

Simulation of the growth of hydrogenated amorphous silicon films from an rf discharge plasma

Yu. E. Gorbachev, M. A. Zetevakhin, and I. D. Kaganovich

Institute of Interphase Interactions, 194291 St. Petersburg, Russia; A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia; St. Petersburg State Technical University, 195251 St. Petersburg, Russia

(Submitted June 8, 1996; resubmitted March 28, 1996)

Zh. Tekh. Fiz. 66, 89–110 (December 1996)

A model describing the growth of a film of amorphous silicon from an rf silane discharge plasma is constructed. Estimates are obtained on the basis of recent experimental data for several constants of electron-stimulated dissociation reactions. The role of different components and the influence of the principal parameters (pressure, electrode spacing, electron density) on the film growth process are analyzed by numerically solving a system of chemical-kinetic equations. Analytical dependences on the system parameters, characterizing the growth rate of the film and its quality, respectively, are obtained for fluxes of silane and silyl onto the surface. The analytical expressions closely approximate the results of the numerical calculations and permit the performance of parametric investigations. © 1996 American Institute of Physics. [S1063-7842(96)00912-9]

INTRODUCTION

The simulation of a film growth process is an effective means for investigating the growth mechanisms and permits optimization of the corresponding technological processes. The number of studies devoted to the complete simulation of a film growth process from an rf discharge plasma is very limited because of the complexity of faithfully describing a large number of plasma-chemical and adsorption processes. The information that can be derived is restricted to the film growth rate and, at best, to descriptive characteristics of its quality. These statements also apply to films of amorphous hydrogenated silicon (α -Si:H). The role of such studies, however, has increased as a result of the recent advances in understanding the nature of the defects formed in films and as a result of the newly achieved possibilities for directly measuring the defect concentration,¹ the concentrations of Si-H and Si-H₂ complexes, and the refractive indices² as a function of the conditions in the growth chamber.

The most complete model of the growth process of α -Si:H films from an rf discharge plasma was constructed by M. Kushner.³ His research was based on cumbersome calculations for a system of more than forty components (neutral and charged species having the general formula Si_mH_n with $n \leq 2m + 2$) and use of the Monte Carlo method to calculate the electron energy distribution function.

Studies recently performed by several investigators⁴⁻⁷ have led to refinement of the values of the rate constants for several plasma-chemical processes. The analysis that we performed showed that the new rate constants lead to qualitative changes in the paths of formation of the different components.

The question of which component makes the predominant contribution to the growth of films has been discussed in connection with the attempts to simulate film growth processes. The main contenders for the role of the decisive components were SiH₃, Si₂H₄, and SiH₂. After the *in situ* experiments in Refs. 8 and 9 and the analysis performed in Refs.

6–8 for films of so-called device quality, this question was resolved in favor of silyl (SiH₃). The other radicals, including the polysilanes, were assigned the role of components that lead to deterioration of the film quality.^{2,3,10,13-15}

In our opinion, cumbersome numerical calculations are still not justified, because the constants of many chemical processes are known with insufficient accuracy and reliability. This also applies to the constants of processes stimulated by electron impact, since even in such detailed investigations, as Ref. 3, the calculation of the discharge was not self-consistent. Moreover, calculations based on models of the type used in Ref. 3 require such great expenditures of machine time that they do not make it possible to obtain results covering time periods that are of interest from the standpoint of practical applications, i.e., to obtain stationary solutions. Therefore, the purpose of the present work is to construct a qualitative model of the bulk chemical kinetics and the growth of hydrogenated amorphous silicon films from an rf silane discharge plasma.

In this paper we formulate a considerably simpler model than in Ref. 3, which makes it possible to perform quick evaluations of all the principal growth parameters (the dependence of the growth rate and the film quality on the conditions in the deposition chamber) with sufficient accuracy. A numerical investigation of the physicochemical processes in a silane plasma is performed, and analytical expressions are obtained for the fluxes of silyl and silylyl (SiH₂) onto the surface. If refined values of the rate constants are used in these expressions, it is easy to obtain more exact data on the film growth characteristics. It is difficult to expect such results from cumbersome calculations with uncontrolled accuracy.

1. SELECTION OF THE MODEL

First of all, on the basis of an analysis of the data presented in Ref. 3 regarding the characteristic values of the rate constants of different chemical reactions and the hypothesis

that the concentration of the radicals is considerably smaller than the concentration of the principal component SiH_4 (which is confirmed both by the results in Ref. 3, as well as by our evaluations¹⁶ and the calculations performed in the present work), it is possible to establish that to describe film growth it is sufficient to take into account only 12 species (besides the sustaining component, i.e., silane): SiH_n ; $n = 1-3$; H ; H_2 ; Si_2H_n , $n = 3-6$; Si_2H_6^* ; $\text{Si}_2\text{H}_6^{**}$ (the asterisks denote electronically excited states); Si_3H_8 .

The active formation of polysilanes,¹⁷ i.e., Si_mH_n particles with $m > 2$ (when $m > 5$ they are referred to as "dust"³) takes place under the usually employed regimes for growing films. Their impingement on the surface results in deterioration of the film parameters. As the estimates and the calculations performed show, the influence of the polysilanes, which are not taken into account in our model, on the concentrations of the components considered (at least in the range of parameters considered in this work) is not decisive, allowing us to neglect them and still obtain a qualitatively correct description of the film growth process.

To describe the gas-phase processes in the system under consideration, we restrict ourselves to consideration of only convective and diffusion transport processes. The corresponding system of chemical-kinetic equations has the form

$$\frac{\partial n_i}{\partial t} + u \nabla n_i = \nabla (D_i \nabla n_i) + F_i,$$

$$F_i = \sum_j n_j \left(n_e k_{ji} + \sum_l K_{jli} n_l \right) - n_i \sum_j \left(n_e k_{ij} + \sum_l K_{jli} n_l \right), \quad (1)$$

where the k_{ij} are the rate constants of processes induced by electron impact, the K_{jli} are the rate constants of chemical reactions, the D_i are the diffusion coefficients, n_i is the concentration of component i , and u is the hydrodynamic velocity.

To complete the formulation of the problem under consideration we must assign the boundary conditions and rate constants of the various processes. As for the rate constants of the chemical reactions, we used the data in Refs. 3-6 and 18 to calculate them. More recent data that permit refinement of the values of the rate constants for several key processes were taken into account.

This applies, first of all, to reaction R15 (see Table I): $\text{SiH}_3 + \text{SiH}_3 \rightarrow \text{SiH}_2 + \text{SiH}_4$. As was shown in Ref. 4, the previously used value of the corresponding rate constant was strongly underestimated; therefore, we used the data of Ref. 4. In addition, as was noted in Ref. 18, the value given in Ref. 3 for the rate constant of the reaction $\text{Si}_2\text{H}_4 + \text{H}_2 \rightarrow \text{SiH}_4 + \text{SiH}_2$ (R23) exceeds the frequency of elastic collisions; therefore, we used the value recommended in Ref. 18 for this rate constant.

More recent data on the rate constants of the electron-impact dissociation of silane molecules were also used in the work. The total cross section of this process is known with great reliability. Recent investigations,⁵⁻⁷ however, have shown that the distribution of the products of this reaction among the channels $\text{SiH}_4 + e \rightarrow \text{SiH}_3 + \text{H}$ (R1), $\text{SiH}_2 + 2\text{H}$ (R2), $\text{SiH} + \text{H} + \text{H}_2$ (R3), and $\text{SiH}_2 + \text{H}$ (R4) differs significantly from that previously adopted: 83% are products of

TABLE I. Rate constants of reactions.

