Collision Processes of Hydride Species in Hydrogen Plasmas: III. The Silane Family

R. K. Janev[1,2] and D. Reiter[1,3]

Abstract

Cross sections are provided for most important collision processes of the Silicon-Hydrides from the "Silane-family": SiH_y $(y = 1 - 4)$ molecules and their ions SiH_y^+, with (plasma) electrons and protons. The processes include: electron impact ionization and dissociation of SiH_y, dissociative excitation, ionization and recombination of SiH_y^+ ions with electrons, and charge - and atom - exchange in proton collisions with SiH_y. All important channels of dissociative processes are considered. Information is also provided on the energetics (reactants/products energy loss / gain) of each individual reaction channel. Total and partial cross sections are presented in compact analytic forms.

The critical assessment of data, derivation of new data and presentation of results follow closely the concepts of the recently published related databases for Carbon-Hydrides, namely for the Methane family [1, 2], and for the Ethane- and the Propane families [3], respectively.

[1]Institut für Plasmaphysik, Forschungszentrum Jülich GmbH, EURATOM Association, Trilateral Euregio Cluster, D-52425 Jülich, Germany

[2]Macedonian Academy of Sciences and Arts, 1000 Skopje, Macedonia

[3]Institut für Laser- und Plasmaphysik, Heinrich-Heine-Universität, D-40225 Düsseldorf, Germany

Contents

1 Introduction **3**

2 General properties of SiH_y molecules and their collision processes with electrons and protons **4**

2.1 Structural and thermochemical properties of SiH_y 4
2.2 Reaction energetics 5
2.3 General properties of collision cross sections 9

3 Cross sections and energetics of collision processes **12**

3.1 Electron-impact ionization of SiH_y (I, DI) 12
3.2 Dissociative excitation of SiH_y to neutrals (DE) and vibrational excitation of SiH_4 15
3.3 Dissociative excitation of SiH_y^+ (DE^+) 18
3.4 Dissociative ionization of SiH_y^+ (DI^+) 19
3.5 Dissociative recombination of SiH_y^+ (DR) 20
3.6 Charge exchange and particle rearrangement reactions 20

4 Concluding remarks **23**

5 References **25**

6 Tables **27**

1 Introduction

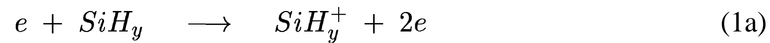
Collision processes of SiH_y $(y = 1 - 4)$ molecules and their ions with electrons and protons play an important role in plasma processing technologies (e.g. microelectronic industry, integrated circuit technology, logic devices) [4]...[6], and in certain astrophysical enviroments (planetary atmospheres, hydrogen rich gaseous nebulae, etc) [7]. SiH_y molecules may also appear in the cold plasma periphery of fusion devices, if Si is present as an admixture in plasma facing materials [8]. Finally, SiH_4 may be (and has been in TEXTOR) deliberately injected into fusion edge plasmas for transport and spectroscopic studies [9].

Despite the significant efforts in the past to estabish a self-consistent database for SiH_y and SiH_y^+ collision processes with electrons and protons [5, 6], [10] - [13], the absence of experimental and / or theoretical cross section information for the majority of these processes has prevented the success of these efforts. The gaps are particularly significant for collision processes of SiH_y $(y = 1 - 3)$ radicals and their ions. There are significant discrepancies in these data collections even for SiH_4 (e.g. in the identification of dominant dissociative ionization, excitation and recombination channels).

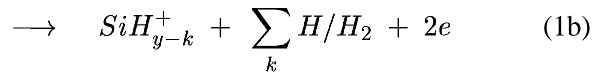
The purpose of this present work is to establish a comprehensive dataset for all collision processes of SiH_y and $SiH_y^+ (y = 1 - 4)$ with electrons and protons that are deemed to be the most important ones in the physical kinetics of a hydrogen plasma with relevant collision energies in the range from thermal to several hundreds eV. The establishment of this database will be based upon a critical assessment of available experimental and theoretical cross section information and on the use of physically well founded semi-empirical cross section scaling relationships for the considered processes.

The following electron impact processes will be considered in the database:

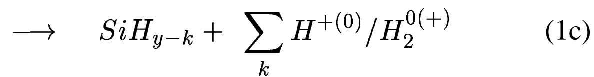
1) Direct (I) and dissociative (DI) ionisation of SiH_y :



$$e + SiH_y \longrightarrow SiH_y^+ + 2e \quad (1a)$$

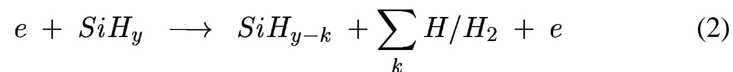


$$\longrightarrow SiH_{y-k}^+ + \sum_k H/H_2 + 2e \quad (1b)$$



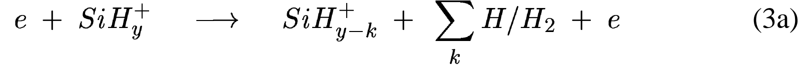
$$\longrightarrow SiH_{y-k} + \sum_k H^{+(0)}/H_2^{0(+)} \quad (1c)$$

2) Dissociative excitation of SiH_y to neutrals (DE):

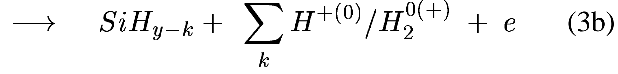


$$e + SiH_y \longrightarrow SiH_{y-k} + \sum_k H/H_2 + e \quad (2)$$

3) Dissociative excitation of SiH$_y^+$ ions (DE$^+$):

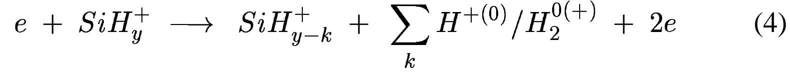


$$e + SiH_y^+ \longrightarrow SiH_{y-k}^+ + \sum_k H/H_2 + e \quad (3a)$$



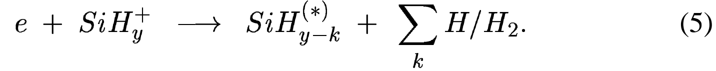
$$\longrightarrow SiH_{y-k} + \sum_k H^{+(0)}/H_2^{0(+)} + e \quad (3b)$$

4) Dissociative ionization of SiH$_y^+$ ions (DI$^+$) :



$$e + SiH_y^+ \longrightarrow SiH_{y-k}^+ + \sum_k H^{+(0)}/H_2^{0(+)} + 2e \quad (4)$$

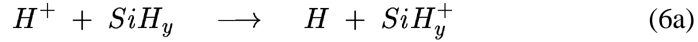
5) Dissociative recombination (DR) of electrons with SiH$_y^+$:



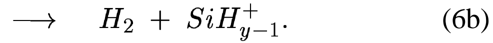
$$e + SiH_y^+ \longrightarrow SiH_{y-k}^{(*)} + \sum_k H/H_2. \quad (5)$$

Under the considered plasma conditions, and assuming small concentrations of SiH$_y$ in the plasma, the only important heavy-particle collision processes are

6) Proton impact charge exchange and particle rearrangement (CX):



$$H^+ + SiH_y \longrightarrow H + SiH_y^+ \quad (6a)$$



$$\longrightarrow H_2 + SiH_{y-1}^+. \quad (6b)$$

The summations in Eqs. (1)−(5) run over all dissociative channels. The asterisk on SiH$_{y-k}$ in Eq.(5) indicates that this DR product is (normally) in an electronically excited state.

In the next section we give the basic information on the properties of SiH$_y$ molecules and their collision processes with electrons and protons. In Section 3, we present the cross section information for processes (1) - (6) and their energetics. In Section 4 we give some concluding remarks.

2 General properties of SiH$_y$ molecules and their collision processes with electrons and protons

2.1 Structural and thermochemical properties of SiH$_y$

The similarity of the outer-shell electronic structure of $Si(3s^2 3p^2)$ with that of carbon atoms, $C(2s^2 2p^2)$ results in a structural similarity of SiH$_y$ molecules with CH$_y$ ($y = 1 - 4$). On this basis, one can expect that there should be a certain

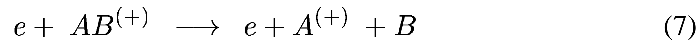
degree of similarity in the collision dynamics of SiH_y and CH_y molecules colliding with electrons and protons. However, there are still considerable differences in electronic properties (such as ionization potentials, polarizabilities, etc) between the two systems that introduce differences also in the collision dynamics. These differences manifest themselves in the magnitudes of collision cross sections rather than in the underlying dynamic mechanisms of the processes. In Table 1, we give the values of heat of formation, ΔH_f^0 (at 293K), and ionization potential, I_p, of all SiH_y molecules ($y = 1 - 4$), Si, H and H_2, and their ions. This information is needed when calculating the reaction exothermicities and reaction energetics. Si, H, H_2 are included in Table 1 because they appear as products in some reactions. The values of ΔH_f^0 and I_p were taken from Ref. [14]. Only for SiH_2 and SiH_3, the values of ΔH_f^0, not found in [14], were taken from Ref. [15]. We note that the value ΔH_f^0 for an ion A^+ is related to that of the neutral A by the thermochemical relation: $\Delta H_f^0(A^+) = \Delta H_f^0(A) + I_p(A)$. The lowest excited states of the species involved in processes (1)$-$(6), together with their excitation energies (taken from Refs. [14] and [16]), are also given in Table 1.

2.2 Reaction energetics

All electron impact inelastic processes (1)$-$(4) are characterized by an energy threshold, E_{th}. Dissociative recombination reactions (5) can proceed even for zero-energy electrons (no reaction threshold), while the charge- and particle-exchange reactions (6a) and (6b), respectively, have a threshold only when they are endothermic. Only in the case of direct electron-impact ionization of SiH_y, the threshold energy coincides with the ionization potential. The dissociative processes (1b)$-$(4) are characterized by an "appearance potential", A_p: the energy lost by incident electron for producing a specific fragmentation of SiH_y or SiH_y^+.

