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Electrical characteristics and reheat-treatment effects in a ZnO varistor fabricated by two-stage heat-treatment

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Conventional ZnO varistors are generally fabricated by sintering ZnO powder mixed with additives such as Bi_2O_3, Sb_2O_3, Cr_2O_3, Co_2O_3, and MnO_2. To reduce abnormal grain growth and change in electrical characteristics in the conventional ZnO varistors caused by volatilization of Bi_2O_3, the ZnO powder with all additive oxides except Bi_2O_3 was pressed into disc form and sintered. The disc was then painted with metal oxide paste containing Bi_2O_3 and again fired. The ZnO varistor fabricated by this process, i.e. a two-stage heat-treatment process, showed typical non-linear I–V characteristics with higher breakdown voltage exceeding 800 V mm^{-1}. It was also observed that the non-linear I–V coefficient change rate, $\Delta\alpha$, in the ZnO varistor due to reheat-treatment is almost linearly proportional to the sintered density.

1. Introduction

ZnO varistor is known as a multijunction semiconductor device, whose highly non-ohmic current–voltage (I–V) characteristics are derived from the electrical properties of its grain-boundary region [1]. Conventional ZnO varistors are fabricated by sintering ZnO powder mixed with a number of metal oxide additives, including Bi_2O_3, Sb_2O_3, Cr_2O_3, Co_2O_3 and MnO_2. These oxide additives form multiphase bodies consisting of ZnO grains with $Zn(Zn_{4/3}Sb_{2/3})O_4$ known as the spinel phase and Bi_2O_3-rich $Bi_2Zn_{4/3}Sb_{2/3}O_6$ known as the pyrochlore phase [2]. The amount of these metal oxides incorporated in the ZnO powder affects the electrical characteristics of the ZnO varistor. With Co_2O_3 and MnO_2, remarkable improvement of the I–V non-linearity in the low current density region is achieved through the increased potential barrier height [3–5]. With Sb_2O_3, spinel phase is formed, and the breakdown voltage and non-linearity are increased [6, 7], while with Cr_2O_3, the decomposition temperature of the pyrochlore phase is lowered [8].

Bi_2O_3 plays an important role in inducing varistor characteristics in the ZnO varistor. However, Bi_2O_3 causes problems, such as abnormal grain growth, due to its liquid phase at the sintering temperature and change in electrical characteristics due to its volatilization [9, 10]. A decrease in the non-linearity phenomenon also occurs following the phase transition of Bi_2O_3 when reheated for electrode attachment in the temperature range 600 to 800 °C [11]. Bi_2O_3 can exist in four different phases, α, β, δ and γ [12]. When the phase of Bi_2O_3 changes from β to γ, mechanical stress due to the microscopic volume change is induced at the grain boundaries of ZnO. This stress causes deterioration in the non-linearity [13]. In order to alleviate these problems, ZnO varistor was fabricated through a two-stage heat-treatment process, in which ZnO-based green body (ZnO powder plus all the oxide additives except Bi_2O_3) was sintered by the conventional ceramic process and then Bi_2O_3 was diffused into the grain boundaries of the sintered ZnO-based ceramic through second firing process.

2. Experimental procedure

The conventional ZnO varistor composition, except Bi_2O_3, was prepared by wet ball milling for 24 h, dried and then granulated with PVA as binder. The granulated powder was pressed into discs 10 mm diameter and 1.2 mm thick at a pressure of 1000 kg cm^{-2}. The discs were sintered in the 1200 to 1450 °C temperature range with 50 °C intervals for 1 h in air and then cooled to room temperature. In order to form the electrical barrier at the ZnO grain boundaries, metal oxide paste was silk screened on both sides of the disc which was then fired again at four different temperatures (900, 1000, 1100 and 1200 °C) for six different times (15, 30, 45, 60, 120 and 240 min). The metal oxide paste was composed of 50% PbO, 40% Bi_2O_3 and 10% B_2O_3 by weight with nitrocellulose and diethylene glycol mono-*n*-butyl ether as a solvent. The ZnO varistors prepared by this process were painted with Dotite, an electroconductive silver paste (Fujikura Kasei Co. Ltd, Japan) for electrical characteristics measurement. After the measurement of the characteristics, the Dotite was removed and then the ZnO varistors were reheated in the range 600 to 850 °C for non-linearity change observations. The non-linear coefficient, α, in the current range 0.1 to 10 mA, was used to describe quantitatively the change in non-linearity. Applied current for I–V characteristics measurement was limited to 10 mA to avoid unwanted joule heating.

