On the balance between silylene and silyl radicals in rf glow discharges in silane: The effect on deposition rates of *a*-Si:H

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Plasma enhanced chemical vapor deposition (PECVD) of amorphous hydrogenated silicon (*a*-Si:H) is typically performed in low-pressure ($\leqslant 0.5$ Torr) radio frequency (rf) discharges in gas mixtures containing silane (SiH_4). The initiating step is electron impact dissociation of silane, whose products are primarily the silylene (SiH_2) and silyl (SiH_3) radicals. The ratio of SiH_2 to SiH_3 in the plasma is important because these radicals incorporate differently into the *a*-Si:H film; and therefore the characteristics of the film are a function of the ratio $[SiH_3]/[SiH_2]$. The initial silane dissociation step is followed by a series of hydrogen abstraction, silylene insertion, and silyl association reactions which subsequently alter this ratio. The branching ratios for electron impact dissociation of silane, as well as the rate constants for the subsequent reactions, have not been measured or are uncertain. Using a model for a rf discharge in silane gas mixtures, the effects of branching ratios for silane dissociation, and rate constants for key reactions are investigated. We find that in order for SiH_3 to be the dominant radical, as currently thought, its branching ratio from electron impact dissociation of SiH_4 must exceed 0.75, and the yield for H atoms in the branch for SiH_2 must also exceed 0.75. The deposition rate of *a*-Si:H is then controlled by the yield of H atoms and the subsequent generation of radicals by hydrogen abstraction from SiH_4. These results require that the silyl association reaction has a rate constant $\leqslant 10^{-11}$ cm^3 s^{-1}, and that the rate constant for insertion of SiH_2 into silane exceeds 10^{-11} cm^3 s^{-1}.

I. INTRODUCTION

Plasma enhanced chemical vapor deposition (PECVD) is a process whereby amorphous hydrogenated silicon (*a*-Si:H) films may be fabricated for use in microelectronics, photovoltaic, and photoreceptor applications.[1–6] PECVD of *a*-Si:H is typically performed in a parallel plate, capacitively coupled radio frequency (rf) discharge having electrode separations of a few centimeters and power deposition of tens to hundreds of mW cm^{-3}. Typical gas mixtures may contain one or more of silane (SiH_4) and disilane,[4,7,8] with admixtures of noble gases,[9] or hydrogen[10] at pressures of $\leqslant 0.5$ Torr. Electron impact dissociation of silane (or disilane) generates Si_nH_m radicals [predominantly silylene (SiH_2) and silyl (SiH_3)] which diffuse to a heated substrate, usually one of the electrodes. At the surface, the radicals are adsorbed and incorporated into the growing film.

The electron kinetics and plasma chemistry of rf discharges in silane gas mixtures have been the topic of numerous previous investigations. However, in spite of this effort, the details of the silane plasma chemistry in rf discharges remain controversial. In particular, the identity of the radical primarily responsible for deposition of *a*-Si:H is still debated. It is generally accepted that when using silane as the feed stock under nonpolymerizing conditions, the dominant radicals are SiH_2 and SiH_3. The dominance of these radicals is, in a large part, due to the branching ratios for electron impact dissociation (neutral and dissociative ionization) of silane which favor them. Although the branching ratios for dissociative ionization of silane have been measured, the branching ratios for neutral radicals have not been directly measured. The values of those branching ratios have important implications on the balance of silylene and silyl radicals in the plasma and, therefore, the identity of the dominant radical. The balance between SiH_2 and SiH_3 effects the plasma chemistry following dissociation, the deposition rate of *a*-Si:H, and the properties of the film. In addition to those branching ratios, certain key reactions involving dissociation products also play an important role in determining these characteristics. The values of the rate constants for many of these ractions are also uncertain.

In this paper, the effect of the branching ratios for the neutral dissociation of silane on the plasma chemistry and deposition rate of *a*-Si:H will be investigated with results from a model for a capacitively coupled parallel plate rf discharge in Ar/SiH_4 gas mixtures. The effects of the values of rate constants for certain key reactions will also be investigated for moderately powered plasmas (< 100 mW cm^{-3}). We will parametrize the branching ratio for production of SiH_2 and SiH_3 from the electron impact dissociation of silane, the sticking coefficient of SiH_3, and the values of the rate constants for the following heavy particle reactions: the hydrogen abstraction reaction $H + SiH_4 \rightarrow SiH_3 + H_2$; the silylene insertion reaction $SiH_2 + SiH_4 \rightarrow Si_2H_6^*$; and the bisilyl association reaction $2 \cdot SiH_3 \rightarrow Si_2H_6^{**}$. These reactions involving the dissociation products of silane alter the radical density ratio $[SiH_3]/[SiH_2]$ in the plasma, change the contribution of those radicals to the deposition process, and alter the deposition rate of *a*-Si:H.

In Sec. II, the plasma chemistry model will be briefly

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described. A synopsis of opinion on the values of the branching ratios and rate constants, and their implications, will be presented in Sec. III. The effect of branching ratios for electron impact dissociation of silane on plasma properties will be discussed in Sec. IV, and the effect of the value of key rate constants will be discussed in Sec. V. Concluding remarks are in Sec. VI.

II. DESCRIPTION OF THE MODEL

The processes whereby a-Si:H films are grown in silane glow discharges can be conceptually divided into three areas: the rf discharge electron kinetics, plasma chemistry, and surface deposition kinetics. The electron kinetics include the details of the time and spatially varying electron energy distribution function in the plasma which, when convolved with the appropriate cross sections, provides the electron impact rate constants for momentum transport, excitation, ionization, and dissociation. Plasma chemistry includes the reactions involving collisions between heavy particles, and the transport of those particles within the plasma and to the surface. Surface deposition kinetics includes those processes whereby radicals diffuse out of the plasma to the film, and incorporate into the film.

