The correlation between surge energy capability and Bi$_2$O$_3$ volatilization in ZnO varistors

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This study investigated the correlation between the surge energy capability and Bi$_2$O$_3$ volatilization in ZnO varistors by analyzing the volatilization phenomenon of Bi$_2$O$_3$. A ZnO varistor is composed mainly of Sb$_2$O$_3$, Bi$_2$O$_3$. Bi$_2$O$_3$ has the lowest vapor pressure among these components. Bi$_2$O$_3$ plays an important role, moreover, in forming grain boundaries. These grain boundaries have low conductivity in the leakage current region, but, becomes higher in the region. It also determines the surge energy capability of the varistors. Bismuth oxide has four phases, each with intrinsic ion-conductivity. Formation of the bismuth oxide phase depends on the amount of bismuth at the grain boundary. Volatilization of Bi$_2$O$_3$ should therefore be prevented when developing ZnO varistors was conducted using high energy capabilities. Analysis of the volatilization phenomenon of Bi$_2$O$_3$ X-ray analysis methods such as X-ray fluorescence, X-ray photoelectron spectroscopy and X-ray diffraction. The results confirmed a close correlation among them. Sealed sintering methods were proposed to prevent the volatilization of Bi$_2$O$_3$ by ZnO varistors.

Key-words : ZnO varistor, Bi$_2$O$_3$ volatilization, Bi$_2$O$_3$ phases, Microstructure, Surge energy capability

1. Introduction

The varistor has a role as an active resistor in a circuit for clamping transient voltages, because it has excellent nonlinearity in the operating region. Varistor voltage and energy capacity are also important electrical properties of the ZnO varistor. These properties are depending on the microstructures of ZnO varistor.

The ZnO varistor is a polycrystalline ceramic comprising Bi$_2$O$_3$, Sb$_2$O$_3$. A ZnO varistor has three phases: ZnO grain, which has low resistivity; amorphous grain boundaries which are formed by Bi$_2$O$_3$ and feature high resistivity; and a spinel phase (ZnSb$_2$O$_4$), which play a role as a grain growth inhibitor. These phases are have two different types of interfaces inside of the varistor. ZnO–ZnO or ZnO–Bi$_2$O$_3$–ZnO. The non-homogeneous bonded interface (ZnO–ZnO) assumes leakage properties in the pre-breakdown region, while the homogeneous bonded interface (ZnO–Bi$_2$O$_3$–ZnO) appears to have nonlinear characteristics in the breakdown region. Controlling the microstructures of ZnO varistors is therefore essential for high energy capability. When controlling the microstructure of a ZnO varistor, Bismuth oxide is an important material for forming amorphous grain boundary layers. Since, its vapor pressure is lower than the others, however, it is essential to prevent volatilization of Bi$_2$O$_3$ during the sintering process. If volatilization of Bi$_2$O$_3$ cannot be prevented, it will be difficult to form grain boundary layers.

Other studies have focused on the varistor voltage and leakage current in the pre-breakdown region rather than on the upturn region. In this study, however, a lightning impulse test was conducted to confirm the correlation of electrical properties in the upturn region. When lightning impulse tests conducted to determine the energy capacity of ZnO varistors, varistor samples were checked for varistor voltages before and after the tests, respectively. The varistor voltage after an impulse test should be within a 10% tolerance.

In this study, a sealed sintering method was used to prevent volatilization of Bi$_2$O$_3$. Covered crucibles used to seal the green body of ZnO specimens in a box furnace. Two types of samples were selected, a Non-Volatilization (NV) sample and a Volatilization (V) sample, respectively. The NV is sintered in a sealed covered crucible to prevent volatilization of Bi$_2$O$_3$ [Fig. 1(a)]. On contrary, V is sintered in an opened crucible with no cover [Fig. 1(b)].
ACS reagent, −200 mesh, NOAH technologies, U.S.A), 1 molecular percent of Bi2O3 (NOAH technologies, U.S.A, 99.9% pure, −325 mesh); and 1 molecular percent Sb2O3 (99.9% pure, −325 mesh, 1 micron average, NOAH technologies, U.S.A). Commercial oxides powders were mixed in a polyethylene jar and then ball-milled (UBM-200L, Intec, Republic of Korea) for 24 h in deionized water with zirconia media. They were then spray dried (DJE-FCNM 015R, Dongjin Co., ltd, Republic of Korea) at 110°C and sieved through a −325 mesh. Next, a green body was pressed by uniaxial pressure (SW-100, Samwon Co., LTD, Republic of Korea) at 15 MPa into a disk (90 © 90 © 10 mm). The maximum sintering temperature was 1250°C, and the soaking time was 6 h at ambient atmosphere in a box furnace (TM-EA303040E, KFCT Co., LTD, Republic of Korea).

