Electrical Non-Linearity of SiC Aggregate

By

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1. Introduction

It is well known that SiC is usually coated with an SiO₂ layer at the surface and SiO₂ layer serves as a protective coating for further oxidation. There have been many reports about the oxidation of SiC^{(1), (2), (3)}. Suzuki⁽⁴⁾ has reported the relations among physical properties of SiC, binding materials and the oxidation of SiC.

However, there has been little attention to the effect of SiO₂ layer on the semiconductive properties of SiC. The SiO₂ layer formed at the surface of SiC particles has very important role especially in the SiC non-linear resistor because the non-linear property of this resistor is attributed to contacts among individual SiC particles.

The *I-V* characteristic of SiC particle aggregate has been approximately expressed by the following equation⁽⁵⁾:

$$I = \left(\frac{V}{C} \right)^\alpha \quad \dots\dots\dots (1)$$

where *I* is a current flowing through the aggregate and *V* is a voltage applied to the aggregate. According to Schwertz et al⁽⁵⁾, *C* and α are constants independent of *I* and *V* and are dependent on the dimension and shape of the aggregate or on the preparation conditions. They conclude that the *C* relates to the pressure, *P*, applied to the aggregate by the following equation.

$$C \propto P^{-1/m} \quad \dots\dots\dots (2)$$

where *m* is a constant ranging 3 to 3.5:

The *C*-value is named a non-linear resistance and corresponds to a resistance of usual ohmic resistor having $\alpha=1$.

These *I-V* characteristics of SiC particles have not been discussed in view of the SiO₂ layer formed at the surface of SiC particles. The present paper is to study the voltage non-linear properties of SiC particles while considering the effects of SiO₂ layer on the surfaces of SiC particles.

2. Experimental

2.1 Measurement on SiC Aggregate

The SiC particles having an average size of 60 to 180 μ were placed in a ceramic cylinder of 13 mm in diameter and were pressed by an upper

Table 1 Properties of SiC used in varistor.

Impurity Content (%)		Resistivity (k Ω)	Color
Al	Fe		
0.32	0.18	200	Black

and lower punches acting as electrodes.

The *I-V* characteristics were measured by applying dc current through the both punches while the pressure of the upper punch was changed from 0.1 kg/cm² to 800 kg/cm². Table 1 shows the impurity content and electrical resistance of SiC particles used. The resistance of the SiC particles was conveniently represented by the resistance obtained when dc current of 1 mA was supplied to a compact body pressed at 400 kg/cm². The compact body was composed of SiC particles in an average size of 113 μ and had a dimension of 4 mm in diameter.

2.2 Calculation of α -value and Definition of Non-Linear Resistance *C*

The α -value is calculated by the following equation (3) lead from equation (1):

$$\alpha = \frac{d(\log I)}{d(\log V)} = \frac{dI}{I} \bigg/ \frac{dV}{V} = \frac{\log I_1 - \log I_2}{\log V_1 - \log V_2} \quad \dots\dots\dots (3)$$

where *I*₁ and *I*₂ are current flowing through the varistor at *V*₁ and *V*₂, respectively.

The obtained value is defined as an α -value at a voltage of (*V*₁ + *V*₂)/2. The non-linear resistance *C* is conveniently defined as a resistance when 1 mA of current flows.

3. Results and Discussion

3.1 *I-V* Characteristics

Fig. 1 shows typical *I-V* curves of SiC aggregate. As easily understood by equation (3); the reciprocal of slope of the *I-V* curve indicates α -value; the larger slope results in the smaller α -value. The slope becomes steeper with a decrease in the applied voltage or in the current as well as with an increase in the pressure. It is concluded that the α is not constant but dependent upon applied voltage, current and pressure.

Fig. 2 shows the relation between the compacting pressure and the α -value at a given voltage. Below 5 kg/cm² the α -value increases with incre-

Fig. 1 I - V properties of SiC aggregate as a parameter of applied pressure.

Fig. 2 Relations between compacting pressure and α at constant voltages.

asing compacting pressure. However, the aggregate compacted at a pressure more than 5 kg/cm² shows a constant α -value.

