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Influence of sintering on microstructure and electrical properties of ZnO-based multilayer varistor (MLV)

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Abstract

The effect of sintering on microstructure, dielectric property and varistor property of ZnO-based multilayer varistor (MLV) were investigated. The results show that an optimum microstructure of ZnO-based MLV can be obtained when sintering at 950 °C/1.5 h. The reaction between ZnO and Sb_2O_3 is noted. Also, the segregation of Bi_2O_3 to the inner electrode and thus the reaction of Bi_2O_3 with Pd are observed. The V_B and α value of ZnO-based MLV can be controlled in a straightforward manner through the control of grain size. The decrease in V_B directly relates to the grain growth of ZnO grains when increasing the sintering temperatures from 900 to 1050 °C. Moreover, the increase of capacitance with sintering temperature may mainly result from the coalescence of ZnO matrix grains. The energy absorption capabilities in terms of electro-static discharge (ESD) and peak current (PC) measurements of ZnO-based MLV are reported. The optimum varistor properties of ZnO-based MLV can be obtained when sintering at 950 °C.

Keywords: D. ZnO; E. Varistor; ESD; Breakdown voltage

1. Introduction

The ZnO-based ceramic is one of the most commonly used varistors because of its exceptional nonlinear ohmic characteristic. The roles of individual dopants, which form a potential barrier for electron flow, have been investigated and reported in great detail [1–3]. The physics of doped ZnO varistor have been reviewed in the literatures [4,5]. The microstructure of doped ZnO varistor mainly consists of electrically conductive ZnO grains, surrounded by electrically insulating Bi_2O_3-rich glassy phases. The breakdown voltage (V_B) can be varied in a straightforward manner by changing the grain size through the sintering conditions. The reaction products due to the chemical reaction between Bi_2O_3 and Sb_2O_3 have been reported [6,7].

The present work studies the effect of sintering on microstructures, and electrical properties of doped ZnO varistors. The energy-handling capabilities of ZnO-based varistor such as electro-static discharge (ESD), and peak current (PC) will be emphasized in dependence on the sintering conditions.

2. Experimental procedures

2.1. Preparation of multilayer varistor (MLV)

ZnO-based multilayer varistors (MLV) were fabricated by a conventional multilayer ceramic capacitor (MLCC) technology. ZnO (ZnO, Mitsui Inc., Japan) and dopants including $Al(OH)_3$, MnO, CoO, Sb_2O_3 and Bi_2O_3 were weighed, mixed, dispersed, and milled in deionized water with 2 mm ZrO_2 beads for 6 h. The mean particle size (D_{50}) of milled slurry was about 0.35 μm. The pre-milling slurry were mixed with binder and plasticizer. The resulting slip was cast into a green sheet with a 30 μm in thickness using the Doctor-blade method. The Ag/Pd inner pastes were printed onto the green sheet. These printed sheets were stacked, laminated and cut into chips. The green chips were de-binded at 320 °C and then sintered between 930 and 1000 °C for 1.5 and 2 h.

2.2. Measurements

The microstructures of the specimens were characterized by scanning electron microscope (Leo 1530, Philips Instrument Inc., Netherlands or JSM-5300, JEOL, Japan) equipped with an