Reaction	Reaction No.	Rate constant ^a
$\text{SiH}_4 + e \rightarrow \text{SiH}_3 + \text{H}$	R1	$3.0(-11)^{b,c}$
$\text{SiH}_4 + e \rightarrow \text{SiH}_2 + 2\text{H}$	R2	$1.5(-10)^c$
$\text{SiH}_4 + e \rightarrow \text{SiH} + \text{H} + \text{H}_2$	R3	$9.34(-12)^c$
$\text{SiH}_4 + e \rightarrow \text{SiH}_2 + \text{H}_2$	R4	$7.19(-12)^c$
$\text{H}_2 + e \rightarrow 2\text{H}$	R5	$4.49(-12)^c$
$\text{Si}_2\text{H}_6 + e \rightarrow \text{SiH}_4 + \text{SiH}_2$	R6	$2.86(-10)^c$
$\text{Si}_2\text{H}_6 + e \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2$	R7	$1.23(-10)^c$
$\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$	R8	$2.53(-12)^{d,e}$
$\text{SiH}_4 + \text{SiH}_2 \rightarrow \text{Si}_2\text{H}_6^*$	R9	$1.0(-11)^f$
$\text{SiH}_4 + \text{SiH} \rightarrow \text{Si}_2\text{H}_5 + \text{H}_2$	R10	$1.7(-12)$
$\text{SiH}_4 + \text{SiH} \rightarrow \text{Si}_2\text{H}_5$	R11	$2.5(-12)$
$\text{SiH}_4 + \text{Si}_2\text{H}_5 \rightarrow \text{SiH}_3 + \text{Si}_2\text{H}_6$	R12	$5.0(-13)$
$\text{SiH}_4 + \text{Si}_2\text{H}_4 \rightarrow \text{Si}_3\text{H}_8$	R13	$1.0(-10)^d$
$\text{SiH}_3 + \text{H} \rightarrow \text{SiH}_2 + \text{H}_2$	R14	$1.0(-10)^d$
$\text{SiH}_3 + \text{SiH}_3 \rightarrow \text{SiH}_4 + \text{SiH}_2$	R15	$1.5(-10)^d$
$\text{SiH}_3 + \text{SiH}_2 \rightarrow \text{Si}_2\text{H}_5^{**}$	R16	$1.0(-11)$
$\text{SiH}_3 + \text{Si}_2\text{H}_5 \rightarrow \text{SiH}_4 + \text{Si}_2\text{H}_4$	R17	$1.0(-10)^d$
$\text{SiH}_3 + \text{Si}_2\text{H}_5 \rightarrow \text{Si}_3\text{H}_8$	R18	$1.0(-11)$
$\text{SiH}_3 + \text{Si}_2\text{H}_6 \rightarrow \text{SiH}_4 + \text{Si}_2\text{H}_5$	R19	$3.27(-12)^{d,e}$
$\text{SiH}_2 + \text{H} \rightarrow \text{SiH} + \text{H}_2$	R20	$7.96(-13)$
$\text{SiH}_2 + \text{Si}_2\text{H}_6 \rightarrow \text{Si}_3\text{H}_8$	R21	$1.2(-10)$
$\text{Si}_2\text{H}_3 + \text{H}_2 \rightarrow \text{Si}_2\text{H}_5$	R22	$1.7(-12)$
$\text{Si}_2\text{H}_4 + \text{H}_2 \rightarrow \text{SiH}_4 + \text{SiH}_2$	R23	$1.0(-10)^d$
$\text{Si}_2\text{H}_6 + \text{H} \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2$	R24	$1.0(-10)^d$
$\text{Si}_2\text{H}_6 + \text{H} \rightarrow \text{SiH}_4 + \text{SiH}_3$	R25	$7.16(-12)^{d,e}$
$\text{Si}_2\text{H}_6 + \text{H} \rightarrow \text{Si}_2\text{H}_5 + \text{H}_2$	R26	$1.43(-11)^{d,e}$
$\text{Si}_2\text{H}_6^* \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2$	R27	$5.0(6) \text{ s}^{-1}$
$\text{Si}_2\text{H}_6^* + M \rightarrow \text{Si}_2\text{H}_6 + M$	R28	$1.0(-1)^g$
$\text{Si}_2\text{H}_6^{**} \rightarrow \text{SiH}_4 + \text{SiH}_2$	R29	$2.3(7) \text{ s}^{-1}$
$\text{Si}_2\text{H}_6^{**} \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2$	R30	$2.3(7) \text{ s}^{-1}$
$\text{Si}_3\text{H}_8 + \text{H} \rightarrow \text{Si}_2\text{H}_5 + \text{SiH}_4$	R31	$2.17(-11)^{d,e}$
$\text{Si}_3\text{H}_8 + \text{SiH}_3 \rightarrow \text{Si}_4\text{H}_9 + \text{H}_2$	R32	$1.0(-11)$

^aUnless indicated otherwise, the dimensions of the constants presented correspond to $\text{cm}^3 \cdot \text{s}^{-1}$. Also, unless stated otherwise, their values were taken from Ref. 3.

^b $3.00(-11) = 3 \times 10^{-11}$.

^cData are presented for an electrode spacing $L_0 = 2.5$ cm, a partial pressure of silane in the growth chamber $p_0 = 0.125$ Torr, a temperature $T = 520$ K, and a specific power $W' = 0.25$ mW/cm³.

^dData from Ref. 18.

^eThe constants were calculated under the assumption that the rotational translation temperatures are equal.

^fWith regard to the ratio between the constants proposed in Refs. 3 and 18, see the text at the end of Sec. 4.

^g M is an arbitrary particle that acts as the collision partner with Si_2H_6^* .

reaction R2, and 17% are products of reaction R1 (the yields of the remaining reactions were not determined in view of their smallness). We shall use the data presented in Ref. 3 for the sum of the rate constants of reactions R1-R4 and assume that the ratio between the rate constants of reactions R1 and R2 is equal to the ratio between the yields of these reactions (17:83), and we take the data of Ref. 3 for the rate constants of reactions R3 and R4. Then the corresponding rate constants for an electrode spacing $L_0 = 2.5$ cm, a partial pressure of silane in the growth chamber $P_0 = 0.125$ Torr, and a specific power $W' = 0.25$ mW/cm³ are $k(R1) = 3.00 \times 10^{-11}$, $k(R2) = 1.50 \times 10^{-10}$, $k(R3) = 9.34 \times 10^{-12}$, and $k(R4) = 7.19 \times 10^{-12}$.

It was shown in Ref. 12 that the most effective channels for the electron-impact dissociation of Si_2H_6 are the reac-

tions $\text{Si}_2\text{H}_6 + e = \text{SiH}_3 + \text{SiH}_2 + \text{H}$ ($91 \pm 9\%$ yield) and $\text{Si}_2\text{H}_6 + e = \text{H}_3\text{SiSiH} + 2\text{H}$ ($9 \pm 9\%$ yield), but it was not possible to reconstruct the corresponding rate constants.

An approximate method is proposed for determining the dependences of the constants of processes initiated by electron impact on the discharge parameters. To obtain this parametrization the electron energy distribution function is modeled in the Boltzmann form, but it is taken into account that the electron temperature T_e appearing therein corresponds to the high-energy "tail" of the electron distribution and depends on the pressure of the gas and the electrode spacing. The balance relationship of the particles is used to determine T_e : the ionization frequency $\nu_i = Nk_i$ is equal to the frequency of the diffusion-controlled depletion of particles from the bulk, where k_i is the ionization constant and N is the number density of the neutral gas. It follows from the assumption of quasineutrality that the frequency of the depletion of electrons is equal to the frequency of the depletion of the ions. As a result, we obtain

$$\pi^2 D_a / L^2 = Nk_i = N\pi m_e \left(\frac{2}{\pi m_e T_e} \right)^{3/2} \int_{\varepsilon_i}^{\infty} \varepsilon \sigma_i \times \exp(-\varepsilon/T_e) d\varepsilon, \quad (2)$$

where $D_a = b_i T_e$ is the ambipolar diffusion coefficient, b_i is the mobility of the ions, m_e is the mass of the electron, σ_i is the ionization cross section, ε_i is the ionization threshold, and L is the electrode spacing.

For not excessively low pressures we can assume that D_a is inversely proportional to the pressure p in the chamber.

If the electron temperature is sufficiently small, i.e., if $T_e \ll \varepsilon_i$, we can approximate the ionization cross section by the linear function $\sigma_i = c_1(\varepsilon - \varepsilon_i)$, where $c_1 = \text{const}$, and obtain the following asymptotic expression for the ionization constant

$$k_i = 2c_1 \varepsilon_i (2T_e / \pi m_e)^{1/2} \exp(\varepsilon_i / T_e). \quad (3)$$

Since the expressions for the rate constants k_r of the reactions stimulated by electron impact have the same form as the ionization constant (2) and only have different values of the parameters ε_i and σ_i , approximations like (3) with the appropriate changes are obtained for them. For the ratio between the rate constants calculated for different values of the electron temperature it is easy to obtain the expression $k_r / k_r^0 = (T_e / T_{e0})^{1/2} \exp[-\varepsilon_r (T_e^{-1} - T_{e0}^{-1})]$, where ε_r is the reaction threshold. A similar relation can be written for the ionization constants. Using it to determine the relationship of the electron temperature to the pressure and electrode spacing with the aid of the balance relation (2), we obtain the final expression explicitly specifying the dependence of k_r on the current values of the pressure p and the electrode spacing L :

$$k_r(p, L) / k_r^0 = \left(\frac{p_0 L_0}{pL} \right)^{2\varepsilon_r / \varepsilon_i}, \quad (4)$$

where $k_r^0 = k_r(p_0, L_0)$, and p_0 and L_0 are certain fixed values of p and L .

When Eq. (4) is used, certain precautions should be taken, since several fairly rough approximations were made during its derivation. For example, in an rf discharge the electron distribution function can be non-Maxwellian at pressures greater than 0.3 Torr, the recombination losses are significant in addition to the diffusion losses, at large powers high-energy γ electrons can make a significant contribution to the ionization, the presence of negative ions can be manifested,^{18,19} etc. However, since pressures below 0.3 Torr and small powers are usually used in real systems, the proposed approximation should provide a correct description of the dependences considered at least on the qualitative level.

