

IR laser-induced thermolysis of silacyclopent-3-ene: extrusion of silylene and chemical vapour deposition of polycarbosilane phases via reactions of silylene, buta-1,3-diene and methylene

Josef Pola ^{a,*}, Markéta Urbanová ^a, Luis Díaz ^b, Magna Santos ^b, Zdeněk Bastl ^c, Jan Šubrt ^d

^a Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic

^b Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006 Madrid, Spain

^c J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic

^d Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řez near Prague, Czech Republic

Received 18 April 2000; accepted 18 May 2000

Abstract

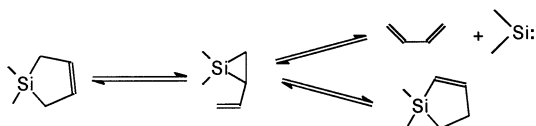
Infrared laser-induced (SF_6) photosensitized decomposition and infrared laser multiphoton decomposition of silacyclopent-3-ene occur as extrusion of silylene, yielding butadiene as a major gaseous product and affording chemical vapour deposition of solid saturated polycarbosilane films. The involvement of H_2Si , H_2C : and buta-1,3-diene in the formation of the films is revealed through quantification of the gaseous products and identification of H_2Si : and H_2C : by laser induced fluorescence. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silacyclopent-3-ene; Laser-induced thermolysis; Silylene; Chemical vapour deposition; Si/C/H polymers

1. Introduction

Thermal or photolytic decomposition of silacyclopent-3-enes is regarded [1–3] as a reversible process [4] occurring via transient 2-vinyl-1-silirane [5,6] and affording products of rearrangement and silylene extrusion (Scheme 1).

These two pathways have different significance depending on the substituents at the silicon [1,2,5,6]. The decomposition of the parent silacyclopent-3-ene (SCP) might have been expected to occur as a clean extrusion



Scheme 1.

of H_2Si : and subsequent self-polymerization of this species into rare poly(hydridosilanes). However, UV laser photolysis of gaseous SCP, although being a neat extrusion of silylene and yielding buta-1,3-diene as a major gaseous product, affords chemical vapour deposition of Si/C/H phases. The formation of these phases is due to the occurrence of polymerization steps of both H_2Si : and the products of buta-1,3-diene photolysis [7].

It was our aim to compare SCP decomposition from the electronically excited state and vibrationally excited ground state. In this study we examined IR laser-induced thermolysis of SCP in the absence and presence of photosensitizing SF_6 in an effort to elucidate the mechanism and to find out whether silylene is involved in reactions with other products of SCP thermolysis.

2. Experimental

Laser thermolysis experiments were conducted with a tunable TEA CO_2 laser (Plovdiv University) operating on the P(14) and P(18) line of the $00^0_1 \rightarrow 10^0_0$ transition

* Corresponding author. Tel.: +420-2-20390308; fax: +420-2-20920661.

E-mail address: pola@icpf.cas.cz (J. Pola).

(949.50 and 945.98 cm^{-1} , respectively). The former line was used for the irradiation of SCP (10 Torr) and the latter for the irradiation of the equimolar mixtures of SCP and sensitizing SF_6 (total pressure 20 Torr). The unfocused radiation at both lines was of the same fluence (0.5 J cm^{-2}). The wavelength and fluence were checked by a model 16-A spectrum analyser (Optical Eng. Co.) and by a pyroelectric detector (ml-1 JU, Charles University).

Gaseous samples of SCP were irradiated in a Pyrex vessel (45 mm i.d., 10 cm length) equipped with two NaCl windows, a PTFE stopcock and a sleeve with a rubber septum. The cell accommodated metal substrates which after the irradiation of SCP were covered with solid deposited materials and transferred for measurements of their properties by SEM, FTIR and XPS. Changes in the composition of the gaseous content of the vessel after laser irradiation were monitored by an FTIR (Nicolet, model Impact 400) spectrometer. The depletion of SCP was followed using the diagnostic band at 2163 cm^{-1} . Some gaseous products (silane, ethene, ethyne, methane and buta-1,3-diene) were detected using the diagnostic absorption bands of these compounds. Identification of the gaseous products was also accomplished by GC/MS. The GC/MS and GC analyses of the gaseous samples after irradiation were performed on a Shimadzu QP 1000 mass spectrometer and Shimadzu 14A chromatograph with FID detector which was coupled with a Chromatopac C-R5A computing integrator. Both instruments were equipped with Porapak P and SE-30 columns and were operated at the programmed temperature (20–150°C) using helium carrier gas. The quantitative GC analyses were based on knowledge of the response factors for the identified products, which were determined or taken from ref. [8].

