This would be the first report that transmission line pulse (TLP) analysis for stability against electrostatic discharge (ESD) of Cu-MLCVs reveals the effect of ZnO grain resistivity under ESD zapping. The influence has been evident from results over a wide range of $V-I$ characteristics provided by TLP measurement. ESD stability is found to be closely related to variations of ZnO grain resistivity, greatly depending on oxygen partial pressure ($P_{O_2}$) during sintering. The lowering of ZnO resistance leads to high stability against ESD. Thus, the stability is demonstrated to be drastically improved with decreasing ohmic resistance down to the lowest levels by sintering below $P_{O_2}$ of $1.6 \times 10^{-9}$ MPa. Then, influence of Cu diffusion on their properties of MLCVs was investigated in bulk-disks of SrCoO$_3$ doped-ZnO with various CuO additions. The enhancement of ZnO grain resistivity is caused by the slight diffusion of Cu$^+$ during the sintering in a relatively weak reducing $P_{O_2}$ above $2.2 \times 10^{-9}$ MPa, resulting in low ESD stability. However, ZnO grain resistivity is not influenced by Cu diffusion below 0.005 mol % as CuO, thus Cu-MLCVs containing Cu-O~1mA~ as breakdown voltage have been considered bringing high ESD performance. It was confirmed experimentally that sintering of Cu-MLCVs in the optimum reducing atmosphere provides high ESD stability and significant suppression (about 1100 to 150 V) for ESD zapping at 8 kV under IEC61000-4-2. Cu-MLCVs obtained are able to have high protection performance as well as ESD stability at the same level as a device in practical use. Lowering of ZnO resistivity by a decrease of Cu diffusion is believed to give benefits to overall performance of Cu-MLCVs.

Key-words: ZnO varistors, Electrostatic discharge, Stability, Transmission line pulse, Base metal electrodes, Suppression performance, Resistivity, Cu diffusion

1. Introduction

Recently, because of highly non-linear $V-I$ characteristics, ZnO-based ceramic varistors are used as the standard for dangerous overvoltage-protection in various electrical equipment.

In particular, integrated circuits (ICs) used in mobile equipment are very susceptible to damage and easily destroyed by electrostatic discharge (ESD). ZnO-based multilayer ceramic varistors (MLCVs) in which are widely employed, due to the very excellent protection performance combined with small size. To protect rapidly advanced ICs for a variety of uses such as mobile and automotive equipment, an improvement of ESD suppression effect and cost reduction are further required for MLCVs in future. Because the effect of ESD suppression is able to be usually improved by lowering the varistor voltage ($V_{1mA}$), it is necessary for resolving this matter to lower $V_{1mA}$ as breakdown voltage. However, as lowering their varistor voltage, the non-linearity and stability against ESD are generally degraded. Conventional Pt- and Bi-doped MLCVs show the lower limit of $V_{1mA}$ = 6.8-8 and 12 V, respectively, which are produced using precious metals such as Ag, Pd, Au and Pt as internal electrodes. Thus, if base metals are able to be applicable to internal electrodes in low voltage MLCVs, the issues, including those related to protection performance, reliability and economy may be resolved simultaneously. For such a reason, SrCoO$_3$-doped ZnO varistors are one of the new candidates for MLCVs instead of conventional. Due to the low voltage characteristics of SrCoO$_3$-doped ZnO varistors, the MLCVs are able to have $V_{1mA}$ = 5.6 V with high non-linearity as well as ESD stability despite below the conventional lower limits. Further, the newly developed varistors can give us to reduce the cost of MLCVs as well. Non-linear $V-I$ property has been found to be obtained also by a combination of sintering in a reducing atmosphere and post-annealing. On the basis of this procedure, the MLCVs co-fired with Cu internal electrodes (Cu-MLCVs) could have the same level of electrical properties as those of sintered in air. During producing Cu-MLCVs, co-firing with Cu in which can affect the varistor properties by sintering and post-annealing conditions. For example, the post-annealing temperatures are thus limited to about 700°C, due to minimizing the influence of co-fired Cu electrodes such as the diffusion and oxidation on electrical properties. In specific, ESD stability greatly depends on oxygen partial pressure ($P_{O_2}$) during sintering, which is believed to be closely related to variations of ZnO grain resistivity and the microstructure. As described previously, the enhancement of ZnO grain resistivity when sintered in a relatively weak reducing ($P_{O_2}$ = $2.2 \times 10^{-9}$-$6.5 \times 10^{-9}$ MPa) probably has been caused by the slight diffusion of Cu$^+$ during the sintering (which is
detected by EPMA), resulting in low ESD stability. However, to the best of the authors’ knowledge, the resistivity of ZnO grains in varistor ceramics has never been evaluated under ESD stress, thereby, the relation between the resistivity and ESD stability has not been fully revealed. In the present study, we analyzed the resistivity of Cu-MLCVs up to high current region (eg., 10 A) under ESD zapping event by using transmission line pulse (TLP) technique. TLP is a short pulse (e.g., 50–200 nsec) measurement of $V-I$ property. Being similar to the ESD pulse, it should be used to characterize the electrical behavior of MLCVs under ESD testing. Therefore, the effect of co-firing with Cu electrodes on the resistivity was examined for Cu-MLCVs by TLP measurement. The results of TLP analysis show that the enhancement of Cu diffusion significantly provides the high resistivity of ZnO grains, causing decrement of ESD stability.

