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PREPARATION AND CHARACTERIZATION

A STUDY OF THE SILANE GLOW DISCHARGE DEPOSITION BY ISOTOPIC LABELLING

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Neutral and ionic species in SiH_4–SiD_4–He and SiH_4–H_2–D_2 r.f. glow discharges at pressures of 0.15–1 Torr were measured by mass spectrometry. We found partially deuterated monosilanes (SiH_2D_2 and $SiHD_3$). The disilane formed, $Si_2H_{6-n}D_n$, exhibits all the degrees of deuteration ($n = 0$–6). These results are consistent with the presence of SiH_2 and SiH_3 radicals in the discharge. Reaction pathways are proposed to account for these results.

The observed plasma etching of an a-Si:H film in a D_2 plasma and the IR analysis of the Si—D bonds in the film showed that the formation of these bonds is the result of both silane deuteration and of deuterium incorporation in the growing film.

1. INTRODUCTION

The plasma deposition of an a-Si film from silane has been known since 1969[1]. Although the study of the material itself is still an important research field, studies of the deposition mechanisms are rather scarce, probably because of the great complexity of reactive molecular plasmas.

We have recently reported the results of a kinetic study of the silane discharge[2] and mass spectrometric measurements of the SiH_4 plasma[3]. A mechanism was proposed for formation of a-Si:H films which was based upon the existence of neutral radicals. These radicals were formed by the dissociation of silane through the reactions

$$e^- + SiH_4 \rightarrow SiH_3 + H + e^- \qquad \Delta H = 4.1\,eV \qquad (1)$$

$$e^- + SiH_4 \rightarrow SiH_2 + H_2 + e^- \qquad \Delta H = 2.2\,eV \qquad (2)$$

$$e^- + SiH_3 \rightarrow SiH_2 + H + e^- \qquad \Delta H = 2.6\,eV \qquad (3)$$

$$SiH_2^+ + SiH_4 \rightarrow SiH_3^+ + SiH_3 \qquad \Delta H = -0.04\,eV \qquad (4)$$

Knights[4] has drawn a similar conclusion about the role of SiH_2 and SiH_3 radicals from a study of the growth morphology of the a-Si:H films.

Haller[5] has recently studied the ions issued from an r.f. glow discharge in SiH_4 in the pressure range 17–100 mTorr. Drevillon *et al.*[6] have studied the dissociation

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mechanisms of silane in a multipole plasma at a pressure of 0.1–5 mTorr. Scott *et al.*[7] have studied the plasma deposition of a-Si:H films from Si_2H_6 and Si_3H_8.

It is important to identify the intermediate radicals and the reactions which occur while the film is being formed. In the present paper we use an isotopic labelling technique to determine the various reaction steps in discharges in SiH_4–He and SiH_4–H_2 mixtures. Neutral deuterated monosilanes and disilanes are detected by mass spectrometry. The Si—D bonds in the film are analysed by IR spectroscopy.

2. EXPERIMENTAL

The experimental set-up has been described in a previous paper[3]. The gas is sampled from the discharge through an orifice of diameter 200 μm bored in the wall. The neutral and ionic species are measured by means of a quadrupole mass spectrometer. In order to improve the sensitivity for the detection of neutral species, the valve of the intermediate vacuum chamber is throttled. Thus a pressure of 1 Torr in the discharge tube gives rise to a pressure of 2×10^{-6} Torr in the spectrometer. The SiH_4 and SiD_4 gases are diluted in helium, hydrogen or deuterium (5% concentration).

3. RESULTS AND DISCUSSION

3.1. Discharge in SiH_4–SiD_4–He

3.1.1. Disilane (Si_2H_6) formation

Figure 1(a) shows the evolution of the partial pressure of Si_2H_6 formed in an SiH_4–He discharge as a function of the pressure. Disilane is still observed at pressures as low as 0.15 Torr, the typical pressures used for a-Si:H deposition. The molar fraction of Si_2H_6 remains constant over the complete pressure range (0.15–2 Torr). By analogy with photochemistry studies[8] we assume that two separate pathways, the existence of which has been demonstrated[9], account for the formation

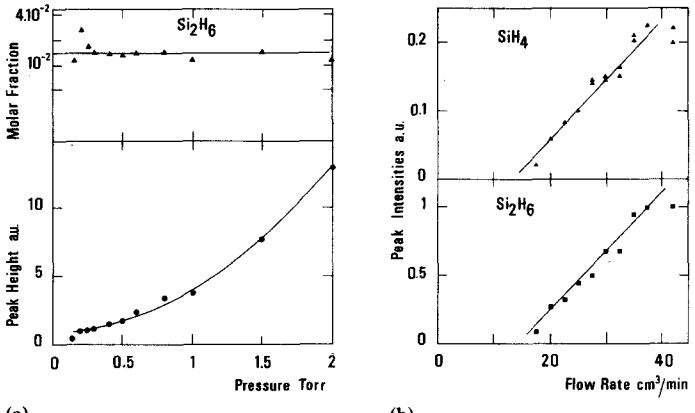

Fig. 1. (a) Pressure dependence of Si_2H_6 ($m/e = 60$) in an SiH_4–He discharge (flow rate, 42 $cm^3\ min^{-1}$ STP; r.f. power, 12 W). (b) Evolution of undissociated SiH_4 ($m/e = 30$) and Si_2H_6 ($m/e = 60$) as a function of the flow rate in an SiH_4–He discharge (total pressure, 1 Torr; r.f. power, 4 W).