As for boundary conditions, the question of their correct formulation has been examined, for example in Refs. 20 and 21. However, because of the lack of detailed information on the laws governing the interaction of the components under consideration with the surface we confine ourselves to the results of a primitive kinetic theory, which are similar to those obtained in Ref. 22 and follow from the simple relation between the fluxes of the incident and reflected particles $\Gamma_{i\text{out}} = (1 - s_i) \Gamma_{i\text{in}}$. Here $\Gamma_{i\text{in,out}} = n_i c_i / 4 \mp (D_i / 2) \partial n_i / \partial x$ defines the incident and reflected fluxes of particles of species i , $c_i = 2(2T / \pi m_i)^{1/2}$ is the thermal speed, m_i is the mass of a particle of the i th component, and s_i is the sticking coefficient of the particles of species i . Then for the values of the gasdynamic parameters on the absorbing surface we obtain the relation (a diffusion law for reflection of the particles from the surface is assumed)

$$D_i \frac{\partial n_i}{\partial x} = \frac{s_i c_i}{2(2 - s_i)} n_i, \quad (5)$$

where $\partial / \partial x$ is the derivative with respect to the outer normal to the surface.

Generally speaking, evaporation from the surface must be taken into account in obtaining the boundary conditions. In this case a term of the form $s_i n_i^e c_i / 4$, where n_i^e is the concentration of the saturated vapor, appears on the right-hand side of the flux balance relation. Consequently, the replacement $n_i \rightarrow n_i - n_i^e$ should have been performed on the right-hand side of (5). However, since intense deposition of the species under consideration takes place on the wall under the conditions of interest to us, the supersaturation must be great, i.e., $n_i / n_i^e \gg 1$, and we shall use Eq. (5) in our calculations.

It is seen from (5) that in the case of complete reflection of the particles, in which $s_i = 0$, the boundary condition of usual form $\partial n_i / \partial x = 0$ is obtained, but when $s_i \neq 0$, a condition which takes into account the concentration jumps is obtained. It transforms into the ordinarily used condition $n_i = 0$ only in the limit of a zero mean free path $l_j \propto D_i / c_i$ and fixed s_i (i.e., when $l_j = 0$).

Within such an analysis it is possible to obtain an expression for the film growth rate $R = \sum_i v q_i (\Gamma_{i\text{in}} - \Gamma_{i\text{out}})$, where v is the volume occupied by an atom participating in the growth of the film (Si), and q_i is the number of such atoms in the particle of species i being deposited. From the form of the expression for the fluxes we obtain the final expression

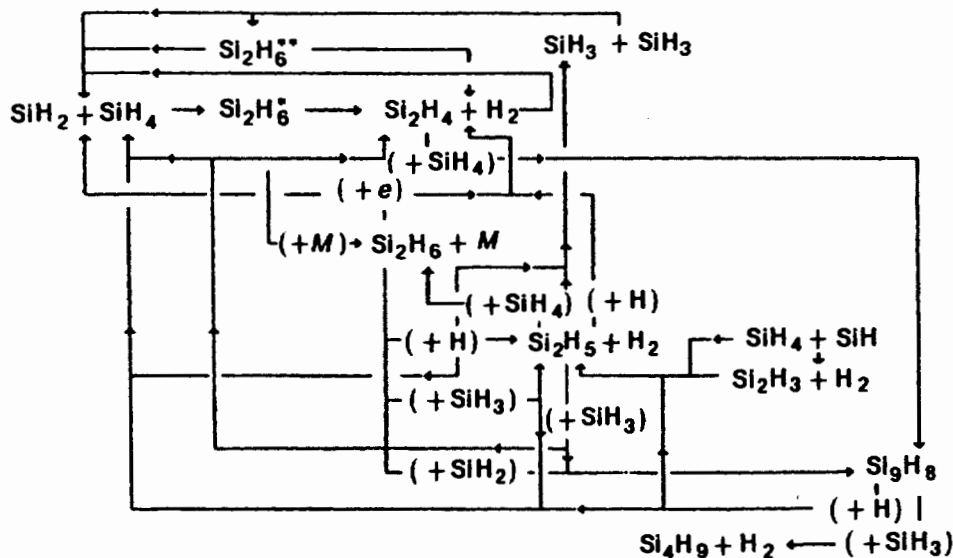
$$R = - \sum_i v q_i D_i \partial n_i / \partial x. \quad (6)$$

It should be noted that, unlike the expression in Ref. 3, this expression does not contain the factors s_i . The influence of incomplete sticking or reflection is automatically taken into account here by the boundary conditions (5). The proposed approach for determining the film growth rate is more systematic. The largest error in the determination of R using the expressions from Ref. 3 appears at small, but finite sticking coefficients s_i ($s_i > Kn = l_f / l_h$, where l_h is the characteristic spatial scale). Let us examine the situation in which $1 \gg s_i \gg Kn$. It then follows from (5) that the ordinary boundary condition $n_i = 0$ can be used, as was done, for example, in Ref. 3. The partial contribution of the i th component to the film growth rate in Ref. 3 was underestimated due to the presence of the additional factors s_i in the expression for R . Here we note the erroneous conclusions regarding the contribution of particular components to film growth drawn on the basis of the assumption that the fluxes of the components onto the surface are proportional to s_i (see, for example, Ref. 23): as is seen from (5) and (6), when $Kn = l_f / l_h \gg s_i$, neither the boundary conditions nor the film growth rate depend on the sticking coefficient.

2. PRELIMINARY EVALUATIONS

Let us make some estimates, which will enable us to investigate the influence of the external conditions on the principal characteristics of the problem, i.e., the growth rate of the films and their quality. For this purpose we introduce several simplifications, on the basis of which we shall obtain the dependence of the concentrations and fluxes of various components onto the surface.

We, first of all, note that in calculating the concentrations of H, Si_2H_4 , Si_2H_6^* , and $\text{Si}_2\text{H}_6^{**}$, their diffusion can be neglected in view of the high rates of the reactions in which they participate. The diffusion of H_2 , Si_2H_6 , and Si_3H_8 can be neglected, because the changes in their concentrations as a result of their interaction with the walls are not taken into account. The corresponding equilibrium values of the density can be found easily (see the Appendix). We note that the equilibrium values of the density of several components in the growth process are not attained. For convenience, the paths of the principal reactions are presented in the scheme.



The particles which are not results of the preceding reaction but participate in the subsequent reaction are indicated in parentheses. The arrows pointing to an element signify its appearance as a result of a given reaction, and the arrows pointing to a plus sign signify the appearance of both components. We note that for such components as Si_2H_6^* , $\text{Si}_2\text{H}_6^{**}$, Si_2H_6 , Si_2H_5 , Si_2H_4 , and Si_2H_3 , all the reactions in which they participate are presented in the scheme (only the reactions of SiH_4 , SiH_3 , SiH_2 , and H_2 with electrons or nascent hydrogen are not represented in the scheme).

To evaluate the film growth rate we first consider the deposition of silyl as the component which makes the decisive contribution to this process. Since the diffusion coefficient of this component is fairly great,^{9,11} the condition $u < D_{\text{SiH}_3} / L$ holds over a broad range of values of the pumping rate u , permitting neglect of its convective transport. Besides deposition on the walls as a result of diffusion, another important mechanism for the depletion of silyl is its disappearance as a result of bulk chemical reactions. The most

important path for such depletion is its reaction with Si_3H_8 , which leads to the formation of higher silanes (reaction R32 in Table 1). Using the equilibrium value of the concentration of Si_3H_8 (see the Appendix), we obtain for the rate of depletion of silyl $K(R32)n_3n_{\text{Si}_3\text{H}_8} = K(R9)n_{\text{SiH}_4}n_{\text{SiH}_2}$.

Using the data in Table I for the rate constants of the electron-stimulated processes, we can conclude that the formation of silyl is mainly determined not by electron impact, but by the reaction with nascent hydrogen $\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$, which is an order of magnitude more effective. Attention was focused on the important role of hydrogen in the formation of silyl back in Ref. 11. Thus, using the expression for the equilibrium concentration of nascent hydrogen (see the Appendix), we can write the expression for the formation of silyl in the form $2k(R2)n_{\text{SiH}_4}n_e$. As a result, the combined influence of the chemical reactions determining the silyl balance can be described in the form of the effective source

$$R_{\text{ef3}}^+ = (2k(R2)n_e - K(R9)n_{\text{SiH}_2})n_{\text{SiH}_4}.$$

Finally, considering the one-dimensional formulation of the problem, we can write the following equation for the silyl balance (the subscript 3 denotes SiH_3)

$$-D_3 d^2 n_3 / dx^2 = R_{\text{ef3}}^+. \quad (7)$$

Using the dependence of the silyl concentration on the coordinate obtained from Eq. (13), for the flux of silyl onto the wall we find [L_{D2} is defined in (14)]:

$$\Gamma_{\text{SiH}_3} = k(R2)n_e n_{\text{SiH}_4} L \left(1 - \frac{1}{2} \times \left(1 - \frac{2L_{D2}}{L} \tanh(L/2L_{D2}) \right) \right). \quad (8)$$

Here we have neglected the variation of the electron density n_e along the interelectrode coordinate; therefore, the corresponding average quantity is replaced by its current value. We note that the quantity defined by (8) can easily be generalized to the spatially inhomogeneous case. To accomplish this, the frequency of the formation of silyl $k(R2)n_e$ in the expression for R_{ef3}^+ should be replaced by the value averaged over the electrode gap:

$$k(R2)n_e \rightarrow \frac{1}{L} \int_{-L/2}^{L/2} k(R2)n_e dx.$$

To evaluate the electron density we take advantage of its relation to the power W supplied to the rf discharge. For not very large values of the power, the energy supplied to the discharge is utilized mainly to heat the electrons. Then we can write

$$W = \frac{j_0 E_0 L}{2} = (pL/2)n_e \left(\frac{E_0}{p} b_e p \right) \frac{E_0}{p}, \quad (9)$$

where j_0 is the current in the discharge, p is the pressure in the chamber, E_0 is the amplitude of the field in the discharge, b_e is the mobility of the electrons, and L is the electrode spacing.

