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UV laser-induced photolysis of silacyclopent-3-ene: unseparable photochemistry of reactant and product for chemical vapour deposition of Si/C/H polymer

Josef Pola [a],*, Akihiko Ouchi [b], Markéta Urbanová [a], Yoshinori Koga [a], Zdeněk Bastl [c], Jan Šubrt [d]

[a] *Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojova Str. 135, 16502 Prague 6, Czech Republic*
[b] *National Institute of Materials and Chemical Research, AIST, MITI, Tsukuba, Ibaraki 305, Japan*
[c] *J Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 18223 Prague 8, Czech Republic*
[d] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Řež near Prague, Czech Republic*

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Abstract

UV laser-induced photolysis of silacyclopent-3-ene in the gas phase is a clean extrusion of silylene yielding buta-1,3-diene. Silylene self-polymerisation and consequent deposition of Si_nH_{2n} agglomerates is precluded by concurrently occurring photolysis of buta-1,3-diene. The solid polymeric deposit being produced through polymerisation steps involving both H_2Si: and the products of the buta-1,3-diene photolysis makes the reaction suitable for chemical vapour deposition of Si/C/H films. © 1999 Elsevier Science S.A. All rights reserved.

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

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1. Introduction

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

The extent of these paths depends on the substituents at the silicon: while the extrusion of $(CH_3)_2Si$: from methyl-substituted silacyclopent-3-enes is accompanied with formation of the rearranged products (silacyclopent-2-enes and siladienes) [2,5], the addition of $H(CH_3)Si$: to buta-1,3-diene (the inverse of the decomposition of 1-methyl-1-silacyclopent-3-ene) gives only 1-methyl-1-silacyclopent-3-ene [6], and both addition of Cl_2Si: to 1,3-dienes [1] and thermal decomposition 1,1-dichloro-1-silacyclopent-3-enes [1] are not involved in the rearrrangement at all. The decomposition of the parent silacyclopent-3-ene (SCP), which has not been yet studied, might occur only as an extrusion of H_2Si: and thus serve as a clean source of silylene.

The H_2Si: species was earlier generated and spectroscopically identified in the lamp, UV and IR laser photolysis of $RSiH_3$ (R = H, alkyl, phenyl), Si_nH_{2n+2} ($n = 1-3$) and H_3SiI compounds [7] and transiently produced [8] in thermolysis of Si_nH_{2n+2} ($n = 1-4$) and $RSiH_3$ (R = H, alkyl, phenyl, alkenyl and alkynyl) compounds (e.g. Refs. [8–15]). Its gas-phase reactivity has been the subject of intensive research (e.g. Refs. [9,16]); it has been assessed [17] that the self-reaction into $H_2Si{=}SiH_2$ and $H_3Si(H)Si$: as well as the H_2Si: polymerisation have a zero activation barrier and are accompanied by disilene and silylsilylene dehydrogenation. The latter steps partly occur on a hot reactor surface [18] and impair formation of yet uncom-

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* Corresponding author. Tel.: +42-2-24311498; fax: +42-2-20920661; e-mail: pola@icpf.cas.cz.

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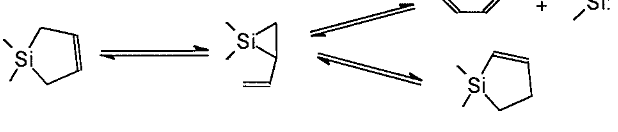
mon saturated poly(hydridosilanes). Consequently, a-Si:H films prepared by thermally-, plasma- and laser photolysis-assisted decomposition of silanes (e.g. Refs. [19–21]) are poor in H and those of the highest H content possess 40–50 at. %H at most [22–24]. Also, a-Si:H films produced with 185 nm light at heated substrate contain [25] less hydrogen and have the SiH_2/SiH bond density ratio below 0.6. The dehydrogenative steps were considered not to occur in VUV (147 nm) gas-phase photolysis of silane or disilane in a cold reactor [26,27], but the films obtained in this photolysis were not characterised.

Presuming that UV photolysis of gaseous SCP in a cold-wall reactor using high intensity laser radiation can afford high concentrations of H_2Si: and result in deposition of rare poly(hydridosilanes) Si_nH_{2n}, we examined ArF laser-induced photolysis of gaseous SCP and report here on its mechanism and the nature of the deposited material.

