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MASS SPECTROMETRY OF A SILANE GLOW DISCHARGE DURING PLASMA DEPOSITION OF a-Si:H FILMS

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We undertook a mass spectrometric investigation of the ionic and neutral species present during the deposition of a-Si:H using an r.f. glow discharge in silane (mixed with helium or hydrogen). A correlation between the neutral composition of the plasma and the nature of the IR vibrational modes in the deposited film is proposed. The ionic species extracted from the silane discharge are not characteristic of the direct ionization of SiH_4. The predominance of the SiH_3^+ ion is attributed to the ion–molecule reaction

$$SiH_2^+ + SiH_4 \longrightarrow SiH_3^+ + SiH_3$$

Secondary ions $Si_2H_n^+$ ($n = 1$–7) are also observed. Mass spectrometry of the ionic species resulting from the interaction of a hydrogen plasma with the a-Si:H film suggests that atomic hydrogen plays an active role during the growth of the film.

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1. INTRODUCTION

Recent studies[1–7] concerning the deposition of a-Si:H films by the glow discharge decomposition of SiH_4 have shown that there must be a correlation, which has not yet been explained, between the kinetics of the discharge and the properties of the films. Until now this correlation has been rather empirical because attention has mainly been drawn to the properties of the films in view of the potential applications of thin film a-Si solar cells.

We have begun to study in more detail the reaction mechanisms involved in the silane glow discharge process[8]. In this paper we report some new results dealing with the mass spectrometric sampling of the glow discharge during the deposition process. Particular attention was paid to the effects of power, pressure, flow rate and gas composition of the neutral and ionic species present in the plasma. The purpose of these measurements was to provide some insights into the numerous reactions occurring in the silane glow discharge.

2. EXPERIMENTAL

2.1. *Plasma reactor*

The experimental apparatus used in this work is illustrated in Fig. 1. The plasma reactor consists of a glass tube 70 mm in diameter and 400 mm long with two parallel internal electrodes 5 cm apart and of length 15 cm. The 13.56 MHz r.f. power is capacitatively coupled into the plasma via the upper electrode C and an L-section matching network. The lower electrode A is held at ground potential and is the substrate holder. With this small interelectrode spacing, the glow discharge established between the electrodes is of the obstructed type. The r.f. power coupled into the system was measured by a conventional wattmeter and was varied from 2.5 to 50 W. Since one electrode is grounded the system is asymmetric. As a result the excitation electrode C self biases to a negative potential of 20–300 V depending on the power. The gas mixture used was 5% SiH_4 in either helium, hydrogen or argon. The pressure was measured using a Baratron capacitance manometer. Pressure variations were achieved by throttling the vacuum pump. The flow rate of the gas mixture was monitored by a rotameter and controlled by a needle valve. In these experiments the range of variations of these two parameters was 0.05–0.5 Torr for the total pressure and 4–42 standard cm^3 min^{-1} for the flow rate. In these conditions the residence time for species is in the range 0.1–1 s.

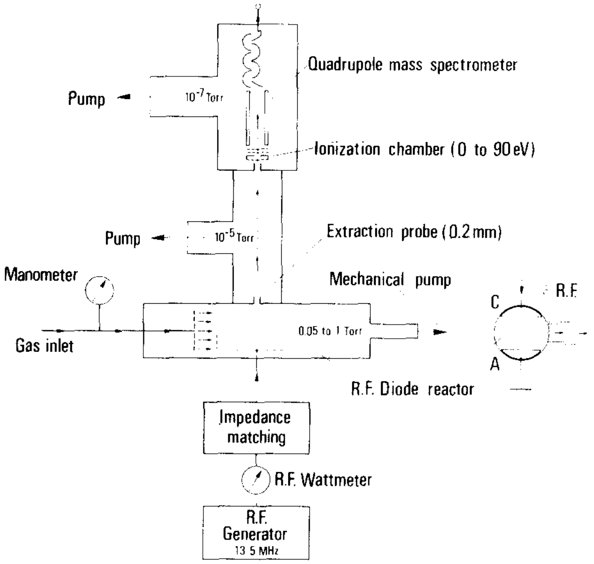


Fig. 1. The experimental set-up for the mass spectrometric study.

