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Fabrication of Low-Voltage ZnO Varistors by a Two-Step Process

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Abstract

In order to make a low-voltage ZnO varistor of uniformly large-grained microstructure, a pure ZnO powder compact was first sintered at 1500°C. The abnormal grain growth that occurred during the sintering of the ZnO resulted in a relatively uniform matrix of very large grains. Subsequent heat-treatment in contact with a Bi_2O_3 *powder mixture resulted in the formation of a low-voltage ZnO varistor.*

1 Introduction

Low-voltage ZnO varistors are now widely used for surge protection in integrated circuits and in automobiles.[1,2] Since the breakdown voltage (V_b) of the varistor is proportional to the number of ZnO grains in series between the electrodes,[3,4] low voltage varistors can be obtained either by decreasing the thickness of the specimen or by increasing the size of ZnO grains. The thin ZnO varistors are, however, difficult to prepare and apt to break. Note also that the energy absorption capability of the thin ZnO varistor is very poor due to its small volume.[5–8] On the other hand, low voltage ZnO varistors with grains of large size have been fabricated by using grain growth-enhancing additives,[6,9] or exceptionally large seed ZnO grains.[7,8] Consequently, its microstructure exhibits a nonuniform distribution of grain size, which causes an irregular current distribution and makes the varistor susceptible to hot spots.[10–12]

In this paper, a new processing technique for the production of a low-voltage ZnO varistor of uniformly large-grained microstructure will be described. Instead of conventional fabrication by sintering of ZnO powder which has been previously mixed with Bi_2O_3 and other oxides, the two-step process consisting of the sintering of pure ZnO alone and subsequent heat-treatment has been adopted for fabrication of the low-voltage ZnO varistor. The uniformity in grain size and low porosity of ZnO varistors obtained by this process are expected to enhance its reliability and lifetime.

2 Experimental Procedures

Commercial grade ZnO powder of 99·9% purity (Aldrich Chem. Co. Inc., Milwakee, Wis., USA) was used. Its average particle size determined by sedimentation technique was 0·5 μm. The powder was pressed to a cylindrical compact (10 mm in diameter) with a hole (3 mm in diameter) in the center, and then pressed hydrostatically at 100 MPa. The obtained compacts were sintered at 1500°C for 1 h in air to induce an extensive grain growth. In order to minimize the ZnO vaporization and consequent pore formation during sintering at such a high temperature, the specimens were put together with the same ZnO powders in a closed alumina crucible. Platinum foil was used to isolate the specimen from the surrounding powders. The sintered specimens were then ground and its thickness was controlled to be 4 mm. On the other hand, high purity Bi_2O_3 and MnO_2 powders were mixed with ZnO to give $1Bi_2O_3$–$1MnO_2$–98ZnO (in mol%). This powder mixture was then manually rubbed into the central hole of the sintered ZnO specimen. The specimen was then heat-treated at 1200°C for 1 h with Bi_2O_3 powders in a closed alumina crucible, as illustrated in Fig. 1. Preliminary experiments showed that this heat-treatment condition is most appropriate for making a varistor of the desirable I–V characteristic.

The photomicrographs of the polished section for pure ZnO, i.e. before the Bi_2O_3 atmosphere treatment were obtained after the thermal etching for 30 min at 1200°C. After the atmosphere treatment, however, etching was not needed for microstructural observation. The presence of the

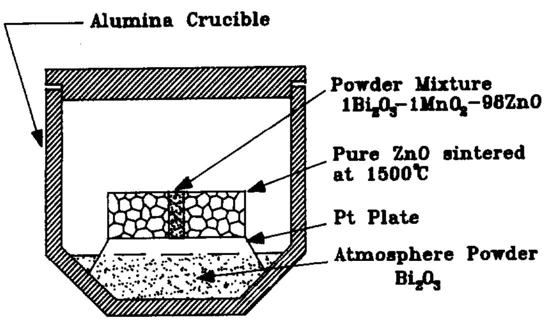

Fig. 1. Schematic illustration for heat-treatment of large-grained pure ZnO specimen in Bi_2O_3 atmosphere.