of disilane:

$$SiH_3 + SiH_3 \xrightarrow[W]{M} Si_2H_6 \qquad \Delta H = -3.17\,eV \tag{5}$$

$$SiH_2 + SiH_4 \xrightarrow[W]{M} Si_2H_6 \qquad \Delta H = -2.15\,eV \tag{6}$$

These reactions are exothermic and the disilane formed is vibrationally excited. Hence it must be stabilized by either a third body (M) or the walls of the reactor (W). In the pressure range of these experiments both homogeneous and heterogeneous reactions may occur.

The probability of forming SiH_2 and SiH_3 radicals through electron impact (reactions (1)–(3)) is not known. However, following the considerations of Winters[10] about the dissociation of the CF_4 molecule, it is believed that the probability of creation of SiH_2 through reactions (2) and (3) is of the order of 0.7, which is the probability of formation of the SiH_2^+ ion by electron impact just above the threshold of ionization (12.5 eV). It should be noted that ion–molecule reactions such as reaction (4) will also produce radicals and will modify the relative population of SiH_2 and SiH_3.

The only certainty is the presence of Si_2H_6 in the discharge which certainly implies the existence of these intermediate radicals.

Figure 1(b) shows that the partial pressures of undissociated SiH_4 and Si_2H_6 increase linearly as a function of the inlet flow rate of SiH_4. Such an evolution does not necessarily mean that reaction (6) prevails over reaction (5).

The mass balance of SiH_4 in the discharge may be written as

$$N_M = Q_M V^{-1}\left(\frac{1}{t_R} + \frac{1}{t_1}\right)^{-1} \tag{I}$$

where N_M is the silane concentration (in molecules per cubic centimetre), Q_M the inlet flow rate of SiH_4 (in molecules per second), V the volume of the reactor, t_R the mean residence time of molecules in the reactor and t_1 the characteristic time for dissociation of SiH_4 [2].

Similarly the radical concentration in the discharge may be expressed as

$$N_R = \frac{N_M {t_1}^{-1}}{\{{t_R}^{-1} + (2R/s\bar{v} + R^2/5.78D)^{-1}\} + k_v N_M} \tag{II}$$

where s is the sticking coefficient of radicals on the growing film, R the radius of the discharge tube, D the diffusion coefficient of radicals in the gas phase and k_v the rate constant for radical recombination.

In discharge conditions leading to film formation, *i.e.* with essentially no gas phase nucleation, $k_v N_M$ is negligible compared with the expression in braces. Thus N_R will be approximately proportional to N_M, *i.e.* to Q_M (eqns. (I) and (II)). The results reported in Fig. 1(b) are in agreement with these relations. A short residence time (less than 1 s) will produce no further increase in the formation of Si_2H_6 [2].

An increase in the r.f. power from 2.5 to 20 W leads to a marked decrease in the Si_2H_6 concentration. Indeed disilane is an even more unstable compound than SiH_4 ($\Delta H = 0.74$ eV) and the observed concentration is the result of the opposing effects of its formation through reactions (5) and (6) and of its destruction in the discharge.

3.1.2. Formation of $SiH_{4-n}D_n$ and $Si_2H_{6-n}D_n$

Figures 2 and 3 give a picture of the neutral molecules formed in a discharge in SiH_4–SiD_4–He. Figure 2(a) shows the dependence of the H_2 and HD intensities on the gas phase composition. As expected, the maximum of HD formation is observed for a 1:1 SiH_4–SiD_4 mixture. Figures 2(b) and 2(c) illustrate the evolution of peak intensities in the range 29–34 a.m.u. as a function of the gas phase composition. The parent molecules of these peaks are monodeuterosilanes $SiH_{4-n}D_n$. The ionic fragmentation spectra of SiH_4 and SiD_4 are given in Table I. Fragmentation patterns for intermediate deuterosilane: silane-d_1 (SiH_3D), silane-d_2 (SiH_2D_2) and silane-d_3 ($SiHD_3$) are not available. However the peak at $m/e = 33$ can unambiguously be assigned to $SiHD_2^+$ whose parent molecules are SiH_2D_2 and $SiHD_3$.

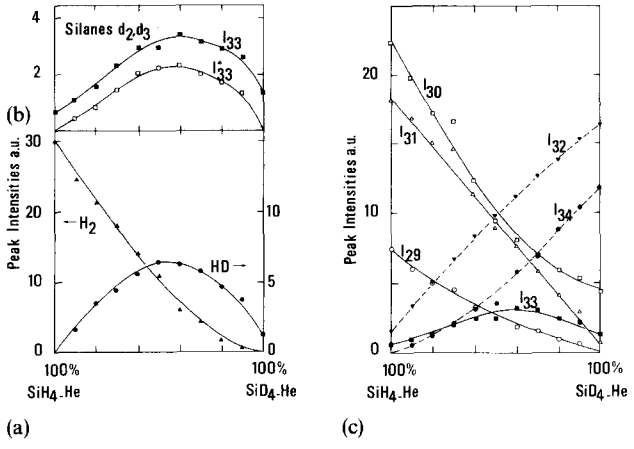

Fig. 2. Evolution of the peaks at $m/e = 2$, 3 and 29–34 as a function of the initial gas phase composition in an SiH_4–SiD_4–He discharge (flow rate, 42 cm^3 min^{-1}; pressure, 1 Torr; r.f. power, 5 W).

