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Current-voltage Characteristics of Ceramics with Positive Temperature Coefficient of Resistance

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ABSTRACT

A current-voltage relation for Positive Temperature Coefficient of Resistance (PTCR) ceramic was derived and compared with the experimental data. The new current-voltage relation was developed based on Heywangs double Schottky barrier model and a bias distribution across the grain boundary. The voltage limitation $V<4\Phi_b$ suggested by Heywang is no longer necessary in the new expression for the voltage dependence of the resistance. The pulsed voltages were applied to the PTCR ceramic specimen in order to avoid possible temperature variation during the measurement.

Key words* : *PTCR effect, Barium titanate, Ceramics, Current-voltage relation, Grain boundary, DC bias

1. Introduction

The Positive Temperature Coefficient of Resistance (PTCR) effect of Barium titanate-based ceramic is resulted from the Schottky barriers formed at the grain boundaries.[1] The electrical properties of the grain boundaries have been investigated using C-V relations either developed for the metal-semiconductor Schottky junctions or modified for ceramics such as ZnO varistors.[2-4] Recently a new C-V relation was proposed for PTCR ceramics.[5,6]

Although various papers were published for the electrical properties of Barium titnate-based PTCR ceramics, a limited number of publications are available for the current-voltage relation of this ceramic.[1] Considering back-to-back double Schottky barriers at the grain boundary, the barrier lowering by the applied bias determines the current flow across the grain boundary. Then the correct expression for the forward bias is critical to derive an appropriate current-voltage relation.

In this paper the authors investigated the significance of the potential barrier height in the pre-exponential term of the resistance expression and compared the forward bias proposed by Heywang and the one developed in this study. Comparing various I-V relations with the experimental data, the best expression describing the actual I-V relation was suggested.

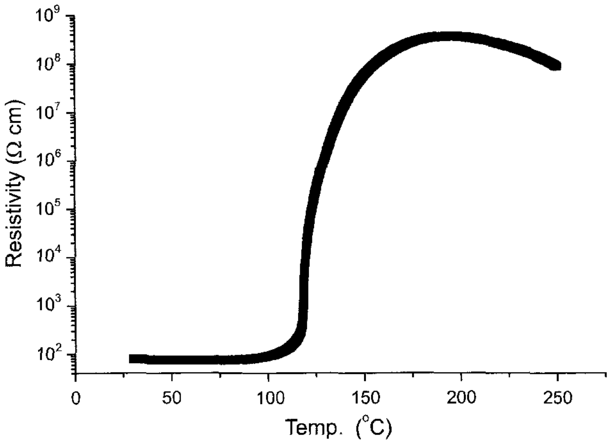

Fig. 1. Electrical resistivity of the PTCR specimen as a function of temperature.

2. Experimental

A $BaTiO_3$-based PTCR ceramic was prepared using conventional ceramic process. Sb_2O_3 and MnO_2 were added to $BaTiO_3$ for obtaining semiconductivity and enhancing PTCR effect, respectively. The electrical resistivity of the specimen as a function of temperature shown in Fig. 1 assures that the specimen prepared in this study is a good PTCR ceramic.

An equivalent circuit for PTCR ceramic can be expressed as Fig. 2, where R_g and R_b are the resistances of a grain and a grain boundary, and C_b is the capacitance of a grain boundary. When a voltage V is applied to a PTCR ceramic at $t=t_0$, the current flowing in the specimen changes with time as shown in Fig. 3(b). In general the resistance of the grain

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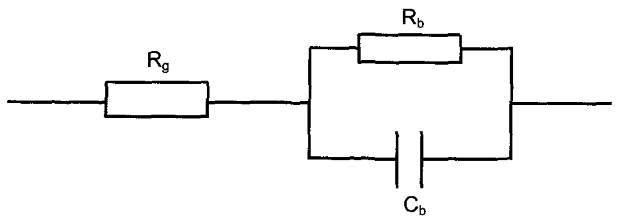

Fig. 2. Equivalent circuit of PTCR ceramic.