Bi-rich liquid phase at the grain boundary was observed by transmission electron microscopy. Disks of 3 mm in diameter were cut from the specimen and reduced to a thickness of ≈ 5–10 μm in the center by mechanical grinding and dimpling. A further thinning was carried out by using an ion-miller. The I–V characteristic of the specimen prepared was measured with a picoammeter (Model: 4140B pA Meter/DC voltage source, Yokogawa Hewlett Packard Co., Yokogawa, Japan). The individual specimen was ground on silicon carbide paper (No. 1200) and the electrode was made by sputtering Au on each surface of the cylindrical specimen. The voltage per unit thickness (1 mm) at a current of 1 mA/cm^2 was regarded as the breakdown voltage of the varistor specimen.[10,13,14]

3 Results and Discussion

Previous studies[15–17] on sintering of pure ZnO have shown that its densification begins at a rather low temperature such as 700°C and the full densification is achieved in a few minutes of sintering at 1200°C. On the other hand, a decrease in bulk density, which can be referred to as overfiring has been reported to occur during sintering of ZnO if the sintering temperature is too high.[18] From these works, the optimum temperature for the densification of ZnO powder compact is expected to be around 1100°C. In this investigation, however, the ZnO powder compacts were sintered at 1500°C to induce a rapid grain growth and Fig. 2 (a) and (b) show the microstructure of the specimen sintered for 0·5 and 1 h, respectively. In spite of an excessively high sintering temperature, a notable increase of porosity was not observed in this experiment. It appears likely that the atmosphere powders have minimized the ZnO evaporation from the specimen and consequent pore formation. For the specimen shown in Fig. 2 (a) and (b), most of the pores were trapped inside the grain as a result of extensive grain growth. The porosities determined by the point counting method were 0·2 and 0·5%, respectively.

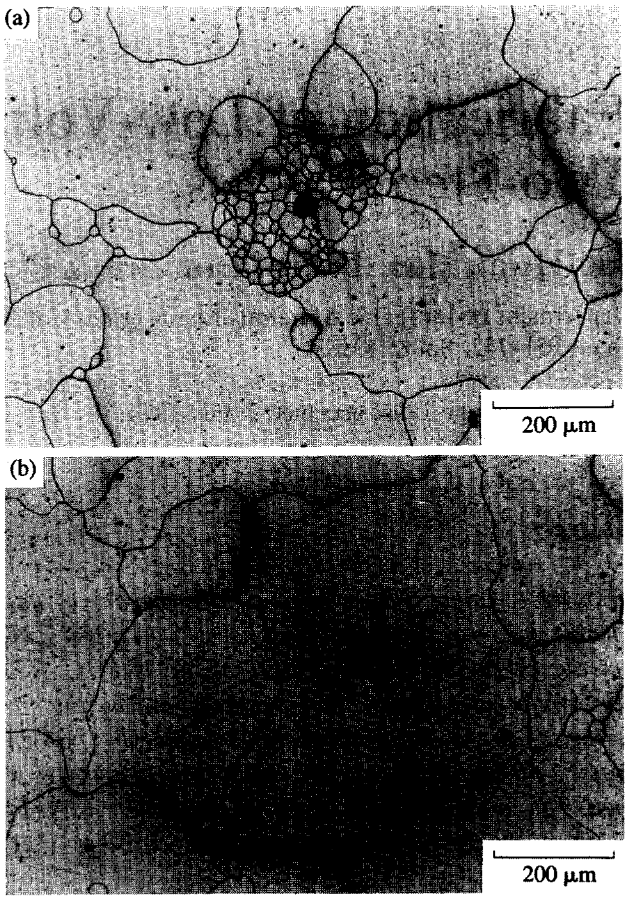

Fig. 2. Microstructures of the pure ZnO specimen sintered at 1500°C for (a) 0·5 and (b) 1 h.

In comparison with the initial ZnO particle size (≈ 0·5 μm), the grains observed in the specimen shown in Fig. 2 are exceptionally large. Note that the specimens were made from fine powder and therefore a few particles of a size substantially larger than the average may be present, which acted as embryos for abnormal grain growth.[19,20] It has been suggested that the grains two times larger than the average may be able to start the abnormal grain growth. The assembly of small grains observed in the specimen sintered for 0·5 h (Fig. 2 (a)) may show the initial fine grained structure. Once those few abnormally growing grains reach a size where they impinge each other, the grain boundaries tend to be flat so that the driving force for migration is practically eliminated. Fig. 2 (b) is expected to exhibit such a new set of exceptionally large grains which replace completely the initial fine grained structure. For this specimen, the average grain size was determined to be ≈ 500 μm through the linear intercept method.

Inside those abnormally grown grains, the entrapped small grains were frequently observed as indicated by the arrow in Fig. 2 (b). Such grain entrapment during abnormal grain growth has also been reported in other ceramic materials and attributed to the very rapid boundary migration.[21] It is expected, however, that the grain entrapment is related to the size and orientation of shrinking grains adjacent to the rapidly growing grains. As the shrinking grains vary in size and have random orientation, the growth rate along the advancing boundary will be uneven from point to point. The slowly shrinking grains and/or the relatively large size grains will become entrapped and be left behind to remain in an apparent metastable state. It is further expected that the grains once trapped shrink rapidly, which may explain their rare experimental observation.

