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UV laser photolysis of silacyclopent-3-ene: effect of admixtures on nature of chemically vapour-deposited organosilicon films

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Examination of ArF laser-induced gas-phase photolysis of silacyclopent-3-ene, occuring as extrusion of silylene, in the presence of admixtures reveals that photolysis is not interfered with in the presence of N_2, CO and CO_2, but it is in the presence of O_2, 2-C_4F_8, CH_3OH, CD_3OH, CF_3CH_2OH and CH_3CO_2H. Formation of volatile products and solid deposited films incorporating fluorine or oxygen atoms is interpreted in terms of reactions of silylene with the admixtures. Copyright © 2002 John Wiley & Sons, Ltd.

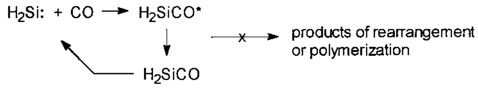
KEYWORDS: chemical vapour deposition; organosilicon films; laser photolysis; silacyclopent-3-ene

INTRODUCTION

Silylenes are important intermediates in organosilicon chemistry. They undergo a number of reactions, such as insertion into Si—H, Si—OR, and O—H bonds, as well as addition to alkenes and akynes.[1–4] The occurrence of these reactions was first proved experimentally by identification of end-products, and later by time-resolved kinetic studies.[5–7]

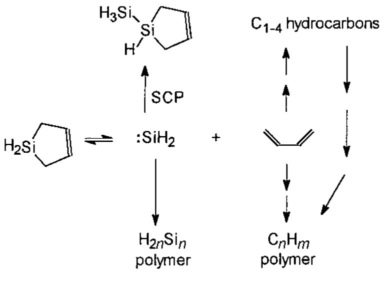
Recent time-resolved studies[8–12] on silylene reactions with oxygen-containing molecules were explained as initiated by an attack of H_2Si: to the oxygen centre, this interaction getting support from *ab initio* calculations and fits of kinetic data with RRKM (Rice, Ramsperger, Kassel and Marcus) modelling assuming transition states leading to a three-membered 3,3-dimethylsiloxirane.

Silylene generated by UV laser photolysis of phenylsilane was described[11,12] to undergo an association reaction with CO facilitated by a third body and yielding a $H_2Si{\cdot}CO$ adduct (possibly silaketene) that underwent reversion to the initial reactants. This description relying on *ab initio* and RRKM calculations fitting the kinetic data rejected other possible routes, such as $H_2Si{\cdot}CO$ polymerization and rearrangements (Scheme 1), but was not supported by the analysis of final products.



Scheme 1.

We have recently studied IR[13] and UV[14] laser photolysis of silacyclopent-3-ene (SCP) and described the UV laser-induced reaction as an extrusion of silylene and yielding buta-1,3-diene together with solid polycarbosilane originated from co-polymerization of silylene and products of concurrent photolysis of buta-1,3-diene. This major route is accompanied by insertion of silylene into SCP to yield 1-silyl-1-silacyclopent-3-ene (minor route) (Scheme 2).



Scheme 2.

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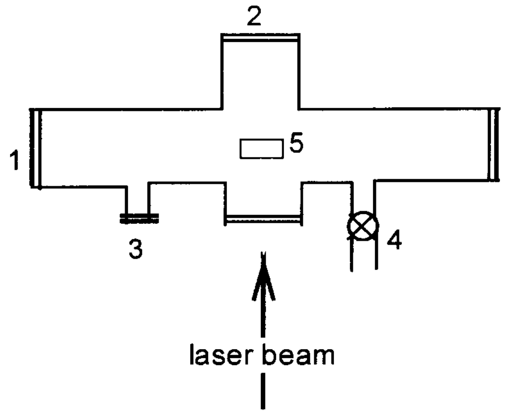


Figure 1. Pyrex reactor. 1, KBr window; 2, quartz window; 3, rubber septum; 4, PTFE valve; 5, KBr substrate.