Computer models have been developed to describe the electron kinetics and plasma chemistry of rf discharges in silane. The electron distribution function is obtained by performing a Monte Carlo simulation of electron trajectories in a parallel plate capacitively coupled rf discharge, as described in Refs. 11 and 12. Self-consistent discharge conditions (e.g., sheath voltage, electric field in the bulk plasma) are obtained by requiring a power balance; the power deposition in the plasma as given by the time-averaged value of voltage current must equal the rate of power dissipation by electron and ion impact reactions.[12] There is a unique value of sheath voltage and bulk electric field for which this equality holds.

From results of the rf discharge kinetics model, one obtains electron impact rate coefficients as a function of position within the discharge and as a function of phase during the rf cycle. The electron impact rate constants are then used as input to the plasma chemistry model. The plasma chemistry model is functionally similar to that described in Ref. 12, and therefore will be only briefly described here.

The plasma chemistry model consists of a set of partial differential equations which describe the time rate of change and transport of radicals and ions in one-dimension perpendicular to the electrodes. We assume plug flow for the gases in the dimension parallel to the electrodes. For a given flowrate, integration in time is therefore equivalent to integration along the direction of flow. The species included in the model are listed in Table I. Different from the model described in Ref. 12, in this work, we included higher silane molecules and radicals through Si_5H_{11} and Si_5H_{12}, and grouped all higher silane molecules into "DUST." The polymerization chain is based on lower silane insertion into saturated molecules (e.g., $SiH_2 + Si_nH_{2(n+1)} \rightarrow Si_{n+1}H_{2(n+2)}$. The chain is propagated with uniform rate constant of 1.0×10^{-11} $cm^3\,s^{-1}$. A similar chain is invoked for charge exchange for ions $Si_nH_{2n}^+$, $n \leqslant 5$. Charge exchange collisions are categorized into endothermic and exothermic reactions based on the gas temperature. Exothermic reactions occur throughout the plasma; endothermic reactions occur only in the sheaths where, for electropositive plasmas, the ion energy is sufficiently high to allow such reactions. Including the excitation of the vibrational modes of SiH_4 is important because a large fraction of power deposition by electrons is through this excitation process.

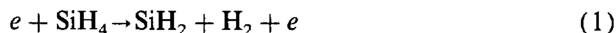
TABLE I. Species in the plasma chemistry model.

Neutral species:						
Ar	$Ar^*(4s)$	$Ar^{**}(4p)$	H_2	H_2^*	H	H^*
SiH_4	$SiH_4(v1,3)$		$SiH_4(v2,4)$		SiH_n, $n = 0$–3	
Si_2H_n, $n = 2$–6		$Si_2H_6^*$	$Si_2H_6(v1,3)$		$Si_2H_6(v2,4)$	
Si_nH_{2n+1}, $n = 3$–5		$Si_nH_{2(n+1)}$, $n = 3$–5			DUST	
Charged species:						
Ar^+	ArH^+	H^+	H_2^+	H_3^+	SiH_n^+, $n = 0$–3	
$Si_2H_n^+$, $n = 1$–7		$Si_nH_{2n}^+$, $n = 3$–5		e	H^-	SiH_n^-, $n = 2,3$

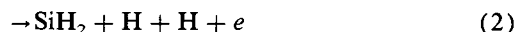
III. BRANCHING RATIOS FOR NEUTRAL ELECTRON IMPACT DISSOCIATION OF SILANE, AND RATE CONSTANTS FOR IMPORTANT REACTIONS

A. Branching ratios for electron impact dissociation of SiH_4

The initiating step in the PECVD of a-Si:H is electron impact dissociation of silane. Electron impact dissociation proceeds through both neutral[13] and ion channels.[14] Due to the lower threshold energy for dissociation through the neutral channel, the majority of radicals are generated by this method. Typical rate constants for neutral dissociation and dissociative ionization in rf deposition plasmas are 10^{-10}–10^{-9} $cm^3\,s^{-1}$ and 10^{-12}–10^{-11} $cm^3\,s^{-1}$, respectively, netting a ratio of neutral to ion products of 50–100.[11,12,14–16] The major branching channels for neutral dissociation are[16]



$$e + SiH_4 \rightarrow SiH_2 + H_2 + e \quad (1)$$



$$\rightarrow SiH_2 + H + H + e \quad (2)$$

$$\rightarrow SiH_3 + H + e. \quad (3)$$

Although the total cross sections for electron impact dissociation of SiH_4 have been measured,[13] the branching ratios for Reactions (1)–(3) have not been directly measured. Therefore, the branching ratios have been inferred from other dissociative processes, and by measurements of discharge properties and fitting the experimental data to models. The branching ratio for dissociative ionization of silane, though, has been recently measured by Chatham *et al.*,[14] giving a ratio of yields of $[SiH_3^+]/[SiH_2^+]$ of 0.8 over a large range of electron energy ($\leqslant 200$ eV). Making a direct analogy to the neutral channel would therefore favor SiH_2 as the dominant neutral dissociation product. Based on measurements of the dissociative ionization cross sections of si-

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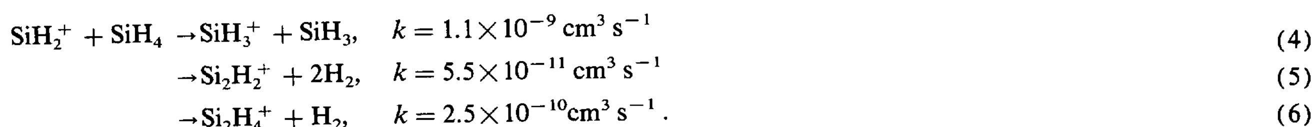
lane, and scaling the neutral to the ion channel in a manner similar to that of methane, Winters[17] suggested a ratio of neutral branching ratios of $[SiH_3]/[SiH_2]$ of 0.45, thereby also favoring SiH_2 as the dominant dissociation product. Having SiH_2 as the dominant product would also appear to be supported by making an analogy to the dissociation of silane by homogeneous pyrolysis. Dissociation by pyrolysis favors branching to SiH_2 due to the higher activation energy for the branch to SiH_3 (52 kcal/mol for SiH_2 compared to 93 kcal/mol for SiH_3).[18]

