Russian Chemical Reviews **70** (4) 321 – 332 (2001) © 2001 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2001v070n04ABEH000603

Mechanism of thermal decomposition of silanes

A A Onischuk, V N Panfilov

Contents

I.	Introduction	321
II.	Thermal decomposition of monosilane	322
III.	Homogeneous pyrolysis of disilane	325
IV.	Heterogeneous decomposition of silanes	326
V.	Aerosol formation in the pyrolysis of silanes	327
VI.	The composition of the solid product	329
VII.	Conclusion	330

Abstract. Data on the mechanism of thermal decomposition of silanes are generalised. The main stages of the process are distinguished and characterised. Attention is concentrated on the elementary homogeneous reactions, deposition of silicon from the gas phase and formation of aerosols. Various models of formation of aerosols are considered. The results of theoretical and experimental investigations of this process are discussed. Data on the chemical composition of the solid product of silane pyrolysis (wall deposit and aerosol particles) are presented. It is noted that the hydrogen content in the solid product varies over wide limits. The bibliography includes 211 references.

I. Introduction

Thermal decomposition (pyrolysis) of silanes is used in microelectronics to obtain polycrystalline silicon and amorphous silicon layers, which explains the researchers' interest in this process. Dozens of investigations devoted to pyrolysis of silane are published annually, however, it should be emphasised that this process has been studied to a much lesser extent than pyrolysis of their closest structural analogues, *viz*. alkanes. For example, it is known that the homogeneous pyrolysis (cracking) of alkanes follows a non-branched chain mechanism. Rice's quantitative scheme suggested back in the 1930s (Ref. 1) allows one to calculate the composition of cracking products for any individual hydrocarbon. The results of the calculations obtained by this scheme fit the experimental data. The study of the influence of heterogeneous factors on the pyrolysis of hydrocarbons [2] has led to a concept of the involvement of surface in both the stages of chain initiation and termination and the stages of chain propagation.

By now, the mechanism of silane pyrolysis (unlike that of hydrocarbon pyrolysis) has not been studied adequately. Due to the lower Si—H and Si—Si bond strengths in silanes in comparison to those of the C—C and C—H bonds in hydrocarbons, pyrolysis of silanes occurs at much lower temperatures and high-molecular-mass silane derivatives are not the final products, but rather intermediates. The final products of the thermal decomposition of silanes are gaseous hydrogen and the solid phase, *viz*., silicon

$$Si_nH_{2n+2} \longrightarrow n\,Si + (n+1)\,H_2\,. \qquad (1)$$

It should be noted that the reaction generally cannot go to completion due to the experimental conditions. So the solid product is usually hydrogenated (containing chemically bound hydrogen) rather than pure silicon. The lower the reaction temperature the higher the hydrogen content in the solid product. Besides, under real conditions, stable gaseous substances (Si_2H_6, Si_3H_8, Si_4H_{10}, *etc*.) are obtained in addition to hydrogen.

Silane pyrolysis is a complex process including numerous homogeneous and heterogeneous elementary steps. At lower pressure ($P < 1$ kPa), heterogeneous stages prevail [3–7] and the solid product deposits on the reactor walls, while at high pressures homogeneous elementary reactions dominate and the solid product is obtained mainly in the form of aerosol particles.[8,9] Usually, the thermal decomposition of silanes is studied in a static reactor ($600 < T < 750$ K),[10–19] in a flow reactor ($800 < T < 1000$ K) [10,14,20–29] and in shock tubes ($900 < T < 2000$ K).[30–35] The solid product is most often amorphous hydrogenated silicon. The content of hydrogen in the solid product expressed as the [H]/[Si] ratio varies from ~ 2 (Ref. 15) 0.5 (Ref. 27) and 0.15 (Ref. 8) at low temperature and a short reaction period to < 0.01 (Ref. 36) at high temperature and a long reaction time.

Under definite conditions, the intermediate solid product (hydrogenated silicon) formed in the course of pyrolysis influences the kinetics and mechanism of this process. In particular, such influence results in acceleration of the reaction when silicon with a highly developed surface (owing to the precipitation of aerosol particles) is obtained.[37,38] As the composition of the solid product changes during the reaction, its reactivity changes, *i.e*., a solid phase of variable composition is formed, which affects the kinetics and mechanism of the process.[3] This is the key feature of the pyrolysis of silanes.

In the present review, elementary reactions, the processes of silicon precipitation on the reactor walls, the formation of aerosols and elementary reactions occurring in the solid product in the pyrolysis are considered. It should be mentioned that certain aspects of the thermal decomposition of silanes have been

A A Onischuk, V N Panfilov Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, ul. Institutskaya 3, 630090 Novosibirsk, Russian Federation. Fax (7-383) 234 23 50. Tel. (7-383) 233 13 22.
E-mail: onischuk@ns.kinetics.nsc.ru (A A Onischuk)
Tel. (7-383) 233 23 81. E-mail: panfilov@ns.kinetics.nsc.ru (V N Panfilov)

Received 10 May 2000
Uspekhi Khimii **70** (4) 368 – 381 (2001); translated by A V Serov

discussed in detail. Thus homogeneous elementary stages of the process have been described thoroughly in a number of publications.[39–44] In the reviews,[45,46] the data on chemical vapour deposition (CVD) are systematised and some peculiarities of this process are explained. The results of studies on aerosol formation in the silane pyrolysis have been analysed.[8,9,47] In the present review, we avoid repeating the above-mentioned publications; in particular, elementary homogeneous reactions and CVD processes are not considered in detail. The attention is concentrated on those aspects which, in our opinion, either require an additional discussion (for example, the contribution of radical reactions) or provide more complete information on the pyrolysis of silanes.

II. Thermal decomposition of monosilane

1. Primary decomposition of the monosilane molecule

The reactions of the thermal decomposition of monosilane have been described most thoroughly. There are many viewpoints on whether the process of primary decomposition of SiH_4 into SiH_2 and H_2 under different conditions is homogeneous or heterogeneous. Thus according to an investigation of the silane pyrolysis in a static reactor ($P = 5-30$ kPa, $T = 650-700$ K) where the initial reaction rate did not depend on the surface to the volume ratio (S/V), the authors came to the conclusion that the primary reaction proceeds homogeneously.[15] This process was studied in static and flow reactors [10] (under lower pressure) and a conclusion as to the heterogeneity of the primary pyrolysis reaction in the whole range of pressures from 1 to 10^4 Pa was made assuming that the rate of the initial decomposition of silane at $P = 10$ Pa is proportional to the S/V ratio. This conclusion [10] was the subject of criticism. In particular, O'Neal and Ring [48] on the basis of results obtained earlier [15] reinterpreted the data given in the paper cited [10]. Taking into consideration that the heterogeneous primary decomposition prevails at pressures below 100 Pa, they proved convincingly that under high pressure (> 1 kPa) the primary decomposition proceeds as a homogeneous process. Studies on monosilane pyrolysis by laser heating (without influence of the reactor walls) confirm this conclusion. The activation energy of the laser-induced monosilane pyrolysis at 2.7 kPa (Ref. 49) was measured to be 221 ± 29 kJ mol^{-1}, which corresponds to the results obtained earlier in shock tubes [30] and in a static reactor.[15] Investigations into the silane pyrolysis under continuous wave (c.w.) CO_2 laser radiation and a total pressure of the mixture equal to 4×10^4 Pa allowed representation of the effective rate constant for the silane pyrolysis as $10^{11.5\pm0.6}\exp[-219\pm8(\text{kJ mol}^{-1})/RT]$ (Ref. 50); the value of the activation energy obtained in this study agrees with those given elsewhere.[15,30,49]

At present, it is believed that at $P > 1$ kPa the primary monosilane decomposition occurs as a homogeneous reaction and at lower pressures it is heterogeneous.[5,51]

2. The role of radical reactions in the monosilane pyrolysis

A detailed study of the mechanism of the homogeneous monosilane pyrolysis in a static reactor was first carried out by Purnell and Walsh.[15] The kinetics of the pyrolysis was characterised in the initial (conversion below 3%) and middle (conversion of 10%–20%) stages of the process. In the initial stage, the reaction had the order $\sim3/2$ with respect to monosilane, and the stoichiometry was described by the equation

$$2.39\,SiH_4 = Si_2H_6 + 0.13\,Si_3H_8 + 1.26\,H_2.$$

The total pressure in the reactor did not change with time and the solid product was not deposited. In the intermediate stage, the reaction was first order with respect to monosilane, the total pressure in the reactor increased and the formation of the solid product was observed.

Two alternative mechanisms were suggested which explained the experimental result, *viz*., the molecular mechanism

$$SiH_4 \longrightarrow SiH_2 + H_2, \quad (2)$$

$$SiH_2 + SiH_4 \longrightarrow Si_2H_6, \quad (3)$$

$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \quad (4)$$

and the radical mechanism

$$SiH_4 \longrightarrow {}^{\bullet}SiH_3 + H^{\bullet}, \quad (5)$$

$$H^{\bullet} + SiH_4 \longrightarrow H_2 + {}^{\bullet}SiH_3, \quad (6)$$

$${}^{\bullet}SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H^{\bullet}, \quad (7)$$

$$2\,{}^{\bullet}SiH_3 \longrightarrow Si_2H_6. \quad (8)$$

It was noted that the reaction order 3/2 can be explained both by the radical and the molecular mechanism (it is suggested that the process in the latter proceeds in the region of the dependence of the rate constant on pressure, *viz*., in the 'fall-off' regime). Later, the calculations of the reaction constant of the unimolecular decomposition of monosilane (reaction 2) by the Rice–Ramsperger–Kassel–Marcus (RRKM) method [30] confirmed the reaction order 3/2 observed by Purnell and Walsh. Nevertheless, the discussion on the possible role of radical reactions in the thermal decomposition of monosilane continues to be topical for the last two decades.

Cleavage of the Si–H bond rupture in the SiH_4 molecule (reaction 5) is the key reaction in the radical mechanism. The Si–H bond energy was measured both by the experimental and theoretical methods. For example, interpreting the experimental data on the kinetics of the reaction between I_2 and SiH_4 in the gas phase, Doncaster and Walsh [52] estimated the H_3Si-H bond energy as 378 ± 5.1 kJ mol^{-1}. The energy of this bond found in the investigation of the reaction of SiH_3 with HI (HBr) was 384 ± 2.0 kJ mol^{-1} (298 K),[53] and in the experiments on SiH_4 photo-ionisation at 150 K it was found to be equal to 372 ± 7 kJ mol^{-1} (Ref. 54).

It should be mentioned that the values of the H_3Si-H bond energy found experimentally agree with the theoretical values. Thus Sax and Kalcher [55] have calculated the enthalpies of formation and Gibbs energies of silicon hydrides containing up to three silicon atoms. According to these calculations, the dissociation energy of the H_3Si-H bond is 383.7 kJ mol^{-1}. The H_3Si-H bond energy obtained in the determination of atomisation energies for a series of AH_n hydrides (where A is an element of the I–VII groups of the second and third periods of the Periodic Table) is 384 kJ mol^{-1}.[56] According to the calculation carried out by Ho *et al*.,[57] the value of the energy is 384 kJ mol^{-1}, later,[58] it was established as 382 kJ mol^{-1}.