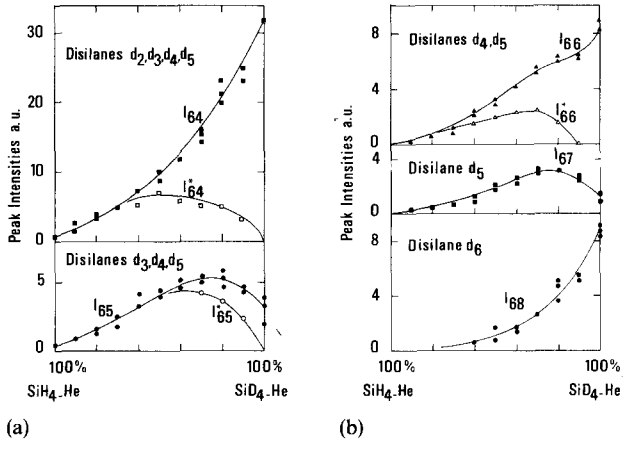

Fig. 3. Variations in the peaks at $m/e = 64$–68 as a function of the initial gas phase composition in an SiH_4–SiD_4–He discharge, where I^* are corrected intensities (see text) (flow rate, 42 cm^3 min^{-1}; pressure, 1 Torr; r.f. power, 5 W).

TABLE I
FRAGMENTATION PATTERN[a] OF SiH_4 AND SiD_4

m/e	*Relative intensity*	
	From SiH_4	*From SiD_4*
28	20	20
29	24	1
30	100	21
31	77	2
32		100
33		5
34		71

[a] For an electron energy of 90 eV.

From the results of Figs. 2(b) and 2(c) we can conclude that silane-d_2 and silane-d_3 are formed in the discharge. The other peaks are obscured by mass interferences and it is not possible to detect the presence of SiH_3D. However, for reasons of symmetry with silane-d_3 it is reasonable to suppose that SiH_3D is also formed.

The formation of silane-d_1, -d_2 and -d_3 in the SiH_4–SiD_4–He discharge is attributed to the recombination (7), disproportionation (8) and displacement (9) reactions[8,11,12]

$$D + SiH_3 \rightarrow SiH_3D \qquad \Delta H = -4.14\,\text{eV} \tag{7}$$

$$SiH_3 + SiD_3 \rightarrow SiH_mD_{4-m} + SiH_nD_{2-n} \qquad \Delta H = 1.57\,\text{eV} \tag{8}$$

$$D + SiH_3 \rightarrow SiH_2D + H \qquad \Delta H \approx 0 \tag{9}$$

The formation of the SiH_2D and $SiHD_2$ radicals followed by reaction (7) is a possible route for the formation of silane-d_2.

The intensity of peak 33 relative to peaks 30 and 31 shows that silane-d_2 and -d_3 account for at least 10% of the silane present in the discharge under the conditions of Fig. 2(c). The existence of such silanes implies the formation in the discharge of the partially deuterated radicals SiHD, SiH_2D and $SiHD_2$.

Figure 3 gives the evolution of the peaks between 64 and 68 a.m.u., the parent molecules of which are the deuterodisilanes $Si_2H_{6-n}D_n$. The fragmentation spectra of Si_2H_6 and Si_2D_6 are reported in Table II. A discrepancy with the values of Ring[13] is observed at masses 62 and 68 and this is attributed to the use of different mass spectrometers. We were therefore not able to use the fragmentation pattern of the partially deuterodisilanes given by Ring[13] to determine the exact amounts of the various disilanes. The peak at $m/e = 68$ arises solely from Si_2D_6, apart from silicon isotopes. The contribution of Si_2D_6 to masses 64–67 have been subtracted and the resulting intensities are denoted by I^*. An estimate of the proportions of disilane-d_2, -d_3, -d_4 and -d_5 based on the corrected intensities and the data of Ring[13] showed that all these disilanes are present in the discharge. A comparison of I^*_{65} and I^*_{66} shows that the presence of disilane-d_3 is certain. These results differ somewhat from those from silane photochemistry[12,13], in which no formation of disilane-d_3 is observed, but they are in agreement with those of Ring[13] for a silent electric discharge in SiH_4–SiD_4 at a pressure of 10 Torr.

