Barrier formation of single junctions with oxidation in SrCoO₃-doped ZnO varistors sintered in a reducing atmosphere

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Nonlinear electrical properties of individual grain boundaries in SrCoO₃-doped ZnO varistor ceramics are investigated using a nano-prober system. In particular, the effect of post-annealing is clarified for them after sintering in a reducing atmosphere. The nonlinear characteristics are enhanced by annealing in air at above 600°C. The resulting characteristics are attributed to an increase of p-type carrier concentration in SrCoO₃ phase at grain boundaries. By annealing at a higher temperature (e.g., 800°C), the grain boundaries possess nonlinear characteristics similar to conventional Bi-doped ZnO varistors, as well as bulk-bodies.

Key-words : ZnO varistors, Grain boundary, SrCoO₃, Single junctions, Nonlinearity, Annealing, Oxidation, Barrier formation, Nano-prober, Reduction

1. Introduction

ZnO-based ceramic varistors are generally used to protect integrated circuits (ICs) in various electrical equipment from overvoltage surges because of high nonlinearity in their V–I properties.¹ In particular, since multilayer ceramic varistors (MLCVs) show excellent protection performance with small size, they are commonly employed in mobile devices.²–⁴ Advanced ICs are more susceptible to damage by overvoltage as electrostatic discharge and load dump surge.⁵ Enhancing protection performance is therefore, a most important requirement for MLCVs, which is provided by lowering varistor voltage (i.e., V₁mA which is voltages at a current of 1 mA) as break down voltage.⁵ However, because degradation of nonlinearity and stability occurs with decreasing V₁mA, the control of V₁mA is limited within practical characteristics.⁶⁻⁷ The lower limits of V₁mA in conventional Pr- and Bi-based MLCVs are thus V₁mA = 6.8–8 and 12 V, respectively.⁸ The authors have recently found that SrCoO₃-doped ZnO varistors exhibit remarkably low V₁mA such as 5.6 V with high nonlinearity and stability despite below the conventional limits.⁹ This excellent varistor property is attributed to lower potential barriers comprised of n–p (ZnO/SrCoO₃) and p–n (SrCoO₃/ZnO) heterojunctions.¹⁰ The nonlinearity is able to be obtained also by combination of sintering in a reducing atmosphere and post-annealing in air.¹⁰ MLCVs co-fired with Cu internal electrodes (Cu-MLCVs) are thus produced with practical characteristics.¹⁰ Nonlinearity in varistors sintered in a reducing atmosphere is provided with increasing p-type carriers in SrCoO₃ at grain boundaries, due to post-annealing effect.¹¹,¹² However, behaviors of individual single grain boundaries have yet to be revealed in the microstructure. Thus, we evaluated the variation in nonlinearity of many single grain boundaries in SrCoO₃-doped ZnO varistors by the direct measurement using a nano-prober system as reported in our previous study.¹³ In the present, from the results with various post-annealing temperatures, the process of barrier formation in the varistors is shown with the influence of conductive characteristics of SrCoO₃.

2. Experimental

All the samples used in this study were prepared by the solid-state reaction method using reagent-grade powders of ZnO and additives (SrCoO₃). SrCoO₃ as a precursor was synthesized from SrCO₃ and Co₃O₄. The nominal composition of samples in this study is ZnO + 2 mol % SrCoO₃. ZnO and SrCoO₃ were weighted in the stoichiometric ratio and ball-milled in wet mixing using polyethylene bottles with Zirconia balls and water for 20h. Dried mixed powders were granulated with an organic binder and passed through a mesh screen, then uniaxially pressed into cylindrical shapes. They were sintered at...
1040°C for 5 h in $P_{02} = 1.60 \times 10^{-9}$ MPa and post-annealed 400–800°C for 0.5 h in air.