Part of this examination was UV laser photolysis of SCP in the presence of some admixtures, which we now report. We show that the final products of the SCP photolysis are virtually the same when silylene is generated in the presence of CO and CO_2, that solid polycarbosilane obtained in the presence of 2-perfluoropropene incorporates fluorine, and that that obtained in the presence of molecular oxygen, methanol, methanol-*d*$_3$, 1,1,1-trifluoroethanol or acetic acid contains oxygen. These findings contribute to laser chemical vapour deposition studies of organosilicon films and show that reactions of silylene with the admixtures modify properties of the deposited organosilicon film. They also give support to the decomposition of the $H_2Si{\cdot}CO$ adduct solely into H_2Si: and CO[12] and show the lack of irreversible reaction between H_2Si and CO_2.

EXPERIMENTAL

Laser photolysis of SCP (20 Torr) in the presence of CO, CO_2 or N_2 (total pressure 790 Torr) and in the presence of CH_3OH, CD_3OH, CF_3CH_2OH, $CF_3CF{=}CFCF_3$ and CH_3CO_2H (all 20 Torr) and N_2 (total pressure 760 Torr) or of O_2 (180 Torr) were carried out in a Pyrex reactor (Fig. 1) equipped with a sleeve with a rubber septum and PTFE valve, and which consisted of two orthogonally positioned tubes, one fitted with two quartz windows and the other furnished with two NaCl windows. The ArF (ELI 94 model) laser operated at 193 nm with a repetition frequency of 10 Hz and an incident energy of 90 mJ effective on an area of 2 cm^2. The reactor contained a KBr substrate whose position could be changed from horizontal (parallel to the laser beam) to vertical (perpendicular to the infrared spectrometer beam). The progress of the photolysis was monitored by periodically removing the reactor and placing it in the cell compartment of the FTIR (Nicolet impact) spectrometer. The depletion of SCP was followed at its diagnostic absorption band at 862 cm^{-1} and the accumulation of volatile products was monitored by FTIR spectroscopy and gas chromatography (GC; a Shimadzu GC 14A chromatograph coupled with a Chromatopac C-R5A computing integrator, Porapak P column, programmed 20–160 °C temperature, helium carrier gas). The volatile products were identified on a Shimadzu model QP 1000 quadrupole mass spectrometer (ionizing voltage 70 eV). Quantitative analysis of the volatile products relied on knowledge of the flame ionization detector (FID) response factors of the authentic samples that were taken from our stock.

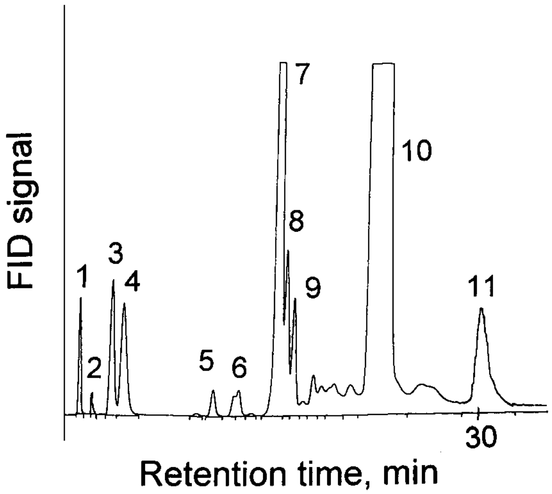


Figure 2. Typical GC trace of SCP–N_2 mixture photolysed by ArF laser. Porapak P column, peak designation: 1, methane; 2, silane; 3, ethene; 4, ethyne; 5, propene; 6, allene; 7, buta-1,3-diene; 8, buta-1,2-diene; 9, 1-buten-3-yne; 10, SCP; 11, 1-silyl-1-silacyclopent-3-ene.