2. Experimental details

Laser photolysis experiments were carried out in a reactor which was equipped with a sleeve with rubber septum and PTFE valve, and consisted of two orthogonally positioned Pyrex tubes, one fitted with two quartz windows and the other furnished with two NaCl windows. SCP (20 Torr) was irradiated at a repetition frequency of 10 Hz by pulses from an ArF (Lambda Physik LPX 200 or ELI 94) laser at an incident fluence of 10 mJ cm^{-2} effective on the area of 1 cm^2. The progress of the photolysis was monitored by FTIR spectroscopy (a Shimadzu FTIR 4000 spectrometer) using an absorption band of SCP at 670 and 840 cm^{-1}, and by gas chromatography on a Gasukuro Kogyo 370 chromatograph (programmed temperature 30–150°C, a 60 m long capillary Neutra Bond-1 and 2 m long SUS Unipak S columns) connected with a Shimadzu CR 5A Chromatopac data processor. Some GC analyses were performed on a Shimadzu (GC 14 A chromatograph equipped with 1 m long Porapak P column and a C-R5A Chromatopac data processor). Identification of gaseous products was accomplished by means of the gas chromatography and GC/MS technique (a Shimadzu QP-1000 mass spectrometer). Properties of the deposits on KBr, quartz and Co substrates accommodated in the reactor were measured by FTIR spectroscopy, X-ray photoelectron spectroscopy (a VG ESCA 3 MK II electron spectrometer), transmission electron spectroscopy (a Philips 201 microscope) and scanning electron microscopy (a Tesla BS 350 ultra high vacuum instrument).



Scheme 1.

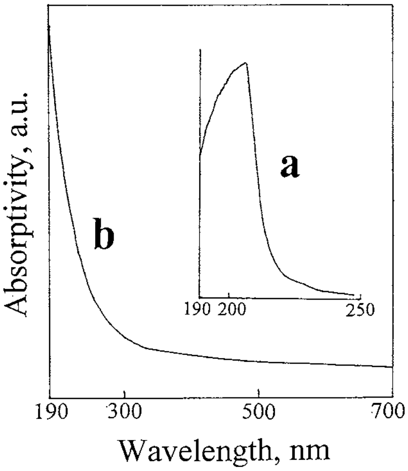


Fig. 1. UV–vis absorption spectrum of gaseous SCP (a) and of the thin film of deposit obtained by ArF laser photolysis of SCP (b).

SCP was prepared using the procedure described in the literature [28] and its purity (> 98%) was checked by gas chromatography.

3. Results and discussion

The ArF laser-induced photolysis of gaseous SCP was achieved by tuning radiation into the absorption band (Fig. 1a) centered at 207 nm ($\varepsilon = 1.43 \times 10^{-2}$ $torr^{-1}$ cm^{-1}). It results in the formation of volatile hydrocarbons, silane (traces) and 1-silyl-1-silacyclopent-3-ene [*m*/*z* (relative intensity): 114(19), 113(12), 85(13), 84(15), 83(100), 82(79), 81(34), 69(12), 67(14), 58(16), 57(22), 56(13), 55(46), 54(15), 53(24), 43(20), 29(16), 28(12)] and in deposition of a white solid which coats the inside of the reactor close to the front quartz window. The film is opaque to the 193 nm radiation (Fig. 1b) and detrimental to the photolytic progress: thus only 30% decomposition can be achieved by a prolonged irradiation (ca. 6×10^3 pulses) utilizing both quartz windows.

The hydrocarbon products distribution (in relative mole %)—buta-1,3-diene (60–90), buta-1,2-diene (< 5), ethane (8–22), ethene (5–8) ethyne (1–4), propane and methane (both < 1)—varies at different photolysis stages (Fig. 2a). The main product being buta-1,3-diene reveals that the major decomposition channel of SCP is extrusion of silylene. The observation of 1-silyl-silacyclopent-3-ene and silane confirm this view, since these are the products of silylene reaction with SCP and H_2, respectively. The availability of hydrogen in the system can be explained by 1,1-H_2 elimination, the path common for decomposition of organylsilanes [8–15]. Silane being a very minor product (its amounts are comparable to those of methane) confirms that this channel is negligible. However, amounts of 1-silyl-1-silacyclopent-3-ene range within 10–30% photolytic progress between 35 and 45% of those of buta-1,3-diene and reveal that the insertion of silylene into SCP is an important step.

Ethyne and methanol are efficient trapping reagents of silylene [4], but ArF laser irradiation of SCP (20 torr) in excess of these compounds (110 torr of methanol or 250 torr of ethyne, conditions similar to those suitable for scavenging reactive silenes [29,30]) revealed no formation of silylene products with these traps. The deposit formation not being impeded may imply that the products of trapping may themselves polymerise or be decomposed to polymer.

