

Mechanism of the Activation of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane in Plasma Chemical Vapor Deposition

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Plasma chemical vapor deposition (PCVD) using 1,1,3,3-tetramethyl-1,3-disilacyclobutane (DSCB) as a source compound for the formation of hydrogenated amorphous silicon-carbon (a-Si_{1-x}C_x:H) films was studied in terms of the mechanism of the activation step. The comparative deposition experiments were performed for suitable model compounds representing the respective structural units in DSCB molecule. The PCVD processes were characterized by measurements of the pressure increase in the reactor (resulting from plasma fragmentation of a source compound) and calculation of the deposition yield. These data revealed that the ring-opening reaction dominates over fragmentation of methylsilyl groups in the activation step.

Introduction

Among a variety of organosilicon compounds which can be used for the production of thin-film materials by plasma chemical vapor deposition carbosilanes are the least explored group of the source compounds. They are generally recognized as the compounds with alternating silicon and carbon atoms in the molecular skeleton.¹ Owing to this inherent structural feature, carbosilanes may serve as a single-source CVD precursors for the a-Si_{1-x}C_x:H films. Conventional polycarbosilanes are known to convert into high-quality silicon carbide when subjected to pyrolysis.²⁻⁴

Judging from the literature data, very few papers deal with the use of carbosilane source compounds for the PCVD process. Inagaki et al.⁵ only fragmentarily report on plasma polymerization of bis(trimethylsilyl)methane and gas permeability characteristics of the resulting plasma polymer films. Beyer et al.⁶ and Li and Fieselmann⁷ found marked improvement of the photoelectric properties of the PCVD a-Si_{1-x}C_x:H films produced from disilylmethane/silane and trisilylmethane/silane mixtures, respectively. Most recently, Folsch et al.⁸ revealed excellent optoelectronic properties of the same group of thin-film materials deposited from di-, tri-, and tetrasilylmethane admixed with silane.

In the present work we have been exploring the use of 1,1,3,3-tetramethyl-1,3-disilacyclobutane as a novel source compound for PCVD. This compound, due to high reactivity resulting from a significant strain energy

present in the four-membered carbosilane ring (103 kJ mol⁻¹),⁹ is particularly attractive in terms of the CVD processes as it offers the prospect of lower deposition temperatures. It is interesting to note that structurally related compounds, i.e., 1,3-dimethyl-3-methylsilylmethylene-1,3-disilacyclobutane and 1,3-disilacyclobutane, were found to be potential single-source precursors to polycrystalline and single-crystal silicon carbide in thermal CVD.^{10,11}

An important step in PCVD, determining the structure of film-forming precursors is the activation of a source compound which in the case of DSCB, is anticipated to take place via at least two competitive reactions: ring-opening and fragmentation of the ring substituents. To evaluate the contribution from the particular reaction in the activation step, we have undertaken the study involving suitable model source compounds which represent respective structural units in DSCB molecule. The results of the deposition experiments and structural study of the deposit reported in this paper give insight into the mechanism of the activation of DSCB.

Experimental Section

The PCVDs were carried out in a capacitively coupled parallel plate reactor operated at radio frequency (rf) 13.56 MHz. The reactor schematically illustrated in Figure 1, consisted of two glass parts (made by HWS, Mainz) containing greaseless conical vacuum joints and 20-cm-diameter flat flanges which were sealed with an O-ring. The plasma was induced between two aluminum electrodes, 13 cm in diameter and spaced 2 cm apart. The vapor of a source compound was fed through the upper, powered electrode, and the film was deposited onto Corning glass substrate placed on the lower, grounded electrode, equipped with a heater. The deposition

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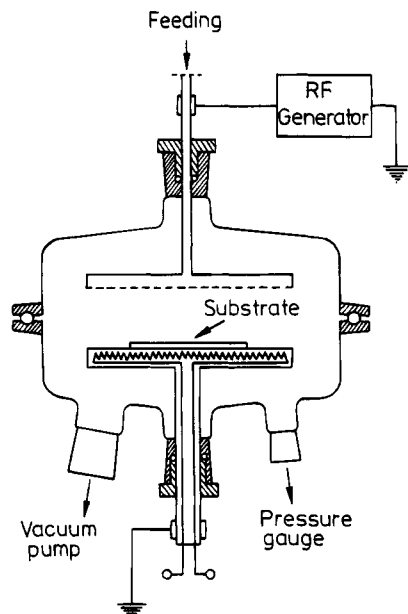


