INFRARED LASER-INDUCED DECOMPOSITION OF *tert*-BUTYLSILANE FOR CHEMICAL VAPOUR DEPOSITION OF Si/C/H PHASES

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Abstract: TEA CO_2 laser induced decomposition of *tert*-butylsilane is controlled by elimination of isobutene and affords solid Si/C/H films whose H-content is dependent on the laser fluence. The process of the chemical vapour deposition of Si/C/H phases is a unique from the viewpoint that depending on the irradiation conditions different major component of the solid films (either elemental silicon or silicon carbide) can be obtained from the only single precursor.

Introduction

Thermal and photolytic decomposition of organosilanes is of current interest due to its potential for chemical vapour deposition (CVD) of hydrogenated amorphous $Si_{1-x}C_x$ phases which are used in optoelectronic applications. 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 (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], 1,4-disilabutane[15] divinylsilane[16], tetravinylsilane[17], diethylsilane[18] and monoorganylsilanes[19-21] have been examined. We have shown that the irradiation of silacyclobutane, 1,3-disilacyclobutane and 2-chloroethenylsilane with the low fluence IR laser pulses yields Si/C/H phases which are mainly polycarbosilanes in which silicon carbide is only a minor constituent, whereas high fluence IR laser irradiation of these compounds affords mostly silicon carbide along with a minor portion of polycarbosilanes[10,19]. High fluence IR laser irradiation into tetravinylsilane[17] and 1,4-disilabutane[15] affords materials composed of elemental silicon and polycarbosilane, and SiC, polycarbosilane and Si, respectively. The same type of irradiation of 2-propenylsilane[21] yields phases composed of SiC (major constituent) and polycarbosilane. The most efficient (explosive) formation of SiC takes place upon high fluence irradiation of ethynylsilane[21], but SiC was also produced as a major constituent by infrared multiphoton decomposition (IRMPD) of tetramethylsilane[14]. In contrast to these results (refs.[22-24]), UV laser photolysis of monoorganylsilanes results in deposition of exclusively saturated polycarbosilanes[11,20,25].

Monoorganylsilanes $RSiH_3$ (R = alkyl) are eminently good absorbers of CO_2 laser radiation and can decompose via several different pathways which are homolysis of the Si-C bond, 1,2-H_2 and 1,1-H_2 as well as alkane and alkene elimination. Major primary stages in the shock induced thermolysis of $RSiH_3$ are dominated by 1,2-H_2 and 1,1-H_2 elimination[26,27], but those of IRMPD are judged to be a four-centre transition state elimination of SiH_4 (refs. [28,29]) or 1,1-H_2 elimination[30]. It is conceivable that some decomposition paths can be ruled out by the selection of the R group; this would simplify the decomposition mechanism and consequently lead to a more predictable stoichiometry of the deposited films. For example, tert-alkylsilanes not possessing β-hydrogen cannot undergo 1,2-H_2 elimination.

In this work we examined IRMPD of *tert*-butylsilane and showed that this process, even though dominated by high-yield expulsion of isobutene, affords not Si/H but Si/C/H phases in which the carbon content is controlled by the fluence of the laser radiation.

Materials and Methods

The experiments were conducted with a tunable TEA CO_2 laser (Plovdiv University) operating on the P(30) and P(40) lines of the $00^01 \varnothing 10^00$ transition (934.90 and 924.97 cm^{-1},

respectively). 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). The unfocused radiation at the P(30) and P(40) lines was of the same incident energy (0.5 J), but differed in fluence which was 0.25 and 1.25 $J.cm^{-2}$, respectively. In experiments with focused radiation, the radiation was focused with a NaCl lens (f.l. 8 cm) 2 cm behind the entrance window of the reaction vessel.