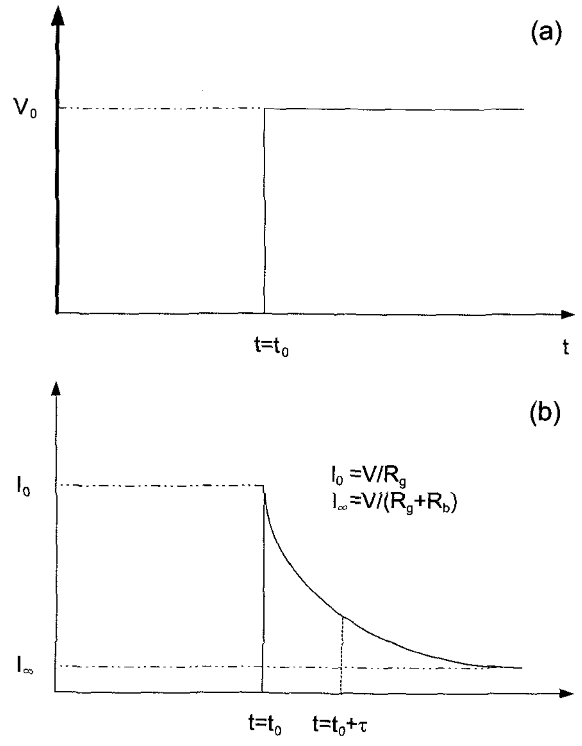

Fig. 3. Charging of PTCR ceramic after applying voltage.

boundary is much larger than that of the grain above Curie temperature, the time constant, therefore, can be expressed as $\tau \cong R_g C_b$. In order to obtain a saturation current, the current should be measured after several times of the time constant (for example, 5 times of τ gives 99.33% of the saturation value) from the onset of the applied voltage. However, when a voltage is applied to the specimen, the temperature of the specimen changes due to Joule heating, results in the change of the resistance. For the correct measurement of the current, the charging time of the capacitor should be considered properly, while the temperature rise of the specimen during measurement due to self-heating is avoided.

The heat capacity of $BaTiO_3$ is 115 ~ 125 J/kmol, which is approximately 0.123 cal/g, above 130°C. The instrument used for measuring current-voltage relation (Keithley 237 Source/measure unit) allows maximum current of 100 mA below 110 V. If the current of 100 mA flows in the specimen at 100 V and the heat generated is used only for raising the temperature of the specimen, the temperature change of the specimen (the weight is 1.2 g) is

$$\Delta T = \frac{VIt}{mC_p} < \frac{100\times0.1\times0.24t}{0.123} = 16.3t\,(^\circ\mathrm{C}) \qquad (1)$$

where t is the duration time of voltage applying, m is the weight and C_p is the heat capacity of the specimen. When the applied voltage is maintained for 1 second, the temperature of the specimen is raised by about 16°C, which is a serious problem for correct measurement.

The PTCR ceramics prepared in this study show the grain resistances and the grain boundary capacitances less than 1000 Ω and 200 nF, respectively, above Curie temperature. Therefore, time constant τ, which is the product of the grain resistance and the grain boundary capacitance, is less than 0.2 ms. We applied a pulsed voltage as shown in Fig. 4. The current is measured after 2 ms of voltage applying, which is 10 times of the time constant and long enough to charge the grain boundary capacitor. The temperature of the specimen during the measurement is raised by 0.033°C according to Eq. (1). The pulse interval is chosen as 30 seconds to prevent a possible heat accumulation by the successive measurements. A current-voltage curve measured at 130°C for a PTCR specimen is given in Fig. 5.

