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# Production of silicon containing particles by laser induced reaction of silane with methane, ethane and acetylene

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**Abstract**

Silicon containing ultrafine particles (Si and SiC) have been obtained by pulsed IR laser irradiation of gaseous $SiH_4$/hydrocarbon ($CH_4$, $C_2H_6$ and $C_2H_2$) mixtures. The chemical composition and structure of the powders formed were determined by scanning and transmission electron microscopy (SEM and TEM), X-ray diffraction (XRD) and I.R. and UV-v spectroscopy. The particles are small, uniform, loosely agglomerated spheres with a mean size of approximately 19 nm. To complete the characterisation of these ultrafine silicon-containing particles, the X-ray absorption spectra (XAS) were obtained using synchrotron radiation at the silicon absorption K-edge. We show that the use of pulsed laser radiation results in the generation of amorphous Si and crystalline SiC particles depending on the gas mixtue used, among other parameters such as composition of the mixture, laser fluence, pressure and number of laser pulses.

*Keywords:* Powders-gas phase reaction; SiC; Si; X-ray absorption spectra

## 1. Introduction

There has been a great deal of recent research interest in the synthesis of nanophase materials by means of a variety of methods, and this development has resulted in a new class of materials with special chemical and physical properties.[1] They are dominated by their ultrafine grain sizes ($<100$ nm) and by the large number of interfaces associated with their small sizes. However, other structural features, such as pores, grain boundary junctions and crystal lattice defects that depend on the manner in which these materials are synthesized and processed, also play a significant role in determining their properties. It has become increasingly clear during the past several years that all of these structural aspects must be carefully considered in trying to fully understand the properties of nanophase materials.

It is well established that the laser induced reaction technique is one of the best methods for the production of ultrafine particles, which are very pure and uniform in composition and particle size.[2] The development of powerful $CO_2$ lasers, which have reached the market for applications to industrial processes both from technical and economical points of view, pushed researchers to consider laser assisted photodecomposition of at least one of the gas-phase precursors as a possible way to prepare high purity ceramic powders. In fact, previous studies on vibrational multiphoton excitation of molecules showed that IR photons can selectively excite a molecule up to dissociation in different chemical environments.[3] Photochemical reactions can be devoted to the production of high purity compounds, since the laser assisted process is localized along the laser beam and no contamination from hot surfaces is possible. In laser-induced gas-phase reactions, the laser beam starts a reaction, which takes place in a compartment where the walls remain cold and thus, non reactive.[4] This ensures that the process is clean while the low reaction volume and ability to maintain steep temperature gradients allows for a precise control of the nucleation and growth rates favouring the formation of very small and uniform particles.

Much interest has been focused, in the past few years, on the production of silicon carbide due to its excellent chemical and thermal shock resistance, superior electrical properties, chemical stability, mechanical strength and high thermal conductivity.[5] Strong covalent

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bonding between the constituent elements in this material gives rise to a combination of properties very important for designing high-performance materials. Thus, SiC nanosized powder is frequently used as a main constituent of ceramic nanocomposite materials.

In the case of laser synthesis of silicon-containing powders, $SiH_4$ is generally used as a suitable gas-phase precursor because the $\nu_4$ vibrational band is at resonance with the $CO_2$ laser emission in the 10.6 μm region.[6,7] The production of Si[4] and SiC[4,8] from $SiH_4$ absorption by infrared radiation from a continuous wave (cw) $CO_2$ laser, can be explained according to the following overall gas-phase reactions:

$$SiH_4(g) \xrightarrow{h\nu} Si(s) + 2\ H_2(g) \tag{1}$$

$$2\ SiH_4(g) + C_2H_4(g) \xrightarrow{h\nu} 2\ SiC(s) + 6\ H_2(g) \tag{2}$$

$$SiH_4(g) + CH_4(g) \xrightarrow{h\nu} SiC(s) + 4\ H_2(g) \tag{3}$$

$$2\ SiH_4(g) + C_2H_2(g) \xrightarrow{h\nu} 2\ SiC(s) + 5\ H_2(g) \tag{4}$$

In this work, we studied the pulsed laser generation of silicon containing powders (Si and SiC). The production of Si and SiC after absorption of *m* IR quanta of frequency $\nu_4$ by $SiH_4$, can be explained according to the following overall gas-phase reactions:

$$SiH_4(g) + CH_4(g) \xrightarrow{mh\nu} Si(s) + C(s) + 4\ H_2(g) \tag{5}$$

$$SiH_4(g) + C_2H_6(g) \xrightarrow{mh\nu} Si(s) + 2\ C(s) + 5\ H_2(g) \tag{6}$$

$$2\ SiH_4(g) + C_2H_2(g) \xrightarrow{mh\nu} 2\ SiC(s) + 5\ H_2(g) \tag{7}$$

This technique seems to be promising for the production of nanostructured materials, since an adequate control of the experimental conditions allows for the synthesis of both amorphous and crystalline particles.[9] Regarding the laser production of SiC powders, all previously reported work using continuous IR laser irradiation, shows the formation of crystalline particles[8] regardless of the initial $SiH_4$/hydrocarbon mixture used (reactions 2–4). From the chemical and physical characterization of the powders obtained in this work, using pulsed IR radiation, we determined that the formation of crystalline SiC particles occurs only with mixtures of $SiH_4/C_2H_2$ whereas amorphous Si powders are formed with mixtures of $SiH_4$ and $CH_4$ or $C_2H_6$.

From a mechanistic point of view, it has been well established that silylene ($SiH_2$) is a key intermediate in a wide range of decomposition processes of silicon hydrides including pyrolysis,[10,11] chemical vapor deposition,[12] glow discharge[13] and IR laser-induced dissociation.[14] When $SiH_2$ is formed in the $^1A_1$ ground state, as in the thermal reaction, the dominant mechanism involves its insertion into undissociated $SiH_4$ giving rise to higher silanes.[10,11] Otherwise, silicon or silicon carbide formation followed by particle nucleation and condensation is observed when $SiH_2$ is produced in the excited $^1B_1$ electronic state.[14] Laser based kinetic studies have measured the removal rate constants for silylene in its ground vibrational and electronic state. The reported values, as upper limits, for the reactions of $SiH_2 + CH_4$ and $SiH_2 + C_2H_6$, determined at 298 K and 5 Torr total pressure with He were $(2.5 \pm 0.5)\ 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$ and $(1.2 \pm 0.5)\ 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$, respectively.[15] The rate coefficient for the addition reaction of $SiH_2$ to $C_2H_2$ at 298 K and 5 Torr (He) has been determined as $(9.8 \pm 1.2)\ 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$.[15]

In the present study, in order to complete the characterization of the ultrafine silicon containing powders, the X-ray absorption spectra (XAS) of the samples at the silicon absorption K-edge[16,17] were obtained using synchrotron radiation. This technique has the advantage that the spectra obtained are specific of the element under analysis since the absorption steps of the inner shells take place at defined energies of the X-rays characteristic of the atomic number of the absorbing elements. Therefore, the absorption spectrum of each element can be obtained from samples of a complex mixture of different elements simply by changing the wavelength of the incident X-rays.

These results allowed us to characterize the particles generated by infrared multiple photon decomposition (IRMPD) with respect to chemical composition and structure for comparison with results obtained by other experimental methods.

## 2. Experimental

Experiments were performed with a pulsed TEA $CO_2$ laser (Tachisto model 217-G, Laser System Inc) as the source of IR radiation, tuned at the P (20) line of the $00^01$–$10^00$ transition at 944.19 $cm^{-1}$, which is resonant with the $\nu_4$ mode of $SiH_4$ at 10.6 μm. A spectrum analyzer (Optical Engineering) was used to tune the laser to the desired wavelength. The energy of the beam was measured with a power meter (Scientech 38–0102). Runs were carried out in a cylindrical Pyrex cell (2.6 cm diameter), 8.0–20.0 cm optical path length, sealed with removable KBr windows. The experiments were carried out only with a focused beam in order to reach the reaction threshold. The fluence was 30 J $cm^{-2}$ when the beam was focused with a $BaF_2$ converging lens. $SiH_4$, $CH_4$, $C_2H_6$ and $C_2H_2$ were commercially obtained and gas chromatography, infrared spectroscopy and mass spectrometry verified their purity. $SiH_4$ is a highly hazardous compound in its reaction with oxygen. It is known to react explosively with oxygen under certain conditions, therefore extreme care is required in its handling. The following mixtures were used: $SiH_4$ + $CH_4$; $SiH_4$ + $C_2H_6$ and $SiH_4$ + $C_2H_2$. Experiments were conducted at room temperature irradiating samples of $SiH_4$ at pressures between 20 and 900 Torr, in the presence of $CH_4$ at pressures between 20 and 100 Torr, or $C_2H_6$ at pressures between 50 and 350 Torr or $C_2H_2$ at pressures between 20 and 300 Torr measured with a MKS Baratron capacitance manometer model 220-B.