Therefore, the V - α curves are represented by an identical line as shown in Fig. 3 even when the aggregate is pressed at various pressures

Fig. 3 V - α properties of SiC aggregate at various compacting pressures.

above 5 kg/cm². V - α relation of Fig. 3 is approximately linear in logarithmic scale and can be expressed by the following experimental equation:

$$\alpha = bV^a \dots\dots\dots (4)$$

where a and b are constants independent of the voltage. Fig. 3 indicates that at a pressure above 5 kg/cm² a and b are also independent of the compacting pressure. From equations (3) and (4),

$$\frac{d(\log I)}{d(\log V)} = bV^a = be^a \log V$$

Accordingly,

$$I = ke^{\frac{b}{a}V^a} = ke^{b_0V^a} \dots\dots\dots (5)$$

where k is constant.

Fig. 3 exhibits that the SiC has about 1/2 of α -value for a pressure above 5 kg/cm². According to the measurements with various SiC particles, the α -value above 5 kg/cm² was independent of the kinds of SiC particles and was also about 1/2. The b -value depended on the kinds of SiC particles and decreased with an increase in the resistivity of SiC particles.

3.2 Effect of Oxidation of SiC Particles

The voltage non-linear properties of the SiC aggregate are known to be attributed to contacts among individual SiC particles⁶⁾. The surface state of SiC particle is greatly responsible for the non-linear property of aggregate. Therefore, it is interesting to examine the effect of SiO₂ film formed on SiC particle on the α -value.

Fig. 4 Relation of C and bulk density of SiC aggregate as a function of applied pressure.

The SiC particles as crushed were heated at a temperature of 800° to 1300°C for 1 hour in order to from a thin SiO₂ film on the surface. Fig. 4 shows a relation between applied pressure and non-linear resistance C , or bulk density of SiC particles oxidized at various temperature. The SiC particles show a logarithmic decrease in the non-linear resistance C and a linear increase in the bulk density with increasing pressure. The non-linear resistance C decreases initially steeply

Fig. 5 $V-\alpha$ properties of SiC aggregate pressed at 150 kg/cm². SiC particles are fired in air at various temperatures.

with a compacting pressure below 150 kg/cm² and gradually above 150 kg/cm². The higher oxidation temperature results in the higher non-linear resistance C ; the bulk density does not vary with the oxidation temperature.

As shown in Fig. 5, the $V-\alpha$ curve did not vary with the heating temperature of 800° to 1300°C for 1 hour and was similar to that of unheated SiC particles when the SiC particles were pressed at 150 kg/cm². The SiC particles heated in air at 1300°C for 15 hours, however, exhibited a $V-\alpha$ curve different from that of SiC particles heated in air at 1300°C for 1 hour.

Fig. 6 $V-\alpha$ properties of SiC aggregate pressed at 5 kg/cm². SiC particles are fired in air at various temperatures for 1 hour.

The $V-\alpha$ curve at 5 kg/cm², however, varied with the heating temperature of SiC particles. Fig. 6 shows that the $V-\alpha$ curve shifts toward the higher voltage as the heating temperature of SiC particles rises. The $V-\alpha$ curve for SiC particles heated at 800°C is exactly similar to that for SiC particles heated at 1000°C. From the comparison of Fig. 5 with Fig. 6, it can be seen that there is no difference in $V-\alpha$ curve between the SiC particles pressed at 150 kg/cm² and 5 kg/cm² when the SiC particles are heated at 800° to 1000°C.

The $V-\alpha$ curves of Fig. 5 and 6 will be explained by considering the thickness of thin film of SiO₂ formed by oxidation. The thickness of thin film can be expressed by the following equation²⁾:

$$\left. \begin{aligned} \delta_0^2 &= Kt \\ \log K &= 13.7 - 17500/T, \end{aligned} \right\} \text{.....(6)}$$

where δ_0 is a thickness of SiO₂ film (mμ); t , a heating time (minute); and T is a temperature in absolute (°K). The thickness of SiO₂ film is calculated to be 20 mμ and 70 mμ when the SiC particles are heated in air at 1300°C for 1 hour and 15 hours, respectively.