Figure 1. Scheme of the reactor used for plasma chemical vapor deposition.

experiments were performed at a constant initial pressure of the source compound vapor $p_i = 17$ Pa (0.13 Torr) and the rf power input $P = 100$ W, using unheated substrate. The substrate temperature during the deposition did not exceed 50°C . The pressure was measured by means of a capacitive pressure gauge (MKS Baratron, Model 127A). The flow rate was determined gravimetrically from the difference in the mass of the source compound in the evaporator before and after the deposition process. Prior to film deposition the loaded reactor was cleaned with an argon plasma for 5 min. The DSCB source compound and 1,1,1,3,3-pentamethyldisilylmethylene (DSM) model compound, were synthesized in our laboratory according to the procedures in refs 12 and 13, respectively; their purity as checked by the gas chromatography was better than 99%. Tetramethylsilane (TMS) model compound of NMR grade was supplied by Petrarch Systems. The liquids were evaporated to the reactor at the following temperatures: DSCB and DSM at 25°C and TMS at -5°C .

The gaseous products of plasma reactions were examined by the gas chromatography/mass spectrometry (GC/MS) combined technique. The products were sampled during PCVD process to the ampoule of about 50 cm^3 in capacity, which was attached to the reactor through a stopcock. Prior to sampling, the ampoule was evacuated to a pressure of less than 10^{-5} Torr and the products were sucked in by opening the stopcock. The content of the ampoule was then inject into a JEOL Model JGC 1100 gas chromatograph, equipped with a flame ionization detector and a $1\text{ m} \times 3\text{ mm}$ stainless steel separation column filled with a 5A 60/80 mesh molecular sieve. The column was heated from 30 to 270°C using a linear heating rate of $10^\circ\text{C min}^{-1}$ and a steady helium flow of $40\text{ cm}^3\text{ min}^{-1}$. The separated products were analyzed using a LKB Model 2091 mass spectrometer.

Film thickness was measured interferometrically. The infrared (IR) spectrum of the film deposited on Corning glass coated with aluminum was recorded on a Carl Zeiss Jena Specord Model M80 spectrophotometer, using the attenuated total reflection (ATR) technique.

Results and Discussion

To obtain information regarding the mechanism of the activation step, the plasma reactivity of particular structural units in DSCB molecule was examined using

selected model compounds such as DSM and TMS, which represent opened DSCB-like structure and methylsilyl groups, respectively. To avoid an undesirable effect from thermal activation which might interfere with plasma activation, the films were deposited onto unheated substrate. The PCVDs were characterized by three most principal parameters:

(1) The energy input per mass unit of the source compound, P/FM ,¹⁴ where P is the rf power input, F is the feed-in volumetric flow rate of the source compound vapor, and M is the molecular weight of the source compound.

(2) The relative pressure increase in the reactor $\Delta p/p_i$, where $\Delta p = p_g - p_i$; p_g is a steady pressure during glow discharge. This parameter determines susceptibility of the source compound toward plasma fragmentation.¹⁵

(3) The yield of the deposition process expressed by the thickness or mass of the deposit per mass unit of the source compound fed to the reactor, i.e., R/FM ,^{16,17} where R is the deposition rate.

The values of these parameters evaluated for DSCB and the investigated model compounds are listed in Table 1. For precise determination of the deposition rates, they were calculated from the slopes of linear plots of time dependence of the film thickness shown in Figure 2. To make a reasonable comparison between yields of the deposition, the real R/FM data calculated for the model source compounds were normalized to the P/FM value of DSCB (Table 1), assuming a linear dependence of R/FM on P/FM (within the range of calculated P/FM values), as reported by Nomura et al.¹⁸