Real time studies of the IR multiphoton decomposition of SCP were carried out using experimental set-ups for monitoring laser-induced fluorescence (LIF) and spontaneous luminescence emission (SL) of the formed photofragments. For these studies, a Lumonics K-103 TEA CO_2 laser tuned to the 10P(14) line was employed to initiate the decomposition of gaseous SCP in Pyrex cells similar to that mentioned above but with a lateral quartz window to detect the LIF and SL emissions. At the low fluences obtained with unfocused geometry, the signal-to-noise ratio was not sufficient to collect the spectrum; real time detection of the fragments was therefore carried out at higher fluences using focused geometry. The CO_2 laser beam was focused at the centre of the cell with a 24 cm NaCl lens. The fluence was calculated as the ratio of the pulse energy, as measured with a Lumonics 20D pyroelectric detector, and the FWHM cross-sectional beam area, measured at the cell position with a pyroelectric array Delta Development Mark IV. The resulting fluence was ca. 20 J cm^{-2} . Fluorescence in the formed fragments was in-

duced by an N_2 -pumped dye laser (PRA LN107) with a bandwidth of 1.6 cm^{-1} at 580 nm. The dye laser beam, counter-propagating to the CO_2 laser beam, was focused by a 50 cm quartz lens at the focus of the IR laser. The SL and LIF signals were detected through the lateral window and focused onto an R928 Hamamatsu photomultiplier. The LIF excitation spectrum was collected through a Schott RG610 glass filter and the SL emission through the same filter for SiH_2 ($A^1B_1 \rightarrow X^1A_1$) detection and through an interference filter centred at 560 nm (10 nm FWHM) for the C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$) $\Delta v = -1$ Swan band detection.

The LIF signal could be detected only with low pressures of SCP (0.02–0.45 Torr). With higher SCP pressures, an intense visible spontaneous luminescence signal appears that makes detection of the induced fluorescence impossible. The appearance of the spontaneous luminescence background poses limits on the fluence that can be used in the irradiation of SCP for LIF detection.

The photoelectron spectra were acquired using ESCA 3 Mk II (VG Scientific) and ESCA 310 (Gammadata Scientia) electron spectrometers equipped with an Al- K_α X-ray source ($h\nu = 1486.6$ eV). The background pressure during spectra acquisition was typically of the order of 10^{-6} Pa. The spectrometers were operated in the fixed analyser transmission mode. Detailed spectral scans were taken over Si (2p), C (KLL) and Si (KLL) regions. The XPS peak positions and areas were determined by fitting the unsmoothed experimental spectra after subtraction of Shirley [9] background. The surface concentrations of elements were determined using theoretical photoionization cross-sections [10].

SEM and TEM studies of the deposits were carried out on an ultrahigh vacuum Tesla BS 350 instrument and a Philips 201 microscope.

SCP was prepared following the procedure in ref. [11] and its purity was better than 98% as checked by gas chromatography.

3. Results and discussion

The TEA CO_2 laser-induced decomposition of SCP carried out by irradiating SCP (10 Torr) in $\delta(\text{SiH}_2)$ mode (absorptivity of SCP at 950 cm^{-1} , 6.8×10^{-3} Torr $^{-1}$ cm^{-1}) is a much slower process than decomposition carried out by irradiating mixtures of SCP and SF_6 (each 10 Torr). In the former, IR multiphoton decomposition (IRMPD, e.g. [12,13]), SCP is vibrationally excited through direct absorption and a 30% decomposition of SCP is accomplished with as many as 6000 pulses. In the latter, laser-photosensitized decomposition (LPD, e.g. [14,15]), SCP is vibrationally excited mostly through collisions with better absorbing SF_6 (absorptivity of SF_6 at 946 cm^{-1} , 230 Torr $^{-1}$ cm^{-1})