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3. Results and discussion

As shown in Fig. 1, the electrical resistivity of the sintered disc without Bi_2O_3 decreases with sintering temperature. Such a decrease in disc resistance may be attributed to the effective increase of the conducting area by the densification and also to the reduced number of grain boundaries by grain growth. It is also shown that the sintered discs have nearly ohmic *I–V* characteristics in the measured current range.

Fig. 2 shows the effect of Bi_2O_3 diffusion into the grain boundary of the sintered disc body. When the metal oxide paste is painted on both sides of the disc and fired at 1000 °C for 1 h in air, a typical non-ohmic property can be obtained. Comparing the results in Figs 1 and 2, we can see that melted Bi_2O_3 paste penetrates into the grain boundary during the second firing process and forms intergranular layers which, in turn, may give rise to the increased barrier height at the grain boundary.

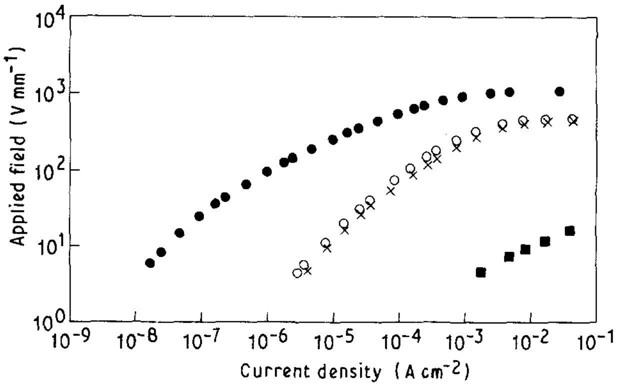

Figure 1 *I–V* curves of the discs sintered at four different temperatures: (●) 1200, (○) 1250, (×) 1300 and (■) 1350 °C.

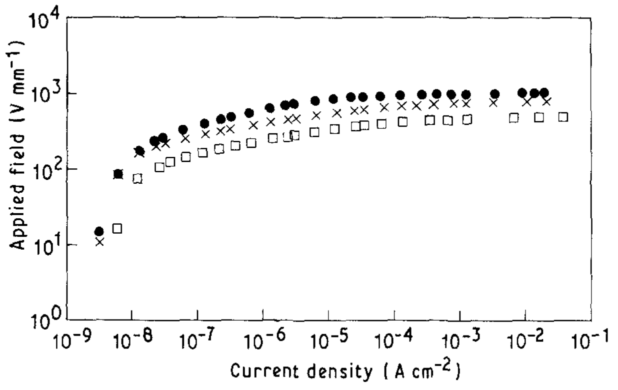

Figure 2 *I–V* curves of the discs fired for a second time at 1000 °C for 1 h. All the discs were initially sintered at (●) 1200, (×) 1300 and (□) 1400 °C.

