Relation between nonlinearity and semiconducting characteristics of SrCoO₃ additive in ZnO varistors sintered in a reducing atmosphere

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Air-sintered SrCoO₃ is strongly reduced at 1020°C in P\(_{\text{O}_2}\) = 1.6 × 10⁻⁹ MPa and then post-annealed at various temperatures in air. The conductive and structural characteristics are examined, comparing them with those of air-sintered. Although annealing in a reducing atmosphere breaks down SrCoO₃ to several compounds, SrCoO₃ is re-synthesized by post-annealing above 800°C. When post-annealed at 1000°C, the oxidation state of SrCoO₃ is believed to be the same higher level as that of sintered in air. The result shows that, enhancement of p-type carriers in SrCoO₃ at grain boundaries leads to nonlinearity improvement of SrCoO₃-doped ZnO varistors sintered in reducing atmospheres.

Key-words : ZnO varistors, Grain boundary, Reduction, Annealing, Oxidation, SrCoO₃, Electrostatic discharge, Stability, Suppression performance, Resistivity

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1. Introduction

ZnO-based ceramic varistors are used as a means to protect integrated circuits (ICs) in various electronic devices against overvoltage surges due to excellent nonlinear \(V-I\) characteristics. Because of the protection performance with small size, multilayer ceramic varistors (MLCVs) are frequently employed mainly in mobile equipment. Recent advanced ICs have been low stability to electrostatic discharge (ESD), tending to be easily destroyed. Therefore, it is strongly required for MLCVs to enhance ESD protection performance as an important characteristic. Improvement of ESD suppression is generally given by lowering varistor voltage \((V\text{\textsubscript{imA}})\) as breakdown voltage. However, since degradation of stability against ESD and nonlinearity usually occurs with a decrease in \(V\text{\textsubscript{imA}}\) the improvement by the control of \(V\text{\textsubscript{imA}}\) is limited within characteristics as practical devices. Conventional Pr- and Bi-based MLCVs thus have lower \(V\text{\textsubscript{imA}}\) limits of 6.8–8 and 12 V, respectively. Recently, authors have found that MLCVs using SrCoO₃-doped ZnO ceramics exhibit lower \(V\text{\textsubscript{imA}}\) of 5.6 V than conventional two types, maintaining both high nonlinearity and ESD stability. Additionally, cost reduction also is strongly needed for MLCVs. Conventional MLCVs were covered with precious metals (Ag, Pd, Au and Pt) as internal electrodes, which have a large proportion of internal electrode cost to overall. It is shown from previous studies that Cu-MLCVs have the probability of considerable cost reduction as well as enhanced performance. MLCVs using SrCoO₃-doped ZnO are reported to be able to possess both practical nonlinearity and ESD stability, being sintered with base metals such as Cu in a reducing.

Nonlinearity of SrCoO₃-doped ZnO varistors when sintered in a reducing atmosphere is found to arise due to post-annealing effect above 600°C. As stated in our previous paper, nonlinear characteristics of SrCoO₃-doped ZnO originates from barriers comprised of n-p (ZnO/SrCoO₃) and p-n (SrCoO₃/ZnO) hetero junctions. It is believed that ZnO grains keep n-type conductivity regardless of post-annealing. On the other hand, because SrCoO₃ at grain boundaries has a certain degree of oxygen deficiency as a perovskite-like compound with SrCoO₃−δ, it should be extremely sensitive to annealing condition. This suggests that the formation of potential barriers is closely related to variations in the oxygen non-stoichiometry. It, therefore, seems likely that SrCoO₃−δ in a higher oxidation state by post-annealing would bring the barriers at grain boundaries, causing enhanced nonlinearity. However the mechanism of barrier formation giving rise to non-ohmic behavior is not yet clarified in the ZnO varistors by the combination of sintering in a reducing atmosphere and post-annealing. To reveal it, semiconducting characteristics with p/n-types are examined for pre-reduced SrCoO₃−δ when post-annealed at various temperatures. This study is intended to report the mechanism of barrier formation causing nonlinearity of SrCoO₃-doped ZnO varistors, which are produced by reduction-sintering and air-annealing.

