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Electrical properties and microstructure of zno varistor with high surge protective characteristics

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We fabricated ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor and investigated the effect of sintering temperature on its microstructures and electrical properties. As the sintering temperature increases, crystalline grain growth and phase change are observed owing to the volatilization of Bi_2O_3. The varistor voltage decreased from 280 V/mm to 195 V/mm with the increase in sintering temperature, and the nonlinear coefficient (α) and leakage current of the varistor sintered at 1120 °C were 42.3 and 2.8 μA, respectively. For the varistor sintered at 1120 °C, the surface temperature and current increased from 45.3 °C to 87.9 °C and from 2.8 kA to 7.44 kA, respectively, under the surge voltage (waveform of 1.2/50 ms) of 6 kV to 15 kV. According to a repeated surge test (waveform: 1.2/50 ms and 8/20 ms, surge voltage 6.6 kV/3 kA, interval: 60 s), the varistor exhibited excellent surge-withstanding capability with the variation rate of voltage 0.8% and the variation rate of leakage current within 1.5%.

Key words: Varistor, Sintering temperature, Nonlinear coefficient, Surge voltage.

Introduction

ZnO-based varistors are widely used owing to their advantages such as high nonlinear coefficient (~50), fast response, high surge energy capacity, and high voltage gradient, which are important factors for evaluating the performance of a varistor. Therefore, ZnO-based varistors are widely used as surge protective devices in electronic and electrical systems to suppress the overvoltage. Although voltage gradient can be enhanced by employing low sintering temperature and short sintering time, it causes low nonlinearity. To solve this problem, ZnO varistor has been studied using various additives, such as Bi_2O_3, Sb_2O_3, CoO, Al_2O_3, and NiO to reduce the sintering temperature and time. These additives produce a Bi-rich liquid phase upon sintering. The Bi liquid phase including Co, Al, Ni, and excess O ions at ZnO/ZnO grain boundaries provides a continuous path. The transition-metal oxides (CoO, Al_2O_3, NiO) serve to provide ions and form interstitial start and deep bulk traps, resulting in a high potential barrier. Sb_2O_3 effectively inhibits the grain growth of ZnO [1-4]. In a power system, a large amount of instantaneous electrical energy such as a lightning surge, switching surge, and transient overvoltage is discharged to the ground and applied to protect electronic devices and it has been applied to photovoltaic systems. Typical ZnO varistors are used for protection against various surge and transient overvoltages in low-voltage circuits at commercial frequency. However, these varistors are deteriorated by commercial frequency voltage and harmonic components during continuous operation for a long time. Currently, high-surge-withstanding varistors are required to satisfy the strengthening standard of UL 1449 3rd edition test method (3000 A, 6 kV (1.2 μs/50 μs)-3 kA (8/20 μs)) [5,6].

There are three methods of fabricating a high-surge-withstanding varistor: i) increasing the volume of the ZnO varistor, ii) increasing the thickness of the electrode when forming the electrode in the varistor, and iii) adding a rare earth oxide to the existing composition. In this study, we investigated the microstructure and electrical properties at different sintering temperatures after optimizing the additive composition and thereafter developed a high-surge varistor with high energy absorption capability. In order to test the ZnO varistor, the surge characteristics were measured by increasing the surge voltage (waveform of 1.2 μs/50 μs) from 6 kV to 15 kV [6,7].

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Experimental

ZnO, Bi_2O_3, Sb_2O_3, Al_2O_3, Co_3O_4, NiO, and Mn_3O_4 were prepared as starting materials for the fabrication of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO and thereafter, the powders were ball-milled with deionized water for 24 h using a zirconia ball. Subsequently, an organic binder was added to the slurry and granulated using a spray dryer. The particle size of the granule material was sieved to 60-140 µm; subsequently, it was placed in a cylindrical mold, and thereafter uniaxially pressed at 25 MPa and hydrostatic pressed at 98 MPa. The samples were sintered in air at 1080-1200 °C for 2 h at the heating and cooling rate of 5 °C/min. The sintered samples were processed to a thickness of approximately 2.0 mm, and Ag electrode was coated on both sides with a silk screen, followed by heat treatment at 600 °C for 10 min to measure the electrical properties of the samples. The structural properties of the samples were analyzed using scanning electron microscopy (S-4200, Hitachi, Japan) and X-ray diffractometry (XRD, M03X-HF, MAC Science Co. Ltd., Japan). The distribution of the phases was observed using backscattered electron imaging (BEI, RBH-4200 5MC, Robinson, Australia). The electrical properties such as varistor voltage (V1mA), nonlinear coefficient (α), and leakage current (IL) were measured using a high-voltage SourceMeter (Keithley, 237, USA). The surge test was performed under different voltages with waveforms of 1.2/50 ms & 8/20 ms (Combination Wave) using the NoiseKen Lighting Surge Simulator. Furthermore, the rate of change of characteristics was measured with 15 repetitions.