TABLE II
FRAGMENTATION PATTERN OF Si_2H_6 AND Si_2D_6

m/e	*Relative intensity from Si_2H_6*		*Relative intensity from Si_2D_6*	
	This work	*Ref. 13*	*This work*	*Ref. 13*
56	21.3	24.6	19.2	23.2
57	33.5	35.6	0	3.4
58	74.6	69.9	32.5	36.2
59	32.6	40.1	4.9	4.7
60	100	100	80.5	79.6
61	40.5	44.4	7.0	11.2
62	33.9	55.9	23.0	24.4
63	7.1	9.5	7.9	3.2
64	2.5	5.2	100	100
65			9.7	13.8
66			24.3	33.0
67			3.2	4.7
68			24.7	60.6

Reactions (5) and (6) between partially deuterated radicals and molecules obtained through reactions (7)–(9) may explain the appearance of these disilanes. In particular the formation of disilane-d_5 implies such reactions as

$$SiHD + SiD_4 \rightarrow Si_2HD_5 \tag{10}$$

$$SiD_2 + SiHD_3 \rightarrow Si_2HD_5 \tag{11}$$

Thus from the results of Figs. 2 and 3 we can conclude that partially deuterated silanes and radicals are present in the discharge.

A similar evolution is observed when the pressure is 0.15 Torr instead of 1 Torr. An increase in the pressure does not greatly modify the repartition of the various peak intensities. Only a slight increase in the intensities of the peaks at $m/e = 33, 67$ and 68 is observed. The variation of the input power between 2 and 20 W has no marked effects on the repartition of the intensities at $m/e = 30$–34 and 64–68.

In contrast, increasing the residence time t_R of the molecules from 1 to 5 s results in an increase from 0.6 to 1 in the ratio I_{33}/I_{34} for an equimolar SiH_4–SiD_4 mixture. Thus the scrambling characterized by the formation of silane-d_2 and -d_3 is favoured by the low flow rates.

3.2. *Discharge in SiH_4–H_2–D_2*

Figure 4 shows that the addition of hydrogen to the SiH_4–He mixture results in a twofold increase in the disilane concentration in the discharge. It has also been observed that the presence of hydrogen promoted the formation of powder in the reactor. The increase in the disilane concentration occurs because of the abstraction reaction[8,12]

$$H + SiH_4 \rightarrow SiH_3 + H_2 \qquad \Delta H = -0.39\ \text{eV} \tag{12}$$

This reaction (rate constant $k_v = 4.6 \times 10^{-13}$ cm^{-3} molecule^{-1} s^{-1}) always occurs in an SiH_4 discharge owing to the atomic hydrogen produced by the dissociation of silane. However, in the SiH_4–H_2 mixture the amount of atomic hydrogen is much

greater and this increases the production of SiH_3 radicals which in turn lead to the formation of Si_2H_6 through reaction (5).

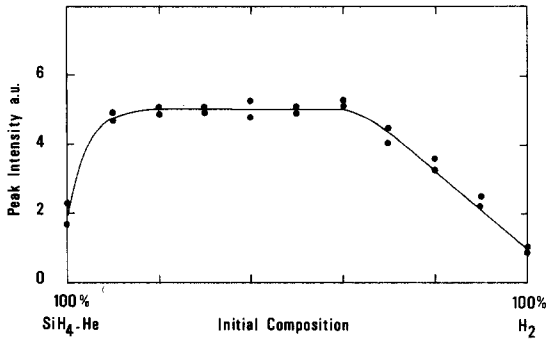

Fig. 4. Relative evolution of the neutral disilane concentration in an SiH_4–He–H_2 discharge as a function of the initial gas phase composition (Si_2H_6, m/e = 60) (flow rate, 42 cm^3 min^{-1}; pressure, 1 Torr; r.f. power, 10 W).

The reactions of deuteration of the silane in the SiH_4–H_2–D_2 discharge are illustrated in Fig. 5. The amounts of silane-d_1, -d_2, -d_3 and -d_4 (masses 32–34) increase gradually with the D_2 concentration. Such a deuteration occurs through reactions (7)–(9). In particular for the conditions of Fig. 5(a) the peak I_{32} in the SiH_4–D_2 mixture, which arises from all the deuterated silanes (d_1 to d_4), corresponds to 40% of the peak I_{30} in the SiH_4–H_2 mixture. Thus, under our experimental conditions at least 20% of the Si—H bonds of the silane present in the discharge were rebuilt.

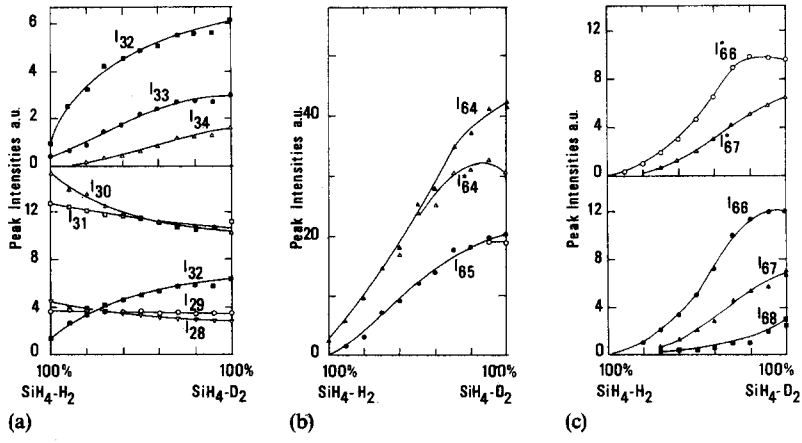

Fig. 5. Evolution of the peaks at m/e = 28–34 and 64–68 as a function of the initial gas phase composition in an SiH_4–H_2–D_2 discharge (flow rate, 42 cm^3 min^{-1}; pressure, 1 Torr; r.f. power, 15 W).