2.2. *Mass spectrometric sampling*

The ionic and neutral species present in the discharge were studied by means of a Balzers quadrupole spectrometer, model QMG 311. The mass filter is located in the second stage of a differential pumping system. The first stage is pumped by a 150 l s^{-1} diffusion pump (Edwards) and the second stage by a 300 l s^{-1} diffusion pump (Edwards). The sampling orifice is a hole of diameter 200 μm which was perforated in a ceramic cylinder. Such a dielectric material was chosen in order to avoid any possible spurious discharges which sometimes occur with metallic sampling in an r.f. plasma. In this way it is believed that the sampled species are a correct picture of those which impinge on the reactor wall. In the mass spectrometric experiments the gas inlet is located 15 mm upstream of the sampling orifice so as to obtain a sufficient signal in the spectrometer.

When neutrals were measured the positive ions were magnetically deflected out of the intermediate chamber and a conventional electron impact ionization source was used after this chamber (90 eV). For ionic measurements the positive ions were directly extracted from the glow discharge and effused without special focusing to avoid, as far as possible, further reactions in the sheath around the orifice. In this case the ionization chamber of the mass filter was switched off.

3. IR VIBRATIONAL PROPERTIES OF THE FILM

3.1. *Measurements*

Our primary interest in this section is the relationship between the deposition parameters and the IR spectra of the film. These measurements were made to clarify the kinetic conditions of the discharge which determine the presence of SiH groups or SiH_2 groups in the film. Samples were deposited at room temperature on $\langle 111 \rangle$ n-doped monocrystalline silicon wafers of resistivity 150–250 Ω cm. The IR transmission spectra were performed with a double-beam spectrophotometer.

The spectra display modes attributed to SiH groups and SiH_2 groups[2,6,7]. Special attention was focused on the stretching band region, namely 2000–2100 cm^{-1}. In general we observed an absorption doublet in this region. This doublet was deconvoluted into two components centred at 2000 and 2090 cm^{-1} using symmetric line shapes. To estimate the relative concentration of SiH groups to SiH_2 groups the product of the maximum absorbance and the bandwidth at half absorbance was taken as an approximation of the integrated intensity of each band.

3.2. *Results*

We investigated two parameters which are known to be very important in plasma chemical vapour deposition, namely the flow rate and the r.f. power. In Fig. 2 the $[SiH]/([SiH]+[SiH_2])$ ratio is plotted as a function of the axial position of the substrate on the grounded electrode for various flow rates and powers. The most significant effect is the increasing concentration of SiH groups relative to SiH_2 groups when the flow rate is increased from 4 to 42 $cm^3\ min^{-1}$. Another interesting feature is the decrease in the SiH group concentration with increasing power for a constant flow rate. Finally it is observed that, for a set of parameter values, the SiH units are always more abundant near the point of silane injection than far from it. The same behaviour was found with films deposited on the excitation electrode (cathodic films).

4. MASS SPECTROMETRY OF THE NEUTRAL SPECIES

4.1. *Neutral radicals*

In a previous paper[8] we have developed a kinetic model of the silane discharge. The proposed mechanism for the glow discharge deposition process is as follows.

(1) The silane is decomposed in the gas phase by inelastic collisions between the free electrons of the plasma and the molecules.

(2) This decomposition, as recognized in molecular glow discharges, provides many more neutral fragments than ionic fragments.

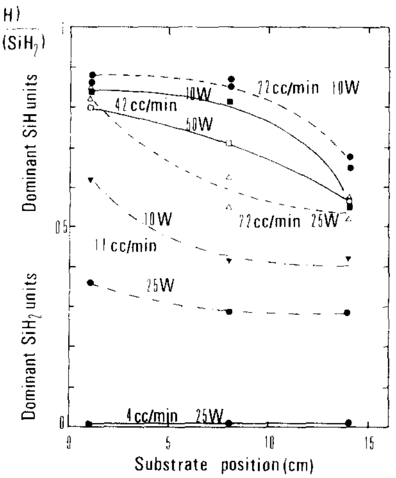


Fig. 2. The $[SiH]/([SiH]+[SiH_2])$ ratio from integrated IR absorptions as a function of the substrate position: —■—, $Q = 42$ cm^3 min^{-1}, $W = 10$ W; --□—, $Q = 42$ cm^3 min^{-1}, $W = 50$ W; -- ○ --, $Q = 22$ cm^3 min^{-1}, $W = 10$ W; -- △ --, $Q = 22$ cm^3 min^{-1}, $W = 25$ W; ·–▼–·, $Q = 11$ cm^3 min^{-1}, $W = 10$ W; ·–●–·, $Q = 11$ cm^3 min^{-1}, $W = 25$ W; —●—, $Q = 4$ cm^3 min^{-1}, $W = 25$ W. Deposition conditions: SiH_4–He mixture, $p = 0.15$ Torr, room temperature.