The average value of the H_3Si-H bond energy obtained in the above-mentioned studies is 381 ± 13 kJ mol^{-1}. This does not agree with the experimental activation energy (233 kJ mol^{-1}) of monosilane decomposition in the initial stage of the process.[15] (Besides, for the rate of the monosilane chain decay to fit the experimentally observed rates, the chain length should exceed 10^6, but as it follows from the experimental results obtained in shock tubes,[30] the average number of collisions of the monosilane molecule with the molecules of products does not exceed 50 under these conditions.) However, the activation energy value equal to 233 kJ mol^{-1} agrees with the calculated data on the activation energy of the reaction (2).[59–64]

At present, it is acknowledged that the primary stage of the monosilane decomposition is the dissociation of the SiH_4 molecule into SiH_2 and H_2 and not H_3Si-H bond cleavage; but the significance of the contribution of the radical reactions to the next pyrolysis stages still remains an open question. Numerous publications deal with the role of SiH_3 in the process of the thermal monosilane decomposition. Thus the pyrolysis of an equimolar mixture of SiH_4 and SiD_4 was studied in flow and static reactors.[14] The formation of mixed silanes and disilanes and the differences in the results obtained in static and flow reactors could be rationalised by the mechanism implying the involvement of SiH_3.

Thermal decomposition of monosilane in the presence of acetylene in a flow reactor at 690–710 K was studied by Haas

and Ring.[24] Based on the analysis of the reaction products, it was suggested that the silyl radicals were the major products of the initial decomposition.

In an investigation into the decomposition of monosilane in a single-pulse shock tube at 1200–1300 K, it was concluded [33] that the observed decomposition rate of monosilane cannot be explained by the radical mechanism; therefore, the primary act of the monosilane decomposition is the unimolecular elimination of H_2. The rate constants for the H_2 elimination from SiH_4 were calculated by the RRKM method. Comparison of the calculated and experimental [15] values showed that they differ more than forty-fold, which led to the conclusion that the chain mechanism is predominant under the static reactor conditions.

The thermal decomposition of SiH_4 in a static reactor in the presence of ethylene was carried out in order to determine whether the primary act of the monosilane decomposition occurs according to the molecular mechanism (*i.e.*, as the result of H_2 elimination from the SiH_4 molecule).[18] The analysis of the pyrolysis products suggested that the SiH_3 radicals formed in the slow heterogeneous process of the Si—H bond cleavage participate, though to a minor extent, in the pyrolysis of silane. This suggestion was confirmed by performing a pyrolysis of a SiH_4–SiD_4 mixture and detecting a rather high content of HD in the hydrogen fraction.

The initial acceleration of the silane pyrolysis in static and flow reactors in the range of pressures from 1 to 10^4 Pa was found,[10] which could be explained by the liberation of radicals from the surface into the gas phase or by the hydrogen atom elimination into the gas phase followed by chain reaction [processes (6) and (7)].

The gas-phase pyrolysis of monosilane in the mixture of Ar and SF_6 under c.w. CO_2-laser radiation was investigated.[50] The total pressure of the mixture was 4×10^4 Pa, while the partial pressure of monosilane was 10^2–10^3 Pa. The influence of propene additives as an inhibitor of radical reactions was studied experimentally. It was established that the effective rate constant for the silane pyrolysis decreases on the addition of propene. Presumably, in the presence of an inhibitor the reaction proceeds in accordance with the molecular mechanism and is characterised by an activation energy of 281.5 kJ mol^{-1}. In the absence of an inhibitor, the radical stages become sifnificant and the effective activation energy of this process decreases to 217 kJ mol^{-1}.

A series of experiments on the monosilane decomposition in the presence of alkenes and acetylene in a static reactor was carried out in order to find out whether silyl radicals take part in the pyrolysis of monosilane.[11] The analysis of the kinetics of the pyrolysis of the silane–acetylene mixture gave additional information on the nature of the monosilane thermal decomposition. According to the first-order kinetics obtained for this mixture, it was determined that silyl radicals do not participate in the decomposition under conditions examined. A possible scheme of the radical mechanism of monosilane decomposition in the presence of alkenes, according to which lower alkanes should be formed, was suggested. The absence of lower alkanes among the experimentally detected products led to the conclusion that the silyl radicals do not contribute considerably to the reaction.

The results of the investigation on the pyrolysis of a SiH_4–SiD_4 mixture under static conditions and under reduced pressures, in particular, the kinetic curves of the H_2, HD and D_2 formation, showed [12] that HD concentration in the initial stage of the process increased more slowly than in the following stages. The analysis of the formation of isotopic hydrogen molecules shows that the molecular mechanism of the monosilane decomposition is predominant. The sequence of the formation of mixed deuteriosilanes

$$\left.\begin{array}{l} SiH_4 \longrightarrow SiH_3D \\ SiD_4 \longrightarrow SiHD_3 \end{array}\right\} \longrightarrow SiH_2D_2,$$

was determined as being due to the exchange reactions involving the SiH_3 radical, *e.g.*

$$^{\bullet}SiH_3 + SiD_4 \longrightarrow SiH_3D + {}^{\bullet}SiD_3. \quad (9)$$

The concentrations of Si_2H_6, $Si_2H_2D_4$ and Si_2D_6 in the initial stage of the pyrolysis exceed those of other deuteriodisilanes. This fact proves the predominance of the disilane formation upon the reaction SiH_2 with SiH_4. Thus, the features of formation of isotopic hydrogen molecules and deuteriodisilanes points to the significance of the contribution made by the molecular mechanism.

In studies on the heterogeneous decomposition of monosilane at 0.5–4 Pa, the liberation of hydrogen atoms and SiH_3 radicals into the gas phase was observed.[61] The heated surface was placed directly close to the ionisation source in such a way that practically all the radicals evolved from the surface into the gas phase could reach the inlet of the ionisation chamber virtually without collisions with the gas molecules. At $T > 1800$ K, almost all the hydrogen obtained upon the decomposition SiH_4 is liberated as H atoms, while a part of hydrogen is liberated as H_2 molecules at $T < 1800$ K. The elimination of hydrogen in the temperature range 1300–1800 K is characterised by the activation energy 176 kJ mol^{-1}, while at $T < 1300$ K the activation energy is 46 kJ mol^{-1}. The effectiveness of the formation of SiH_3 radicals in the heterogeneous silane decomposition is 0.014–0.05. The liberation of SiH_3 radicals from the surface takes place as the result of the exchange of the hydrogen atom between the SiH_4 molecule and the free bond localised on the surface.

Direct detection of SiH_3 radicals in the thermal decomposition of monosilane in a flow reactor was investigated by the method of laser magnetic resonance.[28] A mixture of monosilane and argon (the total pressure was 60–500 Pa, the partial pressure of monosilane was 2.3–18 Pa) was used. The concentration of SiH_3 radicals changed from 10^{10} to 10^{12} cm^{-3} as the temperature of the reactor was raised from 830 to 1250 K (10% of SiH_4 at the total pressure of 400 Pa). It was suggested that SiH_3 radicals are formed in the heterogeneous processes.

The possibility of the chemical induction of the monosilane pyrolysis was shown.[19] This was carried out in a cylindrical metal reactor. A mixture of SiH_4 and O_2 with the oxygen percentage below 2% was introduced at room temperature and the reaction was initiated by spark ignition or by chemical ignition. The degree of conversion of monosilane was up to 60%. At definite concentration ratio of SiH_4 and O_2 and pressures, the mixture can ignite spontaneously even at room temperature, which is the chemical method of ignition. If the necessary $[SiH_4]:[O_2]$ ratio is established in a small volume of a reactor, self-ignition occurs. Then the burning front spreads over the whole volume, which results in the significant burnout of monosilane. The decomposition of silane presumably has branched-chain character under these conditions. Oxygen is required only in the stage of chain initiation. The atoms and radicals formed in this stage take part in the chain reactions of the monosilane decomposition, which results in significant consumption of monosilane. The average chain length is ~ 10.

Studies of the monosilane pyrolysis under static conditions at $P = 0.2$–5 kPa show that an increase in the specific surface (S/V) at $T = 669$ K gives rise to an increase in the decomposition rate, while at $T = 779$ K it results in its reduction.[4] The dependences obtained were interpreted in the terms of the radical chain mechanism and it was suggested that the rate of the heterogeneous decomposition of monosilane increases with the increase in the ratio S/V at low temperatures, while at high temperatures the rate of the heterogeneous chain termination increases.

It was supposed that the chain process plays a considerable role in the pyrolysis of monosilane [reactions (6) and (7)].[62] The activation energies obtained by *ab initio* quantum-chemical calculations were found to be 36 and 133 kJ mol^{-1} for these reactions, respectively.

Hydrogen atom formation during the monosilane pyrolysis in a shock tube was studied.[35] The reaction was followed by monitoring light absorption by the hydrogen atoms at the wavelength $\lambda = 121.6$ nm. An Ar/SiH_4 mixture was used (the total

pressure was 1 – 1.5 atm, the relative concentration of monosilane in the mixture was $\sim 10^{-5}$). The time dependence of the hydrogen atom concentration was obtained. The features of this dependence are as follows: the change in the concentration at low temperatures is S-shaped; the maximum concentration increases as the temperature increases to ~ 1600 K and decreases as the temperature increases from 1600 to 2300 K. Furthermore, at $T \geqslant 1800$ K the two-stage formation of hydrogen atoms is evident, as the characteristic time of the accumulation of hydrogen exceeds significantly the decomposition time of SiH_4. These features confirm the complex character of the processes of the hydrogen atom formation

$$Si + SiH_2 \longrightarrow {}^{\bullet}Si(H)Si + H^{\bullet}, \quad (10)$$

$$Si + H_2 \longrightarrow {}^{\bullet}SiH + H^{\bullet}, \quad (11)$$

$$Si + Si(H_2)Si \longrightarrow {}^{\bullet}Si_3H + H^{\bullet}, \quad (12)$$

$$H_2 + M \longrightarrow H^{\bullet} + H^{\bullet} + M. \quad (13)$$

Thus, the monosilane pyrolysis results in significant amount of hydrogen (5% – 10% of the initial silane concentration) even under homogeneous conditions and at high dilution. The hydrogen atoms are formed not upon the decomposition of SiH_4 or SiH_2, but rather in the secondary bimolecular reactions. It was concluded that the hydrogen might take part in the chain process which includes the reaction (6) and

$$ {}^{\bullet}SiH_3 + M \longrightarrow {}^{\bullet}SiH + H_2 + M, \quad (14)$$

$$SiH_4 + SiH \longrightarrow {}^{\bullet}Si_2H_4 + H^{\bullet}. \quad (15)$$

The rate constants for the radical reactions should be determined to evaluate the importance of these reactions in the thermal decomposition of monosilane. Unfortunately, the information on these reactions in the literature is poor. The rate constants [63] for the reactions of SiH_3 with Si_2H_6, of SiH_3 with SiD_4 and of H with SiH_4 ($T = 300$ K) are $\leqslant (7\pm4)\times10^{-15}$, $\leqslant (4\pm2)\times10^{-14}$, $\leqslant (2.5\pm0.5)\times10^{-13}$ cm^3 s^{-1}, respectively.[63] According to the calculations of the activation energy, the rate constant for the reaction (7) should be $1\times10^{-10}\exp[-56.1(\text{kJ mol}^{-1})/RT]$ cm^3 s^{-1}.[64] The calculated activation energy for the reaction (7) is 133 kJ mol^{-1}.[62] For the reaction [65]

$$ {}^{\bullet}SiH_3 + SiH_4 \longrightarrow {}^{\bullet}Si_2H_5 + H_2 \quad (16)$$

the rate constant is

$$k_{16} = 2.94\times10^{-12}\exp\left[-\frac{18.4\ (\text{kJ mol}^{-1})}{RT}\right].$$

The values of the rate constant for reaction (5) calculated based on the variation theory of the transition state for the temperature range 200 – 1000 K (Ref. 66) agree with the experimental values.

