Effect of Argon and Hydrogen on Deposition of Silicon From Tetrachlorosilane in Cold Plasmas

R.R. Manory
Lewis Research Center
Cleveland, Ohio

and

R. Avni and A. Grill
Ben Gurion University of the Negev
Beer Sheva, Israel

Prepared for the
Fall Meeting of the Materials Research Society
Boston, Massachusetts, December 2-7, 1985
EFFECT OF ARGON AND HYDROGEN ON DEPOSITION OF SILICON FROM TETRACHLOROSILANE IN COLD PLASMAS

R.R. Manory*
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

R. Avn1 and A. Grill
Ben Gurion University of the Negev
Beer Sheva, Israel

SUMMARY

The roles of Ar and H₂ on the decomposition of SiCl₄ in cold plasma were investigated by Langmuir probes and mass spectrometry. Decomposition of the reactant by Ar only has been found to be very slow. In presence of H₂ in the plasma SiCl₄ is decomposed by fast radical-molecule reactions which are further enhanced by Ar due to additional ion-molecule reactions in which more H radicals are produced. A model for the plasma-surface interactions during deposition of μC-Si in the Ar + H₂ + SiCl₄ system is presented.

INTRODUCTION

The deposition of microcrystalline silicon in cold plasmas of silane (SiH₄) has been extensively studied for about 10 yr (refs. 1 to 3), but the deposition of microcrystalline silicon from cold plasmas of tetrachlorosilane (SiCl₄) has been studied very little, probably because of the belief that the residual chlorine in such films would be detrimental for their electronic properties. In spite of this belief, such studies have been conducted by several groups (refs. 4 to 7) as SiCl₄ is both cheaper and less hazardous than SiH₄ and conversion efficiencies as high as 7.5 percent are reported for Si-Cl solar cells (ref. 6). Recent studies by Chevallier et al. (ref. 8) indicate that the halogen incorporated in such films annihilates the dangling bonds of silicon and thus improves the films' electronic properties in a manner similar to the role of hydrogen in films deposited from SiH₄.

The model presented herein is intended to broaden understanding of the deposition of silicon in the Ar + H₂ + SiCl₄ system. The systems Ar + SiCl₄ and H₂ + SiCl₄ were also investigated to elucidate the roles of the different diluent gases on the deposition process. In the system in which argon and hydrogen both participate, the deposition was performed better than in the other two systems (i.e., deposition rates were higher and the deposit contained less chlorine). As will be shown, this is due to the specific roles of argon and hydrogen in the different stages of deposition.

*Ben Gurion University of the Negev, Beer Sheva, Israel, and NRC-NASA Research Associate.
METHODS

The techniques used for plasma diagnostics were Langmuir probes and mass spectrometry. The films were deposited on graphite substrates. Their thickness was measured by scanning electron microscopy (SEM), and their chlorine content was measured by energy-dispersive x-ray analysis (EDAX).

The experimental systems consisted mainly of a quartz tube in which inductively coupled plasma was excited from gaseous mixtures of 4 to 5 vol % SiCl₄ diluted in argon only, in hydrogen only, or in a mixture of Ar + 15 vol % H₂. Plasmas without SiCl₄ were also analyzed for Langmuir probe measurements. The mass-spectrometric system, the double-floating-probe system (DFPS), and the deposition system are described in detail, respectively, in (refs. 9 to 11). The analysis included reaction kinetics (total and local reaction rates), determination of plasma species, measurements of charge-carrier density and electron temperature, and measurements of the deposition rates and chlorine contents of the films under different deposition conditions.

The plasma was sampled and the films deposited separately in three regions labeled by the letters H, G, and F (ref. 10) (fig. 1). Position H was located 1.5 cm before the plasma excitation center, position G was at the plasma center, and position F was 1.5 cm after it. This form of measurement gives a kinetic picture of the plasma processes and allows rates of the reactions taking place in the plasma to be determined by the method of Field, Franklin, and Munson (ref. 12).

For the DFPS measurements a similar system was used, except that instead of the quadrupole mass spectrometer (QMS) port shown in figure 1 the probes were installed. The theoretical considerations of this technique are detailed in (refs. 10 and 13). The expressions for the calculation of electron energy $E_e$ and electron density $n_e$ are quite elaborate and are not given herein. The precautions taken in these measurements and in their interpretation are detailed in (ref. 14).