(a) Contact pressed below critical pressure. (b) Contact pressed above critical pressure.

Fig. 7 Model of SiC to SiC contact.

The SiC particles are brittle and show no plastic deformation like metal powders when pressed at high pressure. In view of similarity in $V-\alpha$ curve at 150 kg/cm² between SiC particles heated at 1300°C for 1 hour and unheated SiC particles, it will be concluded that the compacting pressure of 150 kg/cm² makes it possible to break partially the SiO₂ film of 20 mμ in thickness and to bring the SiC particles into direct contacts as shown in Fig. 7. The difference in $V-\alpha$ curve for SiC particles heated at 1300°C for 15 hours and that for SiC particles heated at 1300°C for 1 hour indicates that the SiO₂ film of 77 mμ in thickness can not be broken by the pressure of 150 kg/cm² and prevents direct contacts between the SiC particles. The change in the bulk density and the C with increasing pressure is also attributed to an increase in the contact area among the SiC particles, which is due to a promotion of pulverization at the edge contacts as shown in Fig. 7. Such pulverization was proved by microscopic observation of aggregate pressed at a high pressure.

It is interesting to know a relation between the thickness of SiO₂ film and a critical pressure by which the SiO₂ film starts to be broken. The SiC particles were heated in air at various temperature for various heating time periods so that their surfaces are coated by SiO₂ films having various thicknesses. The thickness can be calculated in accordance with the equation (6). The α of SiC particles coated with SiO₂ films in various thicknesses was plotted against the pressure in

Fig. 8 Relations between applied pressures and α for SiC particles having SiO₂ layers of various thicknesses.

Fig. 9 Relations between SiO₂ thickness and critical pressure.

Fig. 8; the α was measured at 60 V/mm. Fig. 8 indicates that the α increases with an increase in the pressure and is constant above a critical pressure. The constant α -value above the critical pressure may be resulted from the direct contacts of SiC particles due to the damage of the SiO₂ film. Note that the unheated SiC particles has a critical pressure of about 5 kg/cm².

The critical pressure increases linearly with the thickness of SiO₂ film as shown in Fig. 9. In view of a critical pressure of 5 kg/cm² for unheated SiC particles, it will be concluded that the unheated SiC particles are coated with SiO₂ film in about 1 mμ thickness. It is noteworthy that the value of 1 mμ in thickness corresponds to that of previous reports^{7), 8)}.

3.3 Pressure Dependence of α and C

The relation between the α -value and the applied pressure below critical pressure can be explained with a simple aggregate model in which SiC particles coated with ohmic SiO₂ films are in

Fig. 10 Simplified model of SiC aggregate.

contact to each other.

Assume a simple aggregate composed of m trains, each of which comprises n SiC spheres aligned in a longitudinal line as shown in Fig. 10. An electric voltage V_1 applied across the top layer and the bottom layer causes a current I_1 to flow through the aggregate in a longitudinal direction. Since the SiC particles themselves have a resistance extremely lower than that of the contact between SiC particles, the V_1 and I_1 can be expressed by the following equation:

$$\left. \begin{aligned} V_1 &= n v_1 \\ I_1 &= m i_1 \end{aligned} \right\} \dots \dots \dots (7)$$

where v_1 is a voltage applied to each of contacts between SiC particles and i_1 is a current flowing through each of the trains. When the SiC particles have no SiO₂ layer on the surfaces, the V - I characteristic of each m trains containing n SiC particles aligned in a longitudinal direction is assumed by the following equation:

$$i_1 = K_1 v_1^{\alpha_1} \dots \dots \dots (8)$$

where α_1 is defined as the non-linear exponent of SiC particles having no SiO₂ layer. By combining the equation (7) and (8), one obtains;

$$I_1 = m K_1 \left(\frac{V_1}{n} \right)^{\alpha_1}$$

When the SiC particles of the aggregate are coated with the SiO₂ films formed by oxidation, the voltage V applied to the aggregate is divided into two parts: One is the voltage, V_1 applied to SiC particles and the other is the voltage, V_2 applied to SiO₂ films. Therefore, one can obtain,

$$V = V_1 + V_2$$

Assume that the SiO₂ films have a constant resistance R_0 , and one obtain:

$$\begin{aligned} V_2/V_1 &= \frac{\text{Resistance of SiO}_2 \text{ films}}{\text{Resistance of SiC particles}} \\ &= I_1 R_0 / V_1 \\ &= \frac{R_0 m K_1}{n^{\alpha_1}} V_1^{\alpha_1 - 1} \end{aligned}$$