The above-mentioned data show that the role of the radical reactions in the monosilane pyrolysis is not clear. Nevertheless, the following conclusions can be made. First, under the conditions of the homogeneous pyrolysis, the primary reaction of the silane decomposition is the dissociation of SiH_4 to H_2 and SiH_2 [reaction (2)]. Second, the conditions under which radical reactions make considerable contribution exist probably even at relatively high pressures (where homogeneous reactions are predominant). In static and flow reactors, the radicals are apparently formed in heterogeneous reactions.[67]

The later statement can be confirmed by the following data. Studies of monosilane pyrolysis in a flow reactor for a mixture of 5% SiH_4 and 95% Ar (the total pressure was 6.6 kPa) gave the constants of the decomposition of monosilane at 843 and 933 K, *viz*., 0.25 and 3.6 s^{-1}, respectively. Let us estimate the possible contribution of the radical reactions to this process. The concentration of SiH_3 radicals formed in the monosilane pyrolysis in a flow reactor for a mixture of 10% SiH_4 and 90% Ar (the total pressure was 400 Pa) was measured by the method of laser magnetic resonance and was found to be 1×10^{10} and 5×10^{10} cm^{-3} at 843 and 933 K, respectively.[28] The signal for SiH_3 was proportional to the total pressure squared (the content of the silane in the initial mixture was constant) and to the partial pressure of the silane (the total pressure was fixed). Extrapolating the results obtained [28] for the mixture of 5% SiH_4 and 95% Ar (the total pressure was 6.6 kPa), we obtain $[SiH_3] \approx 1\times10^{12}$ and 5×10^{12} cm^{-3} at $T = 843$ and 933 K, respectively. The ratio of the (Ref. 65) reaction rate to $[SiH_4]$ can be calculated using the rate constant for the reaction (16). At 843 and 933 K, this ratio is 0.2 and 1.37 s^{-1}, respectively. Thus the estimated rate of the reaction (16) is close to the rate of the monosilane decomposition measured experimentally. Unfortunately, the development of the expression for the rate constant for the reaction (16) has not been described in detail.[65] Thus, the estimate given may suggest that the contribution of the radical reactions to the process of pyrolysis can be significant.

3. The mechanism of homogeneous pyrolysis of monosilane

At present, it is believed (see *e.g*. Ref. 39) that the main contribution to the process of the homogeneous monosilane pyrolysis (at least, in the early stages) is made by the following reactions

$$\begin{aligned} &SiH_4 \rightleftharpoons SiH_2 + H_2, \\ &SiH_2 + SiH_4 \rightleftharpoons Si_2H_6, \\ &SiH_2 + Si_2H_6 \rightleftharpoons Si_3H_8, \\ &SiH_2 + Si_3H_8 \rightleftharpoons Si_4H_{10}. \end{aligned} \quad (17)$$

Silylene (SiH_2) formed in the reaction of primary monosilane decomposition reacts with another molecule of monosilane to give disilane. Silylene reacts consecutively with disilane to give trisilane, with trisilane to give tetrasilane, *etc*. The formation of polysilanes is accompanied by their dissociation and the formation of substituted silylenes

$$Si_2H_6 \rightleftharpoons H_3SiSiH + H_2, \quad (18)$$

$$Si_3H_8 \rightleftharpoons SiH_3SiH_2SiH + H_2. \quad (19)$$

The reactions of substituted silylenes with monosilane result in the formation of trisilane, tetrasilane, *etc*.

$$SiH_4 + H_3SiSiH \rightleftharpoons Si_3H_8, \quad (20)$$

$$SiH_4 + SiH_3SiH_2SiH \rightleftharpoons Si_4H_{10}. \quad (21)$$

In addition, the isomerisation reactions

$$H_3SiSiH \rightleftharpoons Si_2H_4, \quad (22)$$

$$SiH_3SiH_2SiH \rightleftharpoons Si_3H_6, \quad (23)$$

unimolecular elimination of hydrogen, *e.g*.,

$$Si_2H_4 \rightleftharpoons Si_2H_2 + H_2, \quad (24)$$

$$Si_2H_2 \rightleftharpoons Si_2 + H_2, \quad (25)$$

$$Si_3H_6 \rightleftharpoons Si_3H_4 + H_2, \quad (26)$$

etc, take place.

The intermediate product Si_2H_2 is represented by two isomers, $Si(H_2)Si$ being more stable.[39,68] The Si_3H_4 species also has two isomers.[47]

Transition from the initial stage of the pyrolysis to intermediate one is accompanied by the acceleration of the process. Devyatykh and coworkers [16] were the first to investigate this phenomenon. This transition was described in more detail by Purnell and Walsh,[15] and the first mechanism of the initial acceleration was suggested in their monograph (Ref. 69). The reactions are autocatalytic processes with SiH_3SiH as an intermediate product.

$$\begin{aligned} &SiH_2 + SiH_4 \rightleftharpoons Si_2H_6 \longrightarrow SiH_3SiH + H_2, \\ &SiH_3SiH + SiH_4 \rightleftharpoons Si_3H_8 \longrightarrow SiH_2 + Si_2H_6. \end{aligned} \quad (27)$$

The results of simulation [39] have shown that the initial acceleration observed under the conditions of a static reactor [15] agree with the mechanism involving reactions (27). It should be noted that the initial acceleration in the process of the monosilane pyrolysis in a flow reactor was also described based on the mechanism of the reactions (27).[27, 67]

An alternative heterogeneous mechanism of the initial acceleration of the silane pyrolysis under the conditions of a static reactor [15] was suggested.[13, 70] Modification of the surface during the reaction was supposed to be the reason for the initial acceleration. As the result, SiH_2 is liberated from the surface into the gas phase accelerating the homogeneous process. This mechanism was criticised,[39] as the pyrolysis rate and the product ratio did not depend on the S/V ratio.[15] Furthermore, the homogeneous mechanism of the initial acceleration was supported by the results obtained in the silane pyrolysis where the influence of the reactor walls was eliminated (shock tubes [30] and laser pyrolysis [49]).

At present, the rate constants for numerous homogeneous elementary reactions occurring in the monosilane pyrolysis have been established. In particular, for the numerical simulation of the monosilane pyrolysis, one can use the parameters of the Arrhenius equation

$$k = A\exp\left(-\frac{E}{RT}\right),$$

where A is a pre-exponential factor, E is the activation energy.

The parameters A and E for the initial decomposition of the monosilane molecule [reaction (2)] in the pyrolysis of undiluted silane for the range of pressures are given in Table 1.

Table 1. Parameters of the Arrhenius equation for the reaction of primary monosilane decomposition in the range of temperatures 800 – 1500 K.[60]

P /Pa	A /s^{-1}	E /kJ mol^{-1}
0.1	1.5×10^{7}	214.4
1.3	1.5×10^{8}	214.4
13	1.5×10^{9}	214.4
1.3×10^{2}	1.5×10^{10}	214.4
1.3×10^{3}	1.5×10^{11}	214.8
1.3×10^{4}	1.8×10^{12}	218.6
1.3×10^{5}	1.7×10^{13}	223.6
∞	3.4×10^{15}	250.4

Table 2. Parameters of the Arrhenius equation (A /cm^3 s^{-1} or s^{-1}; E /kJ mol^{-1}) for the reactions occurring in the silane pyrolysis.

Reaction	A	E	Ref.
$SiH_2 + H_2 \rightarrow SiH_4$	9.8×10^{-13}	−2.3	40
$SiH_4 + SiH_2 \rightarrow Si_2H_6$	1.3×10^{-10}	−3.0	40
$Si_2H_6 \rightarrow SiH_2 + SiH_4$	1.3×10^{15}	213	43
$Si_2H_6 + SiH_2 \rightarrow Si_3H_8$	3.1×10^{-10}	−1.9	40
$Si_3H_8 \rightarrow SiH_2 + Si_2H_6$	4.9×10^{15}	222	42
$Si_3H_8 + SiH_2 \rightarrow Si_4H_{10}$	3.7×10^{-10}	−2.0	40
$Si_4H_{10} \rightarrow Si_3H_8 + SiH_2$	6.31×10^{15}	223.6	70
$Si_2H_6 \rightarrow H_3SiSiH + H_2$	7.9×10^{15}	237	70
$H_3SiSiH + H_2 \rightarrow Si_2H_6$	2.8×10^{-10}	9.2	70
$Si_3H_8 \rightarrow SiH_3SiH_2SiH + H_2$	1.8×10^{15}	229	70
$SiH_3SiH_2SiH + H_2 \rightarrow Si_3H_8$	2.83×10^{-10}	9.2	70
$SiH_4 + H_3SiSiH \rightarrow Si_3H_8$	6.6×10^{-11}	−10.9	70
$Si_3H_8 \rightarrow SiH_4 + H_3SiSiH$	9.3×10^{14}	209	42
$SiH_4 + SiH_3SiH_2SiH \rightarrow Si_4H_{10}$	6.6×10^{-11}	−10.9	70
$Si_4H_{10} \rightarrow SiH_4 + SiH_3SiH_2SiH$	4.4×10^{15}	210.3	70
$H_3SiSiH \rightarrow Si_2H_4$	6.2×10^{9}	6.5	72
$Si_2H_4 \rightarrow H_3SiSiH$	1.3×10^{10}	52.7	72
$SiH_3SiH_2SiH \rightarrow SiH_3SiHSiH_2$	6.2×10^{9}	6.5	70, 71
$SiH_3SiHSiH_2 \rightarrow SiH_3SiH_2SiH$	1.3×10^{10}	52.7	70, 71

In order to apply the data of Table 1 to the mixture of monosilane and argon, the parameters of the Arrhenius equation for several other elementary reactions of the silane pyrolysis are given in Table 2.

III. Homogeneous pyrolysis of disilane

Possible elementary reactions occurring in the thermal decomposition of disilane are described in the theoretical studies (Refs 72 – 75), while experimental investigations into the pyrolysis of disilane and higher silanes are presented in other papers (Refs 32, 42 – 44, 76, 77). Chromatographic analysis of the pyrolysis products of disilane carried out under static conditions at $P = 3\times10^3 - 10^4$ Pa and $T = 560 - 610$ K shows that the products are monosilane, trisilane, two tetrasilane isomers and hydrogen.[76] The parameters of the Arrhenius equation for the reactions of formation of monosilane, trisilane and hydrogen were determined. The mechanism of decomposition of disilane is following: the initial stage is the Si_2H_6 dissociation into SiH_2 and SiH_4, SiH_2 reacts further with Si_2H_6 to form Si_3H_8 and with Si_3H_8 to form Si_4H_{10}, *etc*. The experimental data suggest that hydrogen is a secondary reaction product.

The kinetics of the disilane decomposition was studied in a single-pulse shock tube in the temperature range 850 – 1000 K and at $P = (3.1 - 3.6)\times10^5$ Pa.[44] It was considered that two primary reactions of the disilane decomposition, *viz*., the forward reaction (18) and the reverse reaction (3) occur simultaneously. The parameters of the Arrhenius equation for these reactions were found (see Table 2).

Thermolysis of disilane under static conditions was experimentally studied by Martin, Ring and O'Neal.[43] The dependences of rate constants for this process on temperature and pressure were obtained. The calculated parameters of the Arrhenius equation differ substantially from those found by Bowrey and Purnell.[76]

The experimental investigation of the thermolysis of disilane, as well as tri- and tetrasilane under the conditions of a static reactor was continued later.[42] The parameters of the Arrhenius equation for the primary decomposition reactions of these silanes were found.