This paper attempts to initially illustrate the relation between ESD stability of Cu-MLCVs and linear resistivity in ESD stress by means of TLP measurement. It would be the first report that characterizing using TLP is shown to be useful to analyze the electrical property under an ESD event. Furthermore, influence of Cu diffusion on their properties of MLCVs was investigated in bulk-disks of SrCoO$_3$ doped-ZnO with various CuO additions. Finally, ESD suppression performance was evaluated for Cu-MLCVs with stabilization against ESD by the lowering of ZnO grains resistivity.

2. Experimental

All the samples used in this research were produced from reagent-grade powders of ZnO and additives (SrCoO$_3$) by the solid-state reaction method. SrCoO$_3$ was synthesized from SrCO$_3$ and Co$_3$O$_4$ as a precursor preliminarily. The nominal composition of the specimens in this paper was from ZnO + 0.5–2 mol % SrCoO$_3$ in typical commercial formulations for SrCoO$_3$-doped ZnO varistors on the basis of our United States Patent. ZnO and SrCoO$_3$ were weighed in the stoichiometric ratio, respectively. These raw materials were then ball-milled in wet blending using polyethylene bottles with zirconia balls and water for 20 h. Cu-MLCVs were produced using the conventional multilayer ceramic process. Details on the synthesis condition of MLCVs are given in our previous paper. The green chips with a functional layer between two internal electrodes were constructed into 1.17 mm in length (L), 0.6 mm in width (W) and 0.6 mm in height (H) and sintered at 1030°C for 5 h in $P_{O_2}$ = 5.3 × 10$^{-10}$–6.5 × 10$^{-9}$ MPa. After sintering, Cu-MLCVs were post-annealed at 700°C for 0.5 h in air. Resulting MLCVs was the size of 1.0 mm × 1.0 mm × 0.5 mm in L, W and H, respectively, having the functional layer thickness of 17 μm. And their edge faces were grinded with SiC sandpaper and terminated with In/Ga alloy-electrodes, electrical measurements were performed to obtain their $V-I$ characteristics. Their $V-I$ properties were evaluated using TLP measurement from 1 mA–15 A for an elevated voltage of a short pulse of 200 nsec. (HED-T5000-HC, HANWA Electronic Ind. Co., Ltd., Japan), and voltages at the measured currents were defined as $V_{10A}$, $V_{10mA}$, $V_{100mA}$ and $V_{15A}$, respectively.

The effect of co-firing with Cu internal electrodes was examined for bulk-bodies with CuO additions. The CuO levels were 0.003, 0.005, 0.03 and 0.05 mol % for ZnO in the nominal varistor composition. The bulk-disks with CuO were produced by conventional solid state reaction as mentioned above. The powder was uniaxially pressed into cylindrical shapes with a diameter of 13 mm and a thickness of about 1.5 mm. They were sintered at 1080°C for 5 h in $P_{O_2}$ = 1.6 × 10$^{-5}$ MPa. After annealing at 700°C for 0.5 h in air for disks, Au electrodes were formed on the upper and lower surfaces, and electrical measurements were then conducted. Their $V-I$ properties were evaluated using DC current from 1 μA–1 mA, and voltages at the measured currents were defined in the same way with TLP measurement. Similarly to evaluation of MLCVs, TLP measurement with small risk of destruction in high current, was used as well as for disks to characterize voltage as resistivity above 1 mA.

The ESD suppression was evaluated by applying ESD pulse of 8 kV by contact discharge, in accordance with International Electrotechnical Commission (IEC) 61000-4-2, using an ESD simulator. The values of the charged capacitor and discharge resistor were 150 pF and 330 ohm under ESD stress on human body model (HBM). The ESD testing circuit on MLCVs is shown in Fig. 1. The wave shape suppressed by Cu-MLCV was observed using an oscilloscope, and suppression voltage was determined from a maximum peak value.