Result and Discussion

Fig. 1 shows the sintering densities of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistors at different sintering temperatures. The density decreased from 5.608 g/cm^3 (theoretical density: 5.78 g/cm^3) to 5.568 g/cm^3 with the increase in sintering temperature. Above 1000 °C, the result indicates that the ZnO-Bi_2O_3 system exhibits volatilization of the Bi-rich liquid phase at the intergranular junctions, resulting in the decrease in the sintering density, which has been previously reported.

Fig. 2 shows the results of thermogravimetric and differential thermal analysis to confirm sintering behavior at different sintering temperatures. We can observe weight loss owing to the volatilization of water and organic binder up to 400 °C. Moreover, a weight loss of 0.15% in the region of 750 °C to 900 °C and a weight loss of 1.14% in the region of 900 °C to 1200 °C can be observed and the weight loss progresses significantly above 1050 °C. The weight loss in the range 750 °C to 900 °C is considered to be related to the formation of a pyrochlore phase as an intermediate phase near 740 °C, which is the eutectic temperature of ZnO and Bi_2O_3. Above 960 °C, the pyrochlore phase is changed to the spinal phase and the weight is reduced sharply. This can be explained by the increase in volatilization of Bi_2O_3, as shown in Equation 1 [8, 9].

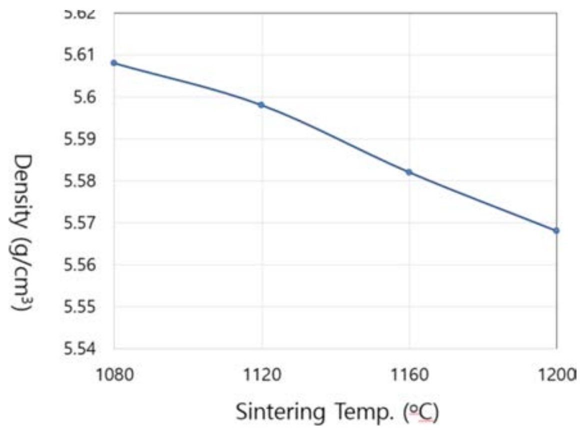


Fig. 1. Sintering density of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor with different sintering temperatures.

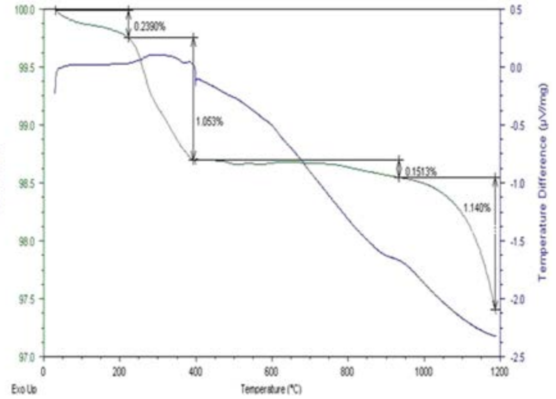


Fig. 2. TG-DTA curve of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor.

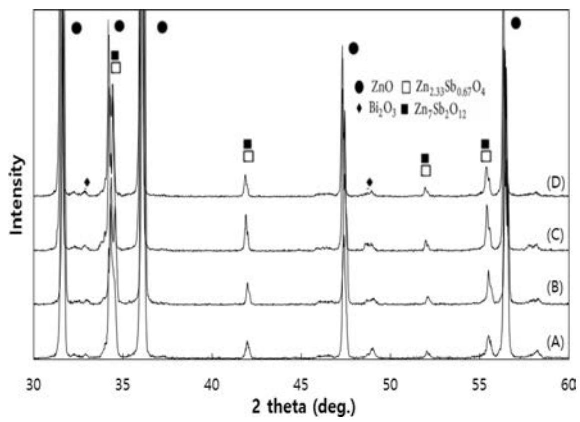


Fig. 3. XRD patterns of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor with sintering temperatures

$$2ZnBi_3Sb_3O_{14} + 17ZnO \rightarrow 3Zn_7Sb_2O_{12}(\alpha) + 3Bi_2O_3\ (\ell) \quad (1)$$

