Production of disilane and silyl sticking coefficients during plasma-enhanced chemical vapor deposition of hydrogenated amorphous silicon

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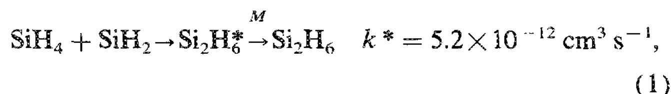
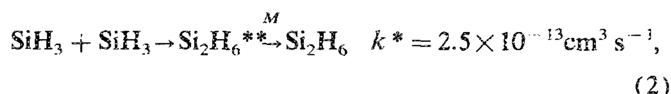
The rate of production of disilane (Si_2H_6) in silane (SiH_4) plasmas by gas phase and surface-catalyzed processes is examined. The discussion is based on results from plasma chemistry and surface deposition computer models. The surface model simulates the adsorption of silane radicals from the plasma on a growing amorphous silicon film and the subsequent desorption from the surface of the nonadhering SiH_3 radicals as Si_2H_6. The rate of generation of Si_2H_6 from the surface reactions is compared to the rate of generation due to plasma reactions. We find that for conditions which are typical of those used for deposition of amorphous silicon, production of disilane is likely dominated by surface-catalyzed processes. The rate of production, though, depends on the sticking coefficient of SiH_3, which we find to be a function of plasma conditions.

Plasma-enhanced chemical vapor deposition (PECVD) of hydrogenated amorphous silicon (*a*-Si:H) thin films in silane discharges is being investigated by many research groups with the goal of fabricating solar cells, photodetectors, and thin-film transistors.[1-3] The current understanding of plasma and film growth kinetics postulates that neutral monosilane radicals, particularly SiH_3, are dominantly responsible for the film growth in the low power ($\lesssim 10$ mW cm^{-3}), low pressure (<0.5 Torr) discharges which produce device quality films.[4] However, SiH_3 radicals, which may comprise $>90\%$ of the radical flux incident on the substrate, require an activated site ($\equiv$Si—•) on the surface of the growing *a*-Si:H film for incorporation into the lattice. Since the surface of the film in typical discharges is highly passivated by atomic hydrogen ($\equiv$Si – H), a large fraction of the adsorbed SiH_3 desorbs from the surface as SiH_3, or as the saturated molecules SiH_4 and Si_2H_6 which result from surface-catalyzed reactions. The effective sticking coefficient[5] of SiH_3 has been estimated as being 0.03–0.10 depending on discharge conditions,[4,6] implying that surface-catalyzed reactions may contribute a large flux of products to the plasma. In fact it has been suggested that surface-catalyzed reactions of SiH_3 may be an important source of disilane in silane glow discharges.[4] Since electron impact dissociation of disilane (Si_2H_6) is 1.5–2.0 times faster and produces different radicals than dissociation of SiH_4,[7,8] the production of significant amounts of Si_2H_6 from surface reactions could alter the volumetric plasma chemistry. Kuznetsov *et al.* have attributed large growth rates of *a*-Si:H in SiH_4 discharges at high-power deposition to the generation of Si_2H_6.[9]

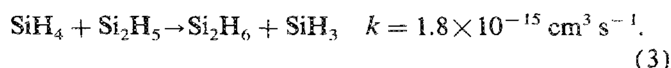
In this letter, we examine the production of Si_2H_6 in silane glow discharges by volumetric plasma and surface-catalyzed processes, and its dependence on the sticking coefficient of SiH_3 radicals. Results from computer models for the plasma chemistry of silane glow discharges and for *a*-Si:H thin-film growth have been used in this study. These models have been validated by comparison to experiments, as described in Refs. 10 and 11. The plasma chemistry model[10] simulates the electron distribution function, electron impact dissociation of silane into various radicals, and subsequent reactions and transport of those radicals to the surface. Disilane is one product of these gas phase reactions. The three most important reactions for gas phase production of disilane and their rate constants (k) as used in this study are[10]



$$SiH_4 + SiH_2 \rightarrow Si_2H_6^* \xrightarrow{M} Si_2H_6 \quad k^* = 5.2\times 10^{-12}\ \mathrm{cm^3\ s^{-1}}, \tag{1}$$

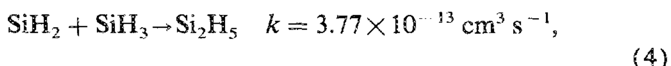


$$SiH_3 + SiH_3 \rightarrow Si_2H_6^{**} \xrightarrow{M} Si_2H_6 \quad k^* = 2.5\times 10^{-13}\ \mathrm{cm^3\ s^{-1}}, \tag{2}$$

