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Preparation of SiC ultrafine particles from SiH_2Cl_2 and C_2H_4 gas mixtures by a CO_2 laser

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Preparation of SiC ultrafine particles from SiH_2Cl_2–C_2H_4 mixtures by a CO_2 laser was investigated. The powders with specific surface area in the 8–150 $m^2\,g^{-1}$ range were obtained by irradiating SiH_2Cl_2–C_2H_4 gas mixtures with a CO_2 laser at atmospheric pressure. X-ray diffraction of the products showed that silicon, SiC and free carbon were produced and the composition of the powders depended on the C_2H_4/SiH_2Cl_2 ratio. The reaction flame temperature changed from less than 1273 K to more than 3073 K with the laser power density and C_2H_4/SiH_2Cl_2 ratio. When SiH_2Cl_2 was irradiated with the CO_2 laser, the reaction temperature was less than 1273 K and silicon particles were formed. When the SiH_2Cl_2–C_2H_4 mixture was irradiated with a CO_2 laser, the reaction temperature was low (< 1273 K) at low power density and low C_2H_4/SiH_2Cl_2 ratio, but it increased rapidly to around 3000 K at high laser power density and high C_2H_4/SiH_2Cl_2 ratio (> 0.3). SiC was formed at both high and low reaction flame temperatures. It was considered that the rapid increase in the reaction flame temperature was caused by the initiation of exothermic reactions and the increase in laser absorption which was caused mainly by carbon particle formation. Hysteresis was observed between the reaction flame temperature and the power density of the laser beam. It was found that SiH_2Cl_2 underwent a disproportionation reaction on irradiation with the CO_2 laser, and silicon and SiC particles were formed through the various products of the disproportionation reaction. In particular, at low reaction flame temperature, the reactive species, such as SiH_4 and SiH_3Cl, produced by the disproportionation of SiH_2Cl_2 were considered to play an important role in the formation of silicon and SiC particles.

1. Introduction

Ultrafine SiC and Si_3N_4 particles are attracting a great deal of attention as starting materials for sintered ceramics. Recently, investigations on the production of ceramic fine particles using lasers have been increasing. A CO_2 laser [1–6] was used during most investigations, but in some investigations an Excimer laser [7] or a YAG laser [8] have been used. Most researchers prepared SiC and Si_3N_4 particles using CO_2 lasers with SiH_4 as the starting material under reduced pressure. SiH_4 strongly absorbs the CO_2 laser beam. SiH_4 is suitable for the production of high-purity particles because no elements other than silicon and hydrogen are used, but it is chemically unstable and extremely expensive. The process would be more economical if a compound other than SiH_4 was available as the silicon source and could be reacted at atmospheric pressure. Bauer *et al.* [5] reported the preparation of silicon and Si_3N_4 particles at atmospheric pressure using SiH_2Cl_2 and $SiCl_4$, which are more easily handled than SiH_4. In this work, we studied the preparation conditions of SiC ultrafine particles using SiH_2Cl_2 and the formation mechanism.

2. Experimental procedure

The experimental apparatus was described previously [9]. The wavelength of the CO_2 laser was 10.6 μm and the maximum laser power was 150 W. The laser beam was focused by a lens and the beam diameter was about 2 mm at the reaction zone. The temperature of reaction flame was measured using a pyroscope having a measurable range from 1273–3073 K. The powder product gave off a strong HCl odour, and was dried at about 373 K for at least 2 h in a nitrogen flow until no odour remained. The powder prepared by the CO_2 laser was subsequently analysed by X-ray diffraction (XRD) for the crystalline phase, the one-point BET method for surface area, coulometry for the carbon content, N/O analysis (EMGA-650, HORIBA Ltd) to determine the oxygen content and by transmission electron microscope (TEM) and selected area

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electron diffraction (SAED) to determine morphology and structure. Chlorine present in the powder as an impurity was determined by atomic absorption analysis indirectly to measure silver. Photoacoustic emission (PAS) spectra were taken for several powders.

