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D.C. electrical conductivity of amorphous Si_3N_4–C composites prepared by chemical vapour deposition

TAKASHI GOTO, TOSHIO HIRAI
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, 980, Japan

Amorphous Si_3N_4–C[Am.CVD-(Si_3N_4–C)] composites containing 0.07 to 6 wt % carbon were prepared on a graphite substrate by chemical vapour deposition using $SiCl_4$, H_2, NH_3 and C_3H_8 as the source gases. The d.c. electrical conductivities of the Am.CVD-(Si_3N_4–C) composites in the directions perpendicular ($\sigma_\perp$) and parallel ($\sigma_\parallel$) to the substrate were measured. The variation of $\sigma_\perp$ with temperature in the range 250 to 950° C, and also the difference between $\sigma_\perp$ and $\sigma_\parallel$ at room temperature, were investigated. The $\sigma_\perp$ of the Am.CVD-(Si_3N_4–C) composites containing 0.2 wt % or more carbon was 10^9 to 10^{10} times greater than that of amorphous CVD-Si_3N_4 at a temperature of about 500° C, and $\sigma_\parallel$ was 10 to 30 times greater than $\sigma_\perp$ at room temperature. The activation energy for electrical conduction obtained from the measured temperature dependence of the $\sigma_\perp$ ($E_\perp$) for the electrically conductive Am.CVD-(Si_3N_4–C) composites was 0.02 to 0.06 eV. This result suggests that the electricity is conducted through a carbon network in the amorphous Si_3N_4 matrix.

1. Introduction

Amorphous silicon nitride films have been widely used in semiconductor processing as diffusion masks, surface passivators and gate dielectric films because of their superior chemical stability and high electrical resistance. In order to develop new materials the authors have been studying the preparation of Si_3N_4-based composite materials by chemical vapour deposition (CVD). One such attempt was to produce electrically conductive Si_3N_4–C composite materials by CVD.

The present authors have prepared amorphous Si_3N_4 containing carbon [Am.CVD-(Si_3N_4–C) composites] by CVD [1], and investigated their structures and properties [2, 3]. In particular, we showed that the carbon in the Am.CVD-(Si_3N_4–C) composites is present as an amorphous carbon phase within an amorphous Si_3N_4 matrix [1, 4].

The present paper describes the temperature dependence of the d.c. electrical conductivity in the temperature range 250 to 950° C for the composites in the direction perpendicular to the substrate ($\sigma_\perp$), and also discusses the difference between $\sigma_\perp$ and the conductivity in the direction parallel to the substrate ($\sigma_\parallel$) at room temperature. Finally, a discussion on the electrical conduction mechanism of the Am.CVD-(Si_3N_4–C) composites is presented.

2. Experimental procedure

2.1. Sample preparation

The Am.CVD-(Si_3N_4–C) composites containing 0.07 to 6 wt % carbon were prepared on a graphite substrate by CVD using $SiCl_4$, NH_3, C_3H_8 and H_2 as the source gases, and carbon-free amorphous CVD-Si_3N_4 was also prepared for comparison purposes. The details of these preparation procedures have been reported earlier [1]. All samples were prepared at deposition temperatures (T_{dep}) of 1200 and 1300° C and a total gas pressure of 30 torr. The carbon content of the Am.CVD-(Si_3N_4–C) composites was controlled by regulating C_3H_8 gas-flow rates [FR(C_3H_8)]. Table I

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TABLE I The deposition conditions and some properties of the specimens

T_{dep} (° C)	FR(C_3H_8) ($cm^3\ min^{-1}$)	Colour	Density ($g\ cm^{-3}$)	Carbon content (wt%)
1200	0	White	2.97	0
	10	Grey	2.95	0.1
	25	Black	2.96	0.6
	40	Black	2.96	0.7
	70	Black	2.92	2
	100	Black	2.81	3
1300	0	White	3.00	0
	10	Grey	3.00	0.07
	25	Black	2.98	0.2
	40	Black	2.98	0.6
	70	Black	2.95	2
	100	Black	2.85	6

summarizes the deposition conditions and several properties of the prepared samples.

