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# Siliconated Pyrolytic Graphite

## Part 3 *Structural Features*

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The structural features of several samples of siliconated pyrolytic graphite (0.02 to 4 wt % silicon) prepared at various deposition temperatures, total gas pressures and partial pressures of silicon tetrachloride vapour have been examined by X-ray diffraction. The structural features investigated include interlayer spacing, ordering, intercrystallite porosity, preferred orientation and crystallite size. These features are affected by the preparation conditions. By the addition of silicon tetrachloride vapour, the ordering and the crystallite size of the graphite matrix are developed, the preferred orientation improved and the porosity diminished. The effects of the addition of silicon tetrachloride on the structural features are marked at high total gas pressures, at high partial pressures of silicon tetrachloride vapour and in the medium temperature range of 1600 to 1700° C.

## 1. Introduction

Pyrolytic graphite (PG) compounds may be divided into two types, "PG-lamellar compounds", which are prepared by diffusing foreign atoms or molecules into the graphite matrix, and "PG-deposited compounds", prepared by co-depositing a foreign element by pyrolysing a hydrocarbon gas mixed with vapour containing the doping element. PG-lamellar compounds have been investigated by many workers and their crystal structures are well understood [1]. On the other hand, the structures of PG-deposited compounds are not clear in detail. Recently, Katz and Gazzara [2] examined the structural features of the PG-boron deposited compound (PG(B)), and reported that they depend on the amounts of boron in PG(B).

In our laboratory, PG-silicon deposited compounds (siliconated PG, PG(Si)) containing 0.02 to 4 wt % silicon have been prepared, and several properties examined as part of an investigation of PG-compounds. As reported in previous papers [3, 4], the microstructure of PG(Si) was still "fine regenerative structure" at fairly low temperatures, and the density of PG(Si) prepared at the low and medium temperatures (1400 to 1800°C) was 70 to 80 % greater than that of PG. Moreover, it was found that silicon in PG(Si) formed $\beta$-SiC.

In the present study, we have investigated the effect of preparation conditions on structural features, such as interlayer spacing, ordering, intercrystallite porosity, preferred orientation, and crystallite size.

## 2. Experimental Procedures

### 2.1. PG(Si) Samples

PG(Si) was prepared by pyrolysis of a mixture of propane gas and silicon tetrachloride vapour by direct heating of the graphite substrate. The conditions of preparation were as follows: deposition temperatures ($T_{\text{dep}}$) = 1440 to 2025°C, total gas pressure ($P_{\text{total}}$) = 10 or 50 torr, partial pressure of silicon tetrachloride vapour ($P_{\text{SiCl}_4}$) = 0 to 13 torr. The procedures have been fully described elsewhere [3].

Fig. 1 shows the amounts of silicon in PG(Si). In fig. 1 the bars show the range of variation of silicon content with $P_{\text{SiCl}_4}$.

### 2.2. X-ray Diffraction Analysis

X-ray measurements were made on a diffractometer using Ni-filtered CuK$\alpha$ radiation on the powdered or block samples of PG(Si) prepared under various conditions. For measurement of

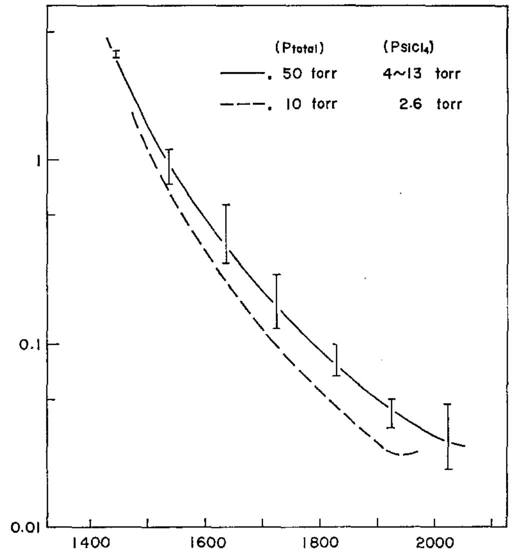


*Figure 1* Silicon content in PG(Si) prepared under various conditions.

preferred orientation, the diffractometer was used as a single-crystal unit. The specimens (0.2 to 0.5 mm square rods with a length of about 10 mm) were mounted on a single-crystal orienter which permitted controlled changes of the specimen orientation relative to the incident and diffracted X-ray beams. The details of X-ray diffraction analysis have been reported in previous papers [5-7]. Therefore, a simple description suffices here:

(i) Interlayer spacing ($c_0/2$) was determined from the (002) and (004) reflections from powdered samples (200 to 325 mesh); the (004) reflections were mainly used.