Gaseous samples of *tert*-butylsilane were irradiated in a Pyrex vessel (45 mm i.d., 10 cm length) equipped with two NaCl windows, a P.T.F.E. stopcock and a sleeve with rubber septum. The cell accommodated metal substrates which, covered with the solid deposited material, were transferred for measurements of their properties by scanning electron microscopy and FTIR and XPS spectroscopy. Changes in the composition of the cell gaseous content after the laser radiation were monitored by an FTIR (Nicolet, model Impact 400) spectrometer. The depletion of *tert*-butylsilane was followed by using a diagnostic band at 925 and 933 cm^{-1}. GC-MS and GC analyses of the gaseous samples after the 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 using programmed temperature (20-150°C) and helium and nitrogen carrier gas. The quantitative GC analyses are based on the knowledge of response factors for the identified products which were determined or taken from ref. 31.

The photoelectron spectra were acquired using ESCA 3 Mk II (VG Scientific) and ESCA 310 (Gammadata Scienta) electron spectrometers equipped with Al Kα X-ray source (hν = 1486.6 eV). The background pressure during spectra acquizition 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 (1s), O (1s) and Si (KLL) regions. The XPS peak positions and areas were determined by fitting the unsmoothed experimental spectra after subtraction of Shirley[32] background. The surface concentrations of elements were determined using theoretical photoionization cross-sections[33].

SEM studies of the deposits were carried out on an ultrahigh vacuum Tesla BS 350 instrument.

tert-Butylsilane was prepared after procedure[34] and its purity was better than 98 per cent as checked by gas chromatography.

Results and discussion

The TEA CO_2 laser irradiation into the δ (H_3Si) mode of *tert*-butylsilane with the unfocused low fluence radiation at the P(30) line (beam profile 2 cm^2) and high fluence radiation at the P(40) line (beam profile 0.4 cm^2) affords the same gaseous compounds - silane, methylsilane, ethylene, propene, isobutane and isobutene - along with a pale solid material deposited on the inside of the vessel. In both cases, isobutene was a dominant product and the other compounds were formed in very minor amounts. The distribution of these gaseous products does not differ much with the individual irradiation lines and it is, with each of them, practically constant within the decomposition course 10-60 % (Table 1).

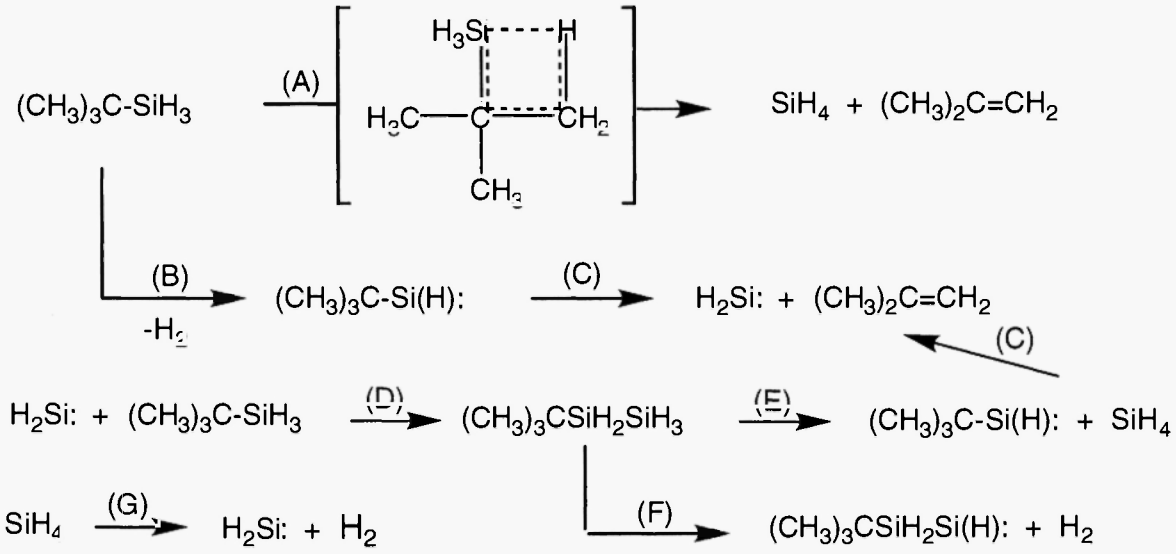
Table 1. Gaseous products yields obtained with the high and low fluence radiation.

