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ADDITIVES DISTRIBUTION AND ELECTRICAL PROPERTIES IN ZINC OXIDE VARISTOR PREPARED BY A WET CHEMICAL METHOD

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Abstract – Cobalt-, praseodymium-added zinc oxide varistor was prepared through a wet chemical method followed by sintering with or without calcination. Changes in grain size, compact density, additives distribution, and voltage-current/capacitance-voltage relations were investigated for the characterization of the samples sintered at temperatures from 1473 to 1573 K without calcination or with calcination at 773 K for 2 h. The electrical properties were compared with those of samples prepared by two types of ball mill methods. The wet chemical method provided almost the same additives-distribution profile and less impurities in comparison with the ball grinding method carried out for 10-100 h. The donor concentration and the potential-barrier height for the samples were evaluated by Double Schottky Barrier Model. Addition of small amount of both cobalt and praseodymium in preparation by the wet chemical method was effective for a better nonlinearity relation between voltage and current, which has potential for a smaller sized varistor.

Key words: Zinc Oxide, Varistor, Wet Chemical Method, Electrical Property, Additives

INTRODUCTION

The zinc oxide varistor has an excellent nonlinearity relation between applied voltage and current, and enormous surge capabilities; so that applications are expected for home electronic instruments, circuits in automobile, and CPUs in the nearest future. To lower threshold voltage and to develop a multilayer type are urgent for producing a smaller size or a surface mount device [Utsumi, 1989; Yen et al., 1994], As compared with a larger device of the same performance, defects have rather big influence on the characteristics of thinner or multilayer type of functional material. Especially, it is well known that non-uniformity of grain size and defects cause excessive dropping in electric performance of zinc oxide varistor [Eda, 1984; Amiji et al., 1986; Sumiyoshi and Matsuoka, 1986; Sun et al., 1993]. Therefore uniformity is one of the most important factors in the aspects of chemical component and physical texture for a multilayer-type zinc-oxide varistor.

Conventionally, it is well known to grind particles in a medium to obtain homogeneous materials [Tanaka et al., 1988; Kondo et al., 1993]. A promising alternative is a wet chemical method such as sol-gel and coprecipitation. However, little work has been done on the zinc oxide varistor preparation by a wet chemical method, except one on ZnO-Bi varistor investigation [Westin et al., 1994]. It is a difficult problem that internal Pd electrode and Bi react each other in ZnO-Bi varistor. On the other hand, a Pd electrode is inactive in ZnO-Co-Pr varistor.

In this study, for fundamental study on multilayer type zinc oxide varistor development, we carried out experiments to improve homogeneity of the ZnO-Co-Pr varistor material with a wet chemical method, and compared the results with those obtained by two types of ball mill methods.

EXPERIMENTAL

1. Preparation Methods

1-1. Preparation by a Wet Chemical Method

Preparation procedure of ZnO-Co-Pr precursor by a precipitation method is shown in Fig. 1. Praseodymium oxide in hydrochloric acid and cobalt chloride were consecutively dissolved in zinc acetate solution with ethanol. Precipitation was conducted by adding oxalic acid aqueous solution. Zinc oxide precursor was obtained by filtration and drying the precipitate at 333 K. Two kinds of sample were prepared by a wet chemical method: calcined precursor at 773 K for 2h and dried precursor without calcination.

1-2. Preparation by Ball Mill Methods

A conventional ball mill method was applied to mixing or grinding of cobalt oxide, praseodymium oxide and zinc oxide. Two kinds of sample were prepared by ball milling: a precursor ground with ZrO_2 balls of 2 mm diameter for 4, 16, 40, 64 and 100h, and a precursor ground with resin coated steel-balls for 4 h. Each precursor is referred to a sample prepared by a ball grinding method and by a ball mixing method, respectively. Both methods were treated with 20% slurry and 50 rpm rotation speed, and the weight ratio of sample to milling medium was 1 to 10.