For microstructural analysis, sintered disks were ground to about the mid-plane in thickness by SiC sandpapers and polished to remove mechanical damaged surface with water slurry containing finer alumina powders carefully. The polished surfaces are etched by dry etching process using CF$_4$. Electrical measurements of individual single grain junctions between two adjacent ZnO grains were performed using a nano prober system as shown in Fig. 1. Tungsten probes which have ohmic contact of W/ZnO with the grains were used for evaluation by direct contact by the same way of our previous study. 13) 20 measurement points were selected randomly in the surface for each sample, according to previous studies. 13),14) To confirm data reproducibility, the measurements were conducted four times at the same point. As the junction area between ZnO grains are unknown owing to having a large variation of grain sizes in the microstructure, we are not able to analyze them with the same current density. 13) Nonlinearity of a single junction was thus evaluated on the basis of the method by our previous study. 13) $V$–$I$ properties of single junctions were measured by applying voltage of 0 to 15 V with 0.1 V step. The maximum nonlinearity index ($\alpha_{\text{max}}$) was determined by $\alpha$-values [$\alpha = (\log I_2 - \log I_1)/(\log V_2 - \log V_1)$] which were calculated from the highest nonlinear point of $V$–$I$ property. 13) $V_{\text{max}}$ was defined with a voltage corresponding to obtained $\alpha_{\text{max}}$. 13) It is also a breakdown voltage at a grain boundary. Electrical measurements of bulk-samples were performed with Au electrodes ($\phi = 6$ mm) formed by sputter deposition on their upper and lower surfaces. $V$–$I$ properties of bulk-disks were evaluated using DC current from 1 mA to 1 mA, and voltages at measured currents were defined as $V_{\text{1mA}}$, $V_{\text{100mA}}$, $V_{\text{10mA}}$ and $V_{\text{1mA}}$, respectively. $\alpha_{\text{1mA}}$ is nonlinearity index defined by $V_{\text{1mA}}/V_{\text{10mA}}$. When the value of $\alpha_{\text{1mA}}$ is closer to 1, the resistance rapidly decreases with increasing of a current between 10 mA and 1 mA, and the nonlinearity is enhanced to ideal. 15) The break down voltage per a grain boundary ($V_{gb}$) is usually given as follows: $V_{gb} = V_{\text{1mA}}/N$, where $V_{\text{1mA}}$ is the voltage at a current of 1 mA and $N$ is numbers of grain boundaries between electrodes. 13) Conductive characteristics of SrCoO$_3$ post-annealed at various temperatures were quoted from our previous study. 12)

3. Results and discussion

3.1 $V$–$I$ characteristics for single junctions sintered in a reducing atmosphere

Shown in Fig. 2 are $V$–$I$ curves for the individual three single junctions at different grain boundaries in SrCoO$_3$-doped ZnO varistors, which are annealed at 800°C after sintering in a reducing atmosphere. Nonlinear $V$–$I$ properties of single grain boundaries are able to be obtained using direct measurement. It seems that they have various types of $V$–$I$ properties by $\alpha_{\text{max}}$ (e.g., single junction 1 = 1.1, single junction 2 = 4.4 and single junction 3 = 24.7). Such a variation in nonlinearity of them is found also in the microstructure within Bi-based ZnO varistors. 13) As reported in the previous studies, nonlinearity of single junctions of SrCoO$_3$-doped ZnO varistors also are distinguished by the degree of $\alpha_{\text{max}}$ as follows: 13),14) Good junctions with high nonlinearity ($\alpha_{\text{max}} \geq 10$) and bad junctions having low nonlinearity ($\alpha_{\text{max}} < 10$). It is reported in the previous research that $V$–$I$ characteristics of grain junctions are significantly affected by not only grain size (junction area) but also crystal orientation and donor concentrations of ZnO grains. 13),14)

As stated in the previous study, the precise measurement of nonlinearity is needed to be performed by statistically analyzing many ZnO/ZnO grain junctions. 13) In the present, $V$–$I$ curves are evaluated for 20 single junctions between ZnO grains, each of which is post-annealed at various temperatures. From the results of SrCoO$_3$-doped ZnO varistors by reduced sintering, we discuss variations of the electrical barrier state and bulk properties with oxidation at grain boundaries.