Studies of the kinetics of the disilane thermal decomposition in a shock tube at 1000 – 3100 K have shown that disilane generally decomposes into SiH_2 and SiH_4.[32]

The process of the thermolysis of disilane at $T = 300 - 1000$ K and $P = 100 - 1000$ Pa was studied by resonance enhanced multiphoton ionisation (REMPI) and multiphoton ionisation (MPI) methods.[78] The formation of silicon atoms during the pyrolysis was detected by REMPI method.

Thus, according to the above-mentioned data, the reactions

$$Si_2H_6 \longrightarrow SiH_2 + SiH_4,$$

$$Si_2H_6 + SiH_2 \longrightarrow Si_3H_8,$$

$$Si_3H_8 + SiH_2 \longrightarrow Si_4H_{10} \quad etc.$$

are predominant in the primary stage of the disilane pyrolysis.

Furthermore, the formation of silylsilylene H_3SiSiH and hydrogen as a result of dissociation of disilane, *viz*., the forward reaction (18), takes place. Silylsilylene is in equilibrium with its isomer disilene Si_2H_4 [equilibrium (22)].

Silylsilylene reacts actively with disilane (and other silanes), for example,

$$H_3SiSiH + Si_2H_6 \longrightarrow Si_4H_{10}. \qquad (28)$$

Thus, pyrolysis of disilane can proceed with an acceleration of the process due to the additional consumption of Si_2H_6 as the result of its reaction with H_3SiSiH and other substituted silylenes.

IV. Heterogeneous decomposition of silanes

Silicon deposition on the surface as the result of the heterogeneous silane decomposition has been described in detail in several reviews (see *e.g.* 45, 46). Hence, the processes of CVD are considered only in brief in the present review. The publications on the heterogeneous pyrolysis can arbitrarily be divided into two groups: the first group includes studies on the rate of formation of silicon films depending on macroscopic conditions (such as temperature, pressure and composition of a gas mixture); the second group deals with investigations into elementary heterogeneous reactions on the well-characterised ideal surface of single-crystal silicon using modern methods of analysis of the surface.

1. Growth of silicon films upon heterogeneous decomposition of silanes

Studies on the rate of formation of silicon films by the CVD method are aimed at the search for the optimum deposition conditions. Generally, this is associated with technological demands for microelectronics. Experiments were mostly carried out at reduced pressures to avoid the formation of aerosol particles, the deposition of which on the surface of growing layers impairs the product quality. In majority of investigations into CVD, silane [5, 60, 79–93] and disilane [5, 60, 80, 81, 89, 94–99] served as precursors of silicon films. The conditions of deposition in these investigations were so chosen, that the contribution of the homogeneous reactions was negligible. Thus, using the data from these publications, one can determine the reaction sticking coefficient of monosilane (ε_s) and disilane (ε_{ds}). For instance, ε_s is calculated using the equation

$$\varepsilon_s = \frac{W\rho}{Zm}, \tag{29}$$

where W is the rate of the film growth (cm s^{-1}); ρ is the density of the growing silicon film ($\rho \approx 2$ g cm^{-3}); Z is the collision frequency of the monosilane molecules with the unit surface area; m is the mass of the silicon atom. The value of ε_{ds} is calculated by the same manner.

Summing up the results given in the above-cited papers, we derived the equations for the reaction sticking coefficient of monosilane and disilane for a wide range of temperatures and partial pressures of these substances ($750 < T < 1000$ K, $2 \times 10^{-4} < p_s < 2$ kPa, $1 \times 10^{-4} < p_{ds} < 1$ kPa) [27]

$$\varepsilon_s = 10^{3.0}\exp\left[-\frac{148\ (\text{kJ mol}^{-1})}{RT}\right](p_s)^{-0.59}, \tag{30}$$

$$\varepsilon_{ds} = 10^{1.6}\exp\left[-\frac{119\ (\text{kJ mol}^{-1})}{RT}\right](p_{ds})^{-0.70}, \tag{31}$$

where p_s and p_{ds} are partial pressures of silane and disilane, respectively. The dependences of the reaction sticking coefficient of mono- and disilanes on their partial pressures are shown in Figs 1 ang 2.

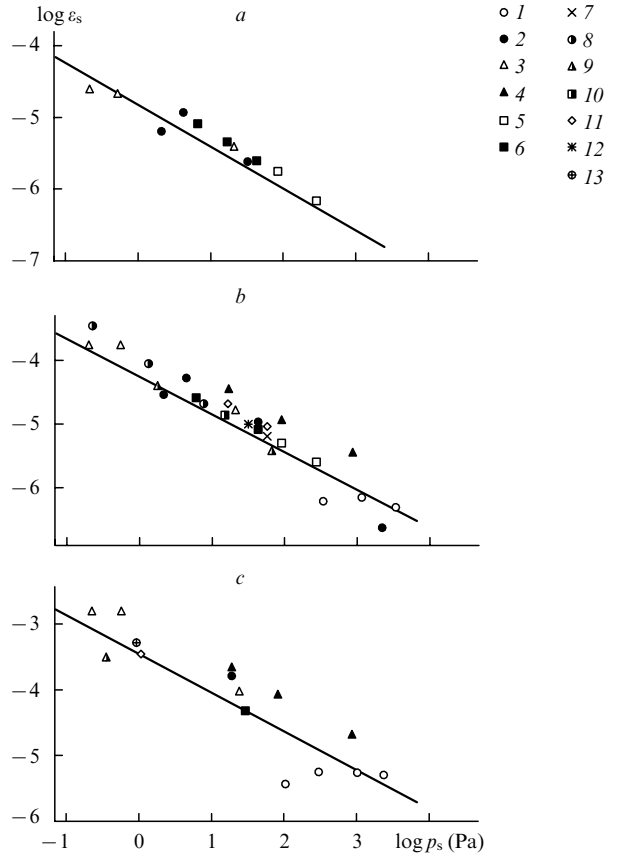


Figure 1. Dependence of the reaction sticking coefficient of monosilane on its partial pressure over the surface of the growing silicon layer at 813 (*a*), 863 (*b*) and 950 K (*c*).
Straight lines are plotted using the Eqn (30), the experimental points (*1*)–(*13*) are taken from Refs 92, 5, 81, 87, 86, 84, 88, 96, 95, 91, 85, 93 and 82, respectively.

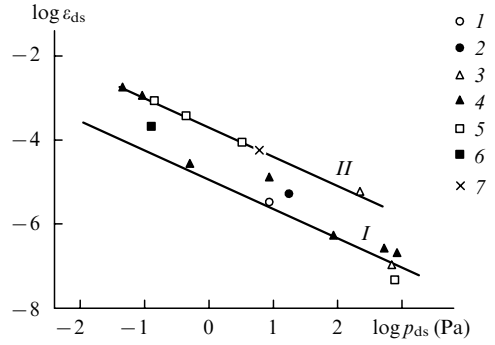


Figure 2. Dependence of the reaction sticking coefficient of disilane on its partial pressure over the surface of the growing silicon layer at 738 (*I*) and 863 K (*II*).
Straight lines are plotted using the Eqn (31), the experimental points (*1*)–(7) are taken from Refs 5, 96, 79, 99, 95, 91 and 94, respectively.

The reaction sticking coefficient of trisilane is approximately the same as those of disilane (for the same range of partial pressures).[89] It is noteworthy that the transport of the molecules from the gas phase to the reactor walls does not limit the process of film growth in the range of temperatures mentioned.[46] Using the Eqns (29)–(31), the growth rate of the silicon film in the heterogeneous decomposition of silane and disilane can be estimated for a wide range of temperatures and pressures.

2. Dissociative adsorption of silanes on the ideal surface of single-crystal silicon

Information on heterogeneous elementary reactions which occur in the pyrolysis of silane on the surface of a solid product formed, *viz.*, amorphous hydrogenated silicon is rather scarce. However, the mechanism of silicon growth on the well-characterised ideal Si(111) and Si(100) surfaces is discussed in numerous studies. Modern methods of the analysis of surface such as thermodesorption,[98] low-energy electron diffraction,[98, 100, 101] secondary-ion mass spectrometry,[102] scanning tunnelling microscopy,[103–108] reflection high-energy electron diffraction [109–111] are used in these investigations.

It was found that two neighbouring dangling bonds participate in elementary reactions of heterogeneous decomposition of mono- and disilane.[104, 107] The elementary reaction of the heterogeneous monosilane decomposition can be represented by the reaction [104, 108, 112–114]

$$SiH_4 + 2_ \longrightarrow \underline{H} + \underline{SiH_3}. \quad (32)$$

Hereinafter, the symbol _ denotes an active centre of the surface (dangling bond), $\underline{H}$ and $\underline{SiH_3}$ mean that H and SiH_3 are bound to the surface (mono- and trihydride groups, respectively).

The elementary reaction of the heterogeneous decomposition of disilane occurs as follows [105, 115, 116]:

$$Si_2H_6 + 2_ \longrightarrow \underline{SiH_3} + \underline{SiH_3}. \quad (33)$$

Alternatively, the following version is possible (Refs 115, 117, 118):

$$Si_2H_6 + 2_ \longrightarrow \underline{Si_2H_5} + \underline{H}. \quad (34)$$

Trihydride groups are unstable at high temperatures and decompose in the reaction presented below [105, 113, 116, 119–121]:

$$SiH_3 + 2_ \longrightarrow \underline{\underline{SiH_2}} + \underline{H}, \quad (35)$$

where $\underline{\underline{SiH_2}}$ is the group bound to two surface silicon atoms.

V. Aerosol formation in the pyrolysis of silanes

Three characteristic stages of aerosol formation in the pyrolysis of silanes can be distinguished: (1) nucleation, *i.e.*, the formation of nuclei which grow much faster than they decompose; (2) growth of single particles in the processes of 'condensation' and coagulation; (3) the formation of agglomerates consisting of individual primary particles. The stage of nucleation is the least studied.

1. Experimental investigation into aerosol formation

Aerosol formation can take place in the process of thermal decomposition of silane under certain conditions. The regimes of an epitaxial reactor which favour aerosol formation were studied by Eversteijn.[122] Mixtures of silane with hydrogen under atmosphere pressure were used. Aerosol formation occurred above certain critical concentration of silane, and this lower limit of silane concentration was registered at different temperatures. The critical silane concentration depended on the temperature of the reactor and changed from 0.248% to 0.002% as temperature increased from 1050 to 1410 K.

The process of aerosol formation in an epitaxial reactor was also studied by Murthy *et al.*[123] Mixtures of silane with argon under atmosphere pressure were used. If the concentration of silane at the reactor entrance exceeded 0.2%, 'smoke' was observed at the exit from the reactor at 1370 K. The onset of gas-phase nucleation was determined from 'smoke' formation. The critical concentration of silane decreased with the increase in temperature.

Investigations into aerosol formation in flow reactors were carried out.[9, 26, 124–129] Critical concentrations of silane in the decomposition of its mixtures with inert gases and hydrogen at low temperatures were determined by Slootman and Parent.[9] These experiments were carried out in a vertical flow reactor under atmosphere pressure. It was found that the critical concentration of silane for all carrier gases is inversely proportional to temperature. Homogeneous nucleation in inert gases began at relatively low temperatures. In the experiments with mixtures of silane with hydrogen, aerosol formation was observed at much higher temperatures. It is necessary to consider chemical reactions inhibiting the formation of aerosol particles to rationalise the increase in temperatures. It was suggested that the large excess of hydrogen influences kinetics of gas-phase processes, *viz.*, favours reverse reactions with silylene, which results in the decrease in the concentration of aerosol particle precursors.