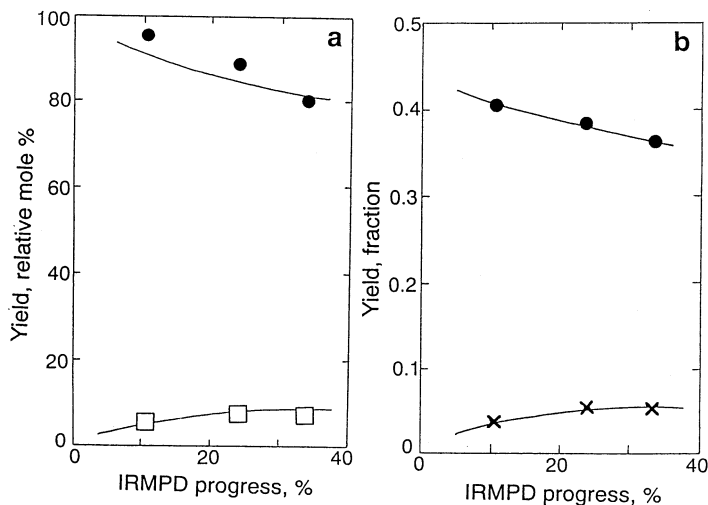


Fig. 1. Yield of gaseous products (in relative mole per cent (a) and in mole/mole of SCP decomposed (b)) at different stages of IRMPD of SCP. 1,3-C₄H₆ (●); C₂H₄ (□); C₂H₄ + C₂H₂ (×).

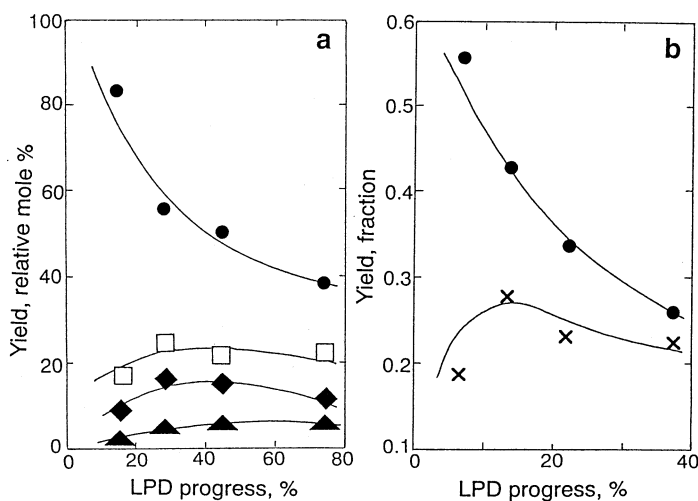


Fig. 2. Yield of gaseous products (in relative mole per cent (a) and in mole/mole of SCP decomposed (b)) at different stages of LPD of SCP. 1,3-C₄H₆ (●); C₂H₄ (□); C₂H₂ (◆); CH₄ (▲); C₂H₄ + C₂H₂ (×).

and the same 30% decomposition of SCP can be achieved with as few as 30 pulses of the same fluence.

3.1. Final products

Both processes result in the deposition of a faintly yellow solid deposit and in the formation of hydrocarbons, silane and 1-silyl-1-silacyclopent-3-ene. The relative amounts of hydrocarbons for both processes are different. In IRMPD, the distribution of the volatile products (in relative mole per cent) is as follows: buta-1,3-diene (80–96), buta-1,2-diene (< 1), ethene (5–8), ethyne (2–3), methane (< 1), propene (1–2), silane (2–3), 1-silyl-1-silacyclopent-3-ene (< 1). These values are hardly altered as the decomposition progresses, ca. 10–35%, buta-1,3-diene being the dominant product

(Fig. 1a). In LPD, the distribution of the volatile products (in relative mole per cent) is as follows: buta-1,3-diene (40–83), buta-1,2-diene (< 1), ethene (15–24), ethyne (10–16), methane (2–6), propene (2–4), silane (1–2), 1-silyl-1-silacyclopent-3-ene (1–2). These values are rather different; buta-1,3-diene is still a major product but it is accompanied with significant amounts of ethene and ethyne (Fig. 2a).