FTIR spectra of solid films deposited from the gas phase on the KBr substrates were obtained after withdrawal of gaseous samples for GC and GC–Mass Spectrometry analyses and evacuation of the reactor. FTIR spectra of the deposited films in contact with air were also measured.

SCP was prepared using the procedure described in the literature.[15] The purities of all the compounds used were checked by GC.

RESULTS AND DISCUSSION

Photolysis of SCP in N_2

The ArF laser photolysis of gaseous SCP in excess of N_2 was achieved by irradiation into an absorption band centred at 207 nm ($\varepsilon = 1.4 \times 10^{-2}$ $Torr^{-1}$ cm^{-1}). It results in the formation of volatile hydrocarbons, silane and 1-silyl-1-silacyclopent-3-ene and in deposition of a white solid that coats the inner surface of the reactor. The film is opaque to 193 nm radiation and, being also deposited on the quartz window, it inhibits photolysis progress; thus, only ~30% photolysis is accomplished by firing *ca* 5×10^3 pulses and utilizing both quartz windows of the reactor. The observation of 1-silyl-1-

Table 1. UV laser photolysis[a] of SCP

		Volatile products							
		Hydrocarbons (relative mol%)							
Irradiated mixture	Admixture depletion (%)	CH_4	C_2H_4	C_2H_2	C_3H_6	C_3H_4	1,3-C_4H_6	C_4H_x[c]	Other[b]
SCP + N_2	0	<5	<12	15	<2	<2	56	9	–
SCP + CO + N_2	0	7	9	11	1	2	60	10	–
SCP + CO_2 + N_2	0	<1	<9	12	<1	1	72	4	–
SCP + 2-C_4F_8 + N_2	2	<2	10	27	–[d]	–[d]	52	9	(C_3F_5H and $SiC_2F_4H_2$)[e]
SCP + CH_3OH + N_2	7	3	14	20	<1	3	44	15	CH_3CHO[f] CO
SCP + CD_3OH + N_2	15	2	11	18	<1	<3	50	14	CH_3CHO[f] CO
SCP + CF_3CH_2OH + N_2	8	<2	12	20	1	2	62	–[d]	CO
SCP + CH_3CO_2H + N_2	16	3	14	23	<1	<4	43	11	$(H_3Si)_2O$, $HC{\equiv}CCHO$, CO_2, CH_3OH, $H_3CC(O)OSiH_3$[g]
SCP + O_2		<2	15	25	<1	<3	55		C_6H_6, $CH_3{\cdot}C_6H_5$

[a] Conditions: see Experimental, photolysis progress *ca* 30%.

[b] Silane and 1-silyl-1-silacyclopent-3-ene produced in all runs are not noted.

[c] 1,2-Butadiene, 1-buten-3-yne, 1-butyne and 2-butyne.

[d] Cannot be determined due to GC interference of admixture.

[e] Mixture; tentative assignment on basis of mass spectrum (*m/z*: 132, 113, 101, 86, 84, 82, 66, 47, 31).

[f] Amounts comparable to those of methane.

[g] Tentative assignment on basis of mass spectrum [*m/z* (relative intensity): 90 (1), 75 (100), 43 (65)].

Table 2. UV laser photolysis of SCP: FTIR spectra of solid phase[a]