Figure 6 illustrates the influence of the pressure, the r.f. power and the flow rate on the deuteration of the silane. This deuteration is much more sensitive to these parameters than was the case for the SiH_4–SiD_4–He mixture.

It should be noted that long residence times (4.5 s) markedly increase the amount of SiD_4 formed ($m/e = 34$). A similar evolution has been observed for the disilane.

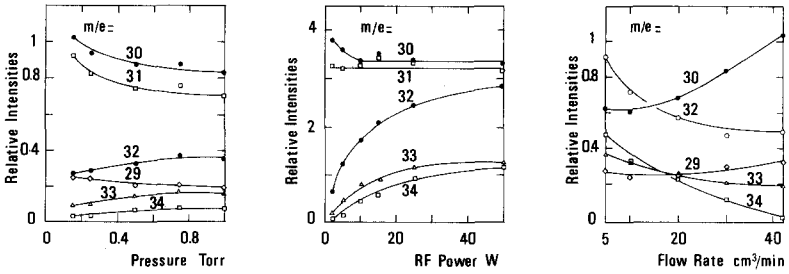

Fig. 6. Relative evolution of the intensity of peaks at $m/e = 29$–34 as a function of the discharge parameters in an SiH_4–D_2 mixture: (a) pressure dependence of peaks (relative to the peak at mass 30 in an SiH_4–H_2 discharge) (flow rate, 42 $cm^3\ min^{-1}$; r.f. power, 10 W); (b) power dependence of the peaks (relative to the peak at mass 29) (flow rate, 42 $cm^3\ min^{-1}$; pressure, 1 Torr); (c) flow rate dependence of the peaks (relative to the peak at mass 30 in an SiH_4–H_2 discharge) (pressure, 1 Torr; r.f. power, 10 W).

3.3. *Etching of a-Si:H films in an H_2 (D_2) plasma*

In a previous paper[3] it has been shown that the atomic hydrogen produced in an H_2 plasma reacts with a freshly deposited a-Si:H film. Figure 7(a) shows the evolution of the partial pressure of the neutral SiH_4 released in these conditions. The molar fraction of SiH_4 is about 2‰ for an H_2 pressure between 0.15 to 1 Torr. With a deuterium plasma the silane formed is completely deuterated (Figs. 7(b) and 7(c)). We also observed the formation of Si_2D_6, the evolution of which as a function of flow rate and r.f. power is similar to that of SiD_4. The hydrogen contained in an

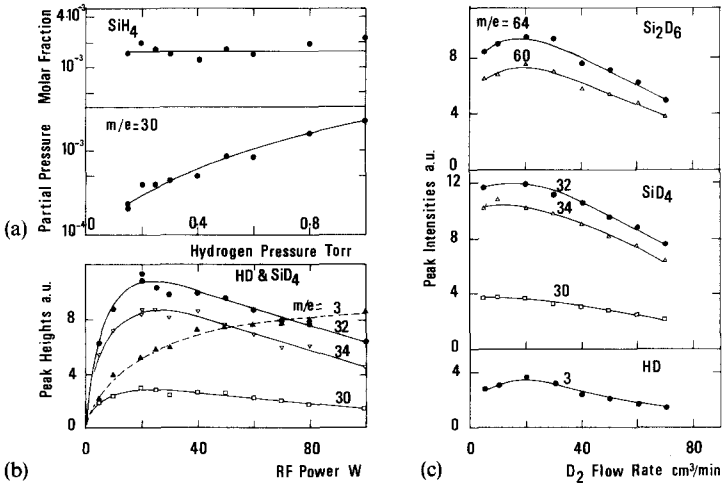

Fig. 7. Neutral molecules released during the etching of an a-Si:H film in an $H_2(D_2)$ plasma: (a) partial pressure of SiH_4 as a function of H_2 pressure (flow rate, 42 $cm^3\ min^{-1}$; r.f. power, 20 W); (b) relative variations in HD and SiD_4 as a function of the r.f. power (flow rate, 42 $cm^3\ min^{-1}$; pressure, 1 Torr); (c) relative evolution of HD, SiD_4 and Si_2D_6 as a function of the flow rate (pressure, 1 Torr; r.f. power, 20 W).

a-Si:H film is released as an HD molecule according to the reaction

$$yD + SiH_x(\text{film}) \rightarrow SiD_4 + HD \tag{13}$$

Similar results have been obtained by Niki and Mains[14] and Austin and Lampe[12] in silane photosensitization experiments. These authors observed that SiH_4 is released from an SiH_x polymer exposed to atomic hydrogen created by the irradiation of an H_2–Hg mixture. We thus consider that the results of Fig. 7 show that hydrogen atoms produced in an H_2 discharge etch the a-Si:H film.

The SiH_4 flux can be expressed by the relation

$$Q_{SiH_4} = \tfrac{1}{16} N_H \varepsilon \bar{v} A \tag{III}$$

where N_H is the hydrogen atoms concentration in the discharge, ε the etching probability, $\bar{v}$ the mean thermal velocity of hydrogen atoms and A the film area subjected to the discharge. Relation (III) together with relation (I) shows that the evolution of the SiD_4 concentration as a function of the power and the flow rate (Figs. 7(b) and 7(c)) is the result of a competition between the etch rate and the silane decomposition rate.