The minimum energy that is required for dissociation of a molecule AB (or molecular ion AB^+) to ground state (electronically and vibrationally unexcited) fragments in the reaction

$$e + AB^{(+)} \longrightarrow e + A^{(+)} + B \qquad (7)$$

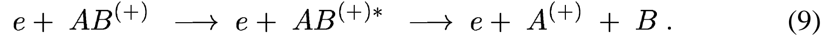


is

$$D_0(AB^{(+)}) = \Delta H_f^0(A^{(+)}) + \Delta H_f^0(B) - \Delta H_f^0(AB^{(+)}) , \qquad (8)$$

where $\Delta H_f^0(X)$ is the heat of formation of particle X. The dissociation energy (8) defines the case of ground-state products with zero kinetic energy. This dissociation channel is usually very weak since it involves a direct transition of the

molecule $AB^{(+)}$ from its initial (ground) vibrational state to the vibrational continuum (with a small overlap of corresponding vibrational wavefunctions). Dissociation is much more efficient if an electronic transition from the initial (ground) electronic state of $AB^{(+)}$ to an anti-bonding (repulsive) electronic excited state $AB^{(+)*}$ is involved, i.e. if the process proceeds as



$$e + AB^{(+)} \longrightarrow e + AB^{(+)*} \longrightarrow e + A^{(+)} + B \, . \tag{9}$$

In this case, the energy lost by the incident electron to excite the repulsive $AB^{(+)*}$ state defines the appearance potential (or the threshold) for reaction (9), and is equal to

$$E_{th}^{DE(+)} = E_{exc}(AB^{(+)*}) = D_0(AB^{(+)}) + \Delta E_{exc}(AB^{(+)*}) \, , \tag{10}$$

where $D_0(AB^{(+)})$ is given by Eq.(8), and $\Delta E_{exc}(AB^{(+)*})$ is the amount of excitation energy above the dissociation limit at the equilibrium distance of $AB^{(+)}$ (vertical Franck-Condon transition). Obviously, the excess of excitation energy $\Delta E_{exc}(AB^{(+)*})$ represents the total kinetic energy of dissociation product $A^{(+)}$ and B, i.e.

$$E_K = \Delta E_{exc}(AB^{(+)*}) \, . \tag{11}$$

We note that Eqs.(7) and (9) have a symbolic character in the sense that AB may be a complex polyatomic molecule, and the products A or B can represent several atomic or molecular products. The total kinetic energy E_K given by Eq.(11) is shared among the heavy dissociation products according to

$$E_{K,j} = \frac{\mu}{M_j} E_K \, , \qquad \sum_j E_{K,j} = E_K \, , \tag{12}$$

where M_j is the mass of the product j and μ is the reduced mass of all dissociation products.

In view of the finite range of the Franck-Condon region of the initial (ground) vibrational state of $AB^{(+)}$ within which the vertical transition to the excited state $AB^{(+)*}$ takes place, the total kinetic energy E_K of the products is spread over a certain (relatively narrow) range. Therefore, E_K in Eqs.(11) and (12) has the meaning of an average of E_K over its distribution in the Franck-Condon region.

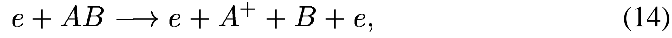
As we have seen above, the determination of energy threshold, electron energy loss and kinetic energy of products in dissociative reactions depends on the knowledge of the energy of $AB^{(+)*}$ excited repulsive state in the Franck-Condon region of ground vibrational state of $AB^{(+)}$. For the $SiH_y^{(+)}$ systems, however,

the energies of excited repulsive states are not known (e.g. neither from quantum - chemistry calculations, nor from experimental measurements of the energy distribution of dissociation products). Based on our experience with the analysis of dissociative processes in $C_xH_y^{(+)}$ systems [1, 2, 3], we have adopted the relation

$$\Delta E_{exc}(AB^{(+)*}) = \chi D_0(AB^{(+)}) \equiv \overline{E}_k, \tag{13}$$

where $D_0(AB^{(+)})$ is given by Eq.(8) and χ is a numerical factor with values in the range $\chi \simeq 0.3 - 2.0$. According to the experience with $C_xH_y^{(+)}$ systems, supported partly by quantum - chemistry calculations (e.g. for $CH^{(+)}$) and partly by experimental observations of the energy distribution of dissociation products, χ attains smaller values ($\sim 0.3 - 0.5$) when $D_0(AB^{(+)})$ is large ($> 4 - 5$ eV), and larger values ($\sim 1 - 2$) when $D_0(AB^{(+)})$ is small ($< 1 - 2$ eV). These criteria were applied when determining $\Delta E_{exc}(AB^{(+)*})$ for dissociative reactions of $SiH_y^{(+)}$ as well.

In the case of dissociative ionization (DI) reactions of AB,

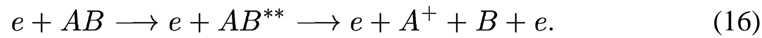


$$e + AB \longrightarrow e + A^+ + B + e, \tag{14}$$

the threshold energy (= appearance potential) is given by

$$\begin{aligned} E_{th,DI}(A^+, B/AB) &= \Delta E_f^0(A^+) + \Delta H_f^0(b) - \Delta H_f^0(AB) \\ &= I_p(AB) + D_0(AB^+). \end{aligned} \tag{15}$$

Since an electronic transition is involved in this reaction, it is efficient even in the threshold region, where the products A^+ and B have zero kinetic energy. However, the reaction becomes much more efficient when dissociation takes place by exciting an auto-ionizing state AB^{**} of AB, i.e. when it proceeds as



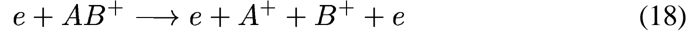
$$e + AB \longrightarrow e + AB^{**} \longrightarrow e + A^+ + B + e. \tag{16}$$

The doubly excited state AB^{**} is in fact an electronic state with the ionic core AB^+ of the AB molecule excited to a dissociative (repulsive) state AB^{+*}. Since in most cases this is the dominant dissociation mechanism (i.e. the main part of dissociative excitation cross section is due to this mechanism), it is more reasonable for the electron energy loss in a DI reaction to take

$$E_{el,DI}^{(-)} = I_p(AB) + D_0(AB^+) + \Delta E_{exc}(AB^+) \tag{17}$$

where $\Delta E_{exc}(AB^+)$ is the excess of excitation energy of AB^{+*} above the dissociation limit of AB^+. As in the case of earlier discussed DE^+ processes, $\Delta E_{exc}(AB^+)$

is released as total kinetic energy of reaction products (A^+ and B, in the present case), which is shared between (among) them in accordance with relation (12). The process of dissociative ionization of AB^+ ions



$$e + AB^+ \longrightarrow e + A^+ + B^+ + e \tag{18}$$

proceeds via excitation of (A^+,B^+) Coulomb (repulsive) state by a vertical Franck-Condon transition form the initial (ground) vibrational state of AB^+. The energy threshold for this process is

$$E_{th,DI^+} = I_p(AB^+) + \Delta E_{exc}(A^+, B^+) \tag{19}$$

where

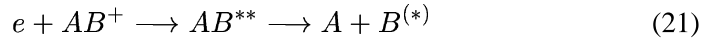
$$I_p(AB^+) = D_0(AB^+ \to A^+ + B) + I_p(B) = D_0(AB^+ \to A + B^+) + I_p(A),$$

and

$$\Delta E_{exc}(A^+, B^+) \simeq \frac{27.2eV}{R_e(AB^+)a_0} \equiv E_K \tag{20}$$

where $r_e(AB^+)$ is the equilibrium distance between the nuclei in AB^+ ion, expressed in units of the Bohr radius, a_0. The relation (20) follows from the fact (or very plausible assumption) that the Franck-Condon transition from AB^+ to (A^+, B^+) is vertical, and from the Coulomb character of the interaction between A^+ and B^+ in the (A^+, B^+) continuum state. Eq.(20) also gives the total kinetic energy of charged product. (If additional neutral products are produced in reaction (18), their kinetic energy is close to zero.)

The energetics of dissociative recombination (DR) process



$$e + AB^+ \longrightarrow AB^{**} \longrightarrow A + B^{(*)} \tag{21}$$

is characterized by absence of threshold. The reaction is always exothermic, with an exothermicity

$$\Delta E_{DR} = E_K^{(0)} = \Delta H_f^0(AB^+) - \Delta H_f^0(A) - \Delta H_f^0(B). \tag{22}$$

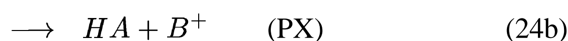
$E_K^{(0)}$ represents the total kinetic energy of the products when they are produced in their ground (electronic and vibrational) states, and when the kinetic energy of incident electron is zero. In the general case, the total kinetic energy of DR products is

$$E_K = E_{CM}^{el} + E_K^{(0)} - E_{exc}(B^*), \tag{23}$$

where E$^{el}_{CM}$ is the energy of incident electron in center-of-mass system, and E$_{exc}(B^*)$ is the excitation energy of excited product B^*.

The ionization potentials of SiH$_y$ molecules are smaller than that of hydrogen atom, and charge exchange reactions of H$^+$ with SiH$_y$ are all exothermic. The exothermicities ΔE of charge-, or particle-exchange reactions

$$H^+ + AB \quad \longrightarrow \quad H + B^+ \qquad \text{(CX)} \tag{24a}$$



$$\longrightarrow \quad HA + B^+ \qquad \text{(PX)} \tag{24b}$$

are calculated as

$$\Delta E = \sum \Delta H^0_f(\text{reactants}) - \sum \Delta H^0_f(\text{products}), \tag{25}$$

where the ΔH^0_f values for all reactants or products are included in corresponding sums. If some of the products are electronically or vibrationally (most often) excited, then the amount of their excitation energy has to be subtracted from ΔE given by Eq.(25).