Qian *et al.*[124] carried out experiments in a low-pressure flow reactor using pure silane. The residence time of silane in a hot zone was ~ 1 s. The beginning of the homogeneous nucleation was established by appearance of a weak smoke-forming flash. The critical concentration of silane (above which the nucleation was observed) increased ~ 1.26-fold on the increase in temperature from 970 to 1020 K.

The mechanism of deposition of polycrystalline silicon from silane was studied in a low-pressure flow reactor.[125] Mixtures of silane with nitrogen were used. The formation of aerosol particles was determined from laser light scattering. If the pressure of the silane exceeded the critical value (the initial content of silane in the mixture being the same), the intensity of the scattered light increased sharply. Thus for the initial mole fraction of silane equal to 0.3, the flow rate 400 $cm^3\ min^{-1}$ and temperature 1000 K, an abrupt increase in the intensity of the scattered light was observed at ~ 85 Pa. Electron microscopic studies of particles formed at 130 Pa suggest that these particles are single crystals with characteristic sizes from 5 to 10 nm.

Studies of the growth of silicon particles formed upon pyrolysis of silane in a multistage flow reactor followed by condensation, showed that the formation of the primary silicon particles as the result of homogeneous nucleation took place in the first stage.[126, 127] In the second stage, the primary particles served as the 'condensation nuclei' for the products of heterogeneous decomposition of silane and the intermediate products formed in the homogeneous pyrolysis. It was noted that the regime of spontaneous homogeneous nucleation can be realised provided such parameters as flow rate, silane concentration and temperature profile are properly selected. The morphology of the particles and their crystal structure were studied by electron microscopy. It was found that the particles are non-agglomerated spheres with the size of ~ 0.1 μm. The major part of the particles has crystal structures.

A method of synthesis of spherical particles homogeneous in size in a reactor with five heating zones was described.[128] The particle morphology was determined by electron transmission microscopy method and their crystal structures were determined by X-ray and electron diffraction.

Particles obtained in a flow reactor were shown to be clusters resulting from the homogeneous decomposition of silane, nucleation and coagulation.[26] The sizes of the clusters varied from 1 to 10 μm. X-Ray diffraction analysis revealed that the particles have crystalline structures.

The results of an experimental study of aerosol formation under static conditions were given in Refs 4 and 17. The formation of aerosols upon thermal decomposition of silane under pressure of 0.3–4.5 Pa and 750–830 K was investigated.[4] The aerosol particle formation was followed by monitoring changes in optical transmission at wavelengths of 515 and 755 nm. It was suggested that the precursors of aerosol are silicon atoms.

The critical character of the dependence of aerosol formation on the silane pressure was rationalised as being due to competition of the homogeneous nucleation and silicon deposition on the reactor walls.[17]

The investigation of aerosol formation in the pyrolysis of mono- and disilane diluted with argon was carried out in a shock tube.[8] The aerosol particle formation was followed by monitoring the absorption of laser radiation at two different wavelengths. Information on the sizes, compositions and the number concentrations of particles was obtained. The investigation of the particles by such methods as electron diffraction, electron transmission microscopy and secondary-ion mass spectroscopy shows that the particles are spherical with their diameters ranging from 10 to 40 nm. These particles are weakly agglomerated and contain 15 at.% of hydrogen.

A number of investigations [130–135] was devoted to the study of aerosol formation upon heating of silane by laser radiation. The formation of particles in mixtures of silane with argon under the action of a CO_2-laser was investigated by Flint and coworkers.[130, 131] The sizes and number concentrations of the particles were determined from the results of the measurement of

scattered and passed radiation. It was concluded that silicon particles are formed as amorphous silicon with subsequent crystallisation on passing into hotter reaction zones.

The silicon powder obtained upon laser heating of silane was analysed.[133, 134] Physicochemical parameters of the powder were determined, using a number of methods: the sizes of the particles and crystallites were determined by electron transmission microscopy and scanning electron microscopy, while the density was determined by the method of helium pycnometry. The crystal structures and sizes of the crystallites were determined by X-ray diffraction (considering the width of X-ray diffraction lines using the Debye–Sherrer formula), electron diffraction and dark-field electron microscopy. It was found that both separate spherical silicon particles and chain agglomerates are formed in the laser pyrolysis. The sizes of the primary particles incorporated in these agglomerates are in the range 10–100 nm. The particles are built of separate crystallites with the size ~ 15 nm.

The morphology of aerosol silicon particles formed upon decomposition of silane is of particular interest. Coagulation of these particles results in agglomerates of irregular structures.[128, 136] Analogous agglomerates of Ag,[137, 138] TiO_2,[136, 139–144] SiO_2[141, 144–147] and soot[148–150] are formed in natural and industrial processes.[151] These structures can be characterised by the fractal dimension $D_f < 3$, which is the exponent in the ratio

$$M \propto \left(\frac{R}{a}\right)^{D_f}, \tag{36}$$

which relates the mass of the agglomerate M to its radius R, a is the average radius of the primary particles. The silicon agglomerates formed upon pyrolysis of monosilane at temperatures 800–1720 K had the fractal dimension $D_f = 1.5–1.7$ (Refs 29, 136).

2. The mechanism of aerosol formation

Much attention has been paid to the mechanism of aerosol formation in the thermal decomposition of silanes. A mechanism of the formation of particles from silicon atoms was suggested based on investigation of aerosol formation upon thermal decomposition of monosilane under static conditions in the range of temperatures 723–1070 K and pressures 66–1335 kPa.[17] Studies of thermal decomposition of silane at 770–1070 K have led to a conclusion that the particles could be formed from Si and Si_2 atoms.[21, 22] A model of homogeneous polymerisation in the gas phase for the conditions of low-pressure reactors was suggested.[125] According to this model, the particles are formed from SiH_2. A model of particle formation from disilane was considered by White *et al.*[13] and Ring and O'Neal.[70] An assumption was made that trisilane could be a precursor of the solid product in the processes of the deposition on the reactor walls and homogeneous polymerisation.[39] Decomposition of pentasilane was considered to be the initial stage of aerosol formation.[152] A model of aerosol formation in low-pressure reactors which allows identification of the conditions of homogeneous nucleation and those under which heterogeneous reactions predominate was suggested by Sladek.[153] This model is based on the competition of nucleation processes and diffusion of aerosol precursors to the reactor walls.

A model of aerosol formation upon silane pyrolysis was given.[154] The calculations for the temperature range 900–2400 K were made based on the classical nucleation theory and assumption that aerosols are formed from silicon atoms. The critical nucleus contained several silicon atoms at 900–2000 K. Yet another theoretical investigation of silicon nucleation in silane decomposition was made based on the classical nucleation theory.[155]

Simulation of the aerosol formation process in the silicon layer deposition from mono- and disilane at atmospheric pressure showed that the basis of the mechanism is the growth of aerosol particles as the result of the consecutive addition of silylenes.[77]

A kinetic model of aerosol formation in thermal decomposition of silane was described.[156] The essence of this model is that a nucleus of an $(SiH_m)_n$ particle is formed in the initial stage as the result of homogeneous reactions; its further growth occurs due to its reaction with silane.

A mechanism of the formation of silicon hydride clusters in the silane pyrolysis was discussed.[47] This model contains detailed chemical information on the relative stabilities and reactivities of different possible silicon hydride clusters. The model allows one to calculate the rate of the particle nucleation. Thermodynamic properties of the silicon hydride clusters were estimated. The mechanism includes reversible and irreversible formation of silicon hydrides: the former reactions involve particles containing up to 10 Si atoms, while the latter reactions involve particles containing 11–20 Si atoms. The key intermediates and reactions leading to the formation of the particles were determined, the dependence of their formation on the conditions of the reaction was studied.

A detailed kinetic model describing pyrolysis of the initial molecules and the homogeneous nucleation of the silicon particles under shock tube conditions was considered.[8] The kinetic scheme contains 117 elementary reactions and includes 42 types of molecules (from fully hydrogenated Si_nH_{2n+2} to unsaturated Si_nH_{2n}, Si_2H_2 and non-hydrogenated silicon Si_n clusters). The model describes the process of coagulation of aerosol particles and their growth due to the CVD process.

Numerical solutions of discrete-sectional equations of the aerosol dynamics, which take account of the interaction of separate clusters for various reactor types were described.[128, 157] Simplified equations of reaction and coagulation which permit one to predict rapidly the aerosol evolution were derived. The influence of the initial vapour concentration, reaction time, seeds and temperature profile on the properties of the highly dispersed particles formed in silane pyrolysis was estimated.

Numerical stimulation of aerosol formation under the heterogeneous-homogeneous thermal decomposition of silane was made.[67] The model allows one to calculate the following time-dependent parameters: the degree of silane decomposition, di- and trisilane concentration, the concentration and dispersity of aerosol particles formed, the hydrogen content and the concentration of active centers (in the form of dangling bonds) in particles. These data agree reasonably with the experimental results.

The results of the above-mentioned studies show that the modern concepts on the process of aerosol formation are contradictory and its mechanism is not sufficiently studied. A reason for the disagreement as to the mechanism of aerosol formation is the insufficiency of experimental data. As a rule, the experiment gives only some parameters of the process such as the sizes of the particles,[8, 128] or temperature and the concentration of silane required for the onset of homogeneous nucleation.[4, 9, 17, 122–126] Nevertheless, based on the available literature data general features of aerosol formation in the silane pyrolysis can be formulated. The initial stage of this process is the formation of Si_mH_n clusters. The thermochemical calculations[47] show that for small sizes of clusters ($m \leqslant 10$) the rate of their decomposition is relatively high, which leads to a decrease in the number of silicon atoms in the clusters

$$Si_{m+l}H_{2(n+k)} \longrightarrow Si_mH_{2n} + Si_lH_{2k}. \tag{37}$$

In other words, the concentration of this kind of clusters depends on a quasi-equilibrium between the formation reactions of these clusters due to the agglomeration of smaller clusters

$$Si_mH_{2n} + Si_lH_{2k} \longrightarrow Si_{m+l}H_{2(n+k)}, \tag{38}$$

and the decay of lager clusters [see reaction (37)], on one side, and involvement of these clusters in analogous reactions of agglomeration and decay, on the other side. The rate of cluster decomposition is relatively small for larger cluster sizes ($m > 10$); since the dissociation of a large cluster requires that larger numbers of the Si–Si bonds were cleaved than in the dissociation of a smaller

cluster. Thus, the clusters with $m > 10$ may be regarded as particles and the rate of the formation of clusters with $m > 10$, as the rate of nucleation.[47] Further, the rate of the particle growth is determined largely by coagulation.[67]

VI. The composition of the solid product

The detailed investigations on the chemical composition of aerosol particles formed in thermal decomposition of silane are virtually not documented and the data on the solid product of the reaction which deposits on the reactor walls during the silane pyrolysis are very scarce. Therefore, the experimental data concerning this aspect should be analysed in more detail than in the previous sections.

The solid product (a deposit on the reactor walls and aerosol particles) of thermal decomposition of silane represents polycrystalline silicon [8] (high temperatures and/or long reaction time) or amorphous hydrogenated silicon [3] (mild temperatures and/or short reaction periods). The content of hydrogen in the solid pyrolysis product vary over a wide range (see Section I).