Plate-like deposits with dimensions of 40 mm x 12 mm and 1 to 1.5 mm thick were ultrasonically cut to a disc of 5 to 10 mm diameter and to a stick with dimensions of 3 mm x 15 mm. Two surfaces of each sample were then shaved plane parallel to a thickness of 0.5 to 0.8 mm using a diamond-grinder, then ultrasonically cleaned in acetone before the sample was subjected to the electrical conductivity measurements.

2.2. Measurements of d.c. electrical conductivity

2.2.1. Temperature dependence of d.c. electrical conductivity

The $\sigma_\perp$ of disc-shaped specimens was measured by the two-point technique. The measurements were made at temperatures between 250 and 950° C, and in an electric field up to 150 V cm^{-1}. The specimens were measured in a reducing atmosphere of 97% He–3% H_2 to prevent oxidation of the specimen surfaces.

The lead wires were made of platinum, and gold paste (Du Pont: DP-8760) was used for making ohmic electrical contact. At very low $\sigma_\perp$, a guard ring was used to remove the surface current.

Fig. 1 illustrates the specimen-holding apparatus for heating the specimens. Each platinum lead wire was insulated by a quartz tube. The quartz tubes and the holding apparatus were enclosed in an earthed stainless steel pipe in order to prevent current leaks through the quartz tubes as well as to eliminate any external electrical noise. The electric current was supplied through a stabilized voltage source (Metronix: 652), and was measured by a pico-ammeter (Toa Denpa: PM-18) and digital multimeter (Takeda Riken: TR-6855).

2.2.2. Anisotropy of d.c. electrical conductivity

Measurement of $\sigma_\perp$ and $\sigma_\parallel$ was performed at room temperature in air. $\sigma_\perp$ was measured by a two-point technique using disc-shaped specimens and $\sigma_\parallel$ was measured by a four-point technique with stick-shaped specimens. The instruments used for these measurements were described in Section 2.2.1. Fig. 2 shows the circuits used for

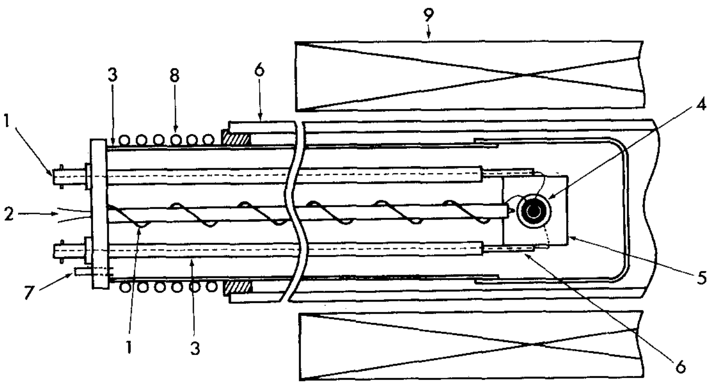

Figure 1 Holding apparatus for heating the specimens. 1 Pt lead wire; 2 Pt–13%Rh thermocouple; 3 stainless steel tube; 4 specimen; 5 specimen holder; 6 quartz tube; 7 gas inlet; 8 water jacket; 9 furnace.

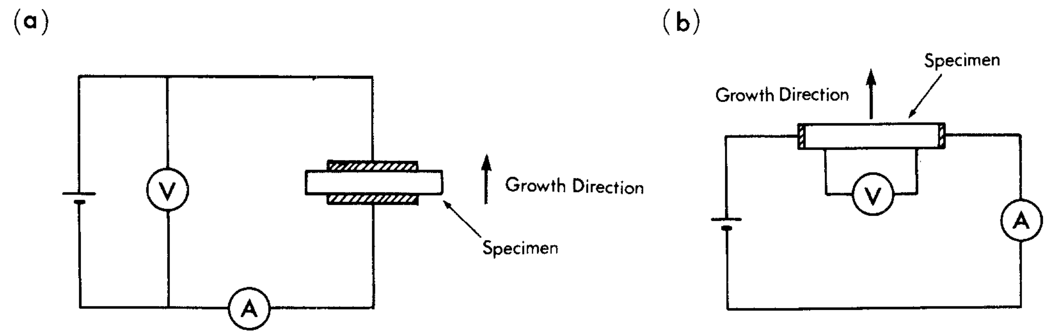

Figure 2 Circuits for the measurements by (a) the two-point and (b) the four-point techniques.

