Radical and Ion Molecule Mechanisms in the Polymerization of Hydrocarbons and Chlorosilanes in rf Plasmas at Low Pressures (>1.0 torr)

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ABSTRACT

The ion-molecule and the radical-molecule mechanisms are responsible for the dissociation of hydrocarbons, and chlorosilane monomers and the formation of polymerized species, respectively, in the plasma state of a rf discharge. In the plasma of a mixture of monomer with Ar, the rate determining step for both dissociation and polymerization is governed by an ion-molecular type interaction. Additions of H₂ or NH₃ to the monomer + Ar mixture commutes the rate determining step from an ion-molecular interaction to a radical-molecule type interaction for both monomer dissociation and polymerization processes.

INTRODUCTION

In radio frequency (rf) discharges, hydrocarbons such as methane, acetylene and propylene (refs. 1 and 2) polymerize resulting in the formation of solid pyrocarbon (PyC) (refs. 3 to 5). A similar discharge in silane (refs. 6 to 9) or in chlorosilanes (refs. 10 to 14) results in the formation of solid...
silicon. Addition of NH$_3$ to silane or chlorosilanes results with the solid deposition of Si$_3$N$_4$ (refs. 15 and 16) while organosilicones such as tetramethyl silane (ref. 17) in rf plasma results with the formation of solid SiC.

Introduction of rare gases (Ar or He) in the rf plasma enhance the dissociation of the monomer, its polymerization and the deposition of both PyC (refs. 3 to 5) and Si (refs. 7 to 13). The role played by argon in the rf discharge was explained by being a charge carrier enhancing the ionization of hydrocarbon species by charge transfer reactions and by Penning ionization (refs. 3 to 5, and 7). The presence of Ar in the discharge enhances, as well, the deposition rate on grounded or negatively biased substrates (refs. 1 to 5).

The aim in the present work is to shed more light on the nature of the mechanism and kinetics in the homogeneous reactions of hydrocarbons or chlorosilanes in rf plasmas. In other words, to determine the rate determining steps in the dissociation of the monomer and in the formation of polymerized species. Two different plasmas, one containing the monomer mixed with argon, while the other containing hydrogen (or ammonia) were diagnosed and compared by the following characteristics:

1. Mean electron energy (T$_e$) and plasma density (n$_i$).
2. Reaction rates for monomer dissociation (k$_o$) and formation of polymerized species (k$_L$).
3. Relative concentration of free radicals (n$_R$) and
4. Deposition rates on floated, grounded and negatively biased solid substrates.

The above diagnostics were performed varying plasma parameters such as: total gas pressure, relative concentration of the monomer in the gas mixtures, (its partial pressure), and net power input to the plasma at different locations in the plasma.
Two general approaches for the mechanism of homogeneous reactions are found in the literature, namely:

(1) the positive ion-molecule type reactions (refs. 18 to 25); and

(2) the radical molecule type (refs. 1, 2, and 26).

To discern which one of the two mechanisms are rate determining in a plasma system a general criterion is needed. Free radicals, positive and negative ions are continuously formed in the plasma as a result of the interaction of the gas monomer molecules with plasmas energetic electrons. The concentration per unit volume or plasma (cm$^{-3}$) of free radicals, $n_R$, positive ions, $n_i$, and negative ions, $n_N$, and their spatial gradients are variables entering into the kinetics of reactions with the monomer molecules. Another variable controlling the kinetics is the reactivity of the radicals and the charged ions, i.e., the cross sections, $\sigma_R$, $\sigma_i$, $\sigma_N$ of such reactions. The probability of reaction, $P$, is defined as the product of $n \times \sigma$ in a given location, $z$, along the plasma system. Thus if:

$$n_R \times \sigma_R > n_i \times \sigma_i,$$

meaning that the probability of radicals interacting with the monomer is higher than the probability for ion-molecule interaction at $z$ and vice versa $P_i > P_R$ when $n_i \sigma_i > n_R \sigma_R$ at $z$.

**EXPERIMENTAL**

The rf plasma system is shown in Fig. 1(a), while the position in the plasma along the gas flow, i.e., H, G, and F are shown in Fig. 1(b). It shows the distances between H to G, and G to F which in terms of time ($\tau_0$) at 10 torr for example are 45 $10^{-3}$ seconds apart.