(ii) Intercrystallite porosity ($I_P$) was calculated from the following equation; $I_P = (d-D)/d \times 100\,(\%)$, where, $D$ is the experimental density and $d$ is the X-ray density.

(iii) Ordering was determined qualitatively from the line shapes of the two-dimensional (10) reflections obtained in the transmitting position on the block and flat specimens.

(iv) The preferred orientation parameter ($\beta$) was estimated from the $\omega$–$I$ curve ($I(\omega)$), where $\omega$ is the inclination angle measured from the normal to a deposition surface, $I$ is the intensity of the (002) reflection for the X-ray beam incident at an angle $\omega$, and $\beta$ is one-half the peak width at half-maximum intensity of the $I(\omega)$ curve.

(v) Crystallite sizes in the $a$-direction ($L_a$) and the $c$-direction ($L_c$) were determined from the line-widths of the (110) reflection obtained in the transmitting position on the block specimens, and the (002) and (004) reflections obtained in the reflecting position on the powdered samples, respectively.

## 3. Experimental Results

### 3.1. Interlayer Spacing ($c_0/2$)

The effect of $P_{SiCl_4}$ on the interlayer spacing of PG(Si) samples prepared under various conditions is shown in figs. 2 and 3.

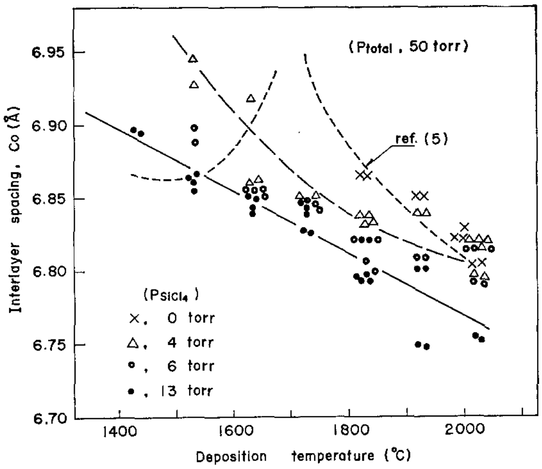


*Figure 2* Effect of preparation conditions on the interlayer spacing at $P_{total} = 50$ torr and $P_{SiCl_4} = 0$ to 13 torr.

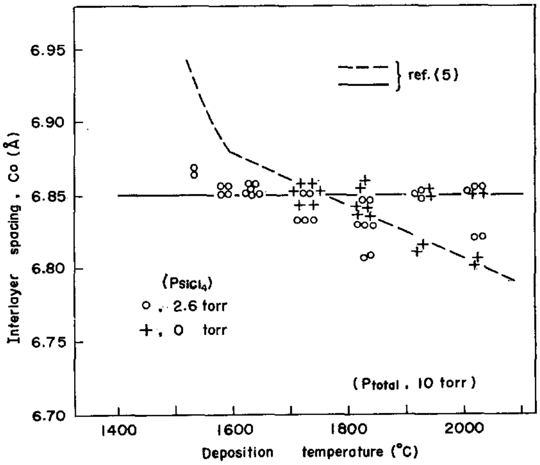


*Figure 3* Effect of preparation conditions on the interlayer spacing at $P_{total} = 10$ torr and $P_{SiCl_4} = 0$ and 2.6 torr.

Fig. 2 was obtained at $P_{total} = 50$ torr. In fig. 2 the broken line represents the result obtained at $P_{SiCl_4} = 0$ torr in the earlier investigation [5].

The dashed line and full line show the results at $P_{\mathrm{SiCl_4}} = 4$ and 13 torr, respectively. At $P_{\mathrm{total}} =$ 50 torr, $c_0$ of PG shows a maximum value at about 1700°C. On the other hand, $c_0$ of PG(Si) decreases with increasing temperature. The value of $c_0$ depends strongly on $P_{\mathrm{SiCl_4}}$, in that it decreases with increasing $P_{\mathrm{SiCl_4}}$. The $P_{\mathrm{SiCl_4}}$-dependence of $c_0$ is marked in the medium temperature range of 1600 to 1700°C. Under these conditions ($P_{\mathrm{total}} = 50$ torr, $T_{\mathrm{dep}} = 1600$ to 1700°C), $c_0$ of PG cannot be obtained because the (002) reflection is weak and diffuse. In contrast, the (002) reflection of PG(Si) is sharp, and $c_0$ is estimated from this at 6.84 Å. This value corresponds to that of PG obtained at about 1900°C. In the low temperature range, below about 1500°C, $c_0$ of PG(Si) is larger than that of PG.