Irradn. line	Fluence[a], J/cm^2	Number of pulses[b]	Products distribution[c], [mole/mole of t-butylsilane decomposed] x 100				
			iso-C_4H_8	C_3H_6	CH_3SiH_3	C_2H_4	SiH_4
P(30)	0.25	10	85 - 98	1 - 3	0.5 - 3	0.5 - 2	0.5 - 3
P(40)	1.25	800	75 - 85	0.3 -1	< 0.5	< 0.2	10 -16

[a]The incident energy at each line 0.5 J; [b]to achieve 25 % decomposition; [c]within 10 – 60 % of the decomposition progress.

The dominance of isobutene and the occurrence of silane among the products is in keeping with the Scheme 1 where isobutene is formed via the four-centre transition state elimination (path A), or by the sequence of 1,1-H_2 elimination (path B) and decomposition of *tert*-butylsilylene (path C). The formation of silane is, in principle, compatible with path A (but also with the sequence of paths B, C, D E); the low yield of silane can be explained by silane

decomposition[35,36] (path G). Silane itself is a good absorber of the CO_2 laser radiation[35,36] and the IR absorption pattern of *tert*-butylsilane and silane (Fig. 1) gives support for less silane decomposition with the P(40) line. This situation not being observed and the fact that infrared multiphoton decomposition of silane at siiane low partial pressures is unlikely[34] are in support of the occurrence of paths B and C. An unambiguous decision on the role of path A and paths B+C is, however, an uneasy task. Our attempt to detect silylene chains (D, E, C) by using buta-1,3-diene as trapping agent[37] failed - we have not detected any products of the silylene addition to buta-1,3-diene and neither observed noticeably slower decomposition.



Scheme 1

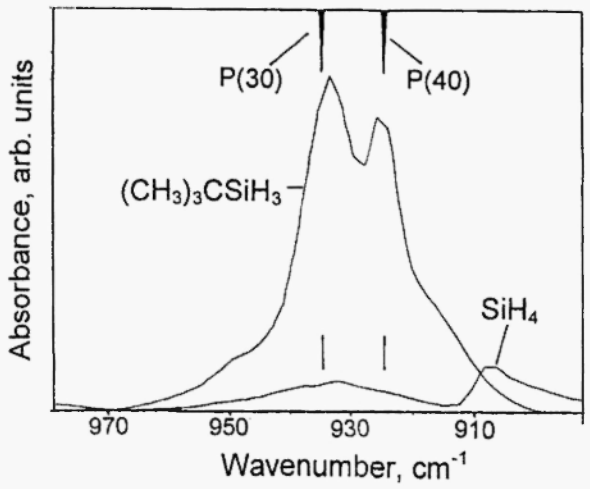


Fig. 1. FTIR spectrum of *tert*-butylsilane and silane (the same pressure of each) in the region of emission of CO_2 laser.

In experiments with focused radiation, the decomposition of *tert*-butylsilane is accompanied with a bright visible luminescence. The energy fluence at luminescence threshold versus *tert*-butylsilane pressure is given in Fig. 2. Neither this phenomenon helps to discriminate between both pathways, since the luminescence can be ascribed to silylene as well as H, H_2 and SiH species[35,38].