The change in *I–V* characteristics for many different combinations of sintering and second firing temperatures are shown in Fig. 3. It was found that the varistor breakdown voltage (defined as V_{1mA} mm^{-1}) and the non-linear *I–V* coefficient ($\alpha = 0.1$ to 10 mA) decrease monotonically with the second firing temperature, as shown in Figs 3a and b. Our varistor samples fired for a second time at 1200 °C have a relatively lower breakdown voltage (V_{1mA} mm^{-1} < 100 V), while most of the ZnO varistors sintered at higher temperature present typical electrical breakdown voltage such as V_{1mA} mm^{-1} = 200 V [14]. It was reported elsewhere that in the case of the conventional sintering process, the volatilization temperature of Bi_2O_3 becomes higher due to the formation of complex compounds with the other metal oxides [14, 15]. We have used the metal oxide paste containing PbO and B_2O_3 as a flux to promote the Bi_2O_3 diffusion effect in the second firing process, and this flux might have enhanced the melting and volatilization of Bi_2O_3 at relatively low temperatures. Therefore, it is suggested that the lowered electrical breakdown voltage and non-linearity in our samples must be strongly attributed to the volatilization of Bi_2O_3. When these disc samples having low non-linear coefficient are heat

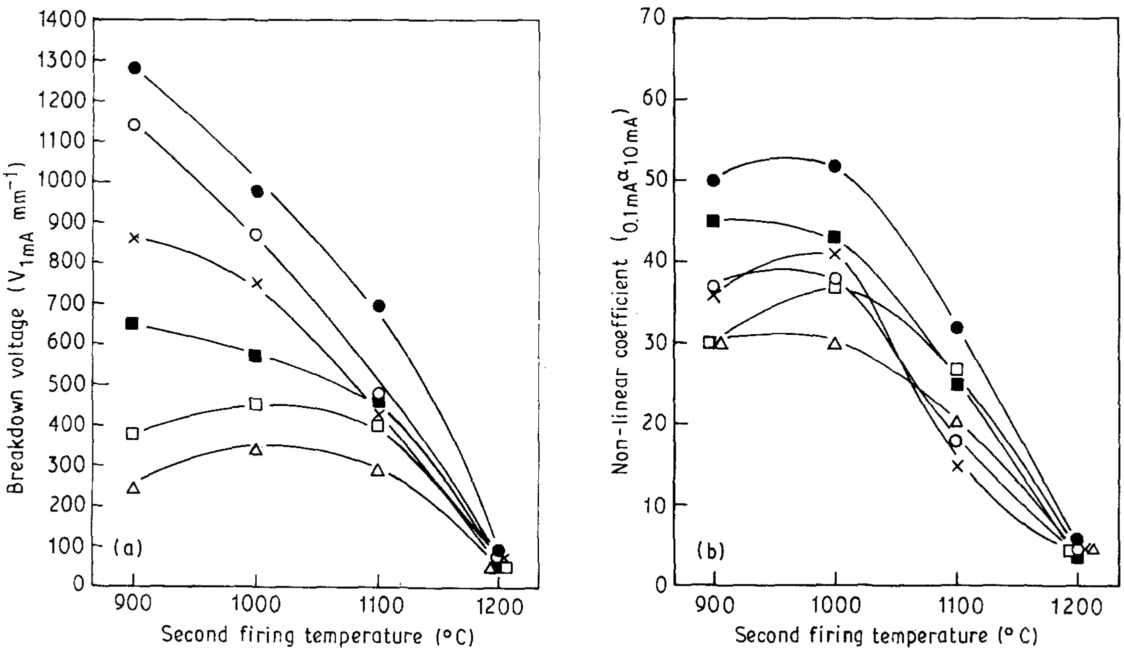

Figure 3 *I–V* characteristics change for various combinations of second firing and sintering temperatures: (a) variations in breakdown voltage (V_{1mA} mm^{-1}), and (b) variations in non-linear coefficient, α. Sintering temperature (°C): (●) 1200, (○) 1250, (×) 1300, (■) 1350, (□) 1400 and (△) 1450.