3. Results and discussion

3.1. Characterization of the powder

Table I summarizes the reactant gas flow rate, reaction flame temperature, specific surface area, crystalline phase and carbon and oxygen contents. These powders were prepared at different reactant gas flow rates at a laser power density of 3.66 $\mathrm{kW\,cm^{-2}}$. In the case of the SiH_2Cl_2 flow rate of 10 standard $\mathrm{cm^3\,min^{-1}}$, the reaction flame temperature was less than 1273 K at a low C_2H_4/SiH_2Cl_2 flow ratio, but increased rapidly to over 3073 K as the C_2H_4/SiH_2Cl_2 ratio exceeded 0.5. The specific surface area became maximum near $C_2H_4/SiH_2Cl_2 = 0.5$. TEM observation showed that the particle size of the powder became minimum near $C_2H_4/SiH_2Cl_2 = 0.5$. The same trend was observed at a SiH_2Cl_2 flow rate of 20 standard $\mathrm{cm^3\,min^{-1}}$. The carbon content of the powder increased linearly with a rise in the C_2H_4/SiH_2Cl_2 ratio [9]. These powders contained a large amount of oxygen, especially when the powder was prepared with SiH_2Cl_2 only or at a low C_2H_4 /SiH_2Cl_2 ratio. It was thought that these powders oxidized in air because they were handled in air. The powders contained a small amount of chlorine: 0.23 wt % in sample 10, 0.26 wt % in sample 11 and 0.24 wt % in sample 13. Based on the results of composition analysis, the amounts of free carbon and SiC were calculated by assuming that the powders consisted of carbon, silicon and oxygen, and oxygen present as SiO_2, and silicon other than SiO_2 present as SiC. The amount of free carbon became minimum (about

TABLE I SiC powders prepared by CO_2 laser. Power density = 3.66 $\mathrm{kW\,cm^{-2}}$, beam diameter = 2 mm

Sample no	SiH_2Cl_2 (standard $\mathrm{cm^3\,min^{-1}}$)	C_2H_4 (standard $\mathrm{cm^3\,min^{-1}}$)	Reaction flame temperature (K)	Specific surface area ($\mathrm{m^2\,g^{-1}}$)	Crystal line phase by XRD	Composition	
						C (wt %)	O (wt %)
1	4	15	–	57.4	C, SiC	72.4	5.4
2	10	0	< 1273	14.1	Si	–	42.3
3	10	3	< 1273	44.9	SiC, Si	19.2	36.1
4	10	5	> 3073	153.3	SiC	21.5	21.2
5	10	8	> 3073	111.8	SiC, C	32.1	16.7
6	10	10	> 3073	78.1	C, SiC	44.4	14.1
7	10	13	> 3073	67.0	C, SiC	53.0	14.4
8	10	15	> 3073	72.9	C, SiC	56.8	9.6
9	20	0	< 1273	8.6	Si	–	20.0
10	20	5	2823–2933	104.9	SiC	18.0	24.6
11	20	10	2573–2693	79.8	SiC	25.7	13.2
12	20	12	> 3073	61.9	SiC	29.3	17.7
13	20	15	> 3073	88.1	SiC, C	36.4	13.4
14	30	15	2113–2193	86.1	SiC	24.0	19.2