	Wavenumber (cm^{-1})/relative absorbance[b]				
Irradiated mixture	$\nu(Si-C) + \delta(H_xSi)$	$\nu(SiO)$	$\nu(Si-H)$	$\nu(C-H)$	$\nu(C-F)$
$SCP + N_2$	764/0.70, 806/1.20, 858/0.80, 950/0.60	1097/0.05	2131/1.0	2887/0.16	–
$SCP + CO$	766/0.47, 813/0.63, 860/0.63, 950/0.55	1095/0.09	2133/1.0	2906/0.16	–
$SCP + CO_2$	764/0.28, 813/0.42, 858/0.40, 951/0.45	1097/0.07	2131/1.0	2887/0.14	–
$SCP + 2\text{-}C_4F_8 + N_2$	762/0.43, 812/0.44, 858/0.68, 950/0.57	1097/0.15	2131/1.0	2914/0.18	1097/0.19 1192/0.16 1284/0.13
$SCP + O_2$	858/1.56, 940/1.13, 977/1.0	1078/3.10	2153/1.0	2923/0.21	–
$SCP + CH_3OH + N_2$	858/0.96, 953/0.78	1089/1.33	2144/1.0	290160.19	–
$SCP + CD_3OH + N_2$	860/0.71, 953/0.69	1095/0.91	2146/1.0	2918/0.20	–
$SCP + CF_3CH_2OH + N_2$	858/0.84, 953/0.80	1093/1.00	2144/1.0	2906/0.17	–
$SCP + CH_3CO_2H + N_2$	710/1.0, 833/4.3, 943/1.63, 978/1.64	1064/>4.7	2188[c]/1.0	2918/0.19	–

[a] Assignment after Ref. 27.

[b] $A_{\nu(Si-H)}$.

[c] Band split to contributions at 2237, 2188 and 2156 cm^{-1}.

silacyclopent-3-ene and silane indicates reactions of silylene with SCP and H_2. The availability of hydrogen is compatible with some 1, 1-H_2 elimination of SCP, which is a common route for the decomposition of alkylsilanes.[16,17]

With 30% SCP decomposition, the main product is buta-1,3-diene, and minor products are ethyne, ethene and methane, along with C_3H_4 hydrocarbons, 1,2-butadiene and 1-buten-3-yne (Fig. 2, Table 1). The C_1–C_4 hydrocarbons are identical to products of UV photolysis of buta-1,3-diene, which takes place[18–20] via: (i) isomerization into buta-1,2-diene and subsequent cleavage into CH_3 and C_3H_3 radicals; (ii) decomposition into a C_2H_4 and C_2H_2 couple; (iii) decomposition into 1-buten-3-yne and H_2; and (iv) polymerization.[19,21] The presence of these hydrocarbons thus confirms that buta-1,3-diene does not survive under photolytic conditions and that its photolysis is a concurrent process. The volatile and solid products can thus be rationalized in terms of Scheme 2, showing that chemical vapour deposition of the solid films involves reactions of silylene and species produced by buta-1,3-diene photolysis.

Rate constants for silylene additions to buta-1,3-diene and insertion into the Si—H bond are somewhat higher[5,7] than those for addition of silylene to ethyne and ethene. High concentrations of SCP and buta-1,3-diene and low concentrations of C_1–C_4 hydrocarbons therefore make reactions between silylene and buta-1,3-diene or SCP (resulting in the respective formation of the initial SCP and of the observed 1-silyl-1-silacyclopent-3-ene) more important than reactions between silylene and C_1–C_4 hydrocarbons (ethyne, ethene, 1,2-butadiene, 1-buten-3-yne). It is thus conceivable that the solid polycarbosilane films are produced mostly by (i) polymerization of silylene, (ii) polymerization of the photolysis products of buta-1-3-diene, and (iii) co-polymerization of silylene and products of buta-1,3-diene polymerization, but not *via* initial addition of silylene to minor olefins[16,22–24] (C_2H_4, C_2H_2, C_3H_4, C_3H_6, C_4H_4) and subsequent UV photolysis of the produced alkenyl- or alkyl-silanes.[25]