The amounts of the C_1–C_3 hydrocarbons and buta-1,2-diene slightly increase in the course of the photolysis while amounts of buta-1,3-diene diminish. The former hydrocarbons are identical to the products of UV photolysis of buta-1,3-diene [31–33] which takes place via (i) isomerisation into buta-1,2-diene and subsequent cleavage into CH_3 and C_3H_3 radical, (ii) decomposition into C_2H_4 and C_2H_2 couple, (iii) decomposition into vinylacetylene and H_2 and (iv) polymerisation [32,34]. They thus confirm that 1,3-butadiene does not survive under photolytic conditions and that its photolysis is a concurrent process. The products observed in the SCP photolysis can thus be rationalised in terms of Scheme 2.

Concurrent photolysis of buta-1,3-diene during the SCP photolysis is harmful to achieving chemical vapour deposition of pure Si_nH_{2n} polymer. The UV photopolymerisation of buta-1,3-diene is judged to involve reactions of volatile primary products of buta-1,3-diene photo-decomposition [34], which implies that the uncontaminated Si_nH_{2n} polymer can only be deposited when the photolysis of buta-1,3-diene has ceased.

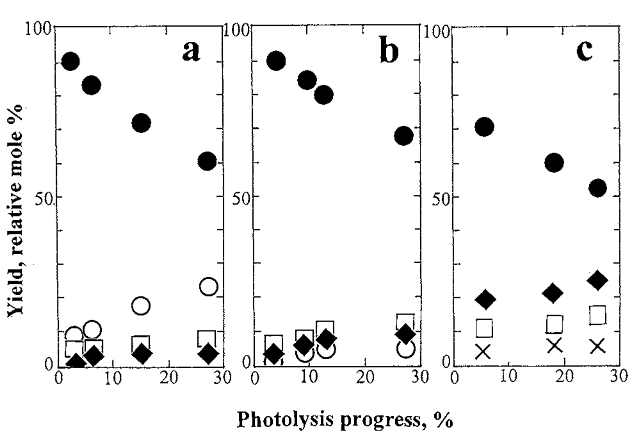
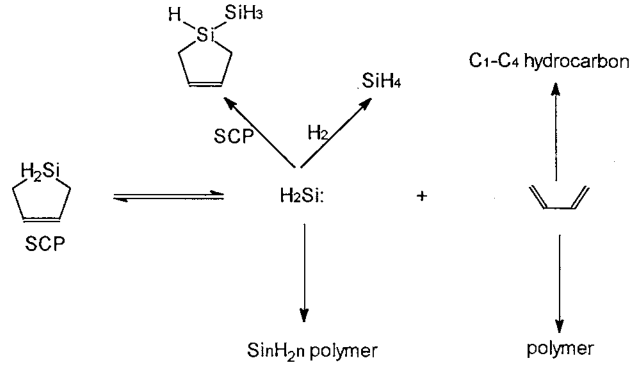


Fig. 2. Gaseous product yield (in relative mole percent) at different stages of SCP photolysis carried out without added gas (a) and in excess of He (b) and N_2 (c). C_4H_6 (●); C_2H_6 (○); C_2H_4 (□); C_2H_2 (◆); $CH_3CH{=}C{=}CH_2$ (×).



Scheme 2.

In an effort to reduce 1,3-butadiene decomposition, the SCP photolysis was carried out in excess of helium or nitrogen. In excess of helium (500 torr), more buta-1,3-diene and less hydrocarbons are obtained, which is in accord with collisional stabilisation of buta-1,3-diene. Ethane being not the major component among the hydrocarbons (Fig. 2b) indicates that the cleavage of buta-1,2-diene into CH_3 and C_3H_3 radicals is somewhat reduced. In excess of nitrogen (200 torr) (Fig. 2c), buta-1,3-diene is not as favoured as in the excess of helium; in this case no ethane, more ethyne and some 1,2-butadiene is produced. This is in line with less decomposition of buta-1,2-diene. The observed changes in relative amounts of buta-1,3-diene and of its decomposition products are, however, rather small and indicate that separation of the photochemistry of SCP and of that of buta-1,3-diene is not possible.