Four methods were used for the diagnosis of the rf plasma:

(1) Double Floating Probes System (DFPS) was described elsewhere (ref. 5) and used for the evaluation of the kinetic energy of electrons ($T_e$) and ion density ($n_i$).
(2) Quadrupole mass spectrometry (QMS) described elsewhere (refs. 3, 24, 27, and 28) and used for kinetic study. Considering different plasma parameters two kinds of kinetic constants were evaluated:

(a) The overall reaction rate constant \( k_o \) for the dissociation of the monomer (refs. 24, 27, and 28) from the plots of m/e normalized concentration \( I/I_0 \) versus positions; and

(b) The local reaction rate constant \( k_L \) for the formation of the polymeric species (refs. 24, 27, and 28) from the plots of \( I/I_0 \) versus gas pressure in the plasma reactor.

(3) Electron Paramagnetic Resonance (EPR) for evaluating the relative concentration of radicals in the plasma. Fig. 1(c) shows the schematic setup for EPR sampling in position F. Radicals from the plasma are adsorbed and stabilized on pretreated alumina (ref. 28). After each sampling the alumina was transferred to an EPR tube and the EPR spectrum was recorded.

(4) Deposition Rate was evaluated on a solid substrate into the plasma for a fixed time. Pyrocarbon was deposited on commercial ATJ graphite placed at position F. Silicon and \( \text{Si}_3\text{N}_4 \) were deposited on a similar graphite substrate and on stainless martensitic steel (AISI-410), both at position H (ref. 27). The substrates were mounted on a metal rod extending out of the reactor such that it could be left floating, grounded by earth connection or connected to an external D.C. power source for biasing purposes (fig. 1(a)).

RESULTS AND DISCUSSION

Electron Energy and Plasma Density

In position G at the center of the rf coil (maximum energy density delivered to the plasma) at 100 watts net input of power, the addition of \( \text{H}_2 \) or \( \text{NH}_3 \) to the plasma inhibits the values of both mean electron energy \( T_e \) and positive ion density \( n_i \) as shown by the ratio values (smaller than
1.0) in table I. For the SiCl₄ + Ar plasma, when hydrogen or ammonia were added, the inhibition effects on Tₑ and nᵢ were stronger compared to the effect of hydrogen on the C₃H₆ + Ar plasma. As shown in table I, the inhibition effect by hydrogen or ammonia increases with increasing pressure in the plasma, i.e., the inhibition is an inverse function of the mean free path of the interacting particles in the plasma.

The lower values of the positive ion density, nᵢ, in the presence of 20 vol% H₂ or 15 vol% NH₃ show an inhibition in the ionization process, for the following reasons:

1. The amount of energetic electrons (above 12 eV), needed for the ionization of SiCl₄, was reduced as shown by the lower Tₑ values in table I.
2. The charge transfer reaction Ar⁺ + SiCl₄ → SiCl₄ + Ar was partly replaced by excited Ar* particles and H⁺ radicals (refs. 28 and 29):

Overall (k₀) and Local (kₗ) Kinetics

The species obtained from the plasma of SiCl₄ + Ar + H₂ (or NH₃) and SiCl₄ + Ar are presented in Fig. 2(a) at various plasma positions. Similar plots (ref. 24) were obtained for the C₃H₆ + Ar plasma and are shown in Fig. 2(b). From Fig. 2 or similar plots (for SiCl₄ + Ar + NH₃) the overall reaction rate k₀ for the dissociation of the monomer and formation of nonidentified products was evaluated (ref. 24):

The overall reaction rate constants, k₀, for the dissociation of C₃H₆ and SiCl₄ between positions H and G, for the rf plasma, is given in table II at 100 W and 1.0 torr. The presence of a high concentration of H₂ in the 66 vol% C₃H₆ + Ar plasma (12 vol% H₂) inhibits the monomer dissociation and the formation of products by a factor of about 3. This
behavior is shown as well in figure 3, where the overall reaction rate con-
stant, $k_0$, of $C_3H_6$ increases by decreasing its concentration in the
gas mixture ($C_3H_6 + Ar$). When 100 vol % $C_3H_6$ is present in the
plasma, its dissociation is due mainly to the interaction with the energetic
plasma electrons, corresponding to a value of $k_0 = 50 \, s^{-1}$ for a pressure
of 1.0 torr. Lowering the hydrocarbon concentration in the gas stream by mix-
ing it with Ar, charge transfer reaction from Ar$^+$ and "penning" ionization
with Ar excited metastable states (11.55 eV) occur as well thus enhancing the
dissociation rate of the monomer.