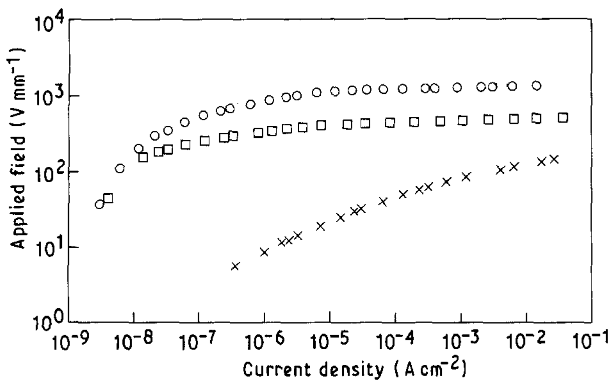

Figure 4 The effects of Bi_2O_3 rediffusion on the ZnO varistor. Sintering temperature 1200 °C. Heat-treatment conditions: (○) 900 °C, 1 h; (×) 1200 °C, 1 h; (□) 1200 °C, 1 h + 900 °C, 1 h.

treated again with Bi_2O_3 paste in the 900 to 1000 °C temperature range, the non-linear characteristics reappear, as shown in Fig. 4.

Fig. 4 shows the effect of the second firing with Bi_2O_3 concentration and the second firing temperature on the *I–V* characteristics of the same disc. The V_{1mA} mm^{-1} value of the heat-treated disc at 900 °C becomes lower than that of the original disc only fired for a second time at 900 °C, because of the ZnO grain growth.

The effects of the second firing time on the *I–V* characteristics of ZnO varistors are shown in Fig. 5. The discs were sintered at 1300 °C and fired for a second time at 1000 °C for six different firing times (15, 30, 45, 60, 120 and 240 min). It can be seen that the peaks appear for non-linear coefficient and breakdown voltage at the second firing times of 45 and 30 min, respectively. Fig. 5 also shows that at least 30 min second firing are needed to obtain non-ohmic *I–V* characteristics, and that when the second firing time exceeds 30 min, the non-linear coefficient of the discs decreases with increasing second firing time, due to the volatilization of Bi_2O_3. It was also found that the breakdown voltage decreases with increasing second firing time due to the grain growth.

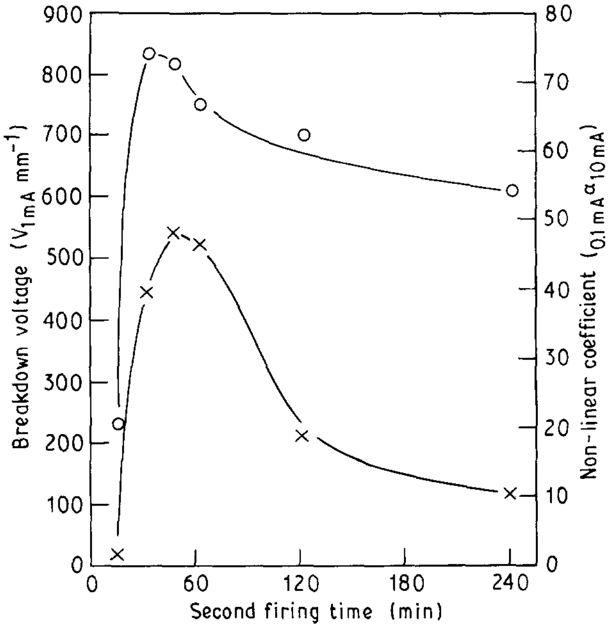

Figure 5 The variation of (○) breakdown voltage (V_{1mA} mm^{-1}) and (×) non-linear coefficient, α, with the second firing time. Samples were sintered at 1300 °C for 1 h.

The *I–V* characteristics of the disc prepared through the second firing process at 1000 °C for 1 h are compared in Fig. 6 with that of the disc fabricated by the conventional process. It can be seen that the breakdown voltage for the disc fired twice is about four times higher than that of the varistor made by the conventional process. This breakdown voltage difference between the discs must originate from their microstructure differences, as shown in Fig. 7.