Photolysis and dissociation by $Hg(6^3P_1)$ photosensitation have also been used to infer branching ratios of SiH_2 and SiH_3 from electron impact dissociation of silane. The results, though, appear to yield contradictory values. Results from the 147-nm photolysis of silane have been interpreted by Perkins *et al.*[19] as yielding a branching ratio of 0.83 for $SiH_2 + 2H$ and 0.17 for $SiH_3 + H$, with a ratio of $[SiH_3]/[SiH_2] = 0.2$. However, Kamaratos and Lampe[20] concluded from their experiments on the Hg* photosensitation of silane that SiH_3 is the primary dissociation product while Niki and Mains[21] concluded that both channels (SiH_2 and SiH_3) must be active during photosensitation. Longeway and Lampe performed experiments on the IR excitation of SiF_4 and photosensitation of silane,[22] and on the IR multiphoton dissociation of silane.[23] The results of both experiments were interpreted as SiH_2 being the primary dissociation product (as much as 98% in the latter study).

Branching ratios have also been estimated from analysis of discharge experiments. A study by Longeway, Estes, and Weaklein[24] showed that in a dc glow discharge SiH_3 is likely to be the primary product of electron impact dissociation of silane. The branching ratio for SiH_3 was estimated to be 0.8–0.9. Longeway's estimate is supported by making an analogy to the electron impact dissociation of methane. The neutral branching ratios for methane were directly measured using a cross beam technique by Melton and Rudolph,[25] and yielded values for CH_3 and CH_2 of 0.80 and 0.13, respectively, a ratio of $[CH_3]/[CH_2] = 6.2$. Robertson and Gallagher[26] support making the analogy to methane for the neutral dissociation branching ratio and recommend the same fractional yields. Other branching ratios used in plasma chemistry models or recommended (expressed as the ratio SiH_3/SiH_2) are 0.36/0.46 (Tachibana[27]) and 0.3/0.7 (Turban, Catherine, and Grolleau).[28]

The apparent discrepancy between the cited branching ratios for SiH_2 and SiH_3 may be partly explained by the recent *ab initio* calculations of silane structure by Tsuda, Oikawa, and Nagayama.[29] They concluded that excitation to the lowest lying triplet state of SiH_4 (9.2 eV) results in dissociation into $SiH_3 + H$ with unity branching ratio; whereas excitation to the lowest lying singlet state results in dissociation into $SiH_2 + H_2$. Hg* photosensitization ($\epsilon = 4.9$ eV) cannot access the triplet state and, if such excitation leads to formation of SiH_3, it must proceed through a different channel. Since the threshold energy for neutral dissociation is ≈ 8.0 eV,[11] electron impact dissociation resulting in SiH_3 at energies a few eV above threshold must also proceed through an excitation channel other than the triplet state or through a channel resulting in SiH_2. This suggests that electron impact dissociation near threshold may result dominantly in SiH_2, whereas dissociation at higher electron energy may result dominantly in SiH_3. This scheme would be consistent with the ordering of enthalpy changes resulting from the electron impact dissociation to neutral products. The smallest change in enthalpy is for dissociation to SiH_2 ($SiH_2 + H_2$, 2.43 eV; $SiH_3 + H$, 3.86 eV; $SiH_2 + 2H$, 6.47 eV), though the change in enthalphy is not necessarily an accurate indication of threshold energy or activation energy.[24] Having low-energy electron impact dissociation favor branching to SiH_2 (and high-energy favor SiH_3) would be consistent with the fact that other low-energy and thermal dissociation processes (e.g., pyrolysis, infrared multiphoton excitation) favor branching to SiH_2.

Thus far, we have ignored the generation of neutral radicals indirectly through the dissociative ionization channel. The effective branching ratios for SiH_2 and SiH_3 can be altered by the contribution of radical ions recombining at the walls and returning to the plasma as their neutral counterparts. SiH_n^+ ions may also dissociatively recombine and undergo ion molecule collisions, both of which contribute to the neutral radical population. By analogy to methane[30] the dissociative recombination coefficient for SiH_n^+ is approximately 7.0×10^{-7} cm^3 s^{-1}. The diffusion constant [31] for SiH_n^+ ions is approximately 400 cm^2 s^{-1}. The diffusion and recombinations times under typical conditions ($[e] \approx 10^9$ cm^{-3}, pressure = 0.5 Torr, electrode separation 1.5 cm) are therefore 0.15 and 1.5 ms, respectively. The most frequent ion-molecule reactions for SiH_2^+ and SiH_3^+ ions are collisions with silane. SiH_2^+ ions are rapidly depleted by the reactions[32]



$$SiH_2^+ + SiH_4 \rightarrow SiH_3^+ + SiH_3, \quad k = 1.1 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}} \tag{4}$$
$$\rightarrow Si_2H_2^+ + 2H_2, \quad k = 5.5 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}} \tag{5}$$
$$\rightarrow Si_2H_4^+ + H_2, \quad k = 2.5 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}. \tag{6}$$

For typical silane densities (4×10^{15} cm^{-3}), the lifetime for SiH_2^+ against these ion molecule reactions is 0.2 μs, which is short compared to either the diffusion or recombination times. SiH_2^+ is more likely to undergo ion molecule reactions than be lost by diffusion or recombination. Therefore, through Reaction (4), SiH_2^+ ions will indirectly increase the branching ratio for SiH_3. However, since the ratio of dissociative ionization to neutral dissociation is $\approx$50–100, the fractional increase in the branching ratio for SiH_3 is at most a few percent to 10%; the contribution to the neutral channel is therefore not large.

