studies have indicated that the presence of a thin(<20 Å) [19-25] and homogeneous [25] layer of Bi at the grain boundaries in ZnO. Generally the Bi-ions trapped at the grain-grain interfaces are thought to be responsible for the electrical activity. This idea is supported by the fact that the varistor characteristic disappears when Bi is eliminated as a dopant(provided sintering is done in a Bi-free atmosphere).

Olsson *et al.* [10, 26, 27] investigated the microstructure of a ZnO varistor material by X-ray diffractometry and analytical electron microscopy. The material was found to consist of ZnO grains (doped with manganese, cobalt, and nickel oxides), smaller spinel grains which hinder the growth of ZnO grains during sintering, intergranular Bi-rich phases (namely α-Bi_2O_3, pyrochlore, and an amorphous phase), and a small proportion of ZnO-ZnO interfaces which did not have any intergranular film but to which bismuth had segregated. The intergranular microstructure is largely a result of processes which occur during liquid-phase sintering and subsequent cooling to room temperature. But, they found that the barriers to electrical conduction from a ZnO interfaces form in the temperature interval 1000°C to 800°C during cooling from the sintering temperature. Interruption of the cooling sequence, by water quenching from temperature of 1000°C and above, gave specimens that did not exhibit varistor behavior, which shows that the mere presence of Bi atoms at the ZnO grain boundaries is not a sufficient condition for the formation of barriers to electrical conduction. Analytical transmission electron microscopy showed that Bi was always present at these interfaces event after quenching from high temperatures. It was found that barriers could be developed in these specimens by application of a post-sintering heat treatment at temperatures of 320°C and above. So, we can think that the grain barriers are formed during the cooling course from the sintering temperature, and it would bring a large difference if the cooling program is not the same. Nonuniformity of grain boundaries exists during their forming courses, which is the origin of nonuniformity of electrical characteristics of ZnO varistors.

The barrier voltages are 3.3V according to Mahan *et al.* [1, 9] and 3.6V according to Kemenade *et al.* [4] And many other researchers had measured the breakdown voltages by different direct methods described above, their measurement results are listed in Table 1. The reported breakdown voltages lie in a range from 1.8V to 6.0V, which covers a wide range. One explanation for this relatively wide spread of results is the difficulty in defining the crossectional area, and secondly, different criteria were used to measure the breakdown voltages. But, even if the same criteria are used, e. g. at 1μA or at the maximum of the nonlinear coefficient α, the barrier voltages are still largely different because of different prescription and different sintering courses. The average value of total values listed in Table 1 is 3.3V per barrier. Although this average value is rough because of different barrier voltage at different measure criterion, but we think this average value over a number of barrier voltages could be used as a reference of barrier voltage of single grain-boundary.

In recent research works [6, 7, 10] on single grain boundaries, ordinary, this method that the breakdown voltage is defined as the voltage at the maximum values of α, is used, the average values of barrier voltages from different literature [6, 7, 10] are close to each other, the average value is 3.2V which can be used as the average value of barrier voltage in simulating analysis to ZnO varistors. The barrier voltage towards 3.2-3.3V for individual ZnO grain boundary was found for a material whose ZnO grain boundaries were mainly devoid of intergranular thin films and the observed α values were in excess of 50 [1, 19], These results are in good agreement with those obtained from different literature by us.

Table 1. Barrier voltages of the ZnO varistors by direct measurements on single grain-boundaries reported from the literature

Materials	Barrier voltage	Ref.
	3.2-3.3V	29
ZnO,1%Sb_2O_3, 0.5%CoO, 0.5% Cr2O3, 0.5%Bi_2O_3	2.3-2.9V at 1μA 2.6-3.3V at 1mA	2
Commercial varistor	4V at 1μA	3
Commercial varistor	3.6V at 1μA	4
ZnO, 1% CoO, 0.2% Nd_2O_3, 0.25% Sn_2O_3	4V	5
	2.3-3.7V at α_{max}	6
ZnO, 1% Bi_2O_3, 1% MnO	6V at 4μA	30
ZnO, 1% Bi_2O_3, 1%MnO, 0.5% TiO_2	5V at 10μA	30
	2.3V at 0.1μA	15
	3.3V	1
	3.5V	8
Commercial varistors	3.0-3.5V at α_{max}	7
90 mol% ZnO, 10 mol% additives of Bi_2O_3, Sb_2O_3 and Co_2O_3	3.2V, 3.6V at α_{max}	10
	3.8-4.0V	13
97 mol% ZnO, 3 mol% additives of Bi_2O_3, Sb_2O_3 and Co_2O_3	1.8-6.0V	31
ZnO, 0.55Bi_2O_3, 0.5% Co_2O_3, 0.5%Mn_3O_4, 0.5% NiO, 0.5% TiO_2	3.5V	32