Fig. 3 shows the relation of $c_0$ to temperature at $P_{\mathrm{total}} = 10$ torr. In fig. 3 the dashed line and full line show the results at $P_{\mathrm{total}} = 10$ and 5 torr (at $P_{\mathrm{SiCl_4}} = 0$ torr), respectively. At low $P_{\mathrm{total}}$, the relation is not clear owing to fluctuation in the experimental data. The results at $P_{\mathrm{SiCl_4}} = 2.6$ torr and $P_{\mathrm{total}} = 10$ torr are between the results at $P_{\mathrm{total}} = 5$ and 10 torr (at $P_{\mathrm{SiCl_4}} = 0$ torr).

### 3.2. Intercrystallite Porosity ($I_p$)

A typical relation between $I_p$ and temperature is given in fig. 4, for the results obtained at $P_{\mathrm{SiCl_4}} = 0$ and 13 torr, and $P_{\mathrm{total}} = 50$ torr. At the medium temperature of about 1700°C, $I_p$ is about 40% at $P_{\mathrm{SiCl_4}} = 0$ torr, but it is about 2% at $P_{\mathrm{SiCl_4}} = 13$ torr. The relation between $I_p$ and temperature corresponds with that between density and temperature [3]. The value of $I_p$ is decreased by the addition of silicon tetrachloride.

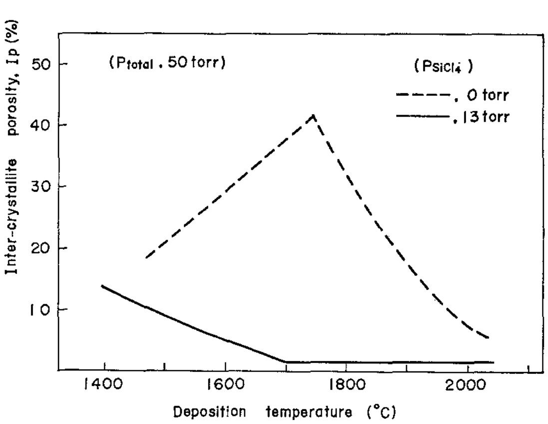


*Figure 4* Effect of preparation conditions on the inter-crystallite porosity at $P_{\mathrm{total}} = 50$ torr and $P_{\mathrm{SiCl_4}} = 0$ and 13 torr.

### 3.3. Ordering

Figs. 5a and b respectively show the (10) reflections of materials with completely disordered layers and partly ordered layers. In the present study the amount of ordering shown in fig. 5a is graded as "none" and that in fig. 5b as "strong", and that intermediate between these as "weak" or "medium", as in the previous work [5].

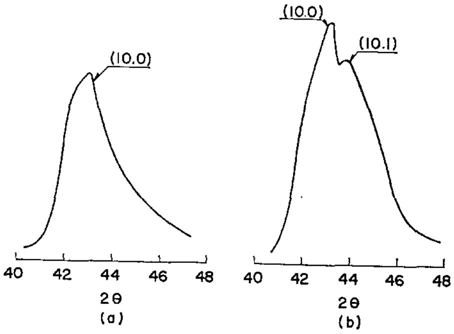


*Figure 5* The (10) reflections of the deposits (a) with no ordering and (b) with ordering.

The effect of $P_{\mathrm{SiCl_4}}$ on the ordering is shown in fig. 6 ($P_{\mathrm{total}} = 50$ torr) and fig. 7 ($P_{\mathrm{total}} = 10$ torr). The amount of ordering increases with increasing $P_{\mathrm{SiCl_4}}$.