Fig. 7 shows scanning electron micrographs of the fracture surface of the samples prepared by second firing and conventional processes. Figs 7a and b show the microstructure of the discs sintered at two different temperatures, 1200 and 1350 °C, respectively, with identical second firings at 1000 °C for 1 h. As shown in these figures, the ZnO grains are similar in size, even with a 150 °C sintering temperature difference. However, the apparent sintered densities differ from each other. The apparent sintered density of the disc at 1200 °C is 3.74 g cm^{-3} and that of the disc at 1350 °C is 4.58 g cm^{-3}. It was also found that the grain size of samples fired a second time is about four times smaller than that of the conventional ones (10 μm) in Fig. 7c. This means that the grain size is dependent on the presence of Bi_2O_3 which is known to promote liquid-phase sintering. Fig. 7d shows the microstructure of the disc prepared by sintering at a second firing temperature of 1200 °C. In this case, it can be seen that the grain size is smaller than that of Fig. 7c, and greater than that of Figs 7a and b.

Fig. 8 shows the relationship between the non-linear coefficient change rate, Δα, and the apparent sintered density for several different sintering temperatures. Δα is defined here as $(\alpha_t - \alpha)/\alpha$, where α_t is the minimum non-linear coefficient value in the reheat-treatment temperature range 600 to 850 °C. It should be noted that Δα increases with sintered density, i.e. the *I–V* non-linearity becomes poor as the sintered density increases. It is believed that these phenomena may

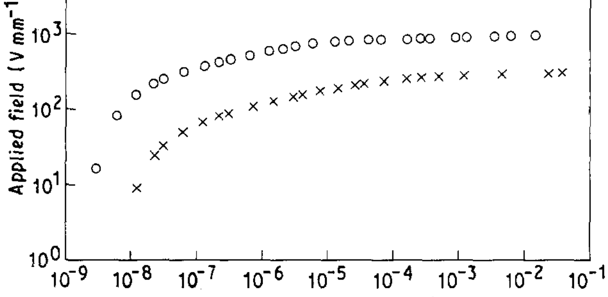

Figure 6 Comparison of *I–V* characteristics of ZnO varistors fabricated through the (○) second firing and (×) conventional processes. Sintering temperature 1200 °C.