From the results listed in Table 1, the barrier voltages from single grain boundaries inside a ZnO varistor by different researchers [2, 6, 7, 10, 13, 29, 31] cover a wide ranges, too. The difference between the maximum and minimum values of barrier voltages are analyzed in Table 2. If we define the nonuniformity coefficient K_n as the ratio between the maximum and minimum values of barrier voltages, different researchers obtained different K_n. then K_n is in the range from 1.03 to 3.33, which covers a large spread. So, the nonuniformity of barrier voltages is very large, which can lead the global electrical characteristics to be lowered.

The average barrier voltages by indirect method can be found in literature, which cover a spread from 2.0 to2.5. The range of barrier voltages by indirect method is narrower than that by direct method. Because the average barrier voltage by indirect method is obtained from the global electrical characteristics of ZnO varistors, the bulk electrical characteristics is the synthetical effect of all single-grain-boundaries. The average barrier voltages by indirect method is 2.3V,[13, 14, 15, 36] which is more lower than 3.3V that is the average obtained from direct method.

The barrier voltages of thin ZnO film are in the range between 2.8 and 3.1V [33], and between 2.3 and 3.0V [34], which are in the middle between the barrier voltage from single grain-boundaries by direct method and that by indirect method from ZnO varistors.

Levinson and Philipp 16) reported the calculated barrier voltage is lower than the measured barrier voltage because the current always seeks the easiest path, i. e. the path with fewest barriers between the electrodes. Emtage 35) showed from theoretical approaches that the mean breakdown voltage per grain in the conductive ceramics is less than that of an isolated grain boundary because there are some chains of long grains through the inside of a ceramic body.

Because the nonuniformity of barrier voltages exists, when voltage is applied on ZnO varistor, electrical current always passes through the lowest barrier voltage path and the least number of grain boundaries between the electrodes. Therefore, the calculated barrier voltage (by indirect method) should be lower than the measured one. The difference between calculated and measured barrier voltages varies like the sigmoidal mode with the standard deviation of average grain sizes, as the standard deviation approaches zero, the difference decreases to zero, and the standard deviation increases, the difference increases too30). So, Sung *et al.* 30) thought that the number of grain boundary barriers for the current path should be conventionally calculated from diving the thickness of the device by the average grain size, and they discussed how to modify the average number of grain boundary barrier, so as to calculate the most probable barrier voltage which is equivalent to the measured one by the indirect method.

Table 2. The nonuniformity of barrier voltages of ZnO varistors reported from literature

Max. Value of Barrier Voltages V_{Bmax}	Min. Value of Barrier Voltages V_{bmin}	$K_n= V_{Bmax} / V_{Bmin}$	Ref.
2.9	2.3	1.26	2
3.3	2.6	1.27	2
3.7	2.3	1.61	6
3.5	3.0	1.09	7
3.6	3.2	1.13	26
3.3	3.2	1.03	29
4.0	3.8	1.05	13
6.0	1.8	3.33	31

3. Classification of Grain Boundaries

The asymmetric *I-V* characteristics were observed in single grain-boundaries 3, 6- 8). Wang *et al.* 7) observed asymmetric grain-boundary potential barriers and *I-V* characteristics, and they thought asymmetry was because of the intergranular differences in chemical composition, distribution of chemisorbed oxygen, and grain boundary microstructure. Einzinger3) thought the asymmetry may be easy to understand, since the Fermi energy levels in the two phases are different.

The Microcontact electrical measurements on multiple-phase ZnO varistors show a wide diversity of grain-boundary characteristics. Nevertheless, these measured results 6, 7, 10, 18, 38) consistently indicate that the *I-V* characteristics for the grain-boundaries could be classified into three representative types: "good" and "bad" nonlinear microjunctions, and ohmic microjunctions. Different grain boundary has different *I-V* characteristic, good grain-boundary has good *I-V* characteristic, and bad grain boundary has bad one.