2.3 General properties of collision cross sections

Both total and partial (i.e. for individual reaction channels) cross sections of electron-impact processes (1)$-$(4) have a similar general behaviour given by

$$\sigma = A\left(1 - \frac{E_{th}}{E}\right)^{\alpha} \frac{1}{E} \ln(e + cE), \tag{26}$$

where E and E$_{th}$ are the collision and threshold energy, respectively, A is constant (or weakly dependent function of E), and e=2.71828... is the base of natural logarithm (introduced for convenience). The power-law term in Eq.(26) describes the cross section behaviour in the threshold region, while the $\ln(cE)/E$ term describes the high-energy cross section behaviour, in accordance with Born theory of inelastic atomic processes. (The form of this term presumes that the dominant mechanism that governs the process includes a dipole-allowed electron transition.) The parameters α and c in Eq.(26) depend on the type of process, and they are the same for all reaction channels of a given process.

For a given process $\lambda(\lambda = I, DI, DE, DE^+, DI^+)$, the general cross section behaviour remains the same for any target molecule; only the relative magnitude of the cross section may change. This is a consequence of the identity of dominant mechanism for a given process for any target. From the Born (for high energies) and classical (for intermediate energies) theories of inelastic atomic processes, it

follows that the magnitude of the cross section for a given inelastic process, as function of reduced energy $E/\Delta E$, is inversely proportional to the square of electron transition energy ΔE (i.e. on the value of reaction threshold), $\sigma \sim E_{th}^{-2}$. This allows to connect the cross sections for the same type of process λ for different targets. Thus, as will be shown in the next section, the experimental total ionization cross sections for CH_y and SiH_y, $(y = 1 - 4)$ systems strictly obey the $\sigma \sim E_{th}^{-2}$ scaling relationship for any given value of y. This scaling should remain valid also for the cross sections of other inelastic electron-impact processes (with exceptions of DR). The charge exchange cross sections also exhibit distinct scaling properties: for E$<$ 25 keV, $\sigma_{cx} \sim I_p^{-1}$, whereas for E$>$ 50 keV, $\sigma_{cx} \sim I_p^{-2}$, where I_p is the ionization potential of the target [17, 18].

Another experimental observation of the electron-impact processes (1)$-$(3) with C_xH_y $(x = 1 - 3; 1 \leq y \leq 2x + 2)$ molecules (see Refs. [1, 2, 3]) is that total cross sections of these processes scale linearly with the number of H-atoms in the molecule. The origin of this scaling is in the "additivity rules" for the strengths of chemical bonds in a given molecule, and, therefore, this scaling should remain valid also for the processes (1)$-$(3) in the case of SiH_y. In the case of ionization of SiH_y, for which experimental data are available for all values of y (see Section 3.1), this scaling has already been explicitly verified.

In the case of electron-impact processes (1)$-$(4) with C_xH_y molecules $(x = 1 - 3; 1 \leq y \leq 2x + 2)$ it was also experimentally observed (see e.g. Refs. [1, 2, 3] and references therein) that the branching ratios R_j^λ for the reaction channels j of a given process λ

$$R_j^\lambda = \frac{\sigma_i^\lambda(E)}{\sigma_i^{tot}(E)} \tag{27}$$

become energy invariant for E$\gtrsim$ 30 $-$ 40 eV. This property of R_j^λ was verified for the case of available partial ionization cross sections for SiH_y, $(y = 1 - 4)$ systems (see Section 3.1). The general character of this property of R_j^λ allows its application to other electron-impact processes of SiH_y. The energy invariance of R_j^λ is brocken only in the energy region where the thresholds of reaction channels j lie. A prescription for determination of energy dependence of R_j^λ in the threshold region was given in Ref. [3]. If the thresholds $E_{th,j} \equiv E_j$ of reaction channels for a given reaction of the molecule SiH_y or SiH_y^+ (with fixed y) are ordered as

$$E_1 < E_2 < E_3 < ...E_k < ..., \tag{28}$$

the modified branching ratios $\tilde{R}_j^\lambda$, that depend on the energy in the near-threshold region and go over into their "asymptotic" values R_j^λ for E$>$ 40 eV, are given by

the recurrence relations [3]

$$\widetilde{R}_1^{\lambda}(E) = \frac{R_1^{\lambda}}{1 - \chi_1 \left(E_1/E\right)^{\beta}} \quad , \quad \chi_1 = 1 - R_1^{\lambda} \tag{29a}$$

$$\widetilde{R}_{k\geq 2}^{\lambda}(E) = \frac{R_k^{\lambda}}{1 - \chi_k \left(E_k/E\right)^{\beta}} \quad , \quad \chi_k = 1 - \frac{R_k^{\lambda}}{1 - \sum\limits_{j=1}^{k-1} \widetilde{R}_j^{\lambda}(E)} \tag{29b}$$

with $\beta \simeq 1.5$. The branching ratios $\tilde{R}_j^{\lambda}(E)$ satisfy the normalization condition $\sum_j \tilde{R}_j^{\lambda} = 1$ at any of the thresholds E= E_k, and for E$\neq$ E_k the deviation is on the few percentage level. (In cases when this deviation is larger, one should adjust the parameter β to another value around 1.5.) The determination of branching ratios R_j^{λ} will be discussed in connection with each of processes λ considered in the next section.

The partial cross section $\sigma_j^{\lambda}(E)$ for a particular reaction channel j is now given by

$$\sigma_j^{\lambda}(E) = \widetilde{R}_j^{\lambda}(E)\sigma_{\lambda}^{tot}(E). \tag{30}$$

When discussing the specific processes λ in the next sections, we shall be giving the analytic expression for $\sigma_{\lambda}^{tot}(E)$ and the values of “asymptotic” branching ratios R_j^{λ}.

3 Cross sections and energetics of collision processes

3.1 Electron-impact ionization of SiH_y (I, DI)

The processes of direct (Eq.(1a)) and dissociative (Eqs.(1b),(1c)) ionization of SiH_y molecules by electron impact have been subject of several experimental [19] - [22] and theoretical [23, 24] studies. Most extensively has been studied the $e + SiH_4$ collision system, for which the partial cross sections for six dissociative ionization channels have been measured in the energy range from threshold to 400 eV [19] and to 100 eV [22]. In the overlapping energy range, the partial cross sections of Refs. [19, 22] for the dominant channels agree well (to within 10-15%) with each other, and so does the total cross section $\sigma_{ion}^{tot}(SiH_4)$. The total ionization cross section of Ref. [20] for this molecule, however, is smaller by 30 - 40 % in the energy region above 40 eV than those of Refs. [19] and [22]. For the collision systems e + SiH_y, $(y = 1 - 3)$, only the partial cross sections for the direct ($\rightarrow$ SiH_y^+ + 2e) and dominant dissociative channel ($\rightarrow$ SiH_{y-1}^+ + H + 2e) have been measured in the energy range from threshold to 200 eV [21].

Theoretical calculations of total ionization cross sections for these systems have been performed within the binary-encounter-Bethe (BEB) model [23]. For the SiH_4 molecule, they agree well ($\sim 10\%$) with the experimental data of Refs. [19, 22], but for SiH_y, $(y = 1 - 3)$ molecules they are consistently smaller (by $\sim 20 - 25\%$) than the sum of the two dominant partial ionization cross sections of Ref. [21].

The total ionization cross sections for e + SiH_y systems adopted in the present database are those of Refs. [19, 22] for SiH_4, and of Ref. [21] for SiH_y, $(y = 1{-}3)$. The latter have been appropriately increased by 2-8 % to account for the contributions of unmeasured dissociation channels (estimated from the contributions of similar channels in SiH_4). In the high energy region (above the range in which experimental data were available), we have extended the adopted cross sections according to their Bethe-Born energy behaviour. All total ionization cross sections for SiH_y systems have broad maxima around E$\simeq$ 70 eV. The adopted total ionization cross sections were fitted to the analytic expression of the following form

$$\sigma_{ion}^{tot}(SiH_y) = A_{ion}(y)\left(1 - \frac{E_{th}}{E}\right)^{\alpha} \frac{1}{E + E_{th}(1 - \delta_{y,4})} \ln(e{+}cE)(\times 10^{-14} cm^2) \quad (31)$$

where the collision and threshold energies, E and E_{th}, are expressed in units of eV, $\delta_{y,4}$ is the Kronecker symbol, and e=2.71828... is the base of natural logarithm.

For the fitting parameters $A_{ion}(y)$, α and c, the following values were obtained

$$A_{ion}(y) = 1.96(1 + 0.116y), \quad \alpha = 3.0, \quad c = 0.10. \tag{32}$$

The analytic fits (31)−(32) reproduce the adopted cross sections well within their experimental uncertainties ($\sim \pm 18\%$).

It is interesting to compare the cross sections $\sigma_{ion}^{tot}(SiH_y)$, given by Eqs. (31)−(32), with the cross sections $\sigma_{ion}^{tot}(CH_y)$, $(y = 1 - 4)$, given in Refs. [1, 2] by an expression similar to Eq.(31). In both cases the values of parameters α and c are the same (c=0.09 in the CH_y case), while for the "structural" factors $A_{ion}(y)$ it was found that they satisfy the relation

$$\frac{A_{ion}(SiH_y)}{A_{ion}(CH_y)} = \xi_y \left[\frac{I_p(CH_y)}{I_p(SiH_y)}\right]^2, \tag{33}$$

where $I_p(X)$ is the ionization potential of molecule X. The proportionality factor ξ_y was found to be $\xi_y \simeq 1$, within 2−4% accuracy for all values of y. Relation (33) confirms the expectations, based on the classical and Born theories, regarding the I_p^{-2} scaling of reduced ionization cross sections. Its strict fulfillment ($\xi \simeq 1.0$), may also be taken as an indication of the accuracy of total ionization cross sections adopted in the present database.