The breakdown voltage of a varistor, V_b, is given by[3]

$$V_b = v_{gb} \frac{D}{r} \tag{1}$$

where v_{gb} is the threshold voltage per grain boundary, which has been estimated to be around 3·6 V,[10,12,13] and D and r are the varistor thickness and average ZnO grain size, respectively. For the low-voltage ZnO varistor, such as $V_b = 7$ V, it has been consequently reported[22] that the thickness should be less than 100 μm, because the average grain size of ZnO grains in conventionally sintered ZnO–Bi_2O_3 is always below 50 μm. Note also that such coarse-grained ZnO–Bi_2O_3 specimens can be obtained by sintering at 1400°C for several hours during which the vaporization of Bi_2O_3 occurs.[23] The vaporization of Bi_2O_3 and concurrent increase of porosity are known[23] to be significant from 1200°C and to deteriorate the varistor characteristic.

As a consequence, the coarse-grained ZnO varistors ensuring the low V_b have been prepared either by using the grain growth enhancing additives[9,22] such as TiO_2 or by adding large ZnO seed grains.[7,8] The varistors thus prepared, however, showed a large spread of grain size and a very high porosity. The presence of a few large grains may result in the high local currents which give rise to a rapid degradation of the varistor.[10–12] In addition, the harmful effects of pores with respect to the mechanical strength are evident.

Assuming that the microstructure of the ZnO varistor is identical to that of Fig. 2 (b), several advantages may appear. First of all, the thickness of a low-voltage varistor (V_b = 7 V) becomes around 2 mm which can be manufactured and handled without great difficulty. The rather uniform distribution of grain size may provide a uniform current flow, and its low porosity enhances the strength and thermal conductivity of the varistor. The high thermal conductivity and fairly large volume may also increase the energy handling capability of the varistor.[10] However, the addition of Bi_2O_3 is known to be essential for ZnO varistors. The Bi ions segregated in the region of the grain boundary have been attributed for the nonlinear characteristics.[24] In order to make a varistor, it is therefore necessary to form a depletion layer by changing the chemistry of the grain boundaries.

Using the specimen shown in Fig. 2(b), the formation of depletion layer was carried out by the heat-treatment with Bi_2O_3 containing powder mixture. The powder mixture of $1Bi_2O_3$–$1MnO_2$–98ZnO was rubbed into the central hole of the sintered ZnO, and then it was heat-treated at 1200°C for 1 h in Bi_2O_3 atmosphere (Fig. 1). During the treatment, the Bi-rich liquid formed in the powder mixture was expected to penetrate into the grain boundaries of ZnO specimens. Note also that the Bi_2O_3 atmosphere powder in the alumina crucible may provide a high vapor pressure of Bi_2O_3.[10,14,23] In fact, Bi_2O_3 was observed to diffuse into almost all of the grain boundaries of pure ZnO specimen when it was treated at 1200°C for 1 h with a small amount of Bi_2O_3 on its surface.[25]

Figure 3 is the microstructure of the specimen obtained. The region of $1Bi_2O_3$–$1MnO_2$–98ZnO (upper part of Fig. 3) showed a typical liquid-phase sintered structure with the solid grains (white) and pores (dark) dispersed in a Bi-rich liquid matrix. Note that the powder mixture was packed by hand into the hole, which is the cause of the rather large fraction of pores. The originally pure ZnO region can be observed in the lower part of Fig. 3. Although a notable microstructural change compared to Fig. 2 (b) was not observed in this microscopic scale, the liquid was observed to present almost all the triple grain boundary junctions.

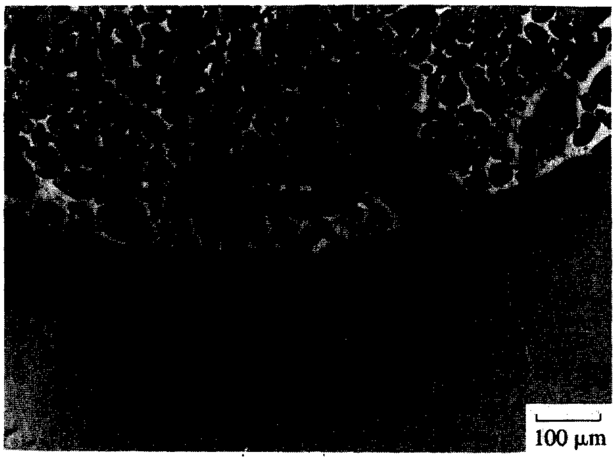

Fig. 3. Microstructure of the ZnO varistor prepared; the pure ZnO was heat-treated at 1200°C for 1 h with the powder mixture ($1Bi_2O_3$–$1MnO_2$–98ZnO in mol%).