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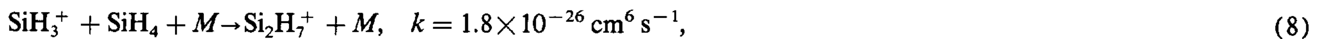
SiH_3^+ ions react with silane by [32,33]

$$SiH_3^+ + SiH_4 \rightarrow Si_2H_5^+ + H_2, \quad k = 2.5\times10^{-11} cm^3\,s^{-1} \tag{7}$$



$$SiH_3^+ + SiH_4 + M \rightarrow Si_2H_7^+ + M, \quad k = 1.8\times10^{-26}\,cm^6\,s^{-1}, \tag{8}$$

neither of which result in neutral SiH_n radicals. For typical discharge conditions, the lifetime for SiH_3^+ ions against Reactions (7) and (8) is $\leqslant 1\,\mu s$, which is short compared to the diffusion and recombination times. Therefore, the contribution to generation of neutral SiH_2 or SiH_3 indirectly through the ion channel by either gas phase or heterogeneous recombination of SiH_2^+ or SiH_3^+ is small.

B. Important reactions subsequent to electron impact dissociation

After being generated by electron impact dissociation of SiH_4, radicals may participate in both plasma chemical reactions and surface deposition kinetics. The ratio $\beta = [SiH_3]/[SiH_2]$ for radicals incident on the surface is particularly important with respect to the method of incorporation of radicals in the a-Si:H film.[34–36] The silylene radical, SiH_2, can insert directly into saturated silicon bonds ($\equiv$Si–H) on the surface of the films. The silyl radical SiH_3, though, can only directly insert into a dangling bond ($\equiv$Si–•). Inserting into a saturated bond ($\equiv$Si–H) requires that hydrogen be concurrently eliminated, a process that may have an activation energy.

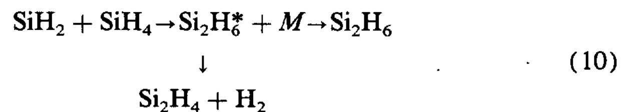
Gas-phase chemical reactions following electron impact dissociation alter the effective branching ratios for silylene and silyl radicals because of their selectivity of reaction for either SiH_2 or SiH_3. Since the relative gas phase densities of these radicals directly effect the characteristics of the a-Si:H film, knowing the relative contribution of these reactions is important. The specific reactions and their potential effect on the balance between SiH_2 and SiH_3 radicals will now be discussed.

Generation of H atoms during electron impact dissociation effectively increases the rate of production of radicals due to the subsequent reaction

$$H + SiH_4 \rightarrow SiH_3 + H_2. \tag{9}$$

Therefore, the single dissociations in Reactions (2) and (3) effectively result in two and one additional radicals, respectively. Therefore, using a gas mixture where reactions may scavange H atoms will reduce the net production of SiH_3. For example, in the PECVD of tungsten silicide, a gas mixture of SiH_4/WF_6 may be used.[37] Reactions of H atoms with flourine containing radicals proceed with gas kinetic rates, and will deplete H atoms, thereby reducing the production of SiH_3. Rate constants for Reactions (9) have been cited in the range of 4×10^{-13}–8×10^{-12} $cm^3\,s^{-1}$.[18,38,39]

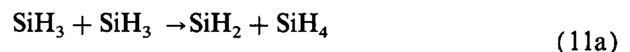
The electron impact dissociation in Reaction (1) (generating $SiH_2 + H_2$) is least favorable for additional production of radicals which participate in the deposition process for two reasons. There are no H atoms generated to participate in Reaction (9); and there is the possibility that the SiH_2 radical will be scavenged by insertion into silane,



$$SiH_2 + SiH_4 \rightarrow Si_2H_6^* + M \rightarrow Si_2H_6 \tag{10}$$
$$\downarrow$$
$$Si_2H_4 + H_2$$

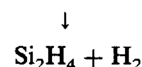
This reaction is potentially rapid. One branch leads to the saturated disilane molecule which does not directly incorporate into the growing film. The branch resulting in Si_2H_4 may contribute to film growth as the radical is likely to have a finite sticking coefficient. Estimates, calculations, and measurements of this rate constant during the past few years have yielded values varying by more than two orders of magnitude. In Tachibana's plasma chemistry model, a rate constant of 9.6×10^{-13} $cm^3\,s^{-1}$ was used for the initiating step.[27] John and Purnell[40] measured the rate constant at high temperature, deriving an Arrhenius parameter and activation energy which yields a rate constant of $\approx 1\times10^{-12}$ $cm^3\,s^{-1}$ for typical plasma conditions.[41] Two recent measurements of the rate constant, though, give values within a factor of 2: 1.0×10^{-10} $cm^3\,s^{-1}$ (Inoue and Suzuki[42]) and 5.0×10^{-11} $cm^3\,s^{-1}$ (Jasinski[43]).

The SiH_3 radical, unlike SiH_2, participates in few rapid reactions subsequent to the dissociation reaction and prior to incorporation into the film. The exceptions are the biradical reactions



$$SiH_3 + SiH_3 \rightarrow SiH_2 + SiH_4 \tag{11a}$$
$$\uparrow$$

$$\rightarrow Si_2H_6^* \underset{M}{\rightarrow} Si_2H_6. \tag{11b}$$
$$\downarrow$$



$$Si_2H_4 + H_2$$

For our plasma conditions, the yield for production of SiH_2 is 0.95. This reaction may represent a self-limiting step for production of large amounts of SiH_3. Should this reaction be important, the rate of generation of radicals (and hence, rate of deposition of a-Si:H) prior to depletion of silane should scale less than linearly with increasing discharge power.[44] The rate coefficient for the initial reaction in Eq. (11) has not been directly measured; estimated values for the rate constants range from 10^{-12} to 10^{-10} $cm^3\,s^{-1}$. Tachibana[27] used rate constants of 7.0×10^{-12} and 1.0×10^{-11} $cm^3\,s^{-1}$ for Reactions (11a) and (11b), respectively, with a net yield for SiH_2 of 0.5 for his conditions. By analogy to the rate of methyl radical recombination, Milhelcic *et al.*,[38] quoting Cadman, Tilsey, and Trotman-Dickenson,[45] suggested a rate constant of 3×10^{-10} $cm^3\,s^{-1}$. Macpherson, Pilling, and Smith[46] recently measured the three-body rate constant for the methyl radical association reaction [6×10^{-29} $\exp(1680/T)$ $cm^6\,s^{-1}$] yielding the equivalent two-body

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rate constant of 1.7×10^{-11} cm^3 s^{-1} at typical densities and pressures.