The distribution of the volatile products in IRMPD is similar to that observed in ArF laser-induced photolysis of SCP carried out in excess helium [7]. The dominant formation of buta-1,3-diene in the IRMPD proves the extrusion of silylene, and the presence of 1-silyl-1-silacyclopent-3-ene indicates insertion of silylene into SCP. The formation of silane can be explained by the secondary photolysis of 1-silyl-1-sila-

cyclopent-3-ene, since addition of H_2 to silylene is significantly slower than insertion of silylene into the Si–H bond [16,17]. The lower yields of buta-1,3-diene and higher yields of ethene and ethyne (and apparently of H_2) in LPD are in accordance with cleavage of buta-1,3-diene [18]. The distribution of the products (in mole/mole of SCP decomposed) reveals that the absolute yields of buta-1,3-diene in both IRMPD and LPD are rather small; thus only the 0.25–0.60 fraction of buta-1,3-diene along with a 0.20–0.27 fraction of C_2 products (ethene + ethyne) persist in the gas phase for LPD (Fig. 2b), and even smaller fractions of buta-1,3-diene (0.36–0.40) together with C_2 products (ca.

0.05) are observed in the gas phase for IRMPD (Fig. 1b).

These findings reveal that buta-1,3-diene (and perhaps also the C_2 products) must react with silylene and be involved in agglomeration reactions leading to the deposition of the solid product. They also show that the decomposition of buta-1,3-diene is less important and the agglomeration reactions of buta-1,3-diene are more feasible in IRMPD compared to LPD.

The assumed intermediate products of SCP decomposition are confirmed by the LIF spectra of the photofragments produced during IRMPD which was conducted at similar incident fluences.

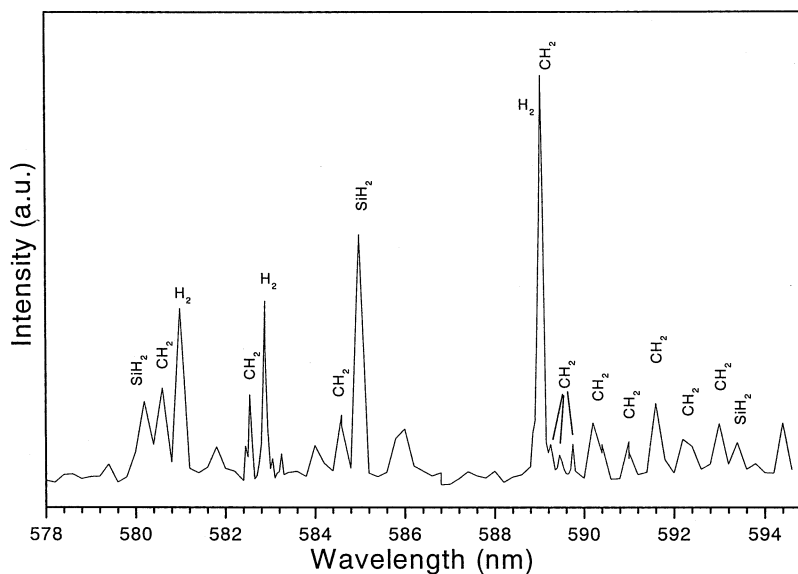


Fig. 3. Excitation spectrum in the 578–594 nm interval of the photofragments formed during IRMPD of 0.15 Torr of SCP.

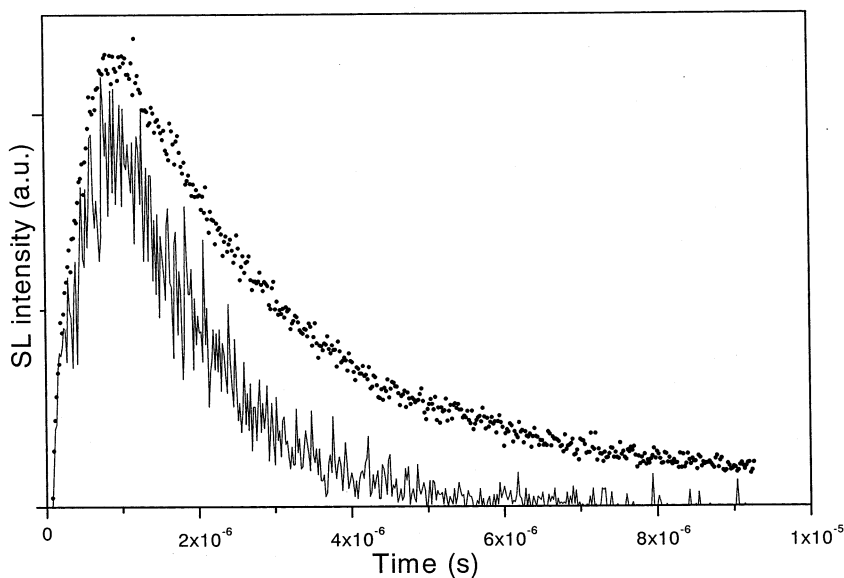
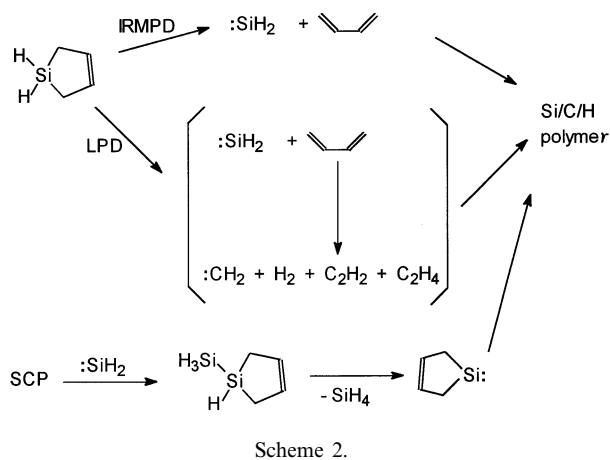