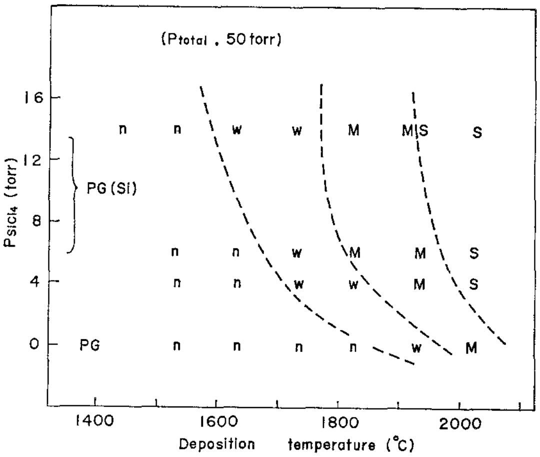


*Figure 6* Effect of preparation conditions on the ordering at $P_{\mathrm{total}} = 50$ torr and $P_{\mathrm{SiCl_4}} = 0$ to 13 torr: S, strong; M, medium; w, weak; n, none.

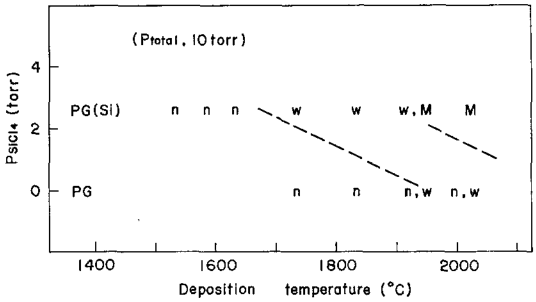


*Figure 7* Effect of preparation conditions on the ordering at $P_{\text{total}} = 10$ torr and $P_{\text{SiCl}_4} = 0$ and 2.6 torr: M, medium; w, weak; n, none.

### 3.4. Preferred Orientation

The effect of $P_{\text{SiCl}_4}$ on the preferred orientation parameter ($\beta$) is shown in fig. 8 ($P_{\text{total}} = 50$ torr) and fig. 9 ($P_{\text{total}} = 10$ torr).

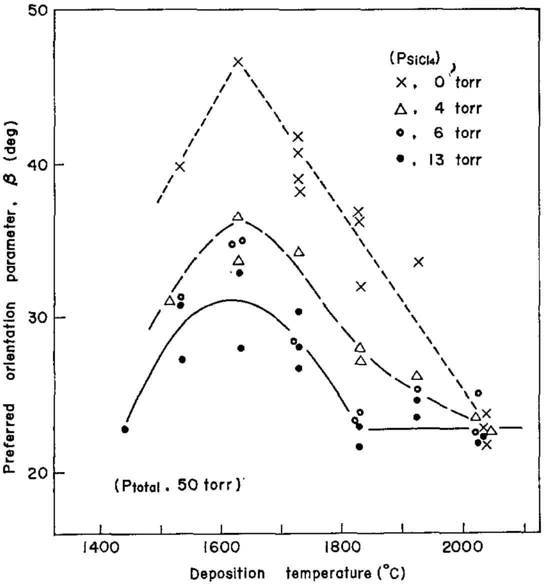


*Figure 8* Effect of preparation conditions on the preferred orientation parameter ($\beta$) at $P_{\text{total}} = 50$ torr and $P_{\text{SiCl}_4} = 0$ to 13 torr.

As shown in fig. 8, $\beta$ decreases with increasing $P_{\text{SiCl}_4}$ at $P_{\text{total}} = 50$ torr, that is, the degree of preferred orientation becomes considerably higher with the addition of silicon tetrachloride. Under these conditions ($P_{\text{total}} = 50$ torr, $P_{\text{SiCl}_4} =$ 0 to 13 torr), $\beta$ shows a maximum value in the medium temperature range of 1600 to 1700° C.

At $P_{\text{total}} = 10$ torr, the effect of $P_{\text{SiCl}_4}$ on $\beta$ is not clear (fig. 9). It seems that $\beta$ shows a maximum value in the medium temperature range as in the case of $P_{\text{total}} = 50$ torr.

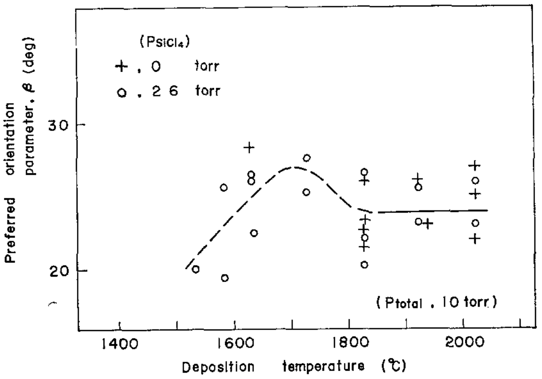


*Figure 9* Effect of preparation conditions on the preferred orientation parameter ($\beta$) at $P_{\text{total}} = 10$ torr and $P_{\text{SiCl}_4} = 0$ and 2.6 torr.