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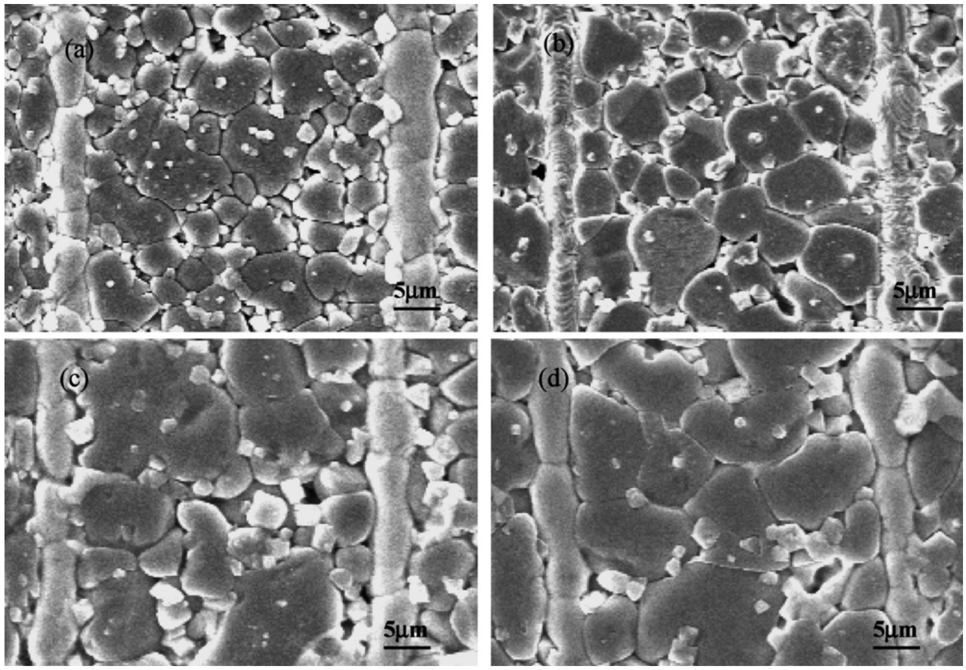

Fig. 1. SEM micrographs of ZnO-based MLV, sintered between (a) 930;(b) 950; (c) 980; and (d) 1000 °C for 2 h.

energy-dispersive spectrometer (EDS, EDAX Inc., USA). The thermal etching was performed at 850 °C for 20 min to reveal the grain boundary. The grain size was measured by using the linear intercept method [8]. The capacitance and dissipation factor (tan δ) were measured at 1 kHz by using a precision LCR network analyzer (4278A, Hewlett-Packard Inc., USA). The nonlinearity (α) was calculated from two pairs of voltage and current values and defined as $\alpha = (\log I_2 - \log I_1)/(\log V_2 - \log V_1)$. The voltage values were recorded at an applied current of 1 and 10 mA, respectively. The evaluation of energy absorption capabilities of ZnO-based MLV including PC and ESD was performed by using surge generator and ESD generator, respectively. All of the testing parameters were followed according to IEC 60060 and IEC61000-4-2.

3. Results and discussion

Fig. 1 shows a series of SEM micrographs of ZnO-based MLV, sintered between 930 and 1000 °C for a soaking time of 2 h. Evidently, abnormal grain growth becomes more significant, especially after sintering at temperatures higher than 950 °C. The grain size of the specimen can be as large as 10 μm. The electrical characteristics of multilayer ZnO varistors are determined by their microstructure. The large grain size distribution will result in poor electrical properties, especially the performance of ESD [9]. Previous investigation shows that it is vital to have a homogeneous microstructure for extended life-time of the multilayer ZnO varistor. The homogeneity of the microstructure is directly related to the quality of multilayer ZnO varistor. It had been also demonstrated that the width of the grain size distribution has an effect on the transport properties.

Fig. 2 shows SEM microstructures of ZnO-based MLV, sintered at 950 °C for 1.5 and 2 h, respectively. A more uniform grain size can be obtained when sintering at 950 °C for 1.5 h. Moreover, a detailed microstructural characterization on the specimens is shown in Fig. 3. The image shows the formation of $Zn_7Sb_2O_{12}$ due to the reaction between ZnO and Sb_2O_3. It is reported that the reaction between ZnO and Sb_2O_3 or Bi_2O_3 leads to the occurrence of spinel or pyrochlore reaction

