

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243882928>

# Reactivity of organosilicon precursors in remote hydrogen microwave plasma chemical vapor deposition of silicon carbide and silicon carbonitride thin-film coatings

ARTICLE *in* APPLIED ORGANOMETALLIC CHEMISTRY · MARCH 2010

Impact Factor: 2.25 · DOI: 10.1002/aoc.1589

---

CITATIONS

6

---

READS

22

## 3 AUTHORS, INCLUDING:



[Aleksander Michael Wrobel](#)

Centre of Molecular and Macromolecular St...

78 PUBLICATIONS 1,297 CITATIONS

SEE PROFILE



[Iwona Krystyna Blaszczyk-Lezak](#)

Instituto de Ciencia y Tecnología de Políme...

46 PUBLICATIONS 387 CITATIONS

SEE PROFILE

# Reactivity of organosilicon precursors in remote hydrogen microwave plasma chemical vapor deposition of silicon carbide and silicon carbonitride thin-film coatings

A. M. Wrobel\*, A. Walkiewicz-Pietrzykowska, and I. Blaszczyk-Lezak

**A number of organosilicon precursors for silicon carbide and silicon carbonitride thin-film coatings, such as silanes, carbosilanes, aminosilanes, and disilazane, respectively, were characterized in terms of their reactivity in a remote microwave plasma chemical vapor deposition process, which was induced using hydrogen as plasma generating gas. The process displayed high selectivity with respect to the activating species and the chemical bonds in the molecular structure of the precursors. In view of very short life times of excited hydrogen plasma species the activation step takes place with an exclusive contribution of ground-state hydrogen atoms. The C–H, C–C, Si–C, Si–N, C–N and N–H bonds present in the molecules of the precursors are non-reactive and only the Si–H or Si–Si bonds play a key role in the activation step. The reactivity of the precursors was characterized in a quantitative way by the yield of the film growth parameter. The yield parameter expressing the mass of film per unit mass of the precursor fed to the reactor was calculated from the slopes of linear plots of time dependencies of film mass and precursor mass, which were determined for each investigated precursor. The reactivity of the precursors was found to be strongly dependent on the number of the Si–H units present in their molecules and those containing two Si–H units appeared to be most reactive.**

Copyright © 2009 John Wiley & Sons, Ltd.

**Keywords:** remote hydrogen plasma CVD; SiC films; SiCN films; organosilicon precursors; reactivity

## Introduction

Of silicon-based thin-film coatings, silicon carbide (SiC) and silicon carbonitride (SiCN) films, owing to their unique optical, electrical and mechanical properties, as well as excellent resistance to high temperatures and aggressive chemical environments, are extremely attractive for a broad range of applications, from microelectronic and optoelectronic devices to tribological or biocompatible protective coatings for artificial organs.<sup>[1–4]</sup> It is noteworthy that silicon carbonitride is even considered to be a serious rival for other superhard materials, such as cubic boron nitride.<sup>[5–7]</sup> Moreover, the SiC and SiCN films are suitable components for the formation of multilayer coatings, SiCN–SiC–SiCN–SiC ···, of superior mechanical performance and other interesting properties.

Among the various methods used for the fabrication of the SiC and SiCN coatings, plasma-induced chemical vapor deposition (CVD) techniques are very beneficial due to relatively low deposition temperatures. These methods include direct plasma CVD (DP-CVD) and remote plasma CVD (RP-CVD), which differ substantially in many aspects. In DP-CVD plasma is generated in film-forming gas (precursor vapor) and film growth takes place in the plasma region. In RP-CVD plasma is generated in non-film-forming gas, which may be either reactive gas (e.g. H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>) or noble gas (e.g. Ar, He) and film growth takes place in the region free of plasma, which is fed with the precursor. The latter technique, RP-CVD, is extremely useful since it offers well-controlled deposition conditions free from film-damaging effects, such as charged-particle bombardment or high-energy ultraviolet irradiation,<sup>[8]</sup> which are inherently present in DP-CVD.<sup>[9]</sup>

Another important aspect is that RP-CVD is exclusively induced via chemical reaction between the uncharged plasma species (e.g. H, N or O atoms) fed from the plasma region, through the remote section (trap for electrons, ions and ultraviolet photons) and the precursor molecules, resulting in the formation of only radical active species. In contrast, the electron impact predominating in DP-CVD involves strong fragmentation of the molecules to a variety of radical, ionic and neutral active species. Moreover, a significantly lower concentration of active species contributing to RP-CVD, compared with that of DP-CVD, markedly reduces the growth step in the gas phase, thereby preventing the formation of powder particles, which often contaminate the DP-CVD films.<sup>[10]</sup> Owing to these aspects, RP-CVD is very advantageous for the production of defect-free and morphologically homogeneous SiC and SiCN films.

In the present study we use molecular hydrogen for the generation of a microwave plasma in RP-CVD and some selected volatile organosilicon precursors, such as alkylsilane and alkylcarbosilane source compounds for the formation of SiC films, as well as alkylaminosilane and alkylidisilazane source compounds for the formation of SiCN films. The use of organosilicon compounds for RP-CVD is particularly attractive for the following reasons: they

\* Correspondence to: A. M. Wrobel, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland, Lodz, Poland. E-mail: amwrobel@bilbo.cbmm.lodz.pl

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

serve as source of the Si–C, Si–N, or C–N bonds which are readily incorporated into the film, they are easy to convert to film-forming precursors of high mobility at the surface, and they are generally non-explosive, non-flammable, non-toxic and inexpensive.

