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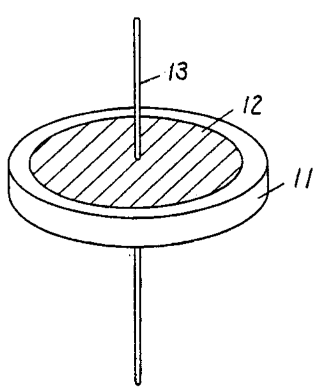
(54) A method for producing a ZnO Varistor.

(57) A method for producing a ZnO-based varistor includes the steps of: heat-treating a mixture of TiO_2 powders and Bi_2O_3 powders so as to prepare composite powders; and adding the composite powders to ZnO varistor materials.

Fig. 1



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BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a method for producing a ZnO-based varistor used for absorbing a surge caused in an electrical circuit, and more particularly to a method for producing a low-voltage ZnO-based varistor widely used for protecting a semi-conductor device in an electronic circuit from various surges.

2. Description of the Related Art:

ZnO-based varistors are formed of a sintered body containing ZnO varistor materials (i.e., zinc oxide (ZnO), basic additives such as bismuth oxide (Bi_2O_3), manganese oxide (MnO_2) and cobalt oxide (CoO), and various oxides to be added for the purpose of improving the performance of the varistors). The clamping voltage of each ZnO-based varistor is known to increase nearly in proportion to the number of grain boundaries present between electrodes. That is to say, the clamping voltage of the ZnO-based varistor increases by 3 to 4 V per one grain boundary. Therefore, in order to produce a low-voltage ZnO-based varistor, it is required that a sintered body containing ZnO grains having a large size is produced. Conventionally, a grain-growth-enhancing additive such as titanium oxide (TiO_2) has been added to enhance the growth of ZnO grains.

However, the addition of TiO_2 sometimes causes an abnormal growth of ZnO grains, resulting in a large distribution in size of ZnO grains. Thus, it has been difficult to uniformly enhance the growth of the grains.

An electric current is likely to flow through a path in the ZnO grains between electrodes, where the least grain boundaries are present. Therefore, in the case where the distribution in size of ZnO grains in the sintered body is large, an electric current intensively flows through that part of the sintered body. Accordingly, there has been problems in that the electrical characteristics of the low-voltage ZnO-based varistor are decreased within a short period of time and so the reliability thereof is low. In addition, since it has been difficult to sufficiently control the abnormal growth of ZnO grains, there has been a large variation of electrical characteristics and the reliability between Zno-based varistors obtained from one lot (in-lot variation) and between ZnO-based varistors obtained from different lots (inter-lot variation).

As described above, according to the conventional production method, low-voltage ZnO-based varistors with excellent electrical characteristics and reliability cannot be stably produced.

SUMMARY OF THE INVENTION

The method for producing a ZnO-based varistor of the present invention, includes the steps of:

heat-treating a mixture of TiO_2 powders and Bi_2O_3 powders to prepare composite powders; and

adding the composite powders to ZnO varistor materials.

In one embodiment of the present invention, the above-mentioned method further includes the step of adding an aluminum component to the ZnO varistor materials.

In another embodiment of the present invention, the aluminum component is added to the ZnO varistor materials so that the weight ratio of Al_2O_3 powders to the ZnO powders is in the range of 0.00062 : 100.0 to 0.372 : 100.0.

In still another embodiment of the present invention, the aluminum component is a solution of an aluminum salt.

In still another embodiment of the present invention, the aluminum salt is aluminum nitrate.

In still another embodiment of the present invention, the aluminum salt is aluminum acetate.

In still another embodiment of the present invention, the above-mentioned method further includes the step of adding an antimony component to the ZnO varistor materials.

In still another embodiment of the present invention, the antimony component is added to the ZnO varistor materials so that the weight ratio of Sb_2O_3 powders to the ZnO powders is in the range of 0.018 : 100.0 to 0.72 : 100.0.

In still another embodiment of the present invention, the above-mentioned method further includes the step of adding a tin component to the ZnO varistor materials.

In still another embodiment of the present invention, the tin component is added to the ZnO varistor materials so that the weight ratio of SnO_2 powders to the ZnO powders is in the range of 0.005 : 100.0 to 0.37 : 100.0.

In still another embodiment of the present invention, the above-mentioned method further includes the step of adding a chrome component to the ZnO varistor materials.

In still another embodiment of the present invention, the chrome component is added to the ZnO varistor materials so that the weight ratio of Cr_2O_3 powders to the ZnO powders is in the range of 0.005 : 100.0 to 0.18 : 100.0.