Fig. 4. Luminescence signals produced during IRMPD of 0.4 Torr of SCP: first shot (—), average of twenty shots (●).



3.2. Real time analysis of IRMPD of SCP

The LIF excitation spectrum in the 578–595 nm region is shown in Fig. 3. The spectrum, collected at a time delay between the pulses of CO₂ and dye lasers of 900 ns and at a pressure of 0.15 Torr of SCP, shows several vibro-rotational bands belonging to :SiH₂, :CH₂ and H₂. These bands were assigned to :SiH₂ [19,20], :CH₂ [21] and H₂ [22,23]. The bands centred at 580.2, 585.0 and 593.4 nm belong to the A¹B₁ ← X¹A₁ Δ*v* = 2 transition of the :SiH₂ fragment. For the :CH₂ species, several lines belonging to the P (591.6, 592.2 and 593 nm), Q (591 and 591.6 nm) and R (589.05, 589.25, 589.45 and 589.75 nm) branches of the ¹B₁(0,14,0) ← ¹A₁(0,0,0) transition and to the P (580.6, 582.5 and 584.6 nm) branch of the ¹B₁(0,16,0) ← ¹A₁(0,1,0) transition were found. The lines at 581 and 582.9 nm can be assigned to molecular hydrogen which also contributes, together with :CH₂, to the strong line at 589.05 nm.

A spontaneous visible luminescence signal is observed with the experiments carried out at high pres-

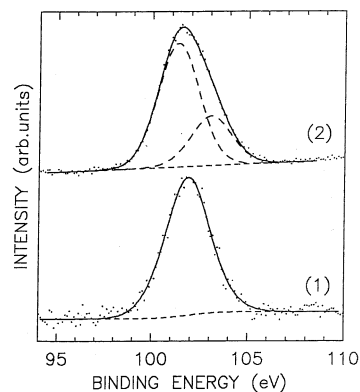


Fig. 6. Fitted photoelectron spectrum of Si 2p electrons of the films obtained by IRMPD (1) and LPD (2).

ures and/or high fluences. This signal was dispersed by placing a monochromator in front of the photomultiplier, but the background, probably originating from scattering of the luminescence in the depositing solid particles, did not allow resolution of the specific bands. It was observed (Fig. 4) that the profile of the SL changes becomes wider with more shots and that it is recovered only after some time is allowed to elapse. This behaviour is likely due to the different nature of the emission in the first and subsequent shots arising from an accumulation of products and their photolysis in the viewing region. The addition of Ar to SCP produces a large increase in the SL signal of H₂C: and an appreciable decrease in the SL signal of :SiH₂. These changes are consistent with the initial unimolecular production of :SiH₂ followed by collisional dissociation of the formed products giving rise to :CH₂.