1-3. Pressing and Sintering Conditions

Each sample was pelletized with adding 1 wt% PVA and applying 1 ton cm^{-2} on a 11.1 mm diameter mold, and sintered

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at 1473-1573 K. Heating and cooling rates were 3.3 Kmin^{-1}, except for temperatures ranged from 473 K to 773 K where 0.2 Kmin^{-1} was applied. The samples were held for 2 h at 873 K and 4 h at final temperatures. The reason of adopting a slower heating rate from 473 to 773 K is to avoid cracks in a sample prepared by a wet chemical method without calcination. Rapid shrinkage occurred with evolution of CO and CO_2 at about 673 K, and resulted in a large weight loss.

2. Analysis and Evaluation of Prepared Samples

Contents of praseodymium, cobalt and other elements in a sample were determined by ICP analysis. The surface and the cross section of sample were observed by SEM (JOEL JSM-5300) and examined by EPMA (JOEL JCMA73) for grain size and additives distribution analysis. Internal surface area was estimated by applying the Dubinin-Polanyi equation to the adsorption isotherm for CO_2 at 273 K (YANACO GAS-10). Grain sizes were measured by marking grain boundaries on a SEM photograph and processing with a two dimensional graphic transaction program supported by the Rise computer system. The number of counted particles was about 300.

The break-down voltage was evaluated by $V_{1.0mA}$ that is the varistor voltage where electric current is 1.0 mA. The non-linearity parameter α for the voltage-current curve defined by Eq. (1) was applied for analyzing varistor characteristics [Lee and Tseng, 1995].

$$\alpha = \log(10/1)/\{\log(V_{10mA}/V_{10mA})\} \quad (1)$$

Voltage-current curves were characterized by a varistor tester (TDK VT-1) and a DC constant current source. Electrode used was In-Ga alloy. The capacitance-voltage analysis (C-V method) was carried out using a multi-frequency LCR meter (Yokogawa-Hewlett-Packard 4274A) at room temperature with 1 kHz frequency.

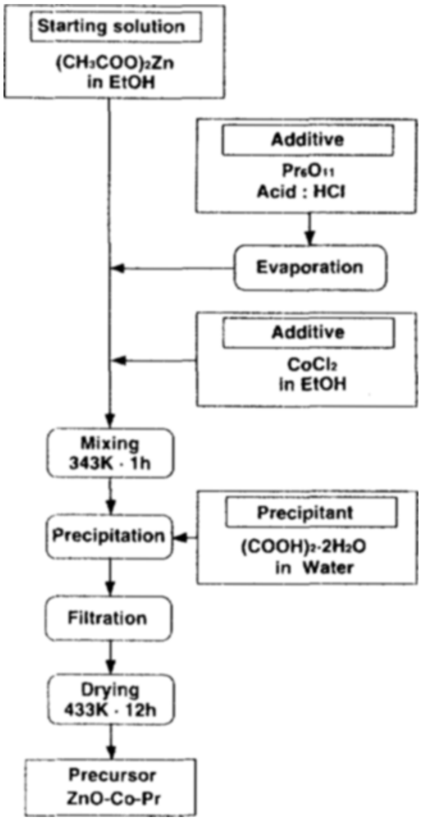

Fig. 1. Preparation procedure of ZnO-Co-Pr precursor.

RESULTS AND DISCUSSION

1. Preparation of Precursor

Component analyses of precursors in mole ratio are listed in Table 1, where initial loading ratio of Zn : Co : Pr=100 : 0.5 : 0.25, in the starting solution or solid is represented as Zn : Co : Pr=100 : 0.5 : 0.25. Time in the table means processing time, i. e., mixing or grinding time for (A) or (B) and stirring time for (C). The component ratio of precursor by a wet chemical method was comparable to that by ball-mill methods. Extent of the recovery of precursor was considered to be satisfactory compared with that by Takehana et al. [Takehana et al., 1996]. The concentrations of filtrate were 5.4 ppm for Zn, <0.1 ppm for Co, and <0.5 ppm for Pr when nominal ratio of 100 : 1.0 : 0.5 was set for Zn : Co : Pr in the precursor. It is seen from Table 1 that content of ZrO_2 increased linearly with grinding time for a sample prepared by a ball grinding method. It is suspected that ZrO_2 was mingled from a medium .