At not very low pressures ($p > 3 \times 10^{-2}$ Torr) the ratio E_0/p and the product $b_e p$ scarcely depend on the pressure and the electrode spacing. This allows us to rewrite the expression for silyl in the form $\Gamma_{\text{SiH}_3} \propto W \cdot k(R2)$. Using (4) to evaluate $k(R2)$, we obtain

$$\Gamma_{\text{SiH}_3} \approx cW(pL)^{-2\varepsilon_d/\varepsilon_i} \left(1 + \frac{2L_{D2}}{L} \tanh(L/2L_{D2}) \right), \quad (10)$$

where $c = \text{const}$ and ε_d is the threshold for the electron-impact dissociation of silane.

It is seen from this expression that at a given power W , the flux of silyl onto the surface and therefore the film growth rate depend on the pressure and the electrode spacing as $(pL)^{-1.4}$, since $\varepsilon_d/\varepsilon_i \approx 0.7$ for the reactions under consideration. At a given specific power $W' = W/L$ the value of Γ depends weakly on L .

To estimate the amount of film being grown we determine the fluxes of the ions and SiH_2 onto the surface, since, according to the existing ideas,^{3,10,13,15} it is these substances that influence the quality of the material obtained when they are deposited. The flux of the ions is determined by the ambipolar diffusion D_a (it is assumed that the blow-through velocity u is sufficiently small that $D_a \gg uL$):

$$\Gamma_i = \pi D_a n_e / L \propto n_e / (pL). \quad (11)$$

Then, for the ratio between the fluxes of the ions and silyl we have $\Gamma_i / \Gamma_{\text{SiH}_3} \propto [(pL)^2 k(R2)]^{-1}$. Using the dependence of $k(R2)$ on p and L , we obtain

$$\Gamma_i / \Gamma_{\text{SiH}_3} \propto (pL)^{-2(1-\varepsilon_d/\varepsilon_i)} \times \left(1 + \frac{2L_{D2}}{L} \tanh(L/2L_{D2}) \right)^{-1}, \quad (12)$$

i.e., the ratio between the fluxes of the ions and silyl is determined by the pressure and the electrode spacing and does not depend on the power.

The formation of silyl takes place mainly upon the electron-impact dissociation of silane and as a result of reaction R23 ($\text{Si}_2\text{H}_4 + \text{H}_2 \rightarrow \text{SiH}_4 + \text{SiH}_2$), and its depletion is mediated by its reaction with silane. Using the expression for the number density of Si_2H_4 (see the Appendix), we can write the reactions taking place that are not associated with electron impact in the form of a reaction resulting in the depletion of silyl with the effective rate constant for the reaction of silyl with silane

$$K_{\text{ef2}}^- = K(R9)K(R13)/(K(R13) + K(R23)n_{\text{H}_2}/n_{\text{SiH}_4}),$$

which coincides with $K(R9)$ at a low concentration of molecular hydrogen. As a result, the equation for the concentration of silyl has the form (the subscript 2 indicates that the respective quantity refers to SiH_2)

$$-D_2 d^2 n_2 / dx^2 = k(R2)n_e n_{\text{SiH}_4} - K_{\text{ef2}}^- n_2 n_{\text{SiH}_4}. \quad (13)$$

For the flux of silyl onto the surface we obtain

$$\Gamma_{\text{SiH}_2} = k(R2)n_e n_{\text{SiH}_4} L_{D2} \tanh(L/2L_{D2}),$$

$$L_{D2} = \left(\frac{D_2}{K_{ef2} n_{\text{SiH}_4}} \right)^{1/2}. \quad (14)$$

Separating the dependence on L and p , we can rewrite this expression in the following form (it was assumed that $K_{ef2} \approx K(R9)$, and the subscript 0 indicates that the respective quantity is calculated for $p = p_0$ and $L = L_0$):

$$\Gamma_{\text{SiH}_2} = k_0(R2)(p_0 L_0 / pL)^{2\varepsilon_r / \varepsilon_i} n_e n_{\text{SiH}_4} L_{D20} \times \tanh(pL/2p_0 L_{D20}). \quad (14a)$$

As a result, for the ratio between the fluxes of SiH_2 and SiH_3 we have

$$\Gamma_{\text{SiH}_2} / \Gamma_{\text{SiH}_3} = \frac{2L_{D2} \tanh\left(\frac{L}{2L_{D2}}\right)}{L} \times \left(1 + \frac{2L_{D2}}{L} \tanh\left(\frac{L}{2L_{D2}}\right) \right)^{-1}. \quad (15)$$

It is seen from this relation that the film quality, which is determined by the deposition of SiH_2 , does not depend on the discharge power or on the electron-stimulated processes and is determined entirely by the electrode spacing L and by L_{D2} , which characterizes the distance over which a silyl particle manages to diffuse before it undergoes a chemical reaction (the reaction diffusion length). The value of L_{D2} , in turn, is determined by the rate constant $K_{ef2} \approx K(R9)$, the diffusion coefficient D_2 , and the silane concentration.

The data on the reaction diffusion lengths (presented in the Appendix) can be used to analyze the roles of SiH , Si_2H_3 , and Si_2H_5 in a similar manner.

3. CALCULATION METHOD

The problem under consideration was numerically simulated in the following formulation. The processes taking place between two parallel electrodes separated by a distance L were considered. Within this region we solved the system of equations

$$\frac{\partial n_i}{\partial t} = D_i \frac{\partial^2 n_i}{\partial x^2} + F_i \quad (16)$$

for 12 components with the F_i from (1). The list of reactions taken into account is presented in Table I.

The rate constants of the reactions were taken from Refs. 3, 4, and 18, the rate constants for reactions R1–R4 being obtained on the basis of the arguments in Sec. 1 and the data in Refs. 5 and 6. The values of the reaction thresholds, which determine the dependence of the electron-stimulated processes according to Eq. (4), were taken from Ref. 18: $\varepsilon_d = 8.4$ eV for the electron-impact dissociation of silane, $\varepsilon_d = 8.85$ eV for the electron-impact dissociation of hydrogen, and $\varepsilon_i = 12$ eV for the electron-impact ionization of silane.

The diffusion coefficients were taken from Ref. 11: $D_n = 1250, 1350, 1470$ cm²/s for SiH_n , where $n = 3-1$, respectively, at $T = 520$ K and a silane number density 4×10^{15} cm⁻³; $D_H = 7000$ cm²/s at $T = 300$ K and the same density. Estimates of the diffusion coefficient for molecular hydrogen were made using expressions from the monograph by Hirschfelder, Curtiss, and Bird²⁴ on the basis of the data on the parameters of the intermolecular potentials presented in Ref. 3.

We note that this system is not closed in the sense that no equation was written out for a product such as Si_4H_9 . This is possible, since the concentration of Si_4H_9 does not appear in any of the equations considered, making the formulation of the problem closed from the mathematical standpoint. Although the conversion of silicon into the higher silanes is crucial from the standpoint of technological applications of the problem, their formation does not influence the chemical kinetics in the bulk over a broad range of values of the parameters but only influences the quality of the films grown and the efficiency of the system. Recalling the possibility of splitting up the problem (the question of the exact determination of the limits for the applicability of this approximation will be considered separately), we restrict ourselves to a calculation of only the principal processes which shape the chemical composition of the mixture and to consideration of the formation of Si_4H_9 . A calculation of the formation of the higher silanes can be performed on the basis of the concentration fields that we obtain.

The choice of the formulation of the problem is governed by two circumstances. First, the range of conditions considered below is characterized by extremely small values of the Peclet diffusion number $Pe = LY/D$ (Ref. 25), which allow us to neglect convective transport and restrict ourselves to consideration of only the diffusion processes. Second, despite the fact that the characteristic diffusion times of the principal reactions are much smaller than the film growth time, which amounts to tens of minutes, the problem under consideration does not have a stationary solution due to the accumulation of several components (and, generally speaking, the decrease in the concentration of silane, which is not taken into account in the present work). Under real conditions the existence of a stationary solution is ensured by the presence of a convective term in Eq. (16), which describes the blowing of the gas mixture through the reactor. A detailed calculation of the processes within the reactor with allowance for blow-through complicates the formulation of the problem significantly; however an analysis of the features of these processes allows us to propose a scheme involving replacement of the original stationary formulation of the problem by a nonstationary formulation that can be solved in some finite time interval $[0, \tau]$, where $\tau = M_0/Q$, and M_0 and Q are the mass of the gas in the bulk and its mass flow rate in the reactor. In fact, in real systems the value of τ is usually much greater than the characteristic diffusion time and the time for the occurrence of the principal reactions. In this case we can consider a simplified integral reactor model, which can be described by equations of the form

$$\frac{dM_i}{dt} = G_i - A_i M_i - \tau^{-1} M_i, \quad (17)$$

where M_i is the mass of the i th component in the bulk of the reactor, and G_i and A_i are the rates of its formation and decomposition due to bulk reactions.