RESULTS AND DISCUSSION

Langmuir Probes

Plasma of argon only. - The behavior of electron energy at 50-W input power at the H, G, and F stations was determined for different pressures (fig. 2). Electron energy generally decreased with pressure at all positions. Also, as expected, electron energy was highest at position G, the plasma excitation center. The behavior of the electron concentration in this plasma at the same input power is shown in figure 3. Assuming quasineutrality of the plasma (i.e., $n_e \approx$ ion density $n_i$), we can state that this is also the behavior of the Ar⁺ ions in this plasma. As shown in figure 3, the values for $n_e$ detected at F at low pressures were higher than those at G. The reason for this is that the measurements were performed in flowing gases and at low pressures more charge carriers are swept to this sampling station. Had these measurements been performed in a static plasma, the values for $n_e$ at F and H would have been similar, as these positions were equidistant from G. The deviation of these values from the ideal values indicates that the measuring method is reliable.
The measurements performed in this simple plasma system served as a reference for the other plasmas analyzed. As argon was the main gas in the Ar + SiCl₄ and Ar + H₂ + SiCl₄ systems, any change in the values of \( n_e \) and electron temperature \( T_e \) measured under similar conditions would be due to the other components of the plasma.

**Plasma of hydrogen only.** - In an attempt to observe the major differences between the two gases hydrogen and argon, measurements were performed in plasmas of hydrogen only for the same pressure and input power as in the argon plasma. Because of the shorter luminous zone of this plasma significant results were obtained only in position G, and no results could be collected when the pressure was raised above 2 mbar as this method is not applicable for low \( n_e \) (<10⁻⁸ cm⁻³) (ref. 13). Comparing the values of \( n_e \) obtained in this plasma at 50 W (table I), with those measured for argon only (fig. 2) shows a decrease by one order of magnitude at 1 mbar. The electron energy however is in the same range as in the argon plasma. We may also note that in argon plasmas an increase in pressure causes a decrease in \( E_e \); but in the hydrogen plasma the behavior of \( E_e \) with pressure is not systematic, indicating a different type of plasma.

**Plasma of Ar + 15 vol % H₂.** - In this plasma the luminous zone was again shorter than in the argon plasma, and only the results for position G are given (table II). Again, there was no systematic trend in the behavior of \( E_e \) with increasing pressure, indicating that from this point of view this plasma resembled more the hydrogen plasma than the argon plasma although the mixture contained 85 percent argon. The total value of \( n_e \) in the Ar + H₂ mixture was higher than that in hydrogen only, but lower than that in argon only. On the other hand, the same \( E_e \) (~4.2 eV) was measured in the argon and hydrogen plasmas for similar conditions (50 W, 1 mbar) at position G. Therefore where did the energy go if less ions were generated? Obviously this energy can only be dissipated by the dissociation of the H₂ molecules into H radicals. This finding may explain the predominance of radical-molecule reactions detected - as will be shown - in the Ar + H₂ + SiCl₄ plasma.

**Plasmas containing SiCl₄.** - Reactive plasmas present problems for the Langmuir probe technique because new material is deposited on the probes during the measuring cycle (ref. 15). We could perform measurements in plasma of Ar + 4 vol % SiCl₄ but not in plasmas containing both H₂ and SiCl₄. This was probably so because the reaction and deposition rates in such plasmas are higher than in the Ar + SiCl₄ plasma - a matter to be discussed in the next section.

From the current-voltage (I-V) characteristics obtained for argon and Ar + SiCl₄ plasmas shown in figure 4, the following results were calculated for \( n_e \) and \( E_e \) at 60 W and 1.2 mbar:

\[
\begin{align*}
\text{Ar only: } & \quad n_e = 3.34 \times 10^{10} \text{ cm}^{-3} \quad E_e = 4.1 \text{ eV} \\
\text{Ar + 4 vol % SiCl₄: } & \quad n_e = 3.5 \times 10^{10} \text{ cm}^{-3} \quad E_e = 4.5 \text{ eV}
\end{align*}
\]

These results indicate that the number of charge carriers in the two plasmas was the same and that the electron temperature in the presence of SiCl₄ was raised by approximately 4500 K (0.4 eV) as a result of the chemical reactions.
Clearly ion-molecule reactions were taking place because in this type of reaction the number of ions remains unchanged although their identity may change in charge transfer reactions of the type

\[ A^+ + B \rightarrow A + B^+ \] (1)

or

\[ A^+ + B \rightarrow AB^+ \] (2)

in which new ions are generated while an equal number of ions are neutralized.