2.2 Microstructures, qualitative and quantitative analysis

The microstructures were observed by field emission-scanning electron microscopy (FE-SEM, S-4800, HITACHI, Japan) with an energy dispersive X-ray (EDX). Qualitative and quantitative analyses were conducted with an XRF (ZSX Primus, Rigaku, Japan) at 110°C and sieved through a −325 mesh. Next, a green body was pressed by uniaxial pressure (SW-100, Samwon Co., LTD, Republic of Korea) at 15 MPa into a disk (90 × 90 × 10 mm). The maximum sintering temperature was 1250°C, and the soaking time was 6 h at ambient atmosphere in a box furnace (TM-EA303040E, KFCT Co., LTD, Republic of Korea).

2.3 Measurement of electrical properties and lightning impulse test

The electrical properties of ZnO varistors such as the varistor voltage at 1 mA, nonlinear coefficient and leakage current were measured by voltage-current characteristic curve analyzer (KERI, Republic of Korea).

A lightning impulse test was conducted by an impulse current generator (10/350μs waveform) designed by KERI. This is an R-L-C-type generator rather than the crowbar type, which is easily affected by a small amount of impedance caused by that of ZnO varistor. When varistors are exposed to a high voltage or current, they play a role similar to a capacitor. Therefore, these effects should be considered. An R-L-C-type generator circuit is shown in Fig. 2(a) with its waveform [Fig. 2(b)]. The impulse was detected by current sensor with a frequency bandwidth from DC to 1.2 MHz (Pearson Electronics, 1423), and the impulse voltages were measured by a high-voltage probe with a frequency bandwidth from DC to 70 MHz (Tektronix, P6015). Those impulse voltages and currents were recorded by a four-channel digital storage oscilloscope with a frequency bandwidth of 300 MHz and a sampling time of 2.5 Gs/s (Tektronix, TDS3032).

3. Results and discussions

Sintered samples show the nonlinearity properties of varistors (Fig. 3). The varistor voltage value should be checked to compare it with the varistor voltage after the impulse test. This value should be within 10% after impulse test. The NVB samples show homogeneous characteristic curves. In contrast, the VB samples show non-homogeneous curves in Fig. 3. This result was caused by volatilization of Bi2O3. Stable grain boundaries cannot form without enough bismuth.

The reason for preventing volatilization of Bi2O3 is to prevent decreases in varistor voltage after the impulse test. According to the IEC 61643 standard, the varistor voltage after a lightning impulse test should be within 10% compared with the varistor voltage before the lightning impulse test.

The results of waveforms in the impulse test are shown in Fig. 3(b). 10/350μs of current was applied to a single varistor sample, and its clamping voltage was 1.15 kV. Single varistors withstand 55 kA current, and this shows that the varistor voltage dropped only 5.5% after the impulse test [Fig. 4(a)].

By contrast, the volatilized sample showed a 26% drop in varistor voltage [Fig. 4(b)]. This results was caused by a
deficiency of bismuth at the grain boundary of ZnO varistor. Additionally, the values of the varistor voltage are not constant with each other. This means these micro-structures are not homogeneous. A deficiency of bismuth oxide at the grain boundary presents formation of form homogeneous varistor microstructures in accordance with the results of the XRD graph [Fig. 7(a)]. Due to non-homogeneous microstructures according to the results of XRD graph [Fig. 7(b)], the electrical properties of the volatilization samples show irregular characteristic curves [Fig. 4(b)].

The microstructures of ZnO varistors in this study are shown in Fig. 5 below. The ZnO grain, Bi$_2$O$_3$ amorphous layer (green color) at the grain boundary and spinel phase are present, mentioned earlier. The volatilization sample shows a lower amount of the bismuth phases at the grain boundary than the non-volatilization sample.

Quantitative analyses of bismuth were conducted by both the EDS and XRF method. They showed the different amounts of bismuth, respectively (Fig. 6). The initial amount (in the batch process) of Bi$_2$O$_3$ was 2.92 wt%. The VB samples showed values under 2%. The reason is that the Bi element was volatilized by the open sintering method [Fig. 1(b)]. Deficiency of bismuth can cause different
types of bismuth oxide phases in the grain boundaries.