(3) These neutral fragments (SiH_n free radicals) diffuse towards the wall.
(4) The polymerization occurs mainly on the surface.

The deposition rate calculated with such a model agrees with the experimental rate. Nevertheless this approach did not consider the detailed mechanism responsible for the different properties of the film. To obtain some direct insights we have tried to detect free radicals by mass spectrometry. The literature on direct photolysis[9] and mercury-sensitized photolysis[10] of silane suggests mechanisms involving either SiH_3 or SiH_2 intermediates. Studies of the optical absorption spectra of discharges in SiH_4 (refs. 11–13) have provided evidence of SiH_2, SiH and Si species. A recent emission spectroscopy study of the SiH_4 glow discharge has reported the observation of the SiH radical[14].

The possible presence of such free radicals in the beam extracted from the discharge was checked by measuring the ion currents at 31 and 30 amu as a function of the electron impact ionization energy (8–90 eV). In theory it should be possible to detect radicals by using electron energies slightly below the value required for the appearance potential (AP) but higher than the ionization potential (IP) of the radical (Table I). At these electron energies the ratio of the ion currents at masses 31 and 30 did not change appreciably with the plasma on or off. However, as a consequence

TABLE I

AP FOR IONS AND IP FOR RADICALS DERIVED FROM SiH_4

Ion	*AP* (eV)	*IP* (eV)
$SiH_3{}^+$	12.3	8.1
$SiH_2{}^+$	11.9	9.5
SiH^+	15.3	7.4
Si^+	13.6	8.15

of operating at such low electron energies, the effective sensitivity of the mass spectrometer is greatly decreased. Furthermore the high reactivity of free radicals makes them very sensitive to collisions with the walls of the sampling orifice and of the instrument. It is therefore difficult to draw conclusions from this negative experiment.

4.2. *Neutral molecules*

Figure 3 gives the dependence of the concentration of SiH_4 relative to its initial concentration as a function of power. Figures 3(a) and 3(b) illustrate the increasing decomposition of silane with power for various pressures and carrier gases. At low power levels (*e.g.* 5 W) up to 50% of the silane is undissociated. In contrast, at high power levels (50 W) up to 80% or more of the silane is decomposed at 1.5 cm of the gas inlet.

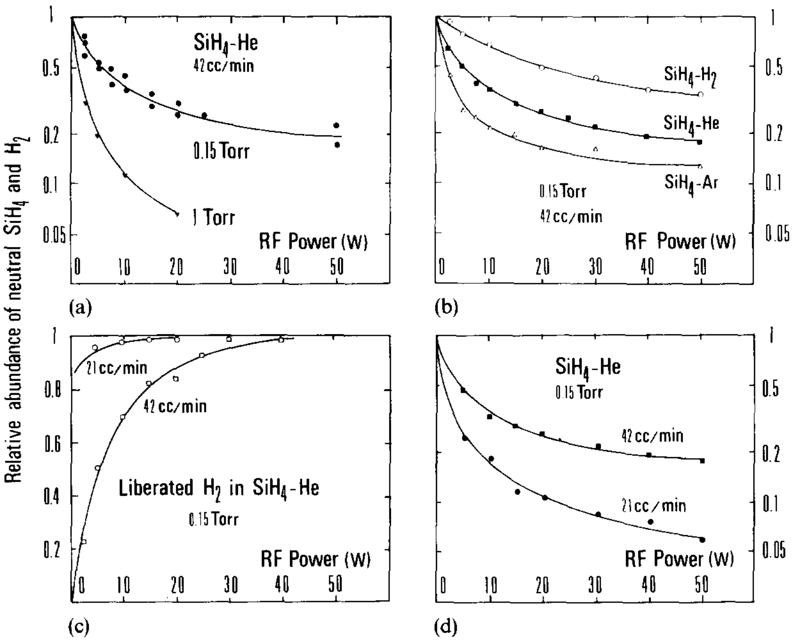


Fig. 3. Relative concentration of neutral molecules in a silane discharge as a function of power: a, b and d, concentration of SiH_4; c, concentration of H_2 released by silane decomposition.