Mass Spectrometry

Plasma species. - Figure 5 presents the plasma and the nonplasma spectra of the Ar + H₂ + SiCl₄ plasma (argon and hydrogen not shown). Polymers of the type SiₓClₓ were observed in this plasma (fig. 5(b)), and they represent a very important feature of this system (ref. 9). Such polymers were detected only in plasmas containing argon (refs. 9 and 16) and were not encountered in H₂ + SiCl₄ (ref. 17), indicating that polymerization is induced by argon. As a higher ne value was also measured in these plasmas, it may be inferred that this polymerization was initiated by ionmolecule reactions. The mass/charge m/e values of all species detected up to m/e = 300 and their assignments are listed in table III. Examination of the x/y values of these species indicates a gradual increase from 1/4 in SiCl₄ toward values greater than 1 in Si₃Cl₂, Si₅Cl, etc., toward infinity in silicon.

Polymerization is a very important step in the deposition process in Ar + H₂ + SiCl₄; it decreases the residual chlorine in the film by enriching the polymers with silicon. As shown by Ross and Jaklik (ref. 18) plasma polymerization may affect film properties. The electronic properties of these films are being studied to clarify this matter (ref. 19). The films were found to be microcrystalline, with crystallite size up to 150 Å.

Reaction kinetics. - The measurements performed at H, G, and F revealed the variation in peak intensity of the plasma species. Assuming pseudofirst-order reactions, the kinetic constants (local and overall) were calculated (refs. 16 and 17). The kinetic constants for reactant decomposition and the formation of silicon and HCl or chlorine are given in table IV for all three plasmas. The data presented are for the best recomposition conditions in each plasma at a fixed input power (100 W). The rate of SiCl₄ decomposition was highest in the Ar + H₂ + SiCl₄ plasma and so was the rate of silicon formation. On the other hand HCl was produced with a higher rate in the H₂ + SiCl₄ plasma. The main difference between the two plasmas being the presence of polymers, we may conclude again that polymers increase the rate of silicon formation.

Fewer charge carriers have been found in hydrogen-containing plasmas, thus ruling out the possibility that the increased reaction rates are due to ion-molecule reactions. The other possible mechanism is radical-molecule reactions. The presence of a high radical concentration in Ar + H₂ + SiCl₄ plasma as compared to Ar + SiCl₄ plasma was confirmed by electron spin resonance measurements in the two plasmas (ref. 16). On the basis of works by Sauer et al. (refs. 20 and 21) at the initiation stage the reaction in a system containing both argon and hydrogen is presumably the ion-molecule reaction:
\[
\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \quad (3)
\]

The \(\text{ArH}^+\) complex, being very reactive, reacts with hydrogen and with electrons:

\[
\text{ArH}^+ + \text{e}^- \rightarrow \text{Ar}^* + \text{H} \quad (4a)
\]

\[
\text{Ar}^* + \text{H}_2 \rightarrow \text{Ar} + \text{H}_2^* \quad (4b)
\]

\[
\text{H}_2^* \rightarrow 2\text{H} \quad (4c)
\]

where the asterisk denotes an excited atom. This is another path by which hydrogen radicals are generated and may explain the higher reaction rates in the plasma containing both argon and hydrogen.

**DEPOSITION RESULTS**

In the deposition system the \(\text{Ar} + \text{SiCl}_4\) plasma deposited no significant silicon layer on graphite substrates. This is attributed to sputtering of the deposit by argon ions and etching of the deposit by chlorine radicals. The extremum (maximum - minimum) results obtained in the \(\text{H}_2 + \text{SiCl}_4\) and \(\text{Ar} + \text{H}_2 + \text{SiCl}_4\) systems are shown in table V. The deposition rates in the \(\text{Ar} + \text{H}_2 + \text{SiCl}_4\) plasma were higher than in the \(\text{H}_2 + \text{SiCl}_4\) plasma. These results are in good agreement with the measurements of reaction kinetics, as higher reaction rates were measured for the homogeneous reactions in the \(\text{Ar} + \text{H}_2 + \text{SiCl}_4\) plasma and these reactions are the precursors for the heterogeneous reactions leading to deposition. Also, the chlorine content of the films was lower when argon was present in the plasma. This is also attributed to the different deposition mechanisms in the two plasmas. The chlorine content of the highly polymerized \(\text{Si}-\text{Cl}\) species in the \(\text{Ar} + \text{H}_2 + \text{SiCl}_4\) plasma diminished in surface reactions of the type

\[
\text{Si}_x\text{Cl}_y (x/y > 1) \rightarrow \text{Si}_x\text{Cl}_y-1 + \text{Cl} \quad (5)
\]

In the \(\text{H}_2 + \text{SiCl}_4\) plasma however the chlorine-rich \(\text{SiCl}_2\) species has been found to have a primary role, in the deposition (ref. 17) in the reactions

\[
\text{SiCl}_2 [\text{ads}] \rightarrow \text{SiCl} [\text{ads}] + \text{Cl} \quad (6)
\]

\[
\text{SiCl} [\text{ads}] \rightarrow \text{Si} [\text{s}] + \text{Cl} \quad (7)
\]

The chlorine radicals formed in reactions (5) to (7) are either reduced by the hydrogen to form \(\text{HCl}\) or participate in \(\text{SiCl}_4\) recombination.