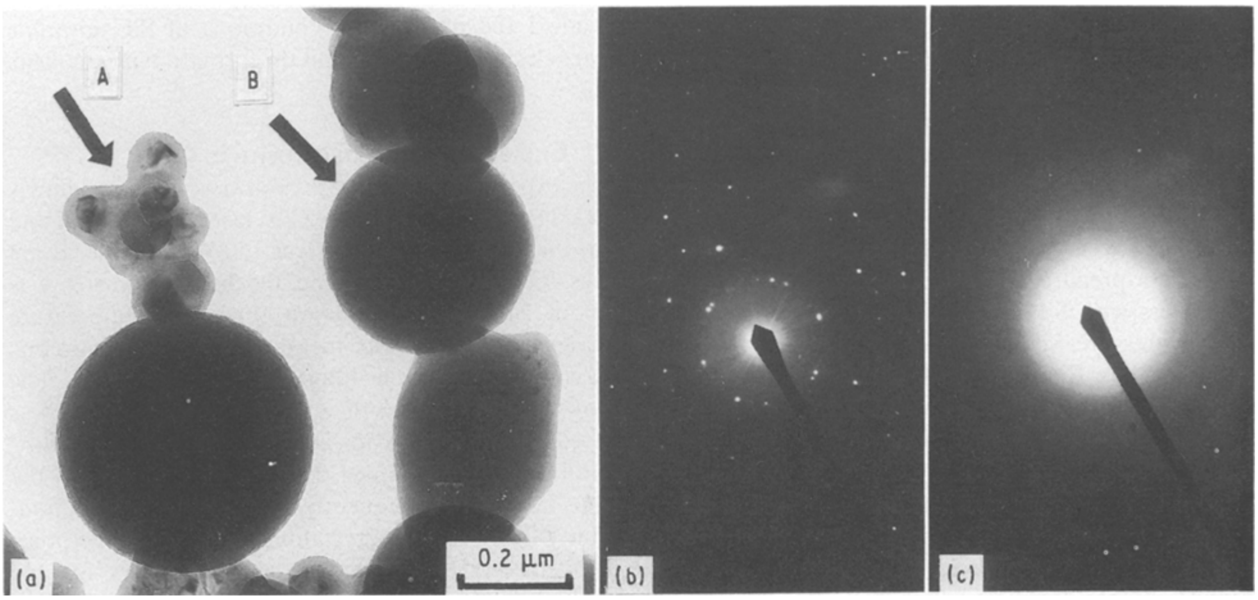

Figure 1 (a) Transmission electron micrograph of the particles prepared by CO_2 laser irradiation with SiH_2Cl_2 = 20 standard $\mathrm{cm^3\,min^{-1}}$, and SAED patterns of part (b) A and (c) B.