IV. THE EFFECT OF BRANCHING RATIO FOR ELECTRON IMPACT DISSOCIATION OF SILANE

To investigate the importance of the branching ratio for dissociation of silane on the radical balance in, and deposition rates of *a*-Si:H from, rf discharges in silane, a parametric study was performed. We varied the branching ratio for production of SiH_2 and SiH_3, and the branching ratio for the production of H and H_2 from the dissociations resulting in SiH_2. The discharge condition are a 0.5-Torr mixture of $Ar/SiH_4 = 3/1$ at a power deposition of 50 mW cm^{-3} (13.56 MHz). The electrode temperature is 500 K and the electrode separation is 1.5 cm. Two sets of conditions for production of SiH_3 were chosen based on the choice of rate constants for Reactions (9) and (11) above: optimistic and pessimistic. The optimistic and pessimistic rates for production of SiH_3 from reaction (9) are 8×10^{-12} cm^3 s^{-1} and 4×10^{-13} cm^3 s^{-1}, respectively; the optimistic and pessimistic rates for Reaction (11) are 1×10^{-12} cm^3 s^{-1} and 3×10^{-10} cm^3 s^{-1}, respectively. These ranges represent the extrema in the values of the reaction rate constants cited by various investigators in the literature. The sticking coefficients for all radicals are unity for these examples and the rate constant for the SiH_2 insertion reaction [Eq. (10)] is 1.0×10^{-11} cm^3 s^{-1}.

The density ratios $\beta = [SiH_3]/[SiH_2]$ for gas phase radicals as a function of branching ratio, and optimistic and pessimistic rate constants for production of SiH_3 are plotted in Fig. 1. For the pessimistic conditions, the density ratio β never exceeds unity. For the optimistic rate constants, $0.5<\beta<13$. When the production of H atoms or SiH_3 is low, β differs little between the two examples. As the H atom production increases, β increases, indicating the importance of the hydrogen extraction Reaction (9). The importance of the silyl association Reaction (11) is indicated by the large difference in β between the two examples for large branching ratios for SiH_3.

The diffusion time for H atoms to reach the walls for our conditions is ≈ 0.3 ms, whereas, even with the pessimistic rate constants the reaction time for hydrogen abstraction from SiH_4 is approximately half that. Therefore, the majority of H atoms produced by dissociation of SiH_4 participate in the radical multiplying reaction. With a unity sticking coefficient, though, the diffusion residence time for SiH_3 in the plasma is ≈ 0.7 ms. The reaction time for the density limiting reactions of Eq. (11) for the pessimistic rates is

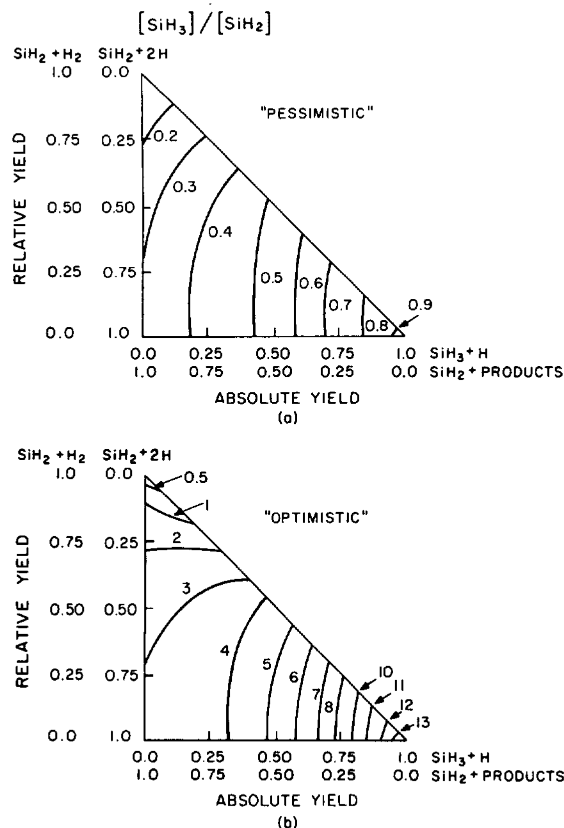

FIG. 1. The ratio of radical densities in the plasma, $\beta = [SiH_3]/[SiH_2]$, as a function of branching ratios for the electron impact dissociation of silane. The scale on the horizontal axis gives the absolute yields for SiH_3 and SiH_2; the scale on the vertical axis gives the relative yields for $SiH_2 + H_2$ and $SiH_2 + 2H$. The results in (a) are for rate constants which minimize the production of SiH_3; (b) is for rate constants which maximize the production rate. Current opinion is that $\beta = [SiH_3]/[SiH_2] \gg 10$. For pessimistic conditions, β does not exceed unity, indicating that the rate constant for the silyl association reaction must be less that 10^{-10} cm^3 s^{-1}. Large values of β ($\gg 10$) require that dissociation resulting in SiH_2 generate a high yield of H atoms.