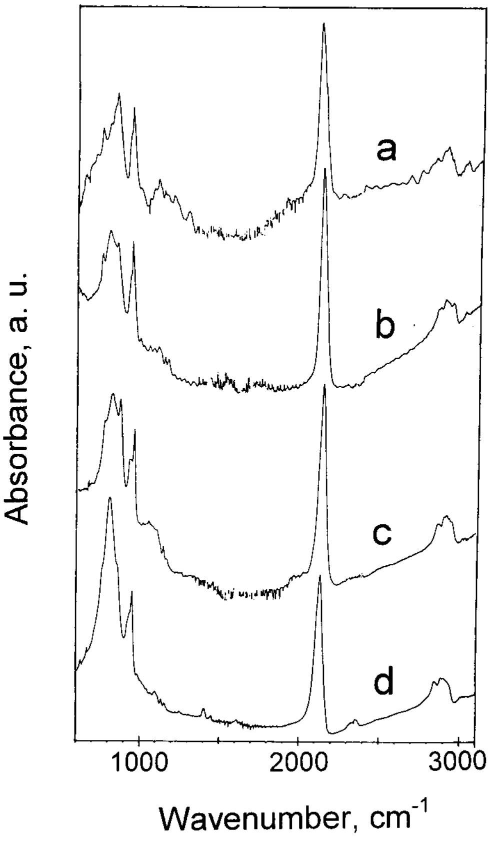


Figure 3. FTIR spectra of the deposit obtained by SCP photolysis in the presence of 2-C_4F_8 (a), CO_2 (b), CO (c) and N_2 (d).

The FTIR spectral pattern of the deposited solid films is independent of photolysis progress and consists of bands assignable to ν(SiC), δ(H_xSi), ν(Si—H) and ν(C—H) vibrations (Table 2, Fig. 3). The ν(Si—H) band centred at $2131\ cm^{-1}$ is typical for polycarbosilanes (ν(Si—H) $\sim$2120–$2150\ cm^{-1}$) produced upon UV laser photolysis of organylsilanes.[25,26] It is known[27] that more carbon incorporation in the Si—Si framework shifts the ν(Si—H) absorption to higher values and that a ν(Si—H) absorption above $2100\ cm^{-1}$ corresponds to a-$Si_{1-x}C_x$:H films with carbon content $x > 0.8$. The observed maximum of the ν(Si—H) band thus reveals that the solid deposit has a very similar content of silicon and carbon atoms.

The absorbance $A_{\nu(C-H)}/A_{\nu(Si-H)}$ ratio is instructive[28] regarding the relative concentrations of the H(C) and H(Si) atoms; the value 0.16 reveals that the incidence of H(C) atoms is *ca* 80% that of the H(Si) atoms and indicates a significant extent of incorporation of carbon-containing moieties in the deposited solid due to the processes (ii) and (iii) above.

Photolysis of SCP in the presence of CO, CO_2 and 2-C_4F_8

The photolysis of SCP carried out in the presence of CO and CO_2 was accomplished to *ca* 20–25% progress with as many as $(3–4) \times 10^3$ pulses, whereas that in the presence of perfluorobutene-2 is rather slower and progresses to *ca* 25% only with more than 10^4 pulses.

Volatile hydrocarbons produced in the photolysis of SCP in the presence of CO and CO_2 and their distribution are very similar to those observed with the photolysis of SCP in N_2 (Table 1). Also, the FTIR spectral patterns of the deposited solid films are practically identical to that observed with the photolysis of SCP in N_2 (Table 2, Fig. 3). These similarities reveal that the photolysis of SCP is not affected by CO and CO_2 admixtures and that transient silylene does not react with these carbon oxides to yield stable volatile or solid products.

The photolysis of SCP in the presence of 2-C_4F_8 affords the hydrocarbons together with a mixture of traces of C_3F_5H and $SiC_2F_4H_2$ compounds (Table 1). The deposited polycarbosilane films possess an IR spectral pattern very similar to that observed for the SCP photolysis in N_2 (Fig. 3, Table 2), but it also contains weak absorption bands at *ca* 1120–$1280\ cm^{-1}$ which are assignable to ν(C—F) vibrations. Both features indicate that photolytic decomposition of SCP is slightly interfered with by products of photolysis of 2-C_4F_8. Perfluoroolefins are reluctant[29] to UV photolysis and cleave at the double bond[30]. We presume that 2-C_4F_8 splits into $F_3C(F)C$, which reacts with silylene and H_2 to yield the observed volatile products. It is plausible that co-polymerizarion of perfluoromethylcarbene and silylene yields the solid fluorine-containing polycarbosilane.

