

Possible contribution of SiH₂ and SiH₃ in the plasma-induced deposition of amorphous silicon from silane

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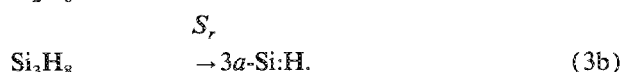
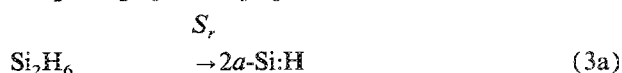
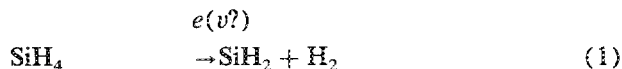
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A self-consistent quantitative analysis of recent kinetic data on the role of di- and trisilane in the plasma-induced deposition of amorphous silicon from monosilane confirms the conclusion that the dominant reactive intermediate responsible for the formation of di- and trisilane and, consequently, for the deposition of a high quality amorphous silicon is SiH₂. The data show that the SiH₃ radical may play only a negligible, if any, role in this process.

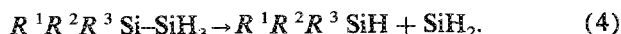
In a recent paper Heintze and Vepřek¹ have shown that the measured deposition rate of amorphous hydrogenated silicon *a*-Si:H correlates with the measured concentration of di- and trisilane. The *a*-Si deposition occurs via a reaction mechanism which is summarized in Eqs. (1)–(3).



A more complete set of kinetic data and their analysis in terms of this mechanism has been published recently.² The rate-determining step of di- and trisilane decomposition on the surface, Eq. (3), is the ion-impact-induced hydrogen desorption. The kinetic data can be quantitatively and self-consistently explained on the basis of this mechanism in a wide range of the discharge-current density between 0.06 and 7.5 mA/cm² (or a "power density" of about 0.006 to >0.3 W/cm³), deposition rate between <0.05 and ≥2 nm/s and a silane concentration between about 100 and <10 mol %. This mechanism is similar to that which is well documented for thermal chemical vapor deposition (CVD) of silicon from silane by Meyerson *et al.*,³ Scott *et al.*,⁴ and other researchers.^{5,6} It has also been proposed to dominate the plasma-induced CVD.^{6–8}

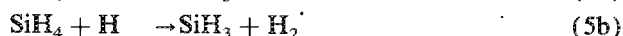
The *a*-Si:H films deposited at a rate up to 3.2 nm/s show excellent homogeneity, very low concentration of Si–H₂ and of Si–H groups on internal surfaces, a high photoconductivity of ≥10^{–4} S/cm, a low dark conductivity of <10^{–9} S/cm, and a relatively small photodegradation.⁹

The fragmentation of monosilane into SiH₂ and H₂ under plasma conditions, Eq. (1), has been identified as the dominant reaction channel by Ensslen and Vepřek.⁸ It is a natural consequence of the electronic structure of silane¹⁰ as documented by a large number of reactions.^{11,12} Accordingly, silanes undergo predominantly an extrusion reaction of a type



Even the ultraviolet photolysis of monosilane yields as a dominant product SiH₂ (83%) and little SiH₃ (17%).¹³ The infrared photolysis by CO₂ laser yields solely SiH₂.¹⁴ Silyl radical, SiR₃, is found to be important in the reaction mechanism only in the case of large or strongly electronegative ligands. Under plasma conditions, the fragmentation of monosilane into SiH₂ and H₂ is probably triggered by electron-impact-induced excitation of vibrational degrees of freedom of monosilane,^{2,7,9,15} which is the dominant channel of electron energy loss in a silane discharge.^{16,17}

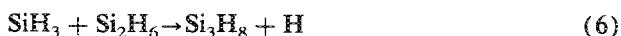
In spite of these facts there is still persisting controversy about the mechanism of plasma-induced deposition of *a*-Si:H as several researchers favor the SiH₃ radical being supposedly the dominant species responsible for the process. For example, Gallagher has criticized our earlier work⁸ and suggested that our results could be more logically explained by the reactions of this radical¹⁸:



However, there are no quantitative arguments given in that paper which would support his statement and this mechanism is in contradiction with several experimental facts. We refer to some recent reviews^{15,19} for further details.

In this letter we present a self-consistent analysis of the experimental data^{1,2} without using any assumption or experimental results regarding reaction (1), i.e., whether SiH₂ or SiH₃ is the dominant fragmentation product. This is possible because there are more kinetic data available in our work than needed for an unambiguous quantitative analysis.