3. Results and Discussion

The electrical resistance at the grain boundary of PTCR ceramic is generally expressed as:[1)]

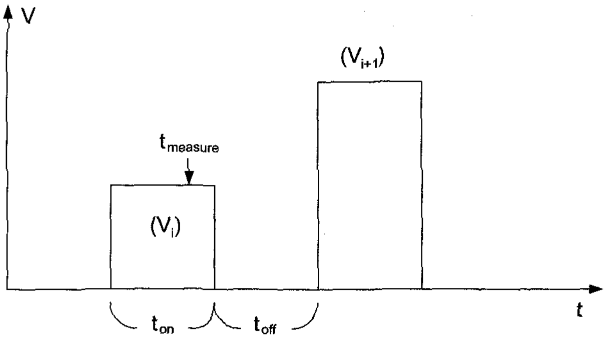

Fig. 4. Voltage pulse waveform for I-V test.

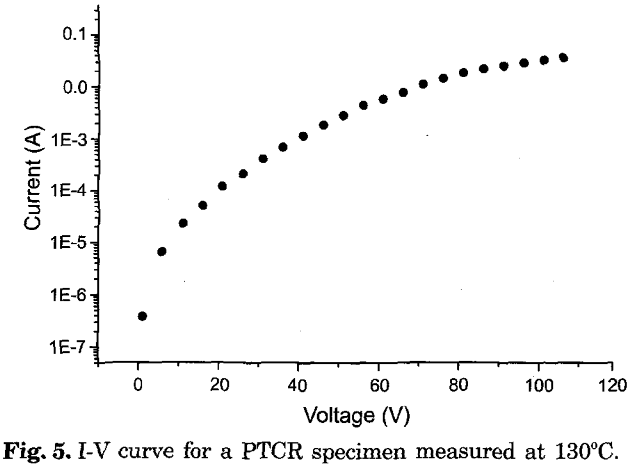

Fig. 5. I-V curve for a PTCR specimen measured at 130°C.

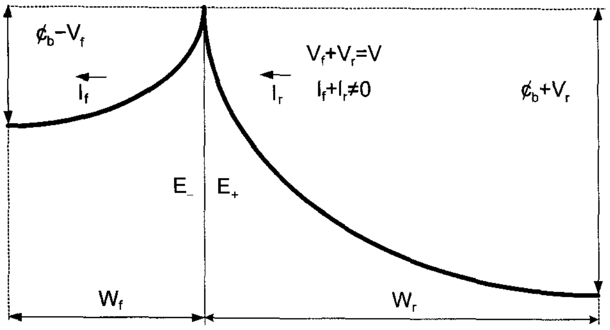

Fig. 6. Potential barrier at the grain boudary of a PTCR ceramic with external voltage.

$$R_b = Ae^{\frac{q\Phi_b}{kT}}, \tag{2}$$

where $A = \frac{\sqrt{2\varepsilon kT}\Phi_b^{-1/2}}{q^{3/2} n_0^{3/2} \mu}$. Eq. (2) is normally acceptable, but when Φ_b approaches zero, the term $\Phi_b^{-1/2}$ becomes significant. Expressing the resistance as a function of potential barrier height:

$$R_b = B\Phi_b^{-1/2} e^{\frac{q\Phi_b}{kT}}, \tag{3}$$

where $B = \frac{\sqrt{2\varepsilon kT}}{q^{3/2} n_0^{3/2} \mu}$.

The potential barrier at the grain boundary is modified by an applied voltage V as shown in Fig. 6. Since the resistance is controlled by the potential barrier in the forward direction, $\Phi_b - V_f$, two different expressions for the resistance at the grain boundary are obtained as follows using Eqs. (2) and (3):

$$R_1 = Ae^{\frac{q(\Phi_b - V_f)}{kT}} = R_0 e^{\frac{-qV_f}{kT}} \tag{4}$$

$$R_2 = \frac{B}{(\Phi_b - V_f)^{1/2}} e^{\frac{q(\Phi_b - V_f)}{kT}} = R_0 \Phi_b^{1/2} (\Phi_b - V_f)^{-1/2} e^{\frac{-qV_f}{kT}} \tag{5}$$

where R_0 is the resistance at $V = 0$. According to Heywang,[1)] the forward bias V_f is

$$V_f = \frac{V}{2} - \frac{V^2}{16\Phi_b}. \tag{6}$$

The authors[5,6)] suggested a bias distribution at the grain boundary of PTCR ceramic as follows:

$$\frac{V_f}{w_f} = \frac{V_r}{w_r}. \tag{7}$$

where w_f and w_r represent the depletion widths at forward and reverse bias, respectively.