In this work we characterize the reactivity of the mentioned organosilicon precursors in the RP-CVD process. Knowledge of the reactivity is very helpful for the selection of suitable precursors, which are most effective for the production of the SiC or SiCN films. Moreover, it may provide an important information on the mechanism of the activation in the investigated RP-CVD. The reactivity was characterized by determining the yield of the CVD process or, in other words, the yield of film growth. The yield parameter, expressing the mass of the deposited film per unit mass of the precursor fed into the CVD system, was developed by Yasuda,<sup>[11–13]</sup> who characterized the reactivity of a number of organic (hydrocarbons, fluorocarbons), organosulfur and some organometallic precursors in DP-CVD. However, the reactivity of organosilicon precursors used for the production of SiC and SiCN films is still little known and therefore we undertook the present study to extend this knowledge. The yield parameter values determined for the examined precursors are discussed in view of proposed hypothetical chemical reactions contributing to the activation step of RP-CVD.

## Experimental

### Remote Microwave Plasma CVD System and Film Deposition Procedure

The RP-CVD system used for the production of SiC and SiCN films was presented and described elsewhere.<sup>[14]</sup> The apparatus consists of three major parts: a plasma generation section (made from Pyrex glass tube, 28 mm i.d.) coupled via a resonant cavity and a waveguide with a microwave (2.45 GHz) power supply unit; a remote tube equipped with a Wood's horn photon trap; and a CVD reactor (made of Pyrex glass by HWS, Mainz) containing greaseless conical joints, 20 cm diameter flat flanges sealed with an O-ring and a stainless steel substrate holder (13 cm in diameter) equipped with a heater. A source compound injector (4 mm i.d.) was located approximately 4 cm in front of the substrate holder. Deposition experiments were performed at total pressure  $p = 75$  Pa, hydrogen flow rate  $F(\text{H}_2) = 100$  sccm, and microwave power input  $P = 150$  W. The precursors were fed into the CVD reactor by evaporation at room temperature. The flow rate of hydrogen was controlled using an MKS mass flow controller. In the case of the precursors, a mass flow controller was used to maintain a constant flow and the flow rate was estimated gravimetrically. Films were deposited on Fisher microscope cover glass plates ( $45 \times 50 \times 0.2$  mm), for kinetic measurements, and on p-type c-Si wafers, for the infrared analysis. The distance between the plasma edge and the substrate was 30 cm. No film deposition was observed in the plasma section, indicating that there was no back diffusion of the precursor.

### Spectroscopic Examination and Materials

The films deposited on c-Si wafers were examined by Fourier transform infrared (FT-IR) absorption spectroscopy. The FT-IR spectra were recorded in a transmission mode on a FTIR-Infinity ATI Matson spectrophotometer. The spectra of gaseous precursors were taken using a gas cell, 10 cm in length, equipped with sodium

chloride windows, whereas the spectra of liquid precursors were recorded for about 0.1 mm thick liquid film.

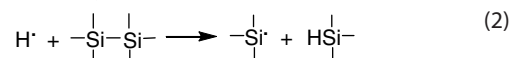
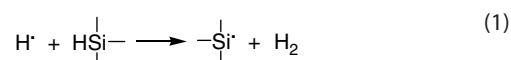
The organosilicon precursors, dimethylsilane (DMS), trimethylsilane (TrMS), triethylsilane (TrES), hexamethyldisilane (HMDS), (dimethylsilyl)(trimethylsilyl)methane (DTMSM) and bis(dimethylsilyl)ethane (BDMSE), used for the formation of the SiC films, as well as (dimethylamino)dimethylsilane (DMADMS), bis(dimethylamino)methylsilane (BDMAMS), tris(dimethylamino)silane (TDMAS) and 1,1,3,3-tetramethyldisilazane (TMDSN), used for the formation of the SiCN films, were mostly ABCR products. The liquid precursors were purified prior to the RP-CVD experiments by distillation in argon atmosphere, following which their purity was tested by gas chromatography. The hydrogen upstream gas used for plasma generation was of 99.99% purity.

