THE ROLE OF H ATOMS AND NEUTRAL RADICALS IN THE SILANE GLOW DISCHARGE DEPOSITION 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.

ABSTRACT

Mass spectrometric analysis were made of the plasma reactions in a silane plasma during the growth of a-Si:H film using isotopic labelling. Recombination and disproportionation reactions between SiH_3 and SiH_2 radicals take place in a SiH_4- SiD_4 plasma.

The formation of $SiH_{4-n} D_n$ (n = 0 to 4) and $Si_2H_{6-m} D_m$ (m = 0 to 6) has been observed. The Si-D bonds in an a-Si:H(D) film deposited in a SiH_4 - D_2 plasma result both from the deuteration of the silyl and silylene radicals in the gas phase and the direct incorporation of D atoms. The etching of the film by a D_2 plasma has also been shown.

1. INTRODUCTION

a-Si:H films deposited by plasma decomposition of silane have interesting properties such as a high photoconductivity which make then attractive for solar energy photovoltaïc converting devices, photoreceptors or image sensors. It is now known that the hydrogen repartition in the film strongly affects the properties of the material.

It is thus important to know the reactive intermediates which are the film precursors and to determine the different pathways which lead to the film formation.

In a previous work (1) we made a modelisation of deposition in a silane plasma which showed that the gaseous precursors accountable for the mass transport to the walls of the discharge tube are neutral SiH_n species i.e. free radicals.

Due to the lack of direct evidence of these radicals we have studied the secondary reactions which may occur during their diffusion towards the walls.

This paper reports on a mass spectrometric study based upon isotopic labelling and the film has been analyzed by I.R. spectroscopy.

2. EXPERIMENTAL

The silane plasma is created in a diode type RF reactor described elsewhere (2). The silane is diluted in helium, hydrogen or deuterium at a concentration of 5 %. The silane d_4 (SiD_4) is diluted in helium. The power density is ∿ 0.13 W/cm². The flow rate of the gases is at most of 42 s cm³/min and the pressure can be varied between 0.15 and 1 torr. The positive ions and the neutral molecules are extracted from the plasma through a 200 µm hole bored in the wall of the discharge tube. The films are deposited on monocrystalline silicon wafers placed either on the RF electrode (cathode) or the ground electrode (anode).

3. RESULTS AND DISCUSSION

1/ The SiH_4 - SiD_4 discharge

Apart from the carrier gas the silane plasma is composed of the following major products : SiH_4, Si_2H_6, H_2, with partial pressures as given in table 1.

Table 1

Partial pressures of neutral products in the SiH_4 - He discharge (12 W, 0.15 torr, 42 s cm³/min).

SiH_4	2,5 mtorr
H_2	12,5 mtorr
Si_2H_6	0,1 mtorr
He	135 mtorr.

The decomposition of the silane in the discharge proceeds mainly through electron impact. The silane electronically excited which results from this impact will dissociates into SiH_2 and SiH_3 radicals. A comparison with the dissociative ionization of silane near the edge of the appearence potential (12 eV), shows undoubtly that the production rate of SiH_2 is about 2 times that of SiH_3 (3). The synthesis of Si_2H_6 in the discharge is an indirect evidence of the existence of these radicals. Indeed, photolysis studies of SiH_4 (4) (5) do not attribute the formation of Si_2H_6 to direct reaction :

(1) $2\,SiH_3 \longrightarrow Si_2H_6^* \quad \Delta H = -3,17$ eV

In our pressure conditions the formation of Si_2H_6 results from the following sequence:

(2) Disproportionation : $2\,SiH_3 \longrightarrow SiH_2 + SiH_4 \quad \Delta H = -1,57$ eV

(3) Termination : $SiH_2 + SiH_4 \xrightarrow[W]{M} Si_2H_6 \quad \Delta H = -2,15$ eV

The fig. 1 shows the evolution of the relative concentrations of silanes d_1 d_2 d_3 obtained in a SiH_4 - SiD_4 plasma by measuring the peak intensities of masses 32 to 34.

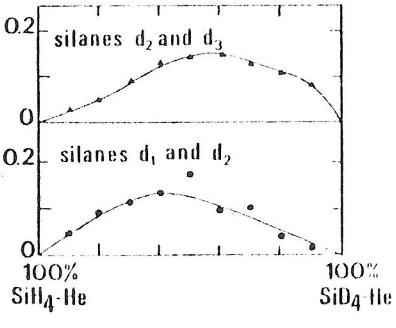

Fig. 1 : Relative concentrations of deuterated silanes in the SiH_4-SiD_4 discharge.