To be specific, four types of bismuth oxide phases exist. First, the monoclinic ($\alpha$-phase) is stable at room temperature. Second, the metastable tetragonal ($\beta$-phase) and third, the cubic ($\gamma$-phase) appear at around 650 and 635°C, respectively, and transform to the cubic ($\delta$-phase) at 730°C. The $\delta$-phase is stable until oxide fusion at 825°C. As the furnace is cooling, the $\alpha$-phase reappears at 500°C.3) The crystal structure of Bi$_2$O$_3$ at the grain boundary also changes from $\alpha$ to $\delta$ due to the addition of Al or Si.7),8) Both the $\gamma$-phase and the $\alpha$-phase are characterized by low ionic conductivity. By contrast, the $\delta$-phase and the $\beta$-phase are good ionic conductors, which intensify the oxygen migration from the grain boundaries. The transport of oxide ions through the grain boundaries is affected by the crystal structure of Bi$_2$O$_3$ and related to the ionic conductivity of a particular crystalline phase of the Bi$_2$O$_3$-rich intergranular layer.9)–11)

XRD analysis was conducted to identify each phase of bismuth oxides. As shown in Fig. 7, the non-volatilized sample has $\beta$ and $\delta$-Bi$_2$O$_3$ phases. The volatilized sample, on the contrary, has only $\alpha$-phase among Bi$_2$O$_3$ phases. And the intensity of the XRD peaks of the volatilized sample is irregular. This means its microstructure is non-homogeneous.12)

$\alpha$-Bi$_2$O$_3$ exhibits p-type electronic conductivity at room temperature. $\delta$-Bi$_2$O$_3$ is predominantly ionic with oxide ions, which are the main charged carriers. $\delta$-Bi$_2$O$_3$ has a defective fluorite-type crystal structure in which two of the eight oxygen sites in the unit cell are vacant. These intrinsic vacancies are highly mobile due to the high polarizability of the cation sub-lattice with the 6s$_2$ lone pair electrons of Bi$^{3+}$. The $\alpha$-phase transforms to the $\delta$-phase temperature range from 650 to 729°C with a rapidly increasing contribution of oxygen vacancies.13) The oxygen ions can jump into the vacancies more freely during the liquid phase sintering.14),15)

As shown in Figs. 8(a) and 8(b), the NVB samples bismuth profiles are slightly higher than these of the VB samples because of bismuth volatilization. These small amount of bismuth can bond with oxides at the grain boundary. They can therefore form the bismuth oxide phase mentioned earlier and show the quality of the IV characteristics16) [Fig. 4(a)].

This is also related to the temperature-driven de-wetting of the grain boundaries by the Bi$_2$O$_3$ phase. The interfacial Bi content is roughly unchanged.7),17)

In the case of the oxygen profile, the VB samples have a higher profile than the NVB samples because oxidation occurred during open sintering.

The changes in the chemical composition can be identified by the XPS method from depth analysis. The important finding from the XPS studies is that the concentration of oxygen ions with bismuth adsorbed at the grain boundaries plays a key role in the conductivity.

Removing the oxygen with bismuth from the grain boundary reduced the barrier height (double Schottky barrier) and decreased the varistor voltage after impulse testing in this study.18),19)

4. Conclusion

In this study, varistor samples of the same composition were manufactured by different types of sintering methods. The correlation between surge energy capability and Bi$_2$O$_3$ volatilization in ZnO varistors was then investigated by analyzing the volatilization phenomenon of Bi$_2$O$_3$.  

![Fig. 6. The amount of bismuth in a sintered varistor (batch is the initial amount of bismuth oxide).](image1)

![Fig. 7. XRD graphs of each sample.](image2)
XRF was used to determine the amount of volatilization of bismuth, and XRD was used to identify the crystallinity of the bismuth oxide. XPS analysis was then performed to measure both the oxygen and bismuth ion concentrations at the grain boundary.

The deterioration of the characteristic I/V curves after lightening impulse test showed a clear difference in energy capacity between the two samples. The reason is that the bismuth oxide was volatilized. The $\beta$, $\delta$-bismuth oxide phase, which should exist in the grain boundary, could therefore not be formed. Since the $\beta$, $\delta$-bismuth phase has high ionic conductivity, transfer of ions in the high voltage region (upturn region) of a varistor can have high electrical conductivity that could pass large currents when the potential barrier of the grain boundary (double Schottky defect) were lowered.

In summary, it was confirmed that there was a close correlation between surge energy capability and Bi$_2$O$_3$ volatilization in ZnO varistors. Also, sealed sintering methods were proposed to prevent the volatilization of bismuth oxide by ZnO varistors.

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