measurements in the two- and four-point techniques. In these figures the growth direction coincides with the direction perpendicular to the substrate.

3. Results

The ohmic characteristics of $\sigma_\perp$ on the carbon-free Am.CVD-Si_3N_4 in the temperature range 450 to 1000° C under an applied electric field of up to $1500\,V\,cm^{-1}$ have been reported previously [5]. $\sigma_\perp$ of the Am.CVD-(Si_3N_4–C) composites containing 0.07 to 0.1 wt% carbon were almost the same as that of the Am.CVD-Si_3N_4. $\sigma_\perp$ of the Am.CVD-(Si_3N_4–C) composites containing 0.2 to 6 wt% carbon showed ohmic characterisitcs in the temperature range 250 to 950° C under a field of up to $150\,V\,cm^{-1}$, and had high values of electrical conductivity. Fig. 3 shows the relationship between the current density in the direction perpendicular to the substrate and the electric field at 200° C for the Am.CVD-(Si_3N_4–C) composites containing 0.6 to 3 wt% carbon prepared at $T_{dep} = 1200°$ C. The figure clearly shows the ohmic characteristics for the test specimens.

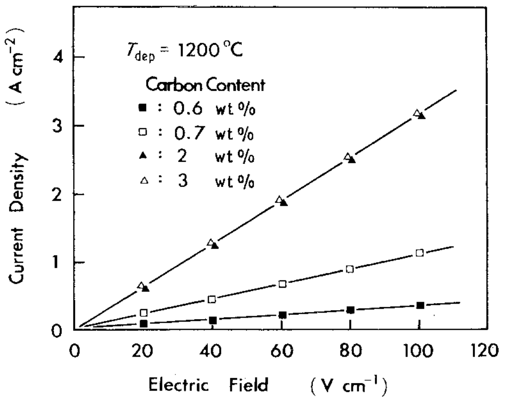

Figure 3 Relationship between current density in the direction perpendicular to the substrate and the electric field at 200° C.

Figs. 4 and 5 describe the temperature dependence of $\sigma_\perp$ of the specimens prepared at T_{dep} = 1200 and 1300° C. When log $\sigma_\perp$ is plotted against the reciprocal temperature all specimens show a linear relationship, which can be expressed according to the following equation:

$$\sigma_\perp = \sigma_0 \exp(E_\perp/kT), \qquad (1)$$

where σ_0 is a constant, $E_\perp$ is the activation energy for electrical conduction in the direction perpendicular to the substrate, k is Boltzmann's constant and T is the absolute temperature. Values of $E_\perp$ obtained from Figs. 4 and 5 were 2.5 eV when the carbon content was 0.1 wt% or less, and 0.02 to 0.06 eV when the carbon content was 0.2 wt% or more.

Fig. 6 shows the effect of carbon content on $\sigma_\perp$ at 500° C. $\sigma_\perp$ of the specimens containing 0.1 wt% or less carbon was about $10^{-11}\,\Omega^{-1}\,cm^{-1}$. This result indicates that the specimens are electrically insulative. $\sigma_\perp$ of the Am.CVD-(Si_3N_4–C) composites containing 0.2 to 6 wt% carbon lay between 10^{-1} and $10^{-2}\,\Omega^{-1}\,cm^{-1}$. Thus, $\sigma_\perp$ was increased 10^9 to 10^{10} times by the addition of 0.2 wt% carbon.