3.3. Gas-phase chemistry

It is conceivable that the observed final and transient products can be reconciled with chemical reactions

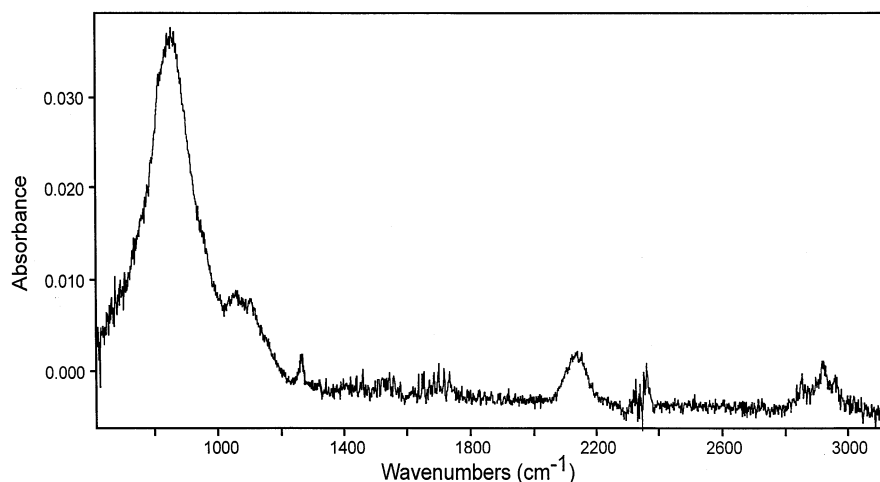


Fig. 5. Typical FTIR spectrum of the deposit from SCP.

described in Scheme 2, where SCP undergoes decomposition to silylene and buta-1,3-diene, and where the latter initial product decomposes into ethene, ethyne,

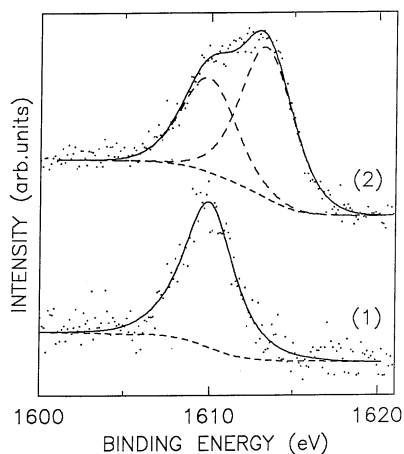


Fig. 7. Fitted photoelectron spectrum of Si KLL Auger electrons of the films obtained by IRMPD (1) and LPD (2).

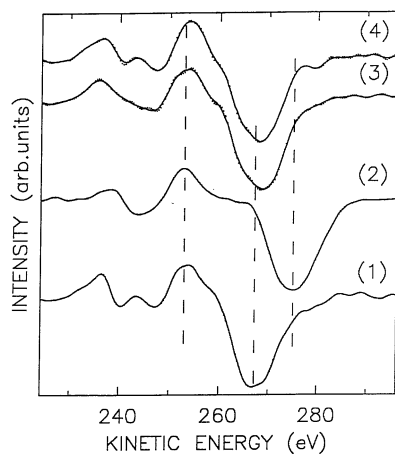


Fig. 8. C KLL derivative Auger spectra of (1) diamond, (2) graphite, (3) the deposit from LPD and (4) the deposit from IRMPD.

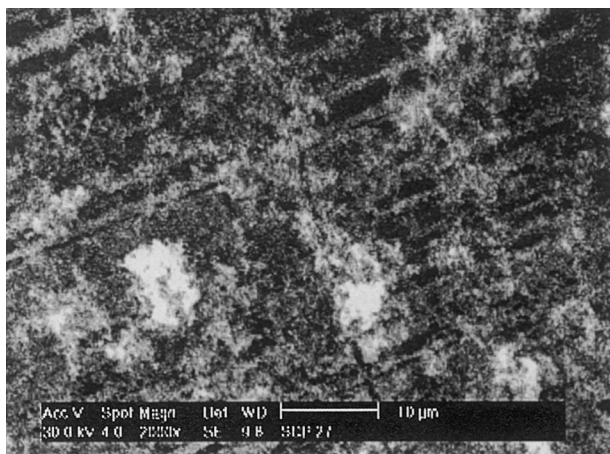


Fig. 9. Scanning electron micrograph of the deposit.

:CH₂ species and hydrogen. The observation of 1-silyl-1-silacyclopent-3-ene and silane among the volatile final products is in line with the insertion of silylene into the Si–H bond of SCP, and with secondary photolysis of 1-silyl-1-silacyclopent-3-ene into silane and silacyclopent-3-enylsilylene (see [16,17]). Other plausible reactions of silylene are those with unsaturated hydrocarbons. All of these contribute to the formation of Si–C–H polymers as confirmed by analysis of the solid material.