2. Density Before and After Sintering

Table 2 shows change in the compact density of samples before and after sintering. The lower values for a sample prepared by a wet chemical method without calcination would be ascribed to pores observed in photographs both taken before and after sintering. For a sample by a wet chemical method without calcination before sintering, compact pressure would be transmitted less properly to powder body, because it was bulkier than other samples. As for a sample prepared by a wet chemical method with calcination before sintering, it implies that compact pressure could not destroy the frame structure which remained after CO and CO_2 evolution by calcination.

3. Sintered Sample and Electrical Properties

3-1. Internal Surface Area

Table 3 represents the values of internal surface area of sam-

Table 1. Contents of Zn, Co, Pr and Zr in precursor [mole ratio]

	(A)	(B)	(B)	(B)	(B)	(B)	(C)
Time	4 h	4 h	16 h	40 h	64 h	100 h	1 h
Zn	100	100	100	100	100	100	100
Co	0.49	0.49	0.47	0.48	0.47	0.49	0.49
Pr	0.23	0.23	0.23	0.23	0.23	0.23	0.24
Zr	-	0.09	0.12	0.14	0.17	0.19	-

(Zn : Co : Pr=100 : 0.5 : 0.25, (A) Ball mixing method, (B) Ball grinding method, (C) Wet chemical method)

Table 2. Sample density before and after sintering [g/cm^3]

	(A)	(B)	(B)	(B)	(B)	(B)	(C)	(D)
Time	4 h	4 h	16 h	40 h	64 h	100 h	1 h	1 h
Before	3.2	3.2	3.2	3.2	3.2	3.2	1.7	2.9
After	5.4	5.4	5.4	5.4	5.4	5.4	4.8	5.5

(Zn :Co : Pr=100 : 0.5 : 0.25, Sintering temperature 1573 K) (A) Ball mixing method, (B) Ball grinding method, (C) Wet chemical method without calcination, (D) Wet chemical method with calcination

Table 3. Internal surface area [m^2/g]

	(A)	(B)	(B)	(B)	(B)	(B)	(C)	(D)
Time	4 h	4 h	16 h	40 h	64 h	100 h	1 h	1 h
	0.59	0.59	0.71	0.79	0.93	1.13	6.21	5.68

(Zn : Co : Pr=100 : 0.5 : 0.25, (A) Ball mixing method, (B) Ball grinding method, (C) Wet chemical method without calcination, (D) Wet chemical method with calcination)

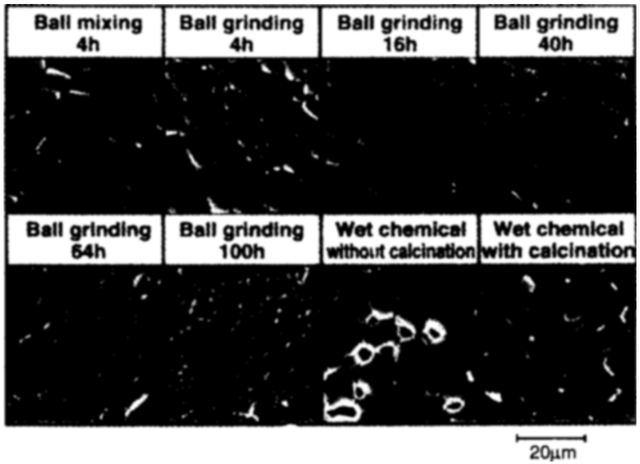

Fig. 2. SEM image of sample surface of ZnO-Co-Pr varistor.
(Zn : Co : Pr=100 : 0.5 : 0.25, Sintering temperature 1573 K)

ples prepared by wet chemical and ball mill methods. Internal surface area of a sample prepared by a wet chemical method was decreased by calcination, but larger than that by a ball mixing or by a grinding method. The result indicates that the wet chemical method develops internal pore structure more than a ball grinding method.