As mentioned at the beginning of this sub-section, partial cross sections for six individual ionization channels of SiH_4 were measured in [19, 20, 22]. The sensitivity of experimental technique employed in Ref. [21] was such that for SiH_y, $(y = 1 - 3)$ the authors could reliably determine only the cross sections for the parent ($SiH_y \rightarrow SiH_y^+$) and dominant dissociative ($SiH_y \rightarrow SiH_{y-1}^+ + H$) ionization channels. The cross sections for other dissociative ionization channels in these systems were estimated to be smaller than $1 \times 10^{-16} cm^2$. (It should be noted that the measurements in Ref. [21] were performed for SiD_y, $(y = 1 - 3)$, but the ionization process does not exhibit an isotope effect.) It is important to note that in all cross sections measurement experiments on SiH_4 [19, 20, 22], the parent ionization channel ($SiH_4 \rightarrow SiH_4^+$) was not observed. The potential well of SiH_4^+ ion is very shallow ($D_0 \simeq 0.57$ eV) and the ion is unstable against auto-dissociation to $SiH_2^+ + H_2$. (The Franck-Condon transition $SiH_4 \rightarrow SiH_4^+$ leads directly to the continuum $SiH_2^+ + H_2$.)

The main electron-impact ionization channels of SiH_y molecules are shown in Table 2. The values of threshold energy (E_{th}), average electron energy loss ($\overline{E_{el}^{(-)}}$) and mean total kinetic energy ($\overline{E}_K$) for each ionization channel, calculated by using Eqs. (15), (17) and (13), respectively, are also given in this table. The

calculated values for E_{th} agree well with the experimentally observed appearance potentials (except for the minor H^+ and H_2^+ ion production channels from SiH_4, where the observed A_p values are about 24 eV. The cross sections of these channels in the threshold region are so small that an experimental error of the order of $\sim$ 5 eV is quite possible. In Table 2 are also given the "asymptotic" branching ratios, $R_{I,DI}$, for all individual ionization channels. For SiH_4, they have been determined from experimental cross sections of Ref. [22]. It has been found that for E$\gtrsim$ 30 $-$ 40 eV these branching ratios are independent (within the accuracy of the cross sections) of the collision energy. For the other SiH_y molecules, the branching ratios were determined after increasing the experimentally available cross section sum of the SiH_y^+ and $SiH_{y-1}^+ + H$ channels [21] by the estimated values of not measured dissociative ionization channels. The latter were determined by assuming that their contribution to the total cross section is in the same proportion as that of the corresponding channels of SiH_4. The ratio of the branching weights for the SiH_y^+ and $SiH_{y-1}^+ + H$ channels, however,was kept the same as in the experiment.

It should be mentioned that the large value of R_{DI} for the SiH_2^+ + H_2 dissociation channel in Table 2 is due to the contribution of the auto-dissociative decay $SiH_4^+ \to SiH_2^+ + H_2$ of the SiH_4^+ ion, formed as an unstable intermediary in the collision. The threshold energy for the formation of this intermediary is 11 eV (see Table 1), close to that for direct SiH_2^+ + H_2 fragmentation (11.6 eV). It has been estimated that the virtual $SiH_4^+ \to SiH_2^+ + H_2$ channel contributes about 50% to the total $SiH_2^+ + H_2$ channel cross section.

The partial cross section for a specific ionization channel $e + SiH_y \to A^+ + ... + 2e$, is given by (see Eq.(30))

$$\sigma_{I,DI}(A^+/SiH_y) = \widetilde{R}_{I,DI}(A^+/SiH_y)\sigma_{ion}^{tot}(SiH_y), \tag{34}$$

where $\tilde{R}_{I,DI}$ is expressed in terms of "asymptotic" values $R_{I,DI}$ (given in Table 2) by Eqs. (29), and σ_{ion}^{tot} is given by Eqs. (31)$-$(32). The cross section for the $e + Si \to e + Si^+ + e$ ionization is given in Ref. [24] in the form

$$\sigma_{ion}(Si) = \frac{10^{-13}}{I_p E}\left[A_0 \ln(E/I_p) + \sum_{j=1}^{3} A_j \left(1 - \frac{I_p}{E}\right)^j\right] (cm^2), \tag{35}$$

where $I_p = 8.15$ eV, collision energy E is expressed in eV units, and the values of fitting parameters A_i are: $A_0 = 1.573, A_1 = 0.722, A_2 = -2.687, A_3 = 1.856.$ The energetics of this reaction is also given in Table 2.

3.2 Dissociative excitation of SiH_y to neutrals (DE) and vibrational excitation of SiH_4

There have been no direct measurements or theoretical calculations of the cross sections for electron-impact dissociative excitation of SiH_y molecules to neutrals. There exists, however, a cross section measurement of the total electron-impact dissociation cross section of SiH_4 to both neutral and ionized fragments [25] in the energy range from threshold to $\sim$ 500 eV. The total cross section for dissociative excitation to neutral fragments of SiH_4, $\sigma_{DE}^{tot}(SiH_4)$, can be obtained by subtracting the total dissociative ionization cross section $\sigma_{DI}^{tot}(SiH_4)$ from the measured total dissociation cross section $\sigma_{diss}^{tot}(SiH_4)$ of Ref. [25],

$$\sigma_{DE}^{tot}(SiH_4) = \sigma_{diss}^{tot}(SiH_4) - \sigma_{DI}^{tot}(SiH_4). \tag{36}$$

By using this relation and the data of Ref. [22] for σ_{DI}^{tot}, we have obtained $\sigma_{DE}^{tot}(SiH_4)$ up to E=200 eV, and have then extended it to higher energies according to the Bethe-Born energy behaviour. The cross section $\sigma_{DE}^{tot}(SiH_4)$ has a threshold $E_{th} \simeq$ 8.0 eV and exhibits a broad maximum around E$\simeq$ 70 eV. The cross section $\sigma_{DE}^{tot}(SiH_4)$ can be related to the similar (also experimentally known) cross section $\sigma_{DE}^{tot}(CH_4)$ [1] by the relation

$$\frac{\sigma_{DE}^{tot}(SiH_4)}{\sigma_{DE}^{tot}(CH_4)} = \eta \left[\frac{A_p(H/CH_4)}{A_p(H/SiH_4)}\right]^2, \tag{37}$$

where $A_p(H/X)$ is the appearance potential for the dominant H-production dissociative channel of molecule X. It was found that above 30-40 eV, the proportionality factor η in Eq.(37) is $\eta \simeq 2.23$. The relation (37), of course, holds for any pair SiH_y and CH_y with the same y. From the known total DE cross sections for CH_y [1, 2], and assuming that the value $\eta \simeq 2.23$ does not depend upon y, one can obtain $\sigma_{DE}^{tot}(SiH_y)$ for y=1$-$3. The cross sections $\sigma_{DE}^{tot}(SiH_y)$ obtained by this procedure can be represented by the analytic expression

$$\sigma_{DE}^{tot}(SiH_y) = A_{DE}(y)\left(1 - \frac{E_{th}}{E}\right)^3 \frac{1}{E}\ln(e + 0.11E)(\times 10^{-14} cm^2), \tag{38a}$$

with

$$A_{DE}(y) = 0.95(1 + 0.50y), \tag{38b}$$

and collision and threshold energies, E and E_{th}, expressed in eV units.

The most important electron-impact dissociative excitation channels of SiH_y molecules are given in Table 3. The threshold energies, E_{th} (= $\overline{E_{el}^{(-)}}$), and the

total mean kinetic energy of the products, $\overline{E}_K$, calculated by using Eqs. (10) and (13), respectively, are also given in this table for each reaction channel. The high-energy branching ratios R_{DE} shown in Table 3 were calculated from the relation

$$R_{DE}(A/SiH_y) \equiv \frac{\sigma_{DE}(A/SiH_y)}{\sigma_{DE}^{tot}(SiH_y)} = \frac{\sigma_{DI}(A^+/SiH_y)}{\sigma_{DI}^{tot}(SiH_y)} \equiv R_{DI}(A^+/SiH_y), \tag{39}$$

i.e. assuming that branching ratios for DE reaction $e + SiH_y \to e + A+$ (products) and DI reaction $e + SiH_y \to 2e + A^+ +$ (products) are the same. The relation (39) reflects the fact that both DE and DI processes are governed by the same physical mechanism: excitation of a dissociative state that lies in the continuum [26, 27]. Autoionization of this state leads to dissociative ionization, whereas its survival leads to dissociation to neutrals. It should be noted that, while autoionization depends only on the coupling of auto-ionizing dissociative state with the continuum, the survival probability of the system in this state depends on the time it spends in that state. Therefore, the DE process exhibits an isotope effect [27].

We note that in the silane-based plasma processing modeling (see e.g. [5, 6, 28]), the DE processes SiH_y, $(y = 1 - 3)$ are usually not included. The $SiH_4 \to SiH_2 + H_2$ channel, which we predict to be a strong DE channel, is also not included in those models (presumably because of lack of cross section data). Instead, the DE channel $SiH_4 \to SiH_2 + 2H$ is usually included (as a sub-dominant channel). However, the dissociation energy for this channel is 7.19 eV (compared to 2.64 eV for the $SiH_2 + H_2$ channel), and its threshold energy should be high ($\sim 12 - 14$ eV). Therefore, this DE channel should be very weak and is not included in Table 3.