3.4. Properties of the solid deposit

The inference about the involvement of buta-1,3-diene and other unsaturated carbon species in the formation of the solid material is in line with the IR and XP spectral analysis of the solid deposit which is shown to contain Si, C and H atoms. The pattern of the IR spectrum (wavenumber (cm⁻¹) (normalized absorptivity)) is as follows: 850 (1), 1245 (ca. 0.075), 2150 (ca. 0.16) and 2930 (ca. 0.05). This does not differ if the films are produced by LPD or IRMPD (Fig. 5) and it can be assigned, in the given order, to $\nu(\text{Si}-\text{C})$, $\delta(\text{CH}_3\text{Si})$, $\nu(\text{Si}-\text{H})$ and $\nu(\text{C}-\text{H})$ vibrations. The absence of absorption bands belonging to the C=C or C≡C bonds indicates that the films can be described as completely saturated polycarbosilanes. The absorptivity at the $\nu(\text{Si}-\text{H})$ and $\nu(\text{C}-\text{H})$ vibrations is instructive of the distribution of H atoms between the Si and C centres [24]; the $A[\nu(\text{C}-\text{H})]:A[\nu(\text{Si}-\text{H})]$ ratio of the films of ca. 0.25–0.30 shows that the concentration of H(C) and H(Si) atoms is almost equal.

XPS analysis of the topmost (ca. 4 nm) layers of the deposit (Figs. 6 and 7) reveals that the films produced by IRMPD and LPD differ. The former possess exclusively silicon at 101.1 eV assignable to an Si–C–H polymer, whereas the latter are composed of silicon in the Si–C–H polymer (63%) and of silicon at 102.8 eV in an Si–O bond (27%) [25,26]. This indicates that the films produced by IRMPD are not oxidized in air when they are transferred from the reactor to the spectrometer. The development of the Si–O component can be attributed to a small concentration of unsaturated Si=C bonds in superficial layers (see for example refs. [27,28]) and to their oxidation in atmosphere by reaction with molecular oxygen [29]. The different propensity of the polycarbosilane to undergo oxidation indicates that the Si–C–H films from IRMPD do not contain significant concentrations of Si=C moieties, in contrast to those from LPD. Comparison of the C KLL Auger spectra of the deposits with those of diamond and graphite [30] reveals that the deposits from LPD and IRMPD possess solely sp³ carbon (Fig. 8) and this supports the conclusion drawn from the FTIR spectra.

SEM images of the deposits obtained from IRMPD and LPD have the same pattern (Fig. 9) and show that

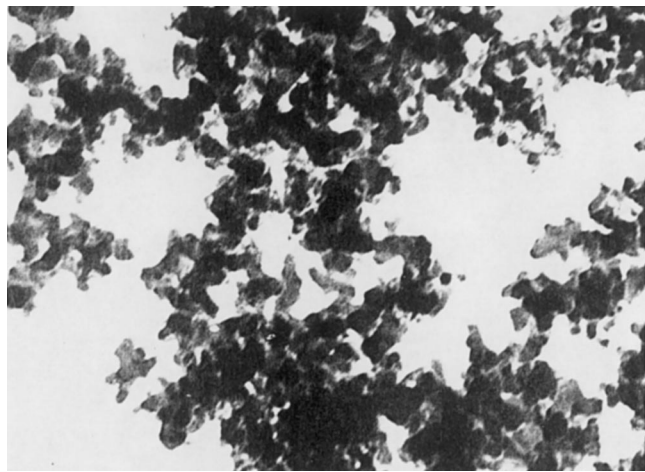


Fig. 10. Transmission electron micrograph of the deposit (magnification 100 000 \times).

these deposits have a particulate structure and consist of fluffy agglomerates. TEM analysis (Fig. 10) reveals that these agglomerates are composed of small chain-like structures several tens of nanometres in size.

4. Conclusion

The CO₂ laser induced IR multiphoton decomposition and photosensitized (SF₆) decomposition of gaseous SCP proceeded as extrusion of silylene and afforded buta-1,3-diene as a major volatile product. The other products of SCP decomposition (silylene, methylene and H₂⁻) were identified by laser induced fluorescence. The transient silylene does not self polymerize to poly(hydridosilanes), but takes part in agglomeration reactions with buta-1,3-diene and presumably with other unsaturated species such as ethene, ethyne and :CH₂. Buta-1,3-diene is utilized more for the formation of the solid polycarbosilane films in IRMPD, whereas in LPD it is more efficiently cleaved into ethene and ethyne. The topmost layers of the films obtained by LPD, but not those of the films obtained by IRMPD, are oxidized upon contact to air.