From 14 % to 27 % of the silane present in the discharge is composed of partially deuterated silane. This relative concentration increases with long residence times (low flow rate) and is practically independant of the pressure (0.15 - 1 torr) and the power (2.5. to 20 W).

These silanes may originate from three reaction types : the disproportionation (reaction 2), the recombination :

(4) $D + SiH_3 \xrightarrow[W]{M} SiH_3D \quad \Delta H = -4,14$ eV

or the ion-molecule reactions :

(5) $SiH_2^+ + SiH_4 \longrightarrow SiH_3^+ + SiH_3$

(6) $SiH_3^+ + SiH_4 \longrightarrow SiH_3^+ + SiH_4$

We have experimentally observed the reaction (5) in a silane plasma (2). These ion reactions are favoured by high silane concentrations (high pressure and flow rate, low power). They are not able to explain the apparition of the deuterated silanes. Thus we attribute the results reported in fig. 1 to reactions 2 and 4, the recombination reaction (4) and the disproportionation reaction (2) do not imply SiH_4 molecules contrary to reactions 5 and 6.

The relative concentrations of the partially deuterated disilanes formed in the SiH_4 - SiD_4 discharge are shown in fig. 2.

This relative concentration has been determined by measuring the peak intensities of the masses 64 to 68 and using the fragmentation spectra of $Si_2H_{6-m}D_m$ given by Ring et al. (6) and that of Si_2D_6 measured in in our experiment. It appears clearly that all the disilanes are formed in the discharge and more particularly disilanes d_3 and d_5.

This result is in agreement with that of Ring (6) for a silent discharge at 10 torr in SiH_4 - SiD_4. On the contrary in photochemical experiments (4) (6) (7) where only SiH_3 and SiD_3 are generated, disilane d_3 is not synthetized because of the preponderance of the disproportionation (2).

The existence of $Si_2H_3D_3$ in the discharge implies that third generation reactions occur, for example :

(7) $SiH_2 + SiHD_3 \longrightarrow Si_2H_3D_3$

(8) $SiHD + SiH_2D_2 \longrightarrow Si_2H_3D_3$

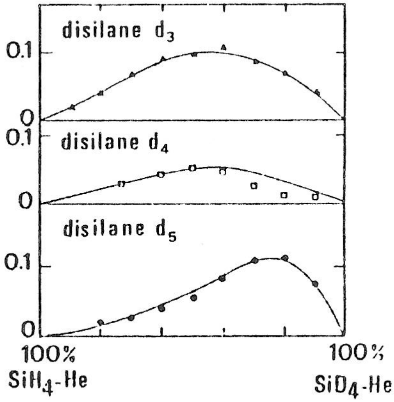

Fig. 2 – Evolution of the ratio of the concentrations of the disilanes $Si_2H_{6-m}D_m$ relative to the concentration of all the disilanes. (42 scm³/min, 1 torr, 5 W).

2/ The role of the hydrogen atoms

The table 1 shows that the SiH_4 plasma contains large amounts of hydrogen. The addition of hydrogen to silane increases the Si_2H_6 partial pressure (2 times) and the formation of powder in the reactor (3). In a $SiH_4 - H_2$ plasma the disilane concentration is about five times greater than what is obtained in a SiH_4- He plasma for the same conditions. It is thought that this increase of the disilane formation originates from the abstraction reaction (8) :

(9) $H + SiH_4 \longrightarrow SiH_3 + H_2$

followed by reactions (2) and (3).

A SiH_4- D_2 plasma possesses large amounts of silanes d_1, d_2, d_3 and d_4(up to 70 % of all the silane). In addition to the reactions (2) (4) (5) (6) which may explain the formation of these silanes one must consider the interaction between the growing film and the hydrogen atoms.

When an a-Si:H film is submitted to a D_2 (or H_2) plasma the formation of SiD_4, Si_2D_6 and HD is observed (Table 2).

Table 2

Partial pressures of silane and disilanes *

plasma	100 % D_2	5 % SiH_4 – 95 % D_2
$p(SiD_4)$	∿ 2,2 mtorr	∿ 17,5 mtorr
$p(Si_2D_6)$	∿ 1,3 mtorr	∿ 4,5 mtorr
$\frac{p(SiD_4)}{p(Si_2D_6)}$	0,59	0,26

* conditions : 1 torr, 42 scm³/min, 10 W.