The silane resulting from the plasma etching is allowed to form a deposit again elsewhere depending on the flow rate and power conditions in the discharge. Webb and Vepřek[15] have reported that in a d.c. discharge in H_2 the chemical transport of silicon occurs with the formation of a polycrystalline silicon film containing 4–6% H.

The question is now to evaluate the importance of this etching of an a-Si:H film by the hydrogen atoms in an SiH_4 discharge during the growth of the film. The partial pressure of SiH_4 in an interacting H_2 plasma represents about 6% of the pressure of undissociated silane in an SiH_4–H_2 discharge for the same conditions (*i.e.* r.f. power, 20 W; flow rate, 42 $cm^3\ min^{-1}$; pressure, 0.15 Torr). Under these conditions the reaction probability ε of the hydrogen atoms with the film is about 10^{-4}.

Figure 8 shows that the gradual substitution of SiH_4–He by D_2 leads to the enhancement of peaks I_{32} and I_{34} of SiD_4 and I_{64} and I_{68} of Si_2D_6. The SiD_4 formed in the plasma may reach 50% of the undissociated SiH_4 in the SiH_4–He discharge.

These results show that the observed deuteration in the SiH_4–D_2 mixture (Figs. 5 and 6, $m/e = 34$) may result in part from an etching of the growing film, especially for low flow rates.

3.4. Ions in the SiH_4–H_2–D_2 discharge

The various Si_1 ions detected in the SiH_4–H_2–D_2 discharge are reported in Table III. Their relative distribution is given on Fig. 9(a). When D_2 is gradually substituted for H_2, the intensity level of the ion at 31 a.m.u. (SiH_3^+) decreases from 0.75 to 0.5. This decrease is accompanied by the formation of ions at $m/e = 32$ and 33. The constancy of the sum of ions at $m/e = 31$–34 as a function of the gas composition leads us to attribute the signals at masses 32 and 33 to SiH_2D^+ and $SiHD_2^+$ respectively.

Figure 9(c) illustrates the variations in the peak intensity of SiH_3^+ (mass 31) and in the peak intensities of masses 32 and 33 with the addition of D_2 to the SiH_4–He

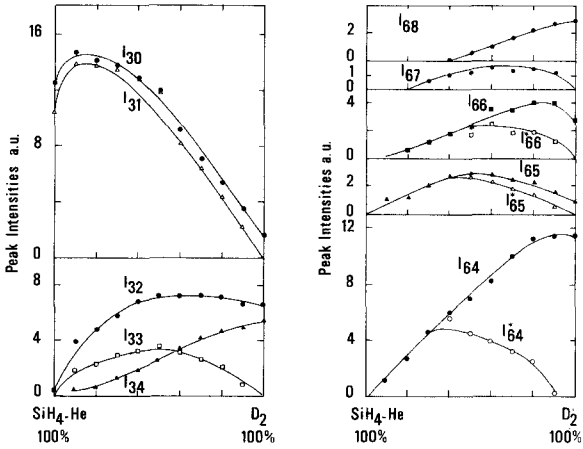

Fig. 8. Variations in the intensities of the peaks at $m/e = 30$–34 and 64–68 as a function of the initial gas phase composition in an SiH_4–He–D_2 discharge (flow rate, 42 $cm^3\ min^{-1}$; pressure, 1 Torr; r.f. power, 10 W).

TABLE III
Si_1 IONS IN THE SiH_4–H_2–D_2 DISCHARGE

m/e	*Ions*
28	Si^+
29	SiH^+
30	SiH_2^+, SiD^+
31	SiH_3^+, $SiHD^+$
32	SiH_2D^+, SiD_2^+
33	$SiHD_2^+$
34	SiD_3^+

mixture. Following Allen *et al.*[16] the two major ion–molecule reactions are

$$D_2^+ + SiH_4 \rightarrow SiH_3^+ + D_2 + H \qquad \sigma = 34\ Å^2 \tag{14}$$

$$D_3^+ + SiH_4 \rightarrow SiH_3^+ + D + HD \qquad \sigma = 34\ Å^2 \tag{15}$$

These reactions account for the slight increase in SiH_3^+ in Fig. 9(c) for a 20–30% D_2 concentration in the gas mixture. The reactions leading to the formation of the partially deuterated ions SiH_2D^+ and $SiHD_2^+$ have very low cross sections ($\sigma < 1$ Å^2). Examination of Fig. 9(c) also indicates that SiH_2D^+ and $SiHD_2^+$ account for the difference between mass 31 in Figs. 9(b) and 9(c). It is believed that these ions at $m/e = 32$ and 33 arise in the main part from the ionization of silane-d_1, -d_2 and -d_3, this initial step being followed by the ion–molecule reaction (4).

Thus the rise of the SiH_3^+ level in the SiH_4–H_2 discharge relative to its level in the SiH_4–He discharge reported in a previous paper[3] is partly due to the ion–molecule reactions (14) and (15) and partly due to reaction (4), which is promoted in the SiH_4–H_2 mixture owing to the increase in the concentration of undissociated silane. The product of reaction (4) appears in the SiH_4–D_2 mixture as the SiH_2D^+ and $SiHD_2^+$ ions.