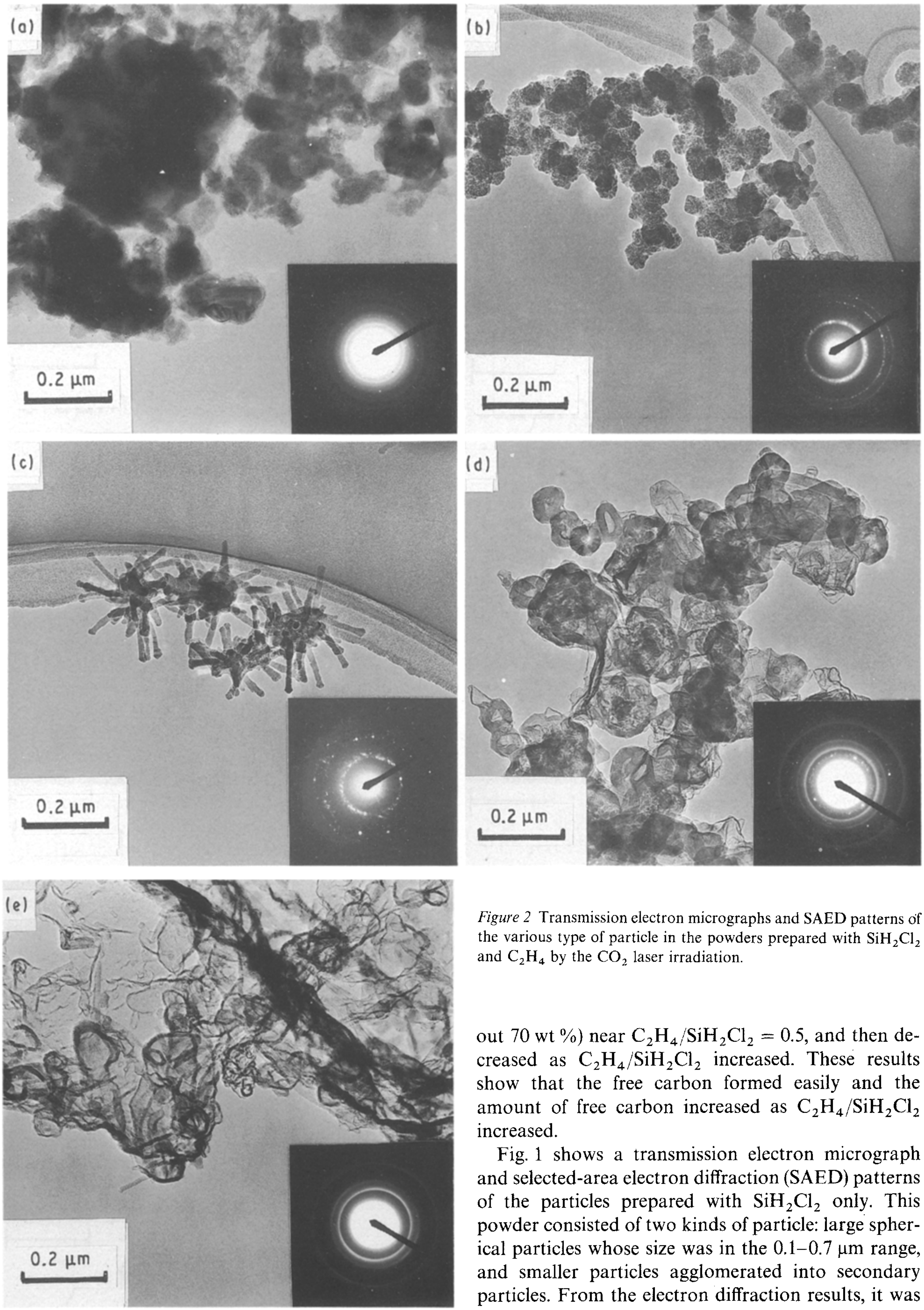

Figure 2 Transmission electron micrographs and SAED patterns of the various type of particle in the powders prepared with SiH_2Cl_2 and C_2H_4 by the CO_2 laser irradiation.

5 wt %) near $C_2H_4/SiH_2Cl_2 = 0.5$, which was the stoichiometric ratio for SiC formation. ($SiH_2Cl_2(g) + 1/2C_2H_4(g) \rightarrow SiC(s) + 2HCl(g) + H_2(g)$). Free carbon increased rapidly as the C_2H_4/SiH_2Cl_2 ratio increased. The amount of SiC became maximum (about 70 wt %) near $C_2H_4/SiH_2Cl_2 = 0.5$, and then decreased as C_2H_4/SiH_2Cl_2 increased. These results show that the free carbon formed easily and the amount of free carbon increased as C_2H_4/SiH_2Cl_2 increased.

Fig. 1 shows a transmission electron micrograph and selected-area electron diffraction (SAED) patterns of the particles prepared with SiH_2Cl_2 only. This powder consisted of two kinds of particle: large spherical particles whose size was in the 0.1–0.7 μm range, and smaller particles agglomerated into secondary particles. From the electron diffraction results, it was found that the large spherical particles were amorphous and the smaller agglomerated particles were crystalline silicon.

Fig. 2 shows transmission electron micrographs and SAED patterns of the various kinds of particle in the powders prepared from a gas mixture of C_2H_4 and SiH_2Cl_2. From the results of TEM observations, the

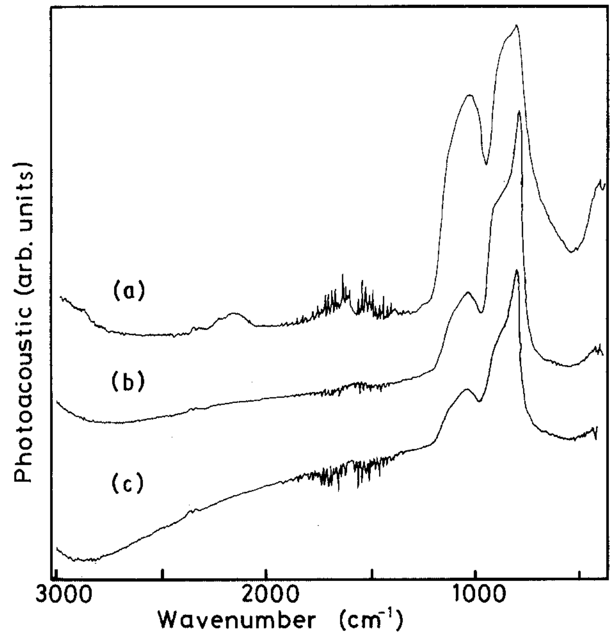

Figure 3 PAS spectra of the powders. (a) $SiH_2Cl_2 = 20$, $C_2H_4 = 5$ standard cm^3 min^{-1} (Sample 10), reaction flame temperature = 2823–2933 K. (b) $SiH_2Cl_2 = 20$, $C_2H_4 = 10$ standard cm^3 min^{-1} (Sample 11), reaction flame temperature = 2573–2693 K. (c) $SiH_2Cl_2 = 20$, $C_2H_4 = 15$ standard cm^3 min^{-1} (Sample 13), reaction flame temperature > 3073K.