## Results and Discussion

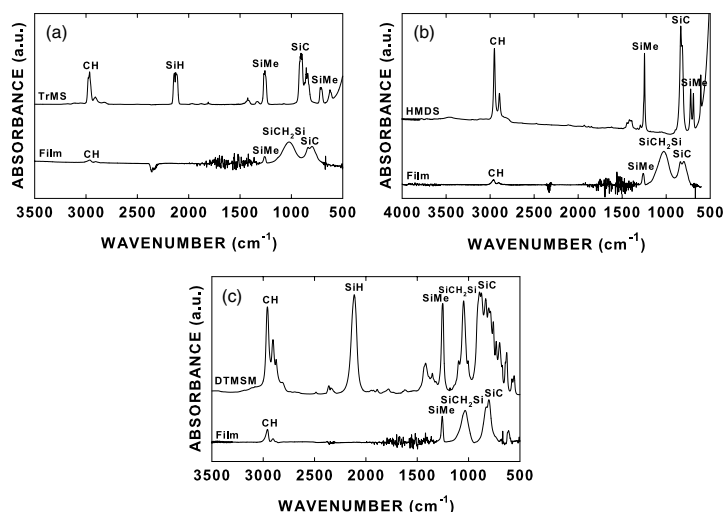
### Reaction System

We used the hydrogen plasma as the effective sources of hydrogen atoms for the activation of the precursor molecules. As charged species and ultraviolet photons have been eliminated from the reaction zone by the remote section equipped with a photon trap, neutral active species important for the investigated CVD process have been considered. The contribution of electronically excited and short radiative lifetime species –  $\text{H}_2(\text{C}^3\Pi_u)$ ,  $\text{H}[(2p)^2P^o]$ ,  $\text{H}[(3p)^2P^o]$  – generated in the hydrogen plasma<sup>[15,16]</sup> is negligible at a relatively long distance (0.3 m) from the plasma section. Therefore, we assume that only ground-state atoms  $\text{H}(^2S)$  play a major role in the activation step. The concentration of atomic hydrogen in the near-substrate region in the CVD reactor was determined using the  $\text{NO}_2$  titration method, that had been applied in our previous work.<sup>[8,17]</sup> Concentration of atomic hydrogen corresponding to the near-substrate region in the CVD reactor determined by the titration measurements<sup>[17]</sup> was  $[\text{H}] = 5 \times 10^{15} \text{ cm}^{-3}$  and its flow (or feeding) rate  $F(\text{H}) = 1.2 \times 10^{-3} \text{ mol min}^{-1}$ .

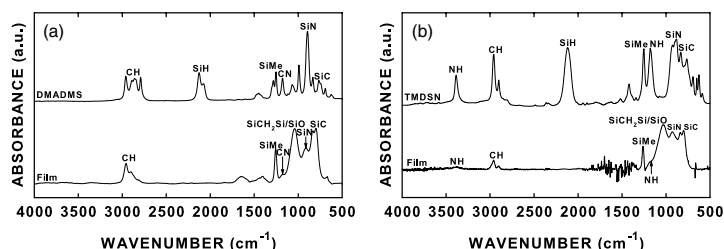
The susceptibility of particular bonds in the molecules of investigated precursors to react with atomic hydrogen was estimated by our earlier comparative RP-CVD experiments involving some permethylated model compounds, such as tetramethylsilane,<sup>[14,17]</sup> tetraethylsilane,<sup>[18]</sup> bis(trimethylsilyl)methane,<sup>[17]</sup> (dimethylamino)trimethylsilane<sup>[19]</sup> and hexamethyldisilazane,<sup>[20]</sup> which are known as effective film-forming precursors for DP-CVD.<sup>[21–23]</sup> The inability of these compounds to form films found for all RP-CVD experiments proved that the C–H, C–C, Si–C, Si–N, C–N and N–H bonds are non-reactive, whereas the observed ability of investigated precursors DMS, TrMS, TrES, HMDS, DTMSM, BDMSE, DMADMS, BDMAMS, TDMAS and TMDSN to form films can be attributed to the major role of their Si–H or Si–Si bonds in the activation step of the investigated RP-CVD process. The elementary reactions of atomic hydrogen with hydrosilyl and disilane units in the precursors are illustrated by equations (1) and (2), respectively.



A high reactivity of the Si–H and Si–Si units in the activation step of RP-CVD, as described by equations (1) and (2), may be



**Figure 1.** FT-IR spectra of TrMS (a), HMDS (b), and DTMSM (c) precursors and their SiC films deposited on c-Si wafers at substrate temperature  $T_S = 30^\circ\text{C}$ .



**Figure 2.** FT-IR spectra of DMADMS (a) and TMDSN (b) precursors, and their SiCN films deposited on c-Si wafers at substrate temperature  $T_S = 30^\circ\text{C}$ .

demonstrated by the results of FT-IR spectroscopy presented in Figs 1 and 2, which exemplifies the FT-IR spectra of TrMS, HMDS, DTMSM, DMADMS and TMDSN precursors and their SiC and SiCN films, respectively. A very intense absorption band corresponding to stretching vibrations of Si–H units present in the spectra of TrMS (Fig. 1a), DTMSM (Fig. 1c), DMADMS (Fig. 2a) and TMDSN (Fig. 2b) precursors near  $2100\text{--}2180\text{ cm}^{-1}$  is undetectable in the spectra of the SiC and SiCN films. The hydrosilyl group formed in the case of HMDS precursor by rupture of the Si–Si bond via equation (2) is not incorporated into the film structure since it readily undergoes reaction with hydrogen atom according to equation (1). This is consistent with the absence of the SiH IR band from the spectrum of the film (Fig. 1b).