**DEPOSITION MODEL**

The findings in the \(\text{Ar} + \text{H}_2 + \text{SiCl}_4\) system are summarized in figure 6. This model specifies the roles of hydrogen and argon in the various stages of deposition. Thus, although hydrogen is the main gas reacting with \(\text{SiCl}_4\) and reacts primarily in radical-molecule reactions, argon is active in the deposition by superimposing ion-molecule reactions. \(\text{ArH}^+\) species are generated and in turn create more hydrogen radicals, and \(\text{Si}_x\text{Cl}_y\) polymers are created and in
turn help decrease the amount of chlorine in the deposit. This deposition model resembles Turban's description of the reactions occurring in \( \text{H}_2 + \text{SiH}_4 \) plasma (ref. 22).

REFERENCES


### TABLE I. - ELECTRON ENERGY AND DENSITY IN HYDROGEN PLASMA AT 50 W

<table>
<thead>
<tr>
<th>Pressure, P, mbar</th>
<th>Electron Energy, $E_e$, eV</th>
<th>Electron Density, $n_e$, cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.6</td>
<td>4.0 x 10^9</td>
</tr>
<tr>
<td>1</td>
<td>4.2</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### TABLE II. - ELECTRON ENERGY AND DENSITY IN Ar + H$_2$ PLASMA AT 50 W

<table>
<thead>
<tr>
<th>Pressure, P, mbar</th>
<th>Electron Energy, $E_e$, eV</th>
<th>Electron Density, $n_e$, cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.77</td>
<td>4.1 x 10^9</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>3.88</td>
<td>1.26</td>
</tr>
</tbody>
</table>

### TABLE III. - SPECIES DETECTED IN Ar + H$_2$ + SiCl$_4$ PLASMA UNDER VARIOUS CONDITIONS

<table>
<thead>
<tr>
<th>S1/Cl ratio</th>
<th>Assigned species</th>
<th>m/e</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>S1</td>
<td>28</td>
<td>(a)</td>
</tr>
<tr>
<td>2:1</td>
<td>Cl$_2$</td>
<td>63</td>
<td>(b)</td>
</tr>
<tr>
<td>1:2</td>
<td>SiCl$_2$</td>
<td>70</td>
<td>(b)</td>
</tr>
<tr>
<td>0</td>
<td>Cl$_3$</td>
<td>91</td>
<td>(b)</td>
</tr>
<tr>
<td>1:1</td>
<td>Si$_2$Cl$_2$</td>
<td>98</td>
<td>(a)</td>
</tr>
<tr>
<td>1:2</td>
<td>SiCl$_3$</td>
<td>105</td>
<td>(c)</td>
</tr>
<tr>
<td>2:3</td>
<td>Si$_2$Cl$_3$</td>
<td>126</td>
<td>(b)</td>
</tr>
<tr>
<td>1:4</td>
<td>SiCl$_4$</td>
<td>133</td>
<td>(a)</td>
</tr>
<tr>
<td>5:1</td>
<td>Si$_5$Cl</td>
<td>161</td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>170</td>
<td>(a)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S1/Cl ratio</th>
<th>Assigned species</th>
<th>m/e</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>S$_2$Cl$_4$</td>
<td>200</td>
<td>(b)</td>
</tr>
<tr>
<td>2:1</td>
<td>S$_5$Cl$_2$</td>
<td>212</td>
<td>(b)</td>
</tr>
<tr>
<td>1:2.5</td>
<td>S$_2$Cl$_5$</td>
<td>233</td>
<td>(b)</td>
</tr>
<tr>
<td>1:1.66</td>
<td>S$_2$Cl$_3$</td>
<td>245</td>
<td>(b)</td>
</tr>
<tr>
<td>1:1</td>
<td>S$_4$Cl$_4$</td>
<td>254</td>
<td>(b)</td>
</tr>
<tr>
<td>1:1.66</td>
<td>S$_3$Cl$_5$</td>
<td>261</td>
<td>(b)</td>
</tr>
<tr>
<td>3.5:1; 1:3</td>
<td>S$_7$Cl$_2$; S$_2$Cl$_6$</td>
<td>266</td>
<td>(c)</td>
</tr>
<tr>
<td>2:1</td>
<td>S$_6$Cl$_3$</td>
<td>273</td>
<td>(b)</td>
</tr>
<tr>
<td>1:2.5</td>
<td>S$_5$Cl$_4$</td>
<td>282</td>
<td>(b)</td>
</tr>
<tr>
<td>1:2; 4:1</td>
<td>S$_3$Cl$_6$; S$_8$Cl$_2$</td>
<td>294</td>
<td>(b)</td>
</tr>
</tbody>
</table>

