Si/C phases from the IR laser-induced decomposition of 1,4-disilabutane

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CO_2 laser-induced decomposition of 1,4-disilabutane (DSB) in the gas phase yields gaseous C_{1-2} hydrocarbons and $RSiH_3$ compounds ($R = H$, CH_3, C_2H_5 and C_2H_3), and it represents a convenient process for chemical vapour deposition of thin films composed of Si/C/H, Si/C and Si components.

Hydrogenated amorphous $Si_{1-x}C_x$ materials, prepared by chemical vapour deposition (CVD) *via* conventional pyrolysis, photolysis or plasma-assisted decomposition of various volatile precursors, have recently attracted much attention due to their importance in photovoltaic and optoelectronic applications and in high-temperature ceramics. Properties of the Si/C films can be improved by the choice of the CVD conditions and by using specially designed hydridocarbosilanes which offer better control of the Si/C stoichiometry and lower deposition temperatures (see, *e.g.*, refs. 1–9). Of these precursors, silacyclobutane,[6,10,11] 1,3-disilacyclobutane,[7,10,11] disilylmethane,[5,12] trisilylmethane,[12] 1,3-disilabutane,[13] tetramethylsilane[14] and monoorganylsilanes[15,16] have been studied. The synthetic approach to another interesting class of Si/C precursor, α,ω-disilaalkanes, has been solved,[17] but the potential of these compounds in the CVD of Si/C materials has not yet been assessed.

Following our previous studies on various Si/C phases prepared from single precursors using excimer-laser[11,16,18] or IR-laser[10,15,19–21] radiation, we report in this paper on the CO_2 laser-induced decomposition of 1,4-disilabutane (DSB) and properties of the Si/C phases deposited in this process.

Experimental

The experiments were carried out with a tunable TEA CO_2 laser (Plovdiv University) operating on the P(38) line of the 0001–1000 transition (927.0 cm^{-1}). 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 DSB was irradiated with a number of pulses at a fluence of 0.3 J cm^{-2} in a glass cell (45 mm i.d., 10 cm length) equipped with two NaCl windows and a valve ended by a septum.

Changes in the composition of the cell content were monitored by gas chromatography (gas chromatograph Shimadzu 14A equipped with FID, and coupled with Chromatopac C-R5A computing integrator; columns packed with Porapak P and OV-1 silicon elastomer, temperature programmed) and by FTIR (Nicolet, model Impact 400 spectrometer) spectroscopy. Reaction progress was estimated by using a diagnostic band of DSB at 927 cm^{-1}. The volatile products of the DSB decomposition were identified by GC–MS (Schimadzu QP 1000 quadrupole mass spectrometer). The quantitative analyses are based on the knowledge of response factors for the identified products which were determined or taken from ref. 22.

Samples of the solid deposits were produced on different substrates (KBr, Cu) housed in the cell before the irradiation. For XPS, SEM and TEM measurements the samples had to be transported from the cell and exposed to ambient atmosphere.

Properties of the deposit were measured on the FTIR spectrometer, a VG ESCA 3 Mk II electron spectrometer and a SEM Tesla BS ultrahigh vacuum instrument equipped with an energy dispersive X-ray analyser (EDXA). Transmission electron microscopy measurements of the solid precipitates were carried out using a Philips 201 microscope.

X-Ray photolelectron spectra and X-ray excited Auger electron spectra were obtained using Al-Kα and Bremsstrahlung radiation, repectively. The energy resolution expressed by the fwhm of the Au $4F_{7/2}$ line was 1.2 eV. The energy scale of the spectrometer was calibrated with the Au $4f_{7/2}$ binding energy fixed at 84.0 eV. Detailed spectral scans were taken over Si 2p, Si ($KL_{23}L_{23}$) and C 1s regions. The overlapping peaks were resolved into individual components using a Shirley-type[23] background, Gaussian–Lorentzian lineshapes and the damped non-linear least-squares technique.[24] Quantification of the element surface concentration ratios was accomplished by correcting the integral intensities of the photoelectron peaks for their cross-sections[25] and accounting for the dependence of the analyser transmission[26] and electron mean free paths on kinetic energy.[27] The results obtained did not depend (within the experimental error) on angle of electron detection, thus showing the absence of measurable surface concentration gradients.

DSB (>99.5% purity) was obtained using the procedure described in ref. 28 and was distilled prior to use.

Results and Discussion

The irradiation of the δ(Si–H) mode of DSB [the absorption band centred at 928 cm^{-1}, Fig. 1(*a*)] leads to a strong visible luminescence which is most intense during the first ten pulses, the formation of volatile hydrocarbons (ethene, ethyne and methane) and organosilanes (silane, vinylsilane, methylsilane, ethylsilane), and also to the deposition of a brown material. The production of this deposit was observed after a single pulse and was most effective within the first 40 pulses.