3-2. Surface microstructure

Fig. 2 shows SEM images of sample surface sintered at 1573 K with preparation ratio Zn : Co : Pr=100 : 0.5 : 0.25. Cracks and pores are observed in a sample prepared by a wet chemical method without calcination. Smaller grains dispersedly recognized in a sample prepared by a wet chemical method with calcination were regarded as praseodymium [Alles et al., 1993]. Many fine particles are observed in a sample prepared by a ball grinding method. They proved to be ZrO_2 by EPMA which came from grinding balls and was separated from solid solution with zinc oxide. They deteriorate the uniformity and quality of product. An example of the grain size distribution of a sample sintered at 1523 K is shown in Fig. 3. The distribution was narrower and the average grain size was smaller with increasing grinding time. A sample prepared by the wet chemical method without calcination had a narrow size distribution with the same average grain size as a sample prepared by ball grinding for 40 h. For a sample prepared by a ball grinding method, ZrO_2 impurity would play an important role in the narrower grain size distribution and the smaller average size as grinding time increased, because it is difficult that zinc oxide particles became smaller with grinding time in the range of particle size used. On the other hand, a sample prepared by a wet chemical method contained no impurities and showed a narrow grain size distribution with a small average grain size. A narrow size distribution contributes a predominant property since zinc oxide varistor is more destructive at nonuniform domains. The average grain size of zinc oxide increased in each sample with an increase of sintering temperature.

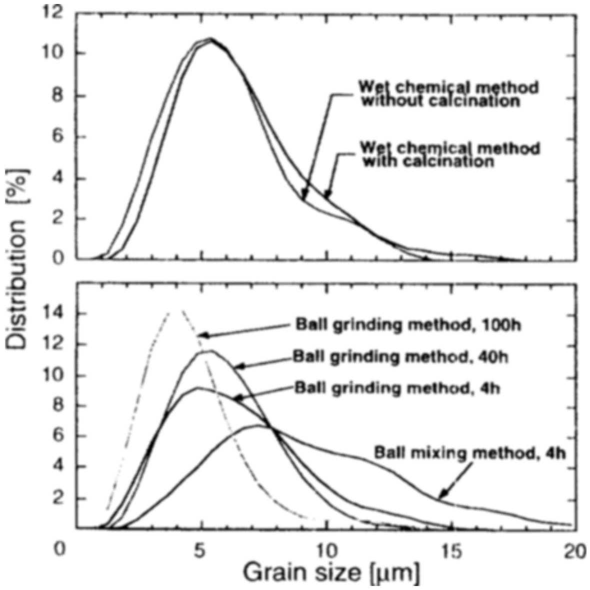

Fig. 3. Grain size distribution of ZnO-Co-Pr varistor.
(Zn : Co : Pr=100 : 0.5 : 0.25, Sintering temperature 1523 K)

3-3. Additives Distribution

The coefficient of variation (C.V.), defined by Eq. (2), was used as an indicator of the extent of segregation of the additives:

$$\mathrm{C.V.}(\%) = (S/\bar{x}) \times 100 \tag{2}$$

where $\bar{x}$ and S are average value and standard deviation, respectively, of number counted by the dot analysis of Co and Pr in the domain 200-200 µm in a compact sample with EPMA. Fig. 4 shows the effect of mixing, grinding, and stirring time on the C.V. values for Pr and Co in compacts; Fig. 5 shows the effect of sintering temperature.

In Fig. 4, the C.V. values for both Pr and Co became smaller with increasing grinding time in a sample prepared by ball grinding. Meanwhile the sample prepared by a wet chemical method only with 1h mixing shows almost the same uniformity as a sample by grinding for 10-100 h. Especially calcination process improved the uniformity of additives distribution as represented by a symbol ◇ compared with △.

In Fig. 5, samples prepared by a ball mixing and a ball grinding methods for 4 h are less uniform for Co in a compact, but the extent of uniformity increased as sintering temperature increased. Good uniformity for Co was obtained in compacts by a 100 h ball grinding method and by a wet chemical method at any sintering temperatures. The C.V. values of Pr became larger for all samples with increasing sintering temperature. Samples prepared by a ball grinding method had a smaller effect of temperature on change in the C.V. values than other samples.