The present invention has been achieved as a result of the earnest study of a mechanism of grain-growth-enhancing by using TiO_2. More specifically, the following was found: When TiO_2 is reacted with ZnO, the growth of ZnO grains cannot be enhanced. On the other hand, when TiO_2 is reacted with Bi_2O_3, the reaction product can enhance the growth of ZnO grains. Therefore, in the case where TiO_2 is merely added as in the conventional method, in some parts of the sintered body, TiO_2 is reacted with ZnO and in other parts thereof, TiO_2 is reacted with Bi_2O_3. Namely, in some parts of the sintered body, the growth of ZnO grains are not enhanced, and in other parts of the sintered body, the growth of ZnO grains are enhanced. Thus, according to the conventional production method, it has been impossible to produce a sintered body with a small distribution in size using ZnO grains. According to the present invention, a mixture of TiO_2 and Bi_2O_3 is previously heat-treated to prepare composite powders. The composite powders can uniformly enhance the growth of ZnO grains.

Moreover, it was found that an antimony component, a tin component, or a chrome component together with an antimony component suppresses the abnormal growth of ZnO grains. The addition of either of these components makes the ZnO grains twin crystal, thereby suppressing the abnormal growth of ZnO grains.

Because of the above-mentioned two phenomenons (i.e., the addition of the composite powders obtained by previously heat-treating the mixture of TiO_2 and Bi_2O_3 and the addition of either of an antimony component, a tin component, or a chrome component together with an antimony component), the ZnO grains having a large average grain size and a small distribution of grain sizes can be obtained. These phenomenons were found by the inventors of the present invention as a result of their earnest study of a method for adding a bismuth component and a titanium component to ZnO varistor materials.

In addition, an aluminum component dissolves in the ZnO grains in a solid state to function as a donor, thereby decreasing electrical resistance.

Thus, the invention described herein makes possible the advantage of providing a method for producing a low-voltage ZnO-based varistor with high yield, which is excellent in electrical characteristics and reliability at a low voltage.

This and other advantages of the present invention will become apparent to those skilled in the art upon reading and understanding the following detailed description with reference to the accompanying figure.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic view showing a ZnO-based varistor produced in the examples according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention will be described by way of illustrative examples with reference to the drawing and tables.

Example 1

TiO_2 fine powders and Bi_2O_3 powders were mixed in a weight ratio of 11.4 : 88.6. The mixture thus obtained was heat-treated at 600°C for 5 hours. Then, the mixture was ground to obtain composite powders. Hereinafter, the composite powders thus obtained will be referred to as TiO_2/Bi_2O_3 composite powders.

ZnO powders, TiO_2/Bi_2O_3 composite powders, CoO powders and MnO_2 powders were mixed in a weight ratio of 100.0 : 2.93 : 0.804 : 0.555 by a wet method and ground. The resulting powders were dried and formed by pressure molding. The molding thus obtained was provisionally sintered at 600°C and ground. Then, the ground molding was formed into a disk shape. The disk-shaped molding was heated in the atmosphere at 100°C/hour and kept at 1250°C for 2 hours. Then, the molding was cooled at 100°C/hour to obtain a sintered body. The sintered body had a thickness of 1.2 mm and a diameter of 14 mm.

Next, referrering to Figure **1**, a method for producing a ZnO-based varistor will be described. Aluminum and then copper were flame-coated onto both sides of a sintered body **11** obtained as described above, whereby electrodes **12** were formed thereon. The electrodes **12** were provided with a lead wire **13** by soldering, and then the sintered body **11** excluding the lead wire **13** was painted in order to produce a ZnO-based varistor.

The electrical characteristics of the ZnO-based varistor thus obtained were evaluated. As initial electrical characteristics, the ZnO-based varistor was measured for $V_{1mA/mm}$ and non-linear resistance index ${}_{0.1}\alpha_{1mA}$. Here, $V_{1mA/mm}$ refers to a voltage with respect to 1 mm thickness of the ZnO-based varistor between electrodes, in a case where an electric current of 1 mA flows through the lead wire **13**; and the non-linear resistance index ${}_{0.1}\alpha_{1mA}$ refers to a value obtained by using V_{1mA} and $V_{0.1mA}$.

