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Development of Low Resistance Ceramics for Multilayer PTC Thermistor Application

논 문
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Abstract

In this study, Semiconducting ceramics (PTC thermistor) have been developed for application to the current limiting element with a multilayer structure. In order to decrease the room temperature resistance and to enhance the PTC property, it was controlled that the effect of additives, sintering temperature and cooling rate on the PTC property. Decreasing the sintering temperature, grain size of sample was largely decreased and room-resistance was increased. It was found that increasing the Nb_2O_5 contents leads to increase in the values of both the room temperature and the maximum resistance. And, the steepness of the plots in the transition region was increased. Also, complex impedance spectra for the grain and grain boundary resistance were investigated so as to find the effect of microstructure. These results are obtained by measuring microstructure and temperature dependence of resistance and complex impedance spectra as a function of frequency range 5 ㎐ to 13 MHz.

Key Words(중요용어) : PTCR, complex impedance, grain, SMD type, Multilayer PTC Termistor, Cooling rate, grain boundary

Ⅰ. Introduction

Donor doped semiconducting barium titanate ($BaTiO_3$) exhibits positive temperature coefficient (PTC) of resistivity in the temperature range above the curie point. This effect involves a substantial nonlinear change of resistivity with temperature, at which phase transition takes place from tetragonal to cubic phase[1]~[3]. It has long been established that the barium titanate PTCR phenomina is a grain boundary resistive effect.

The evidence comes from various studies using the ac impedance method, decoration technique, emission electron microscopy and temperature measurement. These results not only showed that the PTCR effect is a grain boundary resistance phenomenon but also illustrated that even at temperatures well below the curie point the grain boundaries are the primary contributor to the electrical resistance[4]~[5]. It is well known that room temperature resistivity decreases initially with increasing donor concentration and then start to increase again rapidly when donor concentration in increased above about 0.4 at%. Theories accounting for the increase in resistivity in terms of electrical compensation of the donors have also been advanced. On the other hand, H. M. Al-Allak et al[6] suggested that the increase in the resistivity is due to the combined effects of the decrease in grain size with donor concentration and the formation of a Ba vacancy rich insulating grain boundary layer. Thus, high donor concentration can reduce the grain size to about 2㎛. There is a transition from semi conducting to insulating behavior as the donor concentration is increased. It is known that for Nb

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as the donor additive, transition occurs at about Nb 0.5 mol%, and the niobium ions occupy Ti sites, and because Nb has a higher valence than Ti, it behaves as a donor[7].

The purpose of the study is to develop the lower resistance positive temperature coefficient ceramics for the SMD type multilayer PTC thermistor application This study is concentrated to investigate the electrical characteristics of Nb doped $BaTiO_3$ PTC ceramics behind various sintering and cooling condition for the lower room temperature resistance that was notice for the over current devices. The investigation is conducted that nonlinear characteristics on resistance dependent temperature, complex impedance spectra, micro structure of samples.

II. Experimental Procedure

2-1 Sample preparation

The composition of PTC ceramics powder used in this experimental is $(0.8Ba+0.15Sr+0.05Ca)\ TiO_3+0.01TiO_2+0.01SiO_2+0.001MnO_2+xNb_2O_5$ (mol%), where x is varied from 0.14 to 0.20 mol%.

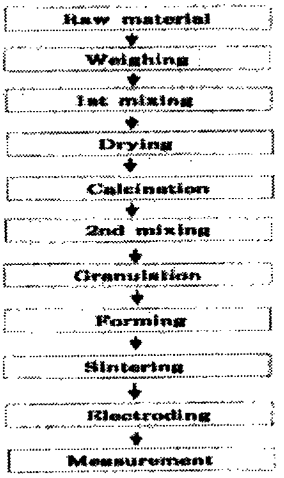

Fig. 1. Processing flow of sample preparation

Fig. 1 shows the processing flow of sample preparation. All of mixture were ball milled in deionized water for 12 hours with zirconia balls. After being dried, powder was calcined at 1050℃ for 2 hours. The powder was ground again by ball milling for 2 hours and granulated by a 100 mesh sieve, and pressed at pressure of 1ton/cm^2. The pressed samples were sintered in an atmosphere of ambient air at temperature range from 1300℃ to 1350℃ for 2 hours with a rate of 300℃/h. They were cooled to 700℃ with a rate 100℃/h and therafter at the natural cooling rate of the furnace to room temperature. The surface of samples were lapped and finally fired on Zn-Ag double electrode, which were used for the ohmic contact and electrical measurement.