When G_i and A_i are constant, the stationary solution of Eqs. (17) has the form

$$M_i = \frac{G_i}{A_i + \tau^{-1}} \approx \begin{cases} G_i/A_i & \text{for } \tau^{-1} \ll A_i, \\ \tau G_i & \text{for } \tau^{-1} \gg A_i. \end{cases} \quad (18)$$

On the other hand, the solution of the nonstationary problem for Eq. (17) after omission of the last term on its right-hand side, which takes into account the influence of the blow-through, gives

$$M_i(\tau) = G_i A_i^{-1} (1 - \exp(-A_i \tau)) \approx \begin{cases} G_i/A_i & \text{for } \tau^{-1} \ll A_i, \\ \tau G_i & \text{for } \tau^{-1} \gg A_i. \end{cases} \quad (19)$$

A comparison of (18) and (19) shows that the proposed approach makes it possible to calculate the concentrations of both the rapidly and slowly reacting components.

The solution of the problem was sought in the region $0 \leq x \leq L$, the condition (5) was imposed on both boundaries, and the sticking coefficients s_i of the particles were chosen according to Ref. 3: $s_i = 0.15$ for SiH_3 and Si_2H_6 ; $s_i = 1$ for SiH , SiH_2 , Si_2H_3 , and Si_2H_4 ; $s_i = 0$ for the remaining components.

The following scheme, which was devised with consideration of the specific properties of the system (16), was used for the numerical solution. The source terms in this system can be represented in the form $F_i = f_i - A_i n_i$, where $f_i \geq 0$, $A_i \geq 0$, and $\partial f_i / \partial n_i = 0$. Then the procedure for solving the system (16) can be represented in the form

$$(1 + \Delta t A_i^l) n_i^{l+1} - \Delta t D_i n_{i,xx}^{l+1} = n_i^l + \Delta t f_i^l, \quad (20)$$

where Δt and l are the duration and number of the time step.

The system (20) is solved in each time step by scalar sweeps, the use of such an approximation for each of the equations ensuring fulfillment of the conditions which guarantee that the sweeping method is correct and that the solution is positive in each time step. Test calculations showed that this scheme makes it possible to obtain stable solutions for $\Delta t \geq t_m$, where t_m is the characteristic time of the fastest reaction.

All the results considered below were obtained in calculations for conditions of constant power, under which $n_e \propto (pL)^{-1}$, and a constant gas flow rate, under which τ is proportional to the pressure. The values corresponding to the standard values $p_0 = 0.125$ Torr and $L_0 = 2.5$ cm were $n_{e0} = 5 \times 10^9 \text{ cm}^{-3}$ and $\tau = 0.33$ s. The latter value refers to the case in which the working volume of the reactor equals 2 liters, and the value of Q corresponds to a volume flow rate of the gas equal to 4 liter/h. The pressure was varied in the range from 0.15 to 1 Torr.

4. DISCUSSION

An analysis of the results obtained showed that the components considered can be divided into three groups: steady, nonsteady, and quasisteady. The first group includes the components whose concentrations reach their steady-state values quickly (within a time much shorter than the characteristic time τ for renewal of the gas in the reactor, which was defined in Sec. 3), the second group includes the components whose concentrations vary as τ is varied, and the third group includes the components whose concentrations depend on the time only through the concentrations of the nonsteady components.

Actually, only such a component as SiH can be assigned to the first group. The reason for this is fairly simple: its formation is determined completely by reaction R3, i.e., by the electron-impact dissociation of silane, and its depletion is mediated by two reactions with the same compound SiH_4 .

The particles which are not radicals (which do not have dangling bonds) H_2 , Si_3H_8 , and Si_2H_6 are assigned to the second group. Molecular hydrogen reacts so slowly with the remaining components that its concentration is practically inversely proportional to the blow-through velocity. At low pressures the concentration of Si_2H_6 nearly manages to reach its equilibrium value after the time τ [$n_{\text{Si}_2\text{H}_6}(t=\tau)/n_{\text{Si}_2\text{H}_6}^e \approx 0.92$ at $p = 0.15$ Torr]. As the pressure rises, the nonsteady behavior of this component becomes stronger, and at $p = 1$ Torr $n_{\text{Si}_2\text{H}_6}(t=\tau)/n_{\text{Si}_2\text{H}_6}^e \approx 0.63$. The concentration of Si_3H_8 manages to come fairly close (to within several percent) to its equilibrium value after the time τ . We note here that variation of the blow-through velocity influences the film growth process through variation of the concentrations of the components, particularly of this group.

The components of the third group are characterized by the extremely small values of the relative imbalance [a quantity equal to the ratio of the difference between their production and depletion (as a result of decomposition and deposition on the walls) to their production]. For most of them this quantity is much smaller than 10^{-4} , but their concentrations depend on the blow-through velocity. The most notable members of this group are Si_2H_5 and Si_2H_3 , the concentration of the latter increasing markedly as the blow-through velocity increases. The reason for this is as follows. The principal suppliers of Si_2H_5 include reactions involving such nonsteady components as Si_3H_8 and Si_2H_3 . The concentration of the latter is completely determined by its reaction with molecular hydrogen, whose concentration drops as the blow-through velocity is increased.

It is also convenient to characterize the components considered by the dimensionless parameters $K_{RDi} = L_{Di}/L$, where L_{Di} is the reaction diffusion length, which was introduced in (14), or simply by the L_{Di} . The results of the classification based on K_{RDi} will be used in a future analysis.

Let us illustrate the results of the numerical calculations. Figure 1 shows the variation of the concentrations of various components as a function of the pressure in the reactor. The relatively slow decrease in the concentrations of Si_2H_6 and Si_2H_3 with increasing pressure is noteworthy. In the case of Si_2H_3 this behavior is attributed to the drop in the concen-

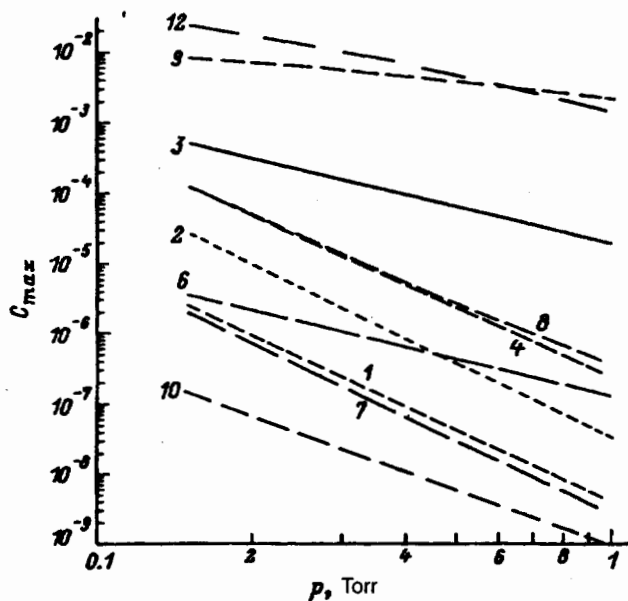


FIG. 1. Maximum values of the concentrations of the components in the bulk of the reactor relative to the concentration of SiH_4 as a function of the pressure for constant power losses in the discharge, i.e., for $n_e p L = n_{e0} p_0 L_0$. 1 — SiH , 2 — SiH_2 , 3 — SiH_3 , 4 — H , 6 — Si_2H_3 , 7 — Si_2H_4 , 8 — Si_2H_5 , 9 — Si_2H_6 , 10 — Si_2H_6^* , 12 — Si_3H_8 .

tration of molecular hydrogen and the decrease in deposition on the wall as the pressure increases. The latter circumstance will be considered again in greater detail below. Practically all the reactions participating in the formation or decomposition of Si_2H_6 make an identical contribution, precluding discrimination of the principal channels determining the behavior of this component.

