STUDY OF THE PLASMA DEPOSITION PROCESSES OF a-Si:H FILMS

G. Turban, Y. Catherine and B. Grolleau
Laboratoire de Physique Corpusculaire, Université de Nantes, 2 rue de la Houssinière — 44072 NANTES CEDEX, France.

Keywords : silane discharge, mass spectrometry.

Compounds : hydrogenated amorphous silicon

ABSTRACT

Thin films of a-Si:H have been prepared by reactive plasma deposition in a SiH_4-He mixture. The kinetic conditions which favour the formation of SiH sites against SiH_2 sites have been determined. For these deposition conditions, mass spectrometric measurements of the ions and neutrals of the discharge have been obtained. The relative abundance of SiH_3^+ and SiH_2^+ ions and the formation of $Si_2H_n^+$ ions are interpreted as the result of ion-molecule reactions.

1. INTRODUCTION

Recent studies (1) (2) concerning the preparation of a-Si:H films by the glow discharge decomposition of SiH_4 have shown that there must be a correlation (not yet clear) between the kinetic of the discharge and the properties of the films. We have recently proposed a kinetic model(3) for the SiH_4 discharge which accounts for the gas-film mass transfer. In this paper we precise the decomposition conditions which enhance the formation of a-Si:H film (instead of SiH_x) and study the relative evolution of the ionic species in a silane discharge.

2. EXPERIMENTAL

The experimental arrangement has been described previously (3). The reactor consists in a pyrex tube with parallel internal electrodes spaced of 5cm. The upper electrode is connected to the rf power source (13.56 MHz) through a matching network. The extraction probe is a ceramic cylinder with an extraction hole of 200 µm in diameter. The gas mixture consists in 5 % SiH_4 in either He or H_2.

3. SILANE DECOMPOSITION

Figures 1 a and b give the decomposition of the silane in the discharge for various carrier gases (He, H_2, Ar). It will be noted that the decomposition of SiH_4 increases when He and Ar are substituted to H_2. This may be the result of the different electronic temperatures and densities at a constant input power.Figure 1d shows that the decomposition level of SiH_4 increases as the flow rate decreases which is indicative of an axial de-

pletion of the gas (3). Obviously the hydrogen formation increases with the silane decomposition (Fig. 1c).

4. CARACTERISATION OF a-Si:H FILMS

The table I gives the hydrogen content of films deposited in a previously described reactor (4). The Figure 2 shows the infrared transmission spectra of films. For low powers and high flow rates the stretching band is located at 2000 cm^{-1} and no absorption band in the 800-950 cm^{-1} region can be observed, which is indicative of a structure containing a large fraction of SiH sites (1). On the other hand layers deposited at high powers and low flow rates have a stretching band located at 2090 cm^{-1}, and the 800-950 cm^{-1} region shows two absorption bands corresponding to the wagging of SiH_2 and SiH_3. Thus, it is believed that the films formed in a region where the silane is not entirely destroyed contain a majority of SiH sites, while those formed in a region where the silane is strongly dissociated contain a majority of SiH_2 sites.

5. EVOLUTION OF THE Si_1 IONS IN SILANE DISCHARGES

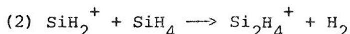
Figures 3a and 3b show typical spectra of the ionic current from the SiH_4-He and SiH_4-H_2 discharge.
We have measured in our spectrometer the electron impact fragmentation pattern of SiH_4 in the range 10-90 eV. From these measurements, the production rates of the ions SiH_3^+, SiH_2^+, SiH^+ and Si^+ have been calculated assuming a maxwellian distribution function for the electrons. (Table II). The relative abundance of the observed Si_1 ions is strongly different of these calculations (Fig. 4). The evolution of the SiH_3^+ and SiH_2^+ ion currents as a function of the discharge pressure is similar to that observed in high pressure mass spectrometry (5). According to these authors we attribute the predominance of the SiH_3^+ ion relative to the SiH_2^+ ion to the following ion-molecule reaction :

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

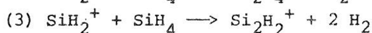
For high flow rates (42 cm^3/min) the relative abundance of the ions remains constant at any pressure, which indicates that we have an excess of SiH_4 accordingly to the decomposition measurements (Fig.1b). An increase of the input rf power (Fig.5) results in a lowering of SiH_3^+ relative to SiH_2^+. This evolution may be interpreted as the result of the depletion of SiH_4 for high powers (Fig. 1). Reaction (1) is then limited by the availability of undissociated SiH_4.

6. EVOLUTION OF THE Si_2 IONS

In the SiH_4-He discharge (Fig.6a) the variation of the relative abundance of $Si_2H_n^+$ions (n = 1 to 7) is similar to that observed by Yu and al. (5). According to this authors it may be assumed that the formation of these Si_2 ions is the result of the following principal ion-molecule reactions:

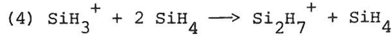


(2) $SiH_2^+ + SiH_4 \longrightarrow Si_2H_4^+ + H_2$



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

for the two principal ions at low pressure ; the $Si_2H_7^+$ ion being formed through the reaction :



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

This last ion is very abundant in the SiH_4-H_2 mixture (Fig.6b) in which it is also observed that the SiH_3^+ion is largely predominant.Reaction (4) agrees with the foregoing observation and also with the lower decomposition of SiH_4 in the SiH_4-H_2 discharge.

