Effect of Ni and Cr on the stability of leakage current for spinel-reduced ZnO varistor ceramics

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With a new concept of reducing the spinel particles in ZnO varistor ceramics (ZVC), the molar ratio of Sb_2O_3 (M_S)/ Bi_2O_3 (M_B) and the effect of the sintering temperature (T_S) on densification behavior and varistor voltage (V_b : $V_{1\text{mA}}/\text{mm}$) were investigated. The densification behavior of ZVC during the sintering process was significantly affected by the M_S/M_B , and the densification curve was shifted to a lower temperature with a decreasing M_S/M_B . Based on these experimental results, four types of spinel-reduced ZnO varistor ceramics (SRZVC) were fabricated to investigate the effect of transition elements such as Ni and Cr on electric stability of the resistive leakage current (I_r). These experiments revealed that electric stability of I_r depended on the contained transition elements, and was influenced by the segregating of transition elements in spinel particles.

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Key-words : Varistor, Zinc oxide, Nickel oxide, Chromium oxide, Spinel

[Received September 6, 2010; Accepted December 16, 2010]

1. Introduction

ZnO varistor ceramics (ZVC) have been widely used for protecting electric products and electronic devices from excessive surge due to their highly nonlinear electric characteristics.¹⁾ It is well known that the switching function of ZVC is derived from the V – I nonlinear characteristics at the ZnO–ZnO grain boundaries, and several authors focused on the intergranular structure, and reported the existence of Bi_2O_3 at the ZnO–ZnO grain boundaries using Transmission Electron Microscope (TEM) analysis.^{2)–5)} Also Sb_2O_3 is a key additive for ZVC, which serves as a ZnO grain growth inhibitor.^{6,7)} During the sintering process, Sb promotes the formation of zinc antimonate spinel particles including various transition elements such as Ni, Cr, Mn and Co, and these spinel particles are mostly located inside the ZnO grains (especially those smaller than 1 μm) and at near the triple junction.

Over the high-current region ($\rho = 0.1$ – $10 \Omega\text{cm}$), the V – I curve of ZVC is considered to be affected by both the resistivity of the ZnO grains and the current path configuration. In terms of the resistivity of spinel particles, most of authors have been reported that spinel particles act as insulator and have less influence on V – I properties in ZVC.⁸⁾ S. Ezhilvalavan et al. reported that under appropriate oxidation conditions, spinel particles act as n-type semiconductor.⁹⁾ Thus, it is possible that reducing the existence ratio of spinel particles in the sintered body leads to extending the current path, and also leads to achieving the low resistivity at the high-current region.

Based on this concept, firstly the effect of the molar ratio of Sb_2O_3 (M_S)/ Bi_2O_3 (M_B) and the sintering temperature (T_S) on the

densification behavior and the varistor voltage V_b ($V_{1\text{mA}}/\text{mm}$) were investigated with the particular aim of reducing the spinel particles in ZVC. Secondly, the effect of transition elements such as Ni and Cr on the stability of the resistive leakage current (I_r), bismuth oxide crystals, and the elemental segregation of transition elements in SRZVC were investigated.

2. Experimental procedure

2.1 Sample preparation

The ZVC samples in this study were prepared by a conventional ceramic process. Industrial grade powders were used as the raw materials. In this study, $M_S + M_B$ for all samples was fixed at 1.27 mol % and the molar ratio of Sb_2O_3 (M_S)/ Bi_2O_3 (M_B) was ranged from 0.33 to 2.0. ZnO powder was mixed with Bi_2O_3 (M_B mol %), Sb_2O_3 (M_S mol %), NiO (0.5 mol %), Cr_2O_3 (0.1 mol %), MnO_2 (0.5 mol %), Co_3O_4 (0.4 mol %), B_2O_3 (0.1 mol %), and Al (NO_3)₃·9H₂O (0.004 mol %), and mixed powder was ball milled with distilled water for 40 h. A Poly Vinyl Alcohol (PVA) solution was used as a binder, and the mixed powder was pressed at 39 MPa into pellets 40 mm in diameter and 10 mm thick. The pressed pellets were sintered at 850–1000°C for 5–10 h in air, and aluminum electrodes were used to characterize the V_b and stability of I_r .