Photolysis of SCP in the presence of O_2

The photolysis of SCP occurring in the presence of molecular oxygen is accomplished with 6×10^3 pulses to *ca* 30%. It yields the same hydrocarbons as in the presence of N_2, together with small quantities of benzene and toluene. The higher yield of ethyne (Table 1) and the occurrence of these aromatic hydrocarbons, typical high-temperature products, are in line with the higher exothermicity of this photolysis.

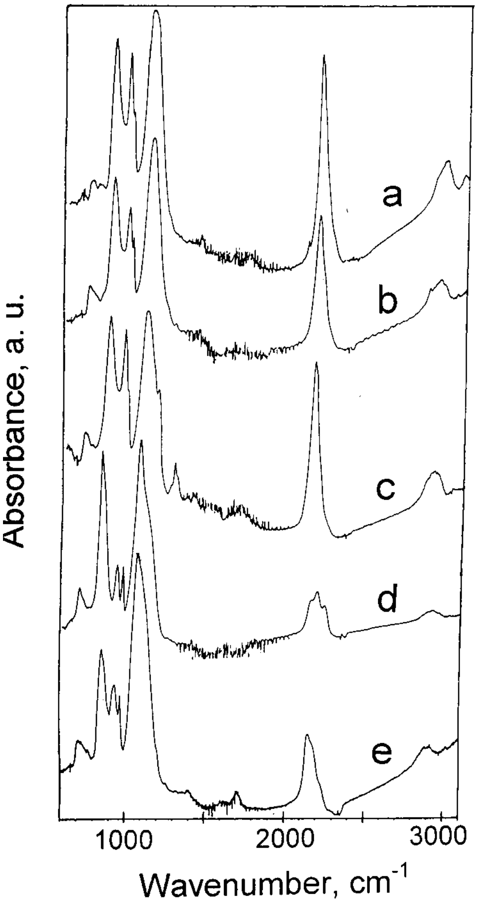
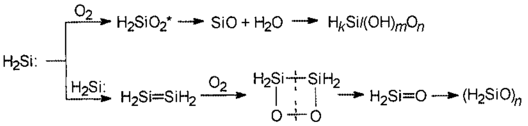


Figure 4. FTIR spectra of the deposit obtained by SCP irradiation in the presence of CD_3OH (a), CH_3OH (b), F_3CCH_2OH (c), CH_3CO_2H (d) and O_2 (e).

The IR spectral pattern of the deposited solid films (Table 2, Fig. 4) differs remarkably from those of the films deposited in the presence of N_2, CO, 2-C_4F_8 and CO_2, and includes a very intense ν(SiOSi) absorption band at $1078\ cm^{-1}$ that is typical[31–33] for polysiloxanes lacking methyl substituents at the silicon. The ν(Si—H) absorption band is centred at $2153\ cm^{-1}$ and its shift to higher wavenumbers can be accounted for[34–36] by the occurrence of $H_2Si(O)$ structures. The $A_{\nu(C-H)}$:$A_{\nu(Si-H)}$ ratio, 0.21, indicates that the relative concentrations of H(Si) and H(C) centres in the deposited film are very similar to those obtained in the presence of N_2, CO, 2-C_4F_8 and CO_2. The $A_{\nu(Si-H)}$:$A_{\nu(SiOSi)}$ ratio, 0.32, reveals the relative content of the Si—H and SiOSi bonds in the deposit and resembles the ratios observed for polyhydrido-



Scheme 3.

alkylsiloxane films obtained by IR laser thermolysis[33,37] (0.24–0.42) or UV laser photolysis[38,39] (0.26–0.47) of $(H_2RSi)_2O$ (R=H, CH_3, C_2H_5) disiloxanes in which the ratio O/Si = 1 determined by photoelectron spectroscopy is in keeping with polymerization of H_2SiO or H_nSiO ($n < 2$) species.