Using Eq. (7) and Heywang model, the forward bias proposed in this study is

$$V_f = \frac{V + 2\Phi_b - \sqrt{4\Phi_b^2 + V^2}}{2}. \tag{8}$$

Combining Eqs. (4), (5), (6), and (8), there can be four different expressions for the resistance at the grain boundary, when a bias V is applied. We denoted R_{11} for the resistance obtained using Eq. (4) and (6), and R_{12} for those determined using Eq. (4) and (8). Similarly, R_{21} is the resistance determined using Eq. (5) and (6), and R_{22} is that acquired using Eq. (5) and (8).

The theoretical values of currents, I_{11}, I_{12}, I_{21}, and I_{22}, can be obtained by inserting R_0, measured at $V = 0$, into Eqs. (4) and (5), and using Eqs. (6) and (8). When a bias V is applied, the current I_{22}, for example, is obtained as follows:

$$I_{22} = \frac{V}{R_{22}} = \frac{V}{R_0} \Phi_b^{-1/2} (\Phi_b - V_f)^{1/2} e^{\frac{qV_f}{kT}} \tag{9}$$

The R_0, measured for the specimen at $V = 0$ and 130°C as shown in Fig. 5, is 23.3 kOhm, and the Φ_b, determined using C-V characteristics, is 0.44 V, then using Eqs. (8) and (9), we can obtain I_{22}.

The theoretical values and the measured value for a PTCR ceramic at 130°C are given in Fig. 7. All the theoretical values are close to the measured one at low applied voltage (approximately below 30 V), but significant deviation from the measured value is observed for I_{11} and I_{21} at high voltage. The currents I_{11} and I_{21} are calculated using Heywangs voltage distribution, Eq. (6). The current I_{12} starts to

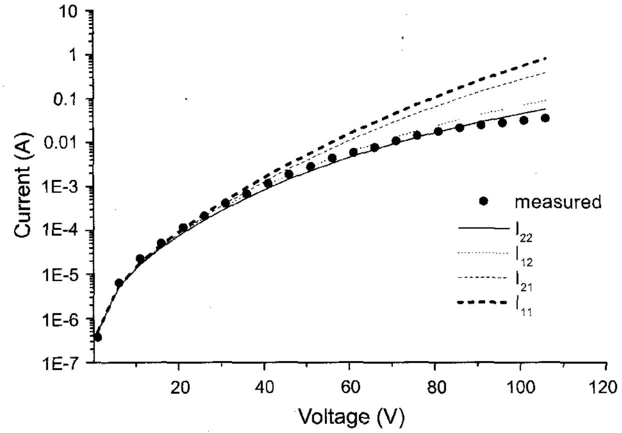

Fig. 7. I-V curves of theoretical and measured values.

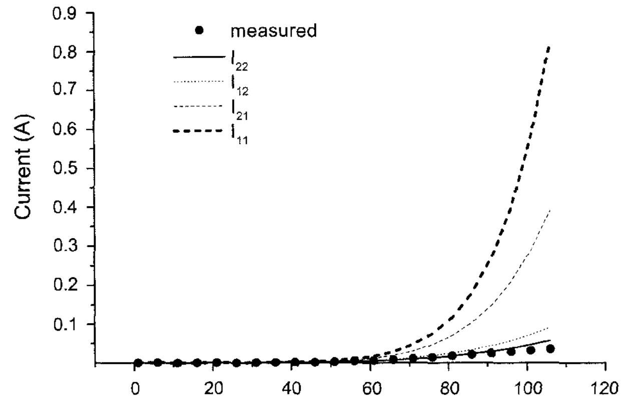

Fig. 8. I-V curves of theoretical and measured values (liner scale).