Figure 3(c) illustrates the formation of molecular hydrogen due to the decomposition of silane. The silane discharge contains an increasing concentration of hydrogen as the silane decomposition increases.

Figure 3(d) shows the influence of two different flow rates on the partial pressure of silane. As expected, high flow rates result in a lower decomposition level of silane than low flow rates. From these measurements we can infer the following.

(1) A high power and a low flow rate mean that most, if not all, of the silane is decomposed in the reactor.

(2) A low power and a high flow rate means that undissociated silane remains in the plasma.

These observations and the IR measurements suggest the following correlation: a-Si:H films deposited from a plasma in which the silane is not entirely decomposed contain a majority of SiH units, while those deposited from a plasma in which the silane is strongly dissociated contain a majority of SiH_2 units. Street *et al.*[6] have obtained a similar correlation between the spin density of the a-Si:H films derived from electron spin resonance and the deposition regimes.

Neutral disilane Si_2H_6 was only observed at total pressures higher than about 1 Torr. It is therefore believed that free radical polymerization is not initiated in the gas phase at a pressure of 0.15 Torr.

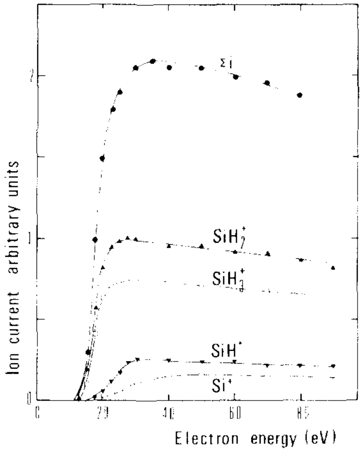
5. MASS SPECTROMETRY OF THE POSITIVE IONS

5.1. *Fragmentation pattern of SiH_4*

In view of the lack of data concerning the partial ionization cross sections of SiH_4 in the literature we have measured the fragmentation pattern of SiH_4 in the range 10–90 eV. The results are shown in Fig. 4. Comparison with ionization of C_2H_4 in the same apparatus gave an ionization current ratio for SiH_4 to C_2H_4 of 0.7 at 70 eV. From these measurements it is observed, in agreement with previous authors[15–18], that SiH_2^+ always predominates over SiH_3^+.

5.2. *Ionic spectra of the silane discharge*

Figure 5 shows typical mass spectra of the discharge ions in SiH_4–He and SiH_4–H_2 mixtures. Apart from 1–5 amu peaks the spectra display two ion groups: the Si_1 ions, Si^+, SiH^+, SiH_2^+ and SiH_3^+; the Si_2 ions, $Si_2H_n^+$ ($n = 1$–7). It is to be noted that some mass interferences may occur for $m/e = 28$ (N_2^+) and $m/e = 29$ (N_2H^+) owing to impurities when the output valve was strongly throttled.



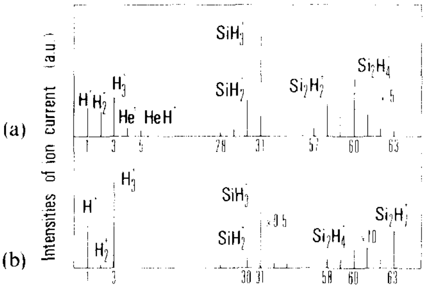


Fig. 4. The fragmentation pattern of SiH_4.

Fig. 5. Ionic spectra of the silane discharges ($W = 10$ W, $p = 0.15$ Torr, $Q = 42$ cm^3 min^{-1}): (a) in an SiH_4–He mixture; (b) in an SiH_4–H_2 mixture.

We studied the evolution of the Si_1 ionic abundance as a function of the three main deposition parameters: total pressure, r.f. power and flow rate. Figure 6 illustrates the pressure dependence of the Si_1 ions. The relative abundance of the observed Si_1 ions differs strongly from that observed in the direct ionization of silane. Except for very low pressures (0.05 Torr) the SiH_2^+ ion is never the most abundant. The evolution shown in Fig. 6 is quite similar to that observed in high pressure mass spectrometry experiments[19]. The predominance of the SiH_3^+ ion relative to the other Si_1 ions is attributed to the ion–molecule reaction

$$SiH_2^+ + SiH_4 \longrightarrow SiH_3^+ + SiH_3 \qquad (1)$$

At high flow rates (42 cm^3 min^{-1}) the SiH_3^+ level remains constant when the pressure is increased (*cf.* Fig. 11). We explain this behaviour as follows: as silane is in excess, reaction (1) is only limited by the formation of SiH_2^+. This explanation agrees with the neutral measurements (Section 4.2).