2. Experimental

All SrCoO₃ samples used in this research were produced by the solid-state reaction method, using reagent-grade powders of SrO, CoO, and CuO. SrO, CoO, and CuO were first weighted in the stoichiometric ratio, respectively. These raw materials were ball-milled in wet blending using polyethylene bottles with zirconia balls and water for 20 h. Dried mixed powders were granulated with an organic binder and passed through a mesh screen, then pressed into cylindrical shapes by uniaxial pressing. Compacted disks were sintered at 1120°C for 10 h in air to synthesize SrCoO₃−δ. They were then reduced in \(P\text{\textsubscript{O}_2}\) = 1.6 × 10⁻⁹ MPa for...
5 h, and post-annealed at 400–1000°C. The crystal structure in the samples was identified by powder X-ray diffraction (XRD) analysis. XRD measurements were conducted from 10 to 80° for 2θ with CuK radiation. Seebeck coefficient was determined from thermal electromotive force and the temperature difference between two points on the surface of specimens, which are caused by heating one side.11) Resistivity was measured by four-terminal method (MCP-T 700, Mitsubishi Chemical Analytech Co., Ltd.). Au electrodes not having contact resistance were formed by sputter deposition on the contact area to perform Seebeck and resistivity measurements. $V-I$ properties of SrCoO$_3$-doped ZnO varistors were evaluated using DC current, and voltages (defined as $V_{1mA}$) at a current of 1 mA are termed varistor voltage. $\alpha_{1mA}$ is nonlinearity index defined by $V_{1mA}/V_{10mA}$.

3. Results and discussion

3.1 Crystal structure of reduced and post-annealed SrCoO$_3$–δ

XRD measurements were carried out for reduced and post-annealed SrCoO$_3$–δ to analyze the crystal structures within ZnO varistors sintered in a reducing atmosphere. XRD patterns are shown in Fig. 1. The structure when sintered in air is confirmed to be a single phase of SrCoO$_2.52$ on the basis of XRD analysis that annealing in a reducing atmosphere breaks down SrCoO$_3$–δ to compounds as Sr$_2$CoO$_{6.13}$, Co$_3$O$_4$, SrO, Sr$_2$Co$_{2.52}$O$_7$, and SrO.12–15) However, SrCoO$_3$ phases with at most, three different structures are found to again appear instead of their compounds, by reaction annealing above 800°C in air, whereas not being produced below 800°C. Re-synthesized SrCoO$_3$–δ comprises the matrix phase (SrCoO$_2.52$) of hexagonal and a small amount of extra two structures (orthorhombic and tetragonal as SrCoO$_{2.5}$) decreasing with post-annealing temperature.16,17) Eventually, SrCoO$_3$–δ annealed at 1000°C demonstrates the same XRD pattern of the only high oxidation structure as sintered in air. The result on the phase relation indicates that oxidation of reduced SrCoO$_3$ proceeds with an increase of annealing temperature. Weight variation with the oxidation was thus evaluated for them, and could be detected easily after air-annealing. Figure 2 is the change rate of SrCoO$_3$–δ weight before and after post-annealing at various temperatures. Post-annealing up to 700°C is not able to give the variation in the weight change rate from as-annealed in a reducing atmosphere, showing the constant values. In contrast, SrCoO$_3$–δ is found to show an increase in weight with temperature above 800°C. As the variations in the weight and crystal phases occur simultaneously at 800°C, a higher oxidation state in SrCoO$_3$–δ is believed to be produced by air-annealing effect. From their results, the same level of oxidation state as sintered in air is likely to be achieved in reduced SrCoO$_3$–δ as well, when post-annealed at 1000°C.

