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DECOMPOSITION OF SiC14 AND DEPOSITION OF Si IN INDUCTIVELY COUPLED
PLASMAS OF H2 + SiC14.

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ABSTRACT

The mechanism of homogeneous reactions in plasmas of H2+5% SiC14 was
studied by mass-spectrometry and was compared to the mechanism
observed in plasmas of Ar+ H2 + SiC14. Contrary to the behavior with Ar,
the results indicate that without argon the SiC14 molecule undergoes only
fragmentation and the deposition proceeds through SiC12. No
polymerization was observed. The deposition rates of uc-Si were lower and
the amounts of chlorine incorporated in the films were higher in the
plasma of SiC14 + H2 than in the argon containing plasma.

1. INTRODUCTION

Silicon deposition from plasmas of SiC14 has been investigated in the
last years (1-4) as a feasible alternative to the use of silane for
photovoltaic purposes. As shown by Chevallier et al. (5) the chlorine
incorporated in these films saturates the dangling bonds of silicon
forming SiC12 bonds. A certain amount of chlorine is therefore desirable
for the electronic properties of such layers, and this level is still to
be determined. Various aspects of silicon deposition from SiC14 from
gaseous mixtures with H2 and Ar were reported previously (6,7). The
gaseous species in such plasmas were defined, as well as the kinetic
constants of SiC14 dissociation, polymerization and recombination (6,7).
Recently a model for the incorporation of chlorine into the films
deposited in such plasmas has been published (8). In the present paper
we present mass spectrometric results and deposition rates in plasmas
containing 5% SiC14 in H2 only. The scope of this study was to broaden
our understanding of the phenomena occurring in H2+SiC14 plasmas and
compare the results to the results obtained in Ar+H2+SiC14 plasmas, in
respect with homogeneous reactions, polymerization, deposition rates and
C1 content of the films.

2. EXPERIMENTAL

The experimental setups for the deposition of Si and for the study of the
decomposition of SiC14 in the plasma state have been described elsewhere
(4,6). A gas mixture of 5% SiC14 in H2 was used at a total gas flow of 60
scm. Several details of the experimental methods should be mentioned:
The deposition experiments were performed in a inductively coupled rf plasma (27.12 MHz), on graphite substrates. The deposition time for all samples was 1 hour. The substrates were located at 3 different locations with regard to the rf coil - H, G and F, as defined in (9). The decomposition mechanism of the SiCl4 was studied in a microwave plasma (2.45GHz) with the system described in (6), using a quadrupole mass spectrometer (Balzers-QMG 311). The mass spectrometric results analyzed by a computer program are presented as normalized intensities, I/I0. The system was operated in the range of m/e = 4-300, to enable detection of heavy species. Hydrogen was therefore not analyzed. A microwave discharge system was used because it allowed to move the cavity along the reactor while the sampling port of the mass spectrometric system was fixed. This technique enabled the extraction of species from the different plasma regions, by changing the relative position between the \( \lambda/4 \) Evenson antenna and the sampling orifice. The results enabled the calculation of the kinetic constants, as shown in (7). The time required for a particle to travel between positions H to F is a function of pressure. For the experiments conditions this time was 6.8ms/c/torr.

Only the highest peak of each Si-C1 compound was taken into account. Species of the form SiClx and Si(4-x)Cl(x) (like SiCl3 and SiHCl3) were not considered separately. A factor of \( \sim 2 \) was found suitable for correlation between the input powers in the two systems (10).

Scanning electron microscopy, SEM, was used to measure the thickness \( d \) of the Si deposits. The Si deposits obtained under similar conditions have been found to have a microcrystalline structure (\( \sim 130 \) Å) and the degree of crystallinity obtained directly from the rf plasma reactor was 56\% (4).

3. RESULTS AND DISCUSSION.

A. MASS SPECTROMETRY.

Effect of location and input power. Figure 1 presents the behaviour of the normalized intensities (I/I0) of the species detected in the plasma at 1 torr at various input powers. The figure indicates that:

(i) At 50 Watt the free C1 radical occurs at all sampling positions, while with increasing power this species is not detected in position F. The appearance of this species and not of HCl only was unexpected due to the excess H2 concentration. Its presence at lower power is attributed to insufficient production of H radicals for the reduction of Cl in this plasma.