### Yield of RP-CVD

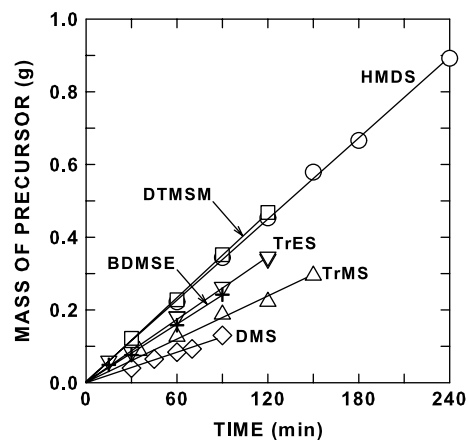
To characterize reactivity of investigated precursors in a quantitative way we have evaluated the yield of the RP-CVD process or film growth ( $k_m$ ) defined by Yasuda<sup>[11–13]</sup> as

$$k_m = r_m/F_m \quad (3)$$

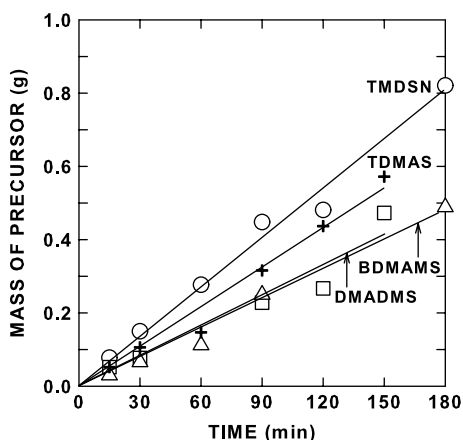
where  $r_m$  denotes the mass-based film growth rate and  $F_m$  is the mass-based precursor flow (or feeding) rate. In a physical meaning, parameter  $k_m$  expresses mass of the film per unit mass of the precursor fed into the CVD reactor, and was found to be very sensitive to the molecular structure of the precursor.<sup>[11–13]</sup> The RP-CVD experiments were carried out at a constant flow rates of the precursors using an unheated substrate ( $T_S = 30^\circ\text{C}$ ) to avoid the undesirable effect that might arise from thermally induced

reactions. The flow rates,  $F$ , and the film growth rates,  $r$ , were precisely determined from the slopes of the linear plots of the time dependencies of evaporated mass of the precursors and the mass of the deposited films shown in Figs 3–6, respectively. The  $F_m$  and  $r_m$  values calculated for the SiC and SiCN films are listed in Table 1 and 2, respectively.

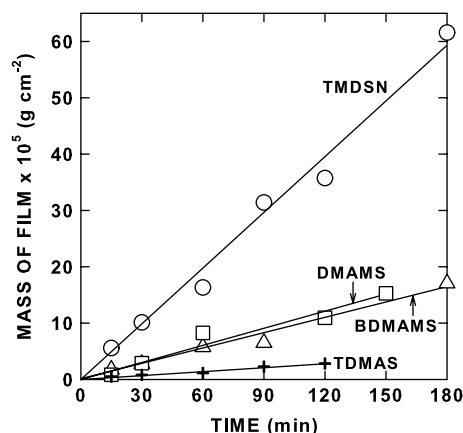
On the basis of the mentioned earlier value of the flow rate of atomic hydrogen  $F(\text{H}) = 1.2 \times 10^{-3}\text{ mol min}^{-1}$  and the values of the flow rate of the precursors  $F_m$  (data from Tables 1 and 2) it was interesting to characterize the reaction system also by evaluating



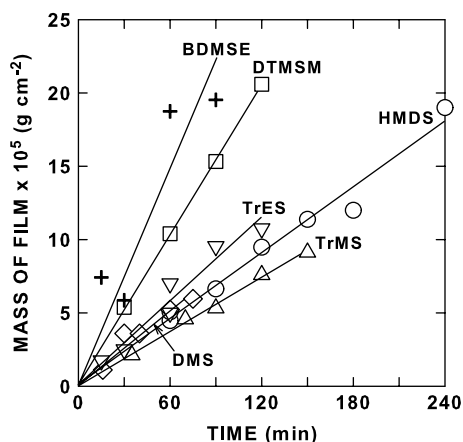
**Figure 3.** Mass of SiC precursors: DMS ( $\diamond$ ), TrMS ( $\Delta$ ), TrES ( $\nabla$ ), HMDS ( $\circ$ ), DTMSM ( $\square$ ) and BDMSE ( $+$ ) fed to the CVD reactor as a function of feeding time.



**Figure 4.** Mass of SiCN precursors: DMADMS ( $\square$ ), BDMAMS ( $\Delta$ ), TDMAS (+) and TMDSN ( $\circ$ ) fed to the CVD reactor as a function of feeding time.



**Figure 6.** Mass of SiCN film deposited at substrate temperature  $T_S = 30^\circ\text{C}$  from DMADMS ( $\square$ ), BDMAMS ( $\Delta$ ), TDMAS (+) and TMDSN ( $\circ$ ) precursors as a function of deposition time.



**Figure 5.** Mass of SiC film deposited at substrate temperature  $T_S = 30^\circ\text{C}$  from DMS ( $\diamond$ ), TrMS ( $\Delta$ ), TrES ( $\nabla$ ), HMDS ( $\circ$ ), DTSM ( $\square$ ) and BDMSE (+) precursors as a function of deposition time.

the approximate number of hydrogen atoms ( $N_H$ ) per single molecule of the precursor as:  $N_H = [F(H) \times M]/F_m$ , where  $M$  denotes the molecular mass of the precursor. We calculated for alkylsilane and alkylcarbosilane precursors (Table 1)  $N_H \approx 50$  atom/molecule and for alkylaminosilane and alkylsilazane precursors (Table 2)  $N_H \approx 40$ –60 atom/molecule. These values account for much lower population of active species contributing to the activation step of RP-CVD compared with those of DP-CVD.