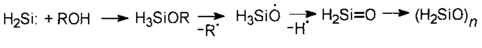
These data prove the occurrence of reactions between molecular oxygen and silylene leading to stable products. It was suggested[10,40] that silylene reacts with O_2 to produce a hot H_2SiO_2 adduct that decomposes into SiO and H_2O. Our recent study of laser ablation of silicon monoxide in the presence of water vapour[41] revealed that SiO_x species react with H_2O to yield solid materials that have an $A_{\nu(Si-H)}$:$A_{\nu(SiOSi)}$ ratio of 0.11, contain different $Si_xO_yH_z$ configurations, and have Si(H) mostly bonded in $(O_3)Si-H$ units manifesting at 2150 cm^{-1}. These findings support the transient occurrence of SiO. Another channel can be dimerization of silylene to disilene, disilene oxidation to silanone[42] and polymerization of silanone.[32,33,43] Both plausible routes are illustrated in Scheme 3.

Photolysis of SCP in the presence of CH_3OH, CD_3OH, F_3CH_2COH and CH_3CO_2H

The photolysis of SCP occurring in the presence of the alcohols and acetic acid yields mixtures of the hydrocarbons in the proportions observed in the presence of N_2 (Table 1) and it interferes with photolysis of the admixtures, although only the absorbance at 193 nm of acetic acid (4×10^{-3} Torr cm^{-1}), but not of the alcohols,[29] is comparable to that of SCP.

The photolysis in the presence of methanol, methanol-d_3 and 1,1,1-trifluoroethanol yields also acetaldehyde (CH_3CHO) together with CO (Table 1).

The formation of CO can only be explained by a sequence of steps involving CH_3O (CD_3O) radicals,[29] whereas that of CH_3CHO in the presence of CH_3OH and CD_3OH must take place only via reactions of CO with CH_3 and H or H_2 species. The FTIR spectra of the deposited films (Table 2, Fig. 4) show intense ν(SiOSi) and ν(Si–H) absorption bands at 1089–1095 cm^{-1} and 2144 cm^{-1} respectively. The $A_{\nu(C-H)}$:$A_{\nu(Si-H)}$ ratios 0.14, 0.17 and 0.22 indicate that the relative concentrations of H(Si) and H(C) centres in the deposited films resemble those in films obtained in N_2. However, the $A_{\nu(Si-H)}$:$A_{\nu(SiOSi)}$ ratios, ranging between 0.75–1.0, imply that the relative occurrence of the SiOSi bonds in these films is significantly lower than in the solid obtained with the SCP photolysis in O_2 or in the polyhydridoalkylsiloxane films produced upon IR laser[33,37] or UV laser[38,39] decomposition of $(H_2RSi)_2O$ (R=H, CH_3, C_2H_5) disiloxanes. The lack of absorption bands due to C–D vibrations indicates insignificant, if any, incorporation of D.


$H_2Si{:} + ROH \rightarrow H_3SiOR \xrightarrow[-R^{\cdot}]{} H_3Si\dot{O} \xrightarrow[-H^{\cdot}]{} H_2Si{=}O \rightarrow (H_2SiO)_n$

Scheme 4.

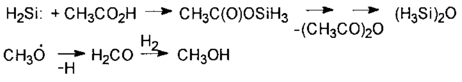
These features allow one to suggest that incorporation of oxygen in the deposit occurs via insertion[3,4] of silylene into ROH and subsequent feasible[38,44] cleavage of alkoxysilane at the O–C bond, as depicted in Scheme 4.