3.2 Variation in nonlinearity of single junctions with post-annealing temperature

Frequency distributions of $\alpha_{\text{max}}$ and $V_{\text{max}}$ of each grain boundaries in the samples post-annealed at 400 and 800°C are presented in Figs. 3 and 4, respectively. Values of

Fig. 1. Scanning electron microscope image of direct measurement of a single junction in SrCoO$_3$-doped ZnO varistors sintered in a reducing atmosphere.

Fig. 2. $V$–$I$ curves of three junctions in SrCoO$_3$-doped ZnO varistors post-annealed at 800°C after reduced sintering ($P_{02} = 1.60 \times 10^{-9}$ MPa).
$V_{1mA \cdot mm^{-1}}$, $V_{gb}$ and $\alpha_{10\mu A}$ of bulks are listed on Table 1 for comparison with those values obtained with micro-prober measurements. $V_{1mA \cdot mm^{-1}}$ is calculated from $V_{1mA}$ normalized by unit thickness of bulk-bodies. As shown in the table, high nonlinearity of bulk varistors appears strongly at post-annealing temperature of 800°C, whereas is not at 400°C. $\alpha_{10\mu A}$ and $V_{1mA \cdot mm^{-1}}$ show significant improvements from 22.9 to 1.04 and 0.8 to 1183 V in the temperature range of 400 to 800°C. It is evident from the result that a considerable difference is found between them. As post-annealing is performed at higher temperature, single junctions with high $\alpha_{max}$ are clearly documented to increase in the microstructure as well as an enhancement of $\alpha_{10\mu A}$ in bulk-disks. From 400 to 800°C, both of $\alpha_{max}$ and $V_{\alpha_{max}}$ increase significantly (e.g., 1.0–7.4 to 0.9–69 and 0–2.5 V to 0–3.8 V).

Figure 5 gives the relation between $\alpha_{max}$ and $V_{\alpha_{max}}$ when post-annealed from 400 to 800°C. We have found that single junctions having high $\alpha_{max}$ show high $V_{\alpha_{max}}$. The correlation is shown also in our previous study on Bi-based. It may be common in polycrystalline varistors, regardless of the additive systems (Bi-, Pr-based and SrCoO$_3$-doped). It is notable that SrCoO$_3$-doped ZnO varistors show the lowest $V_{gb}$, regardless of the same degree of $\alpha_{10\mu A}$. The reason probably is that the barrier structure of grain boundaries is different from conventional varistors.

Also, good junctions with high $V_{\alpha_{max}}$ (e.g., >3V) are obtained due to post-annealing at 800°C. These results indicate strongly that post-annealing has a key role in barrier formation at grain boundaries. Though two points apparently deviate from the correlation, much deviations probably are caused by the measurement error induced by the contact and positioning of probe. And more, Fig. 6 is variations of the mean values of $\alpha_{max}$ and $V_{\alpha_{max}}$ as a func-

![Fig. 3](image_url)

**Fig. 3.** Frequency distributions of $\alpha_{max}$ of SrCoO$_3$-doped ZnO varistors [(a) 400°C and (b) 800°C].

![Fig. 4](image_url)

**Fig. 4.** Frequency distributions of $V_{\alpha_{max}}$ of SrCoO$_3$-doped ZnO varistors [(a) 400°C and (b) 800°C].

![Fig. 5](image_url)

**Fig. 5.** Relation between $\alpha_{max}$ and $V_{\alpha_{max}}$ of SrCoO$_3$-doped ZnO varistors when post-annealed at 400 and 800°C.

| Post-annealing temperature/°C | $V_{1mA \cdot mm^{-1}}$ $\alpha_{10\mu A}$ | $V_{gb}$/V |
|------------------------------|---------------------------------|-----------|
| 400                          | 0.8                             | 22.9, 1183 |
| 800                          | 1183                            | 1.04, 1.70 |