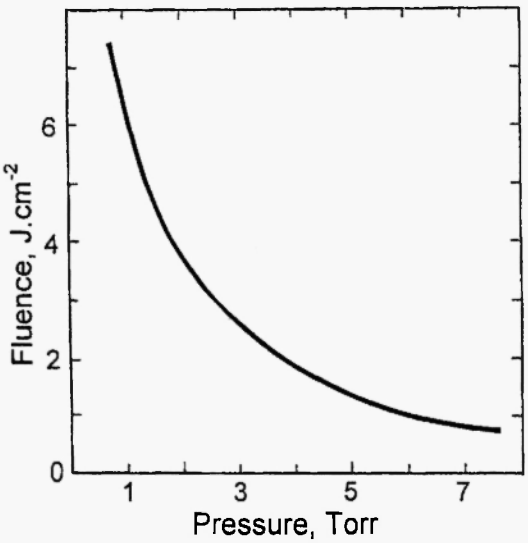


Fig. 2. Energy fluence with the P(30) line at luminescence threshold vs. *tert*-butylsilane pressure.

The comparison of the gaseous products distribution for runs with focused radiation (accompanied by luminescence) and non-focused radiation (Table 2) shows that the luminescence is associated with less silane and isobutene, but more propene and ethene. This indicates that high fluence radiation favours decomposition of isobutene and silane.

Table 2. Gaseous products yields in luminescent and non-luminescent runs[a].

Feature	Products distribution, [mole/mole of t-butylsilane decomposed] x 100				
	iso-C_4H_8	C_3H_6	CH_3SiH_3	C_2H_4	SiH_4
No luminescence	75 - 95	0.04	0.02	0.02	0.24 – 0.30
Bright luminescence	40 -65	0.1 –0.15	< 0.02	0.15 – 0.20	0.03 – 0.08

[a]Within pressures of tert-butylsilane 4-11 Torr, focused radiation, fluence as determined in Fig. 2; decomposition progress 50 – 70 per cent.

The solid films deposited onto the substrates accommodated in the vessel show IR absorption spectra which differ depending on whether they were or not obtained in runs accompanied with luminescence (Fig. 3). The latter – 802 (1.0), 1051 (0.54), 1261 (0.33), 2119 (0.27), 2856 (0.07), 2924 (0.08), 2957 (0.12) – reveal, in the given order, the presence of ν(Si-C), ν(Si-O), δ(CH_3Si), ν(Si-H) and ν(C-H) vibrations, while the former 804 (1.0), 1049 (0.20), 1259 (0.10), 2925 (0.10) have much simpler patterns not showing the band due to ν(Si-H) and possessing much weaker bands due to ν(Si-O), δ(CH_3Si) and ν(C-H) vibrations. The relative content of the Si-H and C-H bonds can be estimated[39,40] by using the Si-H and C-H per bond oscillator strength in MH_4 (M = C, Si); the films obtained in non-luminescence runs have ca. 3 times more H(C) than H(Si) atoms. The presence of the ν(Si-O) bands in the spectra is obviously due to an oxidation of Si=Si intermediates due to leakage of traces of air into the vessel during experiments. The IR spectra thus reveal formation of SiC:H and SiC films in non-luminescent and luminescent runs, respectively. Complementary information on the deposited films can be drawn from the XPS measurements. The surface composition of the deposits calculated from intensities of the Si (2p) and C (1s) photoemission lines together with binding energies of Si (2p) electrons and Auger parameters are given in Table 3.

Table 3. XPS analysis of deposits in luminescent and non-luminescent runs.

Run	Si/C	Binding energy of Si (2p), eV	Auger parameter, eV	Assignment
Non-luminescent	0.91	99.4	1715.5	Si^0
		101.8	1715.1	C-Si-O[a]
		103.3	1712.4	Si^{4+}
Luminescent	0.94	100.3	1715.0	SiC
		101.3	1714.5	C-Si-O
		103.1	1711.7	Si^{4+}

[a]Assignment[41] of these structures is less certain, some partially oxidized carbide phase can be also repsonsible for the peak.