The crucial fact and the starting point of our analysis is the formation of trisilane by the insertion of SiH₂ into disilane, Eq. (2b). This is the only way trisilane can be formed because the reaction of SiH₃ with disilane, Eq. (6), is strongly endothermic (~≥30 kcal/mole) and therefore slow.



Let us recall that the insertion of SiH₂ into Si₂H₆ is very fast with a rate constant close to the molecular collision limit.⁶

In this letter we use only the measured data of the disilane concentration and let open the question of whether the

disilane is formed via the very fast insertion of SiH_2 into SiH_4 according to Eq. (2a) or via a recombination of two SiH_3 radicals, Eq. (7), as proposed by some workers^{18,19}:



Thus, the following analysis is entirely based on the fact that reaction (2b) is the only way the trisilane can be formed.

The measurements of Heintze and Veprek have been done in a homogeneous glow-discharge plasma under conditions of gas flow.^{1,2} Thus, the balance equation for trisilane reads:

$$\frac{d[\text{Si}_3\text{H}_8]}{dt} = k(2b)[\text{SiH}_2][\text{Si}_2\text{H}_6] - k(\text{dec})[\text{Si}_3\text{H}_8] - \frac{[\text{Si}_3\text{H}_8]}{\tau} \quad (8)$$

Here, the first term is the formation of trisilane via reaction (2b), the second term describes its overall loss due to decomposition, and the third term the loss due to gas flow. For a given gas flow rate (i.e., a constant dwell time τ) the concentration of trisilane is constant and Eq. (8) reduces to Eq. (9):

$$\frac{[\text{Si}_3\text{H}_8]}{[\text{Si}_2\text{H}_6]} = \frac{k(2b)[\text{SiH}_2]}{k(\text{dec}) + 1/\tau} = k(2b)[\text{SiH}_2] \left(\frac{\tau}{1 + k(\text{dec})\tau} \right) \quad (9)$$

The concentrations of di- and trisilane have been measured (see Fig. 1 in Ref. 1 and Figs. 2 and 6 in Ref. 2) for various values of the dwell time τ . The rate constant for the insertion reaction (2b) is well documented in the literature.⁶ Thus, the rate constant for the overall decomposition of trisilane and the concentration of SiH_2 are the only unknown quantities in Eq. (9).

SiH_2 is a very fast reacting intermediate for which the steady-state approximation applies.²⁰ Accordingly, its concentration remains constant during the whole range of the dwell time under which the measurements were done.^{20,21} Thus, a plot of the measured ratio of the tri- and disilane concentration versus $\tau/[1 + k(\text{dec})\tau]$ is a straight line passing through zero with a slope corresponding to $k(2b)[\text{SiH}_2]$. Let us recall that for the two unknown quantities $k(2b)[\text{SiH}_2]$ and $k(\text{dec})$ we have Eq. (9) valid for various values of the di- and trisilane concentrations measured at various dwell times which range over two orders of magnitude (see Fig. 1 in Ref. 1). Thus, there is only one algebraic solution for $k(2b)[\text{SiH}_2]$ and $k(\text{dec})$ for Eq. (9) at all the dwell times which can be obtained from the measured data either by a numerical or a graphical iteration. The graphical iteration yields the corresponding values $k(2b)[\text{SiH}_2] = 1.2 \text{ s}^{-1}$ and $k(\text{dec}) = 10 \text{ s}^{-1}$ (for details see Ref. 22).

It should be emphasized that the calculated value of $k(2b)[\text{SiH}_2]$ has been obtained from Eq. (8) based only on the measured data without any assumptions regarding the first step of the decomposition of monosilane and the formation of disilane. Thus, this value can now be used to calculate the rate of the formation of disilane using the measured con-

centration of monosilane [see Fig. 1(a) in Ref. 1] and the rate constants for the insertion of SiH_2 into mono- and disilane reported by Jasinski and Chu.⁶ As a matter of fact, only the ratio of the rate constant $k(2a)/k(2b) \approx 0.6$ (at the given pressure) is needed to calculate the rate of disilane formation equal to

$$\{k(2a)/k(2b)\} \{k(2b)[\text{SiH}_2][\text{SiH}_4]\} = k(2a)[\text{SiH}_2][\text{SiH}_4].$$

As a next step, the calculated rate of the disilane formation is used to calculate the steady-state concentration of disilane at a given value of the dwell time from the corresponding balance equation (10):

$$0 = \frac{d(\text{Si}_2\text{H}_6)}{dt} = k(2a)[\text{SiH}_2][\text{SiH}_4] - [\text{Si}_2\text{H}_6] \{k(3a) + k(2b)[\text{SiH}_2] + 1/\tau\}. \quad (10)$$

The rate constant $k(3a)$ can be calculated from the measured deposition rate of *a*-Si [see Fig. 1(c) in Ref. 1] using the measured values of the di- and trisilane concentration and the above-determined value of the rate constant for the trisilane decomposition, $k(\text{dec})$. The resultant calculated concentration of disilane together with the experimental data^{1,2} is shown in Fig. 1.