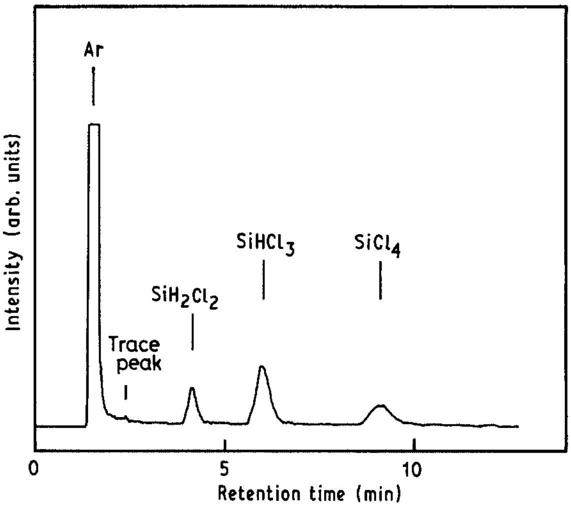

Figure 4 The results of the gas chromatographic analysis of the chlorosilanes in the exhausted gas from the reactor when 30 standard cm^3 min^{-1} SiH_2Cl_2 was irradiated by a CO_2 laser of power 3.2 kW cm^{-2} and diameter 2 mm. Sampling gas 1.0 ml, column DC550 (15%) supported Serite 545, SUS 3 mm diameter, 5 m, Column temperature 323 K, detector temperature 353 K, carrier gas He 30 ml min^{-1}.

powders prepared at a low C_2H_4/SiH_2Cl_2 ratio (0.3) consisted of strongly agglomerated particles (Fig. 2a) with a size of 0.3 µm. The powders prepared at $C_2H_4/SiH_2Cl_2 = 0.5$ consisted of basically spherical particles (Fig. 2b), whose size was in the 0.04–0.07 µm range, and the particles (Fig. 2c) which had radial projections. The powders at the high C_2H_4/SiH_2Cl_2 ratio (1.3) consisted of particles as in Fig. 2c and particles as in Fig. 2d with a shape close to hexagonal, and a film-like material (Fig. 2e). From the results of SAED, it was found that particles in Fig. 2a were a mixture of silicon and SiC; particles in Fig. 2b and c were SiC; particles in Fig. 2d were mostly carbon including a small amount of SiC; and the film-like material was carbon. The formation mechanism of the particles in Fig. 2c was not clearly understood, but it was speculated that SiH_2Cl_2 or chlorine might play a role in the formation of these particles, because they could not be observed in other SiH_4–C_2H_4 systems [2].

Fig. 3 shows typical photoacoustic emission spectra (PAS) of the powders. SiC (around 800 cm^{-1}) and SiO_2 (around 1100 cm^{-1}) were observed in all the samples. A small peak of the Si–H bond (2150 cm^{-1}) was observed in the powder (a) prepared with $SiH_2Cl_2 = 20$ and $C_2H_4 = 5$ standard cm^3 min^{-1} at a reaction flame temperature of 2823–2933 K.

3.2. Reaction mechanism

3.2.1. Silicon formation

Silicon particles were produced by irradiating SiH_2Cl_2 with a CO_2 laser. In the case of SiH_2Cl_2 only, the reaction flame temperature was less than 1273 K. In this temperature range, silicon particle formation by direct decomposition of SiH_2Cl_2 was difficult because the equilibrium constant of direct decomposition of SiH_2Cl_2 was small ($SiH_2Cl_2(g) \rightarrow Si(s) + 2HCl(g)$, $\log K_p = 0.237$, 1300 K) [10]. The equilibrium phase diagram of the Si–H–Cl system [11] shows that $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, $SiCl_2$, and $SiCl_3$ are present in a gaseous phase below 1273 K. Therefore, it was considered that SiH_2Cl_2 underwent a disproportionation reaction during CO_2 laser irradiation and more reactive species, such as SiH_3Cl, were formed. A gas chromatographic analysis of the chlorosilanes was performed to check the occurrence of the disproportionation reaction of SiH_2Cl_2. Fig. 4 shows the result of the gas chromatographic analysis of the chlorosilanes in the exhausted gas from the reactor when 30 standard cm^3 min^{-1} was irradiated with a 3.2 kW cm^{-2} CO_2 laser having a 2 mm beam diameter. The large argon peak as the carrier gas, and peaks of $SiCl_4$, $SiHCl_3$, SiH_2Cl_2 were observed. Moreover, the trace peak, which was speculated to be SiH_3Cl from its peak position, was observed. This result shows that the disproportionation reaction of SiH_2Cl_2 took place and various kinds of chlorosilanes were formed. Silicon particles were considered to be formed mainly from the highly reactive species such as SiH_3Cl and SiH_4 produced by the disproportionation reaction. Even though SiH_4 could not be detected under this gas chromatographic analysis condition, it is possible that SiH_4 could be formed if the material balance is considered.