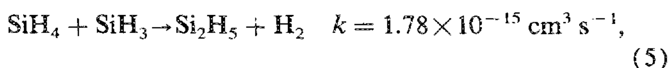


$$SiH_4 + Si_2H_5 \rightarrow Si_2H_6 + SiH_3 \quad k = 1.8\times 10^{-15}\ \mathrm{cm^3\ s^{-1}}. \tag{3}$$

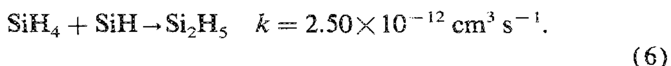
The first two reactions require a third body for stabilization and the rate constants (k^*) shown are the effective two-body rate constants for our conditions[12] (300 mTorr, $T_g = 575$ K). The stabilizing collisions for reactions (1) and (2) have estimated rate constants of 10^{-10} cm^3 s^{-1}. The reaction in Eq. (3) first requires production of Si_2H_5, primarily by[10]



$$SiH_2 + SiH_3 \rightarrow Si_2H_5 \quad k = 3.77\times 10^{-13}\ \mathrm{cm^3\ s^{-1}}, \tag{4}$$



$$SiH_4 + SiH_3 \rightarrow Si_2H_5 + H_2 \quad k = 1.78\times 10^{-15}\ \mathrm{cm^3\ s^{-1}}, \tag{5}$$



$$SiH_4 + SiH \rightarrow Si_2H_5 \quad k = 2.50\times 10^{-12}\ \mathrm{cm^3\ s^{-1}}. \tag{6}$$

Reaction (6) is the main contributing process for the conditions of interest.

The film growth model[11] uses the radical, ion, and hydrogen fluxes produced by the plasma model as input in simulating the film growth process. In this model, adsorbed SiH_n ($n \leqslant 2$) radicals immediately incorporate into the film by bond substitution with $\equiv$Si—H surface sites or by bonding with sites that have been previously activated by the sputtering of passivating hydrogen atoms by ion bombardment or by hydrogen scouring reactions. Silyl (SiH_3) radicals, which require an activated site for incorporation, are

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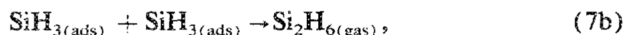
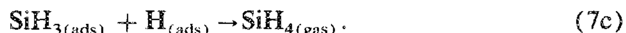
adsorbed and remain mobile on the surface until finding such a site. Before doing so, the radical may desorb and return to the plasma as SiH_3, SiH_4, or Si_2H_6 by the reactions

$$SiH_{3(ads)} \rightarrow SiH_{3(gas)}, \quad (7a)$$



$$SiH_{3(ads)} + SiH_{3(ads)} \rightarrow Si_2H_{6(gas)}, \quad (7b)$$



$$SiH_{3(ads)} + H_{(ads)} \rightarrow SiH_{4(gas)}. \quad (7c)$$

The branchings from the surface of adsorbed SiH_3 for gas phase production of SiH_3 (γ_0), $SiH_4(\gamma_1)$, and $Si_2H_6(\gamma_2)$ have been estimated as $\gamma_0 \approx 0.80$, $(\gamma_1 + \gamma_2) \approx 0.2$,[4] and $\gamma_0 \approx 0.87$, $(\gamma_1 + \gamma_2) \approx 0.13$, with $\gamma_1/\gamma_2 > 1$.[8,13] For the results first discussed in this letter, we have assumed that all desorbed SiH_3 radicals return to the plasma as Si_2H_6 which sets an upper limit on production of disilane by surface-catalyzed reactions. The implications of these estimated values of γ_2 are discussed later.

The combined models were used to simulate Ar/SiH_4, H_2/SiH_4, and pure silane discharges under various conditions. The computed fractional contributions to production of disilane from all plasma sources are shown in Fig. 1 as a function of Ar fraction in an Ar/SiH_4 rf parallel-plate discharge (300 mTorr, 15 mW/cm^3, electrode separation 2.5 cm). Production of disilane is dominated by SiH_2 insertion into silane [reaction (1)] for all conditions. The second largest source of disilane is by abstraction of hydrogen from silane by Si_2H_5 [reaction (3)], followed by the association of silyl radicals [reaction (2)] which contributes $< 10\%$ of the total. At intermediate Ar fractions, the rate of production of silane radicals is maximum so that production of disilane by the two-step Si_2H_5 reaction is also a maximum. The contribution of this reaction decreases with decreasing silane mole fraction as the probability of two-step reactions decreases. SiH_2 insertion represents a larger fraction of total disilane production in H_2/SiH_4 discharges since the density of SiH is depressed by reactions with H_2, thereby reducing the contributions from reactions (3) and (6) (see Fig. 1). In pure silane discharges, the two-step reaction resulting in Si_2H_5 abstracting H from silane becomes increasingly more important with increasing pressure.