2-2 Microstructure and Electrical measurement

The microstructures of the sample were investigated by the scanning electron microscope (SEM). The average grain size was obtained by the linear intercept method. The DC electrical resistances were measured using two probe method by a digital multimeter from 30℃ to 300℃ in a temperature controlled chamber. AC complex impedance spectra of the samples were measured using a impedance analyzer(HP 4192A) in the frequency range of 5 Hz to 13 MHz.

III. Results and Discussion

3-1 Effect of Nb_2O_5 contents

Fig. 2 shows electrical resistivity of the specimens with the Nb_2O_5 contents which were sintered at 1350℃ for 2 hours. It is shown that increasing the Nb_2O_5 contents leads to increase in the values of both the room temperature and the maximum resistance. Also, the steepness of the plots in the transition region (curie temperature) was increased. Essentially Nb_2O_5 additive was well known to form a grain boundary and to roles to obstruct the grain growth[8]. As the Nb concentration is increased, however, the ceramics becomes insulating material. Thus, the resistance of grain boundary incereases because of formation resistive insulating layers.

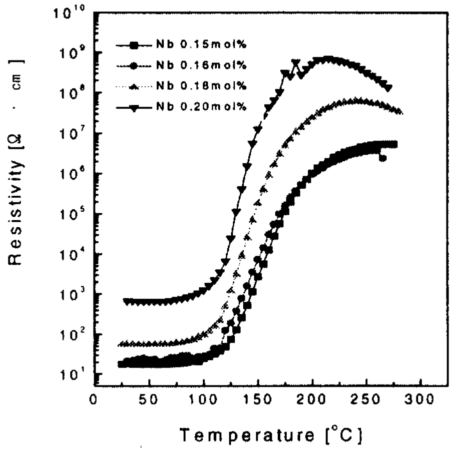

Fig. 2. Resistivity of the specimens with the Nb_2O_5 contents

3-2 Complex impedance spectra

The difficulty with D.C measurement on polycrystalline ceramics is that bulk and grain resistance are limped together and can not easily be separated. On the other hand, by A.C. method it is possible to resolve both bulk and grain boundary components with the aid of complex plane analysis. Grain boundary impedance be directly identified experimentally. One of the most direct method for probing grain boundary impedance is complex impedance measurements. This method has been used for sometime on intermediate resistance ceramics and base on the fact that on RC network produces a semicircles. And this plots useful for determining an appropriate equivalent circuit for system and for estimating the values of the circuit parameters. Semicircular arc corresponds to a lumped R-C combination. The resistance values are derivable from the circular arc intercepts on the R-axis and capacitance values, which can be derived from repressions involving the frequencies at the peaks of the circular arc. This method is perhaps best illustrated by specific examples of simple circuit(Fig. 3)[9]~[11]. The interpretation of frequency dependence conduction and capacitance can be greatly facilitated by the combined use of complex plane diagrams and equivalent circuit.

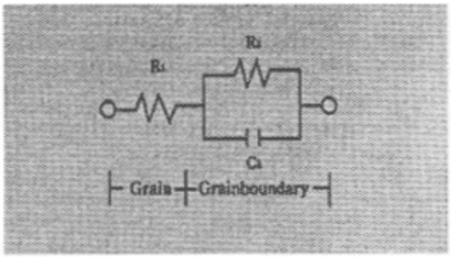

Fig. 3. Equivalent circuit of PTC ceramics

The impedance of this circuit is given by

$$Z(\omega)=R_1+\frac{R_2}{1+\omega^2{C_2}^2{R_2}^2}-j\frac{\omega{R_2}^2C_2}{1+\omega^2{C_2}^2{R_2}^2}$$

where R_1 is grain bulk resistance, R_2 is grain boundary resistance, C_2 is capacitance of grain boundary and ω is angular frequency. In high frequency region, it is expected to become $Z(\omega)=R_1$. From the intercepts of the semicircle, it is possible to determine the values of the resistance in the equivalent circuit and to obtain the capacitance value C_2. Fig. 4 shows complex impedance plots for Nb_2O_5 contents. Semicircle plots agree the principle with a diagram in Fig. 3.

In the Fig. 3, the first intercept of real resistance gives the bulk resistance(R_1), and the second intercept gives the sum of grain and grain boundary resistance(R_1+R_2). It is possible to obtain reasonable values of the grain boundary capacitance (C_2) by using ω $R_2C_2=1$(at the peak of semicircle).

