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# Direct Measurements of Voltage–Current Characteristics of Single Grain Boundary of ZnO Varistors

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***Abstract***

*In order to comprehend electrical properties of grain boundaries and other microscopic regions of electroceramics, an analytical apparatus based on scanning electron microscope (SEM) was newly developed. The apparatus was composed of SEM in which two micro probes made of Pt–Ir alloy were attached at the sample stage, an outer electric DC power supply and energy dispersion type X-ray analyzer (EDX), so that element analysis of specific area of samples was possible. Direct measurements of voltage–current* (V–I) *characteristics of single grain boundary of ZnO varistors having small grain size (≤10 μm) were attempted by the apparatus. As a result, nonlinear behavior of* V–I *characteristics of ZnO varistors was confirmed to take place at one grain boundary and, furthermore, inhomogeneity of the nonlinear* V–I *characteristics was observed. © 1999 Elsevier Science Limited. All rights reserved*

*Keywords*: inhomogeneity, grain boundaries, electrical conductivity, ZnO, varistors.

## 1 Introduction

In the past two and a half decades, ZnO varistors have attracted a great degree of attention due to their peculiar nonlinear voltage–current (*V–I*) characteristics, which allow to fabricate several types of surge absorbers in various electrical fields.[1] It is generally considered that die nonlinear phenomena of ZnO varistors are explained by the presence of a double Schottoky type potential barrier which forms at the grain boundary. However, essential comprehension about ZnO varistors such as the conduction mechanism, structure of grain boundaries, electrical degradation phenomenon has not wholly proceeded because ZnO varistors have many factors which remained ambiguously. For that reason, development of ZnO varistors having good performance still strongly depends on experiential approaches. In order to control and improve the electrical properties of varistors, adequate knowledge and information about the characteristics of each grain boundary is necessary. For this purpose, suitable analytical apparatus for electrical properties of grain boundaries are required to obtain effective data of ZnO varistors for practical use having small grain size (≤10 $\mu$m). Some excellent methods about evaluation of individual grain boundaries of various types of electroceramics have been reported so far. For example, a technique using micro metal electrodes deposited on a mirror-polished sample by photolithography method is representative among them.[2–5] However, such technique is so complicated, especially on sample preparation, that it does not always become general. Based on this background, in this paper, a new experimental apparatus is explained. Then, direct measurements of *V–I* characteristics of single grain boundary of ZnO varistors containing several metal oxides are described.

## 2 Experimental

### 2.1 Experimental apparatus

In order to evaluate electrical properties of micro region of ZnO varistors, ordinary SEM (S-2400, Hitachi Ltd) was improved. Two micro probes, which were made of platinum (Pt)–iridium (Ir) alloy, were attached at the sample stage of the SEM. They were movable independently toward XYZ direction by piezoceramics (M) with 1 $\mu$m precision. Figure 1 shows a SEM photograph in which two micro probes face each other across one

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grain boundary of ceramics. Two micro probes are connected to an outer electric power supply. Range of the applied voltage between two micro probes is ±10 VDC, and maximum current ±200 nA. The features of this experimental apparatus is as follows:

1. The area to measure electrical properties is able to be chosen using SEM image of the sample.
2. Element analysis of the specific area of sample is possible using EDX.
3. Temperature of the sample is able to be controlled from −100 to 200 °C.
4. Electron beam induced current (EBIC) method to analyze internal electrical field of electroceramics is applicable.

In this paper, we describe the three features (1)–(3) of the apparatus. EBIC analysis using the apparatus will be discussed elsewhere.