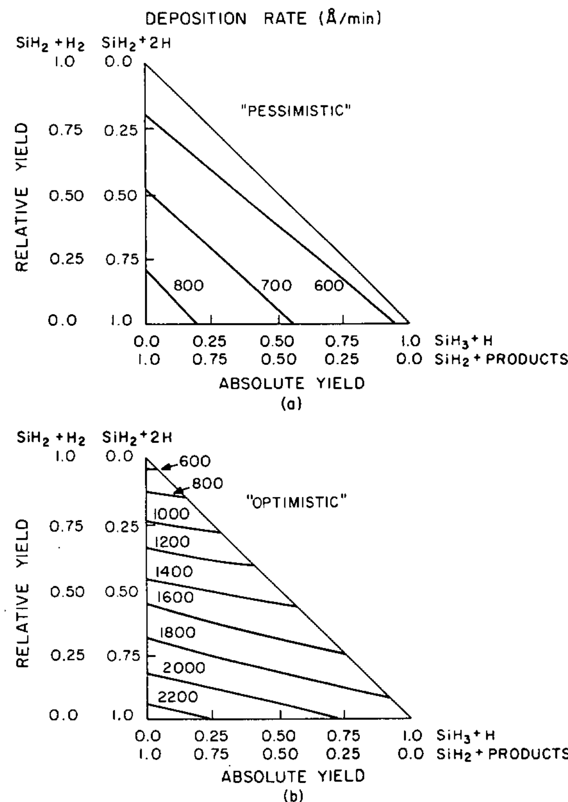

FIG. 2. Deposition rates of *a*-Si:H for the conditions of Fig. 1. (a) Pessimistic rate constants for production of SiH_3 and (b) optimistic rate constants. High deposition rates correlate with intermediate to large values of $[SiH_3]/[SiH_2]$ and high yields of H atoms. The deposition rate is less sensitive to the relative yield of SiH_3 to SiH_2, and more sensitive to the yield of H atoms.

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$\approx (3.0/N_{SiH_3})$ ms, where N_{SiH_3} is the density of SiH_3 in units of 10^{12} cm^{-3}. Therefore, with these conditions (unity sticking coefficient) SiH_3 production is rate limited to densities of $3–5\times10^{12}$ cm^{-3}. Current opinion and measurements support that $\beta \geqslant 10$ for discharge conditions similar to those simulated there.[24,26,35] To obtain this value for β, the rate constants must approach optimistic for production of SiH_3. That is, Reaction (11) must have a rate constant significantly less than 3×10^{-10} cm^3 $-$ s^{-1}. In addition, the branching ratios for SiH_3 and for $SiH_2 + 2H$ (as opposed to $SiH_2 + H_2$) must both exceed 0.75.

The deposition rates of a-Si:H for the conditions in Fig. 1 are plotted in Fig. 2. Since the sticking coefficient for all radicals is unity for these examples, the deposition rate is also a measure of the total radical density. High deposition rates and, hence, large radical densities, correlate with intermediate values of $\beta = [SiH_3]/[SiH_2]$, low branching ratios for SiH_3, and large branching ratios for $SiH_2 + 2H$. The deposition rate is most adversely effected by reducing the production of H atoms and, secondarily, by increasing the production of SiH_3. These conditions imply that the maximum radical production is obtained by minimizing the rate of the silyl association reaction [Eq. (11)] and by maximizing the production of hydrogen atoms, thereby maximizing the rate of radical multiplication by hydrogen abstraction from silane [Eq. (9)]. The deposition rate at the suggested branching ratio for SiH_3 (≈ 0.75) is only 10%–15% less than the maximum value for a given set of reaction rates. Deposition rates appear to be not as sensitive to the branching ratio for SiH_3 (as compared to SiH_2), but rather to the fractional production of H atoms.

The results discussed above are a function of discharge power deposition. At higher power deposition than that used here (50 mW cm^{-3}), radical-radical reactions become progressively more important and the $[SiH_3]/[SiH_2]$ ratio generally decreases, as shown in Fig. 3. It has been observed, though, that film quality degrades as the power deposition significantly exceeds 100 mW cm^{-3}: therefore, our results apply to values of power deposition which yield high quality films.

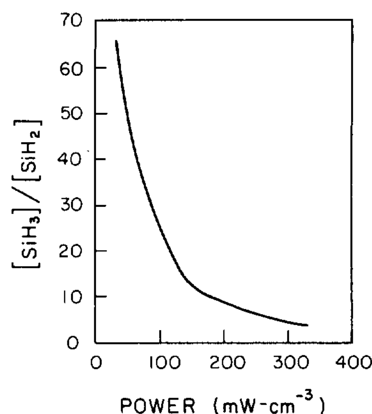

FIG. 3. The ratio of plasma radical densities, $\beta = [SiH_3]/[SiH_2]$, as a function of power deposition. At high power deposition the SiH_3 association reactions become increasingly more important, thereby decreasing β.

V. SiH_2 INSERTION INTO SiH_4, AND STICKING COEFFICIENT FOR SiH_3

In addition to the branching ratios for SiH_2 and SiH_3, two other factors can significantly effect the density ratio $\beta = [SiH_3]/[SiH_2]$ and the deposition rate. The first is the rate constant for the insertion of SiH_2 into silane [Eq. (10)] the second factor is the sticking coefficient for SiH_3. The former process is important because it is the single largest method of depleting SiH_2 in the gas phase. The latter parameter is important because under certain conditions, the dominant mode of depletion of SiH_3 can be incorporated into the a-Si:H film or other heterogenous reactions at the wall. If this is the case, the density of SiH_3 should scale inversely proportional to its sticking coefficient. The manner in which SiH_2 and SiH_3 radicals are incorporated into the film differ with respect to the fraction of hydrogen retained in the film. The sticking coefficient of SiH_3, which changes the relative contribution of SiH_3 to the film growth process, therefore directly effects the film properties, particularly the fraction of hydrogen in the film.[34,35]

The sticking coefficient, or the surface reaction probability, of SiH_3 for the conditions of interest has not been directly measured. Perrin and Broekhuizen[47] estimate that the reaction probability of SiH_3 on a-Si:H grown on heated substrates during Hg* photosensitized decomposition of silane is 0.1–0.2. Of the reacting SiH_3, $\leqslant 40\%$ incorporates into the film, and $\geqslant 60\%$ recombine on the surface desorbing as a stable molecule. Robertson and Gallagher[26] estimate the reaction probability of SiH_3 to be ≈ 0.5 on room-temperature films.