Hence,

$$V_2 = (R_0 m K_1 / n^{\alpha_1}) V_1^{\alpha_1} \equiv k V_1^{\alpha_1}$$

One can calculate the α -value of the aggregate of SiC particles coated with SiO₂ films as follows:

$$\begin{aligned}
\alpha &= \frac{dI_1}{I_1} \bigg/ \frac{dV}{V} \\
&= \frac{dI_1}{I_1} \bigg/ \frac{(1+\alpha_1 k V_1^{\alpha_1-1}) dV_1}{(V_1 + k V_1^{\alpha_1})} \\
&= \frac{dI_1}{I_1} \bigg/ \frac{(V_1 + \alpha_1 V_2) dV_1}{(V_1 + V_2) V_1} \\
&= \left(\frac{V_1 + V_2}{V_1 + \alpha_1 V_2} \right) \alpha_1 \\
&= \left(1 + \frac{V_2}{V_1} \right) \alpha_1 \bigg/ \left(1 + \frac{\alpha_1 V_2}{V_1} \right) \\
&= \alpha_1 \left\{ 1 + (1 - \alpha_1) \frac{V_2}{V_1} - \alpha_1 (1 - \alpha_1) \left(\frac{V_2}{V_1} \right)^2 + \right. \\
&\quad \left. \alpha_1^2 (1 - \alpha_1) \left(\frac{V_2}{V_1} \right)^3 + \dots \right\} \\
&\approx \alpha_1 \left\{ 1 - (\alpha_1 - 1) \frac{V_2}{V_1} \right\} \dots \dots \dots (9)
\end{aligned}$$

The ratio V_2/V_1 decreases as the thickness of SiO_2 film is lowered by the pulverization due to the increasing pressure. When the two particles are in direct contact to each other at the critical pressure, the ratio V_2/V_1 becomes 0 and α is in accord with α_1 . From the equation (9), it will be clear that the α -value of aggregate increases with an increase in the pressure below the critical pressure and reaches α_1 when the two SiC particles are in direct contact to each other above the critical pressure.

Fig. 4 indicates that the C -value still decreases with an increase in the pressure above critical value. The relation between C and pressure can be explained as follows:

The direct contact between SiC particles above critical pressure is responsible for the constant α at a given voltage as stated above. An area of direct contact between SiC particles, however, increases as the applied pressure increases. Since the current passing through the SiC particles is found to be proportional to the direct contact areas of SiC particles, the current at a given voltage increases with an increase in the applied pressure. This means that the voltage at a given current decreases inversely with an increase in the applied pressure. The voltage at a given current is equivalent to the C in view of the definition shown in 2-2. Therefore, the C decreases monotonously with an increase in the applied pressure though the voltage at a given α is independent of the pressure above critical value. It should be noted that the direct contact of SiC particles is resulted in a constant α but not in the constant C -value.

The area of direct contact between SiC particles decreases with an increase in a thickness of SiO_2 layer formed on SiC particle at a given pressure. Therefore, as seen in Fig. 4, the SiC particles heated at a higher temperature show a higher C -value at a given pressure because they have a thicker SiO_2 layer.

4. Conclusion

The V - I property of SiC aggregate is expressed by the following equation:

$$I = \left(\frac{V}{C} \right)^a$$

where α is a nonlinear exponent and C is a constant corresponding with the resistance in an ohmic resistor. The study on the non-linearity of SiC aggregate has led the following conclusions:

1) The SiC particles as crushed is provided with the α which increase with an increase in the applied pressure below a critical pressure of 5 kg/cm². Above the critical pressure, the α at a given voltage keeps constant regardless of a change in the pressure.