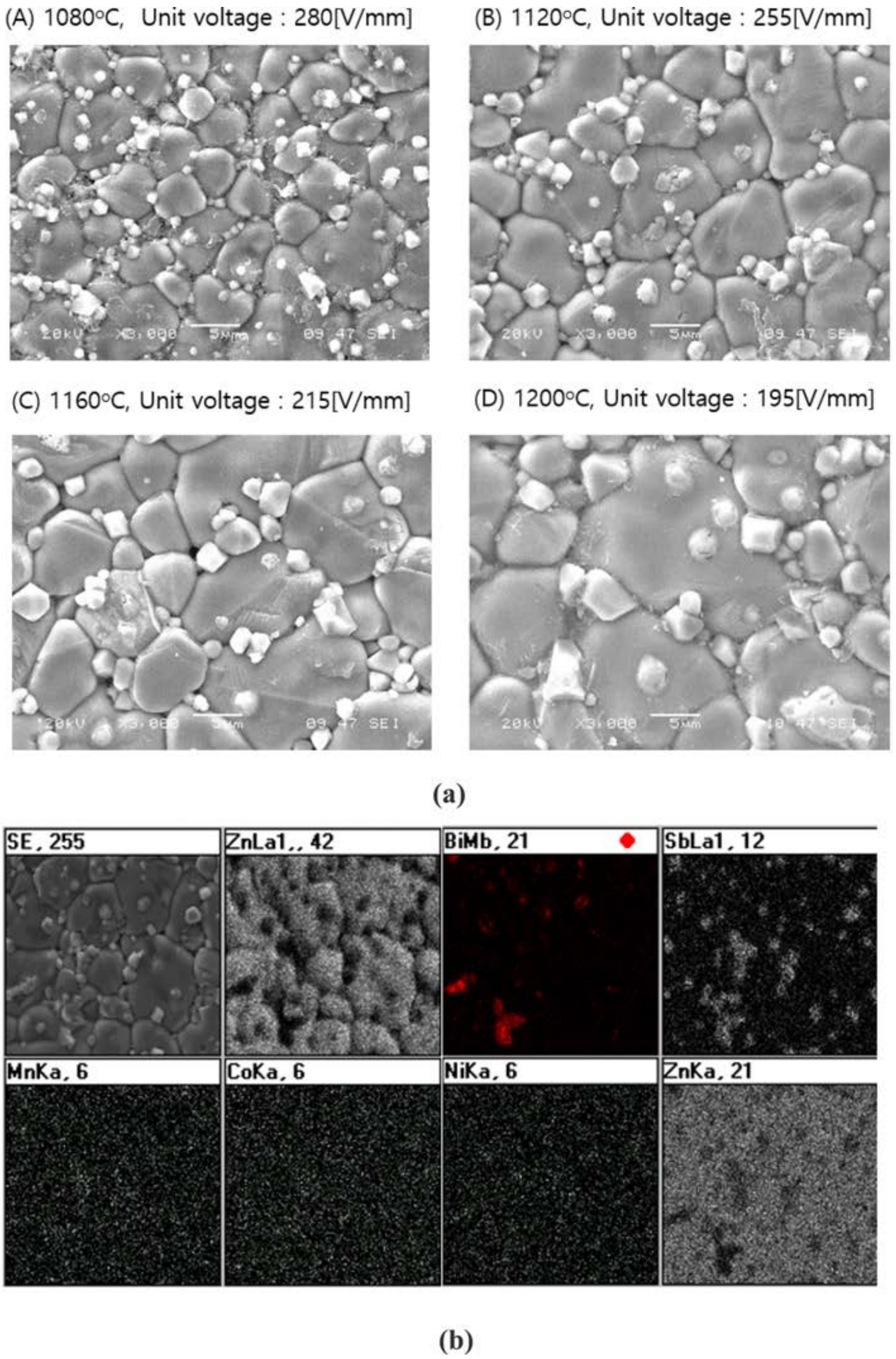
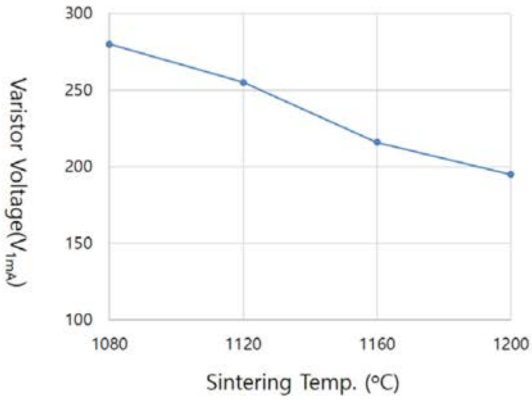