In addition, the ZnO-based varistor was evaluated for reliability with respect to a DC load. The ZnO-based varistor was added with a DC load of 0.2 watts at 80 °C for 500 hours. In this way, the change rate $\Delta V_{1mA}/V_{1mA}$ (change rate due to a DC load) of a clamping voltage V_{1mA} of the ZnO-based varistor was measured. Moreover, the ZnO-based varistor was evaluated for reliability with respect to a surge. The ZnO-based varistor was twice applied with a pulse of 0.5 kA for 8 x 20 μsec to obtain the change rate $\Delta V_{1mA}/V_{1mA}$ (change rate due to a surge). The composition of the specimen of the present example is shown in Table 1, and the evaluation results of the electrical characteristics thereof are shown in Table 2. The numerals representing the evaluation results are the maximum and the minimum values of in each lot.

Table 1

specimen	ZnO (wt ratio)	$Bi_2O_3 + TiO_2$ (heat-treated) (wt ratio)	CoO (wt ratio)	MnO_2 (wt ratio)
#001	100.0	2.93	0.804	0.555

Table 2

specimen	V_1 mA/mm (V)	${}_{0.1}\alpha_1$ mA	Change rate due to a DC load $\Delta V_1 mA/V_1 mA$ (%)	Change rate due to a surge $\Delta V_1 mA/V_1 mA$ (%)
#001	16-18	30-34	-1--2	-4-1

As is understood from Tables 1 and 2, the ZnO-based varistor produced by the method of the present example has excellent reliability. That is to say, in the ZnO-based varistor of the present invention, the clamping voltage V_{1mA} was low and the absolute value of the change rate $\Delta V_{1mA}/V_{1mA}$ of the clamping voltage V_{1mA} with respect to the application of a DC load or a surge for a long period of time was not more than 5%. In addition, as shown in Table 2, the variation of the electrical characteristics between the ZnO-based varistors obtained from one lot was small.

Moreover, in the present example, the variation of the electrical characteristics between the ZnO-based varistors obtained from different lots was also small (not shown in Table 2).

As described above, according to the method of the present example, the yield of the ZnO-based varistors were remarkably improved.

Comparative Example

A ZnO-based varistor was produced by a conventional method, using a sintered body having the same composition as that of Example 1.

ZnO powders, Bi_2O_3 powders, TiO_2 fine powders, CoO powders, and MnO_2 powders were mixed in a weight ratio of 100.0 : 2.60 : 0.33 : 0.804 : 0.555 by a wet method and ground. The powders thus obtained were dried and formed by pressure molding. The molding thus obtained was provisionally sintered at 600 °C and ground. Then, the ground molding was formed into a disk shape. The disk-shaped molding was heated in the atmosphere at 100 °C/hour and kept at 1250 °C for 2 hours. Then, the molding was cooled at 100 °C/hour to obtain a sintered body. The sintered body had a thickness of 1.2 mm and a diameter of 14 mm.

Hereinafter, in the same way as in Example 1, a ZnO-based varistor was produced. Also, in the same way as in Example 1, the ZnO-based varistor thus obtained was evaluated for electrical characteristics. Table 3 shows the composition of the specimen of this comparative example, and Table 4 shows the evaluation results of the electrical characteristics thereof.

Table 3

specimen	ZnO (wt ratio)	Bi_2O_3 (wt ratio)	TiO_2 (wt ratio)	CoO (wt ratio)	MnO_2 (wt ratio)
#002	100.0	2.60	0.33	0.804	0.555

Table 4

specimen	V_1 mA/mm (v)	$_{0.1}\alpha_1$ mA	Change rate due to a DC load Δ V_1 mA/V_1 mA (%)	Change rate due to a surge Δ V_1 mA/V_1 mA (%)
#002	24-33	10-23	-25--40	-45--60

As is understood from Tables 3 and 4, in the ZnO-based varistor produced by the conventional method, the clamping voltage V_{1mA} after the application of a DC load of 0.2 watts was remarkably decreased, and the absolute value of the change rate Δ V_{1mA}/V_{1mA} of the clamping voltage V_{1mA} with respect to the application of a DC load was not less than 25%. Moreover, the absolute value of the change rate Δ V_{1mA}/V_{1mA} of the application of a surge was more than 40%. Thus, the reliability of the ZnO-based varistor produced by the conventional method was remarkably low. As shown in Table 4, the variation of the electrical characteristics between the ZnO-based varistors obtained from one lot was large.

Moreover, the variation of the electrical characteristics between the ZnO-based varistors obtained from different lots was larger than that from one lot (not shown in Table 4). In some cases, the ZnO-based varistors had $V_{1mA/mm}$ and a non-linear resistance index $_{0.1}\alpha_{1mA}$ lower than those shown in Table 4.

As is apparent from the comparison between Example 1 and Comparative Example, the ZnO-based varistor produced by the method of the present invention is more excellent than the ZnO-based varistor produced by the conventional method in the initial electrical characteristics, the reliability, and the variation of the electrical characteristics between the ZnO-based varistors obtained from one lot and between the ZnO-based varistors obtained from different lots.