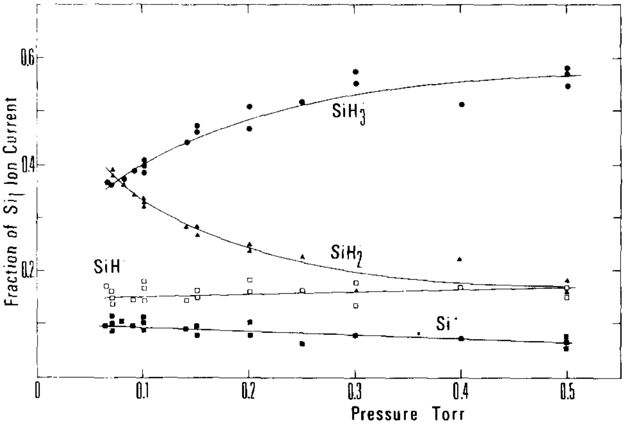


Fig. 6. Relative Si_1 ion intensities observed in an SiH_4–He discharge as a function of pressure (Q = 16 cm^3 min^{-1}, W = 10 W).

Figure 7 illustrates the effects of power on the relative Si_1 ion currents. An increase in the r.f. power results in a fall in the SiH_3^+ current relative to the SiH_2^+ current. This behaviour can be related to the depletion of silane at high power. Reaction (1) is then limited by the availability of silane.

Figure 8 shows the influence of the flow rate on the Si_1 ionic abundance. As noted in Section 4.2, a high flow rate implies a higher partial pressure of silane in the reactor. We therefore observe an increase in the SiH_3^+ ion current relative to the other Si_1 ions owing to reaction (1).

Figure 9 gives the dependences of Si_2 ion currents on the flow rate. Figure 10 illustrates the effects of pressure and power on the relative Si_2 ion currents. The evolution is consistent with that observed by Yu *et al.*[19]

$Si_2H_n^+$ ions are not the result of direct ionization of Si_2H_6 because disilane was not detected in this pressure range. The formation of these ions is attributed to the following ion–molecule reactions[19]:

$$SiH_2^+ + SiH_4 \longrightarrow Si_2H_4^+ + H_2 \qquad (2)$$

$$SiH_2^+ + SiH_4 \longrightarrow Si_2H_2^+ + 2H_2 \qquad (3)$$

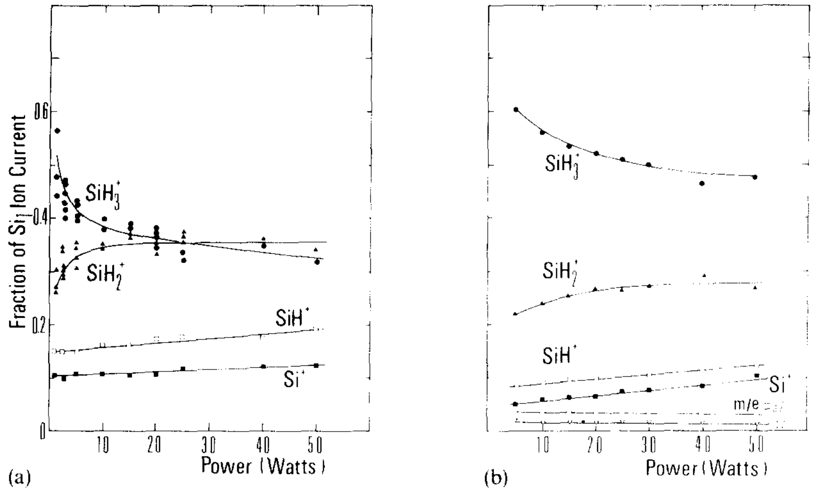
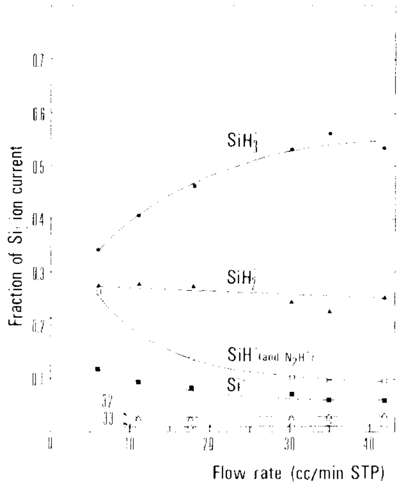