Using the  $F_m$  and  $r_m$  values and equation (3) we calculated the yields of RP-CVD and the values of the parameter  $k_m$  for particular precursors are shown in Tables 1 and 2. It should be noted that  $k_m$  may be considered as the rate constant of the CVD process, but it does not mean a rate constant of chemical reaction in a strict sense.<sup>[13]</sup> Moreover, the values of  $k_m$  calculated for the investigated CVD system cannot be directly compared with those determined for other CVD systems.

### Precursors for SiC Films

Referring to the yield data for alkylsilanes and alkylcarbosilanes presented in Table 1, the higher values of  $k_m$  manifested by the precursors containing Si–H bonds compared with that of HMDSi prove the stronger reactivity of the Si–H unit than that of the Si–Si

unit. This finding is in a good agreement with the energy barrier,  $E_a$ , values reported for dissociation of the Si–H and Si–Si bonds in disilane under attack of hydrogen atom in the gas-phase, which are, respectively,  $E_a = 10 \text{ kJ mol}^{-1}$  and  $E_a = 28$  or  $13 \text{ kJ mol}^{-1}$  (the latter two  $E_a$  values correspond to the reactions involving either a front-side attack or a back-side attack of hydrogen atom on the Si–Si bond, respectively).<sup>[24]</sup> Moreover, the reactivity of the precursor increases markedly with increasing number of the Si–H units in the molecule as proved by the high  $k_m$  values determined for DMS and BDMSE (Table 1). This finding is also supported by the values of real rate constants reported for the gas-phase reactions of hydrogen atoms with DMS and TrMS molecules:<sup>[25–27]</sup>  $k(\text{DMS}) = 3.9 \pm 0.3 (10^{-13} \text{ cm}^3 \text{ s}^{-1})$  and  $k(\text{TrMS}) = 2.8 \pm 0.2 (10^{-13} \text{ cm}^3 \text{ s}^{-1})$ , which remain in a similar trend to that for the determined film growth yields, i.e.  $k_m(\text{DMS}) > k_m(\text{TrMS})$ . Almost the same  $k_m$  values noted for TrMS and TrES (Table 1) indicate that the slight increase in the size of alkyl substituents at the silicon atom, from methyl to ethyl, does not significantly affect the reactivity of the precursors.

In view of the large values of  $k_m$  noted for BDMSE and DMS (Table 1), these precursors appear to be most effective for the formation of SiC films by RP-CVD.

### Precursors for SiCN Films

The SiCN film growth yields determined for methylaminosilanes (Table 2) show that  $k_m$  decreases with increasing number of dimethylamino substituents at the silicon atom reaching approximately a five-fold lower value for TDMAS compared with those of DMADMS and BDMAMS. This trend is evidently attributed to the enhanced screening of the Si–H bond with  $\text{Me}_2\text{N}$  groups and resulting reduced reactivity of the bond with hydrogen atoms. As can be noted from the data in Table 2, the increase in the number of the Si–H unit in the precursor molecule greatly enhances reactivity, as revealed by a large value of the yield parameter  $k_m$  for TMDSN, which is two-fold higher than those of DMADMS and BDMAMS.

A high value of  $k_m$  found for TMDSN (Table 2) accounts for the strong reactivity of this precursor in the investigated RP-CVD process.



**Table 1.** Flow rate of the precursor and growth rate and growth yield of SiC film in remote hydrogen plasma CVD determined for various alkylsilane and alkylcarbosilane precursors at substrate temperature  $T_s = 30^\circ\text{C}$ 

Precursor	Molecular formula	Precursor flow rate, $F_m \times 10^3 \text{ (g min}^{-1}\text{)}$	Film growth rate, $r_m \times 10^7 \text{ (g cm}^{-2} \text{ min}^{-1}\text{)}$	Film growth yield, $k_m \times 10^4 \text{ (cm}^{-2}\text{)}$
Dimethylsilane (DMS)	$\text{Me}_2\text{SiH}_2$	$1.4 \pm 0.1$	$8.6 \pm 0.3$	$6.1 \pm 0.6$
Trimethylsilane (TrMS)	$\text{Me}_3\text{SiH}$	$1.9 \pm 0.1$	$6.2 \pm 0.1$	$3.3 \pm 0.2$
Triethylsilane (TrES)	$\text{Et}_3\text{SiH}$	$2.9 \pm 0.1$	$9.4 \pm 0.5$	$3.2 \pm 0.3$
Hexamethyldisilane (HMDS)	$\text{Me}_3\text{SiSiMe}_3$	$3.7 \pm 0.1$	$7.5 \pm 0.2$	$2.0 \pm 0.1$
(Dimethylsilyl)(trimethylsilyl)methane (DTMSM)	$\text{Me}_3\text{SiCH}_2\text{SiHMe}_2$	$3.9 \pm 0.1$	$17.2 \pm 0.1$	$4.4 \pm 0.2$
Bis(dimethylsilyl)ethane (BDMSE)	$\text{Me}_2\text{HSiCH}_2\text{CH}_2\text{SiHMe}_2$	$2.7 \pm 0.1$	$24.7 \pm 3.5$	$9.1 \pm 1.6$