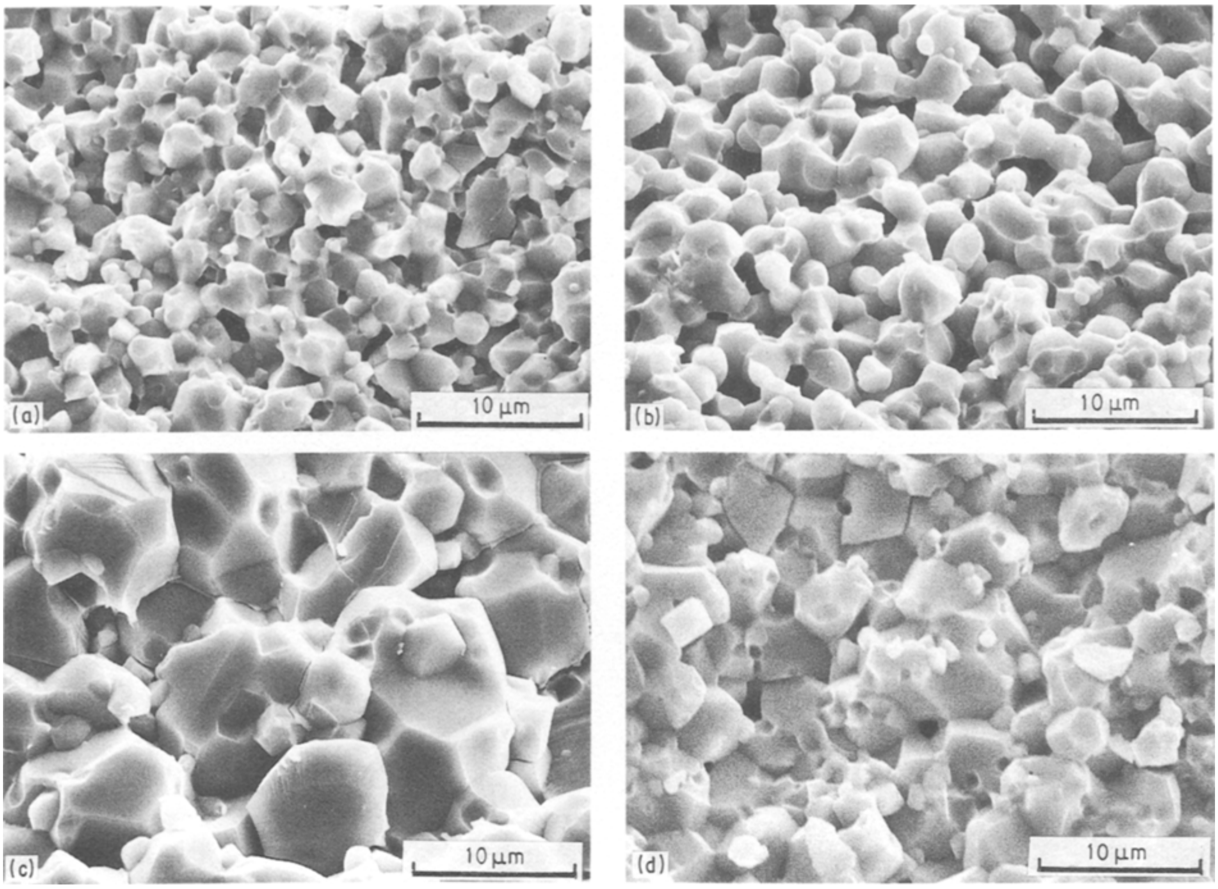

Figure 7 Scanning electron micrographs of the fracture surface for the ZnO varistors after a second firing process. (a) 1000 °C, 1 h after 1200 °C, 1 h; (b) 1000 °C, 1 h after 1350 °C, 1 h; (d) 1200 °C, 1 h after 1200 °C, 1 h. (c) Conventional process, 1200 °C, 1 h.

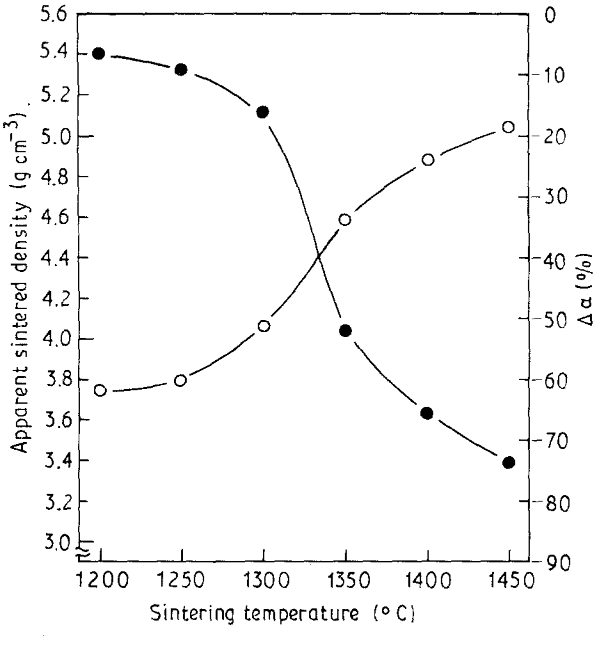

Figure 8 (○) Apparent sintered density and (●) non-linear coefficient change rate, Δα, with sintering temperatures.

result from the internal stress due to the Bi_2O_3 phase transition caused by the reheat-treatment at the ZnO grain boundaries, and furthermore this internal stress could be more easily relieved in the case of the ZnO varistor with low sintered density than that with high sintered density. It is, therefore, supposed that for the porous type of ZnO varistor, the electrical characteristic change due to the reheat-treatment should become less than that of a dense one.

4. Conclusion

ZnO varistor performance, such as thermal stability, can be improved by a second firing process with Bi_2O_3 diffusion into the ZnO ceramic body which is initially sintered without Bi_2O_3 through the conventional fabrication process. It was found that the ZnO varistor fabricated by this second firing method shows a higher breakdown voltage, which is about four times larger than the conventional ones, and also excellent I–V non-linearity ($\alpha > 40$) with relatively smaller thermal dependence.

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