Although the composite parameters P/FM and R/FM have been introduced by Yasuda^{16,19} for the plasma polymerization, they seem to be also very useful for the characterization of the PCVD, since the difference between these processes arises mainly from the different nomenclature used for their determination. Gazicki and Yasuda¹⁶ analyzed, in terms of these parameters, the plasma polymerization of a number of compounds from substantially different four groups such as hydrocarbons, fluorocarbons, organosilicons, and organosulfur compounds. They found that at a lower energy input level (P/FM) the deposition yield R/FM is sensitive to the structure of the monomer and, in particular, to the type of atoms present in the molecule. The differences in the R/FM values for the compounds within a group, tended to diminish as the power input increased, and at very high P/FM levels, all compounds polymerized in an almost identical manner which was reflected in a close values of R/FM . A similar but more quantitative finding is also reported by Sharma¹⁷ for the plasma polymerization of different compounds, including hydrocarbons, fluorocarbons, and organosilicons. He evaluated a threshold value of the power input $P/FM = 10$

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Table 1. Comparative PCVD Data Determined for 1,1,3,3-Tetramethyl-1,3-disilacyclobutane and Model Compounds, at the Initial Vapor Pressure $p_i = 17$ Pa and rf Power Input $P = 100$ W

source compound	mol formula	mol wt, M (g/mol)	flow rate, F (sccm)	P/FM (MJ/g)	pressure increase $\Delta p/p_i$ (%)	deposition rate, R (nm/min)	R/FM (10^2 nm/g)	
							real	normalized ^a
tetramethyldisilacyclobutane	(Me ₂ SiCH ₂) ₂	144.4	2.1	0.44	55	17.0	12.6	12.6
pentamethyldisilylmethylene	Me ₃ SiCH ₂ SiHMe ₂	146.4	2.0	0.46	91	7.5	5.8	5.5
tetramethylsilane	Me ₄ Si	88.3	7.2	0.21	161	7.2	2.5	5.2

^a The values normalized to P/FM for tetramethyldisilacyclobutane.

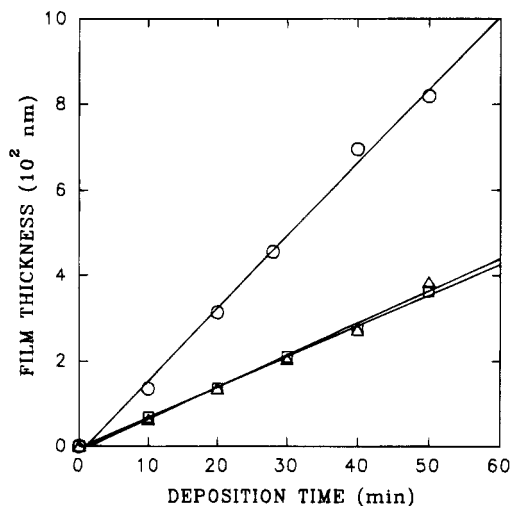


Figure 2. Deposition time dependencies of film thickness determined for DSCB (○), DSM (△), and TMS (□).

MJ/g which determines the nature of the plasma polymerization process. According to this finding, at low values of the power input, $P/FM < 10$ MJ/g, the yield of the deposition, R/FM , strongly depends on structural features of the source compound, thus implying a predominance of a molecular polymerization mechanism over an atomic mechanism. At high values of $P/FM \geq 10$ MJ/g, the majority of compounds polymerize via an atomic mechanism and the molecular structure of the source compound has very little influence on the R/FM value. The latter mechanism is due to the fact that the enthalpy of atomization for most organic compounds is less than 10 MJ/g.

The values of P/FM in Table 1, being lower from the reported threshold value by nearly 2 orders of magnitude, allow us to assume a predominance of a molecular mechanism in the examined PCVDs and resulting effect of the molecular structure (i.e., reactivity) of a source compound on the yield of the deposition. Substantially lower value of $\Delta p/p_i$ observed for DSCB (Table 1) than those of the model compounds, implies that the ring-opening reaction prevails here over fragmentation of the ring substituents. This is consistent with the normalized yields of the deposition (Table 1), which reveal the R/FM for DSCB to be higher more than twice as compared with those of the model compounds. A very close normalized values of R/FM found for DSM and TMS suggest that plasma activation of these compounds proceeds predominantly via fragmentation of the methylsilyl groups.