3-4. Electrical Properties

Figs. 6 and 7 show electrical properties for three different samples having molar ratios, Zn : Co : Pr=100 : 1 : 0.5, 100 : 0.5 : 0.25, and 100 : 0.25 : 0.125. The samples were sintered at 1473-

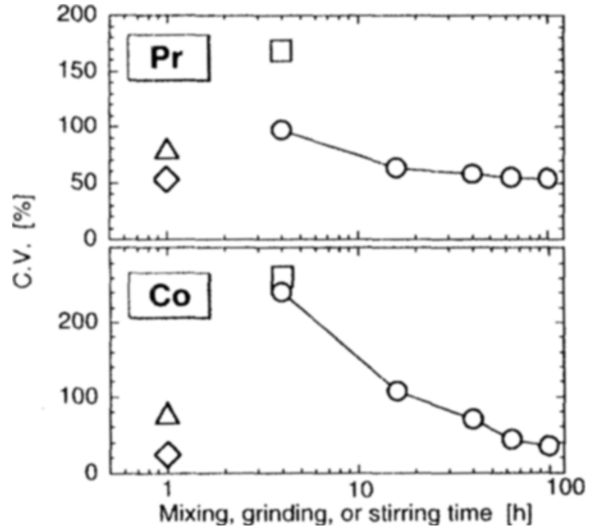

Fig. 4. Change in C.V. value in ZnO-Co-Pr varistor compact with mixing, grinding, or stirring time.
(Zn : Co : Pr=100 : 0.5 : 0.25, □ Ball mixing method, ○ Ball grinding method, △ Wet chemical method without calcination, ◇ Wet chemical method with calcination).

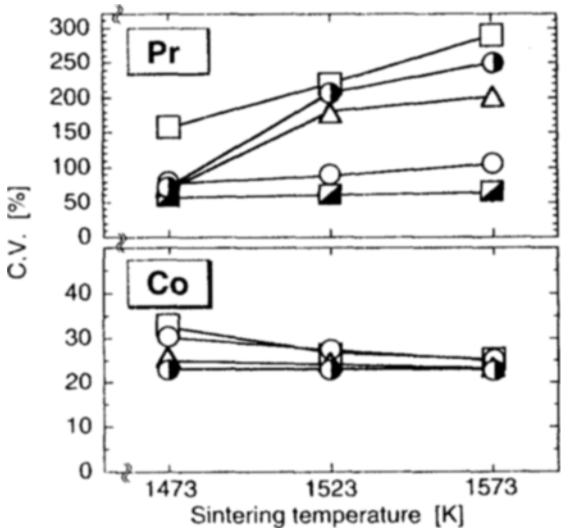

Fig. 5. Change in C.V. value in ZnO-Co-Pr varistor with sintering temperature.
(Zn : Co : Pr=100 : 0.5 : 0.25, □ Ball mixing method, ○ Ball grinding method, 4 h, □ Ball grinding method, 100 h, △ Wet chemical method without calcination, ◑ Wet chemical method with calcination).

1573 K. A sample prepared by a ball grinding method was excluded because ZrO_2 impurity would cause an inferior character. The break-down or varistor voltages for all samples decreased with increasing sintering temperature. Samples prepared by a ball mixing and a wet chemical methods without calcination had the same level of dependence on sintering temperature. But a sample prepared by a wet chemical method with calcination was much more affected by sintering temperature.