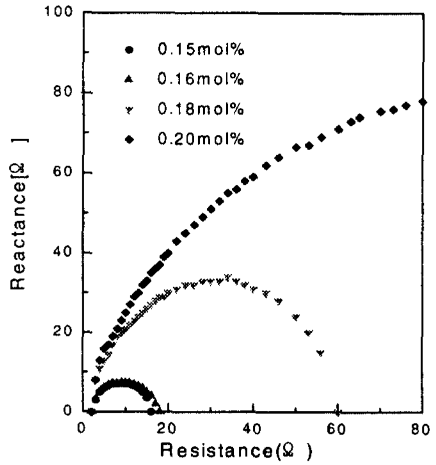

Fig. 4. Complex impedance plots of the specimens with Nb_2O_5 contents

Fig. 5 shows the resistance of grain and grain boundary of samples with various Nb_2O_5 contents. It is shown that increasing the Nb_2O_5 contents leads to increase in the values of R_1+R_2 resistance. Usually three different processes take place during charge transport through a polycrystalline ceramics. (1) bulk conduction or in other words intergrain conduction, (2) conduction across the grain boundary and (3) transports across the electrode-specimen interface. Each of these processes may be represented by independent R-C combination and depending on the relative values or there relaxation times. They may give rise to three independent semicircular arcs in the impedance plots. In our experiment, the highest frequency arc corresponds to the bulk conduction, the lowest frequency arc corresponds to the grain boundary and grain resistance. The effect of electrode-specimen interface can be excluded, because of using a ohmic contact paste for the first electrode. As a this results, it can be concluded that the higher resistivity at room temperature of the sample with Nb_2O_5 contents is attributed to the remarkable increase in grain boundary resistance.

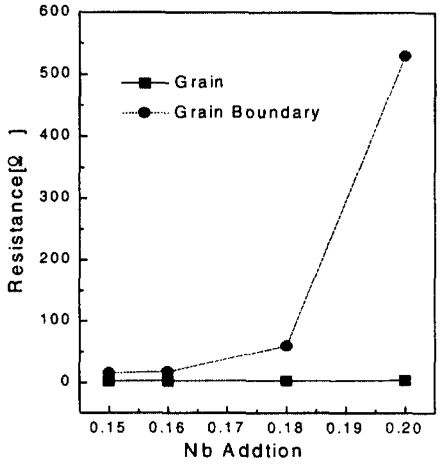

Fig. 5. Resistance of grain and grain boundary of the specimens with Nb_2O_5 contents

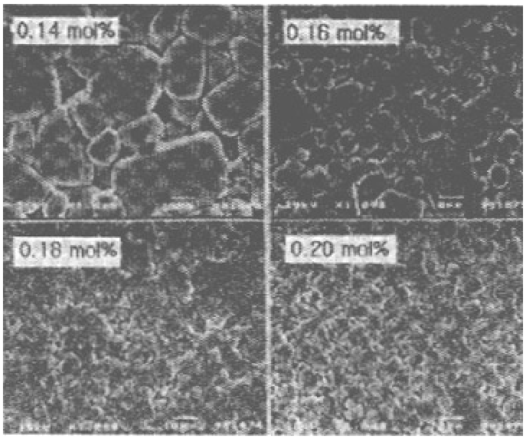

Fig. 6. Microstructure of the samples prepared with different Nb_2O_5 contents

In order to clearly find a effect of grain and grain boundary, typical micrographs of the samples prepared with different Nb_2O_5 amounts shows in Fig. 6. The grain size was decreased with increasing Nb_2O_5 contents. The average grain size of the sample with

Nb_2O_5 0.16㏖% was around 20㎛. This results shows that the addition of Nb donor had significant effect on the decrease of average grain size and increase of area of grain boundary. In fact, $BaTiO_3$ containing substantial amounts of Nb is the basic dielectric formulations for many ceramic capacitor. The Nb acts to decrease the curie temperature and resists to degradation under voltage-temperature stress, because of produce a fine-graind material. In these insulating materials, the donor charge must be balanced by an equivalent negative charge.

3-3 Effect of sintering temperature

Sintering is one of the principal procedure, which can change electrical properties of the PTC ceramics. Sintering procedure attributed to changes of the crystal structures and microstructure such as grain and grain boundary.

Fig. 7 shows the microstructure of PTC ceramics with Nb_2O_5 0.15㏖% under different sintering temperature. The microstucture of PTC ceramics consists of conductive grain and grain boundary surrounded by thin semiconducting layers. The grain size decreased largely with decreasing the sintering temperature. The average grain size of the specimen sintered at 1350℃ was about 20㎛. In the specimen sintered at 1320℃ ~ 1280℃, it was about 1~5㎛. But average grain size of the specimen sintered at temperature below 1320℃ is very small.