Example 2

TiO_2 fine powders and Bi_2O_3 powders were mixed in a weight ratio of 20.5 : 79.5. The mixture thus obtained was heat-treated at 800°C for 5 hours. Then, the mixture was ground to obtain TiO_2/Bi_2O_3 composite powders. The composite powders contained $Bi_4Ti_3O_{12}$ as a main component thereof.

ZnO powders, TiO_2/Bi_2O_3 composite powders, CoO powders and MnO_2 powders were mixed in a weight ratio of 100.0 : 3.15 : 0.922 : 0.534 by a wet method and ground. The resulting powders were dried and formed by pressure molding. The molding thus obtained was provisionally sintered at 600°C and ground. Then, the ground molding was formed into a disk shape. The disk-shaped molding was heated in the atmosphere at 100°C/hour and kept at 1250°C for 2 hours. Then, the molding was cooled at 100°C/hour to obtain a sintered body. The sintered body had a thickness of 1.2 mm and a diameter of 14 mm.

Hereinafter, a ZnO-based varistor was produced in the same way as in Example 1. Moreover, in the same way as in Example 1, the ZnO-based varistor thus obtained was evaluated for electrical characteristics. The composition of the specimen of the present example is shown in Table 5, and the evaluation results of the electrical characteristics thereof are shown in Table 6.

Table 5

specimen	ZnO (wt ratio)	$Bi_4Ti_3O_{12}$ $Bi_2O_3 + TiO_2$ (heat-treated) (wt ratio)	CoO (wt ratio)	MnO_2 (wt ratio)
#003	100.0	3.15	0.92	0.53

Table 6

specimen	V_1mA/mm (V)	$_{0.1}\alpha_1$ mA	Change rate due to a DC load Δ V_1mA/V_1mA (%)	Change rate due to a surge Δ V_1mA/V_1mA (%)
#003	15-16	28-32	-1--2	-1--2

As is understood from Tables 5 and 6, the ZnO-based varistor produced by the method of the present example has excellent reliability. That is to say, in the ZnO-based varistor of the present invention, the clamping voltage V_{1mA} was low and the absolute value of the change rate V_{1mA}/V_{1mA} of the clamping voltage V_{1mA} with respect to the application of a DC load or a surge for a long period of time was not more than 5%. In addition, as shown in Table 6, the variation of the electrical characteristics between the ZnO-based varistors obtained from one lot was small.

Moreover, in the present example, the variation of the electrical characteristics between the ZnO-based varistors obtained from different lots was also small (not shown in Table 6).

As described above, according to the method of the present example, the yield of the ZnO-based varistors were remarkably improved.

Example 3

TiO_2 fine powders and Bi_2O_3 powders were mixed in a weight ratio of 11.4 : 88.6. The mixture thus obtained was heat-treated at 600°C for 5 hours. Then, the mixture was ground to obtain TiO_2/Bi_2O_3 composite powders.

ZnO powders, CoO powders, MnO_2 powders, SnO_2 powders, and TiO_2/Bi_2O_3 composite powders were mixed in a weight ratio of 100.0 : 0.804 : 0.555 : 0.518 : X (X = 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0, 20.0) by a wet method and ground. The resulting powders were dried and formed by pressure molding. The molding thus obtained was provisionally sintered at 600°C. An aqueous solution of aluminum nitrate was added to the molding so that the weight ratio of the ZnO powders to Al_2O_3 was 100.0 : 0.007 and ground. Then, the ground molding was formed into a disk shape. The disk-shaped molding was heated in the atmosphere at 100°C/hour and kept at 1200°C for 2 hours. Then, the molding was cooled at 100°C/hour to obtain a sintered body. The sintered body had a thickness of 1.2 mm and a diameter of 14 mm.

Hereinafter, a ZnO-based varistor was produced in the same way as in Example 1. Also, in the same way as in Example 1, the ZnO-based varistor was evaluated for electrical characteristics. The composition of the specimen of the present example is shown in Table 7, and the evaluation results of the electrical characteristics thereof are shown in Table 8.