Volatile compounds and the gas-phase chemistry

Regarding the volatile products (Fig. 2) and their alteration with the decomposition progress (Fig. 3), the relative yield of

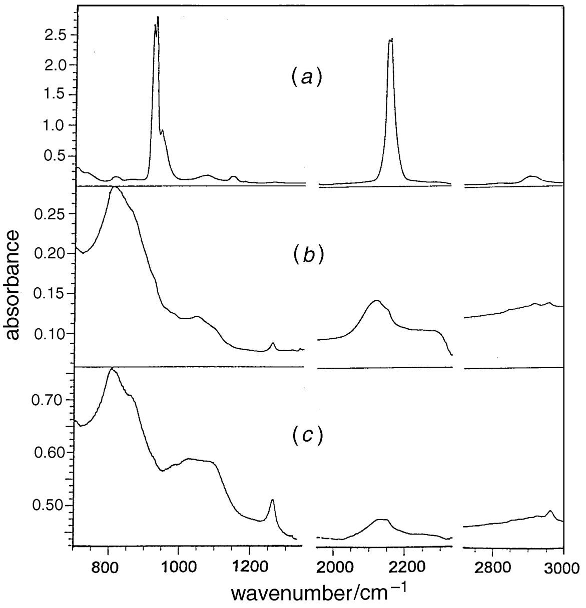

Fig. 1 FTIR spectra of DSB (1.3 kPa) (*a*) and of the deposit before (*b*) and after (*c*) exposure to air

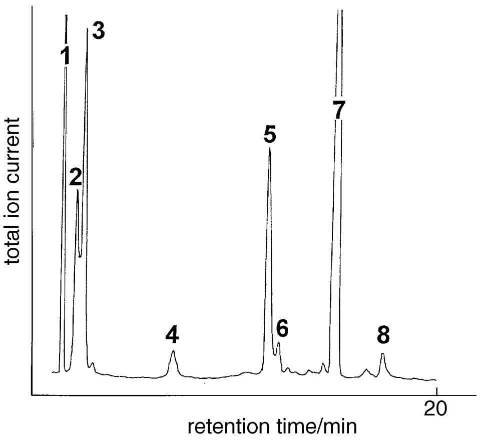

Fig. 2 Typical GLC–MS trace of the mixture obtained on laser irradiation of DSB. Column: Porapak P. Peak identification: 1, air; 2, SiH_4; 3, C_2H_4; 4, CH_3SiH_3; 5, $H_2C{=}CHSiH_3$; 6, $H_5C_2SiH_3$; 7, DSB; 8, $H_3SiSiH_2CH_2CH_2SiH_3$.

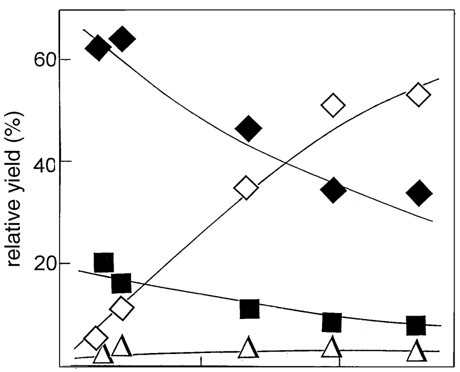

Fig. 3 Major product distribution (mol%) in irradiated DSB *vs.* decomposition progress. ◆, C_2H_4; △, C_2H_2; ■, $H_2C{=}CHSiH_3$; ◇, SiH_4.

silane (5–60%) increases and those of ethene (*ca.* 30–60%) and vinylsilane (20–10%) decrease. The other volatile products are formed in only very small quantities: ethyne (2–4%), methane (*ca.* 1%), ethylsilane (<1%), methylsilane (1–2%) and 1,2,5-trisilapentane (*ca.* 0.5%). The residual pressure in the reactor after freezing the volatile products in a trap indicated the presence of hydrogen. The identified volatile products were estimated to be formed by less than 20% of the DSB, which implies that the parent compound is mostly utilized for the formation of the solid deposit. The volatile products indicate that the DSB decomposition is initiated by at least four primary reactions which are 1,1-H_2 (1), 1,2-H_2 (2), alkane (ethylsilane, 3) and alkene (vinylsilane, 4) elimination pathways (Scheme 1). These reaction prototypes are commonly known to operate in the decompositions of alkylsilanes (see, *e.g.*, refs. 29–32).

$$H_3SiCH_2CH_2SiH_3 \xrightarrow{(1,\,1\text{-}H_2)} :SiH(CH_2)_2SiH_3 \qquad (1)$$

$$\xrightarrow{(1,\,2\text{-}H_2)} H_3SiCH_2CH{=}SiH_2 \qquad (2)$$

$$\xrightarrow{(alkane)} :SiH_2{+}C_2H_5SiH_3 \qquad (3)$$

$$\xrightarrow{(alkane)} :SiH_4{+}H_2C{=}CHSiH_3 \qquad (4)$$

Scheme 1

Other plausible pathways are 1,4-H_2 elimination or intramolecular β-C—H insertion into $:SiH(CH_2)_2SiH_3$ leading to $H_2SiCH_2CHSiH_3$ and further to $:SiH_2 + H_2C{=}CHSiH_3$ (ref. 33).