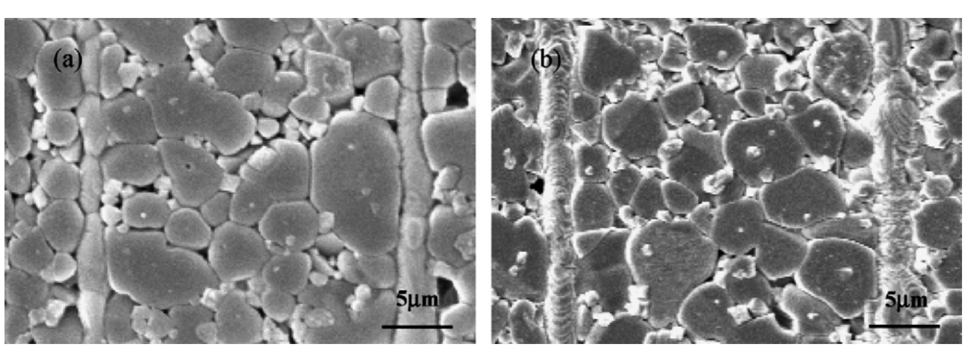

Fig. 2. SEM micrographs of ZnO-based MLV, sintered at 950 °C for (a) 1.5 and (b) 2 h.

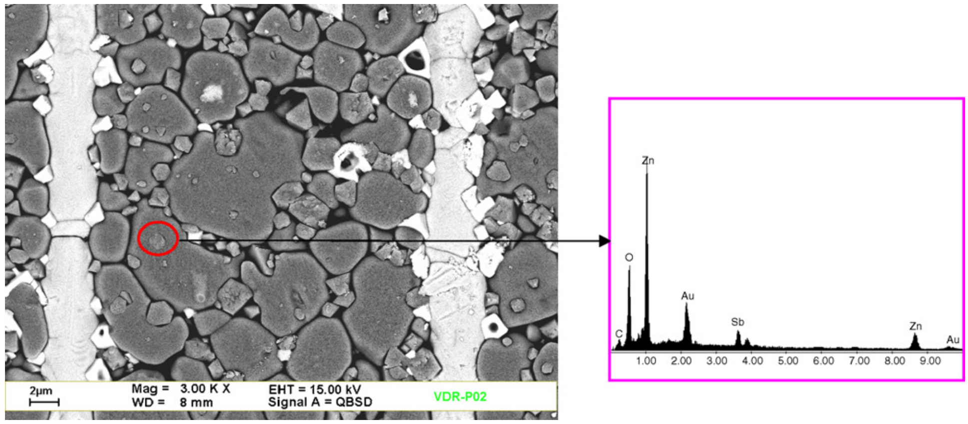

Fig. 3. SEM micrograph of ZnO-based MLV, illustrating the formation of $Zn_7Sb_2O_{12}$, segregation of Bi_2O_3 and reaction of Bi–Pd. The specimens were sintered at 950 °C/1.5 h.

products [7,8]. Moreover, the image illustrates the segregation of Bi_2O_3-rich phase to the inner electrode and thus the reaction of Bi_2O_3 with Pd. The reaction of Bi_2O_3 with Pd is reported in literatures in great detail [10].

Fig. 4 demonstrates the variation of grain size ZnO-based MLV, sintered at temperatures of 900–1000 °C for a soaking time of 1.5 h. The grain size increases with sintering temperature. A typical grain size distribution of the specimens, sintered at 950 °C/1.5 h is shown in Fig. 5. The average grain of the specimen is about 5.2 μm. However, the distribution of grain size is still large, due to the liquid phase sintering in the presence of Bi_2O_3. The grain size can be as small as 2.0 μm and as big as 12.0 μm. A further improvement in the grain size distribution is necessary to obtain a more uniform microstructure.