Table 7

specimen	ZnO (wt ratio)	$Bi_2O_3 + TiO_2$ (heat-treated) (wt ratio)	CoO (wt ratio)	MnO_2 (wt ratio)	SnO_2 (wt ratio)	Al_2O_3 (wt ratio)
#011	100.0	0.1	0.804	0.555	0.518	0.007
#012	100.0	0.2	0.804	0.555	0.518	0.007
#013	100.0	0.5	0.804	0.555	0.518	0.007
#014	100.0	1.0	0.804	0.555	0.518	0.007
#015	100.0	2.0	0.804	0.555	0.518	0.007
#016	100.0	5.0	0.804	0.555	0.518	0.007
#017	100.0	10.0	0.804	0.555	0.518	0.007
#018	100.0	15.0	0.804	0.555	0.518	0.007
#019	100.0	20.0	0.804	0.555	0.518	0.007

Table 8

specimen	V_1 mA/mm (V)	$_{0.1}\alpha_1$ mA	Change rate due to a DC load ΔV_1 mA/V_1 mA (%)	Change rate due to a surge ΔV_1 mA/V_1 mA (%)
#011	6-18	6-10	-10 --20	-25--35
#012	19-22	12-18	-2 --4	-4- + 1
#013	18-20	28-32	-1 --2	-1- + 1
#014	15-16	26-30	-1 --2	-1- + 1
#015	16-19	25-31	-1 --2	-1- + 1
#016	16-19	24-30	-1 --2	-1- + 1
#017	15-17	24-30	-1 --2	-1- + 1
#018	16-18	25-29	-1 --2	-1- + 1
#019	16-19	25-30	-1 --2	-1- + 1

As is understood from Tables 7 and 8, the ZnO-based varistor produced by the method of the present example has excellent reliability. That is to say, in the ZnO-based varistor of the present example, the non-linear resistance index $_{0.1}\alpha_{1mA}$ was large in the case where the added amount of the TiO_2/Bi_2O_3 composite powders was not less than 0.2 in a weight ratio (Specimen Nos. 012 - 018), and the absolute value of the change rate $\Delta V_{1mA}/V_{1mA}$ of the clamping voltage V_{1mA} with respect to the application of a DC load or a surge for a long period of time was not more than 5%. In the case where the added amount of the TiO_2/Bi_2O_3 composite powders was not less than 20 in a weight ratio (Specimen No. 019), if a plurality of moldings were sintered under the condition that the moldings were layered, the sintered bodies stuck to each other, decreasing mass production. Thus, this added amount was not suitable for mass production.

Example 4

TiO_2 fine powders and Bi_2O_3 powders were mixed so that the weight ratio of the Bi_2O_3 powders to the TiO_2 fine powders was in the range of 1.5 to 59. The mixture thus obtained was heat-treated at 500 °C for 5 hours. Then, the mixture was ground to obtain TiO_2/Bi_2O_3 composite powders.

ZnO powders, CoO powders, MnO_2 powders, Sb_2O_3 powders, and TiO_2/Bi_2O_3 composite powders were mixed in a weight ratio of 100.0 : 0.555 : 0.291 : 3.0 by a wet method and ground. The resulting powders were dried and formed by pressure molding. The molding thus obtained was provisionally sintered at 600 °C. An aqueous solution of aluminum nitrate was added to the molding so that the weight ratio of ZnO to Al_2O_3 was 100.0 : 0.001 and ground. Then, the ground molding was formed into a disk shape. The disk-shaped molding was heated in the atmosphere at 100 °C/hour and kept at 1200 °C for 2 hours. Then, the molding was cooled at 100 °C/hour to obtain a sintered body. The sintered body had a thickness of 1.2 mm and a diameter of 14 mm.

The sintered body thus obtained was observed by a scanning electron microscope (SEM), revealing that the sintered body had a characteristic fine structure having twin crystal grains of ZnO.

Hereinafter, a ZnO-based varistor was produced in the same way as in Example 1. Also, in the same way as in Example 1, the ZnO-based varistor was evaluated for electrical characteristics. In particular, in order to inspect the reliability of the ZnO-based varistor with respect to a surge in detail, the change rate $\Delta V_{0.01mA}/V_{0.01mA}$ of the clamping voltage $V_{0.01mA}$ of the ZnO-based varistor was measured, since the change of the reliability at 0.01 mA with respect to a surge was remarkably exhibited. Furthermore, the ZnO-based varistor was applied with a pulse of 1.0 kA for 8 x 20 µsec to obtain the change rate $\Delta V_{0.01mA}/V_{0.01mA}$ of the clamping voltage $V_{0.01mA}$ thereof. The composition of the specimen of the present example is shown in Table 9, and the evaluation results of the electrical characteristics thereof are shown in Table 10.