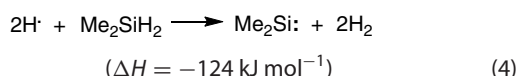
**Table 2.** Flow rate of the precursor and growth rate and growth yield of SiCN film in remote hydrogen plasma CVD determined for various alkylaminosilane and alkylidisilazane precursors at substrate temperature  $T_s = 30^\circ\text{C}$ 

Precursor	Molecular formula	Precursor flow rate, $F_m \times 10^3 \text{ (g min}^{-1}\text{)}$	Film growth rate, $r_m \times 10^7 \text{ (g cm}^{-2} \text{ min}^{-1}\text{)}$	Film growth yield, $k_m \times 10^4 \text{ (cm}^{-2}\text{)}$
(Dimethylamino)dimethylsilane (DMADMS)	$(\text{Me}_2\text{N})\text{SiHMe}_2$	$2.8 \pm 0.3$	$10.1 \pm 0.6$	$3.6 \pm 0.6$
Bis(dimethylamino)methylsilane (BDMAMS)	$(\text{Me}_2\text{N})_2\text{SiHMe}$	$2.7 \pm 0.2$	$9.2 \pm 0.5$	$3.4 \pm 0.4$
Tris(dimethylamino)silane (TDMAS)	$(\text{Me}_2\text{N})_3\text{SiH}$	$3.6 \pm 0.3$	$2.4 \pm 0.1$	$0.7 \pm 0.1$
1,1,3,3-Tetramethyldisilazane (TMDSN)	$(\text{Me}_2\text{HSi})_2\text{NH}$	$4.5 \pm 0.5$	$32.8 \pm 1.0$	$7.3 \pm 1.0$

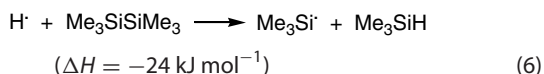
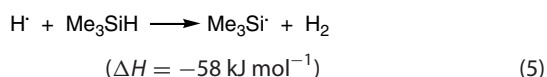
## Chemistry of the Activation Step

Assuming that reactivity of the precursors remains in a close relation with the nature of their active intermediates, we postulate some hypothetical reactions which may contribute to the activation step of investigated RP-CVD.

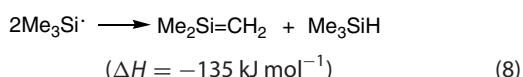
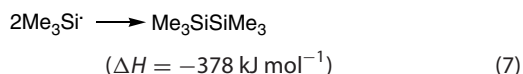
Referring to precursors for SiC films, a relatively large value of  $k_m = 6.1 \times 10^{-4} \text{ cm}^{-2}$  determined for DMS (Table 1) is due to its facile conversion into dimethylsilene,  $\text{Me}_2\text{Si}$ , an extremely reactive biradical transient intermediate [equation (4)].



The TrMS and HMDS precursors are activated via their conversion to trimethylsilyl radicals [equations (5) and (6)].



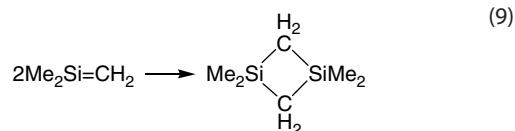
Trimethylsilyl radicals formed via equations (5) and (6) may undergo either recombination or disproportionation reactions [equations (7) and (8), respectively].<sup>[28,29]</sup>



The ratio of gas-phase disproportionation to recombination rate constants for trimethylsilyl radicals was found to be 0.5.<sup>[28,29]</sup>

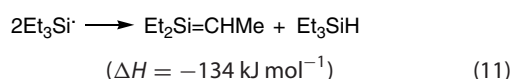
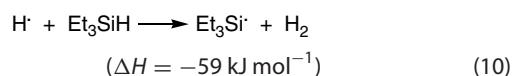
1,1-Dimethylsilene,  $\text{Me}_2\text{Si}=\text{CH}_2$ , a strongly reactive transient intermediate produced via equation (8), is considered to be an important SiC film-forming precursor.<sup>[14,30]</sup>

The presented activation reactions of the TrMS and HMDS precursors are consistent with the results of our gas chromatography/mass spectrometry (GC/MS) examination of the conversion products sampled from the gas phase during RP-CVD.<sup>[30]</sup> The GC/MS data revealed the presence of HMDS as the major conversion product of TrMS formed via equations (5) and (7), whereas TrMS predominated among the conversion products of HMDS, thus accounting for equation (6). The presence of 1,1,3,3-tetramethyl-1,3-disilacyclobutane found in the conversion products of both TrMS and HMDS precursors<sup>[30]</sup> is indicative of a 'head-to-tail' dimerization of 1,1-dimethylsilene.<sup>[31–33]</sup>



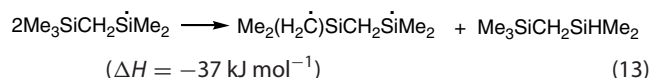
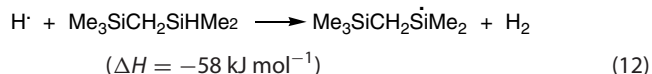
The dimerization [equation (9)] is a strongly exothermic reaction ( $\Delta H = -318 \text{ kJ mol}^{-1}$ ) proceeding with the energy barrier lower than  $58 \text{ kJ mol}^{-1}$ .<sup>[32]</sup>

A TrES precursor is activated via the reactions [equations (10) and (11)] similar to those of TrMS and resulting in the formation of 1,1-diethyl-2-methylsilene transient intermediate [equation (11)], which is assumed to play an important role in the film growth.