(ii) The normalized concentration of SiCl4 decreases from H to F at 50 watts, and at 100W it disappears at position F. Further increase in the input power causes SiCl4 to dissociate completely already after position G.

(iii) Under non plasma conditions the ratio between the intensities of the peaks at m/e=133 and m/e=170 is approximately 2. This ratio has been found to exist also in the spectrum of Ar+H2+SiCl4 plasma. As suggested by Ban(11), a ratio smaller than 2 indicates that SiCl3 is a more reactive specie than its parent. The changes in this ratio with variation of position and input power is presented in the first two lines of Table 1. It can be observed that, while at position H this ratio is approximately 2, at other positions and input powers the ratio changes significantly, indicating separate reactions of SiCl3 and SiCl4. In addition, as shown in Fig.1C, at 150W SiCl3 is the only chlorosilicon specie detected in position G.

(iv) SiCl2 was detected only in position H for all input powers. Its
disappearance at an early stage of the reaction indicates that this specie is generated by the decomposition of SiCl3 and that it is by itself a very reactive component of the plasma, having a role in the formation of the Si film as it will be shown. SiCl also disappears gradually with increasing power, starting at 50W from position F. At higher power input this specie is not detected already at position G. These results indicate the gradual progress of the dissociation reaction along the reactor (from H to F) and with increasing power.

(v). At 100W and 150W the only species detected in the reactor at position F were Si and HCl, both final products of the overall reaction:

\[(1) \text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{HCl}\]

indicating completion of the SiCl dissociation.

Effect of pressure. The effect of increasing pressure at 100 W is presented in Figures 1B,2A and 2B for 1,2 and 6torrs respectively. The shown results indicate that:

(i). The disappearance of SiCl4 along the gas stream at 1 and 2 torrs indicates the completion of the reaction at lower pressures while at the higher pressure the dissociation of SiCl4 is slower.

(ii). The free Cl radical gradually disappears with pressure. At 1 torr it was detected at all sampling positions with intensities approximately equal to those of HCl, while at 2 torr it was not detected after position H and at 6 torr it was undetected. The disappearance of Cl radicals with increasing pressure is due to shorter mean free path and the higher cross section for HCl formation.

(iii). SiCl2, which first disappears after position H at low pressures, was detected again after increasing pressure in position G. This result indicates a decrease in the decomposition rate of this specie (reaction 4 below), as indicated by the opposite inclination of its line as compared to the rest of the lines, Fig.28.

(iv). It should also be mentioned that at 6 torr the formation of certain polymers was observed, but their normalized concentrations was under 1% and are not shown.

Reaction kinetics. According to these results it may be concluded that the homogeneous reactions in the plasma are:

\[(2) \text{SiCl}_4 \rightarrow \text{SiCl}_3 + \text{Cl}\]
\[(3a) \text{SiCl}_3 \rightarrow \text{SiCl}_2 + \text{Cl}\]
\[(3b) \text{SiCl}_3 + \text{Cl} \rightarrow \text{SiCl}_2 + \text{Cl}_2 \text{ (#)}\]
\[(4) \text{SiCl}_2 \rightarrow \text{SiCl} + \text{Cl}\]
\[(5) \text{SiCl} \rightarrow \text{Si} + \text{Cl}\]

(#) C12 was not not detected in this plasma. Due to its low dissociation energy (2.48eV) as compared to HCl (4.43eV), it dissociates easily into Cl radicals.

The kinetic constants for the overall reaction

\[(1) \text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{HCl}\]

were calculated using the procedure described in (7). The reaction mechanism in this plasma was shown to be of the radical-molecule type, as indicated by the reduced density of free electrons detected in a H2 plasma under similar conditions (12). A similar reaction mechanism has been found in plasmas of Ar + H2 + SiCl4 (7). In table 2 the kinetic constants for the two types of plasma are compared for the main species participating in the reaction. As indicated by these results, the presence of Ar in the plasma enhances the decomposition and the formation of Si, and as it will be shown later the deposition rate is also increased in presence of Ar. As for the formation of HCl, it is faster without Ar. It should be noted however that polymers of the type
SixCl₂ were observed in presence of Ar. Their appearance slow down the formation of HCl, but they are important for the deposition.