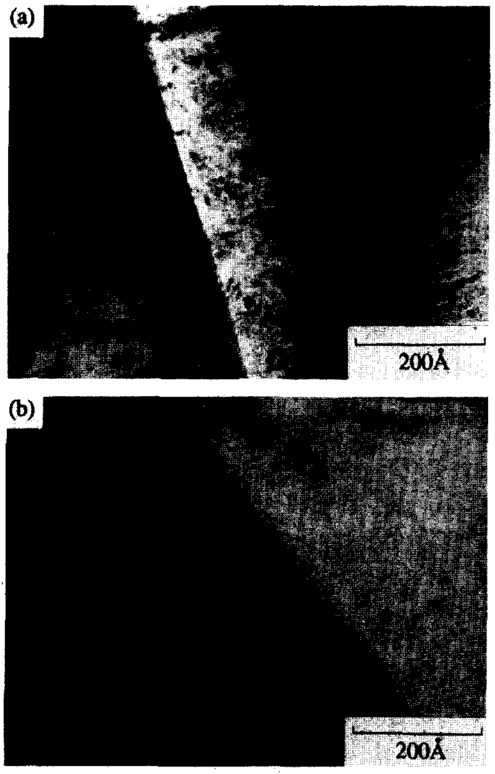

Fig. 4. TEM micrographs of the varistor prepared; (a) some boundaries show the presence of Bi-rich liquid phase and (b) the others show a typical grain boundary.

The grain boundaries and their triple junctions were examined with transmission microscopy. As shown in Fig. 4, some of the grain boundaries showed the presence of a Bi-rich liquid phase (bright region in Fig. 4 (a)), but other boundaries (Fig. 4 (b)) did not show the presence of any Bi-rich liquid phase. Approximately, 80% of the boundaries were observed to be wetted with the Bi-rich liquid and its maximum thickness was around 1 μm. The results may indicate that the grain boundary structure and its energy, which determine the liquid penetration, vary from one grain boundary to another. For ZnO varistors, in fact, three different types of boundary structure were reported,[24] a thick intergranular liquid layer (0·1 ~ 1 μm), a thin intergranular liquid layer (10 ~ 1000 Å), and the grain boundary without any liquid phase.

Figure 5 shows the I–V characteristic of the specimen obtained. The breakdown voltage at a current density of 1 mA/cm^2 is determined to be 3·6 V/mm which is much lower than that of the conventionally fabricated low-voltage varistors. Using ZnO seed grains, for instance, V_b = 6 V/mm has been reported.[7] If the threshold voltage per grain boundary is about 3·6 V, the grain size of the specimen prepared is predicted to be 1000 μm by eqn (1). Note that the current always flows through the easiest path, i.e. the path with the fewest number of grains between the electrodes.

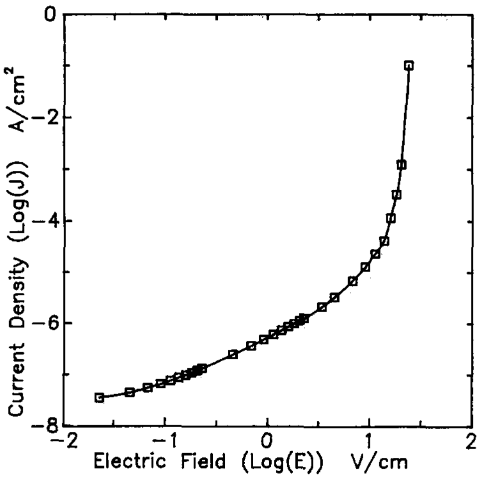

Fig. 5. I–V characteristic of the ZnO varistor prepared.

Therefore, the predicted grain size from the breakdown voltage is always larger than the microstructural average grain size. The nonlinearity coefficient of α for this specimen in the range of 10^{-3} to 10^{-1} A/cm^2 is 20. This value of α is expected to be further increased if other oxides such as CoO, Cr_2O_3, and Sb_2O_3 are incorporated in the Bi_2O_3 containing powder mixture. On the other hand, the amount of leakage current in the pre-breakdown region is acceptable. When the strength of electric field was 10 V/cm, the magnitude of leakage current was 10^{-5} A/cm^2.

4 Conclusions

Low-voltage ZnO varistors have been fabricated by a two-step process consisting of the sintering of pure ZnO and subsequent heat-treatment. The abnormal grain growth that occurred during sintering of ZnO resulted in a relatively uniform matrix of very large grains. After the subsequent treatment with Bi_2O_3 the specimens showed a typical microstructure for a ZnO varistor with a Bi-rich liquid at the triple grain boundary junctions. The breakdown voltage of the specimen obtained was 3·6 V/mm and its nonlinear coefficient α was 20.

Acknowledgement

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