Silicon containing powders were produced by the laser induced reaction of the gaseous mixtures mentioned above using suitable reaction cells. Samples were normally irradiated up to 1000 $CO_2$ laser pulses and after laser irradiation, the cell was evacuated and the powders formed, removed for analysis. Crystalline samples of Si, SiC and $SiO_2$, both in plates and powders were used as standards.

The shape and structure of the particles obtained were examined by scanning electron microscopy (SEM) (Philips 505E with microprobe EDAX) and transmission electron microscopy (TEM) (Zeiss 109 and Siemens 101). The TEM photographs were digitized using a Hewlett Packard 2C Scanner and a high resolution PC monitor and the diameters were determined with an error equal to or less than 1 nm.

X-Ray diffraction (DRX) was used to determine the crystal structure of the powders formed by IRMPD of the silane containing mixtures. The stoichiometric composition of the powders was evaluated using a commercial equipment Leco analyzer, for the determination of carbon (model CS 44) and for the determination of oxygen (model TC 36), calibrated with a standard NBS 112 sample with a certified content of SiC. Accuracy was better than ±1% in each determination.

A Nicolet 5SXC Fourier transform infrared spectrometer (2 $cm^{-1}$ resolution) with a deuterated triglicerin sulfate (DTGS) detector and a Shimadzu UV-visible 1601 Spectrophotometer were used to determine the products formed in the reaction cell in the infrared and UV-v region, respectively. Both the FTIR and UV-v spectra of the $SiH_4$ containing mixtures were taken before and after irradiation. Spectra of pure $SiH_4$ and others gaseous samples were taken and used for final product identification in irradiated samples.

Experimental data for the XAS spectra were collected at the silicon absorption K-edge ($E = 1.841$ keV) using the soft X-ray spectroscopy (SXS) line at the National Synchrotron Light Laboratory (LNLS) in Campinas, Brazil.[18] A double InSb crystal monochromator was used and the detection was performed in the total electron yield mode. Total electron yield mode is a well established method to obtain the absorption spectra of solid samples, whereby the total number of electrons emitted by the sample is determined as a function of photon energy.[16] The pressure in the line was kept down to $10^{-9}$ mbar. For the qualitative analyses, all the XAS spectra were arbitrarily normalized with respect to the energy maximum of the silicon K absorption edge. When necessary, the standards were finely divided and dispersed over adhesive tape and fixed on a stainless steel plate.

The visible luminescence that accompanies powder formation was detected at right angles to the $CO_2$ laser beam through an additional quartz window placed 3 cm apart from the front window of the reaction cell. A Hamamatsu R636 photomultiplier tube was employed for detection of the luminescence spectrum and time analysis of the luminescence signal. The output signal of the photomultiplier tube was digitised and averaged with a Lecroy S43 oscilloscope. It is well known that the overall rise-time of the detection system depends on the polarization voltage of the photomultiplier tube. Thus, the rise-time of the detection system was found to be 200 ns with the photomultiplier tube voltage of 1000 V. The emission spectrum was obtained with a 0.30 m McPherson scanning monochromator model 218, supplied with a 1500 grooves/mm grating. With this equipment the intensity of fluorescence produced after each pulse of the laser was measured every 20 nm wavelength variation.

## 3. Results and discussion

Mixtures of silane and hydrocarbons of different composition ratios were used to obtain the powders by pulsed laser irradiation. The reaction always occurs with an increase of total pressure in the cell and only in the case of $SiH_4/C_2H_2$ mixtures, the reaction was complete with only one laser pulse. With the other mixtures, a large number of pulses (~1000) was necessary to produce a significant extent of reaction.