Similar values of the deposition yield found for DSM and TMS are in a good agreement with the results reported by Inagaki et al. for the rf plasma polymeri-

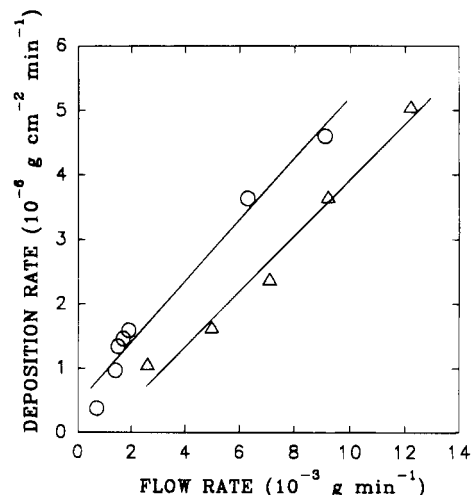
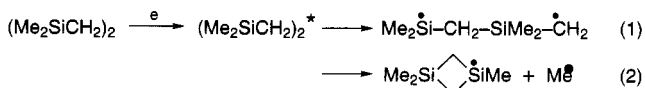


Figure 3. Film deposition rate as a function of the flow rate of bis(trimethylsilyl)methane (△) and tetramethylsilane (○) determined for PCVD at $p_i = 1.3$ Pa and $P(\text{rf}) = 25$ W (data from refs 5 and 20, respectively).

zation of bis(trimethylsilyl)methane (BSM)⁵ and TMS.²⁰ Since the molecular structures of BSM and the examined DSM differ only by one methyl group, this small structural difference seems to be insignificant in terms of the plasma reactivity. The mentioned results are presented in Figure 3 as the dependencies of the gravimetric deposition rate of the film on the mass flow rate (F_w) of BSM and TMS vapors. The yields of the deposition (R/F_w) calculated from the slopes of the plots in Figure 3 are $4.30 \times 10^{-4} \text{ cm}^{-2}$ for BSM and $4.83 \times 10^{-4} \text{ cm}^{-2}$ for TMS. The close values of the deposition yield account for nearly the same plasma reactivities of these compounds and resulting predominant role of the methylsilyl groups in the activation step. It is noteworthy that the deposition yield parameter has successfully been used in our recent study²¹ for the determination of the reactivity of various organosilane source compounds such as TMS, hexamethyldisilane, and tetrakis(trimethylsilyl)silane, in the remote hydrogen plasma CVD.

In the light of data from Table 1 the activation of DSCB under impact of plasma electrons may be described by two major competitive reactions:



Abstraction of methyl group from silicon atom (reaction

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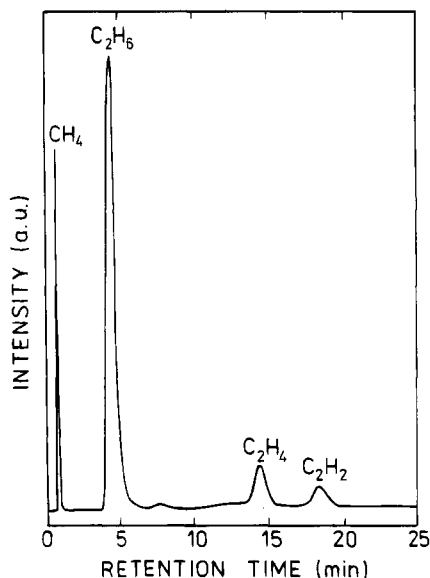


Figure 4. Gas chromatogram of the plasma fragmentation products of DSCB, sampled from the gas phase during PCVD process.

2) is known to be a plasma fragmentation pathway characteristic of methylated organosilicon compounds.²² From the normalized values of R/FM in Table 1, we have evaluated approximate contributions of the respective reactions to the activation step as ca. 60% for reaction 1 and ca. 40% for reaction 2.

The proposed mechanism of the activation step agrees with the results of the GC/MS examination of the plasma fragmentation products and the IR analysis of the deposit. The gas chromatogram of the gas-phase products sampled during PCVD shown in Figure 4, reveals the presence of ethane as the main component and some amount of methane, ethylene, and acetylene. Ethane is formed by the combination of methyl radicals, and its high concentration bears witness to the intense fragmentation of methylsilyl groups. Methane mostly originates from hydrogen abstraction by methyl radicals, whereas ethylene and acetylene probably result from plasma conversion of ethane. These data are strong evidence for reaction 2.