Fig. 7 illustrates the effect of carbon content on $\sigma_\perp$ and $\sigma_\parallel$ at room temperature for the Am.CVD-(Si_3N_4–C) composites prepared at $T_{dep} = 1300°$ C. $\sigma_\perp$ and $\sigma_\parallel$ increase with increasing carbon content, and $\sigma_\parallel$ was 10 to 30 times greater than $\sigma_\perp$.

4. Discussion

Bean *et al.* [6], Brown *et al.* [7] and Voskoboynikov *et al.* [8] reported values of the band gap for Am.CVD-Si_3N_4 prepared using SiH_4 and NH_3 as 4.4, 4.5 and 5.1 eV, respectively. Bauer [9] also reported the value of the band gap for the Am.CVD-Si_3N_4 prepared using $SiCl_4$ and NH_3 as 5.2 eV. Therefore, the values of the band gap

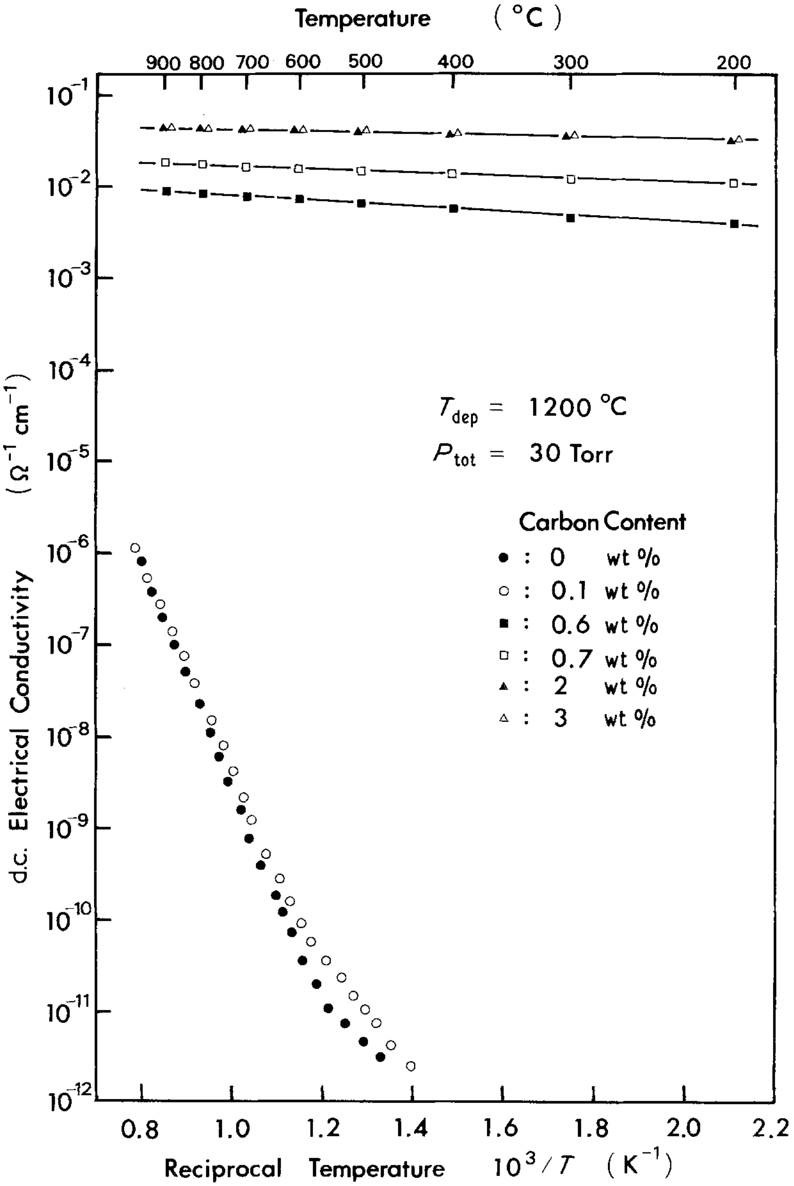

Figure 4 Temperature dependence of $\sigma_{\perp}$ for the specimens prepared at $T_{dep} = 1200°$ C.

for the Am.CVD-Si_3N_4 can be considered to lie between 4.4 to 5.2 eV.