Thus the formed Si_2D_6 arises for one part from the interaction with the film and for the other part from the synthesis on SiD_4.

The interaction between a D_2 plasma and a slightly hydrogenated amorphous silicium film (∿3 %) prepared by conventional chemical vapor deposition of silane also gives rise to the formation of SiD_4 and Si_2D_6.

The formation of SiD_4 and Si_2D_6 through the interaction between atomic hydrogen and a SiH_x film has already been observed (9) (7). Therefore we attribute our results to such a reaction :

(10) $y\,D + SiH_x\,(\text{film}) \longrightarrow SiD_4\ (\text{or } Si_2D_6) + HD.$

Such a plasma etching is probably at the origin of the chemical transport of silicon observed by Veprek (10).

3/ Formation of the SiD bonds in the film.

A study by I.R. absorption spectroscopy of the 2000 cm^{-1} and 1500 cm^{-1} absorption bands of the Si-H and Si-D bonds in an a-Si:H(D) film deposited in a SiH_4-He-D_2 plasma has been done. The results for the integrated absorptions are reported in table 3.

Table 3

Ratio of SiD and SiH bonds *

	anodic films	cathodic films	gaseous phase
$\frac{N(SiD)}{N(SiH)}$	0,38 ± 0,04	0,48 ±0,08	0,24 ± 0,01

* SiH_4 - He - D_2, 0.15 torr, 10 W, 42 scm³/min.

The same ratio has been measured for the silanes in the gaseous phase. A comparison of the ratio for this film with that for the gas phase shows that all the Si-D bonds in the film do not originate from the deuteration in the gaseous phase. A significant part is attributed to the direct incorporation of D atoms in the growing film. Such an interpretation is in agreement with post hydrogenation of a:Si submitted to an hydrogen plasma (11).

The fig. 3 shows the evolution of the ratio of the 2000 cm^{-1} ($\geqslant$SiH) and 2090 cm^{-1} ($>SiH_2$) I.R. absorption bands for anodic and cathodic films as a function of the axial position of the substrate in the reactor.

Knights (12) has shown that anodic films contained more $(SiH_2)_n$ groups than do cathodic films.

Our results are attributed to the effect of the ion bombardment upon the growing layer. The impingement of the surface by ∿ 100 eV ions may enhanced the dissociation of the SiH_2 and SiH_3 radicals chemisorbed on this surface by a mechanism similar to the chemisorption mechanism of CF_3 on Si given by Coburn and Winters (13):

$$(11)\quad SiH_2(ads) + \text{film} \xrightarrow{\text{ions}} Si(ads) + H_2 + \text{film}$$
$$\longrightarrow SiH(ads) + H + \text{film}$$

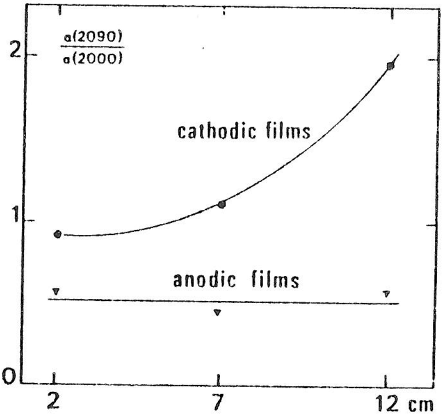

Fig. 3 - Evolution of the ratio of the SiH_2 and SiH I.R. absorption bands in an a Si:H film as a function of the axial position of the substrate.

The formation mechanism for the a-Si:H in the plasma deduced from our experimental results may be resumed as follows :

(1)- chemisorption of SiH_2 and SiH_3 radicals on the walls ;

(2)- dissociation of these chemisorbed radicals, which may be induced by the ion bombardment ;

(3)- direct incorporation of H atoms in the growing film ;

(4)- etching of the film by the H atoms.

The deshydrogenation of the SiH_2 and SiH_3 radicals at the surface may be the result of reaction (11) or of the heterogeneous disproportionation illustrated by reaction (2) (ref. 7).

This study has shown that the SiH_2 and SiH_3 radical population in the gas phase is the result of numerous electron impact, radical-molecule, and ion-molecule reactions. The surface reactions between these radicals, the hydrogen atoms and the plasma ions control the structure of the deposited films.

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