### 3.5. Crystallite Size

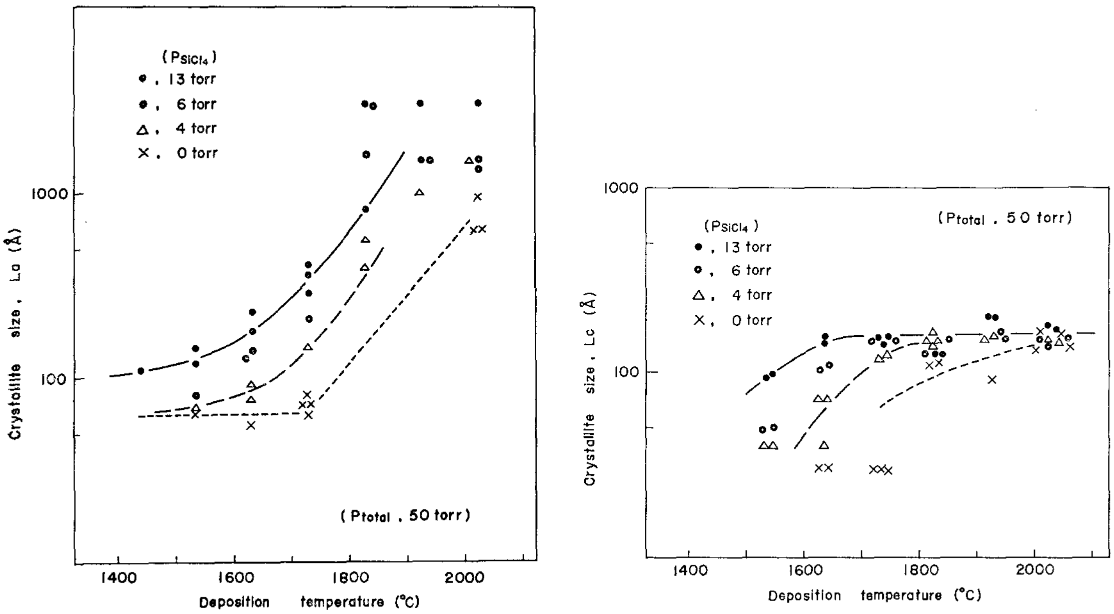
Figs. 10 and 11 show the effects of $P_{\text{SiCl}_4}$ on the crystallite sizes ($L_a$ and $L_c$) at $P_{\text{total}} = 50$ and 10 torr respectively. As shown in fig. 10a, $L_a$ increases with increasing $P_{\text{SiCl}_4}$. At $P_{\text{SiCl}_4} = 0$ torr, $L_a$ is nearly constant in the temperature range of 1535 to 1730° C, and it increases abruptly above this temperature range. At $P_{\text{SiCl}_4} = 13$ torr, however, $L_a$ increases with temperature in the low temperature range of 1400 to 1500° C. Fig. 10b shows that $L_c$ also increases with increasing $P_{\text{SiCl}_4}$ in the temperature range of about 1500 to 1700° C, but it is independent of the addition of silicon tetrachloride at the high temperature of about 2000° C.

In figs. 11a and b, the relation at $P_{\text{total}} = 10$ torr is given. The dashed line and full line represent the results obtained at $P_{\text{total}} = 5$ and 10 torr ($P_{\text{SiCl}_4} = 0$ torr) in the earlier work [5]. As shown in fig. 11, at low $P_{\text{total}}$, the effects of the addition of silicon tetrachloride on $L_a$ and $L_c$ are much less pronounced than those observed at $P_{\text{total}} = 50$ torr.