Figure 5 presents the IR spectra of DSCB and its PCVD film. The IR spectrum of DSCB (Figure 5A) exhibits the presence of the intense absorption band at 940 cm^{-1} attributed to $-\text{CH}_2-$ wagging vibrational mode in the ring.²³ The intensity of this band is seen to be very weak in the film spectrum (Figure 5B) which, on the other hand, shows the presence of a strong new absorption band (absent from the DSCB spectrum) at 1050 cm^{-1} , mostly originating from $-\text{CH}_2-$ wagging mode in the linear $\text{Si}-\text{CH}_2-\text{Si}$ unit.²⁴ The latter structure results from the ring opening process involving reaction 1.

It is interesting to note that the formation of $\text{Si}-\text{CH}_2-\text{Si}$ linkages was found to be a predominant plasma reaction in the case of TMS.²⁵ Mechanisms of the

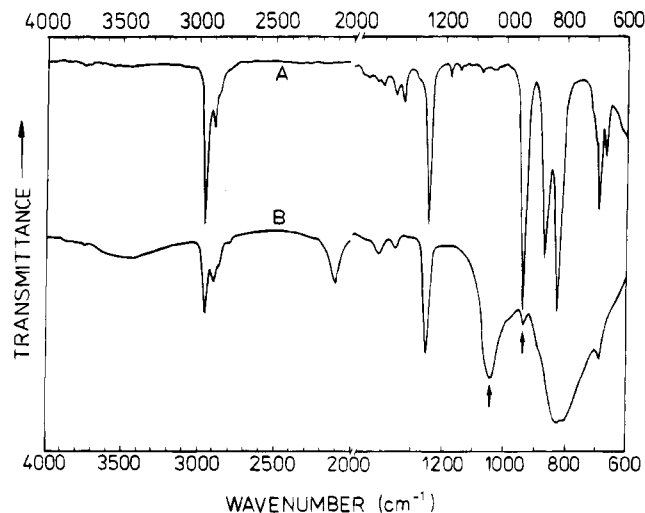
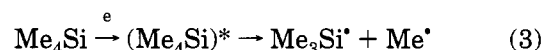


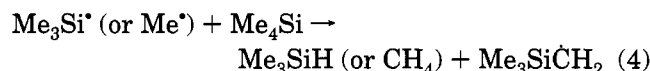
Figure 5. Infrared spectrum of (A) tetramethyl-1,3-disilacyclobutane liquid film (cell thickness 0.07 mm) and (B) its PCVD film, 700 nm thick.

reactions involved in this process may help to explain the observed reactivities of the investigated compounds which are revealed by the deposition yield data in Table 1. In the activation step, TMS is fragmented mostly via cleavage of the $\text{Si}-\text{C}$ bonds:



Due to a distinct difference in the dissociation energy values of $\text{Me}_3\text{SiCH}_2-\text{H}$ (415 kJ mol^{-1}) and $\text{Me}_3\text{Si}-\text{CH}_3$ (376 kJ mol^{-1}) bonds,²⁶ abstraction of a single hydrogen atom from methyl group seems to be unfavorable plasma activation reaction of TMS. This process was found as a very minor in the 147-nm photolysis of TMS in the gas phase, whereas the abstraction of the methyl groups appeared to be a major photochemical reaction.²⁷ Moreover, mechanistic consideration of the activation of TMS in the PCVD reported by Rynders et al.,²⁸ accounts for cleavage of the $\text{Si}-\text{C}$ bonds as a predominant process. Although atomic hydrogen has been detected in the TMS plasma by the optical emission spectroscopy,²⁹ we assume it originates mainly from a number of secondary plasma reactions rather than from the primary reaction involved in the electron impact. Therefore, the latter process has been omitted in favor of reaction 3.

The radical structures formed via reaction 3 may subsequently undergo reaction with TMS:



The radical product of reaction 4 may readily convert into highly reactive transient intermediate, i.e., dimethylsilene:^{1,30}