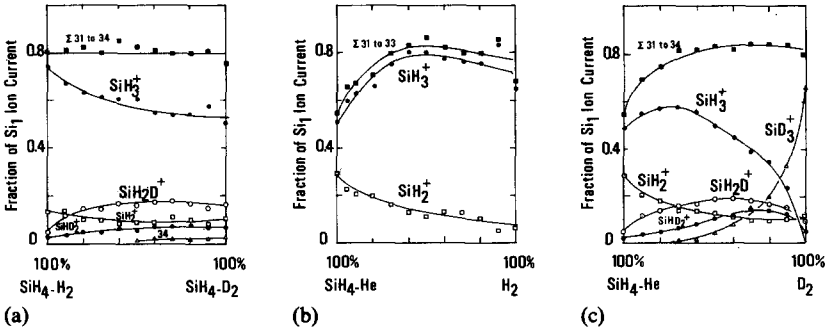

Fig. 9. Relative Si_1 ion intensities as a function of the initial gas phase composition (flow rate, 42 cm^3 min^{-1}; pressure, 0.15 Torr): (a) in an SiH_4–H_2–D_2 discharge (r.f. power, 20 W); (b) in an SiH_4–He–H_2 discharge (r.f. power, 25 W); (c) in an SiH_4–He–D_2 discharge (r.f. power, 25 W).

3.5. Formation mechanisms of a-Si:H films

The a-Si:H(D) films were analysed by IR spectroscopy using the classical technique[3]. Films were deposited in an SiH_4–He–D_2 mixture in a reactor which has previously been described[17]. The band assignments after Knights *et al.*[18] and Freeman and Paul[19] are given in Table IV.

TABLE IV
ASSIGNMENTS FOR IR ABSORPTION BANDS IN AN a-Si:H(D) FILM

Frequency (cm^{-1})	*Mode*	*Groups*
790	Bending	SiHD
845	Wagging	$(SiH_2)_n$
880	Bending	SiH_2
1460	SiD stretching	SiD
1525	SiD stretching	SiD_2, SiHD
2000	SiH stretching	SiH
2090	SiH stretching	SiH_2, SiHD

Figure 10 is a typical spectrum of an a-Si:H(D) film. Figure 11(a) presents the results obtained as a function of the applied power. The amount of incorporated deuterium increases and then saturates. The SiH_2, SiHD, $SiHD_2$ and $(SiH_2)_n$ bands increase gradually as the power is increased.

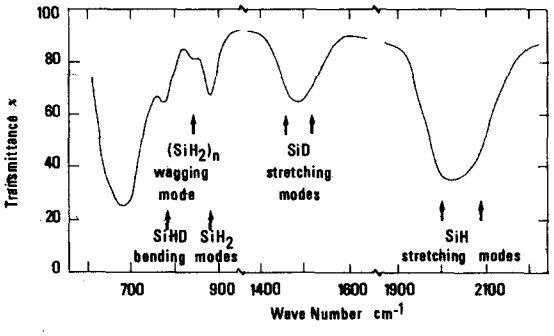

Fig. 10. IR vibrational spectra of an a-Si:H(D) film deposited in an SiH_4–He–D_2 discharge.

The flow rate effect is reported in Fig. 11(b). The deuterium incorporation increases for long residence times. As stated by Turban *et al.*[3], SiH_2, SiHD and SiD_2 bonds are favoured by the low flow rates. It is observed that SiHD and SiD_2 groups are formed in preference to SiH_2. These results are to be compared with those of a recent study[20] concerning the emission spectroscopy of an SiH_4–Ar discharge, in which a correlation has been found between the hydrogen atom concentration in the plasma and the number of SiH_2 groups in the film.

Figure 11(c) illustrates the influence of the pressure. The amount of incorporated deuterium is slightly sensitive to the pressure. The SiH_2, SiHD and SiD_2 groups are favoured at low and high pressures.