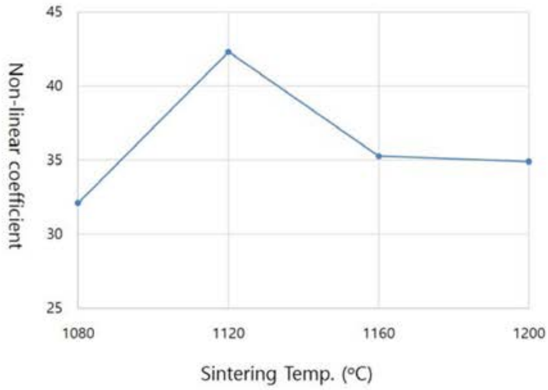
Fig. 4. (a) Microstructures and (b) BEI images of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor with different sintering temperatures.

Fig. 3 shows the XRD patterns of the ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor indicating the crystal structure at different sintering temperatures. It can be observed that there is almost no change in the crystal phase regardless of the sintering temperature. In the ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor, there is a ZnO main phase. Moreover, the secondary phases such as $Zn_2Sb_2O_{12}$, $Zn_{2.33}Sb_{0.67}O_4$, and Bi_2O_3 were observed and the intensities of $Zn_2Sb_2O_{12}$ and $Zn_{2.33}Sb_{0.67}O_4$ increased with the increase in sintering temperature above 1120 °C.

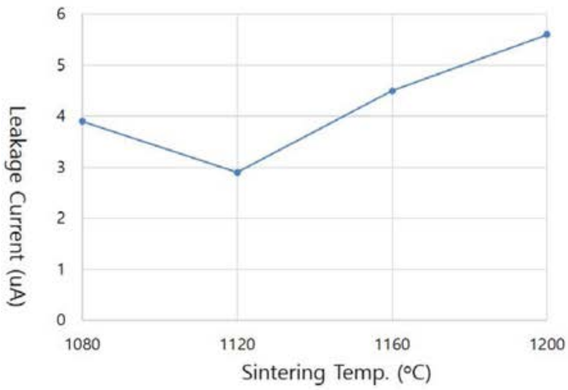
Fig. 4(a) shows the microstructure at different sintering temperatures and Fig. 4(b) shows the BEI image of the sample sintered at 1120 °C. As shown in Fig. 4(a), as the sintering temperature increases, the average particle size of ZnO increases. From BEI analysis, it can be observed that the sample is composed of ZnO particles, spinel phase, and Bi-rich intergranular phase. Co, Mn, and Ni are uniformly distributed in the ZnO particles whereas Sb reacts with



(A)



(B)



(C)

Fig. 5. Electrical properties of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor.

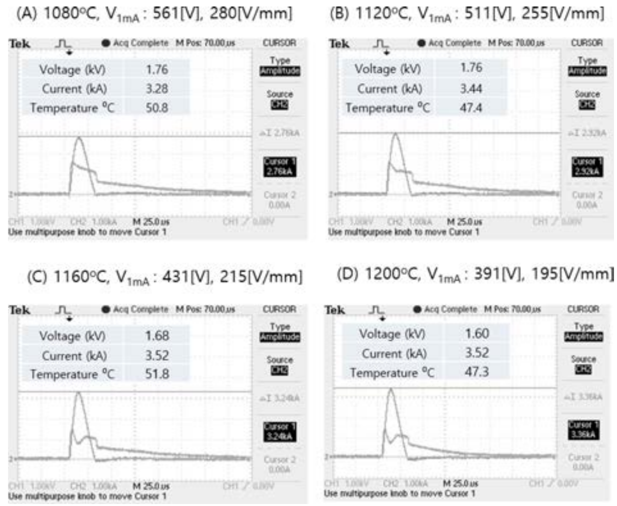


Fig. 6. Surge characteristics of the ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistors according to the rated voltages with sintering temperature.