### 2.2 Sample preparation and measurement

Samples composed of ZnO ceramics containing small amounts of $Bi_2O_3$ (0.5 mol%) and other representative additives, that is, MnO (0.5 mol%), CoO (0.5 mol%), $Sb_2O_3$ (1.5 mol%) were synthesized by the following conventional manufacturing process. Starting powders, whose purity were reagent grade, were mixed by ball-milling with distilled water. The mixed slurry was dried in an electrical oven and then, calcined in air at 700 °C for 4 h. The obtained powder was pressed into disk shapes and sintered in air at 1200 °C for 2 h. Grain size of the samples synthesized via above process was about 10 $\mu$m on an average. Crystalline phase of the sample was identified by X-ray diffraction analysis (XRD:RU-200, Rigaku Co. Ltd) and element analysis was carried out by EDX (Kevex delta III).

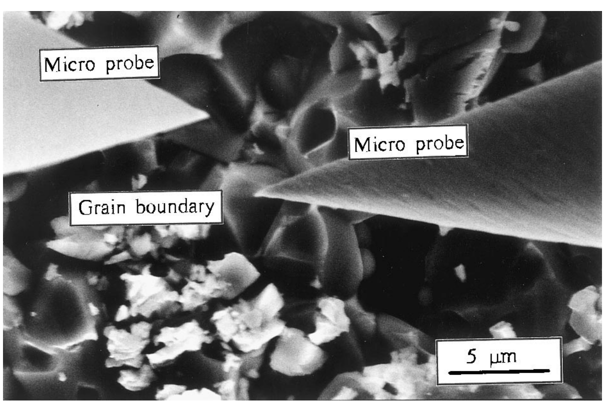


**Fig. 1.** SEM photograph of two micro probes in the experimental apparatus.

The sample was fractured in the atmosphere and set in the experimental apparatus mentioned above. *V–I* measurements of a single grain boundary and other microscopic area of the samples were carried out.

## 3 Results and Discussion

### 3.1 *V–I* characteristics of micro region of the sample

The sample synthesized in this study was confirmed to have two typical crystalline phase of ZnO and Zn–Sb–O complex oxide (spinel oxide) by XRD. Figure 2 shows a SEM photograph of fractured surface of the sample and EDX patterns of large grain (A) and small grains (B) seen in the SEM photograph. As shown in Fig. 2, microstructure of the sample was composed of matrix grains, whose phase was ZnO containing Mn and Co ions and small grains, which were dispersed in the matrix, including a large amount of Sb ions.

Figure 3 shows typical *V–I* characteristics obtained by the experimental apparatus. The horizontal axis of the graph corresponds to the applied voltage and the vertical one to the current. In this

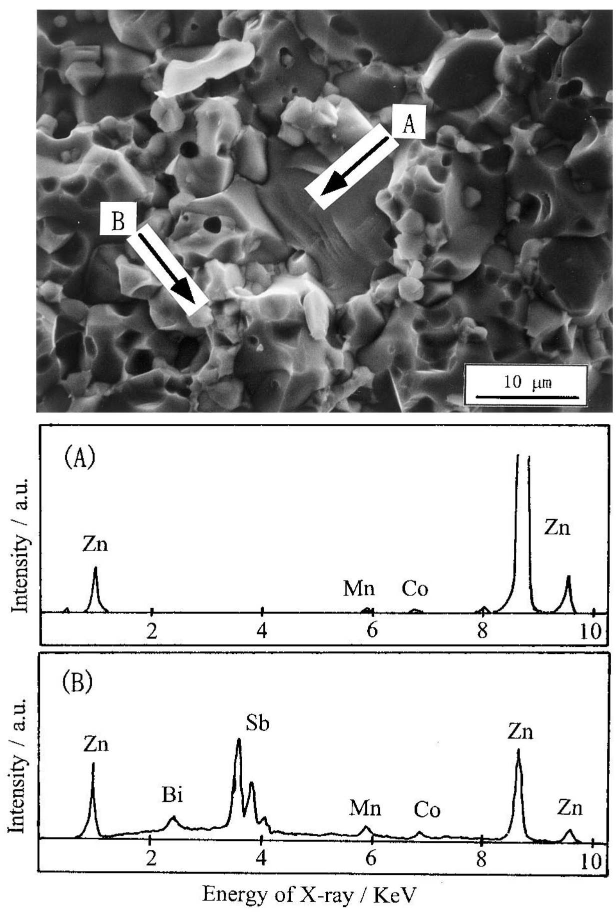


**Fig. 2.** SEM photograph of the fractured surface of the sample and EDX patterns of (A) large grain and (B) small grain of the sample as pointed out in the above SEM photograph.