The small amounts of vinylsilane and ethylsilane indicate that these compounds are intermediary products; it can be inferred[34,35] that they decompose into C_2H_4, $C_2H_5(H)Si:$, $H_2Si:$ and $CH_3CH{=}SiH_2$, and $H_2Si:$ and C_2H_4, respectively. The depletion of ethene in the course of the DSB decomposition indicates that ethene is removed by reactions with silylenes. The intermediacy of the simplest $H_2Si:$ silylene is revealed (i) by the presence of 1,2,5-trisilapentane formed *via* insertion of $:SiH_2$ into DSB, and (ii) by the presence of silane which can only be formed by the reaction of silylene with molecular hydrogen. The accumulation of silane as the DSB decomposition progresses (Fig. 2) serves as evidence of significant amounts of dihydrogen in the decomposition mixture produced by H_2 elimination.

Properties of the deposit

The solid films show [Fig. 1(*b*)] IR absorption at 809 [ν(Si—C)], 1260 [δ(CH_3—Si)], 2120 [ν(Si—H)], 2900 and 2960 [ν(C—H)] cm^{-1} and they develop [Fig. 1(*c*)], upon standing in air, an absorption at *ca.* 1050 cm^{-1} which is assignable to the ν(Si—O) mode. The first three bands constitute the typical pattern of a-SiC:H films[36,37] and reveal characteristic absorptions of Si—H, Si—C and C—H in saturated moieties. Comparison of the FTIR spectra of the deposit and of DSB (Fig. 1) reveals that the solid material is much poorer in hydrogen. The relative contents of the Si—H and C—H bonds can be estimated[38,39] by using the Si—H and C—H per-bond oscillator strength in SiH_4 and CH_4. The absorptivity [normalized to that of the ν(Si—C) band] of ν(Si—C), ν(Si—H) and ν(C—H), in the given order 1.0, 0.28 and 0.02, are compatible with *ca.* 2.5 times more H at Si than at C.

The best fit of the Si 2p (Fig. 4) core level spectrum is obtained using four components of the same widths. The presence of four components is more clearly seen in the Si ($KL_{23}L_{23}$) Auger electron spectrum (Fig. 5) of the deposit. They are consistent with presence of the four different chemical states of Si, namely elemental silicon, silicon in SiC, silicon in