The IRMPD of neat $SiH_4$ samples exhibits a pressure and fluence threshold for the production of Si powders.[6,19] At a fluence of 1 J $cm^{-2}$, powder formation is observed at all pressures of $SiH_4$ above 15 Torr and at pressures greater than 30 Torr, the threshold fluence can be considered pressure independent. Thus, one main difference between the laser decomposition of neat $SiH_4$ samples and the $SiH_4$/hydrocarbon mixtures is that for the latter, powder production exhibits a complex dependence on composition and total pressure whereby total pressures higher than 70 Torr were required to observe a reaction. As a result, for $SiH_4/CH_4$ mixtures, reaction occurs only within a narrow range of experimental conditions. Thus, for a pressure ratio 2:1 ($SiH_4/CH_4$) and partial pressure of $SiH_4$ lower than 120 Torr, reaction is observed. When the ratio decreases to 1.0 or increases to 3.5, the formation of powders is completely suppressed. In the case of $SiH_4/C_2H_6$ mixtures, decomposition takes place for pressure ratios between 2.5 and 3.0 for partial pressures of $SiH_4$ higher than 120.0 Torr. Finally, in mixtures of $SiH_4/C_2H_2$, the decomposition reaction is observed when the pressure ratio is between 1.5 and 2.0 and the $SiH_4$ partial pressure is higher than 250 Torr. The process conditions used in the synthesis experiments and some representative results obtained with the different mixtures are shown in Table 1.

Powder formation is always accompanied by light emission. The strong luminescence is similar to that observed in the photochemical decomposition of neat $SiH_4$.[14] Fig. 1 shows the real time, point to point low resolution emission spectrum obtained in the range 550–800 nm, which exhibits a broad band with a maximum at 720 nm and agrees well with that observed in the IRMPD of $SiH_4$.[14] It has been well established that this emission corresponds to the $^1B_1 \rightarrow {}^1A_1$ transition of $SiH_2$[20] assigned to the decay of $SiH_2$ radicals from the excited $\tilde{A}^1B_1$ electronic state to the fundamental $\tilde{X}^1A_1$ state in accordance with $SiH_4$[6,21] and organosilane decomposition studies.[22,23] The shape of the emission spectra is unaffected by pressure or laser fluence changes under the present experimental conditions. This assignment of the observed fluorescence to the decay of an excited electronic state of $SiH_2$ indicates that this radical is a key intermediate in the reaction mechanism that leads to silicon containing powders.

### 3.1. Characterisation results

To perform the TEM analyses of the samples, we followed two different procedures.

1) In the first, the microscope grid was placed in the cell parallel to the laser beam during the experiment and after deposition of the powders it was directly taken out for analysis.

2) In the second, the particles were brushed off the cell walls and suspended in alcoholic or buffered solutions of different pH using an ultrasonic bath. A drop of the suspension was placed on the microscope grid and allowed to dry. The TEM images show that the particles stick together in clusters. Adequate buffering of the solutions eliminates this agglomeration and the microphotographs studied were the result of samples prepared around pH = 4.

All the silicon containing powder samples analysed by TEM showed that the particles were small, uniform and loosely agglomerated spheres and their sizes varied from 8 to 70 nm, with and average of 19 nm. These mean size values are close to those obtained previously for Si particles produced in the IRMPD of pure $SiH_4$ samples.[9]

#### 3.1.1. $SiH_4/CH_4$ and $SiH_4/C_2H_6$ mixtures

A brownish-yellow deposit was formed on the walls and windows of the cell during laser photolysis. Initial analysis of the powders obtained was carried out by measuring the infrared transmittance of the cell content, previous to evacuation of the gaseous products of the photolysis with the objective of minimizing manipulation of the powders.

The IR spectra obtained from powders formed by IRMPD of $SiH_4/CH_4$ or $SiH_4/C_2H_6$ mixtures are shown in Fig. 2. The spectra are similar and the most prominent features observed in all samples examined are the absorption bands at 2110 $cm^{-1}$, due to Si–H stretching,[24–28] at 895 $cm^{-1}$ for the powders obtained from the mixtures $SiH_4/CH_4$ and 885 $cm^{-1}$ for $C_2H_6$ as reactant, corresponding to the Si–H bending[26–28] and at 635 $cm^{-1}$ for the absorption of the Si–H wagging mode.[26–28] The spectrum of the powders obtained from $CH_4$ as reactant shows two additional absorption features at 1090 and 862 $cm^{-1}$.

The broad band centered at 1090 $cm^{-1}$ is typical of a bridging oxygen between two silicon atoms, Si–O–Si,[24–27] and the feature at 862 $cm^{-1}$ has been assigned to the coupling of Si–H and Si–O–Si motions.[26] These bands could be due to the presence of $O_2$ in the $CH_4$ and since the boiling point of both compounds is quite close, complete separation was not achieved after purification. The fact that the silicon powders obtained from the $SiH_4/CH_4$ mixtures were considerably oxidized is evidenced in the XAS spectra which will be presented below.