Acknowledgements

The work was supported by the Grant Agency of the

Czech Republic (grant no. 104/00/1294) and by Spanish DGES (project no. PB96-0844-C02-02).

References

- [1] E.A. Chernyshev, N.G. Kovalenkova, S.A. Bashkurova, J. Organomet. Chem. 271 (1984) 129.
- [2] D. Lei, P.P. Gaspar, Organometallics 4 (1985) 1471.
- [3] M.G. Steinmetz, C. Yu, Organometallics 11 (1992) 2686.
- [4] D.S. Rogers, H.E. O'Neal, M.A. Ring, Organometallics 5 (1986) 1467.
- [5] P.P. Gaspar, in: H. Sakurai (Ed.), Organosilicon and Bioorganosilicon Chemistry, Horwood, Chichester, 1985, p. 88.
- [6] I.M.T. Davidson, in: E.R. Corey, J.Y. Corey, P.P. Gaspar (Eds.), Silicon Chemistry, Horwood, Chichester, 1988, p. 173.
- [7] J. Pola, A. Ouchi, M. Urbanova, Y. Koga, Z. Bastl, J. Šubrt, J. Organomet. Chem. 575 (1999) 246.
- [8] W.A. Dietz, J. Gas Chromatogr. 49 (1967) 151.
- [9] D.A. Shierly, Phys. Rev. B 5 (1972) 4709.
- [10] J.H. Scofield, J. Electron. Spectrosc. 8 (1976) 129.
- [11] R. Damrauer, R. Simon, A. Laporterie, G. Manuel, Y.T. Park, W.P. Weber, J. Organomet. Chem. 391 (1990) 7.
- [12] C.D. Cantrell (Ed.), Multiple-Photon Excitation and Dissociation of Polyatomic Molecules, Springer, Berlin, 1986.
- [13] R.V. Ambartzumian, S.V. Letokhov, in: C.B. Moore (Ed.), Chemical and Biochemical Applications of Lasers, vol. 3, Academic Press, New York, 1987.
- [14] D.K. Russel, Chem. Soc. Rev. 19 (1990) 407.
- [15] J. Pola, Spectrochim. Acta A 46 (1990) 607.
- [16] J.M. Jasinski, R. Becerra, R. Walsh, Chem. Rev. 95 (1995) 1203.
- [17] J.G. Martin, H.E. O'Neal, M.A. Ring, Int. J. Chem. Kinet. 22 (1990) 613.
- [18] J.H. Kiefer, K.I. Mitchell, H.C. Wei, Int. J. Chem. Kinet. 17 (1985) 225.
- [19] I. Dubois, Can. J. Phys. 46 (1968) 2485.
- [20] M. Fukushima, S. Mayama, K. Obi, J. Chem. Phys. 96 (1992) 44.
- [21] G. Herzberg, J.W.C. Johns, Proc. R. Soc. London Ser. A 295 (1966) 107.
- [22] G. Herzberg, Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules, Van Nostrand, New York, 1950.
- [23] H.G. Gale, G.S. Monk, K.O. Lee, Astrophys. J. 67 (1928) 89.
- [24] H.C. Low, P. John, J. Organomet. Chem. 201 (1980) 363 and refs. therein.
- [25] IST X-ray Photoelectron Spectroscopy Database, US Department of Commerce, NIST, Gaithersburg, MD, 1997.
- [26] M. Urbanová, H. Morita, V. Drinek, Z. Bastl, J. Šubrt, J. Pola, J. Anal. Appl. Pyrol. 44 (1998) 219.
- [27] J. Pola, Z. Bastl, J. Šubrt, R. Taylor, J. Mater. Chem. 5 (1995) 1345.
- [28] J. Pola, Z. Bastl, J. Šubrt, R. Abeyasinghe, R. Taylor, J. Mater. Chem. 6 (1966) 155.
- [29] I.M.T. Davidson, C.E. Dean, F.T. Lawrence, J. Chem. Soc. Chem. Commun. (1981) 52.
- [30] J.C. Lascovich, R. Giorgi, S. Scaglione, Appl. Surf. Sci. 47 (1991) 17.