Kemenade *et al.* 4) postulated an assumption that only a few barriers were electrically active, and the assumption was confirmed experimentally by Tao. *et al.* 6). They measured 54 single grain junctions, and found each single barrier has been found to present its own special electrical characteristics, and their results showed the existence of "good" and "bad" junctions by the third method. And measured breakdown voltage of the "good" junctions is 3.1 V with a nonlinearity coefficient lager than 30,, and a large number of tested junctions (24) belong to the "bad" ones, which have about 3 V breakdown voltage with a low α less than 10. For a voltage equal to half the breakdown voltage, the "good" junctions present a current of about 0.3μA, but the currents are approximately 1mA and 20μA for different "bad" junctions. The measured breakdown voltages are in the range between 2.3V to 3:7V, and average value is 3.0V.

The "good" microjunctions have high leakage resistance and high nonlinearity coefficient ($\alpha \geq 30$), the proportion of "good" junctions are about 15-20% 6), and 65% 31), and 25-33% 19). Estimates of the relative number of such good microjunctions have been reported to vary from 15% to 65% 6, 10, 18, 19, 31). Bad microjunctions have 2 to 3 orders of magnitude lower leakage resistance and much lower nonlinearity coefficient α (about 10) 6, 7, 10, 51). In the microcontact measurements of Cao *et al.* 38), about 30%-35% of the tested microjunctions showed a bad characteristic, but the breakdown voltages of both good and bad microjunctions are nearly identical at about 3 V, the proportion of "bad" junctions is 35% 31). The ohmic microjunctions are nearly linear with a resistance 2 to 5 orders of magnitude lower than the leakage resistance of the good junction 6, 7, 12, 38). The fraction of ohmic junctions has been estimated be about 20%7, 12, 18) and 5-10% 38). Ohmic microjunctions are present in all varistors, including commercial ones, even when their quality is very good 7, 12, 38). The ohmic grain-boundary is called as ineffective grain-boundary, which would leads to the existence of shortcut pathway inside ZnO varistors 31).

As analyzed above, many researchers simply classified the gain boundaries into different types according to their electrical characteristics. We think it is very useful to comprehend the structure and characteristics of grain boundaries. But, in fact, there are distributions in both and the barrier voltage V_B and the grain size in actual ZnO varistors, as had been measured4, 6, 12, 18, 42). The barrier voltages are distributed symmetrically in log-normal distribution 6), an obvious normal distribution exists between barrier voltages and the number of grain boundaries. So the distribution of barrier voltages can be described by normal distribution. This point is very important, we think that the simulating calculation will be better to satisfy the actual electrical characteristics of ZnO varistors if the normal distribution of barrier voltages is used.

The distribution of α is wide and asymmetrical6). A high percent of grain boundaries have bad or ohmic *I-V* characteristics, and only a small percent of grain boundaries have good *I-V* characteristics. But the ZnO varistors have good global *I-V* characteristics, ordinary, the nonlinear coefficient α of ZnO varistor bulks is larger than 30. Tao *et al.* 6) also observed a decrease in α value as a function of sample thickness. The exponential distribution function can be used to describe the distribution of nonlinear coefficient α:.

When we analyzed the effect of Al_2O_3 doping to electrical characteristics of ZnO varistors, we found all samples have high α. It is consequently essential for a better understanding of conduction phenomena in ZnO varistors to consider a distribution and not a mean value of α for all grain-to-grain junctions. So, it is not possible to neglect the α values larger than 30, mostly because they correspond to "good" junctions responsible for a good varistor effect. Moreover, these "good" junctions have small leakage currents than every other junction. Consequently the "good" junctions control the leakage current of ZnO varistor at low values of the applied voltage. [6)]

4. Conclusions

The nonuniformity of electrical characteristics of grain boundaries in ZnO varistors were systematically analyzed. One of the important parameters in the physical models of ZnO varistors explaining the transition phenomena from the low-current region to the high-current region is the value of the barrier voltage, and another important parameter to measure the electrical characteristics is nonlinearity coefficient. The high nonuniformity exist in barrier voltages and nonlinearity coefficients among different grain boundaries.

The barrier voltages have normal distributions, and the nonlinearity coefficients belong to exponential distribution. A high percent of grain boundaries have bad or ohmic *I-V* characteristics, and only a small percent of grain boundaries have good *I-V* characteristics, and the grain boundaries can be simply classified into good, bad, and ohmic ones according to the electrical characteristics of grain boundaries.

A high difference exists between the barrier voltages by direct and indirect measurement methods, the average barrier voltage is equal to 3.3 V by direct method, but it is only 2.3 V by indirect method.

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