To investigate the effect of sticking coefficient and the value of the rate constant for the SiH_2 insertion reaction, rf plasmas were simulated while parametrizing those values, and the $[SiH_3]/[SiH_2]$ ratio and deposition rate were computed. Two sets of branching ratios were selected for the production of SiH_3: optimistic (85% $SiH_3 + H$, 15% $SiH_2 + 2H$) and pessimistic (15% $SiH_3 + H$, 85% $SiH_2 + H_2$). The rate constants for Reactions (9) and (11) were chosen to have intermediate values: 2.7×10^{-12} cm^{-3} s^{-1} and a total of 1.7×10^{-11} cm^3 s^{-1}, respectively.

The results of this parametrization for β are plotted in Fig. 4 for the optimistic and pessimistic branching ratios. The $[SiH_3]/[SiH_2]$ ratio is relatively insensitive to the sticking coefficient, changing by only 50% for an order of magnitude change in sticking coefficient for the pessimistic case and by only 10% for the optimistic case. This effect is due, in part, to the bimolecular SiH_3 reaction in Eq. (11). This reaction both limits the density of SiH_3 at high densities and generates additional SiH_2, which further reduces the $[SiH_3]/[SiH_2]$ ratio. This ratio, though, increases with increasing rate constant for the SiH_2 insertion reaction due to depletion of SiH_2. The increase in β is a factor of 30 for a two orders of magnitude change in rate constant for the pessimistic case, and a factor of 12 for the optimistic case. Sticking coefficients appear to have little effect on β, as will be further discussed below: rather, the density of SiH_2 largely controls the value of this ratio. In order for SiH_3 to be the dominant radical ($\beta > 10$), the rate constant for the SiH_2 insertion must exceed a few times 10^{-11} cm^3 s^{-1}, a value consistent

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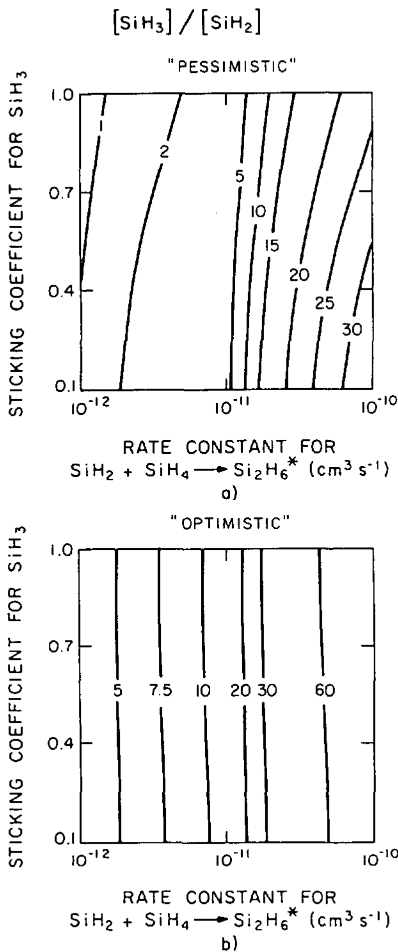

FIG. 4. The ratio of radical densities in the plasma, $\beta = [SiH_3]/[SiH_2]$, as a function of the sticking coefficient for SiH_3 and the rate constant for insertion of SiH_2 into silane. (a) Pessimistic branching ratios for SiH_3 (85% $SiH_2 + H_2$, 15% $SiH_3 + H$ and (b) optimistic branching ratios (15% $SiH_2 + 2H$, 85% $SiH_3 + H$). β is relatively insensitive to the sticking coefficient and is largely determined by the rate of silylene insertion.

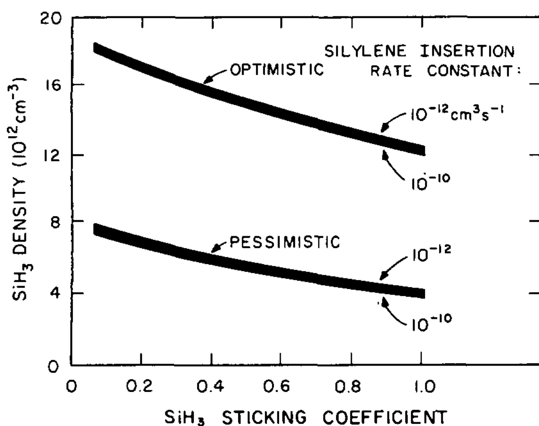

FIG. 5. The number densities of SiH_3 for the conditions of Fig. 4 as a function of sticking coefficient. The band of values represent the SiH_3 densities while the rate constant for SiH_2 insertion is varied between 10^{-12}–10^{-10} $cm^3\ s^{-1}$, indicating a lack of sensitivity to that process. The weak dependence of $[SiH_3]$ on sticking coefficient is an indication of the importance of the silyl association reaction.

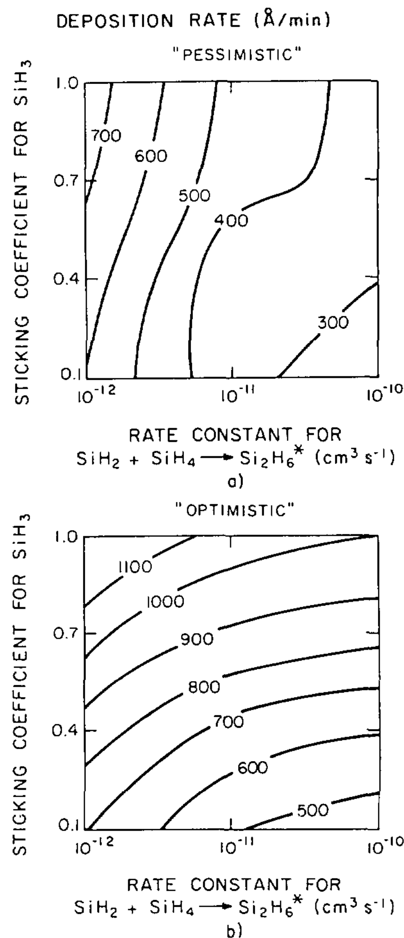

FIG. 6. Deposition rate of a-Si:H for the conditions of Fig. 4. (a) Pessimistic branching ratios for SiH_3 and (b) optimistic branching ratios. The deposition rate correlates well with sticking coefficient for SiH_3 for both cases but is only weakly dependent on the rate constant for SiH_2 insertion for optimistic conditions. This is a result of the importance of the hydrogen abstraction reaction in generating radicals to compensate for losses of radicals by insertion.