Fig. 7. Dependence of Si_1 ion currents on power in an SiH_4–He discharge: (a) $p = 0.07$ Torr, $Q = 16\ cm^3\ min^{-1}$; (b) $p = 0.15$ Torr, $Q = 42\ cm^3\ min^{-1}$.



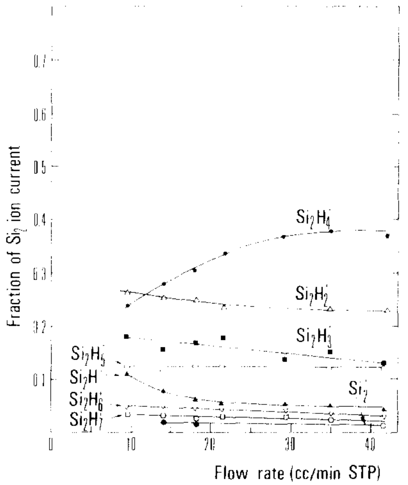


Fig. 8. Dependence of Si_1 ion currents on flow rate in an SiH_4–He discharge ($p = 0.15$ Torr, $W = 10$ W).

Fig. 9. Dependence of Si_2 ion currents on flow rate in an SiH_4–He discharge ($p = 0.15$ Torr, $W = 10$ W).

6. ROLE OF HYDROGEN

6.1. Mass spectrometric results in an SiH_4–H_2 discharge

We performed some experiments with an SiH_4–H_2 mixture. Figure 11 illustrates the evolution of the Si_1 ions as a function of total pressure. If a comparison is made with the Si_1 ions extracted from an SiH_4–He discharge (Fig. 6), it can be seen that both figures exhibit similar trends. However, under the same conditions (namely $42\ cm^3\ min^{-1}$, 0.15 Torr, 10 W) the relative abundance of $SiH_3{}^+$ is 0.65 in SiH_4–He compared with 0.8 in SiH_4–H_2. At the same time the abundance of $SiH_2{}^+$ is 0.2 in SiH_4–He compared with 0.1 in SiH_4–H_2.

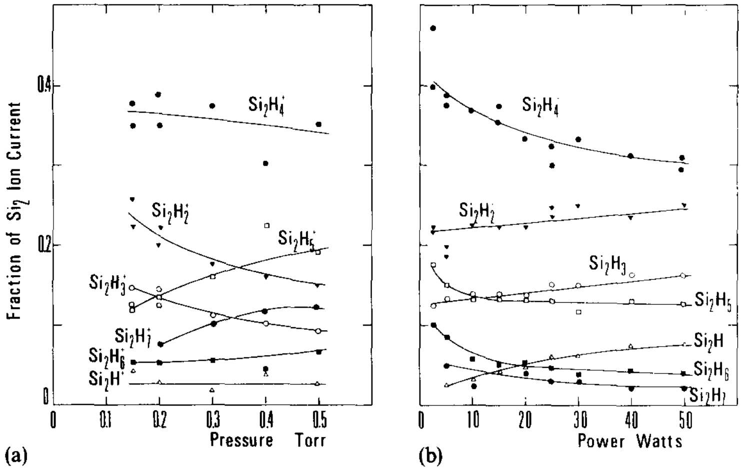
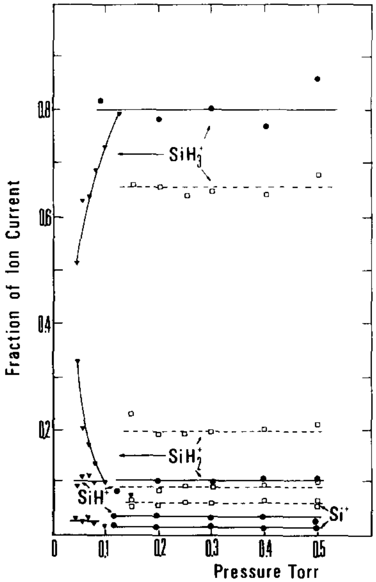


Fig. 10. Dependence of Si_2 ion currents on (a) pressure and (b) power in an SiH_4–He discharge ($Q = 42$ cm^3 min^{-1}, $W = 10$ W).