Table 1. $V_{1mA \cdot mm^{-1}}$ and $\alpha_{10\mu A}$ of SrCoO$_3$-doped ZnO varistors when post-annealed at post-annealed at 400 and 800°C.
tion of post-annealing temperature. The influence of post-annealing temperature is apparent on $V-I$ behavior of junctions. The elevated post-annealing temperature results in an increase of both of them. In particular, the significant enhancement (0.58 to 1.23 V) of $V_{\text{amax}}$ occurs at 600 to 700°C. On the other hand, $\alpha_{\text{max}}$ remarkably increases to 10.9 at 800°C, three times more than 3.36 at a temperature of below 700°C. The temperature gap ($\approx$100°C) between improvements of $\alpha_{\text{max}}$ and $V_{\text{amax}}$ might indicate that the annealing effect is different by characteristics between them. In this regard, further examinations would be needed to clarify that. These results reveal that most of grain-boundary barriers are formed in the microstructure post-annealed over a temperature range of 600 to 800°C. However, nonlinearity of bulk bodies which are sintered in air is higher than that of post-annealed at 800°C after reduced sintering.\(^{6,10}\) Thereby, it is suggested that, by an appropriate heat treatment process such as post-annealing, a further improvement is able to be achieved up to the nonlinear characteristics of air-sintered.

### 3.3 Barrier formation with increasing p-type carrier concentration at grain boundaries

As reported in the previous study, p-type carrier concentration in SrCoO$_3$ at grain boundaries is enhanced by the post-annealing effect after decreased with reduction sintering, providing nonlinear properties.\(^{12}\) This suggests that the formation of potential barriers originates from an increase of p-type carriers of SrCoO$_3$ at grain boundaries. Thus, we have investigated the relation between nonlinear characteristics ($\alpha_{\text{max}}$ and $V_{\text{amax}}$) of single junctions and conductivity of SrCoO$_3$ with various post-annealing temperatures.\(^{12}\) The results are shown in Fig. 7. When post-annealed over 600°C, $\alpha_{\text{max}}$ and $V_{\text{amax}}$ as junctionnonlinearity simultaneously show exponential improvements with SrCoO$_3$ conductivity ($>1.4 \times 10^{-3}$ S cm$^{-1}$).\(^{12}\) It is found from the results that p-type carrier density in the grain boundary region obviously has an important role in nonlinear action of SrCoO$_3$-doped ZnO varistors.

Based on the results, schematics of the barrier-forming process are experimentally given in Fig. 8, depending on p-type carriers of SrCoO$_3$ with post-annealing temperature. As the result, we were able to confirm our speculation on the barrier formation, which is inferred from bulk properties.\(^{10}\) The process is distinguished into three temperature regions [(a) below 600°C, (b) 600–800°C, and (c) above 800°C], being dependent of post-annealing temperature. Usually, ZnO grains should be n-type conductivity, regardless of the heat treatment conditions.\(^{17}\) On the other hand, as described above, p-type carriers are led to increase in SrCoO$_3$ at grain boundaries, owing to the diffusion of O$_2$ by post-annealing from 600 to 800°C, and thereafter (>800°C) further increase with a high level of conductive characteristics.\(^{12}\) Therefore, the barrier-forming process can be considered as the schematics with post-annealing temperature. In region (a), potential barriers should not be formed in varistors because of low density degree of p-type carriers.\(^{12}\) The post-annealing effect in region (b) increases single junctions having high nonlinearity with an enhancement of p-type carrier concentration ($\approx$1.5 $\times$ 10$^{-1}$ S cm$^{-1}$). Further, when post-annealed above 800°C [i.e., region (C)], an increment of nonlinear single junctions saturates in varistors with the same level of a large concentration of p-type carriers as those of sintered in air.