In the present work, the $E_{\perp}$ of the specimens containing 0.1 wt % or less carbon was determined to be 2.3 to 2.5 eV. The value of the band gap for intrinsic conduction can be twice that of activation energy for electrical conduction [10]. Therefore, the value of the band gap for present specimens is estimated to be 4.6 to 5.0 eV. These estimates are in good agreement with the values previously reported [6–9].

The value of the band gap of an amorphous carbon is known to be about 0.1 eV [11]. In the present work, the value of the band gap for the Am.CVD-(Si_3N_4–C) composites containing 0.2 wt% or more carbon is estimated to be 0.04 to 0.12 eV, which is in agreement with that of the amorphous carbon.

Elmer [12] fabricated an electrically conductive SiO_2 glass containing carbon by impregnating porous glass with furfuryly alcohol, and firing it under a reducing atmosphere at 1240° C. He reported that the glass containing more than 2 wt% carbon became electrically conductive. For example, the d.c. electrical conductivity (σ) of the glass containing 4 to 8 wt% carbon was

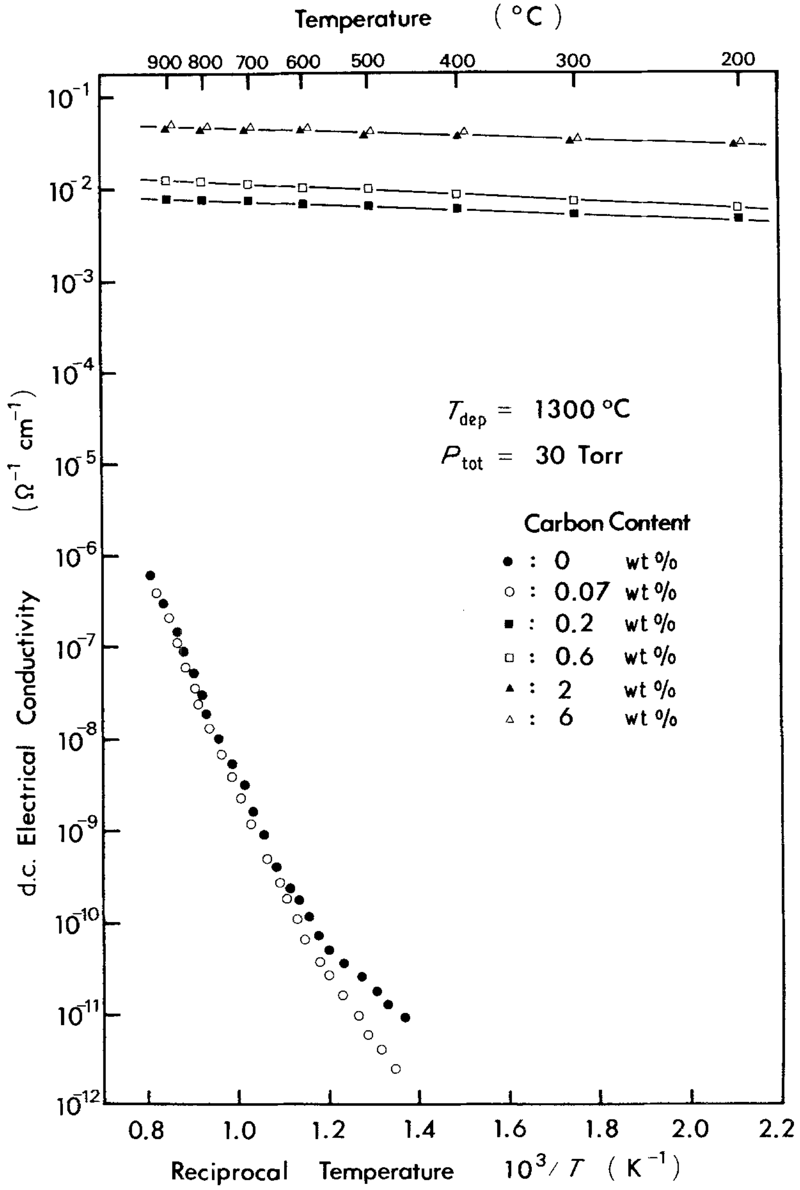

Figure 5 Temperature dependence of $\sigma_\perp$ for the specimens prepared at T_{dep} = 1300° C.

reported to be 0.2 to 4 Ω^{-1} cm^{-1} at room temperature. The activation energy for the electrical conduction was shown to be about 0.06 eV, in agreement with that obtained in the present work for the electrically conductive Am.CVD-(Si_3N_4–C) composites. Elmer [12] concluded that the electricity is conducted through the carbon particles penetrating the voids in the glass. Carrier [13] discovered a large number of voids in the glass by transmission electron microscopy (TEM).