The partial cross section for a given $SiH_y \to A +$ (products) DE channel is given by

$$\sigma_{DE}(A/SiH_y) = \widetilde{R}_{DE}(A/SiH_y)\sigma_{DE}^{tot}(SiH_y), \tag{40}$$

where $\tilde{R}_{DE}$ and R_{DE} are related by Eqs.(29), and σ_{DE}^{tot} is given by Eq.(38).

As it can be seen from Table 3, threshold energies for DE processes of SiH_y all lie above 5 eV. At lower collision energies, SiH_y molecules can be efficiently vibrationally excited by electrons, and this process may be a significant energy loss mechanism for the electrons. Vibrational excitation of SiH_y by protons should also be characterized by large cross sections. Unfortunately, cross section data for these processes are not available except for the electron-impact vibrational excitation of SiH_4.

There are two vibrational modes in SiH_4 for which cross section data are avail-

able: the bending mode (v_2, v_4) and the stretching mode (v_1, v_3), with threshold energies of 0.113 eV and 0.271 eV, respectively. Although the energy quanta of these modes are small, the corresponding cross sections in the energy region below $\sim$ 20 eV are very high (several times $10^{-16}cm^2$). The cross sections for $v_{2,4}$ and $v_{1,3}$ excitations of SiH_4 have not been measured directly, but derived (by many authors) by a Boltzmann equation analysis of experimental electron swarm parameters (drift velocity, net ionization coefficient, etc). This procedure does not provide a unique determination of excitation cross sections of $v_{2,4}$ and $v_{1,3}$ vibrational modes. The cross section data for $\sigma_{exc}(v_{2,4})$ and $\sigma_{exc}(v_{1,3})$ of Refs. [29] and [30] have been used in the modeling of most silane-containing discharges, although in the region above $\sim$ 5 eV these two data sets differ by a factor of 5, or more. Below $\sim$ 1 eV these two cross section data sets are close to each other, and to the data of other authors. For the present database, we have adopted the data of Ref. [29] for the energy region below $\sim$ 20 eV, and for E $>$ 20 eV we have taken a mean value of the cross sections of Ref. [29] and [30]. From the point of view of electron energy loss calculations, relevant is the total vibrational excitation cross section, $\sigma^{tot}_{vib,exc} = \sigma_{exc}(v_{2,4}) + \sigma_{exc}(v_{1,3})$. The sum of adopted $v_{1,3}$ and $v_{2,4}$ excitation cross sections can be represented by the analytic expression

$$\sigma^{tot}_{vib,exc}(SiH_4) =$$

$$\left(1 - \frac{0.2825}{E_1}\right)^{1.40} \frac{16.0}{1 + E_1^{1.58}} + \frac{15.2}{E_2^{-1.65} + 0.38E_2^{0.6} + 0.32E_2^{2.5} + 0.1E_2^{3.5}}$$

$$(\times 10^{-16} cm^2) \qquad (41)$$

where

$$E_1 = \frac{E}{0.4}, \qquad E_2 = \frac{E}{8}, \qquad (42)$$

and the collision energy E is expressed in eV units. For energies E $\leq$ 0.271 eV, the electron energy loss is $E_{el}^{(-)} = 0.113$ eV, for $0.271 < E(eV) \leq 15, E_{el}^{(-)} \simeq 0.192$, ($\sigma_{exc}(v_{2,4}) \simeq \sigma_{exc}(v_{1,3})$ in this energy range), and for E $>$ 15 eV, $E_{el}^{(-)} =$ 0.113 eV (since $\sigma_{exc}(v_{2,4}) \gg \sigma_{exc}(v_{1,3})$ in this region). It should be noted that the SiH_4 excited by this process do not form a separate population of SiH_4 molecules which should be distinguished from the population of unexcited SiH_4 molecules in the kinetic Monte Carlo transport modeling codes. The excitation energy of these vibrationally excited molecules (0.1 - 0.3 eV) is much smaller than the threshold energies of other processes and, therefore, has no effect on their cross sections. In fact, the uncertainties in threshold energies of other electron impact processes are considerably higher ($\sim$ 0.5 eV) than the above vibrational excitation energies.

3.3 Dissociative excitation of SiH$_y^+$ (DE$^+$)

There are no experimental or theoretical cross section data for the process of dissociative electron impact excitation of SiH$_y^+$ ions, Eq.(3). For determining the total cross sections for these processes we shall use the scaling relation

$$\frac{\sigma^{tot}_{DE^+}(SiH_y^+)}{\sigma_{DE^+}(CH_y^+)} = \eta \left[\frac{A_p(A^+/CH_y^+)}{A_p(A^+/SiH_y^+)}\right]^2, \tag{43}$$

where $A_p(A^+/X^+)$ is the appearance potential for the dominant channel of $e + X^+ \to e + A^+ +$ (neutral products) DE$^+$ reaction. By choosing (somewhat conservatively) the value of proportionality constant η in Eq.(43) as $\eta \simeq 1.0$, one obtains $\sigma^{tot}_{DE^+}(SiH_y^+)$ from the known cross sections $\sigma^{tot}_{DE^+}(CH_y^+)$ [1]. The total DE$^+$ cross sections for SiH$_y^+$ derived by this procedure can all be fitted to the analytic expression

$$\sigma^{tot}_{DE^+}(SiH_y^+) = A_{DE^+}(y)\left(1 - \frac{E_{th}}{E}\right)^{2.5} \frac{1}{E} ln(e + 0.8E)(\times 10^{-14} cm^2) \tag{44}$$

$$A_{DE^+}(y) = 0.36[1 + 0.55(y-1)], \tag{45}$$

where E and E$_{th}$ are expressed in eV units, and e = 2.71828.... E$_{th}$ in Eq.(44) is the lowest energy threshold of the individual reaction channels for a given SiH$_y^+$ molecule. The values of E$_{th}$ and the mean total kinetic energies $\overline{E_K}$ of dissociation products calculated by using Eqs.(10) and (13), respectively, are given in Table 4 for the most important DE$^+$ channels. The ion SiH$_4^+$ is excluded from this table since it is not produced by electron-impact ionization of SiH$_4$ (see Section 3.1). This ion is not produced by electron capture in $H^+ + SiH_4$ collisions either, since the vertical Franck - Condon transition SiH$_4$ $\to$ SiH$_4^+$ leads directly to the SiH$_2^+$ + H$_2$ continuum of SiH$_4^+$.

The high-energy values of branching ratios R$_{DE^+}$ of individual reaction channels are also given in Table 4. They have been determined by the procedure described in Ref. [3]. For two different DE$^+$ channels of the same SiH$_y^+$ ion, e.g. SiH$_y^+$ $\to$ A$_1^+$ + (neutrals) and SiH$_y^+$ $\to$ A$_2^+$ + (neutrals), this procedure predicts that

$$\frac{R_{DE^+}(A_1^+/SiH_y^+)}{R_{DE^+}(A_2^+/SiH_y^+)} \simeq \frac{\zeta_1}{\zeta_2}\left(\frac{E_{th_2}}{E_{th_1}}\right)^{2.5} \tag{46}$$

where E$_{th1}$ and E$_{th2}$ are the thresholds of considered DE$^+$ channels, and ζ_1, ζ_2 are additional factors characterizing the channel fragmentation. The exponent 2.5 in Eq.(46) reflects the threshold energy behaviour of DE$^+$ reactions (see Eq.(44)).

The values ζ_i for various types of fragmentation (e.g. release of H, H_2 or H + H_2 neutrals) have been determined from comparing the results of such a procedure, applied to I, DI, and DE processes, and the experimentally known (e.g. for I, DI) or on their basis derived (e.g. for DE) R_λ values (λ = I, DI, DE). The partial cross sections of individual DE^+ channels are given by

$$\sigma_{DE^+}(A^+/SiH_y^+) = \tilde{R}_{DE^+}(A^+/SiH_y^+)\sigma_{DE^+}^{tot}(SiH_y^+) \quad (47)$$

where $\tilde{R}_{DE^+}$ and R_{DE} are related by Eqs.(29), and $\sigma_{DE^+}^{tot}$ is given by Eqs.(44)$-$(45).

3.4 Dissociative ionization of SiH_y^+ (DI^+)

No experimental or theoretical cross section data exist for the electron-impact ionization (DI^+) of SiH_y^+ ions, Eq.(4). These reactions are characterized by large energy thresholds ($\sim$ 25$-$30 eV) and play a role in silicon hydrid kinetics only when the edge plasma temperature is relatively high ($\gtrsim$ 20 eV).

The total cross section for DI^+ processes of SiH_y^+ were determined by the same procedure used in the preceding sub-section for determination of $\sigma_{DE^+}^{tot}(SiH_y^+)$, (cf. Eq.(43)). The total DI^+ cross sections, obtained by this procedure, can be represented by the analytic expression

$$\sigma_{DI^+}^{tot}(SiH_y^+) = A_{DI^+}(y)\left(1-\frac{E_{th}}{E}\right)^{1.55}\frac{1}{E}ln(e+0.5E)(\times 10^{-14}cm^2) \quad (48)$$

$$A_{DI^+}(y) = 0.273[1+0.223(y-1)] \quad (49)$$

where E and E_{th} are expressed in eV, and e = 2.71828....
The main DI^+ channels for $e+SiH_y^+$ collision systems (y = 1 - 3) are given in Table 5. The ion SiH_4^+ has been excluded from this table because it is not formed in the plasmas considered in the present work. Threshold energies, E_{th}, and total kinetic energy of ionized fragments, E_K, calculated using Eqs.(19) and (20), respectively, are also given in this table. The value of $r_e(AB^+)$ in Eq.(20) for SiH^+ was taken from Ref. [16], ($r_e(SiH^+) \simeq 2.87\ a_0$), and was slightly increased for SiH_2^+ (r_e = 2.85 a_0) and SiH_3^+ (r_e = 2.87 a_0), a_0 being the Bohr radius. The branching ratios for individual DI^+ reaction channels were calculated in a similar way as for the DE^+ reactions, considered in preceding sub-section, and are also given in Table 5.