Table 9

specimen	ZnO (wt ratio)	$Bi_2O_3 + TiO_2$ Heat-treated		CoO (wt ratio)	MnO_2 (wt ratio)	Sb_2O_3 (wt ratio)	Al_2O_3 (wt ratio)
		Bi_2O_3 (wt ratio)	TiO_2 (wt ratio)				
#021	100.0	1.8	1.2	0.804	0.555	0.291	0.001
#022	100.0	2.0	1.0	0.804	0.555	0.291	0.001
#023	100.0	2.1	0.9	0.804	0.555	0.291	0.001
#024	100.0	2.2	0.8	0.804	0.555	0.291	0.001
#025	100.0	2.5	0.5	0.804	0.555	0.291	0.001
#026	100.0	2.6	0.4	0.804	0.555	0.291	0.001
#027	100.0	2.8	0.2	0.804	0.555	0.291	0.001
#028	100.0	2.9	0.1	0.804	0.555	0.291	0.001
#029	100.0	2.95	0.05	0.804	0.555	0.291	0.001

Table 10

specimen	V_{1}mA/mm (V)	$_{0.1}\alpha_{1}$mA	Change rate due to a DC load Δ V_{1}mA/V_{1}mA (%)	Change rate due to a surge Δ $V_{0.01}$mA/$V_{0.01}$mA (%)
#021	25-32	4-6	-50--35	-22--18
#022	21-27	12-18	-4--2	-8- + 1
#023	18-23	29-31	-4--1	-5- + 2
#024	18-21	27-29	-2--2	-3- + 1
#025	19-23	27-32	-2--1	-3- + 1
#026	19-22	25-30	-2--1	-2- + 2
#027	18-23	24-32	-3--2	-2- + 1
#028	20-26	10-13	-4--2	-8- + 2
#029	30-36	3-6	-33--40	-20--15

As is understood from Tables 9 and 10, in the case where the weight ratio of the Bi_2O_3 powders to the TiO_2 powders was in the range of 2.0 to 29.0 (Specimen Nos. 022 to 028), ZnO-based varistors with satisfactory electrical characteristics and reliability were obtained. In the case where the weight ratio was not within this range (Specimen Nos. 021 and 029), the absolute value of the change rate Δ $V_{0.01mA}/V_{0.01mA}$ of the clamping voltage $V_{0.01mA}$ with respect to the application of a pulse was not less than 10%, resulting in decreased reliability.

Example 5

TiO_2 fine powders and Bi_2O_3 powders were mixed in a weight ratio of 25 : 75. The mixture thus obtained was heat-treated at 650 °C for 5 hours. Then, the mixture was ground to obtain TiO_2/Bi_2O_3 composite powders.

ZnO powders, TiO_2/Bi_2O_3 composite powders, CoO powders, MnO_2 powders, Sb_2O_3 powders, and Cr_2O_3 powders were mixed in a weight ratio of 100.0 : 2.5 : 0.804 : 0.555 : X : X/4 (X = 0.010, 0.018, 0.030, 0.060, 0.10, 0.20, 0.36, 0.720, 0.80) by a wet method and ground. The resulting powders were dried, and an aqueous solution of aluminum acetate was added to the dried powders so that the weight ratio of the ZnO powders to Al_2O_3 was 100.0 : 0.001. The resulting powders were provisionally sintered at 600 °C. Then, the molding was ground and mixed. The resulting mixture was formed into a disk shape. The disk-shaped molding was heated in the atmosphere at 100 °C/hour and kept at 1200 °C for 2 hours. Then, the molding was cooled at 100 °C/hour to obtain a sintered body. The sintered body had a thickness of 1.2 mm and a diameter of 14 mm.

The sintered body thus obtained was observed by a scanning electron microscope (SEM), revealing that the sintered body had a characteristic fine structure having twin crystal grains of ZnO.

Hereinafter, a ZnO-based varistor was produced in the same way as in Example 1. Also, in the same way as in Example 1, the ZnO-based varistor was evaluated for electrical characteristics. In particular, in order to inspect the reliability of the ZnO-based varistor with respect to a surge in detail, the change rate $\Delta V_{0.01mA}/V_{0.01mA}$ of the clamping voltage $V_{0.01mA}$ of the ZnO-based varistor was measured, since the change of the reliability at 0.01 mA with respect to a surge was remarkably exhibited. Furthermore, the ZnO-based varistor was applied with a pulse of 1.0 kA for 8 x 20 μsec to obtain the change rate $\Delta V_{0.01mA}/V_{0.01mA}$ of the clamping voltage $V_{0.01mA}$ thereof. The composition of the specimen of the present example is shown in Table 11, and the evaluation results of the electrical characteristics thereof are shown in Table 12.