Figure 2 presents calculated plots of the pressure dependence

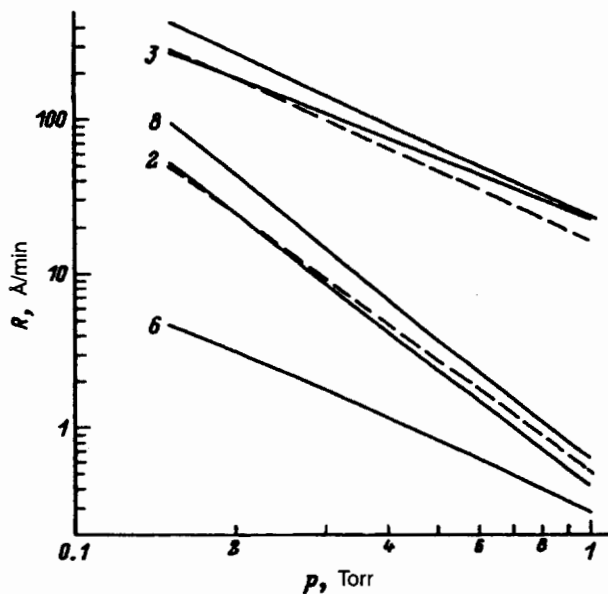


FIG. 2. Dependence of the film growth rate and the contribution of various components on the pressure. The numbering of the curves is the same as in Fig. 1. Dashed curves — results of calculations using analytical formulas (8) and (14).

dence of the film growth rate and of the contributions of individual components to it. The figure also presents the results of a calculation employing the analytical formulas (8) and (14). An analysis of these results reveals the following characteristic features. The growth rate drops as the pressure is increased, i.e., as the amount of silane in the reaction volume increases. An increase in the growth rate leads to deterioration of the film quality: the relative contribution of the flux of SiH_2 increases. The analytical dependences predict the fluxes of SiH_3 and SiH_2 quite well.

Similar conclusions are also true for the dependence on the electrode spacing, which is a consequence of the dependence of the constants for electron-impact dissociation on the product pL obtained in Sec. 1. In addition, two more interesting features should be noted in Fig. 2: the fairly high contribution of Si_2H_5 to film growth, which, generally speaking, decreases as the electrode spacing increases, and the relatively small contribution of Si_2H_3 , although at high pressures its concentration even surpasses the concentration of SiH_2 , as is seen from Fig. 1.

In order to ascertain the cause of these phenomena, let us examine in greater detail the characteristics of the principal processes occurring in the bulk upon the decomposition of silane. We turn to a classification of the components based on the reaction diffusion length L_D . In the case of the quasi-steady components, for which $L_D \ll L$ (which include SiH_2 and Si_2H_4), the small value of the imbalance (see above) is maintained mainly as a result of bulk reactions, and deposition on the wall plays a minor role. Conversely, for the components for which L_D is comparable to the electrode spacing or exceeds it, deposition on the walls makes a significant contribution to the overall balance and thereby determines the values of the concentrations. Two typical members of this subgroup are SiH_3 and Si_2H_3 . Thus a high concentration of Si_2H_3 is maintained only as a result of the slow course of the bulk reactions, while the total production of SiH_2 is almost two orders of magnitude greater, but its deposition takes place only from a thin near-surface layer. This difference is clearly illustrated by Figs. 3 and 4, which present the total balances of SiH_3 and SiH_2 as examples.

An analysis of the results obtained shows that SiH_3 forms mainly as a result of the reaction $\text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2$ and that the main supplier of the nascent hydrogen participating in this reaction is the reaction $\text{SiH}_4 + e \rightarrow \text{SiH}_2 + 2\text{H}$, as was postulated above. The estimate (10), which predicts a drop in the total production of SiH_3 at a constant power due to the dependence of the rate constant of reaction R2 on p and L , is valid here.

The depletion of SiH_3 occurs mainly as a result of diffusion to the walls and as a result of the reaction with Si_3H_8 . As the pressure rises, the role of the depletion of silyl in the reaction with Si_2H_6 increases, although its contribution still does not exceed 28%. When the power deposited in the discharge is constant, one more path for the depletion of SiH_3 from the bulk is manifested. It is the reaction of silyl with itself, i.e., reaction R15, whose role increases with decreasing pressure, since the concentration of electrons then increases fairly rapidly and causes an increase in the concentration of SiH_3 through the formation of nascent hydrogen.

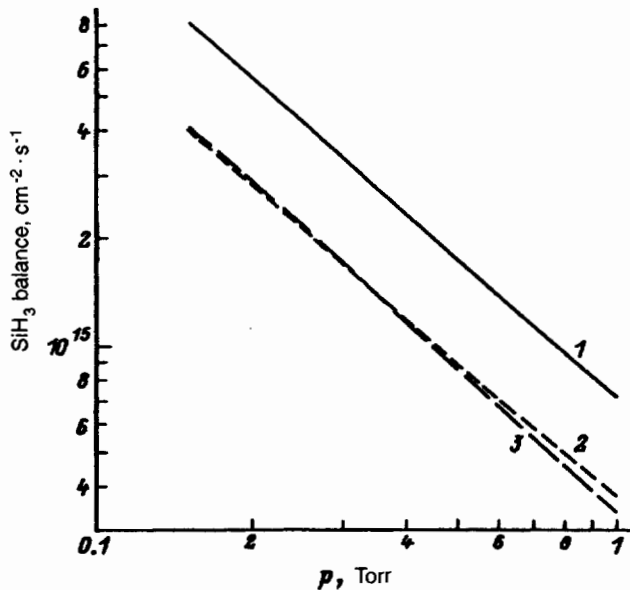


FIG. 3. Silyl balance as a function of the pressure in the reactor for $L=2.5$ cm: 1 — production, 2 — decomposition, 3 — deposition.

The contribution of this reaction does not surpass 30%.

Let us examine the SiH_2 balance (Fig. 4). It is formed mainly as a result of the electron-impact dissociation of silane molecules. The depletion of SiH_2 is mediated practically completely by reaction R9 alone: $\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6^*$. When the pressure is lowered as a result of the cyclic sequence of reactions $\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6^* \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2 \rightarrow \text{SiH}_2 + \text{SiH}_4$, the concentration of silyl is partially restored (to 20% when $p=0.15$ Torr). The flux of SiH_2 onto the walls decreases sharply as the pressure increases, as is clearly seen in Figs. 2 and 4. This is due to two factors acting in the same direction. First, the rate of the

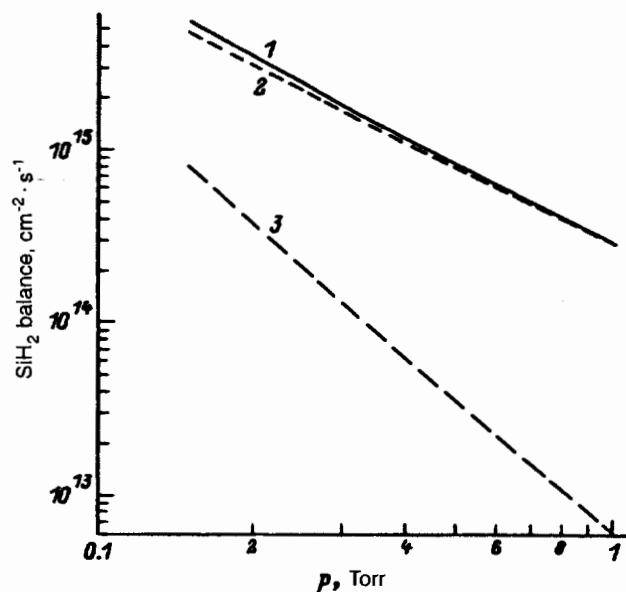


FIG. 4. Silyl balance as a function of the pressure in the reactor. The conditions and notation are the same as in Fig. 3.

formation of silyl from silane due to electron impact then decreases rapidly [$\propto p^{-1.4}$, see Eq. (4)], and, second, the reaction diffusion length decreases ($L_{D2} \propto p^{-1}$), i.e., deposition takes place from a narrow near-surface zone.

When the film growth rate is analyzed, two cases characterized by different values of $K_{RDSiH_2} = L_{D2}/L$ should be distinguished. At small values of K_{RDSiH_2} , at which the concentration of silyl is close to its equilibrium value $n_{SiH_2}^e = n_e k(R2)/K(R9)$, exactly half of the silyl formed disappears from the bulk by reacting with Si_3H_8 [see Eq. (7), as well as $n_{Si_3H_8}^e$ in the Appendix]. Only the remaining half is deposited on the surface. In the case of large values of K_{RDSiH_2} , the bulk depletion of silyl is small, and the concentration of silyl is consequently smaller than its equilibrium value. In this case the concentration of Si_3H_8 is small (see the Appendix) and the bulk depletion of silyl is small. However, as follows from the analysis performed above, these circumstances cannot increase the rate of formation of silyl more than twofold or, therefore, increase the flux of silyl onto the surface more than twofold. This is easily understood on the basis of Eq. (8).

The parameter K_{RDSiH_2} also regulates the formation of "dust." The reaction of Si_3H_8 with silyl is responsible for the formation of higher polysilanes, and silyl is responsible for the increase in the concentration of Si_3H_8 . Thus, the ratio between the surface and bulk growth of silicon formations is determined by the balance between the rate of the formation of Si_3H_8 and the rate of the deposition of silyl on the surface. As was shown by the analysis performed above, both these processes are determined to a large extent by K_{RDSiH_2} . In the case of the predominance of the former process, intense formation of "dust" takes place.