The very good agreement is direct proof that the SiH_2 species is the reactive species responsible for the formation of disilane (and trisilane) and, consequently, for the deposition of *a*-Si:H. There is no need to invoke any other reaction channel.

At this instance it is interesting to ask the question of what concentration of the SiH_3 radical would be necessary to yield the same rate of the disilane formation as obtained from the above analysis of SiH_2 . The concentration of SiH_2 can be estimated from the above-determined value of the product $k(2b)[\text{SiH}_2] = 1.2 \text{ s}^{-1}$ and the value of the rate constant $k(2b) \approx 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ reported, for the given pressure, by Jasinski and Chu.⁶ The resultant value of the SiH_2 con-

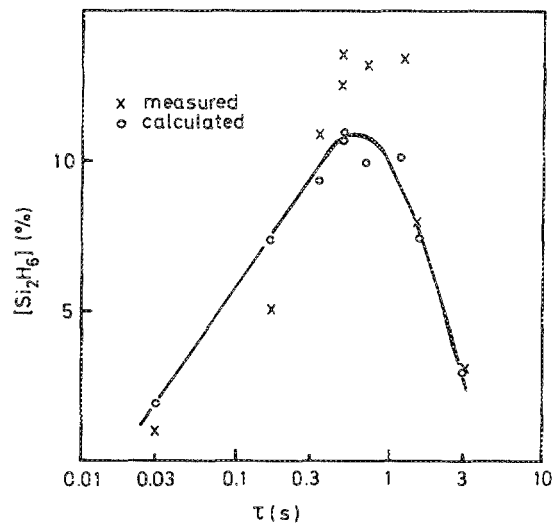


FIG. 1. Comparison of the measured (crosses) and calculated (circles) concentration of disilane according to Eq. (10).

centration of about $1.2 \times 10^{10} \text{ cm}^{-3}$ is sufficient to give the formation rate of

$$r(2a) \approx k(2a) 1.2 \times 10^{10} \times 6 \times 10^{15} \approx k(2a) 7 \times 10^{25} \text{ (mole/cm}^3 \text{ s)}. \quad (11)$$

The corresponding equation for the rate of disilane formation according to Eq. (7) is

$$r(7) = k(7) [\text{SiH}_3]^2. \quad (12)$$

Setting $r(2a) = r(7)$ and accounting for the fact that $k(2a)/k(7) > 1$ one obtains for the necessary concentration of the SiH_3 radical

$$[\text{SiH}_3]_{\text{required}} \approx \{k(2a)/k(7)\}^{1/2} 8.5 \times 10^{12} \geq 10^{13} \text{ (mole/cm}^3 \text{)}. \quad (13)$$

This is almost two orders of magnitude larger than a value evaluated from a measurement of Robertson and Gallagher²³ (but see Ref. 15) and a factor of about 20 larger than the value reported by Itabashi *et al.*²⁴ However, the measurements of Itabashi *et al.* (which are the only ones in which the SiH_3 concentration has been really measured) have been done in a hollow cathode-like discharge operating at a power density of about 0.1 W/cm^3 . Our data, to which the above analysis applies, were measured in a homogeneous plasma of the positive column of a weak glow discharge with a power density of about 0.006 W/cm^3 which is typically used for the deposition of high quality α -Si:H. No absorption signal corresponding to SiH_3 could be observed by Itabashi *et al.* if the power density (or the discharge current) has been reduced by a factor of 10.²⁵ Considering the relatively good signal-to-noise ratio in their paper (see Fig. 2 in Ref. 24) we conclude that their data scaled down to the discharge power used in our measurements yield a concentration of SiH_3 which is at least a factor of 400 (probably even more) lower than that which would be necessary to explain our data. In addition one has to account for the fact that the hollow cathode-like discharge produces orders of magnitude higher degree of ionization and fragmentation than the positive column of a glow discharge.²⁶

In conclusion, the self-consistent analysis of the kinetic data of Heintze and Veprek^{1,2} show that the fragmentation of silane into SiH_2 and H_2 , Eq. (1), followed by fast insertion reactions (2a) and (2b) is the dominant reaction channel of

the formation of di- and trisilane and for the deposition of high optoelectronic quality α -Si:H. There is no need to invoke further additional reaction channels of a comparable importance. The analysis further shows that the SiH_3 radical can play only a negligible, if any, role in this process.

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