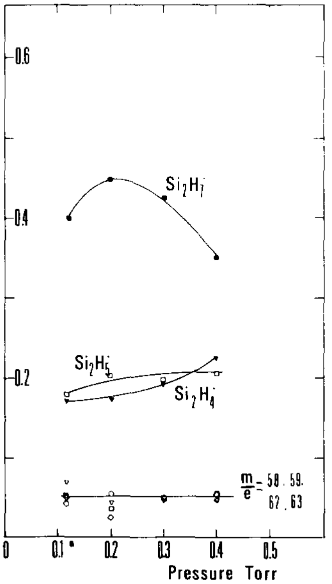


Fig. 11. Pressure dependence of Si_1 ion currents in SiH_4–H_2 and SiH_4–He discharges: ——, SiH_4–H_2 (●, $Q = 42$ cm^3 min^{-1}, $W = 10$ W; ▼, $Q = 8$ cm^3 min^{-1}, $W = 10$ W); —□—, SiH_4–He ($Q = 42$ cm^3 min^{-1}, $W = 10$ W).

Fig. 12. Relative Si_2 ion intensities observed in an SiH_4–H_2 discharge as a function of pressure.

Figure 12 shows the evolution of the Si_2 ion currents in an SiH_4–H_2 mixture as a function of pressure. Contrary to Fig. 10 the dominant secondary ion is not $Si_2H_4^+$ but $Si_2H_7^+$. We recall that in an SiH_4–H_2 mixture the silane is not as decomposed as in an SiH_4–He mixture. Therefore the partial pressure of silane is higher by a factor of 2 in SiH_4–H_2 than in SiH_4–He. As a result a third order ionic reaction can occur:

$$SiH_3^+ + 2SiH_4 \longrightarrow Si_2H_7^+ + SiH_4 \qquad (4)$$

In high pressure mass spectrometry[19] $Si_2H_7^+$ ions dominate at pressures higher than 0.12 Torr.

6.2. *Interaction of a hydrogen plasma with an a-Si:H film*

When the reactor walls and the electrodes were coated with an a-Si:H film that was freshly deposited at room temperature, the hydrogen discharge exhibited the ion spectrum shown in Figs. 13(c) and 13(d). Apart from the fact that the peak 29 cannot be ascribed only to the SiH^+ ion owing to ionic impurities such as N_2H^+, the spectrum displays without any doubt SiH_3^+ and $Si_2H_n^+$ ions. Attempts to detect neutral silane under these conditions failed, probably because in the spectrometer neutral detection is not as sensitive as ionic detection.

In the same reactor and with a helium discharge these ions were not observed (Fig. 13(a)). In the same way after exposure of the a-Si:H film to air the hydrogen discharge did not exhibit silane ions (Fig. 13(b)).

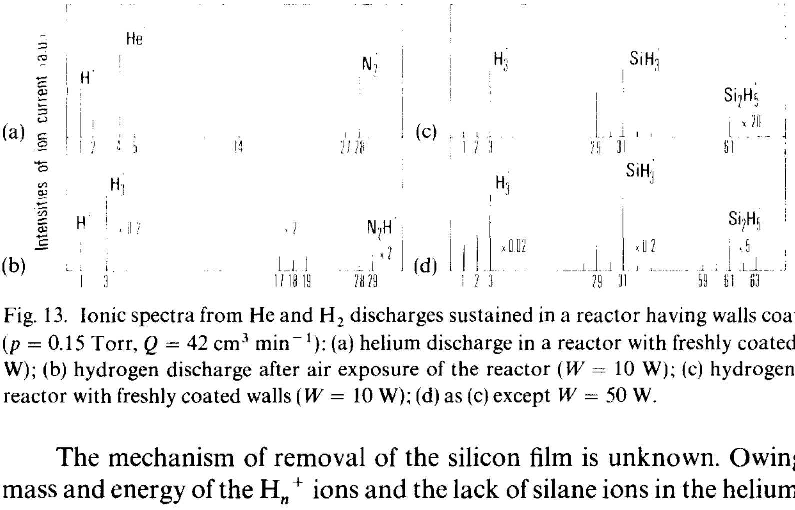


Fig. 13. Ionic spectra from He and H_2 discharges sustained in a reactor having walls coated with a:Si:H ($p = 0.15$ Torr, $Q = 42$ cm^3 min^{-1}): (a) helium discharge in a reactor with freshly coated walls ($W = 10$ W); (b) hydrogen discharge after air exposure of the reactor ($W = 10$ W); (c) hydrogen discharge in a reactor with freshly coated walls ($W = 10$ W); (d) as (c) except $W = 50$ W.