Chen and Diefendorf [14] prepared BN (h-type)-graphite composites (7 to 95 wt% carbon) by CVD at T_{dep} = 1700° C using BCl_3, NH_3 and C_2H_2 gases, and measured its σ. $\sigma_\perp$ and $\sigma_\parallel$ of a deposit containing 10 wt% carbon at room temperature were about 1.6×10^{-3} and 1 Ω^{-1} cm^{-1}, respectively. They explained that the carbon in the deposits existed as a continuous network and the electricity is conducted through this network. The anisotropy of σ results from the preferred orientation of the carbon. Its *c*-direction is preferentially oriented in the direction perpendicular to the substrate. The temperature dependence of σ was found to be as small as that of graphite.

In the present work, an Am.CVD-Si_3N_4 was impregnated with colloidal carbon and heat-

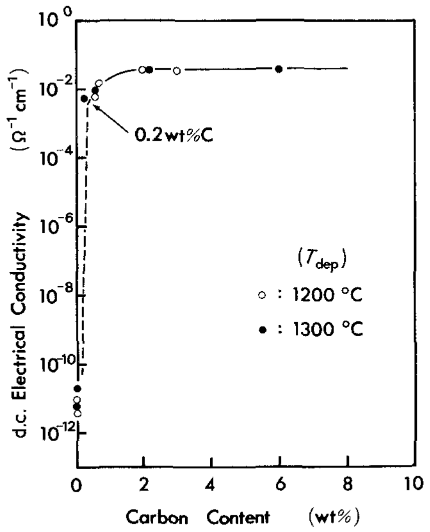

Figure 6 Effect of the carbon content on $\sigma_\perp$ at 500° C.

treated in vacuum at 1000° C, and it was found that the colour of the Am.CVD-Si_3N_4 changed from white to black. $\sigma_\perp$ and its temperature coefficient after impregnation were almost equivalent to those of the electrically conductive Am.CVD-(Si_3N_4–C) composites. Our previous studies by EPMA [1] and positron annihilation [4] revealed that carbon in the Am.CVD-(Si_3N_4–C) composites exists as a carbon phase. Therefore, the cause of the abrupt increase in $\sigma_\perp$ of the Am.CVD-(Si_3N_4–C) composite containing 0.2 wt % carbon might be the conduction of electricity through the carbon phase.