The bound hydrogen present in amorphous hydrogenated silicon has been actively studied over the last three decades. Detailed information on the vibration modes of mono- (SiH) and polyhydride [SiH_2, $(SiH_2)_n$, SiH_3] groups present in amorphous hydrogenated silicon was obtained (see, *e.g.*, Refs 158–162). IR spectra contain three characteristic absorption bands in the range of frequencies 550–750, 800–950 and 1900–2300 cm^{-1} (Ref. 158). Two peaks at ~ 2000 and 2100 cm^{-1} can be found in the range of frequencies 1900–2300 cm^{-1}. A doublet with maxima at 845 and 880 cm^{-1} or a single peak with maximum at 880 cm^{-1} is most often observed in the range 800–950 cm^{-1}. The data allow one to compare different vibration modes with absorption bands observed in the IR spectra of silanes (Table 3).

Table 3. Vibration frequencies of the Si—H bond observed in the IR-spectra of silanes.

Group	Vibration type	Frequencies /cm^{-1}
SiH	stretching	2000
	bending	630
SiH_2	stretching	2090
	scissors	880
	oscillation	630
SiH_3	stretching	2120
	deformation	905, 860
$(SiH_2)_n$	stretching	2090–2140
	scissors	890
	oscillation	845
	the same	630

The absorption peak at ~ 2100 cm^{-1} has to be discussed separately. It was supposed earlier [163, 164] that the stretching vibrations of the monohydride groups manifest themselves only at ~ 2000 cm^{-1}. However, it is well known that the stretching vibrations of the monohydride groups localised on the surface of single-crystal (Refs 116, 165 and references cited therein) and amorphous silicon [166, 167] have the frequencies at ~ 2100 cm^{-1}. Furthermore, lines at 2140,[168] 2100,[169] 2085,[170, 171] 2068 cm^{-1} (Ref. 172) were found in the IR spectra of the amorphous hydrogenated silicon, while absorption at 800–950 cm^{-1} (corresponding to the polyhydride groups, see Table 3) was absent. Heating of amorphous hydrogenated silicon resulted in an increase in the absorption intensity at 2100 cm^{-1} without any absorption at 800–950 cm^{-1}.[173, 174] These results suggest that two types of monohydride groups, which have absorption lines at 2000 and 2100 cm^{-1}, are possible in amorphous hydrogenated silicon. Using aerosol particles of amorphous hydrogenated silicon as an example, it was shown that the SiH groups with the vibration frequency ~ 2000 cm^{-1} do not interact with atmospheric oxygen, unlike the groups with the frequency ~ 2100 cm^{-1} (Refs 3, 175). The interaction of the latter is characterised by a decrease in the line intensity at 2100 cm^{-1} and appearance of absorption in the region 2170–2300 cm^{-1}. The absorption in this region is generally ascribed to monohydride groups where the hydrogen and oxygen atoms are bound to the same silicon atom (Si—O—Si—H).[176–182]

The hydrogen evolution method is a most informative method used for the investigation of amorphous hydrogenated silicon.[183–194] This method allows one to obtain quantitative information on the content of hydrogen in groups of different structures. The essence of this method can be described in the following way. A sample of amorphous hydrogenated silicon is heated at a constant rate (20–40 K min^{-1}), which results in the evolution of hydrogen. The amount of the hydrogen evolved is determined by the increasing pressure or by mass spectroscopy. The sample is heated to the $T \sim 920$–950 K, where crystallisation takes place and all the hydrogen releases to the gas phase. The results of the hydrogen evolution are usually represented as the dependence of the rate of evolution on temperature. Two temperature regions, *viz.*, 570–770 and 770–920 K can be distinguished. In the former region one [185–191, 193, 194] or two [183, 186, 188, 189, 191] peaks are observed. The hydrogen evolution in this temperature region is described by the first-order process and is not diffusion-limited.[185, 190] It is supposed that the low-temperature peak in this region is associated with elimination of hydrogen from the polyhydride groups,[183, 187–189, 194] while the high-temperature peak is determined by elimination of hydrogen from the monohydride groups.[183, 188] In the region 770–920 K, a peak the location of which depends on the rate of heating is observed. Hydrogen evolution in this case is described by the kinetics with an order exceeding the first order.[185–187, 189, 192] This peak is associated with the elimination of hydrogen from the monohydride groups.[183, 185–189] In relation to the interpretation of the peaks in the evolution spectra of hydrogen, it is worthwhile to note the investigations into the thermal desorption of hydrogen from the (111) and (100) faces of silicon single crystal [113, 195–202] and from the surface of porous crystalline sample.[202] It was found [198, 202] that the desorption of hydrogen from di- and trihydride groups occurs at 640–715 K, while from monohydride groups, at 720–820 K.

Detailed comparison of the IR spectra and the hydrogen evolution spectra for the aerosol particles of amorphous hydrogenated silicon formed upon thermal decomposition of monosilane in a flow reactor was described.[36, 175] The evolution spectra of the samples of aerosol particles withdrawn from the flow contain two relatively sharp peaks with the maxima at 670 and 760 K and a broad peak with the maximum at 780 K. It was found that the sharp peaks are determined by the evolution of hydrogen from poly- and monohydride groups with the frequency of stretching vibrations 2000 cm^{-1}, while the broad peak is determined by the evolution of hydrogen from monohydride groups with the frequency of stretching vibrations ~ 2100 cm^{-1}.

The investigations into amorphous hydrogenated silicon by the proton magnetic resonance method (Refs 203–205) show that the spectra represent superposition of two lines, *viz.*, a broad (20–30 kHz) one and a narrow (3–4 kHz) one. The hydrogen giving the broad line is called the 'clustered' phase and hydrogen giving the narrow line is called the 'dilute' phase. Hydrogen atoms of the both phases are bound to silicon atoms by covalent bonds. The difference between these two phases is that hydrogen atoms of the 'clustered' phase are located close to each other, while the hydrogen atoms of the 'dilute' phase are isolated.

For the aerosol particles of the amorphous hydrogenated silicon obtained upon thermal decomposition of monosilane, the data of IR spectroscopy were compared to those of the hydrogen evolution, on one hand, and the data from NMR spectroscopy, on the other hand.[3] It was concluded that the hydrogen of the

'clustered' phase is a constituent of mono- (vibration frequency is 2000 cm^{-1}) and polyhydride groups. The hydrogen of the 'dilute' phase is a constituent of monohydride groups with the vibration frequency 2100 m^{-1}. Experimental results suggest that the SiH groups of the 'clustered' phase are localised inside the amorphous silicon network [206] as 'hydrogen complexes', *viz*., extended defects stabilised by hydrogen.[207–211] The monohydride groups of the 'dilute' phase are localised on the surfaces of interconnected microvoids and microchannels.

VII. Conclusion

Thermal decomposition of silanes is a complex process including different stages. Arbitrarily, the main components of the mechanism of this process are as follows:

1. Homogeneous elementary reactions.

2. Heterogeneous reactions occuring on the surface of the silicon deposited on the reactor walls.

3. The formation of precursors of aerosol particles (molecular clusters Si_mH_n, $m = 10-20$) which exist in the equilibrium with gaseous intermediate products.

4. Homogeneous nucleation, *i.e*., the formation of the smallest aerosol particles, the rates of forward growth reactions for which exceed substantially those of the reverse reactions.

5. Heterogeneous deposition of molecules and smaller clusters on the surface ('condensation').

6. Coagulation and coalescence of particles. In the initial stages where the rate of coalescence exceeds that of the coagulation, more or less spherical particles are formed. In the following stages where the coagulation becomes predominant, particle agglomerates (the so-called primary particles) are formed.

7. Agglomeration of primary particles, *i.e*., the transformation of several neighbouring particles into one primary particle.

8. Chemical and structural changes in aerosol particles.

To explain the pyrolysis mechanism in general each of the above-mentioned stages has to be investigated in detail because of their close relations and mutual influence on each other. Only thorough study with the help of modern physicochemical methods can give the detailed representation of this process.