The variation of DC resistivity of specimen sintered at 1350℃ and 1320℃ against the temperature is shown in Fig. 8. The increasing of sintering temperature leads to abruptly decrease in the room temperature

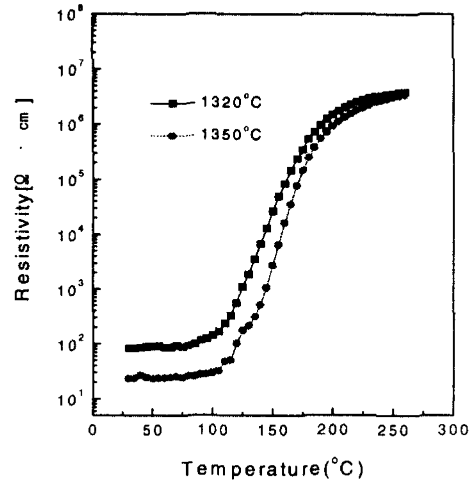

Fig. 8. Temperature characteristics according to the sintering temperature of specimen with Nb_2O_5 0.15㏖%

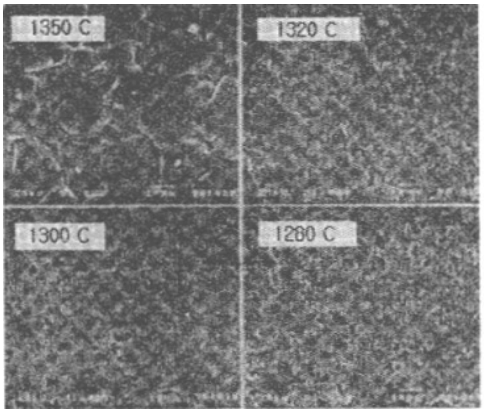

Fig. 7. Microstructure according to sintering temperature of specimen with Nb_2O_5 0.15㏖%

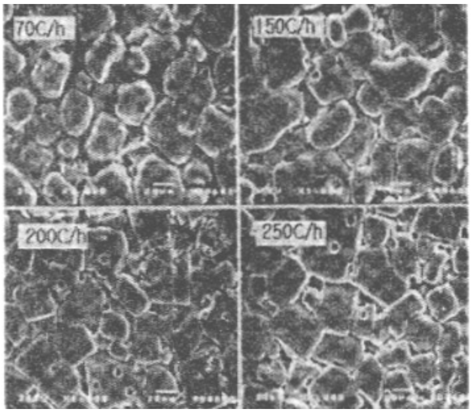

Fig. 9. Microstructure according to cooling rates of specimen with Nb_2O_5 0.15㏖%

resistivity and hardly change in the maximum resistivity. In the specimen sintered at 1300℃ and 1280℃, we could not measure resistivity dependent upon temperature because of deviate from measuring range. As a result, we can conclude that the proper sintering temperature is 1350℃.

3-4 Effect of cooling rate

Electrical characteristics of PTC thermistors are directly related to the sintering conditions such as sintering temperature, time, cooling rate and some other factors. Especially cooling rate can change the microstructure of PTC ceramics, which contribute to the PTC behavior. It is very important to find how a microstructure changes to the cooling rate and what manner those microstructures exist. Because the microstructure is responsible for the electrical characteristics of PTC thermistor. Fig. 9 showed a microstructure of samples Nb_2O_5 0.15mol% with various cooling rates. All sample prepared with different cooling rate had the almost same grain size.

PTC ceramics are polycrystalline ceramics materials which are composed of grains and inter granular regions. All the Nb_2O_5 grains are completely surrounded by a liquid phases during sintering and remains effectively isolated as third phases during cooling. In the ceramics with Nb_2O_5 contents, Nb_2O_5 crystal phases can constitute inter granular layers and continuously spreading in to the ceramics, Those phases are formed by the crystallization of liquid phases in the cooling processes. As we can see in the Fig. 9, at slow cooling rate with 70℃/h which is only shown widely grain boundary regions and some materials overflows throughout grains and grain boundaries. In fast cooling rate above 100℃/h, we found that grain and inter granular layers were observed clearly. But the microstructures in Fig. 9 shows that grain sizes all of samples are about 20㎛ and liquid phases are included in all samples.