As shown in table II, for the $SiCl_4 + Ar$ plasma the addition of $H_2$
or $NH_3$ enhances the dissociation of $SiCl_4$ and the resulting products.
The admixtures of 20 vol % $H_2$ to 3.5 vol % $SiCl_4$ in Ar enhances $K_0$
values about 40 times. For 15 vol % $NH_3$ the $K_0$ values were enhanced
about 25 times.

A partial list of the polymerized products in the plasma state, formed
from the dissociation of the monomer is shown in table III by the values of
$k_L$, the local reaction rate constant. The rate of formation of the polymeric
species, represented by $C_4H_8$, $C_2H_2$, and $C_4H_4$, was hindered by
hydrogen for a higher concentration of propylene in the $C_3H_6 + Ar$ stream.
The local reaction rate ratio, $K_L$, has values below 1.0 and are about of the
same order of magnitude as the overall reaction rate ratio, $K_0$ (table II),
thus indicating that in the hydrocarbon plasma, the dissociation and the for-
formation rates of the polymeric species are governed by the same mechanism.
Comparing the results given in table III and with those of Fig. 3, where the
reaction rate constant increases with increasing Ar concentration in the gas
stream, it might be concluded that an ion-molecule mechanism governs the
kinetics of dissociation ($k_0$) as well as the formation ($k_L$) of the poly-
merized molecules.
For the chlorosilane monomer, the rate of formation of the polymerized silicon species were enhanced by addition of hydrogen or ammonia in the gas stream, as shown in table III. In the SiCl₄ plasma the formation rate ratio values ($K_L$) when compared with the dissociation rate ratio values of the monomer ($K_0$) from table II show a discrepancy of about one order of magnitude, i.e., $K_0 > K_L$. Thus in the presence of $H_2$ or $NH_3$ in the SiCl₄ + Ar plasma another mechanism, besides the ion-molecule, controls the values of both $K_0$ and $K_L$ for the chlorosilicon.

In order to find out if a radical or positive ion mechanism is responsible for the dissociation of the monomer, formation of polymerized species and of Si, Si₃N₄ and PyC deposition, the probability criteria ($n \times \sigma$) should be applied. The following experiments were performed:

(1) electron paramagnetic resonance spectrometry for evaluating the free radical concentration ($n_R$) at a given location in the plasma, and

(2) deposition rate on floating or grounded substrates.

Electron Paramagnetic Resonance (EPR)

A typical EPR spectra with and without hydrogen in the SiCl₄ + Ar plasma is shown in Fig. 4, for $NH_3$ it was shown elsewhere (ref. 15).

The role played by $H_2$ and $NH_3$ in the formation of free radicals from the monomers is indicated in table IV, where EPR intensity ratios ($\beta$) are given for position G at 100 W. Comparing propylene concentrations of 16 vol % and 66 vol % with no hydrogen addition to the gas mixture, the amounts of free radical formed are equal, resulting with $\beta =$ unity. In other hydrocarbon plasma, where 20 percent $H_2$ were added to the gas stream, it enhances the amount of free radicals by at least one order of magnitude. Similar results for $\beta$ were obtained for the chlorosilane with 20 vol % $H_2$ or 15 vol % $NH_3$ in argon. Assuming the concentration trends of the free radicals adsorbed on
alumina represents their trend in the plasma, then addition of 20 vol% H₂ or 15 vol% increases 6 values and promotes the free radical interaction with the monomer, for the same σₙ value.

It can be stated that a higher concentration of free radicals, nₙ, hinders the dissociation and polymerization processes of hydrocarbons, while it enhances the dissociation and polymerization of chlorosilanes.