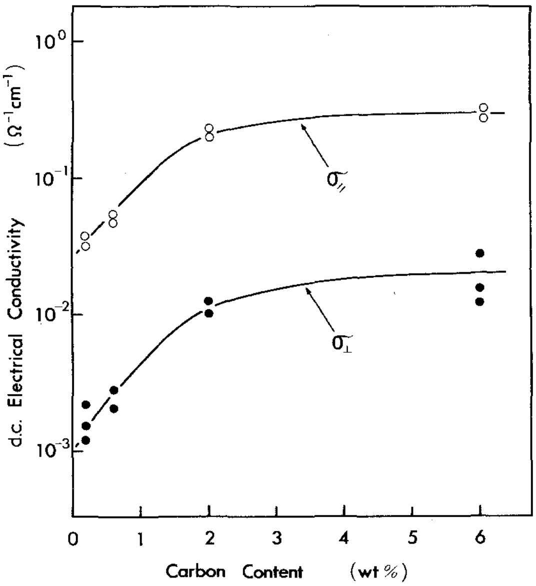

Figure 7 Effect of the carbon content on $\sigma_\perp$ and $\sigma_\parallel$ at room temperature.

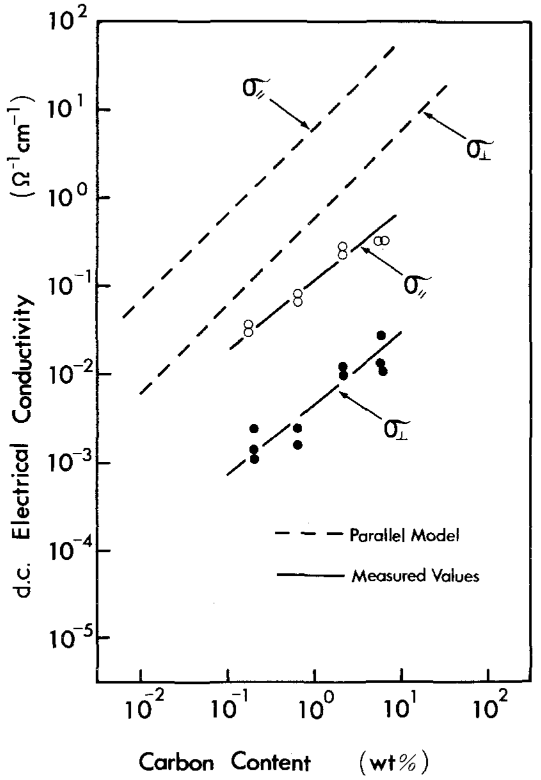

Figure 8 Comparison between the measured and calculated values of $\sigma_\perp$ and $\sigma_\parallel$.

The Hall coefficient in the direction parallel to the substrate for the electrically conductive Am.CVD-(Si_3N_4–C) composite containing 6 wt % carbon was measured in liquid nitrogen in order to clarify the types of carrier for electrical conduction. The Hall coefficient was found to be negative, however, its value was too small to be accurately determined.

Mrozowski and Chaberski [15] measured the Hall coefficient of the soft carbon heat-treated at various temperatures, and reported that the Hall coefficient for the soft carbon heat-treated below 1750° C was about $-0.03\ \text{cm}^3\ \text{C}^{-1}$. Klein [11] investigated the Hall coefficient of the carbon prepared by CVD at $T_{\text{dep}} = 1700$ to 2500° C. He concluded, after comparison with the results of Mrozowski and Chaberski [15], that the Hall coefficient of the soft carbon heat-treated at a certain temperature (T_{ht}) is approximately equal to that of the CVD-carbon prepared at $T_{\text{dep}} = T_{\text{ht}} - 200°$ C. Therefore, the carbon in the Am.CVD-(Si_3N_4–C) composite prepared at $T_{\text{dep}} = 1300°$ C may correspond to the soft carbon heat-treated at $T_{\mathrm{ht}} = 1500°$ C, and its Hall coefficient may be estimated to be about -0.03 cm^3 C^{-1}. As mentioned earlier, a definite value of the Hall coefficient was not determined in this work; however, the estimated value and the measured value were both negative. This fact implies that the electricity is carried by electrons. These results, however, do not contradict the idea that the electricity is conducted through the carbon phase in the Am.CVD-(Si_3N_4–C) composites.