A small portion of the powders obtained from each one of the different initial mixtures was suspended in acetonitrile using an ultrasonic bath in order to obtain

Table 1
Experimental conditions for IRMPD experiments

| Initial cell pressure (Torr) | | | | | | |
|---|---|---|---|---|---|---|
| $SiH_4$ | $CH_4$ | $C_2H_6$ | $C_2H_2$ | Pressure ratio | Powder formation | Powder crystallinity |
| 72.5 | 35 | | | 2.1 | Si | Amorphous |
| 100 | 50 | | | 2 | Si | Amorphous |
| 460 | | 158 | | 2.9 | Si | Amorphous |
| 133.3 | | 131.2 | | 1 | Si | Amorphous |
| 644 | | | 322 | 2 | SiC | Crystalline |
| 260 | | | 174 | 1.5 | SiC | Crystalline |

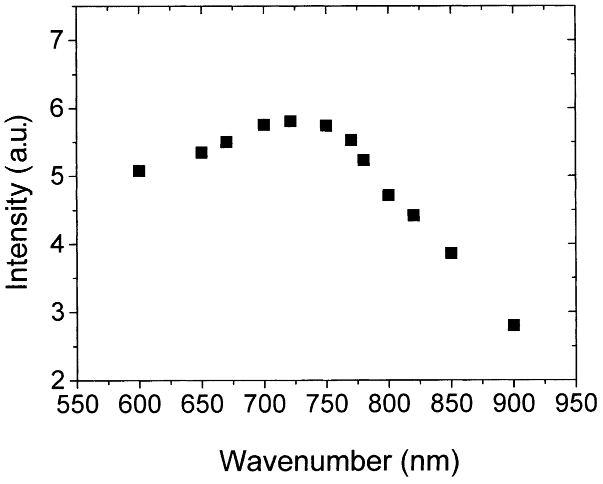

Fig. 1. Visible fluorescence spectrum of the $SiH_2$ radical.

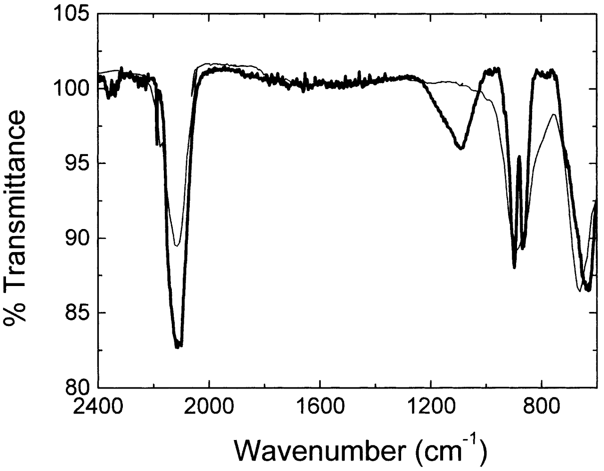

Fig. 2. FTIR spectra of the powders formed from $SiH_4$ + $CH_4/C_2H_6$. —$SiH_4$ + $CH_4$; —$SiH_4$ + $C_2H_6$.

the UV-v spectra. A typical absorption spectrum of a sample of these powders between 200 and 800 nm is shown in Fig. 3. The spectrum is consistent with the small size of the observed Si containing powders and is similar to those reported for 3–8 nm, surface oxidized Si-crystallites.[28,29] There is a weak tail from 370 nm across the visible and stronger absorption from 370 to 230 nm. The shape of the optical absorbance shown in Fig. 3 is actually quite similar to the shape of the expected spectrum of bulk Si in small particles that can be calculated from the electric dipole term of the Mie scattering theory. The absorbance tail is the weak indirect absorption and a higher direct transition occurs at 370 nm.

Characterization of the ultrafine silicon containing particles using synchrotron radiation at the silicon absorption K-edge at 1841 eV was performed obtaining the XAS spectra of the powders and comparing with the ones obtained for the crystalline reference samples of Si, $SiO_2$ and SiC. Results obtained by this method in previous studies based on qualitative analysis of energy shifts and the presence of certain peaks in the spectra were considered.[30,31]

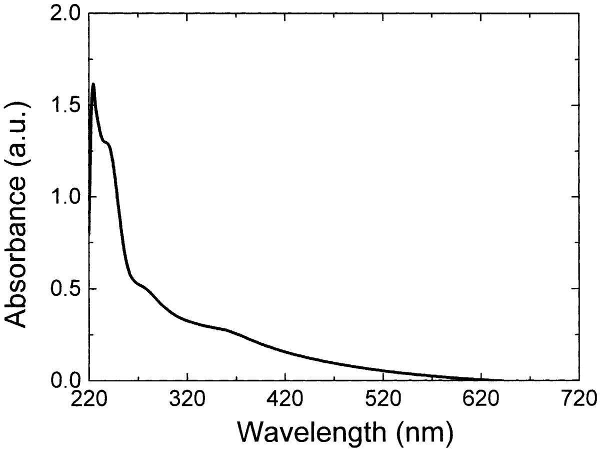

Fig. 3. UV-v spectrum of silicon containing powders suspended in acetonitrile.