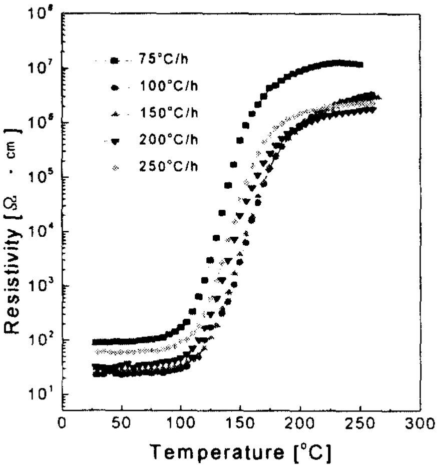

Fig. 10. Resistivity according to cooling rates of specimen with Nb_2O_5 0.15mol%

Fig. 10 shows a resistance according to temperature for cooling rate from 70℃/h to 250℃/h. It is shown that a cooling rate with 70℃/h leads to the largest value of room temperature resistance and maximum resistance. In the between 100℃/h and 250℃/h, increasing the cooling rate leads to increase a room temperature resistance, but maximum resistances had not any tendency. Especially, on the cooling rate 70℃/h, it is shown that widely grain boundary regions and some materials were formed. It was suggested that decrease of the cooling rate results in an increase of the grain boundary thickness. We can suggest, at slow cooling rates below 70℃/h, the grain boundary thickness leads to an increase in the resistivity on the ferroelectric state. It is due to the formation of an inter granular layer of highly increased resistivity on both ferroelectric and paraelectric states.

Ⅳ. Conclusion

The results are as follows :

1) Sintering tempeature and cooling rate seriously affect the electrical resistance of PTC ceramics.
2) As a increasing Nb_2O_5 content, increase of the room temperature resistance is caused by a smaller grain size.
3) Grain boundary resistance increased according to increase Nb_2O_5 content largely, but grain resistance was not changed.
4) The higher resistivity at room temperature is attributed to the remarkable increase in grain boundary resistance.
5) The optimum sintering temperature and cooling rate were 1350℃ for 2 hours and 100℃/h respectively.

Acknowledgements

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References

1. J. Llingsworth, H. M. Al-Allak, A. W. Brinkman and J. Woods, "The influence of Mn on the grain-boundary potential barrier characteristics of donor-doped $BaTiO_3$ ceramics". J. Appl. Phys 67(4), 2088-2092, 1990.
2. D. Y. Wang, "Electrical properties of PTCR barium titanate", J. Am. Ceram. Soc., 73(3), 669-777, 1991.
3. H. Nagamoto, H. Kagotani and T. Okubo, "Positive temperature coefficient of resistivity BaSrPbO creramics", J. Am. Ceram. Soc., 76(8), 2053-2058, 1993.
4. S. H. Tao, Z. L. Ying and Y. Xi, "Grain boundary chracteristics of $BaTiO_3$ PTC thermistor", Ferroelectrics Letter, vol. 14, 45-51, 1992.
5. T. Fukami, "Dependence of Resistivity on Donor Dopant Content in Barium Titanate Ceramics", Jpn. J. App. Phys., Vol. 18, 735-738, 1979.
6. H. M. Al-Allak, A. W. Brinkman, "The effect of donor dopant concentration on the room temperature resistivity of $BaTiO_3$ ceramics with positive temperature coefficients of resistance", J. Appl. Phys 21(3), 1226-1233, 1988.
7. T. Y. Tseng et al, "AC Electrical Properties of High-Curie-Point Barium-Lead Titanate PTCR Ceramics", Materials Letters, Vol. 9, 164-168, 1989.
8. H. M. Chan, M. P. Harmer and D. M. Smyth, "Compansating defects in highly donor-doped $BaTiO_3$", J. Am. Ceram. Soc., 69(6), 507-510, 1987.
9. H. S. Maiti and R. N. Basu, "Complex-Plane impedance analysis for semiconducting barium titanate", Mat. Res. Bull., 21(2), 1107-1114, 1986.
10. I. C. Ho and S. L. Fu, "The core-shell grain resistance in the reduc[illegible]a-doped (Ba, Sr) TiO_3 ceramics", Jpn. J. Appl. Phys., vol. 29(6), 1033-1036, 1990.
11. T. Yamamoto and S. Takao, "Complex impedance analysis of Nb-doped PTC thermistor", Jpn. J. Appl. Phys., vol. 31, 3120-3123, 1992.
12. J. Nowotny and M. Rekas, "Positive temperature coefficient of resistivity for $BaTiO_3$ based materials", Ceramics international, 17, 227-241, 1991.