It should be stated that in the H₂ (NH₃) + Ar plasmas without monomers no EPR spectra was detected due to the rapid formation of H₂ on alumina.

Deposition Rate on Floating and Grounded Substrates

The deposition rate in umh⁻¹ of PyC on a graphite substrate placed in position F (highest deposition rate (ref. 24)) and EPR intensity of free radicals as function of total gas pressure at 16 vol% C₃H₆ in Ar are shown in Fig. 5. The deposition rate on the grounded substrate in the rf plasma shows a maximum value around 7.0 torr. The EPR maximum intensity under identical conditions was obtained at 1.0 torr decreasing with increasing pressure. In a previous publication (ref. 31) the deposition rate of PyC was modelized: From it emerges that the flux of positive ions, accelerated by the electrical field in the sheath formed around the either grounded or negatively biased (-100 V) substrate, impinge on the substrate surface by releasing sputtered particles and secondary electrons from it. These secondary emitted electrons, are accelerated in the sheath towards the plasma thus forming high energy electron beam which reacts and ionizes the free particles in the plasma layer (ref. 31). The maximum rate of deposition in Fig. 5 corresponds to a minimum free radical concentration, thus it might be concluded that an ion-molecule mechanism governs the deposition process of PyC rather than a radical mechanism. At 16 vol% C₃H₆ in argon a maximum deposition rate was obtained indicating the upper limit of propylene concentration in the gas mixture. At
higher than 16 vol% $C_3H_6$ concentration, which evolves higher amounts of $H_2$, the deposition rate decrease continuously; thus at high $H_2$ concentration which hinders the ion-molecule reactions, causes the decrease of the PyC deposition rate. On a floating graphite substrate the PyC deposition rate was reduced to a further minimum (below 1.0 $\mu$m h$^{-1}$). This is in accordance with the ion-molecule mechanism as shown in table V for the deposition rate of Si and Si$_3$N$_4$. If the rate determining step in the presence of $H_2$ or NH$_3$ was an ion-molecule mechanism then the highest deposition rate should be obtained on a negatively biased substrate or grounded substrate. Otherwise, for a radical mechanism a higher deposition rate of Si or Si$_3$N$_4$ should be expected on a floating substrate. This is illustrated by the deposition rate values presented in table V. As shown in the table for a floating substrate a higher deposition rate was obtained for Si and Si$_3$N$_4$ compared to the grounded substrate. Thus in the presence of hydrogen or ammonia a radical mechanism governs the formation and deposition processes of Si and Si$_3$N$_4$.

CONCLUSIONS

It has been shown that two mechanisms are responsible for the dissociation, polymerization and deposition processes in rf plasmas of hydrocarbon and chlorosilane monomers, namely: (a) ion-molecule interactions; and (b) excited radical molecule interaction. In the presence of Ar in the two plasmas, the rate determining step is by an ion-molecule mechanism, while admixtures of $H_2$ and NH$_3$ in the two plasmas the rate determining step are by a radical mechanism.
REFERENCES


TABLE I. - ELECTRON ENERGY ($T_e$) AND ION DENSITY ($n_i$) RATIOS IN THE RADIOFREQUENCY MICROWAVE PLASMAS OF Ar, Ar + H₂, Ar + NH₃, AND Ar + N₂ GAS MIXTURES

[Power input, 100 W; position G; gas mixtures concentrations expressed in volume percent.]

<table>
<thead>
<tr>
<th>Pressure, $P$, torr</th>
<th>Electron energy ratio</th>
<th>Ion density ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\frac{66 \text{C}_3\text{H}_6(12\text{H}_2) + \text{Ar}}{16 \text{C}_3\text{H}_6(4\text{H}_2) + \text{Ar}}$</td>
<td>$\frac{3.5 \text{SiCl}_4 + 20 \text{H}_2(15 \text{NH}_3) + \text{Ar}}{3.5 \text{SiCl}_4 + \text{Ar}}$</td>
</tr>
<tr>
<td>2</td>
<td>0.83</td>
<td>0.91</td>
</tr>
<tr>
<td>4</td>
<td>0.71</td>
<td>0.65</td>
</tr>
<tr>
<td>6</td>
<td>0.66</td>
<td>0.55</td>
</tr>
</tbody>
</table>

\(^a\)12 vol % released from the dissociation of 66 vol % C₃H₆.