The XAS spectra[30,31] obtained for the crystalline reference samples of Si and $SiO_2$, together with the ones for the $SiH_4$ + $CH_4$ gaseous mixture, are shown in Fig. 4 and a strong correspondence between the spectra is observed. These results suggest that highly oxidized silicon powders are formed from the mixture, probably from oxygen contaminated methane. A feature worth mentioning about these spectra is the shift of the silicon edge to higher energies in going from elemental Si to $SiO_2$. This shift is observed when the formal valence of the atom increases. The same correspondence between pure Si and the powders obtained from IR irradiation of the $SiH_4$ + $C_2H_6$ mixture can be observed in the XAS spectra shown in Fig. 5.

X-ray diffraction analysis (XDA) of all the samples obtained by IRMPD of the different mixtures was performed.[32,33] The silicon powders obtained from $SiH_4/CH_4$ and $SiH_4/C_2H_6$ mixtures are amorphous (Table 1) as can be concluded from the X-ray diffraction spectrum of Fig. 6 in which only a background signal is observed and no sharp diffraction peaks are present and by the absence of spots typical of crystalline particles in the electron diffraction pattern.

### 3.1.2. $SiH_4/C_2H_2$ mixture

Chemical analysis shows that the powders formed with mixtures of $SiH_4/C_2H_2$ contain an average of 28% w/w C and a calculated 72% w/w Si content, which is in good agreement with the stoichiometric SiC composition (30% w/w C and 70% w/w Si). The bound Si content was evaluated assuming a complete conversion of C content to SiC and the difference to 100% gives a rough estimate of the remaining Si. The powders were manipulated in the presence of air which would account for them being slightly oxidized (<3% O).

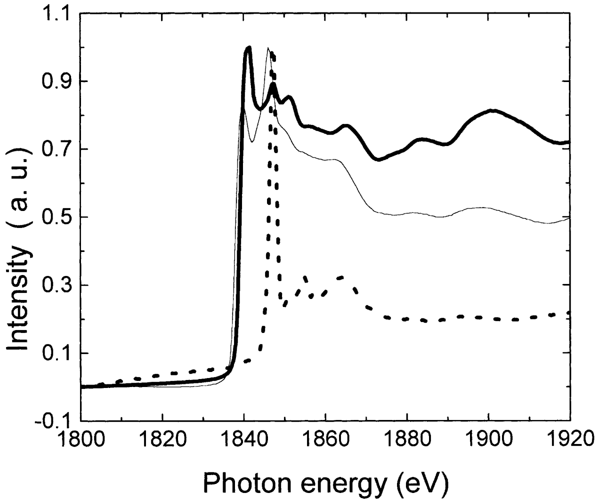

Fig. 4. Comparison of the XAS spectrum obtained for the $SiH_4$–$CH_4$ mixture with spectra of Si and $SiO_2$.—Powders obtained from $SiH_4$/$CH_4$ mixture; —Si standard; . . . $SiO_2$ standard.

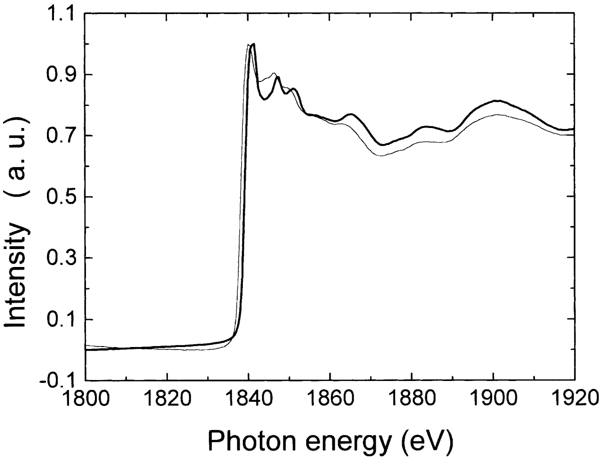

Fig. 5. Comparison of the XAS spectrum obtained for the $SiH_4$-$C_2H_6$ mixture with the spectrum of Si.—Powders obtained from $SiH_4$/$C_2H_6$ mixture; —Si standard.