References

1. F O Rice *J. Am. Chem. Soc*. **55** 3035 (1933)
2. N A Vasil'eva, R A Buyanov, K I Zamaraev *Khim. Fiz*. **3** 688 (1984) [a]
3. A A Onischuk, V P Strunin, R I Samoilova, A V Nosov, M A Ushakova, V N Panfilov *J. Aerosol Sci*. **28** 1425 (1997)
4. R G Aivazyan, V V Azatyan, L F Satunkina *Kinet. Katal*. **37** 492 (1996) [b]
5. B A Scott, R D Estes, J M Jasinski *J. Chem. Phys*. **89** 2544 (1988)
6. A G Gasparyan, G B Rostomyan, R A Badalyan, G A Arutyunyan *Kinet. Katal*. **29** 935 (1988) [b]
7. M S Sukhov *Izv. Akad. Nauk, Neorg. Mater*. **18** 1077 (1982) [c]
8. M Frenklach, L Ting, H Wang, J M Rabinowitz *Isr. J. Chem*. **36** 293 (1996)
9. F Slootman, J-C Parent *J. Aerosol Sci*. **25** 15 (1994)
10. R Robertson, D Hils, A Gallagher *Chem. Phys. Lett*. **103** 397 (1984)
11. J W Erwin, M A Ring, H E O'Neal *Int. J. Chem. Kinet*. **17** 1067 (1985)
12. N K Serdyuk, V P Strunin, E N Chesnokov, V N Panfilov *Kinet. Katal*. **26** 790 (1985) [b]
13. R T White, R L Espino-Rios, D S Rogers, M A Ring, H E O'Neal *Int. J. Chem. Kinet*. **17** 1029 (1985)
14. M A Ring, M J Puentes, H E O'Neal *J. Am. Chem. Soc*. **92** 4845 (1970)
15. J H Purnell, R Walsh *Proc. R. Soc. London, A Math. Phys. Sci*. **293** 543 (1966)
16. G G Devyatykh, V M Kedyarkin, A D Zorin *Zh. Neorg. Khim*. **10** 1528 (1965) [d]
17. S V Maklakov, R G Aivazyan, V V Azatyan, P V Zhirkov, L F Satunkina *Mendeleev Commun*. 120 (1995)
18. P Neudorfl, A Jodhan, O P Strausz *J. Phys. Chem*. **84** 338 (1980)
19. R G Aivazyan, V V Azatyan, V I Kalachev, V I Rubtsov *Fiz. Goreniya Vzryva* **30** 85(1994)
20. G Cochet, H Mellottee, R Delbourgo *J. Chim. Phys*. **71** 1363 (1974)
21. W G Breiland, M E Coltrin, P Ho *J. Appl. Phys*. **59** 3267 (1986)
22. W G Breiland, P Ho, M E Coltrin *J. Appl. Phys*. **60** 1505 (1986)
23. S K Iya, R N Flagella, F S DiPaolo *J. Electrochem. Soc*. **129** 1531 (1982)
24. C H Haas, M A Ring *Inorg. Chem*. **14** 2253 (1975)
25. B A Scott, R D Estes *Appl. Phys. Lett*. **55** 1005 (1989)
26. G Hsu, R Hogle, N Rohatgi, A Morrison *J. Electrochem. Soc*. **131** 660 (1984)
27. A A Onischuk, V P Strunin, M A Ushakova, V N Panfilov *Int. J. Chem. Kinet*. **30** 99 (1998)
28. L N Krasnoperov, V V Nosov, A V Baklanov, V N Panfilov *Khim. Fiz*. **7** 528 (1988) [a]
29. A A Onischuk, A I Levykin, V P Strunin, K K Sabelfeld, V N Panfilov *J. Aerosol Sci*. **31** 1263 (2000)
30. C G Newman, H E O'Neal, M A Ring, F Leska, N Shipley *Int. J. Chem. Kinet*. **11** 1167 (1979)
31. V N Votintsev, I S Zaslonko, V S Mikheev, V N Smirnov *Kinet. Katal*. **27** 972 (1986) [a]
32. H-J Mick, M W Markus, P Roth, V N Smirnov *Ber. Bunsenges. Phys. Chem*. **99** 880 (1995)
33. C G Newman, M A Ring, H E O'Neal *J. Am. Chem. Soc*. **100** 5945 (1978)
34. M Koshi, S Kato, H Matsui *J. Phys. Chem*. **95** 1223 (1991)
35. H-J Mick, P Roth, V N Smirnov, I S Zaslonko *Kinet. Katal*. **35** 485 (1994) [a]
36. A A Onischuk, V P Strunin, M A Ushakova, V N Panfilov *Phys. Status Solidi B* **186** 43 (1994)
37. A A Onischuk, V P Strunin, M A Ushakova, V N Panfilov *Khim. Fiz*. **11** 1136 (1992) [a]
38. A A Onischuk, V P Strunin, M A Ushakova, V N Panfilov *Khim. Fiz*. **13** (5) 129 (1994) [a]
39. R Becerra, R Walsh *J. Phys. Chem*. **96** 10856 (1992)
40. J M Jasinski, R Becerra, R Walsh *Chem. Rev*. **95** 1203 (1995)
41. I Safarik, V Sandhu, E M Lown, O P Starausz, T N Bell *Res. Chem. Intermed*. **14** 105 (1990)
42. J G Martin, H E O'Neal, M A Ring *Int. J. Chem. Kinet*. **22** 613 (1990)
43. J G Martin, M A Ring, H E O'Neal *Int. J. Chem. Kinet*. **19** 715 (1987)
44. J Dzarnoski, S F Rickborn, H E O'Neal, M A Ring *Organometallics* **1** 1217 (1982)
45. J M Jasinski, S M Gates *Acc. Chem. Res*. **24** 9 (1991)
46. J M Jasinski, B S Meyerson, B A Scott *Ann. Rev. Chem*. **38** 109 (1987)
47. M T Swihart, S L Girshick *J. Phys. Chem., B* **103** 64 (1999)
48. H E O'Neal, M A Ring *Chem. Phys. Lett*. **107** 442 (1984)
49. J M Jasinski, R D Estes *Chem. Phys. Lett*. **117** 495 (1985)
50. V V Nosov, S M Repinskii, F N Dul'tsev *Kinet. Katal*. **25** 530 (1984) [a]
51. R Robertson, A Gallagher *J. Chem. Phys*. **85** 3623 (1986)
52. A Doncaster, R Walsh *Int. J. Chem. Kinet*. **13** 503 (1981)
53. J A Seetula, Y Feng, D Gutman, P W Seakins, M J Pilling *J. Phys. Chem*. **95** 1658 (1991)
54. J Berkowitz, J P Greene, H Cho, B Ruščić *J. Chem. Phys*. **86** 1235 (1987)
55. A F Sax, J Kalcher *J. Phys. Chem*. **95** 1768 (1991)
56. J A Pople, B T Luke, M J Frisch, J S Binkley *J. Phys. Chem*. **89** 2198 (1985)
57. P Ho, M E Coltrin, J S Binkley, C F Melius *J. Phys. Chem*. **89** 4647 (1985)
58. P Ho, C F Melius *J. Phys. Chem*. **94** 5120 (1990)
59. M S Gordon, T N Truong, E K Bonderson *J. Am. Chem. Soc*. **108** 1421 (1986)
60. B S Meyerson, J M Jasinski *J. Appl. Phys*. **61** 785 (1987)
61. J Doyle, R Robertson, G H Lin, M Z He, A Gallagher *J. Appl. Phys*. **64** 3215 (1988)
62. A Tachibana, K Yamaguchi, S Kawauchi, Y Kurosaki, T Yamabe *J. Am. Chem. Soc*. **114** 7504 (1992)
63. S K Loh, J M Jasinski *J. Chem. Phys*. **95** 4914 (1991)

64. M S Gordon, D R Gano, J S Binkley, M J Frish *J. Am. Chem. Soc.* **108** 2191 (1986)
65. M E Coltrin, R J Kee, J A Miller *J. Electrochem. Soc.* **133** 1206 (1986)
66. J Espinosa-Garsta, J Sanson, J C Corchado *J. Chem. Phys.* **109** 466 (1998)
67. A A Onischuk, A I Levykin, V P Strunin, M A Ushakova, R I Samoilova, K K Sabelfeld, V N Panfilov *J. Aerosol Sci.* **31** 879 (2000)
68. G Raabe, J Michl *Chem. Rev.* **85** 419 (1985)
69. J H Purnell, R Walsh *Chem. Phys. Lett.* **110** 330 (1984)
70. M A Ring, H E O'Neal *J. Phys. Chem.* **96** 10848 (1992)
71. M E Coltrin, R J Kee, G H Evans *J. Electrochem. Soc.* **136** 819 (1989)
72. P Ho, M E Coltrin, J S Binkley, C F Melius *J. Phys. Chem.* **90** 3399 (1986)
73. P M Agrawal, D L Thompson, L M Raff *J. Chem. Phys.* **92** 1069 (1990)
74. H K Moffat, K F Jensen, R W Carr *J. Phys. Chem.* **96** 7695 (1992)
75. H K Moffat, K F Jensen, R W Carr *J. Phys. Chem.* **96** 7683 (1992)
76. M Bowrey, J H Purnell *Proc. R. Soc. Lond. A, Math Phys. Sci.* **321** 341 (1971)
77. C J Giunta, R J McCurdy, J D Chapple-Sokol, R G Gordon *J. Appl. Phys.* **67** 1062 (1990)
78. J E Johannes, J G Ekerdt *J. Electrochem. Soc.* **141** 2135 (1994)
79. R J Bogaert, B N Baron, M T Klein, T W F Russell, R E Rocheleau *J. Electrochem. Soc.* **136** 2960 (1989)
80. P A Breddels, H Kanoh, O Sugiura, M Matsumura *Jpn. J. Appl. Phys.* **29** L1750 (1990)
81. W A P Claassen, J Bloem, W G J N Valkenburg, C H J van den Brekel *J. Cryst. Growth* **57** 259 (1982)
82. J H Comfort, R Reif *J. Electrochem. Soc.* **136** 2386 (1989)
83. T J Donahue, R Reif *J. Electrochem. Soc.* **133** 1691 (1986)
84. D W Foster, A J Learn, T I Kamins *J. Vac. Sci. Technol. B* **4** 1182 (1986)
85. G Harbeke, L Krausbauer, E F Steigmeier, A E Widmer, H F Kappert, G Neugebauer *J. Electrochem. Soc.* **131** 675 (1984)
86. M K Hatalis, D W Greve *J. Appl. Phys.* **63** 2260 (1988)
87. F Hottier, R Cadoret *J. Cryst. Growth* **52** 199 (1981)
88. T I Kamins, M M Mandurah, K C Saraswat *J. Electrochem. Soc.* **125** 927 (1978)
89. H Kanoh, O Sugiura, M Matsumura *Jpn. J. Appl. Phys.* **32** 2613 (1993)
90. H Kanoh, O Sugiura, P A Breddels, M Matsumura *IEEE Electron Device Lett.* **11** 258 (1990)
91. B S Meyerson, B A Scott, R Tsui *Chemtronics* **1** 150 (1986)
92. A M Beers, J Bloem *Appl. Phys. Lett.* **41** 153 (1982)
93. W L M Weerts, M H J M de Croon, G B Marin *J. Electrochem. Soc.* **145** 1318 (1998)
94. Y Mishima, M Hirose, Y Osaka, K Nagamine, Y Ashida, N Kitagawa, K Isogaya *Jpn. J. Appl. Phys.* **22** L46 (1983)
95. R J Buss, P Ho, W G Breiland, M E Coltrin *J. Appl. Phys.* **63** 2808 (1988)
96. D Meakin, K Papadopoulou, S Friligkos, J Stoemenos, P Migliorato, N A Economou *J. Vac. Sci. Technol. B* **5** 1547 (1987)
97. R S Rosler *Solid State Technol.* **20** (4) 63 (1977)
98. Y M Wu, R M Nix *Surf. Sci.* **306** 59 (1994)
99. M Sadamoto, J H Comfort, R Reif *J. Electron. Mater.* **19** 1395 (1990)
100. C C Cheng, J T Yates Jr *Phys. Rev. B, Condens. Matter* **43** 4041 (1991)
101. R Jones *Physica B* **170** 181 (1991)
102. S M Gates, C M Chiang *Chem. Phys. Lett.* **184** 448 (1991)
103. J J Boland *Phys. Rev. B, Condens. Matter* **44** 1383 (1991)
104. U Memmert, A Berko, R J Behm *Surf. Sci.* **323** L441 (1995)
105. Y Wang, M J Bronikowski, R J Hamers *Surf. Sci.* **311** 64 (1994)
106. D-S Lin, E S Hirschorn, T-C Chiang, R Tsu, D Lubben, J E Greene *Phys. Rev. B, Condens. Matter* **45** 3494 (1992)
107. D Albertini, F Thibaudau, L Masson, F Salvan *Surf. Sci.* **350** L216 (1996)
108. M Fehrenbacher, J Spitzmuller, M Pitter, H Rauscher, R J Behm *Jpn. J. Appl. Phys.* **36** 3804 (1997)
109. M Suemitsu, H Nakazava, N Miyamoto *Surf. Sci.* **357**–**358** 555 (1996)
110. H Hirayama, T Tatsumi, N Aizaki *Appl. Phys. Lett.* **52** 1484 (1988)
111. K Werner, S Butzke, S Radelaar, P Balk *J. Cryst. Growth* **136** 338 (1994)
112. M Suemitsu, K-J Kim, H Nakazawa, N Miyamoto *Appl. Surf. Sci.* **107** 81 (1996)
113. S M Gates, C M Greenlief, D B Beach, P A Holbert *J. Chem. Phys.* **92** 3144 (1990)
114. Z Jing, J L Whitten *Phys. Rev. B, Condens. Matter* **44** 1741 (1991)
115. L-Q Xia, M E Jones, N Maity, J R Engstrom *J. Chem. Phys.* **103** 1691 (1995)
116. K J Uram, U J Jansson *Surf. Sci.* **249** 105 (1991)
117. M Suemitsu, H Nakazawa, T Morita, N Miyamoto *Jpn. J. Appl. Phys.* **36** L625 (1997)
118. J Braun, H Rauscher, R J Behm *Surf. Sci.* **416** 226 (1998)
119. Y Suda, D Lubben, T Motooka, J E Greene *J. Vac. Sci. Technol. A, Vac. Surf. Films* **8** 61 (1990)
120. S M Gates, S K Kulkarni *Appl. Phys. Lett.* **58** 2963 (1991)
121. D Lubben, R Tsu, T R Bramblett, J E Greene *J. Vac. Sci. Technol. A, Vac. Surf. Films* **9** 3003 (1991)
122. F C Eversteijn *Philos. Res. Rep.* **26** 134 (1971)
123. J U M S Murthy, N Miyamoto, M Shimbo, J Nishizava *J. Cryst. Growth* **33** 1 (1976)
124. Z M Qian, H Michiel, A van Ammel, J Nijs, R Mertens *J. Electrochem. Soc.* **135** 2378 (1988)
125. C H J van den Brekel, L J M Bollen *J. Cryst. Growth* **54** 310 (1981)
126. J J Wu, R Flagan *J. Appl. Phys.* **61** 1365 (1987)
127. M K Alam, R C Flagan *Aerosol Sci. Technol.* **5** 237 (1986)
128. J J Wu, H V Nguyen, R C Flagan *Langmuir* **3** 266 (1987)
129. T Kojima, K Usui, T Furusawa *J. Chem. Eng. Jpn.* **22** 683 (1989)
130. J H Flint, R A Marra, J S Haggerty *Aerosol Sci. Technol.* **5** 249 (1986)
131. J H Flint, J S Haggerty *Aerosol Sci. Technol.* **13** 72 (1990)
132. M Ehbrecht, F Huisken *Phys. Rev. B, Condens. Matter* **59** 2975 (1999)
133. W R Cannon, S C Danforth, J S Haggerty, R A Marra *J. Am. Ceram. Soc.* **65** 330 (1982)
134. J S Haggerty, W R Cannon, in *Laser-Induced Chemical Processes* (Ed. J I Steinfeld) (New York; London: Plenum, 1981) p. 183
135. R Fantoni, E Borsella, S Piccirillo, C A Nannetti, R Ceccato, S Enzo *Appl. Surf. Sci.* **43** 308 (1989)
136. S N Rogak, R C Flagan, H V Nguyen *Aerosol Sci. Technol.* **18** 25 (1993)
137. A Schmidt-Ott *J. Aerosol Sci.* **19** 553 (1988)
138. A P Weber, U Baltensperger, H W Gäggeler, A Schmidt-Ott *J. Aerosol Sci.* **27** 915 (1996)
139. H D Jang, S K Friedlander *Aerosol Sci. Technol.* **29** 81 (1998)
140. S Morooka, T Yasutake, A Kobata, K Ikemizu, Y Kato *Int. Chem. Eng.* **29** 119 (1989)
141. S H Ehrmann, S K Friedlander, M Zachariah *J. Aerosol Sci.* **29** 687 (1998)
142. S N Rogak, U Baltensperger, R C Flagan *Aerosol Sci. Technol.* **14** 447 (1991)
143. A Kobata, K Kusakabe, S Morooka *Am. Inst. Chem. Eng. J.* **37** 347 (1991)
144. K Okuyama, Y Kousaka, N Tohge, S Yamamoto, J J Wu, R C Flagan, J H Seinfeld *Am. Inst. Chem. Eng. J.* **32** 2010 (1986)
145. A J Hurd, W L Flower *J. Colloid Interface Sci.* **122** 178 (1988)
146. J E Martin, D W Schaefer, A J Hurd *Phys. Rev. A, Gen. Phys.* **33** 3540 (1986)
147. G D Ulrich, J W Riehl *J. Colloid Interface Sci.* **87** 257 (1982)
148. R J Samson, G W Mulholland, J W Gentry *Langmuir* **3** 272 (1987)
149. S di Stasio *J. Aerosol Sci.* **30** 325 (1999)
150. H X Zhang, C M Sorensen, E R Ramer, B J Olivier, J F Merklin *Langmuir* **4** 867 (1988)
151. A A Onischuk, V P Strunin, M A Ushakova, V N Panfilov *J. Aerosol Sci.* **28** 207 (1997)
152. A Yuuki, Y Matsui, K Tachibana *Jpn. J. Appl. Phys.* **26** 747 (1987)
153. K J Sladek *J. Electrochem. Soc.* **118** 654 (1971)
154. C S Herrick, D W Woodruff *J. Electrochem. Soc.* **131** 2417 (1984)
155. F E Kruis, J Schoonman, B Scarlett, *J. Aerosol Sci.* **25** 1291 (1994)
156. V P Pimenov, V I Chernyak, A I Gorbunov *Khim. Fiz.* **7** 1520 (1988) [a]
157. J J Wu, H V Nguyen, R C Flagan, K Okuyama, Y Kousaka *Am. Inst. Chem. Eng. J.* **34** 1249 (1988)