The dependence on Ar dilution of disilane production in the plasma and by surface catalysis [Eq. 7(b)] is shown in Fig. 2(a). For all conditions, disilane production is dominated by surface catalysis with the contribution being 25–50 times larger than in the plasma volume when $\gamma_2 = 1.0$. The decrease in total disilane production in the volume at higher Ar dilutions is due to the lower total rate of radical production. The decrease in production of Si_2H_6 from the surface is due, in part, to an increase in the sticking coefficient of SiH_3 for incorporation into the lattice. The increase in sticking coefficient is a result of a higher rate of activation of surface sites (to which adsorbed SiH_3 may bond) by ion bombardment, as shown in Fig. 3. Similar trends are observed for production of Si_2H_6 in SiH_4/H_2 mixtures [Figs. 2(b) and 3], although the contribution from the plasma is larger. In each case, sticking coefficients for SiH_3 of 0.05–0.3 are predicted which are commensurate with experiments.[4,13] The higher sticking coefficient in SiH_4/H_2 plasmas is caused by increased surface activation due to scouring of the surface by atomic hydrogen, which removes a passivating H atom.

The decrease in production of Si_2H_6 resulting from an increase in the sticking coefficient of SiH_3 is evident when increasing power deposition in a pure silane discharge (see

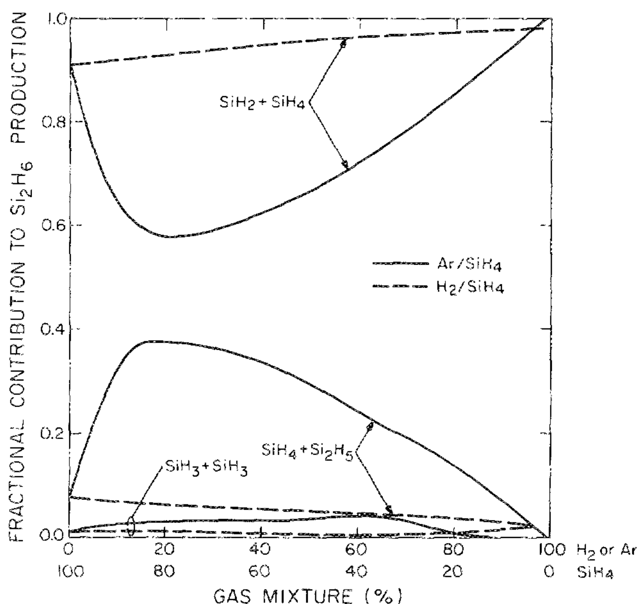


FIG. 1. Relative contributions to disilane production as a function of mole fraction in Ar/SiH_4 and H_2/SiH_4 gas mixtures. The data shown are for a 300 mTorr constant pressure discharge ($T_{sub} = 500$ K) with a rf power deposition of 15 mW cm^{-3}.

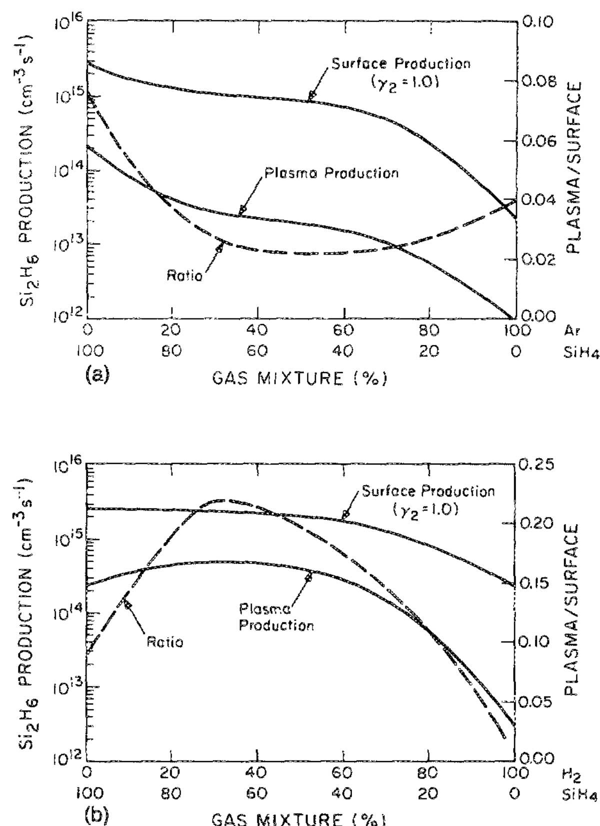


FIG. 2. Total Si_2H_6 production by plasma and surface processes, and their ratio as a function of gas mixture: (a) Ar/SiH_4 and (b) H_2/SiH_4. For these figures the branching ratio for Si_2H_6, $\gamma_2 = 1.0$. Discharge conditions are the same as for Fig. 1. Si_2H_6 production is dominated by surface catalysis provided that $\gamma_2 \gtrsim 0.05$.