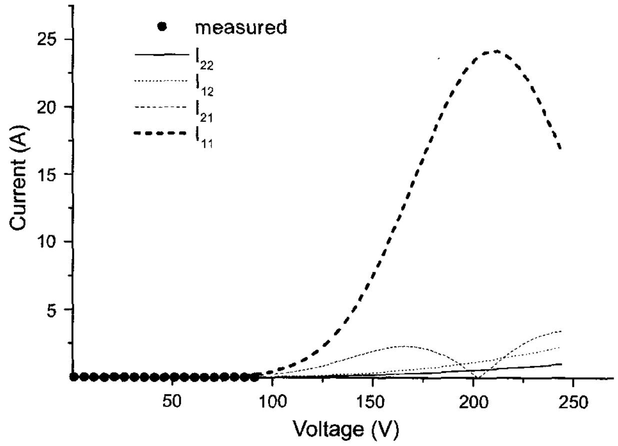

Fig. 9. I-V curves of theoretical and measured values at high voltage.

deviate from the measured value near 80 V, while the current I_{22} fits well with the measured one up to 100 V. This result proves that the voltage distribution proposed by the authors, Eq. (7), is correct. The current-voltage curves expressed using linear scale given in Fig. 8 show the deviation of the theoretical values from the measured one clearly.

It is also observed that the difference in the expression of the resistance does not affect much for the current-voltage curve. There is, however, some effect of $\Phi_b^{-1/2}$ in the pre-exponential term on the resistance expression, which is obvious from the result that I_{22} fits better than I_{12}.

According to the Eq. (6), V_f increases with V up to $V=4\Phi_b$ and decreases as V increases further, which can't happen in real situation. Heywang, therefore, set a limitation of $V<4\Phi_b$ for this equation.[1] On the other hand, the Eq. (8) suggested in this study only allows the increase of V_f with applied voltage V and V_f does not exceed Φ_b, which qualitatively represent the real situation.

The current-voltage curves for the theoretical calculations in the voltage range higher than $4\Phi_b$ are shown in Fig. 9. I_{12} and I_{22} increase gradually with voltage, while I_{11} and I_{21} show unacceptable behavior such as rapid increase of the current with applied voltage and the decrease of the current in a part of the voltage range.

4. Conclusions

Various current-voltage relations applicable to the PTCR ceramics were investigated. When a bias is applied to the PTCR ceramic, the potential barriers at the grain boundaries are lowered by the amount of forward bias. The current-voltage curve obtained using the forward bias derived on the base of a bias distribution across the grain boundary fits very well with the experimental data. Furthermore the voltage limitation $V<4\Phi_b$ suggested by Heywang is no longer necessary in the new expression for the voltage dependence of the resistance. Although there are some effect of $\Phi_b^{-1/2}$ in the pre-exponential term on the resistance expression, the difference is not significant. The application of the pulsed voltage seemed to be appropriate for the PTCR ceramics in order to avoid possible temperature variation during the measurement.

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REFERENCES

1. W. Heywang, "Resistivity Anormaly in Doped Barium Titanate," *J. Am. Ceram. Soc.*, **47** [10] 484-90 (1964).
2. L. M. Levinson and H. R. Philipp, "The Physics of Metal Oxide Varistors," *J. Appl. Phys.*, **46** [3] 1332-41 (1975).
3. W. G. Morris, "Physical Properties of the Electrical Barriers in Varistors," *J. Vac. Sci. Technol.*, **13** [4] 926-31 (1976).
4. K. Mukae, K. Tsuda, and I. Nagasawa, "Capacitance vs Voltage Characteristics of ZnO Varistors," *J. Appl. Phys.*, **50** [6] 4475-76 (1979).
5. Y. G. Li and S. G. Cho, "Capacitance-voltage Relation for Ceramics with Positive Temperature Coefficient of Resistance," *J. Appl. Phys.*, **91** [7] 4535-37 (2002).
6. Y. G. Li and S. G. Cho, "Determination of Potential Barrier Heights at the Grain Boundaries of PTC Ceramics," *J. Kor. Ceram. Soc.*, **38** [7] 639-42 (2001).