2) The relation between the α and the applied voltage is expressed as follows:

$$\alpha = bV^a$$

where a and b are constants. Above the critical pressure, the a -value is independent of the applied pressure and kinds of SiC particles and is about 1/2. The b -value decreases with an increase in the resistivity of SiC. In view of this relation of the α to the applied voltage, the V - I property of SiC particles can be expressed by the following equation:

$$I = k e^{b_0 V^a}, \quad b_0 \equiv b/a$$

where k is a constant.

3) The critical pressure becomes higher as the SiC particles are coated with a thicker SiO_2 film formed by oxidation. The formation of SiO_2 layer on SiC particles causes the lower α below the critical pressure and the higher C -value regardless of the applied pressure.

4) The relation between α and pressure below the critical pressure has been discussed in view of the thickness of SiO_2 layer formed on SiC particles.

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References

- 1) A.C. Lea, *J. Soc. Glass Technol.* **12**, 27-50 (1949).
- 2) G. Ervin, *J. Am. Ceram. Soc.* **41**, 347-52 (1958).
- 3) T.H. Elmer, *U.S. Atomic Energy Doc.* NEPA-1770 (1950).
- 4) S. Yamauchi, "Yogyo no Kenkyu II" Gihodo (1961). pp. 429-86.
- 5) F.A. Schwertz and J.J. Mazenko, *J. Appl. Phys.* **24**, 1015-1024 (1953).

- 6) E.W.J. Mitchell and R.W. Sillars, *Proc. Phys. Soc.* **62 B**, 509-22 (1949).
 7) A. Braun and G. Busch, *Helv. Phys. Acta* **15**, 571-611 (1942).

- 8) H.G. Heine and P. Scherrer, *Helv. Phys. Acta* **13**, 489 (1940).

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SiC 粒子集合体の電気的非直線性

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本論文は SiC 粒子の表面に形成されている SiO₂ の影響を考慮に入れた場合の SiC 粒子集合体の電圧非直線特性についてのべる。

非直線性は $I=(V/C)^a$ の式で表示される。粉碎されたままの SiC 粒子の a は、5 kg/cm² の臨界圧力以下の印加圧力で、圧力の増加とともに大きくなる。臨界圧力以上では、 a は圧力に無関係に一定値を示す。臨界圧は SiC 粒子表面に形成される SiO₂ の厚みが厚くなると大

きくなる。 a と電圧の間には $a=bV^a$ の関係がある。臨界圧以上では a は電圧、圧力、SiC 粒子の種類に無関係に一定である。臨界圧以下における a の圧力依存性は、SiO₂ 層の厚みが圧力とともに変ることによっておこる。SiO₂ 層の厚みは印加圧力が増大するにつれて減少する。SiO₂ 層の a におよぼす影響について論じられている。
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The Properties and Structure of Glasses in the System As₂S₃-Sb₂S₃

(The Properties and Structure of Sulfide Glasses Part IV)

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1. Introduction

The physical and chemical properties of glasses in the system As-S and the structure derived from the various properties were reported in the previous papers^{1,2,3}. We have now intended the investigation of glasses in the system Sb-S in which Sb is of the same group as As in the Periodic Table. However the vitreous material could not be obtained in the binary system Sb-S.

Therefore it was thought advisable to investigate the structure and properties of glasses in which Sb was added to the system As-S for the following reasons; in view of a fact that Sb is more metallic than As and the structure of Sb₂S₃ (a double chain structure, m.p. 548°C) is very different from that of As₂S₃ (a layer structure,

m.p. 310°C) (Fig. 1), it is very interest to investigate how the properties of these glasses change by the addition of Sb to As-S glasses or how the glass in this system is built up.

The tendency of glass formation in the system As-S-Sb has been already reported by Kolomiets et al.⁴, but its range is not determined in detail

Fig. 1 The structure of As₂S₃ crystal (orpiment) (1) and Sb₂S₃ crystal (stibnite) (2).

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