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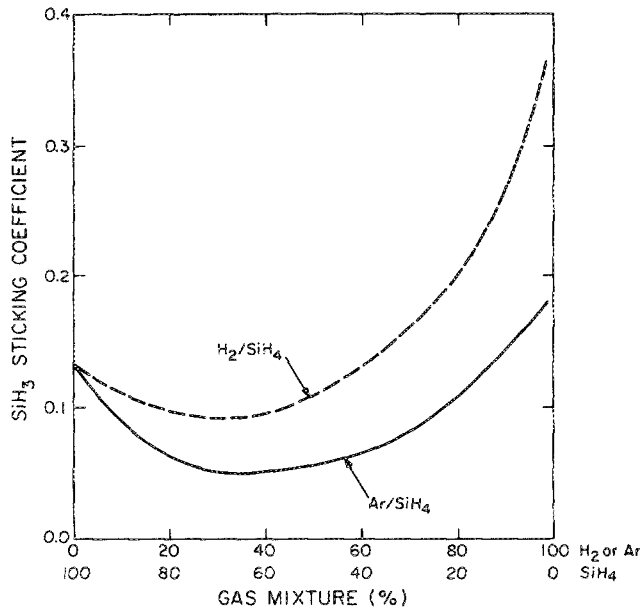

FIG. 3. Sticking coefficients for SiH_3 as a function of Ar and H_2 dilution of silane discharges for the conditions of Fig. 1. The increase in sticking coefficients is due to the increase in ion bombardment and hydrogen abstraction reactions on the surface respectively.

Fig. 4). Increasing power deposition from 20 to 160 mW cm^{-3} increases volumetric production by more than an order of magnitude and increases the sticking coefficient of SiH_3 to a value of ≈ 0.4. Production of disilane from the surface increases by less than a factor of 3 because of the increase in sticking coefficient.

In the previous results, we have used the branching $\gamma_2 = 1.0$ for production of disilane by reaction (7b). In fact, the branching ratio for disilane production is likely a smaller value, with the majority of SiH_3 desorbing in its adsorbed form. Nevertheless, the branching ratio for disilane production may be as small as 0.02–0.04 before the rate of production in the plasma is comparable to that from the surface. These values are in the range previously estimated,[4,8,13] thereby suggesting the disilane production is indeed dominated by surface catalysis.

In conclusion, production of disilane in the plasma is dominated by SiH_2 insertion into silane, with major contributions by reaction of Si_2H_5 with silane at high radical densities and minor contributions by SiH_3 association. The rate of disilane production in silane glow discharges by the surface-catalyzed association of SiH_3 is most sensitive to the discharge conditions which affect the sticking coefficient of

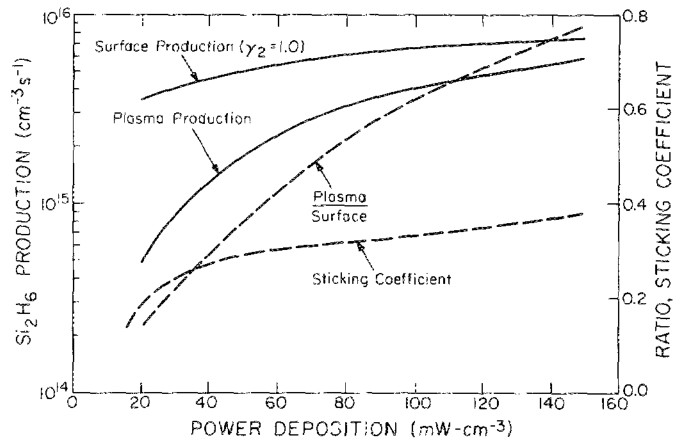

FIG. 4. Production rates of Si_2H_6 as a function of power deposition in pure silane discharges ($\gamma_2 = 1.0$). The ratio of plasma/surface production of Si_2H_6 increases as the SiH_3 sticking coefficient increases.

SiH_3. In all cases of interest, disilane production is dominated by the surface process provided that its branching ratio $\gamma_2 \geqslant 0.05$. Increasing dilution of silane by carrier gases such as Ar and H_2, increases the rate of ion bombardment, and the rate of production of activated surface sites. This increases the sticking coefficient of SiH_3 on the growing film and reduces the production of disilane at the surface. These conditions are typically not associated with high quality films.

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