with the measurements of Inonue and Syzuki,[42] and Jasinski.[43]

The results of the parametrization for sticking coefficient are summarized in Fig. 5, where the density of SiH_3 is plotted as a function of sticking coefficient for the optimistic and pessimistic branching ratios. The density of SiH_3, as well as β, appear to be weak functions of sticking coefficient. The deposition rate for the pessimistic and optimistic branching ratios are plotted in Fig. 6. For pessimistic conditions, the deposition rate correlates only weakly with the sticking coefficient. The correlation is weak because any reduction in the sticking coefficient (η) is compensated for by an increase in the radical density (ρ) such that $\Sigma_i \rho_i \eta_i$ equals the rate of production of radicals, where the sum is over all radical species. Large deposition rates, though, do correlate with small values of β and small values for the SiH_2 insertion rate constant, indicating that larger values for deposition rates are largely a result of larger densities of SiH_2. This trend also qualitatively holds for deposition rates for optimistic branching ratios. The correlation with sticking coefficient, though, is stronger due to the larger value of β and the larger fractional contribution of SiH_3 to the deposition rate, as discussed below.

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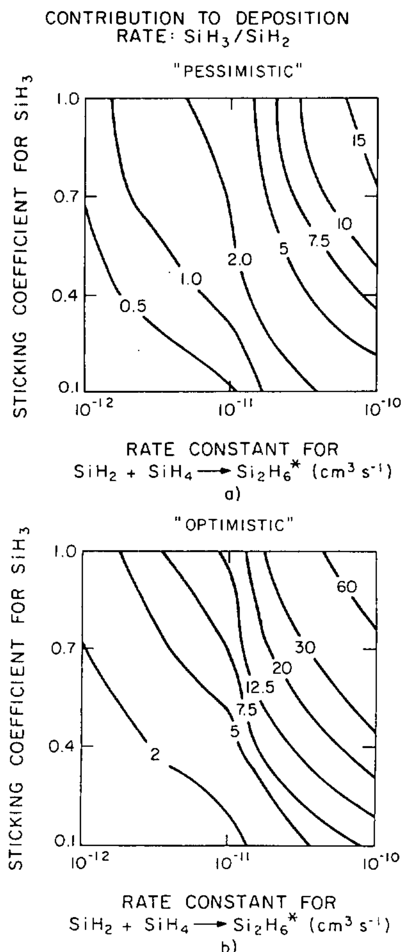

FIG. 7. The contribution to the deposition process for the conditions of Fig. 4.(a) Pessimistic branching ratios for SiH_3 and (b) optimistic branching ratios. Although SiH_3 is the dominant radical based on gas phase density over the entire parameter space of these examples, it is the dominant contributer to film growth, only for large sticking coefficients and large rates of silylene insertion.

The ratios of the contributions of SiH_3 and SiH_2 to the deposition rate are plotted in Fig. 7 for the same conditions as discussed above. Although the density of SiH_3 always exceeds that of SiH_2, its relative contribution to the deposition rate is large (> 10) only with highly optimistic conditions (high rate of depletion of SiH_2 and high sticking coefficient for SiH_3). As a point of reference we used Perrin and Broekhuizen's[47] and Gallagher's[35,44] estimates for the sticking coefficient of SiH_3 (0.1–0.2), and Jasinski's[43] value for the rate constant for the SiH_2 insertion reaction (5×10^{-11} $cm^3\,s^{-1}$). For these conditions, the density ratio and the ratio of contributions to the deposition rate have values of 25–60 and 3–15, respectively, thereby identifying SiH_3 as the dominant radical in both respects. Recall, though, that these results require that the silyl association reaction has a rate constant of $\leqslant 10^{-11}$ $cm^3\,s^{-1}$, consistent with the measurements of Macpherson and co-workers for methyl radical association,[46] and consistent with Robertson and Gallagher's[26] estimate as well. Should this rate constant be significantly larger, the dominant radical is likely to be SiH_2.

VI. CONCLUDING REMARKS

The effect of branching ratios of the electron impact dissociation of silane on the balance of silylene and silyl radicals in rf glow discharges as used for PECVD of *a*-Si:H has been investigated with results from a plasma chemistry model. We find that to be consistent with experimental measurements of the ratio of $[SiH_3]/[SiH_2]$, the branching ratio for SiH_3 must exceed 0.75 and the probability of obtaining H atoms for the SiH_2 branch must also exceed 0.75. These values are close to those for the analogous branching ratios for dissociation of methane. These results, though, require that the silyl association reaction have a rate constant $\leqslant 10^{-11}$ $cm^3\,s^{-1}$, a value close to that measured by Macpherson and co-workers[46] for methyl radical association; and the silylene insertion reaction must have a rate constant $\geqslant 10^{-11}$ $cm^3\,s^{-1}$, consistent with the measurements of Inoue and Suzuki[42] and Jasinksi.[43] The deposition rate of *a*-Si:H is most sensitive to the yield of H atoms from the dissociation branch for SiH_2, and less sensitive the relative yield for SiH_3 and SiH_2. Although the dominant radical in the gas phase, SiH_3 is the dominant contributer to film growth only for sticking coefficients exceeding 0.5.

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