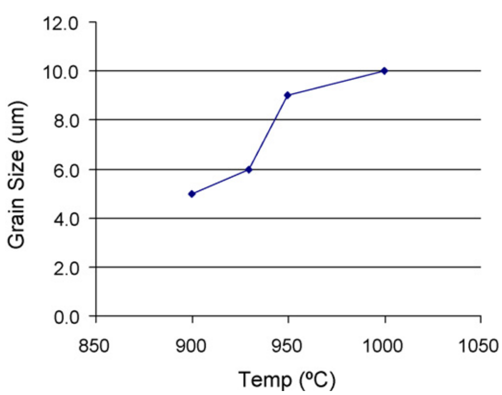

Fig. 4. Variation of grain size with sintering temperature.

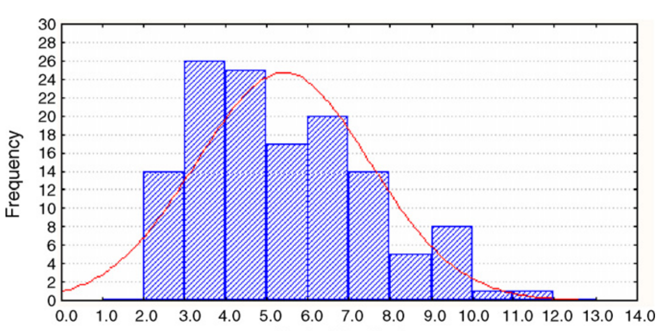

Fig. 5. Grain size distribution of ZnO-based MLV, sintered at 950 °C/1.5 h.

The change of V_B of ZnO-based MLV with sintering temperature is shown in Fig. 6. The result shows that the V_B decreases linearly with sintering temperature, mainly resulting from the grain growth at the elevated temperatures. Usually, a small grain size or thicker layer thickness between two adjourn electrodes will lead to a big V_B. That indicates breakdown voltage of ZnO-based MLV is directly related to the number of grain boundary between two adjourn electrodes. In this study, the layer thickness between two adjourn electrodes is fixed, thus, the working voltage of ZnO-based MLV can be directly controlled in a straightforward manner through the control of grain size.

Fig. 7 shows the variation of capacitance of ZnO-based MLV with sintering temperature. The result shows that the

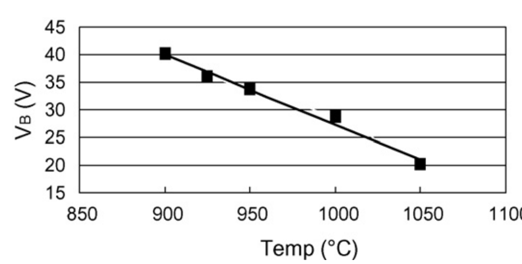

Fig. 6. Variation of V_B as a function of sintering temperature.

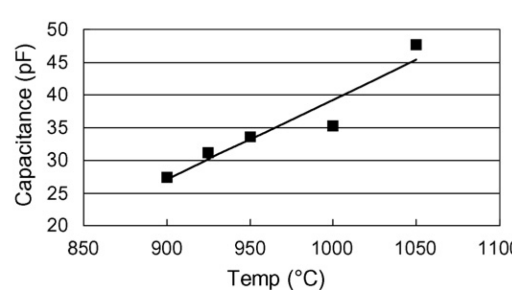

Fig. 7. Variation of capacitance with sintering temperature.

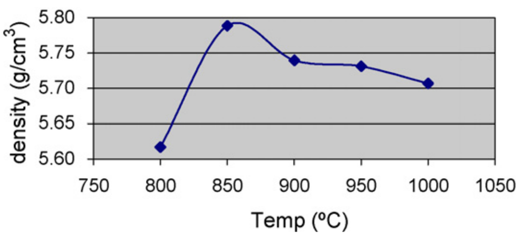

Fig. 8. Density of MLV as a function of sintering temperature.