2.2 Characterization

The densification behavior of three different M_S/M_B samples during sintering process was determined by the Thermo Mechanical Analysis (TMA). The heating rate was 10°C/min. The V_b of each sample was characterized with DC high voltage source. The total AC current through the ZVC is composed of I_r and a capacitive current (I_c).¹⁰⁾ Therefore, the I_c at the constant applied AC (60 Hz) voltage was cancelled with an original system. During the I_r measurement, the applied voltage and

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Fig. 1. Densification behavior of ZVC; Heating rate: 10°C/min.

Fig. 2. Apparent density of ZVC as a function of M_S/M_B and sintering temperature (T_S).

temperature were fixed at $0.8 \times V_b$ and 120°C respectively. After characterizing the electric properties, the surface of the SRZVC samples were polished and chemical etched with 10% NaOH aqueous solution for 2 min. Thin film electrode of Au was applied to the surface of the sample using a sputtering method. The microstructural characterization of the samples was carried out by a Scanning Electron Microscope (SEM) and an Electron Probe Micro Analyzer (EPMA) system (JXA-8621MX, JEOL, Japan). The crystalline phase was also analyzed by the X-ray powder Diffraction (XRD) with CuK α radiation (MXP18V, Bruker AXS, Japan). The X-ray tube voltage and current was fixed at 40 kV, 200 mA.

3. Results

3.1 Densification behavior

Figure 1 shows the densification behavior of ZVC with three different M_S/M_B . Each value on the curve indicates temperatures at half maximum shrinkage. It was confirmed that the densification behavior of ZVC is significantly affected by the M_S/M_B , and the densification curve was shifted to a lower temperature with a decreasing M_S/M_B as J. Kim et al. previously reported.¹¹⁾ These results suggest that SRZVC with a low (around 0.5) M_S/M_B can be sintered at relatively low temperature (around 1000°C).

3.2 Apparent density and V_b

The apparent density and V_b as a function of M_S/M_B sintered at 850–1000°C were investigated. The total amount of $M_B + M_S$ in all samples was fixed at 1.27 mol%. **Figure 2** shows the relationship between M_S/M_B and the apparent density. It is clearly showed that the apparent density of samples sintered

Fig. 3. Varistor voltage (V_b) of ZVC as a function of M_S/M_B and sintering temperature (T_S).

Table 1. Composition of transition elements

Sample	Composition of transition elements				M_S/M_B
A	Ni	Cr	Co	Mn	0.45
B		Cr	Co	Mn	
C	Ni		Co	Mn	
D			Co	Mn	

Table 2. Varistor voltage ($T_S = 950^\circ\text{C}$)

Sample	$V_b(V_{1mA}/\text{mm})$
A	238
B	221
C	227
D	214

at 850°C is lower than those sintered over 900°C. It can be presumed from these results that a T_S of 850°C was insufficient in obtaining enough apparent density compared to other T_S . **Figure 3** shows the relationship between M_S/M_B and V_b . At sintering temperatures of 950°C or higher, the value of V_b was almost proportional to M_S/M_B . At all sintering temperatures, the value of V_b increased with increasing M_S/M_B , implying that ZnO grain growth was more inhibited by increasing amount of spinel particles during sintering process.

As far as these experimental results shown in Figs. 1–3 are concerned, T_S and M_S/M_B conditions for SRZVC experiments were chosen 900 or 950°C and 0.45 respectively.

3.3 Effect of Ni and Cr on V_b and stability of I_r for SRZVC

Sample (A–D) compositions are shown in **Table 1**, and V_b sintered at 950°C for 10 h is shown in **Table 2**. The V_b of samples B–D decreased slightly compared to that of sample A. The electric stability of I_r with two different T_S is shown in **Figure 4**. It was confirmed that the initial slope of I_r was classified into two groups by each composition. In samples A and C contained Ni, I_r continuously decreased in less than 30 h and became almost constant. In contrast to these results, I_r in samples B and D without Ni was continuously increased in 150 h. It has been said that the trend of increase and decrease in I_r with respect to time is derived from the crystalline phase of Bi₂O₃^{12),13)} or density and deepness of the trap level at grain boundary.¹⁴⁾ The crystalline phases of samples A–D sintered at 950°C were

Fig. 4. Stability of resistive leakage current (I_r) in SRZVC; T_S : (a) 900°C, (b) 950°C.