SCP photolysis in the presence of acetic acid also yields carbon dioxide, acetoxysilane, disiloxane, methanol and propargyl aldehyde (HC≡CCHO) (Table 1). Independent experiments showed that ArF laser photolysis of acetic acid yields[45] CH_4 and CO_2 as major products and ethene and ethyne as minor products. Hence, propargyl aldehyde and methanol can be rationalized as arising via reactions of CH_3O radicals and unsaturated hydrocarbons generated from SCP or acetic acid. The occurrence of disiloxane is in keeping with primary insertion of silylene into the H–O bond of acetic acid yielding acetoxysilane, which can undergo scrambling reactions[46] and condensation[47] to disiloxane (Scheme 5) and polysiloxane solid films. Another (direct) source of the hydridosilicone films is[32] disiloxane photolysis at 193 nm.

The FTIR spectrum of the deposited film (Table 2, Fig. 4) shows intense ν(SiOSi) and ν(Si–H) absorption bands at 1064 cm^{-1} and 2188 cm^{-1} respectively. The $A_{\nu(O-H)}$:$A_{\nu(Si-H)}$ ratio, 0.19, is close to that observed in the films deposited in N_2 and indicates that the relative concentration of the H(Si) and H(C) centres in both films is practically the same. The $A_{\nu(Si-H)}$:$A_{\nu(SiOSi)}$ ratio, 0.2, being markedly low, reveals that the films are richer in the SiOSi bonds than the films deposited in O_2 or the polyhydridoalkylsiloxane films laser-deposited from the $(H_2RSi)_2O$ (R=H, CH_3, C_2H_5) disiloxanes. The ν(Si–H) absorption bands at 2156, 2188 and 2237 cm^{-1} are compatible[34–36] with the respective occurrence[41] of $(SiO)SiH_2$, $(O_2)SiH_2$ and $(O_3)SiH$ configurations and reveal pronounced oxidation of silicon in the deposit.

Modification of deposits upon contact with air

The films produced in the presence of the alcohols and acetic acid are stable in prolonged (several days) contact with air, but those deposited in N_2, CO, CO_2 and 2-C_4F_8 change their FTIR spectral pattern: the ν(Si–H) absorption band decreases and the ν(SiOSi) absorption band increases to attain


$H_2Si{:} + CH_3CO_2H \rightarrow CH_3C(O)OSiH_3 \rightarrow \xrightarrow[-(CH_3CO)_2O]{} (H_3Si)_2O$

$CH_3\dot{O} \xrightarrow[-H]{} H_2CO \xrightarrow{H_2} CH_3OH$

Scheme 5.

$A_{\nu(\text{Si}-\text{H})}$:$A_{\nu(\text{SiOSi})}$ ratios up to 0.4–0.6. These changes relate to reactions of residual Si=Si or dangling bonds with moisture and condensation reactions between Si—OH and Si—H centres.

INFERENCES

ArF laser photolysis of SCP is not affected in the presence of CO and CO_2, revealing the absence of irreversible reactions of silylene with carbon oxides.

ArF photolysis in the presence of 2-C_4F_8 is slightly interfered with by perfluoroolefins and yields polycarbosilane films with a low content of C—F bonds.

ArF laser photolysis in the presence of O_2 yields hydridoalkylsilicone films that resemble materials obtained by laser chemical vapour deposition of alkylhydridodisiloxanes.[33,37–39] These materials provide evidence on reaction(s) of silylene and/or disilene with O_2, which can yield final hydridosilicone films through polymerization of intermediate silanone.

ArF laser photolysis of SCP in the presence of alcohols ROH (R = CH_3, CD_3, F_3CCH_2) affords polycarbosilane films with a low content of SiOSi units, whereas that in the presence of acetic acid yields hydridosiloxane films that incorporate more SiOSi units than those obtained by the chemical vapour deposition of disiloxanes. These solids are judged to be formed via a sequence of reactions involving primary insertion of silylene into the O—H bond of alcohols and acetic acid, and intermediate formation of silanone or disiloxane.

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