It is seen that both types of the deposited films have similar Si/C ratio and contain some oxygen, and that their Si(2p) photoelectron spectra (Fig. 4) and Si (KLL) electron spectra (Fig. 5) show the presence of three different chemical states of Si. These are Si^0, (C)-Si-(O) and Si^{4+} states for the films obtained in non-luminescent runs, and SiC, (C)-Si-(O) and Si^{4+} for the films obtained in luminescent runs. The population (in % of total amount of Si present) of these states in order of increasing binding energy of Si (2p) electrons is 39.8, 19.8 and 40.4, and 64.8, 16.2 and 19.0 for for the non-luminescent and luminescent run, respectively. The presence of significant amounts of SiC in the non-luminescent runs is also evidenced by the presence of a component located at 283.3 eV in the spectrum of C (1s) electrons (Fig. 6).

These data indicate the elemental silicon as the major film component in the non-luminescent runs and the SiC as the major component in the luminescent runs; they imply, in accordance with different distributions of gaseous products, that gas phase chemistry for luminescent runs involves different steps. It is plausible that the occurrence of elemental silicon in non-luminescent runs is due to the formation and dehydrogenation of poly(hydridosilicon), while the occurrence of silicon carbide in the luminescent runs is a result of recombination of silylene with propene, ethene (and obviously carbene) and subsequent cleavage and dehydrogenation of products of this reaction.

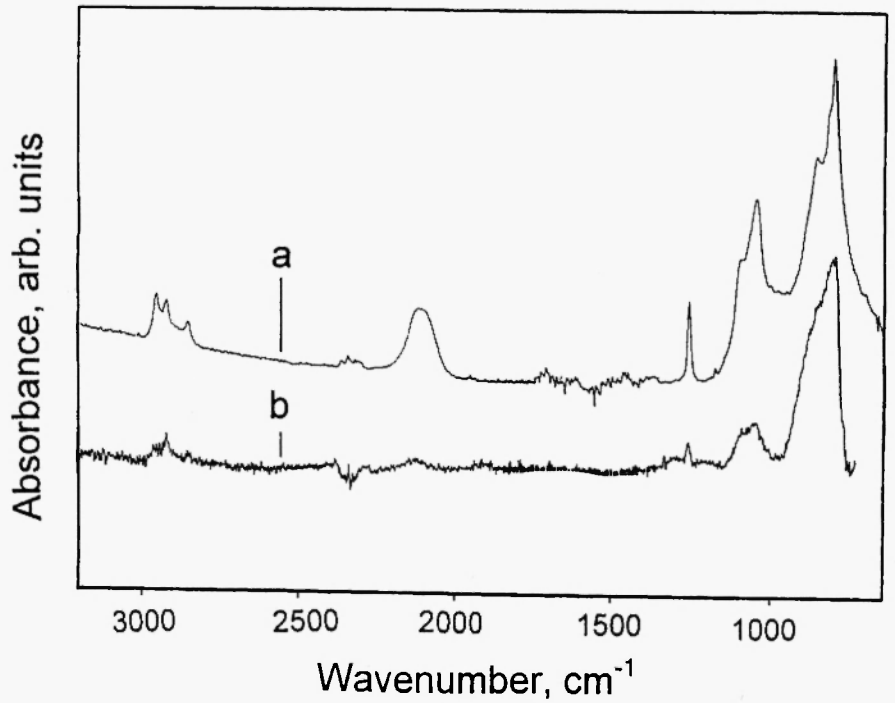


Fig. 3. FTIR spectrum of the deposits obtained by the P(30) line irradiation of *tert*-butylsilane with low fluence (a, non-luminescent run) and high fluence (b, luminescent run).