The question of the contribution of the Si_2H_4 radical to film growth has been discussed often in the literature. Evaluations show that the reaction diffusion length for this radical is of order $L_D \sim 0.08p_0/p$ cm $\approx 0.08l_f/l_{f0}$ cm, i.e., of the order of the mean free path. This means that the concentration of this component in the bulk will be uniform, and a jump will appear in it at the boundary. On the other hand, despite the high rate of the production of Si_2H_4 as a result of the processes $\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6^* \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2$, because of the high efficiency of the reactions of Si_2H_4 both with silane (which leads to the formation of Si_3H_8) and with molecular hydrogen (which leads to its reduction to SiH_4 and SiH_2), its concentration remains low, and the flux onto the surface is small and does not make a significant contribution to film growth. It should be noted here that the sequence of reactions $\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6^* \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2 (+ \text{SiH}_4) \rightarrow \text{Si}_3\text{H}_8 + \text{H}_2$ not only produces a significant part of the hydrogen, but also forms the main portion of the Si_3H_8 . The principal reaction restricting the increase in the concentration of Si_3H_8 is its reaction with silyl to form Si_4H_{10} , which provides for its practically complete depletion at high pressures. Conversely, when the pressure is lowered, a significant portion of the silicon atoms from Si_3H_8 return to the lower compounds by reacting with nascent hydrogen (whose concentration increases with decreasing pressure), and a large portion of the silicon is deposited on the walls, making the film growth

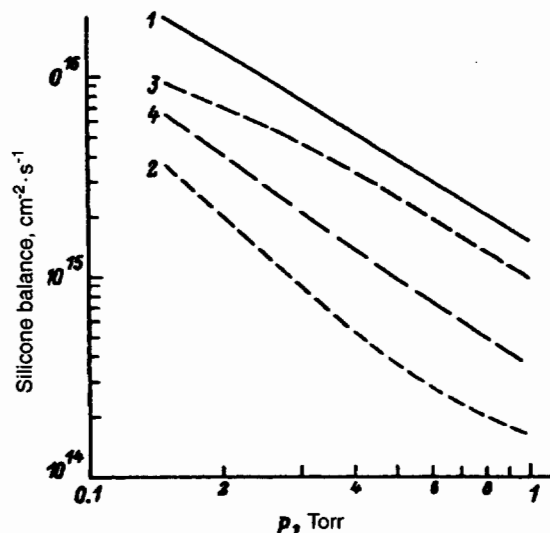


FIG. 5. Balance of silicon atoms in the bulk of the reactor as a function of the pressure in the reactor. The conditions are the same as in Fig. 3; 1 — production, 2 — reduction of SiH_4 , 3 — accumulation in the bulk, 4 — deposition.

process more efficient from the standpoint of the consumption of silane (Fig. 5). The buildup of silicon atoms in the bulk of the reactor is mainly due to the formation of Si_4H_9 and the increases in the concentrations of Si_2H_6 and Si_3H_8 (Fig. 1). We note that the calculated time dependence of the concentration of Si_3H_8 is in good agreement with the data from the calculations in Ref. 3 and that the concentration of Si_2H_6 at $t = 15$ ms is even an order of magnitude smaller than the value in Ref. 3. However, due to the cumbersome nature of the method used, the calculations in Ref. 3 were performed only up to a time of 20 ms, which is considerably shorter than the time needed for the corresponding concentrations to reach their steady-state values.

The calculations performed correspond to fairly large electron densities ($n_{e0} = 5 \times 10^9 \text{ cm}^{-3}$ when $L_0 = 2.5$ cm and $p_0 = 0.125$ Torr). An analysis of the dependence of the characteristics on n_e showed that the concentrations of most of the components are proportional to n_e and $n_{\text{Si}_2\text{H}_6} \propto n_e^{1.5}$ and that the concentrations of silyl, as well as of Si_2H_3 and Si_3H_8 decrease with n_e decreasing somewhat more slowly than according to a linear law. The rate of film growth is approximately proportional to n_e , while the fractions of silyl and silylyl deposited remain practically constant and, as is seen from (15), do not depend on the electron density.

Variation of the blow-through velocity primarily influences the concentration of Si_2H_6 . For example, increasing the blow-through velocity by an order of magnitude leads to a decrease in the concentration of Si_2H_6 by an order of magnitude and a decrease in the concentration of Si_3H_8 by half an order of magnitude. The concentration of silyl and the film growth rate increase slightly.

Let us consider the question of altering the scheme of chemical reactions taken into account. For example, in Refs. 26 and 18 the formation of Si_2H_6^* was not taken into account (although this channel was taken into account in Ref. 14, as

well as in Ref. 3), and it was assumed that the product of the reaction of silane with silylyl is Si_2H_6 . In the range of pressures considered the rate constant of the reaction $\text{SiH}_4 + \text{SiH}_2 \rightarrow \text{Si}_2\text{H}_6$ from Ref. 18 can be rewritten in the form $\hat{K} = 1.76 \times 10^{-13} p$ [Torr]. Thus, \hat{K} is proportional to the pressure, attesting to the participation of a third component in this reaction. Assuming that this reaction is the result of the sequence of reactions $\text{SiH}_4 + \text{SiH}_2 \rightarrow \text{Si}_2\text{H}_6^* + (M) \rightarrow \text{Si}_2\text{H}_6 + (M)$, where M is an arbitrary collision partner, and that the concentration of Si_2H_6^* is equal to the equilibrium value, we can write the rate constant under consideration as

$$\hat{K} = K(R28) \frac{n_{\text{Si}_2\text{H}_6^*}}{n_{\text{SiH}_4} n_{\text{SiH}_2}} n_{\text{tot}} = \frac{K(R28)K(R9)}{K(R27)} n_{\text{tot}} = 3.7 \cdot 10^{-12} p [\text{Torr}]$$

(see the Appendix and Table I; n_{tot} is the total density of the mixture).

The value obtained is approximately 20 times greater than the value of the constant given in Ref. 18. A calculation performed with $K(R9)$ reduced by a factor of 20 (which corresponds to the rate of the reaction $\text{SiH}_4 + \text{SiH}_2 \rightarrow \text{Si}_2\text{H}_6$ given in Refs. 18 and 26) showed that the principal changes affected only two components, viz., SiH_2 and Si_2H_6 . The concentration of silylyl increased by about an order of magnitude, and its flux onto the surface increased by four to fivefold. This is perfectly natural, since reaction R9 is the principal path for the depletion of silylyl from the bulk in a chemical reaction. The concentration of Si_2H_6 decreases by an order of magnitude at low pressures but only twofold at high pressures. The concentrations of Si_3H_8 , Si_2H_6^* , Si_2H_5 , and Si_2H_4 dropped two to threefold at low pressures and remained practically unchanged at high pressures.

The analysis performed indicates that even significant changes in the reaction rate constants, the electron density, and the blow-through velocity have weak effects on the ratios between the concentrations of most of the components. This allows us to conclude that the high concentrations of Si_2H_6 and Si_3H_8 obtained from the calculations, which are inconsistent with the existing models, do, in fact, exist. The only evidence in support of low concentrations of these components is from mass-spectrometric measurements. However, the large number of channels with poorly defined probabilities for the interaction of disilanes and trisilanes with electrons, which include not only ionization, but also pure dissociation processes, compels us to question the surety of the conclusions of the mass-spectrometric measurements with respect to the concentrations of these components.

In conclusion, it should also be stressed that the analytical expressions obtained in this work agree more closely with the results of numerical calculations in areas characterized by a small content of molecular hydrogen, due to the neglect of its concentration in the analytical equations. The agreement between the analytical and numerical calculations also becomes worse for too low a concentration of silyl, since the concentration of Si_3H_8 does not manage to reach its equilibrium value in that case.

CONCLUSIONS

The principal bulk chemical reactions associated with the dissociation of silane and film growth have been determined in this work, making it possible to describe the dependences of the deposition rates of silyl and silylyl on a whole series of parameters. It has been shown that the formation of higher silanes takes place according to a mechanism that is more complicated than the mechanism, for example, in Ref. 17. The important role of such components as Si_2H_6 and Si_3H_8 in shaping the composition of the mixture has been revealed. The mechanism for the influence of the variation of the blow-through velocity of the gas mixture on the film growth process has been ascertained. It is known, however, that the quality of a film is determined not only by the impingement of silylyl and higher radicals on it, but also by the content of hydrogen in the form of various compounds in it. Its concentration is determined mainly by the fluxes of the hydrogen-containing radicals that mediate film growth to the surface, and by its depletion from the surface by silyl radicals and nascent hydrogen, as well as by its thermal destruction. An analysis of similar effects accompanying film growth is possible only when more detailed surface kinetics are taken into account in the boundary conditions.

This work was carried out with partial support from INTAS (Grants Nos. 93-1916 and 94-704), and the Russian Fund for Fundamental Research (Grant No. 93-02-16873).