(a) Belong to spectrum of SiCl$_4$.

(b) Detected only after plasma activation. (Not under all work conditions).

(c) Detected only rarely.
TABLE IV. - OVERALL REACTION RATES FOR VARIOUS PLASMAS CONTAINING SiCl₄ (AT 100 W, 60 sccm)

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Overall reaction rate, k, s⁻¹</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiCl₄</td>
<td>Si(g)</td>
</tr>
<tr>
<td>Ar + SiCl₄</td>
<td>15.6</td>
<td>-71</td>
</tr>
<tr>
<td>H₂ + SiCl₄</td>
<td>241</td>
<td>-365</td>
</tr>
<tr>
<td>Ar + H₂ + SiCl₄</td>
<td>601</td>
<td>-526</td>
</tr>
</tbody>
</table>

⁻Minus designates formation.
    bCalculated at 10 torr.
    cCalculated at 1 torr.

TABLE V. - DEPOSITION RATES AND CHLORINE CONTENT OF SAMPLES FROM TWO TYPES OF PLASMAS CONTAINING SiCl₄

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Minimum and maximum deposition rates, um/hr</th>
<th>Minimum and maximum Cl content in Si, percent</th>
<th>Optimal values¹</th>
<th>Optimal deposition conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ + SiCl₄</td>
<td>0.9 - 4</td>
<td>5.5 - 24</td>
<td>2 µm/hr; 5.5 vol % Cl</td>
<td>2 torr; 100 W; H</td>
</tr>
<tr>
<td>Ar + H₂ + SiCl₄</td>
<td>1.2 - 7</td>
<td>0.7 - 11</td>
<td>6 µm/hr; 1.0 vol % Cl</td>
<td>2 torr; 250 W; H</td>
</tr>
</tbody>
</table>

¹Highest deposition rates with low Cl content.
(a) Sampling in position G.

(b) Sampling before plasma center (position H).

(c) Sampling after plasma center (position F).

Figure 1. - Location of plasma excitation center relative to sampling port.

Figure 2. - Mean kinetic energy of electrons in argon plasma. Input power, 50 W.
Figure 3. - Charge carrier density in argon plasmas. Input power, 50 W.
Figure 4. - Current-voltage characteristics of argon and Ar + SiCl$_4$ plasmas obtained under similar conditions. Input power, 60 W; pressure, 1.2 mbars.

FOR a: $I = 2.5 \times 10^{-5}$ amp/DIVISION
FOR b: $I = 1 \times 10^{-5}$ amp/DIVISION
Figure 5. - Schematic spectrum obtained from Ar + H₂ + SiCl₄ mixture. Input power, 150 W; pressure, 0.6 mbar.
Figure 6. - Deposition model for silicon film in argon + H₂ + SiCl₄ plasma.
Effect of Argon and Hydrogen on Deposition of Silicon From Tetrachlorosilane in Cold Plasmas

R.R. Manory, R. Avn1, and A. Grill

Prepared for the Fall Meeting of the Materials Research Society, Boston, Massachusetts, December 2-7, 1985. R.R. Manory, Ben Gurion University of the Negev, Beer Sheva, Israel and NRC-NASA Research Associate; R. Avn1 and A. Grill, Ben Gurion University of the Negev, Beer Sheva, Israel.

The roles of Ar and H₂ on the decomposition of SiCl₄ in cold plasma were investigated by Langmuir probes and mass spectrometry. Decomposition of the reactant by Ar only has been found to be very slow. In presence of H₂ in the plasma SiCl₄ is decomposed by fast radical-molecule reactions which are further enhanced by Ar due to additional ion-molecule reactions in which more H radicals are produced. A model for the plasma-surface interactions during deposition of µC-Si in the Ar + H₂ + SiCl₄ system is presented.