The mechanism of removal of the silicon film is unknown. Owing to the low mass and energy of the H_n^+ ions and the lack of silane ions in the helium plasma it is doubtful that the observed ions are due to a sputtering phenomenon. In mercury-sensitized photolysis of silane Niki and Mains[10] have observed the formation of gaseous silane when a polymeric silicon hydride was subjected to the reaction of atomic hydrogen. Following these authors we suggest a similar chemical reaction with the hydrogen plasma which is known to be a source of atomic hydrogen.

As a consequence the ionic population of the SiH_4–H_2 discharge is certainly distorted by the contribution of more or less saturated silane evolving from the surface. Such a distortion cannot be excluded in the case of the SiH_4–He discharge because of the hydrogen liberated by the decomposition of the silane.

6.3. *Incorporation of hydrogen during film growth*

Partial deuteration was achieved by adding 10% deuterium to the previous SiH_4–He mixture. IR transmission spectra show that the deuterium content in the film varies from about 20 to 40% of the total hydrogen content when the power is increased.

The ratio H/Si in a-Si:H films, as measured by nuclear reaction, increases also from 0.18 to 0.29 when the power is increased[20].

7. DISCUSSION

From these observations it is believed that the hydrogen atoms from the discharge interfere with the growing film. We recall that even with the SiH_4–He mixture the decomposition of SiH_4 releases hydrogen. Atomic hydrogen is therefore always present in the silane discharge. It can be expected that atomic hydrogen is more involved when the residence time in the discharge is long (low flow rate) or when the concentration is high (high power).

Furthermore, the observed chemical reaction between a hydrogen plasma and an a-Si:H film suggests that the growth of the film during plasma deposition cannot be regarded as an irreversible process from the gas phase to the surface. In fact during the growth more or less saturated silane is probably released from the surface to the gas phase.

No obvious correlation was observed between the ionic composition of the silane discharge and the IR properties of the film. The two deposition parameters which were determined to be important with regard to the properties of the film (namely flow rate and r.f. power) do not determine the ionic composition of the plasma.

We cannot discard the possibility of an ionic path for polymerization. Indeed $Si_2H_n{}^+$ ions are possible precursors of an ionic pathway in the plasma deposition of silane. However, a calculation shows that the flux of ion species impinging on the walls is one or two orders of magnitude lower than the experimental flux obtained from the deposition rate. This ionic mechanism is therefore of minor importance.

Further investigations are needed to obtain a more detailed picture of the deposition process. Furthermore, previous measurements performed by Ring *et al.*[9] have indicated a much greater variety of species in an SiH_4–SiD_4 discharge than in SiH_4–SiD_4 photolysis where the main pathway for decomposition probably proceeds via the free radical SiH_2 (ref. 21).

8. SUMMARY AND CONCLUSION

The primary conclusions of this work are as follows.

(1) The incorporation of SiH groups in the a-Si:H films is clearly favoured by a high flow rate of SiH_4 (*e.g.* 40 $cm^3\ min^{-1}$ of 5% SiH_4 diluted in helium) and low power (5–10 W).

(2) The mass spectrometric sampling of neutral molecules gives evidence that under the foregoing conditions SiH_4 is not completely dissociated. In contrast, completely dissociated SiH_4 is correlated with a film containing a majority of SiH_2 groups.

(3) The mass spectrometric sampling of ionic species from a silane discharge shows that primary ions, especially $SiH_2{}^+$, react with SiH_4 to form $SiH_3{}^+$, $Si_2H_4{}^+$ and $Si_2H_2{}^+$ ions. The evolution of the ionic composition as a function of deposition

parameters does not reveal any clear correlation with the IR properties of the films.

(4) It is believed that atomic hydrogen, which is always present in a silane discharge, interferes with the growing film and may modify both the film itself and the composition of the plasma, especially for long residence time and high concentration.

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