\(^b\)4 vol % released from the dissociation of 16 vol % C₃H₆.
TABLE II. - OVERALL REACTION RATE CONSTANTS \( (k_0) \) FOR THE DISSOCIATION OF \( C_3H_6 \), \( SiH_4 \), and \( SiCl_4 \)

[Power input, 100 W; positions H to G; pressure, 1 torr; \( t_0 = 2.2 \) msec; all gas mixtures expressed in volume percent.]

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>Overall reaction rate constant, ( k_0 ), ( s^{-1} )</th>
<th>( K_0 = k_0 \left[ \frac{Ar + H_2 (NH_3)}{k_0 (Ar)} \right] )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( C_3H_6 )</td>
<td>( SiH_4 )</td>
</tr>
<tr>
<td>( 16 C_3H_6^a + Ar )</td>
<td>228</td>
<td>---</td>
</tr>
<tr>
<td>( 66 C_3H_6^b + Ar )</td>
<td>60</td>
<td>---</td>
</tr>
<tr>
<td>( 5.0 SiH_4 + Ar )</td>
<td>---</td>
<td>330</td>
</tr>
<tr>
<td>( 5.0 SiH_4 + 15 H_2 + Ar )</td>
<td>---</td>
<td>95</td>
</tr>
<tr>
<td>( 3.5 SiCl_4 + Ar )</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( 3.5 SiCl_4 + 20 H_2 + Ar )</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( 3.5 SiCl_4 + 15 NH_3 + Ar )</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\) Releases 4 vol% \( H_2 \) in the plasma.
\(^b\) Releases 12 vol% \( H_2 \) in the plasma.
TABLE III. - LOCAL REACTION RATE CONSTANT \( (k_L) \)

[Power input, 100 W; pressure, 1 torr; all gas mixtures expressed in volume percent.]

(a) Position F

<table>
<thead>
<tr>
<th>Plasma species</th>
<th>Local reaction rate constant, ( \text{cm}^3 \text{ mole}^{-1} \text{s}^{-1} )</th>
<th>( k_L )</th>
<th>( k_L' )</th>
<th>( K_L = \frac{k_L}{k_L'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 66 \text{C}_3\text{H}_6 + \text{Ar} )</td>
<td>( 16 \text{C}_3\text{H}_6 + \text{Ar} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2^+ )</td>
<td>( 0.3 \times 10^{10} )</td>
<td>( 1.9 \times 10^{10} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_4\text{H}_2^+ )</td>
<td>0.6</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_4\text{H}_4^+ )</td>
<td>0.05</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_4\text{H}_8^+ )</td>
<td>0.08</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) Position H

<table>
<thead>
<tr>
<th>Plasma species</th>
<th>Local reaction rate constant, ( \text{cm}^3 \text{ mole}^{-1} \text{s}^{-1} )</th>
<th>( k_L )</th>
<th>( k_L' )</th>
<th>( K_L = \frac{k_L}{k_L'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.5 \text{SiCl}_4 + 20 \text{H}_2 + \text{Ar} )</td>
<td>( 3.5 \text{SiCl}_4 + \text{Ar} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Si}_2\text{Cl}_4^+ )</td>
<td>( 23.0 \times 10^{10} )</td>
<td>( 3.7 \times 10^{10} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Si}_3\text{Cl}_6^+ )</td>
<td>8.8</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Si}_5\text{Cl}_2^+ )</td>
<td>5.0</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Si}_5\text{Cl}^+ )</td>
<td>4.0</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \)Releases 12 vol % \( \text{H}_2 \).
\( ^b \)Releases 4 vol % \( \text{H}_2 \).
\( ^c \)Same \( K_L \) values obtained from

\( 3.5 \text{vol} \% \text{SiCl}_4 + 15 \text{vol} \% \text{NH}_3 + \text{Ar} \)

\( 3.5 \text{vol} \% \text{SiCl}_4 + \text{Ar} \)
### TABLE IV. - EPR INTENSITY RATIO FOR VARIOUS GAS MIXTURES

[Power input, 100 W; pressure, 1 torr; position G; all gas mixtures expressed in volume percent.]