From the present and previous results, because of the post-annealing effect, grain boundaries (SrCoO$_3$) with oxygen deficiency are oxidized, exhibiting the nonlinear electrical behavior with p-type carrier densification.\(^{12,15,16}\) The control of high oxidation state in grain-boundaries is experimentally found to be of extreme importance to give significantly non-ohmic $V-I$ characteristics for SrCoO$_3$-doped ZnO varistors, which is sintered in a reducing atmosphere. From the results of direct measurement, it is evident that potential barriers are produced with increasing the p-type carriers of SrCoO$_3$. However, measurement data is still insufficient to precisely characterize the results. A larger number of experimental points should be statistically required to obtain high-precision results on enhanced nonlinearity with the p-type carrier concentration caused by post-annealing. However, the result obtained clearly gives us the direction of the improvement. It is a further enhancement of single junctions with strongly non-ohmic $V-I$ behavior, owing to high carrier density of SrCoO$_3$ at grain boundaries. The carrier densification probably is not intrinsically sufficient to provide highly nonlinear characteristics, due to the limit (i.e. 700°C) of
annealing temperature so as not to cause oxidation of internal electrodes in porous sintered MLCVs (porosity ≥ 20%). By being oxidized at a higher temperature at 1000°C, reduced SrCoO₃ shows the same conductivity level as air-sintered. Thus, assuming that further dense varistors could be produced by improvement of sintering process, nonlinearity should be enhanced to the same degree as that of SrCoO₃-doped ZnO varistors sintered in air. In consequence, it is conceivable that MLCVs by reduced sintering have a possibility of becoming characteristics of air-sintered bulk-bodies.

3.4 Single junction nonlinearity of SrCoO₃-doped ZnO varistors by reduced sintering, compared to conventional ones

As practical ZnO varistors are multi-junction devices with many nonlinear barriers, $V$–$I$ characteristics of bulk ceramics are examined in this study as well. The results are presented below, and are thus discussed to compare nonlinearities between SrCoO₃-doped and conventional Bi-based ZnO varistors. On the basis of the definition, assuming that the highest nonlinear behavior occurs at around 1 mA, the estimated voltage (i.e., $V_{ph}$) should basically correspond to $V_{max}$ as the mean value of single junctions by direct measurement. In this way, $V$–$I$ curves of each junction can be scaled individually by using the highest nonlinear region, to describe the bulk varistors. Shown in Table 2 are $I_{max}$ of a current giving the highest nonlinearity and $\alpha_{max}$ as the voltage ratio between $I_{max}$ and 0.1 $I_{max}$ in bulk properties when post-annealed at various temperatures. $\alpha_{max}$ is defined by $V_{max}/V_{0.1max}$. $I_{max}$ shifts to lower current with post-annealing temperature, simultaneously showing the improvement of nonlinearity as a decrease of the voltage ratio ($\alpha_{max}$). As the result, bulk varistors post-annealed at 800°C possess the highest nonlinearity between 10 and 100 μA. This result indicates that the microstructure is comprised of junctions aggregated with the development of significantly enhanced nonlinearity, due to post-annealing around 800°C. Because $V$–$I$ property in the current region between 10 μA and 1 mA is very important in practical use, we compare nonlinearities of single junctions and bulk of SrCoO₃-doped ZnO varistors post-annealed at 800°C and those of Bi-based.

Table 3 gives characteristics of them. It is shown from the table that SrCoO₃-doped ZnO varistors sintered in a reducing atmosphere can have the same nonlinear degree as conventional Bi-based, whether polycrystalline or not (i.e., bulk-ceramics and a single junction). From results of $V_{max}$ and $\alpha_{max}$ ($=1.30$ V and 10.86), nonlinear $V$–$I$ curves of single junctions are demonstrated to be similar to those of Bi-based ZnO varistors ($=1.78$ V and 8.71). Also, frequency distributions of $\alpha_{max}$ as nonlinearity in the microstructure are good agreement with each other. Single junctions with high $\alpha_{max}$ (e.g., ≥10) account for 33% of measured points in varistors after post-annealing at 800°C, as well as a proportion of 27% in Bi-based. Since two types of varistors have a large number of grain boundaries between the electrodes, the difference of the numbers does not affect the nonlinear characteristics ($V_{max}$ mm⁻¹ and $\alpha_{max}$) for bulk (Supporting information is shown in Table 4). Thus, $V_{max}$ ($=1.30$ V) by direct measurement is