7. INTERACTION OF AN HYDROGEN PLASMA WITH THE FILM

We have also observed the ion spectrum of a discharge in He or H_2 (Fig.3c and Fig.3d), the walls of the tube and the electrodes being coated by a a-Si:H film freshly deposited at room temperature. Apart from the fact that the peak 29 cannot only be ascribed to the SiH^+ ion but also to ionic impurities such as N_2H^+, the H_2 discharge gives rise to SiH_3^+ and $Si_2H_n^+$ ions. Because of the low mass and energy of the H_n^+ ions it is doubtful that the observed ions are due to a sputtering phenomenon, which is, besides, not observed in the He discharge. A possible interpretation of these results is a chemical reaction of atomic hydrogen, or H_n^+ ions, with deposited films. Indeed these ions are not observed if the reactor walls have been exposed several hours to air. (Fig. 3e).

ACKNOWLEDGEMENT

This work was financially supported by C.N.R.S. and E.D.F. under contract A.T.P. n° 3085.
The authors would like to acknowledge E. Guillet for its technical assistance and J. Fontenille and E. Ligeon (C.E.A. – Grenoble) for the nuclear analysis of the a-Si:H films.

REFERENCES

(1) M.H. Brodsky, M. Cardona and J.J. Cuomo, Phys. Rev. B, 16, 3556 (1977).
(2) R.A. Street, J.C. Knights and D.K. Birgelsen, Phys. Rev. B, 18,1880 (1978).
(3) G. Turban, Y. Catherine and B. Grolleau,Thin Solid Films 59,May(1979)
(4) Y. Catherine and G. Turban, Thin Solid Films, in press.
(5) T.Y. Yu, T.M.H. Cheng, V. Kempter and F.W. Lampe, J. Phys. Chem. 76, 3321 (1972).

Table I

Atomic fraction of hydrogen in a-Si:H films measured by nuclear reaction $^1H(^{11}B,\alpha)2\ \alpha$(*)

pressure torr	power watts	flow rate cc/min STP	substrate temp. °C	H/Si
0.2	100	15	300	0.29
0.15	10	22	300	0.175
0.15	10	4	300	0.195

(*) performed by J. Fontenille and E. Ligeon (C.E.A. – Grenoble)

Table II

Ionization rate constant (cm^3/sec) of SiH_4 (*) for maxwellian electron energy distribution ($x\ 10^{11}$)

$\bar{\varepsilon}$ eV	SiH_3^+	SiH_2^+	SiH^+	Si^+
3	5.98	8.58	0.17	0.05
5	94.8	132.7	7.14	2.8
7	300	414.6	33.6	16.7

(*) calculated from the experimental fragmentation pattern of SiH_4 (10-90 eV). The total ionization cross-section of SiH_4 is evaluated by comparing the ionization current of SiH_4 with that of C_2H_4 at 70 eV.