3.2.2. SiC formation

When SiC powders were prepared by irradiating a mixture of SiH_2Cl_2 and C_2H_4 with a 3.66 kW cm^{-2} CO_2 laser, the reaction flame temperature was low at a low C_2H_4/SiH_2Cl_2 ratio, but it abruptly increased as the C_2H_4/SiH_2Cl_2 ratio increased. When the CO_2 laser was used to irradiate a mixture of SiH_2Cl_2 and

C_2H_4 at $C_2H_4/SiH_2Cl_2 = 0.5$ and 0.6, hysteresis was observed between the reaction flame temperature and the laser power density [9] (Fig. 5). After increasing the laser power gradually, the reaction flame temperature was low (< 1273 K) until the laser power density reached about 3.3 kW cm^{-2}. Then, it suddenly increased and reached ~ 3000 K. Once the reaction flame temperature reached ~ 3000 K, it maintained the high temperature until the laser power density decreased to around 2.0 kW cm^{-2}. Then, it abruptly decreased to less than 1273 K. Table II lists the properties of the powder prepared at low and high reaction flame temperatures at $C_2H_4/SiH_2Cl_2 = 0.5$ and a laser power density of 2.87 kW cm^{-2}. The powder prepared at a low reaction flame temperature was SiC as determined by XRD, but contained less carbon and more oxygen than that prepared at a high reaction flame temperature. The surface area of the powder prepared at a low reaction flame temperature was small, and these particles were found by TEM observation to be strongly agglomerated.

The reason for the steep increase in the reaction flame temperature was assumed to be that two exothermic reactions, which were a decomposition of C_2H_4 ($1/2C_2H_4(g) \rightarrow C(s) + H_2(g)$, $\Delta H = -4.3$ kcal mol^{-1} (1300 K)) and carbonization of silicon ($Si(s) + C(s) \rightarrow \beta\text{-}SiC(s)$, $\Delta H = -17.4$ kcal mol^{-1} (1300 K)) [10], were started by increasing the laser power density, and the reaction flame temperature was increased by their heats of reaction. Assuming that SiH_2Cl_2 was decomposed into Si(s) and 2HCl(g) at 1300 K by using absorbed laser energy, the reaction ($Si(s) + 2HCl(g) + 1/2C_2H_4(g) \rightarrow \beta\text{-}SiC(s) + 2HCl(g) + H_2(g)$, $\Delta H = -21.7$ kcal mol^{-1} (1300 K)) [10] proceeded quantitatively, and the heat of reaction was used entirely to heat all the products, the calculated reaction temperature was about 1900 K (heat capacity $C_p(1300\text{ K}) = 12.2$ cal mol^{-1} K^{-1} for SiC(s), 7.9 for HCl(g), 7.5 for $H_2(g)$ were used) [10]. The actual reaction flame temperature was more than 2600 K (Fig. 5), so the steep increase in the reaction flame temperature could not be explained solely due to the contribution of the heat of the exothermic reactions.

Fig. 6 shows the amount of laser absorption when laser power density was changed. Hysteresis was observed between the amount of laser absorption and laser power density, similar to the case of the reaction flame temperature and laser power density. When the laser power density was increased gradually, the amount of laser absorption was about 4 W until the laser power density reached about 3.0 kW cm^{-2} which was almost equal to the power density at which the reaction temperature abruptly increased. Then, the amount of laser absorption abruptly increased. The degree of the laser absorption change was varied with