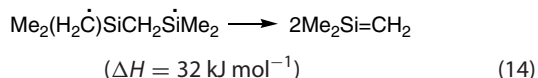


In the case of a DTMSM precursor the radical structure produced via the reaction with hydrogen atom [equation (12)] may undergo

disproportionation reaction resulting in the formation of a biradical structure as described by equation (13).

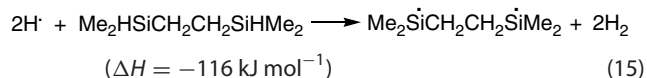


A very unstable biradical product of equation (13) may then readily fragment to 1,1-dimethylsilenes [equation (14)].

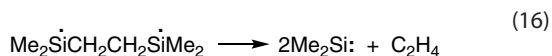


The reaction by equation (14) is slightly endothermic and needs only small amount of energy to occur. We assume that the energy may be transferred via a three-body recombination reaction of hydrogen atoms, strongly exothermic process, involving the molecule in equation (14). The formation of two dimethylsilene molecules in the activation step of DTMSM [equation (14)] is consistent with the relatively high  $k_m$  value evaluated for this precursor (Table 1).

The activation of a BDMSE precursor results in the formation of biradical structure [equation (15)].

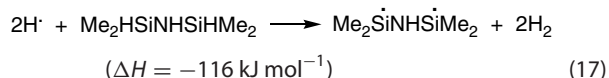


In the next step, a biradical product of equation (15) may undergo fragmentation caused by the energy transfer from a three-body recombination reaction of hydrogen atoms as mentioned earlier. This reaction [equation (16)] leads to the formation of dimethylsililene intermediates and the elimination of ethylene.

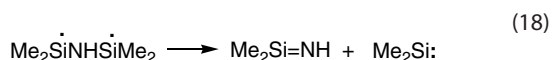


Equation (16) results in the formation of two dimethylsililene molecules, explaining the extremely high value of  $k_m$  determined for a BDMSE precursor (Table 1).

Referring to precursors for SiCN films, a strong reactivity of a TMDSN precursor, as revealed by the high value of  $k_m$  (Table 2), is undoubtedly caused by its easy conversion to a biradical structure [equation (17)].



This biradical product following the energy transfer from the mentioned three-body recombination reaction of atomic hydrogen may readily fragment to 1,1-dimethylsilanimine and dimethylsililene, 'hot species' capable of film formation [equation (18)].



The reaction described by equation (18) seems to be slightly endothermic and needs only a little energy to proceed.

The heats of some presented reactions were evaluated using the thermodynamic data for organosilicon compounds reported by Walsh.<sup>[34]</sup> The  $\Delta H$  values were calculated as the difference between the sum of energies of the bonds dissociated in the reagents,  $\Sigma E_d$ , and the sum of energies of the bonds formed in the reaction products,  $\Sigma E_f$ , as expressed by equation (19):

$$\Delta H = \Sigma E_d - \Sigma E_f \quad (19)$$

It is worth mentioning that the energy of a given bond is not constant and its value is affected by the substituents attached to the bonded atoms.<sup>[34]</sup> Although the values of the reaction heats calculated from equation (19) are very approximate and may differ from the real  $\Delta H$  values, they are assumed to reveal a general thermodynamic character of presented reactions.

The intermediates containing sililene, silene and silanimine units, due to their bifunctional nature, may contribute to film growth either by polymerization or stepwise insertion mechanisms. Their hypothetical reactions resulting in the formation of the SiC and SiCN films are described in our previous reports.<sup>[14,30,35]</sup>

## Conclusions

The results of this study revealed that the Si–H or Si–Si bonds present in the molecules of investigated precursors play a major role in their activation in RP-CVD process. The yield of RP-CVD  $k_m$  (expressing a mass of the film per unit mass of the precursor fed into the CVD reactor) is a useful parameter to characterize the precursor's reactivity. The higher values of  $k_m$  determined for TrMS and TrES compared with that of HMDS prove that the Si–H bond is more reactive in atomic hydrogen environment than the Si–Si bond. The reactivity of the precursor increases markedly with rising number of Si–H bonds in the molecule. The high values of  $k_m$  calculated for the precursors containing two Si–H units – DMS, BDMSE, and TMDSN – indicate that they are most effective for the production of SiC and SiCN films, respectively. A strong reactivity of these precursors is presumably due to their easy conversion to the  $\text{Me}_2\text{Si}^\cdot$  or  $\text{Me}_2\text{Si}=\text{NH}$  'hot' intermediates, respectively, which may readily undergo film-forming reactions.

## Acknowledgment

The present work was supported by the Polish Ministry of Science and Higher Education in a frame of the research project no. NN209117137.