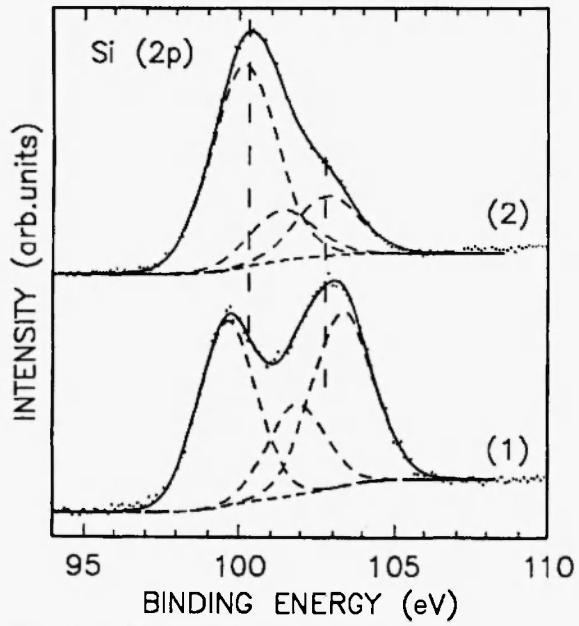


Fig. 4. Si (2p) core level spectra of the deposits in non-luminescent (1) and luminescent (2) runs

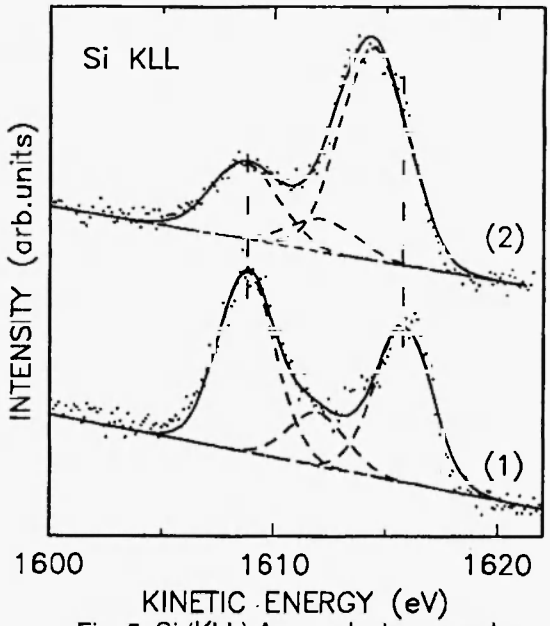


Fig. 5. Si (KLL) Auger electron spectra of the deposits in non-luminescent (1) and luminescent (2) runs.

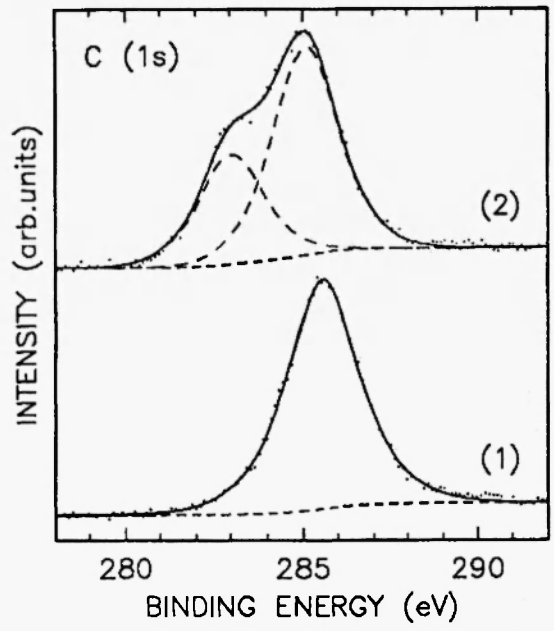


Fig. 6. C (1s) spectra of the deposits in non-luminescent (1) and luminescent (2) runs.

Fig. 7. SEM image of the deposit.

SEM images of the deposits show that they consists of structured agglomerates which are bonded together and have their size larger than 1 mm (Fig. 7).

In conclusion, we point out that the CO_2 laser induced decomposition of *tert*-butylsilane is dominated by high-yield elimination of isobutene, which, although implying formation of H/Si phases, affords H/Si/C phases. The composition of these phases depends on the irradiation conditions. With high laser intensity radiation these materials contain mostly silicon carbide and with low intensity radiation they are composed mostly of elemental silicon. The infrared laser-induced decomposition of tert-butylsilane is thus revealed as a technique enabling to produce two kinds of different solid materials from the only precursor.

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