Table 11

specimen	ZnO (wt ratio)	Bi_2O_3 (75 wt ratio) + TiO_2 (25 wt) (heat-treated) (wt ratio)	CoO (wt ratio)	MnO_2 (wt ratio)	Sb_2O_3 (wt ratio)	Cr_2O_3 (wt ratio)	Al_2O_3 (wt ratio)
#031	100.0	2.5	0.804	0.555	0.010	0.0025	0.001
#032	100.0	2.5	0.804	0.555	0.018	0.0045	0.001
#033	100.0	2.5	0.804	0.555	0.030	0.0075	0.001
#034	100.0	2.5	0.804	0.555	0.060	0.015	0.001
#035	100.0	2.5	0.804	0.555	0.100	0.025	0.001
#036	100.0	2.5	0.804	0.555	0.200	0.050	0.001
#037	100.0	2.5	0.804	0.555	0.360	0.090	0.001
#038	100.0	2.5	0.804	0.555	0.720	0.180	0.001
#039	100.0	2.5	0.804	0.555	0.800	0.200	0.001

Table 12

specimen	V_1mA/mm (V)	${}_{0.1}\alpha_1$mA	Change rate due to a surge $\Delta V_{0.01}$mA/$V_{0.01}$mA (%)
#031	19-23	12-18	-25--20
#032	20-28	18-25	-8--5
#033	20-28	22-30	-7--2
#034	25-35	25-45	-5-+1
#035	30-40	30-40	-3-+1
#036	35-45	35-40	-2-+1
#037	40-43	35-45	+0-+2
#038	40-45	40-45	+2-+4
#039	60-70	50-55	+3-+5

As is understood from Tables 11 and 12, the addition of a small amount of Sb_2O_3 powders to the ZnO varistor materials improved the reliability of the ZnO-based varistor with respect to a surge. That is to say, when the added amount of Sb_2O_3 powders was X = 0.018 or more, and the added amount of Cr_2O_3 was X/4 = 0.0045 or more (Specimen Nos. 032 to 039), the absolute value of the change rate $\Delta V_{0.01mA}/V_{0.01mA}$ with respect to the application of a surge was not more than 10%. However, when the added amount of Sb_2O_3 powders was X = 0.8 or more, and the added amount of Cr_2O_3 was X/4 = 0.2 or more (Specimen No. 039), $V_{1mA/mm}$ exceeded 50 V. In this case, a low-voltage varistor cannot be obtained.

Example 6

ZnO powders, Bi_2O_3 powders, TiO_2/Bi_2O_3 composite powders (which were obtained in the same method as in Example 5), CoO powders, MnO_2 powders, and SnO_2 powders were mixed in a weight ratio of 100.0 : 1.0 : 2.00 : 0.804 0.555 : X (X = 0.003, 0.005, 0.010, 0.030, 0.050, 0.10, 0.20, 0.370, 0.50) by a wet method and ground. The resulting powders were dried, and an aqueous solution of aluminum acetate was added to the dried powders so that the weight ratio of the ZnO powders to Al_2O_3 was 100.0 : 0.001. The resulting powders were provisionally sintered at 600°C. Then, the molding was ground and mixed. The resulting mixture was formed into a disk shape. The disk-shaped molding was heated in the atmosphere at 100°C/hour and kept at 1200°C for 2 hours. Then, the molding was cooled at 100°C/hour to obtain a sintered body. The sintered body had a thickness of 1.2 mm and a diameter of 14 mm.

The sintered body thus obtained was observed by a scanning electron microscope (SEM), revealing that the sintered body had a characteristic fine structure having twin crystal grains of ZnO.

Hereinafter, a ZnO-based varistor was produced in the same way as in Example 1. Also, in the same way as in Example 1, the ZnO-based varistor was evaluated for electrical characteristics. In particular, in order to inspect the reliability of the ZnO-based varistor with respect to a surge in detail, the change rate $\Delta V_{0.01mA}/V_{0.01mA}$ of the clamping voltage $V_{0.01mA}$ of the ZnO-based varistor was measured, since the change of the reliability at 0.01 mA with respect to a surge was remarkably exhibited. Furthermore, the ZnO-based varistor was applied with a pulse of 1.0 kA for 8 x 20 μsec to obtain the change rated $\Delta V_{0.01mA}/V_{0.01mA}$ of the clamping voltage $V_{0.01mA}$ thereof. The composition of the specimen of the present example is shown in Table 13, and the evaluation results of the electrical characteristics thereof are shown in Table 14.