## 4. Discussion

### 4.1. Heat-Treatment Effect

In PG prepared by a direct heating method, several properties of the part which is in contact with the substrate (heater) are known to be different from those in the surface layer [8-12]. This is due to the heat-treatment effect produced by a steep temperature gradient developing in the PG as it thickens, as a result of the low



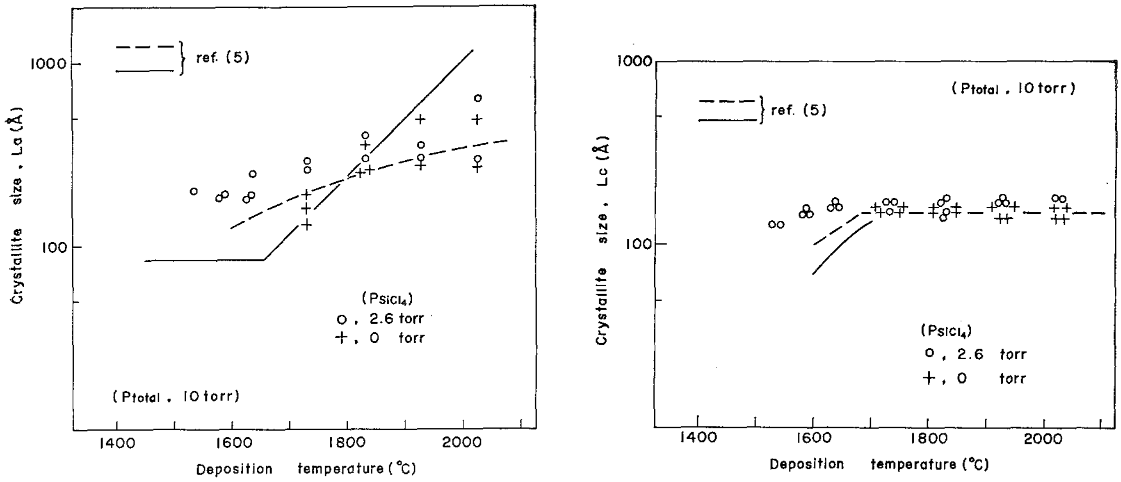
(a) (b)

*Figure 10* (a) Effect of preparation conditions on the crystallite size ($L_a$) at $P_{\text{total}} = 50$ torr and $P_{\text{SiCl}_4} = 0$ to 13 torr. (b) Effect of preparation conditions on the crystallite size ($L_c$) at $P_{\text{total}} = 50$ torr and $P_{\text{SiCl}_4} = 0$ to 13 torr.

$c$-axis thermal conductivity of PG. Therefore, the part which is in contact with the substrate is annealed at temperatures much in excess of the surface temperature in thick PG. In this experiment, to minimise the heat treatment effect, the deposition time for preparation of PG(Si) was curtailed at the high temperature of about 2000°C [13].

### 4.2. Comments on PG(B)

PG(B) is one example of a PG-deposited compound, and its structural features have been investigated by Katz and Gazzara [2], and Kotlensky [14]. Katz and Gazzara examined the effect of boron content on $c_0$ of PG(B) (0.25 to 3.3 wt % B) prepared at 1850°C and reported that boron substituted for carbon up to 0.5 wt %,



(a) (b)

*Figure 11* (a) Effect of preparation conditions on the crystallite size ($L_a$) at $P_{\text{total}} = 10$ torr and $P_{\text{SiCl}_4} = 0$ and 2.6 torr. (b) Effect of preparation conditions on the crystallite size ($L_c$) at $P_{\text{total}} = 10$ torr and $P_{\text{SiCl}_4} = 0$ and 2.6 torr.

with a reduction of $c_0$; above this it was present as $B_4C$, with an increase of $c_0$. They noted a minimum value of $c_0$ (6.735 Å) at 0.5 wt % B. Kotlensky studied the relation between boron content and $c_0$ for PG(B) prepared at 2000° C; he observed a minimum $c_0$ in the boron range of 0.8 to 1.0 wt %.

The results of our investigation on PG(Si) show that it is necessary to regulate $P_{SiCl_4}$ or $P_{total}$ for the preparation of PG(Si) containing the different amounts of silicon at a constant temperature such as 1850° C or 2000° C. In this case, it seems that the structural features of the graphite matrix of PG(Si) vary with the behaviour of the complex intermediate products of the Si–H–Cl–C system which are formed by the pyrolysis, rather than with the amounts of silicon in PG(Si). Similarly to PG(Si), the amount of boron in PG(B) prepared at a constant temperature seems to be regulated by the partial pressure of boron-compound ($P_{B\text{-comp}}$) or $P_{total}$. Since the reaction state in the vapour-phase depends on $P_{B\text{-comp}}$ or $P_{total}$, the structural features of the graphite matrix of PG(B) seems to vary with $P_{B\text{-comp}}$ or $P_{total}$.