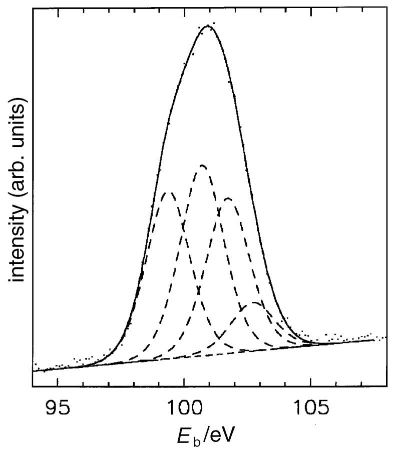

Fig. 4 Fitted photoelectron spectra of Si 2p electrons

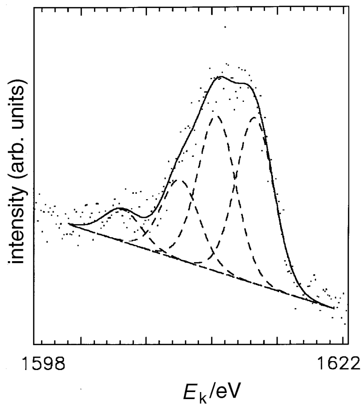

Fig. 5 Fitted photoelectron spectra of Si ($KL_{23}L_{23}$) Auger electrons

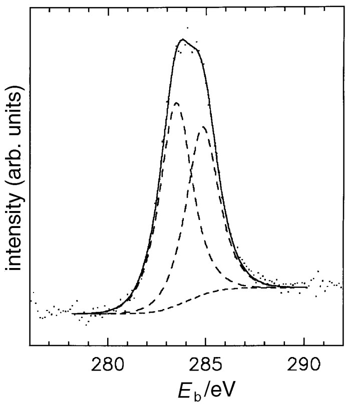

Fig. 6 Fitted photoelectron spectra of C 1s electrons

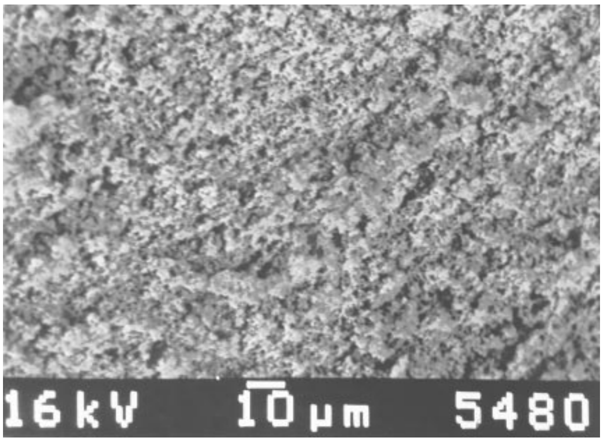

Fig. 7 SEM image of the deposit

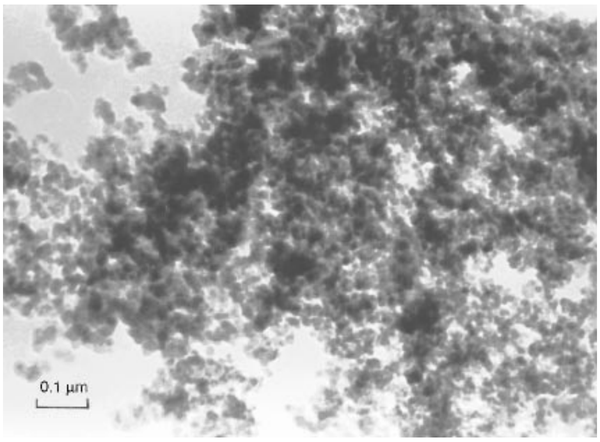

Fig. 8 TEM image of the deposit (magnification 70000×)

Si/C/H polymer, and an oxidized form of silicon. The Si 2p core level binding energies, obtained by fitting the measured spectrum, and their assignments based on comparison of the measured values with the literature data[40–42] are given in Table 1. The C 1s core level spectra (Fig. 6) reveal the presence of two chemical states of carbon, namely carbidic carbon and carbon belonging to organosilicon polymer. Their concentration and the corresponding binding energies are also displayed in Table 1.

The FTIR and XPS analyses show that the gas-phase chemistry results in the formation of three types of materials which reveal the operation of three types of final reaction steps. The formation of a 'polymeric' saturated Si/C/H material is due to polymerization reactions of a number of unsaturated species formed in the gas phase by routes (1)–(4) and consecutive reactions. The occurrence of the elemental silicon is in line with complete dehydrogenation of some gaseous $:SiH_2$ and Si_xH_y intermediates. The presence of silicon carbide is compatible with dehydrogenation of intermediate silenes (possessing strong Si=C bonds); this reaction has been observed under similar conditions upon IR laser irradiation of silacyclobutane and 1,3-disilacyclobutane.[10] We stress that the dehydrogenations leading to Si and SiC are feasible due to direct absorption of the laser radiation in the transients possessing Si—H bonds. The development of the Si—O type component can be explained by a small amount of unsaturated Si=C bonds (see also refs. 10,11,15,16) in the superficial layers and by reaction of these bonds with atmospheric oxygen.[43] We note that the XPS analysis of the deposit (*ca.* 5 nm layers) indicates that the oxygen cannot be removed by ion sputtering, which implies that oxygen can penetrate to some depth of the superficial layers and there react with residual Si=C bonds.

Table 1 The Si 2p and C 1s core level binding energies (E_b) of the fitted photoemission lines (in eV), their assignment, and the calculated atomic concentrations (*c*) of Si and C present in the individual chemical states (normalized to Σ Si = 1)

E_b (Si 2p)	E_b (C 1s)	assignment	*c*
99.6	—	Si^0	0.30
100.8	—	Si carbide	0.34
102.1	—	Si polymer	0.27
103.2	—	Si oxide	0.09
—	283.1	carbidic C	0.35
—	284.4	C in polymer	0.29

SEM images of the deposits (Fig. 7) show that the deposits have particulate structure and consist of agglomerates. TE microscopy (Fig. 8) reveals that these agglomerates consist of small particles of size *ca.* 20 nm.

Conclusion

The CO_2 laser-induced decomposition of DSB is an efficient method of preparing thin layers of Si/C/H phases which are composed of elemental silicon, silicon carbide and an organosilicon polymer. It can be inferred that the major reaction step involved in the DSB decomposition is dehydrogenation of the parent and transient compounds.

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