The partial cross section for an individual DI^+ channel $SiH_y^+ \rightarrow A^+ + B^+ +$ (neutrals) of a given $e+SiH_y^+$ collision system are given by

$$\sigma_{DI^+}(A^+,B^+/SiH_y^+) = \tilde{R}_{DI^+}(A^+,B^+/SiH_y^+)\sigma_{DI^+}^{tot}(SiH_y^+) \quad (50)$$

where $\tilde{R}_{DI^+}$ and R_{DI^+} are related by Eqs.(29).

3.5 Dissociative recombination of SiH_y^+ (DR)

Cross section data of dissociative recombination of electrons on SiH_y^+ ions are not available in the literature. However, total DR rate coefficients for these systems for thermal temperatures have been reported in Refs. [6, 12] and [31]. These data show a weak linear increase with increasing y in SiH_y^+. The rate coefficient $< v\sigma_{DR} >$ has a $T^{-1/2}$ - temperature dependence at low temperatures, that follows from the Wigner law for break-up reactions [32]. At higher temperatures, where other mechanisms contribute to the DR process (T $\sim$ 1 eV) , and, where other processes (such as DE^+) begin to compete with DR ($T \sim$ 10 eV), the $T^{-1/2}$ - temperature dependence changes into a stronger one, $< \sigma_{DR} v > \sim T^{1.05}$ [33]. Using the thermal data on $< v\sigma_{DR} >$ from Refs. [6, 12] and [31], and T-dependence of $< v\sigma_{DR} >$ from Ref. [33], the total DR rate coefficients for SiH_y^+ ions can be represented in the form

$$< \sigma_{DR}^{tot} v > (SiH_y^+) = \frac{2.47(1+0.32y)}{T^{0.5}(1+0.27T^{0.55})}(\times 10^{-8} cm^3/s) \quad (51)$$

where electron temperature T is expressed in eV units.
The main dissociative recombination channels for SiH_y^+ ($y = 1-3$) ions are given in Table 6. Their branching ratios R_{DR}, taken to be the same as the measured branching ratios in the corresponding $e + CH_y^+$ DR reactions [1, 2], are also shown in this table. These branching ratios, determined in the thermal region, are expected to be temperature invariant up to a few eV. Their temperature dependence at higher temperatures is unknown. In Table 6 also shown are the excited products expected to be formed in a given DR channel for collision energies below $\sim$ 1 eV. The exothermicities of DR channels for ground state dissociation products, $E_K^{(0)}$, are also shown in Table 6. The total kinetic energy of dissociation products for an electron impact energy E_{cm}^{el} in the center-of-mass system, with production of an excited product B^*, is given by: $E_K = E_{cm}^{el} + E_K^{(0)} - E_{exc}(B^*)$, where $E_{exc}(B^*)$ is the excitation energy of B^* (see Eq.(23)).

3.6 Charge exchange and particle rearrangement reactions

Cross section measurements or calculations for charge exchange and particle exchange reactions (6a) and (6b), respectively, do not exist in the literature. Total thermal rate coefficients for the sum of these processes, however, do exist [5, 12], but show a spread within a factor of two. The data in these sources are also inconsistent with the Langevin total thermal rate coefficient for these processes, which

requires their increase with the increase of number of H atoms in SiH_y (or, equivalently, with the polarizability of SiH_y). Therefore, staying within the spread of reported K_{cx}^{tot} values, we have chosen to determine them by using the relation

$$K_{cx}^{tot}(SiH_y) = \frac{I_p(CH_y)}{I_p(SiH_y)} K_{cx}^{tot}(CH_y) \tag{52}$$

where $I_p(X)$ is the ionization potential of X, and $K_{cx}^{tot}(CH_y)$ are known (see e.g. [1, 2]). Relation (52) reflects the inverse proportionality of charge exchange cross section with the electron binding energy in the target [17]. The $K_{cx}^{tot}(SiH_y)$ values obtained from Eq.(52) and the data for $K_{cx}^{tot}(CH_y)$ given in Ref. [1] are shown in Table 7. In this table also shown are the values of branching ratios $R_{cx}^{(a),(b)}$ for the proper charge exchange (electron capture) and particle exchange reaction channels, which are close to those for $H^+ + CH_y$ systems [1]. The cross sections for the charge exchange (Eq.(6a)) and particle exchange (Eq.(6b)) processes in the thermal energy region (E $\lesssim 0.1$ eV) can now be written as

$$\sigma_{cx}^{(a)} = 7.26 \frac{R_{cx}^{(a)} K_{cx}^{tot}}{E^{0.5}} (\times 10^{-16} cm^2) \tag{53}$$

$$\sigma_{cx}^{(b)} = 7.26 \frac{R_{cx}^{(b)} K_{cx}^{tot}}{E^{0.5} + cE^{\gamma}} (\times 10^{-16} cm^2) \tag{54}$$

where K_{cx}^{tot} is expressed in units of $10^{-9} cm^3/s$, and collision energy E is in eV units. In fact, Eqs. (53) and (54) can be extended even to somewhat higher energies. The additional term cE^{γ} in the denominator of Eq.(54) takes into account the rapid decrease with energy of the probability for particle exchange. The values of parameters c and γ are also given in Table 7.

In this table are also given the exothermicities ΔE for each of the reaction channels for a given $H^+ + SiH_y$ system, calculated by using Eq.(25) under the assumption that the reaction products are in their ground electronic and vibrational states. It is, however, fairly probable that the SiH_y^+ and SiH_{y-1}^+ products have a significant degree of vibrational excitation. The energy released as total kinetic energy of the products is, therefore

$$E_K = \Delta E - E_{exc}(\text{products}), \tag{55}$$

where E_{exc} is the total (electronic and vibrational) excitation energy of the products. There is no simple way, however, to estimate the amount of E_{exc}. As indicated in Table 7, and mentioned earlier, the electron capture process $H^+ + SiH_4 \rightarrow H +$ (SiH_4^+) is accompanied by a Franck-Condon transition ($SiH_4 \rightarrow SiH_4^+$) which leads

directly to the continuum SiH_2^+ + H_2 of SiH_4^+. The $\sigma_{cx}^{(a)}(SiH_4)$ cross section is, thus, the cross section for production of SiH_2^+ + H_2 fragments. The fact that the SiH_4^+ ion promptly dissociates after the electron capture has taken place, does not affect the character of the electronic transition itself. In the case of the analogous H^+ + CH_4 system, where CH_4^+ is stable, it was experimentally observed that the electron capture process has a resonant character (due to the small exothermicity of about 1.1 eV, that can be absorbed by the internal degrees of freedom of CH_4^+ ion). Because of relatively large exothermicity ($\simeq 2.59$ eV) of the $H^+ + SiH_4$ dissociative charge exchange reaction, one may expect that only part of it can be absorbed by the vibrational modes of SiH_2^+ and H_2 products, so that resonant conditions ($\Delta E \simeq 0$) for this reaction cannot be expected to be fulfilled. The reaction may still have a quasi-resonant character due to the small remaining resonance energy defect. For similar reasons, the charge exchange reaction H^+ + $SiH_3 \rightarrow$ H + SiH_3^+ cannot be expected to have resonant character (contrary to the H^+ + CH_3 case). Nevertheless, the relations

$$\frac{\sigma_{cx}^{(a)}(SiH_y)}{\sigma_{cx}^{(a)}(CH_y)} \simeq \frac{I_p(CH_y)}{I_p(SiH_y)}, \qquad E \lesssim 20keV, \tag{56a}$$

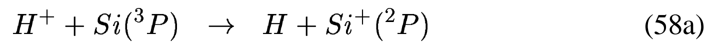
$$\frac{\sigma_{cx}^{a}(SiH_y)}{\sigma_{cx}^{a}(CH_y)} \simeq \left[\frac{I_p(CH_y)}{I_p(SiH_y)}\right]^2, \qquad E \gtrsim 50keV, \tag{56b}$$

resulting from the general theories of low- and high-energy charge exchange reactions [17, 18], are still expected to be valid. We shall use these relations to determine $\sigma_{cx}^{(a)}(SiH_y)$, with due account of the remarks made above for the H^+ + SiH_4 and H^+ + SiH_3 collision systems.

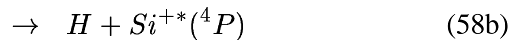
The derived cross sections can be represented by the analytic expression

$$\sigma_{cx}^{(a)}(SiH_y) = \frac{c_1}{E^{0.5} + c_2 E^{c_3}} + \frac{c_4 exp(-c_5/E^{c_6})}{E^{c_7} + c_8 E^{c_9} + c_{10} E^{c_{11}} + c_{12} E^{c_{13}}}(\times 10^{-16} cm^2) \tag{57}$$

where the collision energy is expressed in eV units, and the values of fitting parameters are given in Table 8. The first term in Eq.(57) ensures that with decreasing the energy, the cross section attains its thermal energy value given by Eq.(53). The upper limit of validity of the expression (56) is about 200 - 300 keV. In Table 8, we give also the fitting parameters for the total cross section of reactions



$$H^+ + Si(^3P) \rightarrow H + Si^+(^2P) \tag{58a}$$



$$\rightarrow H + Si^{+*}(^4P) \tag{58b}$$

for which calculations exist in the energy range 1 - 1000 eV [34], as well as a known value of its thermal rate coefficient [12]. In the energy region above 1000

eV, the total cross section of reactions (58) was derived by using the scalings (56). For energies below $\sim 150-200$ eV, the contribution of the channel (58a) can be neglected in the total cross section. The favourable couplings in the channel (58b) lead to a very large cross section for this reaction channel in the energy range below $\sim$ 1000 eV ($\sim 10^{-14} cm^2$), i.e. the process (58b) produces $Si^{+*}(^4P)$ excited ions with rate coefficients of $\gtrsim 10^{-8} cm^3/s$ at plasma temperatures $\gtrsim$ 10 eV [34].