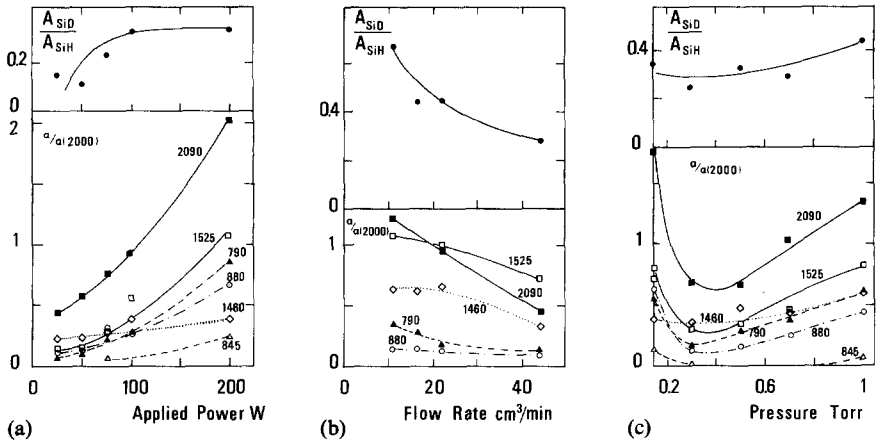

Fig. 11. Ratios of the integrated absorptions A and the peak absorption coefficients α in a-Si:H(D) films deposited from an SiH_4–He–D_2 discharge: (a) as a function of the applied power (flow rate, 42 cm^3 min^{-1}; pressure, 0.15 Torr; deuterium concentration, 5%; substrate temperature, 140 °C); (b) as a function of the flow rate (pressure, 0.15 Torr; r.f. power, 25 W; deuterium concentration, 10%; substrate temperature, 25 °C); (c) as a function of the total pressure (flow rate, 42 cm^3 min^{-1}; r.f. power, 100 W; deuterium concentration, 5%; substrate temperature, 100 °C).

It has been observed that the substrate temperature does not affect the ratio A_{SiD}/A_{SiH} of the integrated absorptions of the stretching vibrations of SiD and SiH. A variation between 5 and 20% in the percentage of D_2 in the SiH_4–He–D_2 mixture involves a change in this ratio of 0.12–0.58. For the same conditions in a 5%SiH_4–D_2 mixture this ratio is 0.56.

A comparison of the gas phase deuteration and of the film deuteration requires a knowledge of the ratio $N_{SiD}/(N_{SiH}+N_{SiD})$ of the number of Si—D bonds to the total number of SiH and SiD bonds. To account for the effect of deuteration on the absorption strength the integrated absorption A_{SiD} must be multiplied by 2. For a film deposited in an r.f. diode reactor in an SiH_4–D_2 mixture (r.f. power, 15 W; flow rate, 22 cm^3 min^{-1}; pressure, 0.15 Torr) this ratio is 0.6. In the same conditions for the gas phase this ratio, calculated from all the deuterated silanes ($m/e = 32$) relative to the total amount of silane, is at most 0.2. This is a rough estimate because we do not know the fragmentation pattern of the partially deuterated silanes. If we assume that the deuteration of the SiH_3 and SiH_2 radicals is similar to that of the silane, we may infer that only some of the Si—D bonds in the films result from these

deuterated radicals. The remainder of the Si—D bonds formed arise from the incorporation of atomic deuterium in the growing film according to the reaction

$$yD + SiH_x(\text{film}) \rightarrow SiH_xD_y(\text{film}) \tag{16}$$

Investigations of the hydrogenation of evaporated silicon[21] and of the rehydrogenation of amorphous silicon[22] have shown that it is possible to incorporate up to 4% H into a film heated to 500 °C and exposed to a hydrogen plasma.

A picture of the deposition mechanism may then be proposed to state more precisely the assumptions of a previous study[2]. The SiH_2 and SiH_3 radicals are generated by electron impact on the silane (reactions (1)–(3)), by ion–molecule reactions (reaction (4)) and by abstraction (reaction (12)). They then diffuse through the gas towards the wall of the reactor. The sticking coefficient for these radicals is unknown but according to Winters[23], it can be assumed to be reasonably large but not unity. These radicals thus have a sufficient lifetime to interact with one another (reactions (5) and (6)) or with atomic hydrogen (reactions (7) and (9)) and to generate new radicals, silane and disilane. The radicals chemisorbed at the surface of the growing film are incorporated after a partial dissociation according to reactions

$$SiH_2 \xrightarrow{W} SiH_x(\text{solid}) + (1 - 0.5x)H_2 \tag{17}$$

$$SiH_3 \xrightarrow{W} SiH_x(\text{solid}) + (1.5 - 0.5x)H_2 \tag{18}$$

The dissociation of the chemisorbed radicals may be promoted by ion bombardment[23]. Such a process would explain the small number of $(SiH_2)_n$ groups observed by Knights *et al.*[24] in cathodic films.

During the growth of the film the atomic hydrogen of the plasma can either be incorporated in the film (reaction (16)) or etch the film (reaction (13)). It is manifest that long residence times and high discharge powers promote the breaking and rearrangements of bonds, and these processes increase the number of SiH_2 groups in the film.

4. CONCLUSIONS

The principal results obtained may be summarized as follows.

(1) The presence of Si_2H_6 in the SiH_4–He and SiH_4–H_2 discharges is indirect evidence for the presence of SiH_2 and SiH_3 radicals in these discharges.

(2) The occurrence of radical–radical, atom–molecule and atom–radical reactions accounts for the formation of the partially deuterated silane observed in the SiH_4–SiD_4–He discharge. All the deuterodisilanes $Si_2H_{6-n}D_n$ are observed in the discharge which involves a set of mixed secondary reactions between radicals and molecules.

(3) The atomic deuterium etches the a-Si:H film to form fully deuterated silane SiD_4 and HD.

(4) The Si—D bonds formed in the film result in part from the deuterated monosilane radicals and molecules generated in the discharge and in part from the direct incorporation of the deuterium atoms in the growing film.

(5) These results support a deposition mechanism which involves the SiH_2 and SiH_3 radicals. The variety of reactions in the gas phase and on the surface implies

that the SiH and SiH_2 groups formed in the film are not correlated straightforwardly with the radicals produced by the decomposition of SiH_4.

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