As for nonlinearity parameter α, a sample prepared by a wet chemical method without calcination showed lower dependence

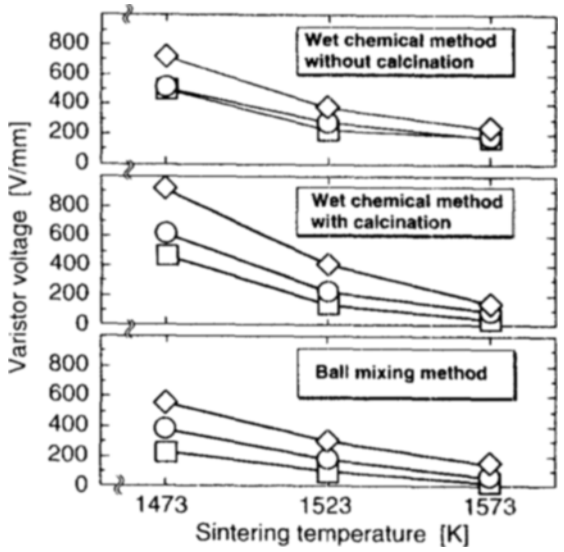

Fig. 6. Change in varistor voltage with sintering temperature.
(□ Zn : Co : Pr=100 : 0.25 : 0.125, ○ Zn : Co : Pr=100 : 0.5 : 0.25, ◇ Zn : Co : Pr=100 : 1 : 0.5).

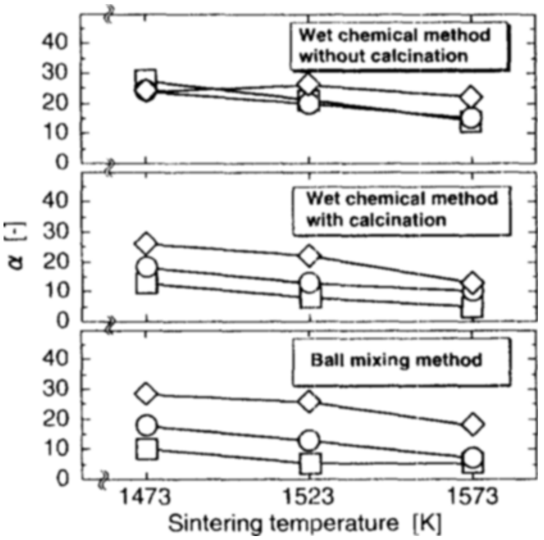

Fig. 7. Change in nonlinearity α with sintering temperature.
(□ Zn : Co : Pr=100 : 0.25 : 0.125, ○ Zn : Co : Pr=100 : 0.5 : 0.25, ◇ Zn : Co : Pr=100 : 1 : 0.5).

on sintering temperature. By precisely examining the effect of additives amount on varistor voltage and nonlinearity characteristics, the sample prepared by a wet chemical method without calcination showed the smallest dependence on sintering temperature. This indicates that smaller amount of addition of Co and Pr is effective for both the varistor voltage and nonlinearity characteristic.

3-5. Examination by a Capacitance-voltage Method

The varistor characteristics have been considered to originate from its grain boundary [Iga, 1992]. The capacitance-voltage relation was measured to evaluate potential barrier height ϕ and donor concentration N_d in the grain boundary which should relate to varistor characteristics [Tsuda, 1989; Mukae, 1991]. Interstitial zinc atom would behave as a donor in the system stu-

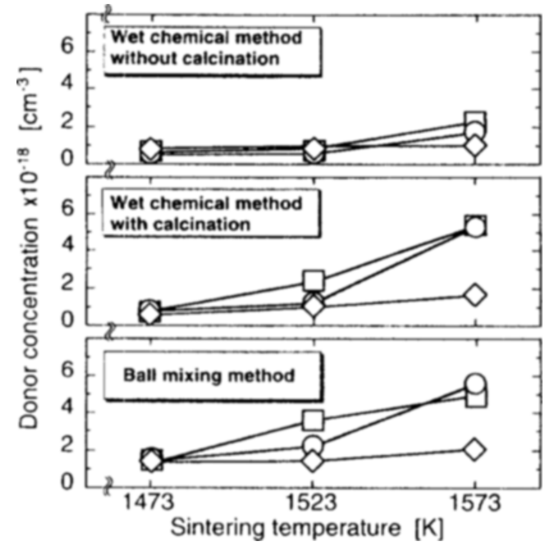

Fig. 8. Change in donor concentration with sintering temperature.
(□ Zn : Co : Pr=100 : 0.25 : 0.125, ○ Zn : Co : Pr=100 : 0.5 : 0.25, ◇ Zn : Co : Pr=100 : 1 : 0.5).