Fig. 7 corresponds to the IR spectrum obtained from powders formed by photolysis of mixtures of $SiH_4$ and $C_2H_2$. A strong absorption band between 900 and 770 $cm^{-1}$, centered at 805 $cm^{-1}$, assigned to the SiC stretching[34,35] can be observed. Characteristic of this band is the shoulder located at 895 $cm^{-1}$.[34]

In Fig. 8, the XAS spectra for SiC and the $SiH_4$ + $C_2H_2$ reaction mixture are compared and a strong coincidence between the spectra is observed, both in the main peak of the silicon edge and the resonance maximum at approximately 12.5 eV after the threshold.[30,36] The energy localization of the main peaks observed in the XAS spectra is summarized in Table 2. The resonance, according to Laffon, Flank and Lagarde[30] is characteristic of a structural order which extends up to

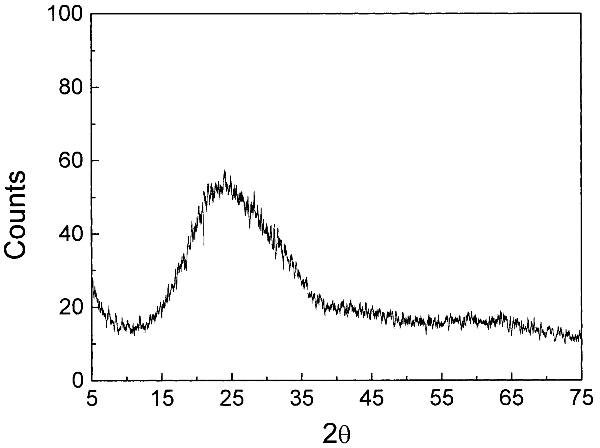

Fig. 6. X-ray diffraction spectrum of amorphous Si obtained for the $SiH_4$–$CH_4$ and $SiH_4$–$C_2H_6$ mixtures.

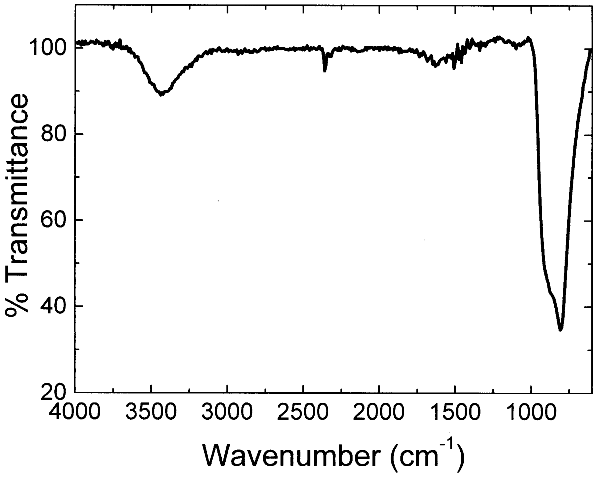

Fig. 7. FTIR spectrum of the powders formed from $SiH_4$ + $C_2H_2$.

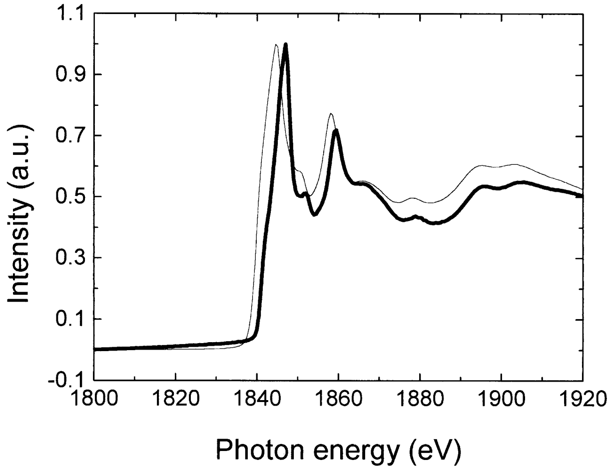

Fig. 8. Comparison of the XAS spectrum obtained for the $SiH_4$–$C_2H_2$ mixture with spectrum of SiC.—Powders obtained from $SiH_4$/$C_2H_2$ mixture; —SiC standard.