This inference is in accord with the IR spectral pattern of the deposits which is the same regardless of the extent of the photolysis and whether or not the photolysis is carried out in the presence of the inert gas. In all the instances, it consists of bands at ν (cm^{-1}): 855m (ν(Si–C)), 950m (δ(Si–H)), 1070m (ν(Si–C–Si) and/or ν(Si–O)), 2130–2150s (ν(Si–H)) and 2920w (ν(C–H)) and is in accord with a polymer possessing H_2Si groups in a Si/C/H skeleton. It is known [35] that more carbon incorporation in the Si–Si framework shifts the ν(Si–H) wavenumber to higher values and that the films showing ν(Si–H) at 2130 cm^{-1} correspond to a-$Si_{1-x}C_x$:H films with carbon content $x > 0.8$. The absorptivity at the ν(Si–H) and ν(C–H) vibrations is instructive of the distribution of H atoms between Si and C centers [36]; the Aν(C–H):Aν(Si–H) ratio of the deposits being 0.21–0.26 is in keeping with roughly equal concentrations of H(C) and H(Si) atoms.

XPS analysis of the topmost (ca. 5 nm) layers of the deposit (Fig. 3) reveals that the Si 2p core level spectrum is best fitted with contributions of two components, the major at 101.1 eV belonging to a Si/C/H polymer and the minor at 102.5 eV assignable to a Si–O bond [37,38]. The curve fitting procedure reveals

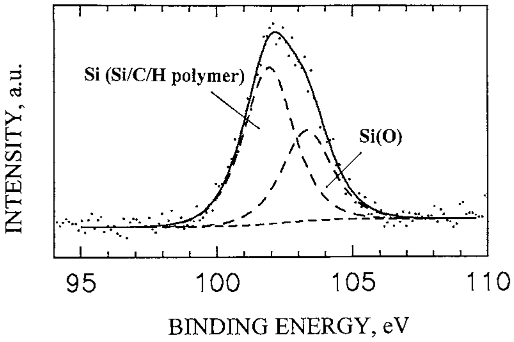


Fig. 3. Fitted photoelectron spectrum of Si 2p electrons.

that an incorporation of the contribution of the a-Si:H component at ca. 99.3 eV is not needed. These data thus rule out the presence of $(H_2Si)_n$ groupings in the polymer and confirm that the solid deposit is produced through polymerisation steps involving both H_2Si: and products of the buta-1,3-diene photolysis. Incorporation of oxygen in the superficial layers indicates deposit reactivity towards ambient atmosphere.

SEM analysis reveals that the deposits have a structure of tightly bonded agglomerates of ca. 1 μm size (Fig. 4), and TEM analysis proves that these agglomerates can be described as a net of ca. 20 nm sized dots (Fig. 5).

The films are not soluble in common organic solvents (benzene, dichloromethane, tetrahydrofuran), which indicates a high degree of cross-linking. They exert excellent adhesion strength to glass and metals and can be scrubbed off the substrates with difficulty.

We conclude that the UV laser photolysis of SCP can be described as a clean extrusion of silylene accompanied by photolysis of the major product, butadiene. The use of the SCP photolysis as a source of Si_nH_{2n} polymer is obstructed by concomittantly occurring photolysis of buta-1,3-diene. The IR spectral pattern of the films deposited by UV laser photolysis of SCP is similar to that of the a-SiC:H films deposited from other organosilicon progenitors through their IR laser photolysis (e.g. [39,40]). The ArF laser photolysis of SCP can be used as a low-temperature chemical vapour deposition of a-SiC:H films possessing high adhesion strength despite the substrates being kept at ambient temperature.

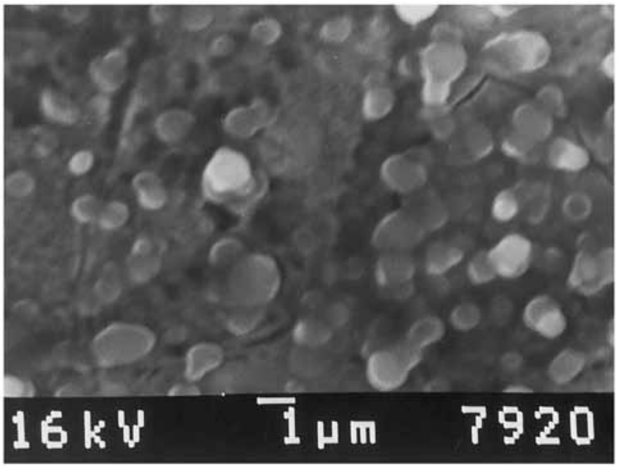


Fig. 4. SEM spectrum of the deposit.

Fig. 5. TEM spectrum of the deposit (magnification × 100 000).

Acknowledgements

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