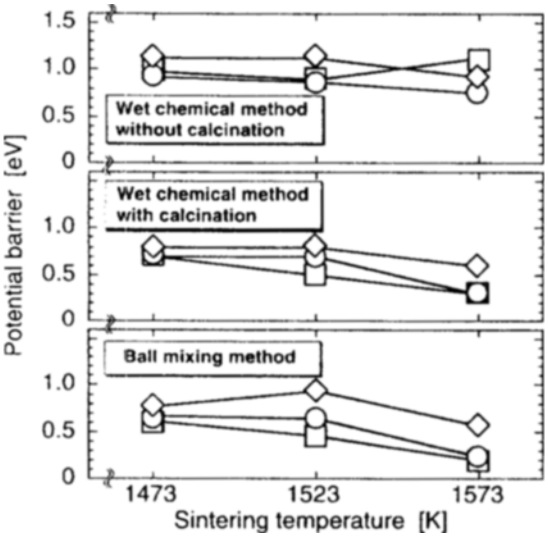

Fig. 9. Change in potential barrier with sintering temperature.
(□ Zn : Co : Pr=100 : 0.25 : 0.125, ○ Zn : Co : Pr=100 : 0.5 : 0.25, ◇ Zn : Co : Pr=100 : 1 : 0.5)

died [Iga, 1992]. Based on Double Schottky Barrier Model, ϕ and N_d are determined by the following equation:

$$\{1/C-1/(2C_0)\}^2=2(\phi+V)/(q\varepsilon_s N_d) \qquad (3)$$

where C or C_0 is capacitance at any applied voltage V or at V=0, q is charge, and ε_s is dielectric constant. Figs. 8 and 9 demonstrate the values of N_d and ϕ for the samples sintered from 1473 K to 1573 K.

Fig. 8 shows that a low level of donor concentration was kept in a sample prepared by a wet chemical method without calcination. While larger amount of addition of Co and Pr was effective in other preparation methods, donor concentration increased with sintering temperature when the addition was low. A wet chemical method without calcination is considered to be superior to the others since the low concentration of donor contributes to the high nonlinearity of varistor [Sogabe et al., 1995; Wakiya et al., 1991].

Higher values of potential barrier height were observed also in a sample prepared by a wet chemical method without calcination as demonstrated in Fig. 9. About 0.8 eV was reported in previous papers [Tsuda and Mukae, 1989; Sogabe et al., 1995], and excellent nonlinearity was mainly due to high potential barrier height [Suyama, 1987].

It has been considered that oxygen in grain boundary is effective for the nonlinearity of varistor. To interpret non-ohmic behavior in porous zinc oxide doped with Al_2O_3, Fuzitu [1991] claimed that the surface potential barrier was formed by adsorbed oxygen in grain boundary. And the adsorbed oxygen in grain boundary was reported to be effective for nonlinear properties [Tsuda and Mukae, 1992]. The observed results showed that a sample prepared by a wet chemical method without calcination had a good nonlinearity characteristics even with small addition of Co and Pr. This result may be explained in terms of oxygen in pores observed more as described in previous sections: oxygen was enough to be supplied to grain boundary from pores.

CONCLUSION

ZnO-Co-Pr varistor was successfully prepared by a wet chemical method. A sample prepared by a wet chemical method has the narrowest grain size distribution and the smallest average grain size without any impurity inclusion in comparison with ball mill methods. The grain size distribution prepared by a ball grinding method was narrower, and the average grain size was smaller with increasing grinding time, but the content of ZrO_2 impurity increased with grinding time. A wet chemical method improved the additives distribution characteristics greatly compared to ball grinding and ball mixing methods. Calcination at 773 K for 2 h after coprecipitaion contributed good uniformity of additives. Smaller amount of addition of Co and Pr in a wet chemical method without calcination was effective for both the varistor voltage and nonlinearity relation between applied voltage and current.

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