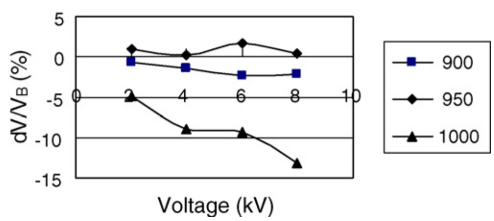

Fig. 9. Variation of V_B of ZnO-based MLV after ESD testing.

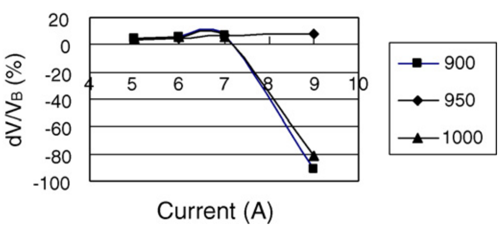

Fig. 10. Variation of V_B of ZnO-based MLV after PC testing.

capacitance of the specimens increases with increasing sintering temperature. The increase in density may be one of the reasons, responsible for the linear increase of capacitance. Fig. 8 shows the density as a function of sintering temperature. The results show that the density increases with temperature, reaches an optimum density at 850 °C and then decreases with sintering temperature probably due to the grain growth. Based on this experimental proof, it is concluded that the increase in capacitance may not only result from the density increment in the temperature of interest.

Besides, it is well-known that the ZnO-based varistor is one of the grain boundary capacitors. The effective dielectric constant of ZnO-based MLV is directly proportional to the dielectric constant of insulting phase (ε_i), and grain size of the matrix (d_g) but reversely proportional to the thickness of insulting phase (d_i). As ε_i is almost a constant and d_i is quite small, d_g may play an important role in the increase in capacitance. As the sintering temperature increases, the grain growth of the specimens takes place significantly, as shown in Figs. 1 and 4. Thus, the increase in capacitance may both result from the contribution of density increment and grain growth of matrix grains.

Fig. 9 shows the variation of $\Delta V/V_B$ of ZnO-based MLV after ESD testing. Generally, the variation of V_B within ±10.0% is acceptable after ESD testing. The results indicate that the variation of V_B of the specimens, sintered between 900 and 1000 °C can be within ±10.0% when testing between 2 and 6 kV. However, the large deviation of V_B of the specimens, sintered at 1000 °C can be found when testing at 8 kV. As previously mentioned, getting worse homogeneity of microstructure for ZnO-based MLV with increasing sintering temperature is responsible for ESD testing results. Moreover, Fig. 10 demonstrates the variation of $\Delta V/V_B$ of ZnO-based MLV after PC testing. As defined in ESD testing, ±10.0% variation in V_B is acceptable after the PC testing. The similar results can be found as the specimens are tested at an applied current up to 7 A. However, the large variation of V_B is noted in the cases of 900 and 1000 °C when testing at 9 A. Insufficient density of specimen sintered at 900 °C and larger grain size distribution causing poor homogeneity of specimen sintered at 1000 °C are both responsible for the PC testing results. In summary, the varistor properties of ZnO-based MLV can be optimized and obtained when sintering at 950 °C.

4. Conclusion

The summary of this work is as follows.

1. The microstructures and electrical properties of ZnO-based MLV have been characterized and correlated. The results indicate that an optimum microstructure of ZnO-based MLV can be obtained when sintering at 950 °C/1.5 h. The reaction between ZnO and Sb_2O_3 is noted. Also, the segregation of Bi_2O_3 to the inner electrode and thus, the reaction of Bi_2O_3 with Pd are observed.
2. The V_B and α value of ZnO-based MLV can be controlled in a straightforward manner through the control of grain size. The decrease in V_B directly relates to the grain growth of ZnO grains when increasing the sintering temperatures from 900 to 1050 °C. Moreover, the increase of capacitance may mainly result from the coarsening of ZnO matrix grains.
3. The capability of ESD and PC of ZnO-based MLV is reported. The optimum varistor properties of ZnO-based MLV can be obtained when sintering at 950 °C.

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