4 Concluding remarks

We have presented a complete cross section database for all important collision processes of electrons and protons with SiH_y ($y = 1 - 4$) molecules and their ions taking place in low density plasmas with temperatures up to several hundreds eV (and even higher). For the sake of completeness, we have also included the electron-impact ionization of Si, as well as its charge exchange process with protons. In establishing this database, we have used the information regarding the mechanisms governing the considered processes. In particular, well established theoretical or semi-empirical cross section scaling relationships have been used for deriving the cross sections of reactions for which such information was not available in the literature.

The limitation regarding the plasma density holds only for low-temperature plasmas with high neutral hydrogen density when the collision processes of SiH_y and SiH_y^+ with hydrogen neutrals become also important. We also assume that plasma conditions are such that formation of heavier silicon hydrides (such as Si_2H_y, etc) does not take place. Under such plasma and gas conditions, the ion SiH_4^+ does not appear among SiH_y^+ ions, and for this reason its processes (DE^+, DI^+ and DR) with plasma electrons have been excluded from the present database. In the opposite case, when Si_2H_6 is present in the plasma, stable SiH_4^+ ion can be formed in the dissociative ionization reaction $e + SiH_6 \rightarrow SiH_4^+ + 2e+$ products (see, e.g. [14]). We note, however, that analytic expressions for the total DE^+ and DI^+ cross sections, Eqs.(44) and (48), respectively, and total DR rate coefficient, Eq.(51), are also applicable for the SiH_4^+ ion. Using the described methodology in Sections 2 and 3, one can also determine the main DE^+, DI^+ and DR reaction channels for SiH_4^+ and their characteristics (branching ratios and energetics).

The cross sections of considered reactions have been presented by compact analytic expressions, valid in a broad energy range (from threshold, or thermal energy region for exothermic reaction, up to several keV for electron-impact pro-

cesses, and several hundreds of keV for electron capture reactions). The accuracy of presented cross sections for electron-impact processes is within $15-20\%$, when the cross sections are derived from experimental sources, and $30-50\%$ when they are derived from scaling relationships. The accuracy of electron capture and particle exchange cross sections is believed to be within $30-50\%$ in the region below $\sim$ 1 eV (where they are determined on the basis of an extension of thermal rate coefficients data), but it may be worse at higher energies. There is also an uncertainly of about 0.5 - 1.0 eV (and in certain cases even more) in the energetics of considered reactions, due to uncertainties in thermochemical data and, more importantly, due to energy uncertainties of dissociative excited states of considered molecules, and state of excitation of reaction products.

5

References

[1] R. K. Janev and D. Reiter, Phys. Plasmas 9, 4071 (2002).

[2] R. K. Janev and D. Reiter, FZJ Report., Juel-3966 (Feb. 2002).

[3] R. K. Janev and D. Reiter, FZJ Report., Juel-4005 (Oct. 2002).

[4] B. Fowler and E.O'Brien, J. Vac. Sci Technol. B 12, 441 (1994).

[5] E. Meeks, R. S. Larson, P.Ho, C. Apblett, S. M. Han, E. Edelberg and E. S. Aydil, J.Vac. Sci. Technol. A 16, 544 (1998).

[6] M. J. Kuschner, J. Appl. Phys. 63, 2532 (1988).

[7] S. E. Butler and J. C. Raymond, Astrophys. J. 240, 680 (1980).

[8] U.Samm, P.Bogen, G.Esser et al. J.Nucl.Mat. 220-222, 25 (1995)

[9] P. Wienhold, V. Philipps, A. Pospieszczyk (2002, private communication).

[10] W. L. Morgan, Plasma Chem. Plasma Proc. 12, 477 (1992).

[11] J. Perrin, O. Leroy and M. C. Bordage, Contrib. Plasma Phys. 36, 3 (1996).

[12] T. J. Millar, P. R. A. Facqular, and K. Willacy, Astron. Astrophys. Sippl. Ser. 121, 139 (1997).

[13] U. Fantz, Plasma Phys. Control. Fusion 40, 1035 (1998).

[14] M. W. Chase, "NIST-JANAF Thermochemical Tables", 4th edition, J. Phys. Chem. Ref. Data Monograph 9, 1-1951 (1998). (See also: www.NIST Chemistry WebBook, 2001).

[15] Y. H. Le Teuff, T. J. Millar, and A. J. Markwick, Astron. Astrophys. Suppl. Ser. 146, 157 (2000).

[16] A. A. Radzig and B. M. Smirnov, "Reference Data on Atoms, Molecules and Ions", (Springer-Verlag, Berlin, 1985).

[17] B. M. Smirnov, "Asymptotic Methods in the Theory of Atomic Collisions", (Nauka, Moscow, 1973), (in Russian).

[18] B. H. Bransden and M. R. C. McDowell, ”Theory of Charge Exchange and Ion-Atom Collisions” (Clarendon Press, Oxford, 1992).

[19] H. Chatham, D. Hills, R. Robertson and A. Gallagher, J. Chem. Phys. 81, 1770 (1984)

[20] E. Krishnakumar and S. K. Srivastava, Contrib. Plasma Phys. 35, 395 (1995).

[21] V. Tarnovsky, H. Deutsch, and K. Becker, J. Chem. Phys. 105, 6315 (1996).

[22] R. Basner, M. Schmidt, V. Tarnovsky, and K. Becker, Int. J. Mass Spectrom. Ion Processes, 171, 83 (1997).

[23] M. A. Ali, Y.-K. Kim, W. Hwang, N.M. Weinberger, and M. E. Rudd, J. Chem. Phys. 106, 9602 (1997).

[24] M. A. Lennon, K. L. Bell, H. B. Gilbody et al. J. Phys. Chem. Ref. Data 17, 1285 (1988).

[25] J. Perrin, J. P. M. Smith, G. De Rosny, B. Devillon, J. Huc and A. Lloret, Chem. Phys. 73, 383 (1982).

[26] R. L. Platzman, Radiat, Res. 17, 419 (1962).

[27] D. A. Vroom and F. J. de Heer, J. Chem. Phys. 50, 573 (1969).

[28] K. Radouane, L. Date, M. Yousfi, B. Despax and H. Caquineau, J. Phys. D: Appl. Phys. 33, 1332 (2000).

[29] M. Hayashi, in: ”Swarm Studies and Inelastic Electron-Molecule Collisions”, ed. L. C. Pitchford et al. (Springer, Berlin, 1987), p. 167.

[30] M. Kurachi and Y. Nakamura, J. Phys. D: Appl. Phys. 22, 107 (1989).

[31] J. L. Turner, Astrophys. J., 213, 286 (1977).

[32] E. P. Wigner, Phys. Rev. 73, 1002 (1948).

[33] R. K. Janev and D. Reiter, J. Nucl. Mater, 313-316, 1202 (2003).

[34] M. Kimura, J. P. Gu, G. Hirsch and R. J. Buenker, Phys. Rev. A 55, 2778 (1997).

6

Table 1

Heat of formation, ΔH_f^0, [14], ionization potential, I_p, ([14]), and lowest stable excited states (with their energies given in parentheses, in eV units, [14, 16]) of H, H_2, SiH_y, $(y = 0 - 4)$, and their ions.

H, H_2, SiH_y	$\Delta_f^0(eV)$	$I_p(eV)$	Lowest stable excited states (E_{exc}, in eV)
H	2.277	13.595	n=2(10.20); n=3(12.09)
H^+	15.872		
H_2	0.015	15.427	B (10.9); a/c (11.5), C (12.0)
H_2^+	15.442		
Si	4.638	8.152	$^1D(0.78);^1S(1.91);^5S^0(4.11);^3P_J^0(4.90)$
Si^+	12.79		
SiH	3.882	7.91	A (2.98)
SiH^+	11.79		A (3.09)
SiH_2	2.98*	8.92	a (0.906); A (1.92); B (2.65)
SiH_2^+	11.90		A (1.63)
SiH_3	2.09*	8.01	A ($<$ 6.0); D (6.14); E (5.98); I (6.94)
SiH_3^+	10.10		no exc. states listed in [14]
SiH_4	0.354	11.00	no exc. states listed in [14]
SiH_4^+	11.354		A (0.094); B (0.61); C(6.92)

(*): Data taken from Ref. [15].

Table 2

Electron-impact ionization channels of SiH_y: Threshold energy (E_{th}), electron energy loss ($\overline{E_{el}^{(-)}}$), mean total kinetic energy of products ($\overline{E}_K$) and high-energy branching ratio ($R_{I,DI}$).