| Post-annealing temperature / °C | (a) ~ 600°C | (b) 600 ~ 800°C | (c) 800°C ~ |
|--------------------------------|-------------|-----------------|-------------|
| Oxidation and barrier formation state |  |  |  |
| [Fig. 8. Schematics showing barrier-forming process with an increase of p-type carrier concentration of SrCoO₃ due to post-annealing effect.](#) |
| Conductivity of SrCoO₃ additive / S · cm⁻¹ | ~1.32 × 10⁻³ | ~1.59 × 10⁻² | 3.06~ |
| Table 2. $I_{max}$ and $\alpha_{max}$ of bulks of SrCoO₃-doped ZnO varistors in each post-annealing temperature |
| $I_{max}$ | 1 mA | 1 mA | 1 mA | 100 μA |
| $\alpha_{max}$ | 1.12 | 1.08 | 1.07 | 1.04 |

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**Table 2.** $I_{max}$ and $\alpha_{max}$ of bulks of SrCoO₃-doped ZnO varistors in each post-annealing temperature

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**Figure 8.** Schematics showing barrier-forming process with an increase of p-type carrier concentration of SrCoO₃ due to post-annealing effect.
confirmed to agree with $V_{gb}$ (≈1.70 V) within 25% error in SrCoO$_3$-doped ZnO varistors post-annealed at 800°C. However, error in our previous study on Bi-based ZnO varistors is about 10%. The difference between $V_{\text{max}}$ and $V_{gb}$ probably arises from the percolation effect along grain boundaries with low nonlinearity. A further examination might be needed for more precise analysis to clarify it. Results obtained in this research demonstrate that an enhancement of p-type carrier concentration in SrCoO$_3$ (i.e., at grain boundary region) plays a crucial role in improving nonlinearity of SrCoO$_3$-doped ZnO varistors to that of Bi-based. Therefore, we emphasize here that substantial diffusion of O$_2$ to grain boundaries within reduced varistors is key to inducing a further improvement of MLCVs co-fired with base metal electrodes. However, it is not clear yet whether oxygen diffusion fully occurs along grain boundaries within the bulk body or not. Further study is required to clarify the limit of the nonlinearity improvement, which is to examine effects of sintered density (i.e., pores) and grain size on oxygen diffusion.

4. Conclusions

In this paper, we have studied the variation in nonlinearity of single junctions within SrCoO$_3$-doped ZnO varistors post-annealed at various temperatures after reduced sintering. $V-I$ curves are evaluated for single junctions by direct measurement using a nano-prober system. Results are presented in comparison with those of Bi-based, including properties of bulk bodies. Our findings are listed below: (1) Nonlinearity of single junctions in the reduced varistors is drastically enhanced with oxidation by post-annealing around 600°C. (2) The enhanced nonlinearity is caused by an increase of p-type carrier concentration in SrCoO$_3$ between ZnO grains with n-type carriers. (3) By post-annealing at a further high temperature (e.g., 800°C), junctions within SrCoO$_3$-doped ZnO varistors become similar nonlinear characteristics to commercial Bi-based, as well as bulk-bodies.

In consequence, in the present, substantial O$_2$ diffusion to the whole grain boundaries (SrCoO$_3$) is found to be essential for a further improvement of MLCVs co-fired with base metal electrodes. Likewise, nonlinear characteristics of conventional Bi/Pr-doped ZnO varistors are improved due to oxidation of grain boundaries as well. Therefore, we believe that the study of SrCoO$_3$-doped ZnO varistors is able to certainly contribute to understanding varistors and the nonlinear properties. Accordingly, it is notable that the results lead to clearly give us the direction of performance enhancement of varistors.

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