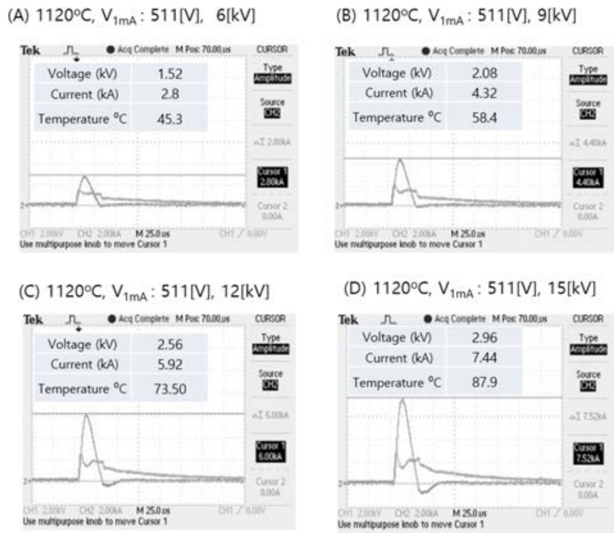


Fig. 7. Surge characteristics of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistor sintered at 1120 °C.

ZnO and exists as spinel phase ($Zn_7Sb_2O_{12}$).

Fig. 5 shows the varistor voltage (V1mA), nonlinear coefficient (α), and leakage current, which are representative properties of the varistor, at different sintering temperatures. The varistor voltage per unit thickness increases with the increase in the number of effective grain boundaries in the conduction path. As the temperature increases, the varistor voltage decreases from 280 V/mm to 195 V/mm. This is because the size of ZnO grains increases and the number of effective grain boundaries decreases, as shown in Fig. 4. Moreover, the nonlinear coefficient is more than 30 at all sintering temperatures, and it shows the highest value of 42.3 at 1120 °C. The leakage current at 1120 °C is 2.8 μA and the increase in leakage current with the increase in sintering temperature is believed to be due to the volatilization of the insulating liquid phase Bi_2O_3.

Fig. 6 shows the surge characteristics of the varistors according to the rated voltages. The applied surge voltage was 7 kV with a waveform of 1.2/50 ms. Although there is a difference depending on the capacitance of varistor, the voltages applied to the varistor were 1.76 kV at 1.60 kV, and currents were 3.52 kA at 3.28 kA. In the case of varistors, energy is consumed via self-heating when a voltage exceeding the limit voltage is applied.

The lower the heating temperature of the varistor, the more stable the characteristic. All the varistors show stable surface temperature in the range 47 °C to 51.8 °C.

Fig. 7 shows the surge characteristics of the varistor sintered at 1120 °C. The applied surge voltage varied from 6 kV to 15 kV with a waveform of 1.2/50 ms. The voltage applied to the varistor increased from 1.52 kV to 2.9 kV as the surge voltage increased, and the surge current showed a sharp increase from 2.8 kA to 7.44 kA. As the resistance decreases rapidly in the breakdown region of the varistor, the current increases. The current increases with the increase in the voltage applied to the varistor and thus, the surface temperature of the varistor rapidly increases from 45.3 °C to 87.9 °C. It can be observed that the varistor exhibits temperature stability up to the applied voltage of 9 kV, satisfying the 3rd edition standard. In addition, the varistor sintered at 1120 °C showed good surge characteristics with the variation rate of varistor voltage of 0.8% and variation rate of leakage current of 1.5% obtained using a repetitive surge test (wave form: 1.2/50 ms and 8/20 ms, surge voltage 6.6 kV/3 kA, interval: 60 s, 15 times)

Conclusions

The microstructure and electrical properties of ZnO-Bi_2O_3-Sb_2O_3-Al_2O_3-CoO-NiO varistors were investigated at different sintering temperatures. As the sintering temperature increased, the crystal phase change owing to Bi_2O_3 volatilization appeared and the grain size increased. The varistor voltage decreased from 280 V/mm to 195 V/mm with the increase in sintering temperature. The nonlinear coefficient (α) and leakage current of the varistor sintered at 1120 °C were 42.3 and 2.8 μA, respectively. When the surge voltage was applied from 6 kV to 15 kV with a waveform of 1.2/50 ms, the surface temperature increased from 45.3 °C to 87.9 °C and the current increased from 2.8 kA to 7.44 kA. According to the repeated surge test, the varistor showed excellent surge characteristics with variation rate of varistor voltage of 0.8% and variation rate of leakage current of less than 1.5%. Therefore, it was confirmed that it is possible to develop a high-surge varistor satisfying the 3rd edition standard by controlling the sintering temperature.

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