## References

- [1] R. Riedel, H. Kleebe, H. Schonfelder, F. Aldinger, *Nature* **1995**, 374, 526.
- [2] W. Luft, Y. Tsuo, *Hydrogenated Amorphous Silicon Alloy Deposition Process*, Marcel Dekker: New York, **1993**, Chap. 2.
- [3] W. J. Choyke, H. Matsunami, G. Pensl, *Silicon Carbide: Recent Major Advances*, Springer: Berlin, **2004**.
- [4] L. M. Fischer, N. Wilding, M. Gel, S. Evoy, *J. Vac. Sci. Technol.* **2007**, B25, 33.
- [5] A. Badzian, T. Badzian, W. D. Drawl, R. Roy, *Diamond Relat. Mater.* **1998**, 7, 1519.
- [6] A. Badzian, T. Badzian, R. Roy, W. D. Drawl, *Thin Solid Films* **1999**, 354, 148.
- [7] A. Badzian, *J. Am. Ceram. Soc.* **2002**, 85, 16.
- [8] A. M. Wrobel, S. Wickramanayaka, Y. Hatanaka, *J. Appl. Phys.* **1994**, 76, 558.

- [9] A. M. Wrobel, G. Czeremuszkin, *Thin Solid Films* **1992**, 216, 203.
- [10] Y. Zhou, D. Probst, A. Thissen, E. Kroke, R. Riedel, R. Hauser, H. Hoche, E. Broszeit, P. Kroll, H. Stafast, *J. Eur. Ceram. Soc.* **2006**, 26, 1325.
- [11] H. Yasuda, *J. Polym. Sci.: Macromol. Rev.* **1981**, 16, 199.
- [12] M. Gazicki, H. Yasuda, *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, 38, 35.
- [13] H. Yasuda, *Plasma Polymerization*, Academic Press: Orlando, FL, **1985**, pp. 169–171.
- [14] A. M. Wrobel, A. Walkiewicz-Pietrzykowska, J. E. Klemberg-Sapieha, Y. Hatanaka, T. Aoki, Y. Nakanishi, *J. Appl. Polym. Sci.* **2002**, 86, 1445.
- [15] J. L. Vossen, J. J. Cuomo, in *Thin Film Processes* (Eds: J. L. Vossen, W. Kern), Academic Press: New York, **1978**, p. 46.
- [16] H. Okabe, *Photochemistry of Small Molecules*, Wiley-Interscience: New York, **1978**.
- [17] A. M. Wrobel, A. Walkiewicz-Pietrzykowska, M. Stasiak, T. Aoki, Y. Hatanaka, J. Szumilewicz, *J. Electrochem. Soc.* **1998**, 145, 1060.
- [18] A. M. Wrobel, A. Walkiewicz-Pietrzykowska, M. Ahola, I. J. Vayrynen, F. J. Ferrer-Fernandez, A. R. Gonzalez-Elipe, *Chem. Vap. Deposition* **2009**, 15, 39.
- [19] I. Blaszczyk-Lezak, A. M. Wrobel, M. P. M. Kivitorra, I. J. Vayrynen, *Chem. Vap. Deposition* **2005**, 11, 44.
- [20] A. M. Wrobel, I. Blaszczyk, A. Walkiewicz-Pietrzykowska, A. Tracz, J. E. Klemberg-Sapieha, T. Aoki, Y. Hatanaka, *J. Mater. Chem.* **2003**, 13, 731.
- [21] N. Inagaki, S. Kondo, M. Hirata, H. Urushibata, *J. Appl. Polym. Sci.* **1985**, 30, 3385.
- [22] N. Inagaki, A. Kishi, *J. Polym. Sci., Polym. Chem. Ed.* **1985**, 21, 2335.
- [23] R. Di Mundo, R. d'Agostino, F. Fracassi, F. Palumbo, *Plasma Process. Polym.* **2005**, 2, 612.
- [24] K. D. Doobs, D. J. Doren, *J. Am. Chem. Soc.* **1993**, 115, 3731.
- [25] N. L. Arthur, L. A. Miles, *Chem. Phys. Lett.* **1998**, 282, 192.
- [26] N. L. Arthur, L. A. Miles, *J. Chem. Soc. Faraday Trans.* **1998**, 94, 1077.
- [27] N. L. Arthur, I. A. Cooper, A. Czerwinsky, L. A. Miles, *Thin Solid Films* **2000**, 368, 176.
- [28] K. Tokach, R. D. Koob, *J. Phys. Chem.* **1979**, 83, 774.
- [29] S. K. Tokach, R. D. Koob, *J. Am. Chem. Soc.* **1980**, 102, 376.
- [30] A. M. Wrobel, A. Walkiewicz-Pietrzykowska, Y. Hatanaka, S. Wickramanayaka, Y. Nakanishi, *Chem. Mater.* **2001**, 13, 1884.
- [31] G. Raabe, J. Michl, *Chem. Rev.* **1985**, 85, 419.
- [32] Y. Apeloig, in *The Chemistry of Organic Silicon Compounds* (Eds: S. Patai, Z. Rappoport), Wiley: New York, **1989**, pp. 105–129.
- [33] G. Fritz, E. Matern, *Carbosilanes*, Springer: Berlin, **1986**.
- [34] R. Walsh, in *The Chemistry of Organic Silicon Compounds* (Eds: S. Patai, Z. Rappoport), Wiley: New York, **1989**, pp. 371–391.
- [35] I. Blaszczyk-Lezak, A. M. Wrobel, T. Aoki, Y. Nakanishi, I. Kucinska, A. Tracz, *Thin Solid Films*, **2006**, 497, 24.