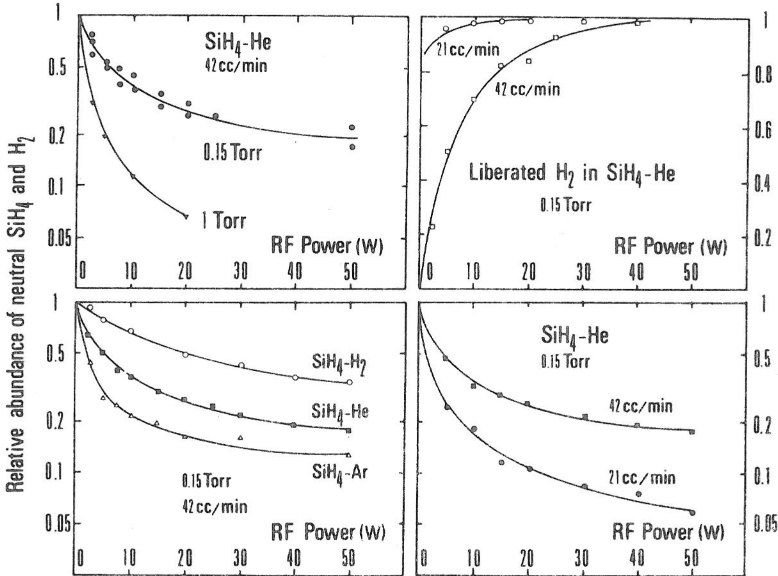


Fig. 1. Normalized signals from neutral SiH_4 and H_2 as a function of power

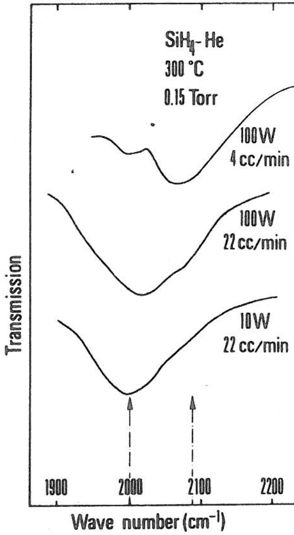


Fig.2. IR spectra of SiH stretching bands

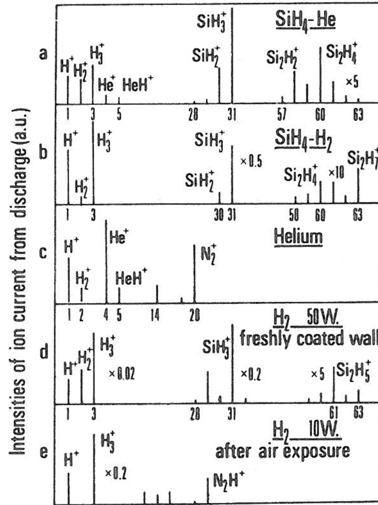


Fig.3. 0.15 Torr discharge ionic spectra.

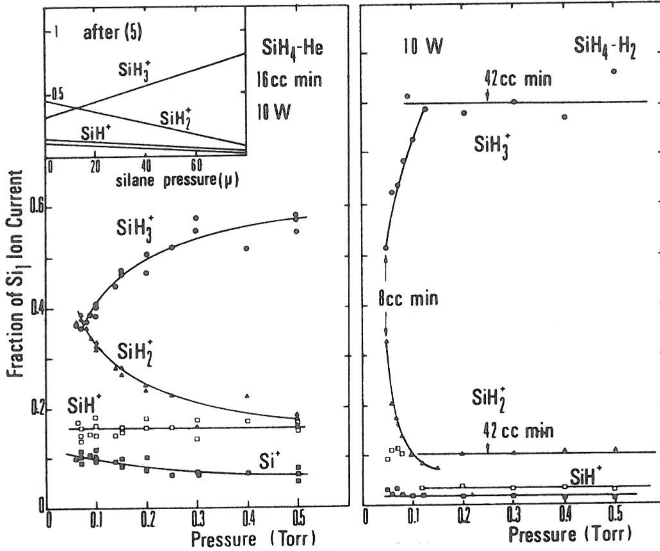


Fig.4. Dependence of Si_1 ion currents on pressure

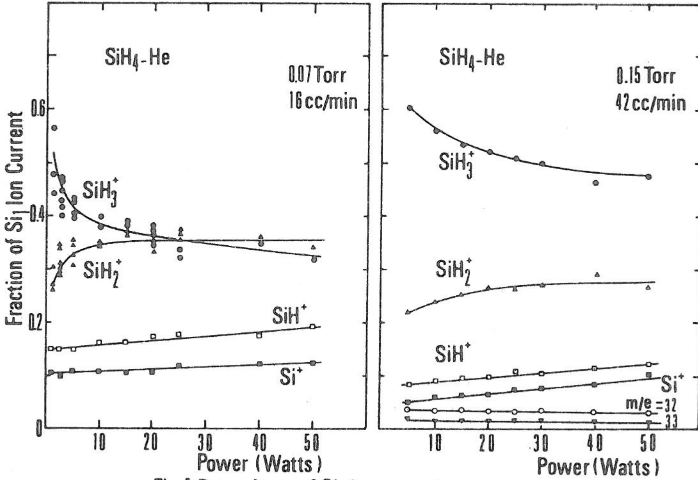


Fig. 5. Dependence of Si_1 ion currents on power

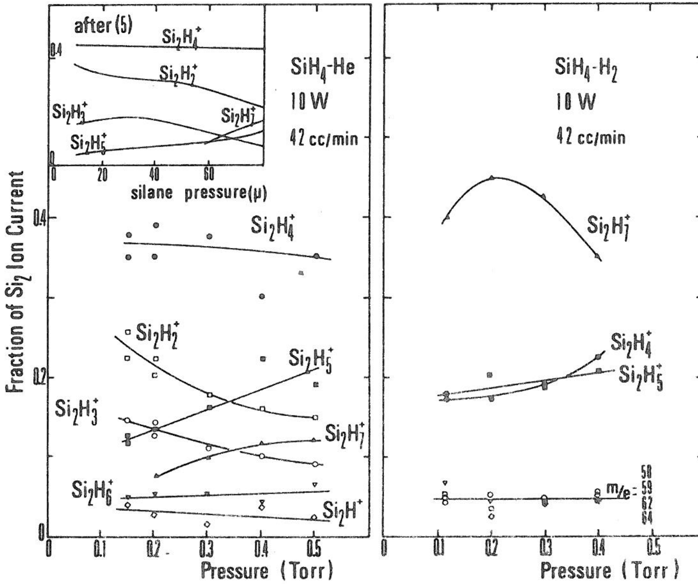


Fig. 6. Dependence of Si_2 ion currents on pressure