Reaction			E_{th} (eV)	$\overline{E_{el}^{(-)}}$ (eV)	$\overline{E_K}$ (eV)	$R_{I,DI}$
$e + SiH_4$	$\rightarrow$	$SiH_3^+ + H + 2e$	12.03	12.85	0.82	0.31
	$\rightarrow$	$SiH_2^+ + H_2 + 2e$	11.57	12.02	0.45	0.42
	$\rightarrow$	$SiH^+ + H + H_2 + 2e$	13.73	15.37	1.64	0.12
	$\rightarrow$	$Si^+ + 2H_2 + 2e$	12.47	13.65	1.18	0.10
	$\rightarrow$	$H^+ + SiH_3 + 2e$	17.61	19.59	1.98	0.04
	$\rightarrow$	$H_2^+ + SiH_2 + 2e$	18.07	20.19	2.12	0.01
$e + SiH_3$	$\rightarrow$	$SiH_3^+ + 2e$	8.01	8.01	—	0.67
	$\rightarrow$	$SiH_2^+ + H + 2e$	12.09	13.31	1.22	0.20
	$\rightarrow$	$SiH^+ + H_2 + 2e$	9.72	10.75	1.03	0.08
	$\rightarrow$	$Si^+ + H_2 + H + 2e$	12.99	14.94	1.95	0.03
	$\rightarrow$	$H^+ + SiH_2 + 2e$	16.76	20.26	3.50	0.02
$e + SiH_2$	$\rightarrow$	$SiH_2^+ + 2e$	8.24	8.24	—	0.72
	$\rightarrow$	$SiH^+ + H + 2e$	11.09	12.39	1.30	0.23
	$\rightarrow$	$Si^+ + H_2 + 2e$	9.83	11.47	1.64	0.05
	$\rightarrow$	$H^+ + SiH + 2e$	16.77	19.31	2.36	0.01
$e + SiH$	$\rightarrow$	$SiH^+ + 2e$	7.91	7.91	—	0.74
	$\rightarrow$	$Si^+ + H + 2e$	11.19	12.17	0.98	0.25
	$\rightarrow$	$H^+ + Si + 2e$	16.63	19.25	2.62	0.01
$e + Si$	$\rightarrow$	$Si^+ + 2e$	8.15	8.15		1.00

Table 3

Main dissociative excitation channels of SiH_y to neutrals: Threshold energies (E_{th}), mean total kinetic energy of products ($\overline{E}_K$), and channel branching ratios (R_{DE}).

Reaction			E_{th} (eV)	$\overline{E}_K$ (eV)	R_{DE}
$e + SiH_4$	$\rightarrow$	$SiH_3 + H + e$	8.04*	4.02	0.46
	$\rightarrow$	$SiH_2 + H_2 + e$	8.26	5.62	0.26
	$\rightarrow$	$SiH + H_2 + H + e$	10.48	4.66	0.15
	$\rightarrow$	$Si + 2H_2 + e$	8.64	4.32	0.13
$e + SiH_3$	$\rightarrow$	$SiH_2 + H + e$	5.71	2.54	0.65
	$\rightarrow$	$SiH + H_2 + e$	5.43	3.62	0.23
	$\rightarrow$	$Si + H_2 + H + e$	8.04	3.20	0.12
$e + SiH_2$	$\rightarrow$	$SiH + H + e$	5.72	2.54	0.78
	$\rightarrow$	$Si + H_2 + e$	5.01	3.34	0.22
$e + SiH$	$\rightarrow$	$Si + H + e$	6.06	3.03	1.00

(*): The total dissociation experiment for SiH_4 [25] indicates a somewhat higher threshold: 8.4 eV. The experimental uncertainty in the threshold region may, however, be fairly large.

Table 4

Main dissociative excitation channels of SiH_y^+: Threshold energies (E_{th}), mean total kinetic energy of products ($\overline{E}_K$), and channel branching ratios (R_{DE^+}).

Reaction			E_{th} (eV)	$\overline{E}_K$ (eV)	R_{DE^+}
$e + SiH_3^+$	$\rightarrow$	$SiH_2^+ + H + e$	5.90	1.84	0.46
	$\rightarrow$	$SiH_2 + H^+ + e$	11.81	3.06	0.08
	$\rightarrow$	$SiH^+ + H_2 + e$	3.76	2.05	0.42
	$\rightarrow$	$Si^+ + H + H_2 + e$	6.83	1.95	0.05
$e + SiH_2^+$	$\rightarrow$	$SiH^+ + H + e$	3.69	1.54	0.30
	$\rightarrow$	$SiH + H^+ + e$	10.60	2.75	0.05
	$\rightarrow$	$Si^+ + H_2 + e$	2.55	1.64	0.55
	$\rightarrow$	$Si^+ + 2H + e$	6.34	1.90	0.10
$e + SiH^+$	$\rightarrow$	$Si^+ + H + e$	4.43	1.15	0.90
	$\rightarrow$	$Si + H^+ + e$	11.77	3.05	0.10

Table 5

Main dissociative ionization channels of SiH_y^+: Threshold energies (E_{th}), kinetic energy of product ions (E_K), and channel branching ratios (R_{DI^+}).

Reaction			E_{th} (eV)	E_K (eV)	R_{DI^+}
$e + SiH_3^+$	$\rightarrow$	$SiH_2^+ + H^+ + 2e$	27.14	9.48	0.47
	$\rightarrow$	$SiH^+ + H_2^+ + 2e$	26.62	9.48	0.24
	$\rightarrow$	$Si^+ + H^+ + H_2 + 2e$	28.02	9.48	0.17
	$\rightarrow$	$Si^+ + H + H_2^+ + 2e$	29.79	9.48	012
$e + SiH_2^+$	$\rightarrow$	$SiH^+ + H^+ + 2e$	24.31	9.54	0.55
	$\rightarrow$	$Si^+ + H_2^+ + 2e$	25.88	9.54	0.29
	$\rightarrow$	$Si^+ + H^+ + H + 2e$	28.58	9.54	0.16
$e + SiH^+$	$\rightarrow$	$Si^+ + H^+ + 2e$	25.48	9.60	1.00

Table 6

Main dissociative recombination channels of SiH_y^+: Reaction exothermicity for ground state products ($E_K^{(0)}$), channel branching ratios (R_{DR}), and possible excited products for $E_{el} \lesssim 1$ eV.

Reaction			$E_K^{(0)}$ (eV)	R_{DR}	Excited products ($E_{el} \lesssim 1$ eV)
$e + SiH_3^+$	$\rightarrow$	$SiH_2 + H$	4.84	0.40	SiH_2 (a; A; B)
	$\rightarrow$	$SiH + H_2$	6.20	0.15	SiH (A)
	$\rightarrow$	$SiH + 2H$	1.67	0.15	SiH (A)
	$\rightarrow$	$Si + H + H_2$	3.17	0.30	Si ($^1D;^1S$)
$e + SiH_2^+$	$\rightarrow$	$SiH + H$	5.74	0.25	SiH (A)
	$\rightarrow$	$Si + H_2$	7.24	0.15	Si ($^1D;^1S;^3P_0^0$)
	$\rightarrow$	$Si + 2H$	2.71	0.60	Si ($^1D;^1S$)
$e + SiH^+$	$\rightarrow$	$Si + H$	4.87	1.00	Si ($^1D;^1S;^3P_0^0$)

Table 7

Charge- and particle- exchange channels in H^+ + SiH_y thermal collisions: Total thermal rate coefficients (K_{CX}^{tot}), branching ratios (R_{CX}), reaction exothermicities (ΔE), and values of parameters c and γ in Eq.(54).

Reaction			$K_{CX}^{tot}(10^{-9}cm^3/s$	R_{CX}	ΔE (eV)	c	γ
$H^+ + SiH_4$	$\rightarrow$	$H + SiH_2^+ H_2$	4.33	0.42	2.59	—	—
	$\rightarrow$	$H_2 + SiH_3^+$	4.33	0.58	6.10	0.5	2.5
$H^+ + SiH_3$	$\rightarrow$	$H + SiH_3^+$	4.18	0.40	5.59	—	—
	$\rightarrow$	$H_2 + SiH_2^+$	4.18	0.60	6.04	0.5	2.5
$H^+ + SiH_2$	$\rightarrow$	$H + SiH_2^+$	3.30	0.38	4.68	—	—
	$\rightarrow$	$H_2 + SiH^+$	3.30	0.62	1.08	0.5	2.5
$H^+ + SiH$	$\rightarrow$	$H + SiH^+$	2.56	0.35	5.69	—	—
	$\rightarrow$	$H_2 + Si^+$	2.56	0.65	6.95	0.1	3.5
$H^+ + Si(^3P)$	$\rightarrow$	$H + Si^+(^2P)$	1.50 (b)	(a)	5.45	—	—
	$\rightarrow$	$H + Si^{+*}(^4P)$	1.50 (b)	(a)	0.14	—	—

(a): Below E $\simeq$ 150 eV, the contribution of H + $Si^+(^2P)$ channel to total cross section of reaction (58) can be neglected. Only for E $\gtrsim$ 500 eV, the contributions of the two channels become approximately equal. (b): Value taken from Ref. [12].

Table 8

Values of fitting parameters c_i in Eq.(57) for electron capture reactions in H^+ + SiH_y collision systems ($y = 0 - 4$).

c_i	SiH_4	SiH_3	SiH_2	SiH	Si
c_1	9.96	12.14	9.10	6.50	10.9
c_2	85	0.010	0.005	0.001	8.25
c_3	2.5	2.5	3.0	3.0	1.85
c_4	30.2	25.4	22.2	29.0	582.0
c_5	0.00	1.22	1.55	5.3	4.98
c_6	—	0.62	0.57	0.35	0.21
c_7	0.015	0.00	0.00	0.00	0.00
c_8	9.0 (-6) $^{(*)}$	2.0 (-9)	2.35 (-7)	1.12 (-6)	2.35 (-5)
c_9	1.20	2.05	1.55	1.45	1.15
c_{10}	2.19 (-18)	4.47 (-21)	4.28 (-21)	6.03 (-20)	7.05 (-21)
c_{11}	3.8	4.3	4.26	4.3	4.3
c_{12}	4.47 (-22)	0.00	0.00	0.00	0.00
c_{13}	4.4	—	—	—	—

(*): $a(-x) = a * 10^{-x}$