As shown in Fig. 7, $\sigma_{\parallel}$ was 10 to 30 times greater than $\sigma_{\perp}$. The cause of this anisotropy may be due to the fact that the *c*-direction of the carbon in the Am.CVD-(Si_3N_4–C) composites is preferentially oriented in the direction perpendicular to the substrate as found in the investigation of Chen and Diefendorf [15] for the BN–C composites. In our previous study [16], the ratio of σ in the *a*-direction (σ_a) to that in the *c*-direction (σ_c) for the CVD-carbon prepared at $T_{\mathrm{dep}} = 1300°$ C was about 10. This value is equal to the ratio of $\sigma_{\parallel}$ to $\sigma_{\perp}$ in the present work. Fig. 8 shows the measured and calculated values* of $\sigma_{\perp}$ and $\sigma_{\parallel}$ of the Am.CVD-(Si_3N_4–C) composites. The calculated values were based on the parallel model*. The model assumes that carbon is present as a continuous network in the amorphous Si_3N_4 matrix, and that the *c*-direction of the carbon is preferentially oriented in the direction perpendicular to the substrate. The values of σ_c and σ_a are assumed to be 10^2 and 10^3 Ω^{-1} cm^{-1}, respectively, as reported in our previous study [16]. Fig. 8 shows that the calculated values are 30 to 100 times greater than the measured values. This result may suggest that only a small part of the carbon in the Am.CVD-(Si_3N_4–C) composites contributes to the electrical conduction. Another possibility may be that the carbon does not form an ideally continuous network but it exists as particles connected to each other and having a certain contact resistance. Indeed, our investigations [17] have revealed that the carbon exists as particles with diameters of about 100 nm.

5. Conclusions

The $\sigma_{\perp}$ of the Am.CVD-(Si_3N_4–C) composites containing 0.2 to 6 wt % carbon were determined to be 10^{-3} to 10^{-1} Ω^{-1} cm^{-1} in the temperature range 250 to 950° C. These values were 10^9 to 10^{10} times greater than $\sigma_{\perp}$ of the carbon-free Am.CVD-Si_3N_4 at 500° C. The activation energy for the electrical conduction in the direction perpendicular to the substrate ($E_{\perp}$) for the electrically conductive Am.CVD-(Si_3N_4–C) composites was 0.02 to 0.06 eV. These values are in agreement with that of the amorphous carbon. $\sigma_{\parallel}$ was 10 to 30 times greater than $\sigma_{\perp}$ at room temperature. These results suggest that the electricity is conducted through a carbon network in the Am.CVD-(Si_3N_4–C) composites.

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$$\sigma_{\mathrm{comp}} = \frac{1}{3}\{\sigma_{\mathrm{carbon}} \times V + \sigma_{\mathrm{Si_3N_4}} \times (1 - V)\},$$

where σ_{carbon}, $\sigma_{\mathrm{Si_3N_4}}$ and σ_{comp} are d.c. electrical conductivities of carbon, amorphous Si_3N_4 and Am.CVD-(Si_3N_4–C) composite, respectively, and V is the volume fraction of carbon.

Because $\sigma_{\mathrm{Si_3N_4}} \ll \sigma_{\mathrm{carbon}}$,

$$\sigma_{\mathrm{comp}} \simeq \frac{1}{3}\sigma_{\mathrm{carbon}} \times V.$$

When $V \ll 1$,

$$V \simeq (\mathrm{wt}\,\%) \times \frac{\rho_{\mathrm{Si_3N_4}}}{\rho_{\mathrm{carbon}}},$$

where $\rho_{\mathrm{Si_3N_4}}$ and ρ_{carbon} are the densities of the amorphous Si_3N_4 matrix and carbon, respectively, and (wt %) is a weight fraction of carbon.

When $\sigma_{\mathrm{Si_3N_4}} = 3.0\,\mathrm{g\,cm^{-3}}$ and $\sigma_{\mathrm{carbon}} = 1.6\,\mathrm{g\,cm^{-3}}$ [2],

$$\sigma_{\mathrm{comp}} = 0.625 \times (\mathrm{wt}\,\%) \times \sigma_{\mathrm{carbon}}.$$

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