3.2 Electrical properties of post-annealed SrCoO$_3$–δ

SrCoO$_3$-doped varistors do not show nonlinearity after sintering in a reducing atmosphere.7) This suggests that electrical barriers of n-p-n junction should not be formed at grain boundaries without post-annealing. First, to analyze carrier type in SrCoO$_3$–δ and the characteristics, which were reduced in $P_{O2} = 1.6 \times 10^{-9}$ MPa for 5 h and post-annealed at various temperatures, we have evaluated electromotive force of them and determined Seebeck coefficient. Illustrated in Fig. 3 is dependence of Seebeck coefficient of SrCoO$_3$–δ for post-annealing temperature. The values of Seebeck coefficient are positive indicating p-type conductivity. Showing lower levels (<170 μV/K) in a temperature range of below 700°C, Seebeck coefficient around 800°C increases drastically more than double for post-annealed at 400 to 700°C. From the results and XRD analysis, the p-type carrier concentration is found to increase at a relatively higher temperature (> approximately 800°C), simultaneously forming a perovskite-like compounds (hexagonal) with the formula SrCoO$_{2.52}$. On the basis of

![Fig. 1. Powder XRD patterns of SrCoO$_3$–δ: sintered in air, reduced and post-annealed (400–1000°C).](image)

![Fig. 2. Change rate of weight of SrCoO$_{3.9}$ after post-annealing (400–1000°C).](image)
heterojunction model comprising n-p (ZnO/SrCoO$_3$) and p-n (SrCoO$_3$/ZnO), SrCoO$_{3.5}$ conductivity with p-type carrier density should have an important role in formation of electrical barriers (n/p/n) between ZnO grains with an n-type.

**Figure 4** gives relation between conductivity of SrCoO$_{3.5}$ and post-annealing temperature. It is evident that the conductivity increases with post-annealing temperature. Conductivity of SrCoO$_{3.5}$ starts to gradually increase owing to enhanced p-type carriers when post-annealed at 600°C, then reaching 3.1 S/cm at 1000°C. In particular, re-synthesis of SrCoO$_{3.5}$ occurring between 800 and 1000°C as presented in Fig. 1, involves a large variation of conductivity ($1.7 \times 10^{-2}$ to 3.1 S/cm) about 10 to 1000 times more than post-annealed below 600°C. As the result, the conductivity for a temperature of 1000°C in Fig. 4, is the approximately similar enhanced level to that (= 4.0 S/cm) of air-sintered (data not shown in Fig. 4), thereby, being a single hexagonal structure with a relatively higher oxidation state (iq., SrCoO$_{2.52}$). Moreover, as described above, Seebeck coefficient reveals the highest value of 350 μV/K around the temperature of 800°C as well. Consequently, it can be seen from the results that annealing over a temperature range of 800 to 1000°C brings enhancing p-type carriers with oxidation in SrCoO$_{3.5}$.

### 3.3 Role of SrCoO$_3$ additive in nonlinearity of SrCoO$_{2.5}$-doped ZnO varistors sintered in a reducing atmosphere