3. Results and discussion

3.1 TLP analysis of effect of ZnO grain resistivity on ESD stability

To examine behavior of Cu-MLCVs under ESD zapping, we obtained $V-I$ characteristics of Cu-MLCVs sintered in various reducing atmospheres by using TLP technique. TLP measurement is very useful for the electrical characteristic analysis of MLCVs during an ESD event. Decreasing resistivity of ZnO grains is found to play an important role in enhancement of stability against ESD. The results of $V-I$ curve measured by TLP are presented in Fig. 2 [(a) overall characteristics between 0 and 20 A, (b) the expanded figure of voltage as a function of log I (0.005 to 0.05 A)], which could be given without damage to MLCVs due to the effect of a short pulse (200 nsec.). Their properties exhibited highly non-linear characteristics in current range up to 1 A, and then changed to linearly ohmic behavior between 1 and 15 A. Based on Schottky barrier model, non-linear characteristics of varistors have been attributed to potential barriers being
formed at grain boundaries, and linearity in high current responsible for ohmic resistance of ZnO grains. In the case of SrCoO$_3$ doped-ZnO, as stated in our previous paper, non-linearity arises from hetero-junctions comprising n-p (ZnO/SrCoO$_3$) and p-n (SrCoO$_3$/ZnO) between ZnO grains. The results over a wide range of current-voltage using TLP suggest that the dominant path of current flow above 1 A is through ohmic ZnO grains without potential barriers, because of linear $V$-$I$ behavior depending on applied voltage. It also is appeared from the results measured by TLP that $V$-$I$ curves especially in ohmic high-current region are significantly dependent on $P_{O_2}$ during sintering. Our previous study has indicated that ESD stability is believed to be mainly related to the lowering of ZnO grain resistivity and the increasing number of grain boundaries. In the present study, the effect of $P_{O_2}$ in sintering on linear resistivity in ESD stress was examined for their MLCVs to analyze the variation of ESD stability by different sintering atmospheres. The linear resistance of ZnO grains was determined from the slope of ohmic behavior at 10 A in $V$-$I$ curves. Figure 3 illustrates relation between $P_{O_2}$ and resistance determined from the slope of $V$-$I$ curves over 1 A in Fig. 2. The result reveals that the lowering of ZnO resistance leads to high stability against ESD. The resistance shows the lowest levels (2.0–3.4 Ω) over a wide range of 0.5 to 1.6 × 10^{-9} MPa in a strong reducing atmosphere, and then increases above 1.6 × 10^{-9} MPa considerably. Consequently, stability against ESD is demonstrated to be drastically improved with decreasing ohmic resistance down to the lowest levels by sintering below $P_{O_2}$ of 1.6 × 10^{-9} MPa. From these results, not only numbers of grain boundaries but also decreasing resistivity of ZnO grains are found to be extremely important for improvement of ESD stability. The lowering of ZnO resistivity should provide the enhancement of protection performance as well as ESD stability, due to capability of a large current flow under ESD zapping.

3.2 Influnc of Cu diffusion on ZnO resistivity and ESD stability

In the previous study, ZnO resistance in MLCVs seemed to be enhanced when sintered in a weak reducing ($\leq 1.6 \times 10^{-9} $MPa), owing to a small amount of Cu$^+$ diffusion which is detectable with EPMA. The variation in the resistance of ZnO grains may be attributed to grain growth, Cu diffusion and oxidation of Cu internal electrodes, depending on $P_{O_2}$ in sintering. In particular, the resistivity of Cu-doped ZnO is high and increased with Cu content. Thus, Cu-diffusion in SrCoO$_3$-doped ZnO would have the possibility to give rise to high resistivity of ZnO grains, resulting in the significant degradation of ESD stability. However, the Cu diffusion effect on $V$-$I$ behavior is still not clarified for SrCoO$_3$-doped ZnO varistors though the Cu diffusion is detected in Cu-MLCVs by means of an electron probe microanalyser (EPMA). $V$-$I$ characteristics was therefore analyzed for bulk-disks of SrCoO$_3$-doped ZnO varistors with CuO additions, using TLP measurement. CuO added as a starting material changes easily to metallic copper by reduction during heating in sintering, giving the same effect as diffusion of Cu-internal electrodes. Figure 4 is dependences of density of sintered body and grain size for various CuO addition levels. Both of them increased clearly with an increase of CuO addition. The results imply that densification and grain growth are accelerated simulta-
The amount of CuO is added. As shown in Fig. 6, CuO additions linear behavior in high current is not affected when even small non-linear region in related as follows:

\[ E = \frac{V_{\text{gb}}}{d} \]

where \( E \) is the electric field strength, \( V_{\text{gb}} \) is the voltage of a grain-boundary, and \( d \) is the thickness of the disk. The variation of \( V_{\text{gb}} \) curves is shown in Fig. 5. The CuO additions were found to have the same level of performance as those of conventional MLCVs, even if CuO below the affected level is contained in the varistors. However, as a small amount of Cu diffusion (e.g., CuO addition level below 0.005 mol%) cannot affect the original varistor property without Cu content, Cu-MLCVs should be able to have the same level of performance as that of conventional, if Cu diffusion is inhibited below the significant level.

### 3.3 ESD suppression performance of Cu-MLCVs

The lowering of ZnO resistivity should bring an enhancement of protection performance in Cu-MLCVs because of increasing current capability. Finally, ESD suppression effect was evaluated for Cu-MLCVs having high ESD stability by sintering in 1.0 and \( 1.6 \times 10^{-8} \) MPa under HBM in accordance with IEC61000-4-2. Figure 8 gives the wave shapes of ESD zapping at 8 kV, which show (a) source pulse and (b) after suppression for Cu-MLCVs. Evaluation results of Cu-MLCVs are presented in Table 1, compared to those of conventional MLCVs for Bi- and Pr-doped types. It is clear, from the results, that the Cu-MLCVs having high ESD stability possess significant ESD suppression effect. The peak voltage was drastically increased.
suppressed from about 1100 to 150 V approximately by the effect of the Cu-MLCV. The similar effect to the significant suppression is obtained for the other sintered in 1.0 × 10⁻⁹ MPa as well (data not shown). As the results, the effect of the lowering of ZnO resistivity could be confirmed also by evaluating ESD suppression performance. Based on $V-I$ properties using TLP in Fig. 2(a), the maximum current corresponding to 150 V of suppression voltage is roughly estimated to be around 40 A by extrapolation of the linear region in the curves, which to be able to flow to Cu-MLCVs during an ESD event. The results reveal that Cu-MLCVs can have ESD stability and suppression performance at the same level as practical devices. By the control of a sintering atmosphere (= 1.0 × 10⁻⁹–1.6 × 10⁻⁹ MPa), Cu diffusion in MLCVs decreases, therefore leading to the improvement of their performance.  

From results described above, due to lowering of ZnO resistivity by a decrease of Cu diffusion, Cu-MLCVs are found to have high protection performance as well as ESD stability at same level as a device in practical use. Consequently, the direction of development of MLCVs with base metal internal electrodes is given clearly for high performance and cost reduction. It is found to be essentially important for further improvement of performance to be a homogeneous microstructure also including in an electrical sense and enhancement of donor concentration in ZnO grains. The issues should be resolved in co-firing processing with base metal.

4. Conclusions

In this paper, we studied the variation in ESD stability of SrCoO$_3$ doped-MLCVs by co-firing with copper in various $P_{O_2}$. The relation between the stability and resistivity of ZnO grains was analyzed using TLP technique, including the effect of Cu diffusion in sintering. Also, ESD suppression performance as a protection device was evaluated for Cu-MLCVs having high ESD stability by sintering in optimum $P_{O_2}$ levels. Our findings are listed below: (1) ESD stability is improved drastically with decreasing of resistivity of ZnO grains, thus it is found to be important for enhancing ESD performance of MLCVs. (2) ZnO grains resistivity in varistors is not influenced by Cu diffusion below 0.005 mol% as CuO. Cu-MLCVs containing below the affected level were considered bringing high ESD stability. (3) It has been confirmed experimentally that sintering of Cu-MLCVs in the optimum reducing atmosphere provides high ESD stability and significant suppression (about 1100 to 150 V) for ESD zapping at 8 kV under IEC61000-4-2.

In the present, it is believed that the enhancement of electrical homogeneity and donor concentration in ZnO grains is essential for further improving performance of MLCVs. The resulting ESD performance of Cu-MLCVs could not outperform that in conventional, as both of which are similar level. Nevertheless, varistors studied, which are sintered in a reducing would have the intrinsic advantage of decreasing ZnO resistivity for the approaches. Thus, we emphasize that MLCVs with base metal electrodes can have strong potential to enhance the performance.

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