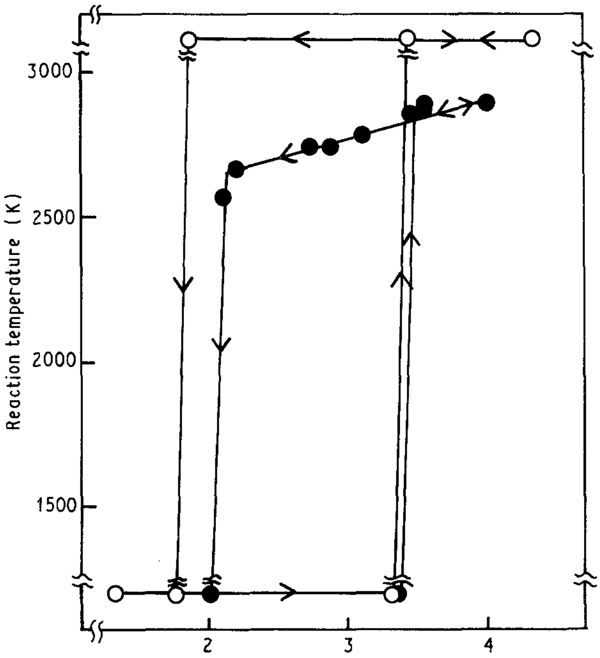

Figure 5 Reaction temperature change as a function of laser power density [9]. 20 standard cm^3 min^{-1} SiH_2Cl_2, and (●) 10 and (○) 12 standard cm^3 min^{-1} C_2H_4.

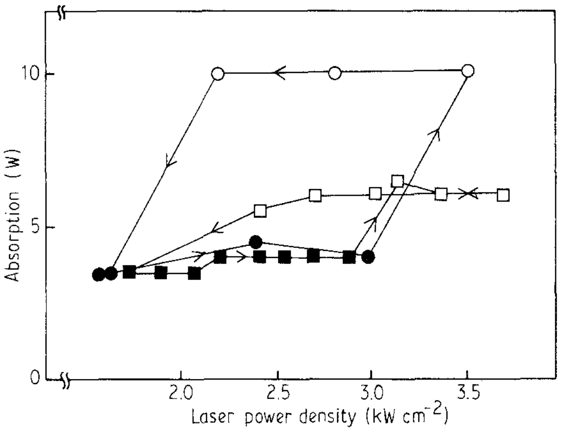

Figure 6 Laser power absorption change as a function of laser power density. (○, □) High flame temperature (> 2753 K), (●, ■) low flame temperature (< 1273 K). 20 standard cm^3 min^{-1} SiH_2Cl_2, (□, ■) 10 standard cm^3 min^{-1} C_2H_4, (○, ●) 15 standard cm^3 min^{-1} C_2H_4.

TABLE II The properties of the powder prepared at high and low reaction flame temperatures. SiH_2Cl_2 = 20 standard cm^3 min^{-1}, C_2H_4 = 10 standard cm^3 min^{-1}, laser power density = 2.87 kW cm^{-2}

Sample	SiH_2Cl_2 (standard cm^3 min^{-1})	C_2H_4 (standard cm^3 min^{-1})	Reaction zone temperature (K)	Specific surface area (m^2 g^{-1})	XRD	Composition	
						C (wt %)	O (wt %)
15	20	10	2773-3073	213.2	SiC	26.5	15.8
16	20	10	< 1273	4.4	SiC (broad)	18.2	23.2

C_2H_4/SiH_2Cl_2 ratio, becoming 2 W at $C_2H_4/SiH_2Cl_2 = 0.5$, 6 W at $C_2H_4/SiH_2Cl_2 = 0.75$. Assuming that the laser absorption increase was all spent to heat the products, the increase in the reaction flame temperature by the laser absorption increase could be calculated (heat capacity $C_p(1300\ K) = 5.5\ cal\,mol^{-1}\,K^{-1}$ for C(s) were used) [10]. In the case of $SiH_2Cl_2 = 20$ and $C_2H_4 = 10$ standard $cm^3\,min^{-1}$, the temperature increase by the 2 W laser power was about 900 K and in the case of $SiH_2Cl_2 = 20$ and $C_2H_4 = 15$ standard $cm^3\,min^{-1}$, the temperature increase by the 6 W laser power was about 2300 K. In the latter case, the increase in laser absorption was enough to explain the steep increase in the reaction flame temperature. However, in the former case, the increase in laser absorption was insufficient to cause a steep increase in the reaction flame temperature by itself, although a steep increase of more than 1800 K took place. Therefore, it was considered that the steep increase in the reaction flame temperature was caused by both the initiation of exothermic reactions and the increase in laser absorption which took place simultaneously.

Solid particles, having a strong absorption band near 10.6 μm (943 cm^{-1}), were considered as a reason for the laser absorption increase. However, silicon did not have an absorption band near 10.6 μm. SiC had a strong absorption band near 10.6 μm [12]. Carbon had a strong absorption in the wide region ranging from 25–2.5 μm, that was confirmed by measuring the infrared transmittance of the carbon black (2 wt %) in the KBr pellet. Therefore, SiC and carbon particles, forming in the reaction flame, were considered to contribute to laser absorption increase. In particular, the formation of carbon particles was considered to have a more important role than SiC, for the following reasons.