B. DEPOSITION RESULTS

Effect of location and input power. The results shown in Figure 3 represent the deposition rates per hour and Cl content in the films at a pressure of 2 torrs. As can be observed, the highest deposition rate was obtained at position G for all input powers. As a rule, in this plasma the Cl content of the films tends to follow the behavior of the deposition rates, as observed also in presence of Ar, with or without dopants (4,13). There is only one exception to this rule: at position F the chlorine content observed at 100W was higher than the one observed in position G, while the deposition rate decreased as compared to position G. The maximum deposition rates were observed at position G, for all input powers, and this coincides with the disappearance of SiCl₂ in the plasma. Thus, it is assumed that the film deposition proceeds by surface reactions starting from SiCl₂:

\[(6) \text{SiCl}_2 + \text{H}_2 \rightarrow \text{SiCl} + \text{HCl}, \text{ followed by} \]
\[(7) \text{SiCl} + \text{H}_2 \rightarrow \text{Si} + \text{HCl}\]

Part of the HCl produced by these reactions remains incorporated in the solid matrix, increasing the Cl/Si content of the film. At low input power a high amount of SiCl₃ was detected in position F together with Cl radicals. The interaction of these two species leads to the reaction (3b), which generates SiCl₂ and enables reaction (6) to occur, in spite of the fact that SiCl₂ was not detected at F.

Effect of pressure. The effect of increasing pressure is shown in Figure 4 for position F at the low input power. The deposition rate (d) decreases with increasing pressure. It should be kept in mind that due to the fact that the decomposition of SiCl₄ was already completed at this location, as indicated by the mass spectrometric data, it was expected that the deposition will be highest at this location. As shown by the deposition results, this assumption proved incorrect. Therefore, it can be assumed that the rate determining step for deposition occurs via reactions (6) and (7) and not via SiCl₄ decomposition. This is further emphasized by the decrease of deposition rate with increasing pressure, Fig.4, and the reappearance of SiCl₂ in the spectrum at 6 torr, Fig.2B.

Comparison with deposition in presence of Ar. The results obtained for similar conditions in plasmas of Ar+H₂+SiCl₄ were presented in (8). A comparison between the two types of plasma indicates that:

(i) The amounts of incorporated Cl in Ar-containing plasmas varied between 0.7% and 12%. In plasmas without Ar for the same input power and pressure (2 torr) the Cl content varied between 6% and 24%.

(ii) The maximum deposition rate in plasmas of Ar+H₂+SiCl₄ was 7 µm/h (pos. G, 100 W, 2 mbar), while for H₂+SiCl₄ it was 4 µm/h. This result is in good agreement with the faster reaction rates for Si formation in Ar-containing plasma.

REFERENCES:

10. R. Avni, A. Inspektor and U. Carmi, This Symposium.

**TABLE 1:** The values of $I(SiCl_3)/I(SiCl_4)$ at positions H, G & F.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>H</th>
<th>G</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.98</td>
<td>1.73</td>
<td>1.6</td>
</tr>
<tr>
<td>100</td>
<td>1.93</td>
<td>1.22</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>1.80</td>
<td>1.77</td>
<td>1.36</td>
</tr>
<tr>
<td>6</td>
<td>1.99</td>
<td>1.66</td>
<td>1.56</td>
</tr>
</tbody>
</table>

(##) both species undetected

**TABLE 2:** Comparison of kinetic constants with or without Ar, at 100W, 1torr.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>H2 + SiCl4</th>
<th>SiCl4</th>
<th>Si</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (1/s) (##)</td>
<td>240</td>
<td>-350</td>
<td>-190</td>
<td></td>
</tr>
<tr>
<td>Ar + H2 + SiCl4</td>
<td>600</td>
<td>-526</td>
<td>-82</td>
<td></td>
</tr>
</tbody>
</table>

(##) minus designates formation.

Fig.1. $I/II$ in microwave plasma at 1torr vs. position.
A. 50W; B. 100W; C. 150W
Fig. 2. $I/\Sigma I$ IN MICROWAVE PLASMA AT 100W VS. POSITION.
A. 2 torr; B. 6 torr

Fig. 3. FILM THICKNESS AND Cl CONTENT VS. POSITION IN RF PLASMA. DEPOSITION AT 2 torr, FOR 1 HOUR.

Fig. 4. FILM THICKNESS VS. POWER IN RF PLASMA. POSITION F, 100W, 1 HOUR DEPOSITION