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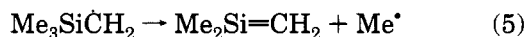
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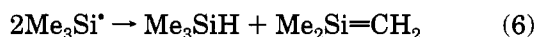
Table 2. Mass Spectrometric Data of Some Low-Molecular Weight Plasma Conversion Products of DSCB, Recorded at an Ionizing Electron Energy of 70 eV

identified structure	ion, <i>m/z</i> (rel intensity, %)
[Me ₃ SiCH ₂ (Me)SiCH ₂] ₂ (BDSCB)	M ⁺ , 288 (<1); (M - Me) ⁺ , 273 (100); (M - Me - CH ₄) ⁺ , 257 (11); (M - Me - Me ₂ SiCH ₂) ⁺ , 201 (49); (M - Me - CH ₄ - Me ₂ SiCH ₂) ⁺ , 185 (63); [M - Me - (Me ₂ SiCH ₂) ₂] ⁺ and/or (M - 2Me) ²⁺ , 129 (14); Me ₃ Si ⁺ , 73 (60)
(Me ₂ SiCH ₂) ₃ (TSCH)	M ⁺ , 216 (1); (M - Me) ⁺ , 201 (100); (M - Me - CH ₄) ⁺ , 185 (15); (M - Me - Me ₂ SiCH ₂) ⁺ , 129 (4); (M - Me - CH ₄ - Me ₂ SiCH ₂) ⁺ , 113 (4); (M - 2Me) ²⁺ , 93 (7); Me ₃ Si ⁺ , 73 (13)

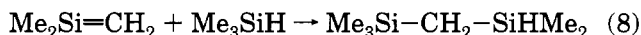
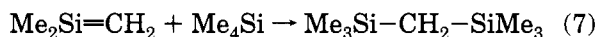
^a *M* denotes the molecular mass.



Another source of dimethylsilene may be disproportionation of trimethylsilyl radicals, which can occur due to relatively high value of the gas-phase disproportionation to combination rate constants ratio $k_d/k_c = 0.5$:^{31,32}

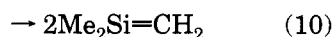
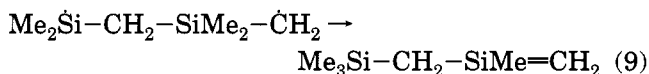


Due to biradical nature, silene may be inserted to the Si-C bond in TMS or to the Si-H bond in trimethylsilane (produced via reactions 4 and 6):³⁰



Reactions 7 and 8 are consistent with the fact that the resulting products, i.e., BSM and DSM, respectively, were found to be the most abundant among low-molecular-weight compounds of plasma conversion of TMS.²⁵ Conversion of TMS to BMS and DMS, according to the presented reaction scheme, well explains a similar plasma reactivities of these three compounds, as revealed by the data in Table 1 and Figure 3.

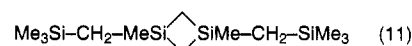
A high plasma reactivity noted for DSCB is attributed to easy formation of silene due to the ring-opening process. Biradical unstable product of reaction 1 may undergo either rearrangement to methyl[(trimethylsilyl)methyl]silene (reaction 9) or fragmentation to dimethylsilenes (reaction 10):



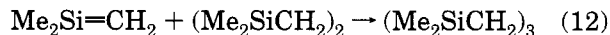
Formation of these silenes is supported by our GC/MS examination of low-molecular-weight plasma conversion products of DSCB which detected the presence of 1,3-bis[(trimethylsilyl)methyl]-1,3-dimethyl-1,3-disilacyclobutane (BDSCB) as the most abundant component and a marked amount of 1,1,3,3,6,6-hexamethyl-

1,3,6-trisilacyclohexane (TSCH). The full account of this study will be published separately, and the mass spectrometric identification data of the mentioned compounds are listed in Table 2.

Dimerization of methyl[(trimethylsilyl)methyl]silene (product of reaction 9) results in the formation of BDSCB (reaction 11). Insertion of dimethylsilene (prod-



uct of reaction 10) to 1,3-disilacyclobutane ring accounts for the formation of TSCH (reaction 12).



Finally, we assume that silenes are an important film-forming precursors in the PCVD of methylated silane and carbosilane source compounds. They are considered to propagate the growth of carbosilane segments in the deposit.

Conclusions

We have shown that in the plasma activation of DSCB the ring-opening reaction prevails over fragmentation of methylsilyl groups. This reaction is involved in the formation of the linear carbosilane segments in the deposit. The proved high reactivity of DSCB makes this compound an attractive precursor for the production of a-Si_{1-x}C_x:H films. The deposition yield was found to be very sensitive to the molecular structure of the source compound. Therefore, this parameter can be applied for the evaluation of reactivity of the source compounds in the PCVD process.

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