1. A steep increase in the reaction flame temperature could not be observed at the low C_2H_4/SiH_2Cl_2 ratio (< 0.3), even though SiC particles were formed at that ratio.

2. The degree of laser absorption increase was larger at $C_2H_4/SiH_2Cl_2 = 0.75$ than at $C_2H_4/SiH_2Cl_2 = 0.5$. In the former case, the product powder showed a high carbon content (36.4 wt %) and free carbon was observed by XRD. However, in the latter case, the carbon content of the powder was 25.7 wt % and free carbon was not observed by XRD.

The hysteresis between the reaction flame temperature and laser power density (Fig. 5) could be explained as follows: when a gas mixture of SiH_2Cl_2 and sufficient C_2H_4 were irradiated with a CO_2 laser, whose power was gradually increased, the exothermic reactions of the decomposition of C_2H_4 to form carbon particles and carbonization of silicon would occur at a certain laser power density. Because the heat of reaction was liberated and carbon particles absorbed more laser beam, the reaction flame temperature increased. The rise in the reaction flame temperature accelerated the decomposition of C_2H_4 and carbon particle formation. These processes could happen in very short time, resulting in a steep increase in the reaction flame temperature. Once the reaction flame temperature became high, the carbon particle formation was continued to some extent by the high flame temperature itself, even if the laser power was decreased. So a high laser absorption and a high flame temperature were maintained to a certain laser power.

It was found by XRD that SiC was formed both at high and low reaction flame temperatures. However, the mechanism of SiC formation could be different in each case.

In the case of low reaction flame temperature (< 1273 K), $SiCl_4$, $SiHCl_3$, SiH_2Cl_2 and a trace peak speculated to be SiH_3Cl, were observed in the exhausted gas from the reactor by gas chromatographic analysis. SiH_2Cl_2 underwent a disproportionation reaction during laser irradiation and various kinds of chlorosilanes and silane were formed. Therefore, the mechanism of SiC formation was very complex, but highly reactive species such as SiH_4 and SiH_3Cl were considered to play a very important role, especially at low temperature. Some SiH_2Cl_2 , $SiHCl_3$ and $SiCl_4$ were exhausted outside without any further reaction.

In the case of the high reaction flame temperature (> 3073 K), all the products of the disproportionation reaction, even the least reactive $SiCl_4$, could react with C_2H_4 forming SiC. However, small amounts of $SiCl_4$, $SiHCl_3$ and a trace of SiH_2Cl_2 were observed in the exhausted gas from the reactor by gas chromatographic analysis in spite of the high reaction flame temperature (> 3073 K). This result indicated that small parts of $SiCl_4$ and $SiHCl_3$ were exhausted outside without any further reaction. Or, some part of these compounds might form a polymeric compound, because a Si–H bond was observed in the PAS spectra (Fig. 3), and in most experiments, a small amount of liquid material was observed near the gas outlet of the reactor. This liquid material was transparent and emitted a strong HCl odour and solidified in air within several tens of minutes. In addition, the polymeric compound might be formed at a low reaction temperature.

In this experiment, the laser beam diameter was so small (2 mm) that the laser power density might be insufficient at the edge of the beam or that the residence time of reactant might be too short to complete the reaction. To complete the reaction, an increase in laser power or enlargement of the beam diameter would be needed.

5. Conclusion

SiC ultrafine particles were prepared by a CO_2 laser at atmospheric pressure from C_2H_4 and SiH_2Cl_2 which are cheaper than SiH_4. The composition of the powder changed with the C_2H_4/SiH_2Cl_2 ratio. The reaction flame temperature was low (< 1273 K) at low C_2H_4/SiH_2Cl_2 ratio, and rapidly increased to around 3000 K when the C_2H_4/SiH_2Cl_2 ratio exceeded 0.3. This rapid temperature increase was caused by initiation of exothermic reactions and the rise in laser absorption mainly caused by carbon particle formation and partly due to SiC particle formation. It was found that SiH_2Cl_2 underwent a disproportionation reaction on CO_2 laser irradiation, and that SiC was formed through the various products of the disproportionation reaction.

This process using SiH_2Cl_2 may possibly be more economical than that using SiH_4.

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