figure, the straight line (A) corresponds to the case that two micro probes attach on one large grain and curve (B) to the case that both sit on the adjacent two grains. Line (C) corresponds to the result obtained from one small grain seen in Fig. 2(B). As shown in Fig. 3, it was recognized that the nonlinear properties in resistivity of ZnO varistors was caused by the single grain boundary's characteristics. On the contrary, the resistivity of one grain was very low compared to that of grain boundary and shows ohmic behavior. In another microscopic region such as small grains composed Zn–Sb–O complex oxides, current could be hardly detected seen in line (C) of Fig. 3. Thus, this result suggests that the two probes method combined with SEM is sufficiently effective to investigate electrical characteristics of microscopic region of ceramics such as grain boundaries.

### 3.2 Inhomogeneity of *V–I* characteristics of grain boundaries

Figure 4 shows *V–I* characteristics obtained from some single grain boundaries (A)–(E) of the sample. As shown in Fig. 4, it was found out that there were many types of grain boundaries in the sample. For instance, at the grain boundary of curve (A)(B), sharp nonlinear behavior and high breakdown voltage, at which current increased rapidly, were recognized. On the other hand, low resistivity was measured at another grain boundary shown in curve (E). Furthermore, as shown in curve (D), there was a grain boundary at which the change of current showed asymmetry to the polarity of applied voltage. Grain boundaries having such a peculiar pattern were often detected. Thus, *V–I* characteristics of ZnO varistors were thought to be inhomogeneous from a point of microscopic view of materials. Such presence of inhomogeneity of the electrical properties of different grain boundaries seen in Fig. 4 (A)–(E) agreed with the result of former works.[2,4,5]

In order to investigate such inhomogeneity, EDX analysis was carried out. However, there was no apparent element difference of each grain boundary region within sensitivity of EDX. According to our experimental results using Auger electron spectroscopy, the additives Bi and Mn ions were segregated at grain boundaries within 2–30 mm thickness, however, their amounts were not absolutely constant.[6,7] Therefore, such inhomogeneity of element distribution in nano scale order was thought to be related to the electrical inhomogeneity of each grain boundary seen in Fig. 4. Thus, Fig. 4 shows the possibility that the method using the apparatus can analyze the behavior of each grain boundary of ZnO varistors from a point of micro/nanoscopic view.

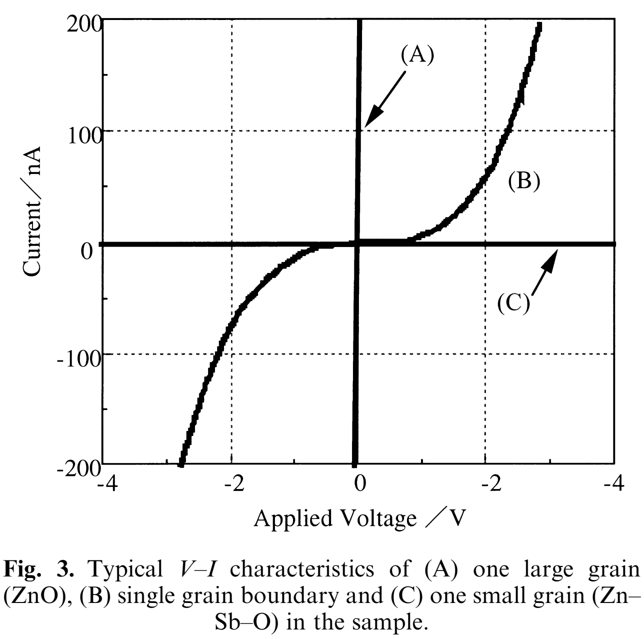


**Fig. 3.** Typical *V–I* characteristics of (A) one large grain (ZnO), (B) single grain boundary and (C) one small grain (Zn–Sb–O) in the sample.