Table 13

specimen	ZnO (wt ratio)	Bi_2O_3 (wt ratio)	Bi_2O_3 + TiO_2 (heat-treated) (wt ratio)	CoO (wt ratio)	MnO_2 (wt ratio)	SnO_2 (wt ratio)	Al_2O_3 (wt ratio)
#041	100.0	1.0	2.0	0.804	0.555	0.003	0.001
#042	100.0	1.0	2.0	0.804	0.555	0.005	0.001
#043	100.0	1.0	2.0	0.804	0.555	0.010	0.001
#044	100.0	1.0	2.0	0.804	0.555	0.030	0.001
#045	100.0	1.0	2.0	0.804	0.555	0.050	0.001
#046	100.0	1.0	2.0	0.804	0.555	0.100	0.001
#047	100.0	1.0	2.0	0.804	0.555	0.200	0.001
#048	100.0	1.0	2.0	0.804	0.555	0.370	0.001
#049	100.0	1.0	2.0	0.804	0.555	0.500	0.001

Table 14

specimen	V_1 mA/mm (V)	$_{0.1}\alpha_1$ mA	Charge rate due to a surge Δ $V_{0.01}$mA/$V_{0.01}$mA (%)
#041	18-22	12-17	-12--10
#042	21-24	16-21	-8- + 1
#043	25-29	20-25	-5- + 2
#044	28-34	20-28	-3- + 1
#045	32-39	22-35	-3- + 1
#046	36-43	30-38	-2- + 2
#047	40-45	35-45	+ 2- + 2
#048	44-48	40-50	+ 4- + 3
#049	65-75	42-55	+ 4- + 5

As is understood from Tables 13 and 14, when the added amount of SnO_2 powders was X = 0.005 or more (Specimen Nos. 042 - 049), the absolute value of the change rate Δ $V_{0.01mA}/V_{0.01mA}$ with respect to the application of a surge was not more than 10%. However, when the added amount of SnO_2 powders was X = 0.5 or more (Specimen No. 049), $V_{1mA/mm}$ exceeded 50 V. In this case, a low-voltage varistor cannot be obtained.

As described above, composite powders obtained by previously heat-treating the mixture of TiO_2 powders and Bi_2O_3 powders can uniformly enhance the growth of ZnO grains. In addition, an antimony component, a tin component, or a chrome component together with an antimony component suppresses the abnormal growth of ZnO grains. Thus, according to the present invention, a ZnO grain having a large average grain size and a small distribution in grain size can be obtained. Namely, a ZnO-based varistor excellent in electrical characteristics and reliability can be produced with a high yield.

Various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the scope and spirit of this invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description as set forth herein, but rather that the claims be broadly construed.

Claims

1. A method for producing a ZnO-based varistor comprising the steps of:
heat-treating a mixture of TiO_2 powders and Bi_2O_3 powders to prepare composite powders; and
adding the composite powders to ZnO varistor materials.

2. A method for producing a ZnO-based varistor according to claim 1, further comprising the step of adding an aluminum component to the ZnO varistor materials.

3. A method for producing a ZnO-based varistor according to claim 2, wherein the aluminum component is added to the ZnO varistor materials so that the weight ratio of Al_2O_3 powders to the ZnO powders is in the range of 0.00062 : 100.0 to 0.372 : 100.0.

4. A method for producing a ZnO-based varistor according to claim 3, wherein the aluminum component is a solution of an aluminum salt.

5. A method for producing a ZnO-based varistor according to claim 4, wherein the aluminum salt is aluminum nitrate.

6. A method for producing a ZnO-based varistor according to claim 4, wherein the aluminum salt is aluminum acetate.

7. A method for producing a ZnO-based varistor according to claim 3, further comprising the step of adding an antimony component to the ZnO varistor materials.

8. A method for producing a ZnO-based varistor according to claim 7, wherein the antimony component is added to the ZnO varistor materials so that the weight ratio of Sb_2O_3 powders to the ZnO powders is in the range of 0.018 : 100.0 to 0.72 : 100.0.

9. A method for producing a ZnO-based varistor according to claim 3, further comprising the step of adding a tin component to the ZnO varistor materials.

10. A method for producing a ZnO-based varistor according to claim 9, wherein the tin component is added to the ZnO varistor materials so that the weight ratio of SnO_2 powders to the ZnO powders is in the range of 0.005 : 100.0 to 0.37 : 100.0.

11. A method for producing a ZnO-based varistor according to claim 8, further comprising the step of adding a chrome component to the ZnO varistor materials.

12. A method for producing a ZnO-based varistor according to claim 11, wherein the chrome component is added to the ZnO varistor materials so that the weight ratio of Cr_2O_3 powders to the ZnO powders is in the range of 0.005 : 100.0 to 0.18 : 100.0.

Fig. 1