Fig. 5. XRD patterns of SRZVC samples ($T_S = 950^\circ\text{C}$).

Table 3. Crystalline phases in SRZVC samples ($T_S = 950^\circ\text{C}$)

Sample	Observed crystalline phase
A	$\text{Bi}_{16}\text{CrO}_{27}$, Sb-spinel
B	$\text{Bi}_{16}\text{CrO}_{27}$, Sb-spinel
C	$\alpha\text{-Bi}_2\text{O}_3$, Sb-spinel
D	$\alpha\text{-Bi}_2\text{O}_3$, Sb-spinel

determined by XRD. The XRD patterns and observed crystalline phases are shown in **Figure 5** and **Table 3** respectively. It is clearly shown that the type of crystalline phases in Bi_2O_3 was attributed to the Cr additive in this study. In contrast, Ni was significantly attributed to the electric stability of I_r for SRZVC, although little difference between the crystalline phases of samples A and B was observed. Several studies have proved that the spinel phase may dissolve almost all other elements present in this system.^{15)–17)} **Figure 6** shows the SEM and EPMA images of samples A and B. In spinel particles, Sb and a small amount of

Co was detected in sample B, although there was little Co in sample A, implying that the spinel composition was significantly changed in SRZVC by Ni doping. Similarly, it was confirmed that a small amount of Co was detected in sample D. It has been said that transition elements such as Co and Mn in particular are responsible for density and deepness of the trap level at grain boundary.^{12),14)} These results suggest that trend of increase and decrease on I_r with respect to time is partially affected by Co distribution in the SRZVC.

4. Discussion

The correlation between dissolved Co in spinel particles and the trend of I_r is now discussed. It is considered that doped Co principally dissolves in ZnO grains and contributes to form a trap level at a grain boundary. In general, Co is not clearly detected with EPMA analysis on ZVC, because Co might be widely distributed over all ZnO grains, and the concentration level of Co might be lower than the minimum detection level of EPMA analysis (e.g. sample A). In contrast, sample B in Fig. 6

Fig. 6. SEM and EPMA images of SRZVC samples ($T_S = 900^\circ\text{C}$).

(Ni-free composition) shows that spinel particles positively dissolved Co.

It was reported by Z. Brankovic et al. that the structural and electrical properties of ZVC depend on the chemical composition of spinel particles.¹⁸⁾ According to this paper, both synthesized Zn–Co–Sb spinel and Zn–Ni–Co–Cr–Mn spinel were relatively stable, and their chemical composition did not change significantly after being mixed and sintered with ZnO. It can be presumed that the Ni doping is responsible for inhibiting the absorption of Co into spinel particles during sintering process on SRZVC. On the contrary, in sample B, spinel particles positively absorb Co, and a smaller Co concentration in ZnO grains might be responsible for decreasing a schottky barrier height due to changing the trap deepness or the trap density.

5. Conclusions

The effect of the M_S/M_B and T_S on the densification behavior and varistor voltage V_b was studied. It was confirmed that the densification behavior of ZVC was significantly affected by the M_S/M_B , and the densification curve was shifted to a lower temperature with decreasing M_S/M_B . Several studies on M_S/M_B and T_S revealed that SRZVC can be obtained over 900°C of T_S with a high apparent density (around 5.5 g/cm^3). In SRZVC, it was found that the trend of increase and decrease in I_r depended on Ni doping. It is suggested that the correlation between I_r trend and Ni doping is attributed to changing the composition of spinel particles. Without Ni doping, poor Co concentration in ZnO grains might be responsible for decreasing the schottky barrier height due to continuously changing the trap level or the trap density.

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