APPENDIX A: DETERMINATION OF CHEMICAL-EQUILIBRIUM CONCENTRATIONS

The principal supplier of nascent hydrogen is reaction R2 ($\text{SiH}_4 + e \rightarrow \text{SiH}_2 + 2\text{H}$), and its depletion is mediated by reaction R8 with silane ($\text{H} + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H}_2$) (see Table I and the reaction scheme). The principal reactions that produce H_2 are R8 and R27 ($\text{Si}_2\text{H}_6^* \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2$), and the process resulting in its depletion is R23/22 ($\text{H}_2 + \text{Si}_2\text{H}_4/\text{Si}_2\text{H}_3 \rightarrow (\text{SiH}_4 + \text{SiH}_2)/\text{Si}_2\text{H}_5$). The production of Si_2H_4 is mediated by reaction R27, and its depletion is mediated by reactions R13 ($\text{Si}_2\text{H}_4 + \text{SiH}_4 \rightarrow \text{Si}_3\text{H}_8$) and R23. Si_2H_6^* forms only as a result of reaction R9 ($\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6^*$), and it disappears mainly as a result of decomposition reaction R27. The only path for the formation of $\text{Si}_2\text{H}_6^{**}$ is reaction R16 ($\text{SiH}_3 + \text{SiH}_3 \rightarrow \text{Si}_2\text{H}_6^{**}$), and its depletion is mediated by the two channels R29/30 ($\text{Si}_2\text{H}_6^{**} \rightarrow \text{Si}_2\text{H}_4 + \text{H}_2/\text{SiH}_2$). The balance of Si_3H_8 is maintained by reactions R13 ($\text{SiH}_4 + \text{Si}_2\text{H}_4 \rightarrow \text{Si}_3\text{H}_8$) and R32 ($\text{Si}_3\text{H}_8 + \text{SiH}_3 \rightarrow \text{Si}_4\text{H}_9 + \text{H}_2$). As a result, for the equilibrium values of the concentrations we obtain

$$n_{\text{H}}^e = (2k(R2)/K(R8))n_e,$$

$$n_{\text{H}_2}^e = \frac{K(R8)n_{\text{H}}n_{\text{SiH}_4} + K(R27)n_{\text{Si}_2\text{H}_6^*}}{K(R23)n_{\text{Si}_2\text{H}_4} + K(R22)n_{\text{Si}_2\text{H}_3}} \\ = \frac{2k(R2)n_e + K(R9)n_{\text{SiH}_2}}{K(R9)n_{\text{SiH}_2}/(n_{\text{H}_2}/n_{\text{SiH}_4} + K(R13)/K(R23)) + K(R22)n_{\text{Si}_2\text{H}_3}} \\ \times n_{\text{SiH}_4},$$

$$n_{\text{Si}_2\text{H}_4}^e = \frac{K(R27)n_{\text{Si}_2\text{H}_6^*}}{K(R23)n_{\text{H}_2} + K(R13)n_{\text{SiH}_4}} \\ = \frac{K(R9)n_{\text{SiH}_2}}{K(R23)n_{\text{H}_2}/n_{\text{SiH}_4} + K(R13)},$$

$$n_{\text{Si}_2\text{H}_6^*}^e = \frac{K(R9)}{K(R27)}n_{\text{SiH}_4}n_{\text{SiH}_2},$$

$$n_{\text{Si}_2\text{H}_6^{**}}^e = \frac{K(R16)}{K(R29) + K(R30)}n_{\text{SiH}_3}^2,$$

$$n_{\text{Si}_3\text{H}_8}^e = \frac{K(R13)K(R9)n_{\text{SiH}_4}n_{\text{SiH}_2}}{K(R32)n_3(K(R23)n_{\text{H}_2}/n_{\text{SiH}_4} + K(R13))} \\ \approx \frac{K(R9)n_{\text{SiH}_4}n_{\text{SiH}_2}}{K(R32)n_{\text{SiH}_3}}.$$

The last relation is valid at low concentrations of H_2 . For the values of the rate constants given in Table I we obtain $n_{\text{Si}_2\text{H}_4} = 0.1$, $n_{\text{SiH}_2}/(1 + n_{\text{H}_2}/n_{\text{SiH}_4})$, $n_{\text{Si}_2\text{H}_6^*}^e = 2 \times 10^{-18}n_{\text{SiH}_4}n_{\text{SiH}_2}$ or $n_{\text{Si}_2\text{H}_6^*}^e = 2.17 \times 10^{-19}n_{\text{SiH}_3}^2$ and $n_{\text{Si}_3\text{H}_8}^e \approx n_{\text{SiH}_4}n_{\text{SiH}_2}/n_{\text{SiH}_3}$.

The reaction diffusion lengths for the components SiH , Si_2H_3 , and Si_2H_5 are

$$L_{D\text{SiH}} = \left(\frac{D_{\text{SiH}}}{(K(R10) + K(R11))n_{\text{SiH}_4}} \right)^{1/2},$$

$$L_{D\text{Si}_2\text{H}_3} = \left(\frac{D_{\text{Si}_2\text{H}_3}}{K(R22)n_{\text{H}_2}} \right)^{1/2},$$

$$L_{D\text{Si}_2\text{H}_5} = \left(\frac{D_{\text{Si}_2\text{H}_5}}{K(R12)n_{\text{SiH}_4}} \right)^{1/2}.$$

For the values of the rate constants from Table I it turns out that $L_{D\text{SiH}}$ is approximately one-and-one-half times greater and $L_{D\text{Si}_2\text{H}_5}$ is approximately five times greater than $L_{D\text{SiH}_2}$. At small hydrogen concentrations $L_{D\text{Si}_2\text{H}_3}$ can significantly exceed $L_{D\text{SiH}_2}$.

¹P. Kounavis, D. Mataras, N. Spiliopoulos *et al.*, *J. Appl. Phys.* **75**, 1599 (1994).

²M. Kawase, T. Masuda, M. Nagashima *et al.*, *Jpn. J. Appl. Phys.* **33**, 3830 (1994).

³M. J. Kushner, *J. Appl. Phys.* **63**, 2532 (1988).

⁴J. Perrin and T. Broekhuizen, *Appl. Phys. Lett.* **50**, 433 (1987).

⁵J. R. Doyle, D. A. Doughty, and A. Gallagher, *J. Appl. Phys.* **68**, 4375 (1990).

⁶D. A. Doughty and A. Gallagher, *Phys. Rev. A* **42**, 6166 (1990).

⁷C. Bohm, J. Perrin, P. Roca i Cabarrocas, *J. Appl. Phys.* **73**, 2160 (1993).

⁸N. Itabashi *et al.*, *Jpn. J. Appl. Phys.* **29**, 1505 (1990).

⁹N. Itabashi *et al.*, *Jpn. J. Appl. Phys.* **29**, 585 (1990).

¹⁰K. Tanaka, *Optoelectron. Devices Technol.* **4**, 133 (1989).

¹¹D. A. Doughty and A. Gallagher, *J. Appl. Phys.* **67**, 139 (1990).

¹²J. R. Doyle, D. A. Doughty, and A. Gallagher, *J. Appl. Phys.* **71**, 4771 (1992).

¹³M. M. Mezdrogina, A. F. Bardamid, O. A. Golikova *et al.*, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **26**, 1809 (1990).

¹⁴M. Shiratani, S. Matsuo, and Y. Watanabe, *Jpn. J. Appl. Phys.* **30**, 1887 (1991).

- ¹⁵L. Boufendi and A. Bouchoule, in *ESCAMPIG-92. Abstracts of Invited Lectures and Contributed Papers*, European Physical Society (1992), pp. 14–17.
- ¹⁶Yu. E. Gorbachev, M. A. Zatevakhin, and I. D. Kaganovich, *ESCAMPIG-92. Abstracts of Invited Lectures and Contributed Papers*, European Physical Society (1992), pp. 425–426.
- ¹⁷N. Sato, M. Shiratani, Yu. Watanabe, *Jpn. J. Appl. Phys.* **33**, 4266 (1994).
- ¹⁸J. Perrin, *J. Phys. D* **26**, 1662 (1993).
- ¹⁹J. Perrin, A. Lioret, J. De Bosny, and J. P. M. Schmitt, *Int. J. Mass Spectrom. Ion Phys.* **57**, 249 (1984).
- ²⁰A. V. Bogdanov and D. V. Shapiro, *Mat. Modelirov.* **4**, 3 (1992).
- ²¹Yu. E. Gorbachev and D. A. Shapiro, Preprint No. 1609, St. Petersburg (1993), 26 pp.
- ²²N. N. Semenov, *Acta Phys. URSS* **18**, 93 (1943).
- ²³A. F. Stekolnikov, D. V. Feshchenko, D. M. Ivanov, and A. E. Pereversev, *ESCAMPIG-92. Abstracts of Invited Lectures and Contributed Papers*, European Physical Society (1992), pp. 453–454.
- ²⁴J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1964) [Russ. transl., IL, Moscow (1961)].
- ²⁵L. G. Loitsyanskii, *Mechanics of Liquids and Gases*, 6th ed., Begell House, New York (1995) [Nauka, Moscow (1995)].
- ²⁶J. M. Jasinski and J. O. Chu, *J. Chem. Phys.* **88**, 1678 (1988).

Translated by P. Shelnitz