Thus, it is difficult to discuss the structural features of PG(B) solely from the amounts of boron in PG(B). An examination of the preparation conditions of PG(B) is important for comparing the experimental results on the structural features of the compound.

### 4.3. Discussion of the Experimental Results

Comparing PG(Si) ($P_{SiCl_4} = 13$ torr) with PG($P_{SiCl_4} = 0$ torr), prepared at $P_{total} = 50$ torr, the structural features represented by $c_0$, $\beta$, $L_a$ and $L_c$ of PG(Si) at the medium temperature range of 1600 to 1700° C correspond to those of PG at 1900° C. When the preferred orientation deteriorates, $I_p$ has the large value of about 40 % in PG, but it is only about 2 % in PG(Si). On the basis of the equivalence just mentioned, comparison with PG at about 1900° C suggests that the value of $I_p$ should be about 15 % in PG(Si) in the medium temperature range. The amount of silicon in PG(Si) in the medium temperature range is 0.2 to 0.5 wt %, as shown in fig. 1. Even if silicon enters into the intercrystallite pore in the form of silicon carbide (density about 3.2 g/cm$^3$), $I_p$ would not be affected by the actual presence of silicon, because of its small amount. The reason for the low value of $I_p$ in PG(Si) at the medium temperature seems to be that the amorphous parts supposed to exist between crystallites in PG are, in PG(Si), graphitised by the presence of silicon or its compounds in the vapour-phase.

Yokokawa *et al* [15] found that carbons (hard carbon) produced from artificial resins underwent rapid graphitisation at temperatures above 1400° C when they were heated with an addition of small amounts of various kinds of metallic compounds with Cu, Ni, Co, Mn and Al. The hard carbons contain well-developed condensed aromatic clusters which linked to each other. They assumed that these elements cleaved the cross-linking carbon-carbon bonds. We suppose that many cross-linked clusters are contained between crystallites in PG at the medium temperatures [5]. This structure corresponds to that of hard carbon. In the present experiment, it is considered that the well-graphitised structure of PG(Si) results from the presence of silicon or the intermediate compounds containing silicon in vapour-phase which cleave the cross-linking.

As reported in the previous paper [4], silicon formed $\beta$–SiC in PG(Si) at low and medium temperatures. Moreover, the form of $\beta$–SiC was flake-like, and its dimensions about 200 Å thick and 2000 Å diameter (in PG(Si) at 1440° C). The size decreased as the temperature was raised.

From these results, and the considerations mentioned above, the structures of PG(Si) at each temperature range are considered to be as shown in fig. 12, in which the structures of PG in the same temperature range are also shown.

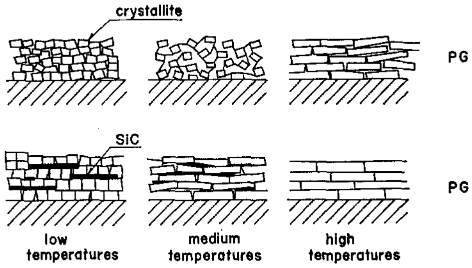


*Figure 12* Schematic diagram of structural features of PG and PG(Si) in the temperature range of 1400 to 2000° C.

## 5. Conclusions

The effect of the addition of silicon tetrachloride on the structural features of PG(Si) is considerably greater at $P_{total} = 50$ torr than that at $P_{total} = 10$ torr; and it is particularly striking in the medium temperature range of 1600 to 1700° C.

At $P_{\mathrm{total}} = 50$ torr, $c_0$ decreases and ordering increases with increasing $P_{\mathrm{SiCl_4}}$. These results indicate that the crystal structure of graphite is improved by the addition of silicon tetrachloride. Moreover $I_p$ decreases, preferred orientation increases, and $L_a$ and $L_c$ become larger with increasing $P_{\mathrm{SiCl_4}}$. These results indicate that the graphite crystallites are developed, and the preferred orientation and boundary fit between the crystallites is improved, by the addition of silicon tetrachloride.

It seems that the complex intermediate products of the Si–H–Cl–C system in the vapour-phase play an important rôle in the change in the structural features of PG(Si).

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