Role by SrCoO$_3$ additive in nonlinearity of SrCoO$_{2.5}$-doped ZnO varistors sintered in a reducing atmosphere, is examined from the basis of properties in the bulk disks described above. It can be understood that increasing nonlinearity by post-annealing in air probably is responsible for an increment of p-type carriers in SrCoO$_3$. Presented in **Fig. 5** is varistor characteristics ($V_{\text{1mA}}$/$\alpha$) as a function of post-annealing temperature. Here, $V_{\text{1mA}}$ is obtained from $V_{\text{1mA}}$ (ie., varistor voltage at 1 mA) normalized by unit thickness of bulk-bodies. As shown in **Fig. 5**, increase of $V_{\text{1mA}}$ and improvement of $\alpha$ are able to be provided because of post-annealing effect. Nonlinearity of SrCoO$_{2.5}$-doped ZnO varistors is currently thought in the potential barrier model as stated in our previous papers, comprising n-p (ZnO/SrCoO$_3$) and p-n (SrCoO$_{3.5}$/ZnO) between ZnO grains. It is thus conceivable from the above bulk-properties of SrCoO$_3$ that the nonlinearity improvement by post-annealing is attributed to an enhancement of conductivity in SrCoO$_{3.5}$ with p-type semi-conducting characteristics. However, from detailed data analysis of Figs. 4 and 5, a slight difference as 600 and 800°C is found between each post-annealing temperature giving two enhancements of SrCoO$_{3.5}$ conductivity and nonlinearity in the varistors. Specifically, nonlinearity improvement of SrCoO$_{2.5}$-doped varistors exhibits a shift toward lower temperature (= 200°C) than an increase in SrCoO$_{3.5}$ conductivity. In general, diffusion along grain boundaries proceeds easier and faster than in bulk grains because diffusion coefficient in grain boundaries is several orders of magnitude higher than in volume. Based on the general understanding of diffusion behavior, oxygen diffusion rate to SrCoO$_{3.5}$ existing in grain boundaries should increase compared to into SrCoO$_{3.5}$ as bulk body. Besides, diffusion along grain boundaries is greatly affected by impurities and non-stoichiometry as reported in the previous study. It is thus likely that lower temperature shift from 800 to 600°C is caused by the difference of diffusion coefficient between grain boundaries and grains. However, it is not yet fully resolved in the present. Even so, this research has revealed that nonlinearity of SrCoO$_{2.5}$-doped ZnO varistors is enhanced with increasing p-type conductivity of SrCoO$_{3.5}$ by post-annealing. Hence, the characteristic variation of SrCoO$_3$ varistors probably affects nonlinear characteristics as a device. To clarify the detailed process of barrier formation in the varistors, electrical analysis of single junctions is considered extremely effective for grain boundaries with n-p (ZnO/SrCoO$_3$) and p-n (SrCoO$_{3.5}$/ZnO) hetero junctions in the microstructure. It is thus believed, further studies to characterize the electrical variation of single junctions are required for understanding the barrier states within varistors, using direct measurement technique of individual grain boundaries.
4. Conclusions

In this paper, we have examined the variation in electrical properties of \( \text{SrCoO}_3\) by post-annealing at various temperatures in air, which is strongly reduced after air-sintering. Influence of the conductive characteristics on nonlinearity of \( \text{SrCoO}_3\)-doped ZnO varistors is analyzed from the basis of results. Our findings are listed below: (1) After being broken down by annealing in a reducing atmosphere, \( \text{SrCoO}_3\) is re-synthesized by post-annealing above 800°C, which possesses the same oxidation state level in the hexagonal structure as air-sintered. (2) Conductivity of \( \text{SrCoO}_3\) with a p-type carrier starts to gradually increase around post-annealing at 600°C, then shows a considerable increment (1.7 \( \times \) 10\(^{-2}\) to 3.1 S/cm) at from 800 up to 1000°C. (3) Nonlinearity improvement of \( \text{SrCoO}_3\)-doped ZnO varistors by post-annealing after reduction sintering probably is attributed to an enhancement of p-type carriers in \( \text{SrCoO}_3\) between ZnO grains with an n-type. However, annealing behavior of \( \text{SrCoO}_3\)-doped ZnO varistors is demonstrated to be slightly different from the bulk and in the grain boundary, in that nonlinearity of varistors improves at a lower temperature than an increase in conductivity of \( \text{SrCoO}_3\)-doped ZnO varistors by post-annealing after reduction sintering probably is attributed to an enhancement of p-type carriers in \( \text{SrCoO}_3\) between ZnO grains with an n-type. Consequently, it is considered that the homogenous control within varistors is an intrinsically important for improvement of MLCVs.

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