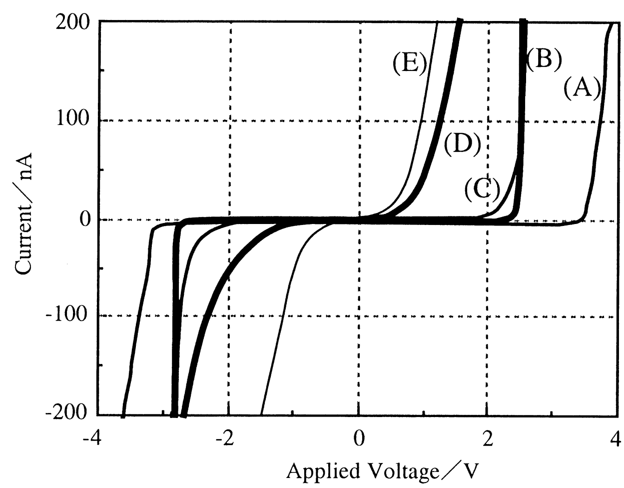


**Fig. 4.** *V–I* characteristics of a microscopic region in the sample; (A)–(E) individual grain boundaries.

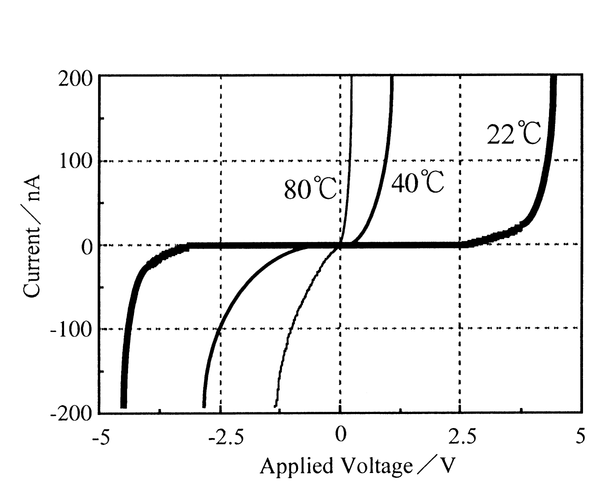


**Fig. 5.** Temperature dependence of *V–I* characteristics of a single grain boundary of the sample; value in the graph corresponds to the measuring temperature.

### 3.3 Temperature dependence of *V–I* characteristics of grain boundaries

Figure 5 shows the temperature dependence of the *V–I* characteristics of a single grain boundary of the sample. As shown in Fig. 5, its nonlinear behavior rapidly vanished under the condition of slight increase in temperature in spite of the grain boundary having excellent *V–I* characteristics at room temperature. Such phenomenon is thought to correspond to the change of the chemical/physical state of ZnO varistors. Though the reason why the nonlinear behavior appears is still not clarified, the experimental result in Fig. 5 suggests at least that such chemical/physical state of grain boundary is easily affected by ambient factors, such as temperature and atmosphere, and that may result in electrical degradation phenomena. This might express that the measuring method proposed in this paper is applicable to investigate degradation phenomena of several electroceramics.

## 4 Conclusion

A new experimental apparatus based on SEM to analyze the *V–I* characteristics of single grain boundaries of ZnO varistors was developed. boundaries and high resistivity of Zn–Sb–O complex oxide in ZnO varistors containing Bi, Mn, Co and Sb oxides were found out directly. Several results show that the method using the new apparatus is effective to analyze the electric behavior in micro/nanoscopic region of electroceramics.

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