Table 2
Silicon absorption K-edge obtained from the XAS spectra

| Silicon K edge energy (eV) | Si (powders) | Si (plate) | SiC | $SiO_2$ | $SiH_4$ + $CH_4$ | $SiH_4$ + $C_2H_6$ | $SiH_4$ + $C_2H_2$ |
|---|---|---|---|---|---|---|---|
| Silicon | 1841 | 1840.5 | 1847 | 1847.5 | 1840 | 1841 | 1846.5 |
| Resonance | | | 1859 | | | | 1859 |

the Si–Si second shell and its carbon neighbours, nevertheless the presence of this feature may be not due just to a particular shell but to the whole set of atoms in the structure taking into account the carbon neighbours. The value of $\Delta E$, which is the energy difference between the absorption edge and the resonance, verifies the relation $(\Delta E)*R^2$ =constant, where $R$ is the characteristic distance of the system which is that of the second shell. Taking $\Delta E = 12.5$ eV and a value of 162.3 eV Å$^2$ for the constant for SiC as reported by Laffon et al.,[30] we obtained, $R = 3.6$ Å. This value is in good agreement with that given by Mastelaro et al.[36] of 3.08 Å for the R(Si–Si) in c-SiC where each Si atom is surrounded by four carbon atoms forming the first shell at 1.89 Å ($R_{Si-C}$) and 12 Si atoms forming the second shell at 3.08 Å. This provides further evidence confirming that the nanoparticles formed from the $SiH_4/C_2H_2$ mixtures are actually SiC crystallites.

The SiC powders obtained from $SiH_4$ and $C_2H_2$ mixtures are crystalline (Table 1) as can be concluded by the presence of sharp diffraction peaks in the X-ray diffraction spectrum, shown in Fig. 9,[8,32] but small contributions from a crystalline Si phase cannot be excluded from the background behaviour. These results are at variance with those reported in works using a continuous $CO_2$ laser[35] as irradiation source, where amorphous SiC particles were obtained under synthesis conditions of thermal decomposition by energy transfer and heating of the reaction mixture.

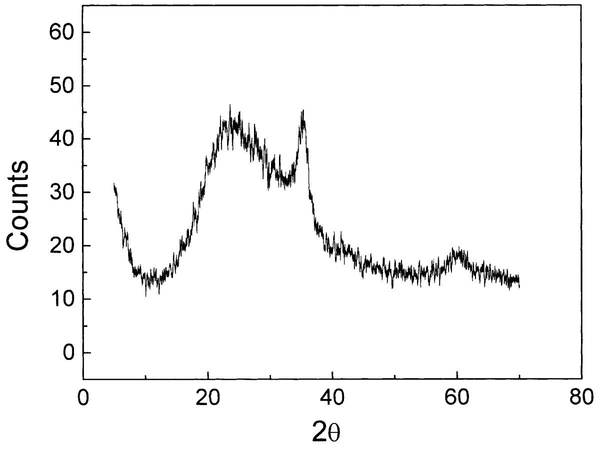

Fig. 9. X-ray diffraction spectrum of crystalline SiC particles obtained for the $SiH_4$–$C_2H_2$ mixture.

## 4. Conclusions

Pulsed IR laser irradiation of $SiH_4$, in mixtures with $CH_4$ and $C_2H_6$, results in the production of amorphous Si nanoparticles. The reaction occurs only within rather narrow pressure and composition conditions, at total pressure higher than 70 Torr. The reaction seems to be initiated by the decomposition of $SiH_4$ to yield $SiH_2$ in the $A^1B_1$ electronic excited state, similarly to the IR multiphoton decomposition of neat $SiH_4$ samples, as indicated by the spectrum of the intense luminescence observed. However, increasing the $CH_4$ or $C_2H_6$ content of the reaction mixture eliminates powder production as well as fluorescence, indicating that collisional relaxation of vibrationally excited $SiH_4$ molecules by the hydrocarbon is taking place, preventing its dissociation to produce electronically excited $SiH_2$.

Irradiation of $SiH_4$ in the presence of $C_2H_2$ showed a different behaviour to that of the IRMPD of mixtures of $SiH_4$ + $CH_4$ and $SiH_4$ + $C_2H_6$. Not only SiC powders are produced predominantly instead of Si but also, complete reaction occurs in one laser pulse. This suggests that the $SiH_2$ radicals formed from initial decomposition of $SiH_4$ react with $C_2H_2$ to generate SiC instead of Si powders.

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