158. G Lucovsky, W B Pollard, in *The Physics of Hydrogenated Amorphous Silicon (II)* (Eds J D Joannopoulous, G Lucovsky) (Berlin; Heidelberg; New York; Tokio: Springer, 1984) p. 86
159. M Cardona *Phys. Status Solidi B* **118** 463 (1983)
160. G Lucovsky *J. Non-Cryst. Solids* **76** 173 (1985)
161. G Lucovsky *J. Non-Cryst. Solids* **141** 241 (1992)
162. W B Pollard, G Lucovsky *Phys. Rev. B, Condens. Matter* **26** 3172 (1982)
163. M H Brodsky, M Cardona, J J Cuomo *Phys. Rev. B, Condens. Matter* **16** 3556 (1977)
164. G Lucovsky, R J Nemanich, J C Knights *Phys. Rev. B, Condens. Matter* **19** 2064 (1979)
165. U Jansson, K J Uram *J. Chem. Phys.* **91** 7978 (1989)
166. Y Toyoshima, K Arai, A Matsuda, K Tanaka *J. Non-Cryst. Solids* **137**/**138** 765 (1991)
167. N Maley, I Szafranek, L Mandrell, M Katiyar, J R Abelson, J A Thornton *J. Non-Cryst. Solids* **114** 163 (1989)
168. E C Freeman, W Paul *Phys. Rev. B, Condens. Matter* **18** 4288 (1978)
169. D Masson, L Paquin, S Poulin-Dandurand, E Sacher, A Yelon *J. Non-Cryst. Solids* **66** 93 (1984)
170. A T M Wilbers, G J Meeusen, M Haverlag, G M W Kroesen, D C Schram, H Kersten *Thin Solid Films* **204** 59 (1991)
171. D Dellafera, R Labusch, H H Roscher *Philos. Mag. B, Phys. Condens. Matter. Electron. Opt. Magn. Prop.* **45** 607 (1982)
172. M J van den Boogaard, B G C van den Ree, H Meiling, R E I Schropp, W F van der Veg *Physica B* **170** 281 (1991)
173. H Shanks, C J Fang, L Ley, M Cardona, F J Demond, S Kalbitzer *Phys. Status Solidi B* **100** 43 (1980)
174. C J Fang, K J Gruntz, L Ley, M Cardona, F J Demond, G Muller, S Kalbitzer *J. Non-Cryst. Solids* **35**/**36** 255 (1980)
175. A A Onischuk, V P Strunin, M A Ushakova, R I Samoilova, V N Panfilov *Phys. Status Solidi B* **193** 25 (1996)
176. G Lucovsky, J Yang, S S Chao, J E Tyler, W Czubatyj *Phys. Rev. B, Condens. Matter* **28** 3225 (1983)
177. G Lucovsky, J Yang, S S Chao, J E Tyler, W Czubatyj *J. Non-Cryst. Solids* **59**/**60** 609 (1983)
178. G Lucovsky, S S Chao, J Yang, J E Tyler, W Czubatyj *J. Vac. Sci. Technol. A, Vac. Surf. Films* **2** 353 (1984)
179. J S Knights, R A Street, G Lucovsky *J. Non-Cryst. Solids* **35**/**36** 279 (1980)
180. P John, I M Odeh, M J K Thomas, M J Tricker, J I B Wilson, *Phys. Status Solidi B* **105** 499 (1981)
181. G Lucovsky, W B Pollard *J. Vac. Sci. Technol. A, Vac. Surf. Films* **1** 313 (1983)
182. G Lucovsky *Solid State Commun.* **29** 517 (1979)
183. M Pinarbasi, N Maley, A Myers, J R Abelson *Thin Solid Films* **171** 217 (1989)
184. S Furukawa, N Matsumoto, T Toriyama, N Yabumoto *J. Appl. Phys.* **58** 4658 (1985)
185. W Beyer, H Wagner *J. Non-Cryst. Solids* **59**/**60** 161 (1983)
186. S R Das, S Charbonneau, D F Williame, J B Webb, J R MacDonald, D R Polk, S Zukotynski, J Perz *Can. J. Phys.* **63** 852 (1985)
187. J A McMillan, E M Peterson *J. Appl. Phys.* **50** 5238 (1979)
188. D K Biegelsen, R A Street, C C Tsai, J C Knights *Phys. Rev. B, Condens. Matter* **20** 4839 (1979)
189. M H Brodsky *Thin Solid Films* **50** 57 (1978)
190. S Oguz, M A Paesler *Phys. Rev. B, Condens. Matter* **22** 6213 (1980)
191. F Kozlowski, V Petrova-Koch, A Kux, W Stadler, A Fleischmann, H Sigmund *J. Non-Cryst. Solids* **137**/**138** 91 (1991)
192. W Beyer, H Wagner *J. Appl. Phys.* **53** 8745 (1982)
193. H Fritzsche, M Tanielian, C C Tsai, J Gaszi *J. Appl. Phys.* **50** 3366 (1979)
194. P John, I M Odeh, M J K Thomas, M J Tricker, F Riddoch, J I B Wilson *Philos. Mag. B, Phys. Condens. Matter. Electron. Opt. Magn. Prop.* **42** 671 (1980)
195. K Sinniah, M G Sherman, L B Lewis, W H Weinberg, J T Yates Jr, K C Janda *J. Chem. Phys.* **92** 5700 (1990)
196. S M Gates *Surf. Sci.* **195** 307 (1988)
197. S M Gates, C M Greenlief, D B Beach *J. Chem. Phys.* **93** 7493 (1990)
198. C M Greenlief, S M Gates, P A Holbert *Chem. Phys. Lett.* **159** 202 (1989)
199. S M Gates, R R Kunz, C M Greenlief *Surf. Sci.* **207** 364 (1989)
200. B G Koehler, C H Mak, D A Arthur, P A Coon, S M George *J. Chem. Phys.* **89** 1709 (1988)
201. M L Wise, B G Koehler, P Gupta, P A Coon, S M George *Surf. Sci.* **258** 166 (1991)
202. P Gupta, V L Colvin, S M George *Phys. Rev. B, Condens. Matter* **37** 8234 (1988)
203. M A Petrich *Magn. Reson. Rev.* **16** 183 (1993)
204. J B Boyce, S E Ready *Physica B* **170** 305 (1991)
205. H Eckert *Progr. Nucl. Magn. Reson. Spectrosc.* **24** 159 (1992)
206. A A Onischuk, R I Samoilova, V P Strunin, E N Chesnokov, R N Musin, V S Bashurova, A G Maryasov, V N Panfilov *Appl. Magn. Reson.* **15** 59 (1998)
207. W B Jackson, S B Zhang *Physica B* **170** 197 (1991)
208. N M Johnson *J. Non-Cryst. Solids* **137**/**138** 11 (1991)
209. F Buda, G L Chiarotti, R Car, M Parinello *Physica B* **170** 98 (1991)
210. A H Mahan, D L Williamson, B P Nelson, R S Crandall *Phys. Rev. B, Condens. Matter* **40** 12024 (1989).
211. M A Robertson, S K Estreicher *Phys. Rev. B, Condens. Matter* **49** 17040 (1994)

[a] — *Chem. Phys. Rep. (Engl. Transl.)*
[b] — *Kinet. Catal. (Engl. Transl.)*
[c] — *Inorg. Mater. (Engl. Transl.)*
[d] — *Russ. J. Inorg. Chem. (Engl. Transl.)*