<table>
<thead>
<tr>
<th>Gas mixture ratio</th>
<th>EPR intensity ratio, $B$</th>
<th>Concentration, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$66 \text{C}_3\text{H}_6 + \text{Ar}$</td>
<td>1.0</td>
<td>$16.0 \text{CH}_4$ $16.0 \text{C}_3\text{H}_6$</td>
</tr>
<tr>
<td>$16 \text{C}_3\text{H}_6 + \text{Ar}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiCl}_4 + \text{H}_2 + \text{Ar}$</td>
<td>15.0</td>
<td>$3.5 \text{SiCl}_4$ $15.0 \text{NH}_3$</td>
</tr>
<tr>
<td>$\text{SiCl}_4 + \text{Ar}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiCl}_4 + \text{NH}_3 + \text{Ar}$</td>
<td>10.0</td>
<td>$20.0 \text{H}_2$ Up to 100 Ar</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{Ar}$</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{H}_2 + \text{Ar}$</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{H}_2 + \text{Ar}$</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{Ar}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_4 + \text{H}_2 + \text{Ar}$</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_4 + \text{Ar}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aNo EPR intensity measured.*
TABLE V. - SILICON AND Si$_3$N$_4$ DEPOSITION RATE
FROM SiCl$_4$ + Ar WITH AND WITHOUT
HYDROGEN (OR AMMONIA) ADDITION FOR
IDENTICAL PLASMA CONDITIONS

[Power input, 150 W; pressure, 2 torr; gas mixtures
expressed in volume percent.]

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>Substrate connection</th>
<th>Deposition rate$^a$ (μm)(h$^{-1}$)</th>
<th>mgh$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 SiCl$_4$ + Ar</td>
<td>Grounded</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>5 SiCl$_4$ + 15 H$_2$ + Ar</td>
<td>Grounded</td>
<td>1.4</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>Floating</td>
<td>2.0</td>
<td>3.1</td>
</tr>
<tr>
<td>5 SiCl$_4$ + 15 NH$_3$ + Ar</td>
<td>Grounded</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Floating</td>
<td>1.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>

$^a$ Measured on one side of 20- by 40-mm steel substrate to compare deposition rates for all substrates, calculated values (for one side) of dG/dt, mgh$^{-1}$ on the grounded are presented. Thickness rates, dh/dt, μm/h$^{-1}$
(a) Plasma deposition of Si and Si$_3$N$_4$.

Figure 1. - Experimental setup.

(b) Three locations, H, G, and F in plasma with regard to the rf coil and gas flow. $\tau_0$ the time spent by the monomer between H, G, and F.

(c) Adsorbing free radicals from plasma. The adsorbing enclave is shown in position F.

Figure 1. - Concluded.
Figure 2. - Normalized concentration $I/\Sigma I$ of chlorosilane species in the plasma in the three positions at 100 watts and 4.0 torr.

Figure 3. - Overall reaction rate constant ($k_0$) versus Ar concentration in the C$_3$H$_6$ plasma at 400 watts.
Figure 4. - EPR spectra of free radicals adsorbed on alumina. (A - plasma of 3.5 v/o SiCl$_4$ + 20 v/o H$_2$ + Ar; B - plasma of 3.5 v/o SiCl$_4$ + Ar.)

Figure 5. - Deposition rate and EPR intensity versus gas pressure for 16 v/o C$_3$H$_6$ + Ar plasma at 400 watts. Position F.
Radical and Ion Molecule Mechanisms in the Polymerization of Hydrocarbons and Chlorosilanes in rf Plasmas at Low Pressures (>1.0 Torr)


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The ion–molecule and the radical–molecule mechanisms are responsible for the dissociation of hydrocarbons, and chlorosilane monomers and the formation of polymerized species, respectively, in the plasma state of a rf discharge. In the plasma, of a mixture of monomer with Ar, the rate determining step for both dissociation and polymerization is governed by an ion–molecular type interaction. Additions of H$_2$ or NH$_3$ to the monomer + Ar mixture transforms the rate determining step from an ion–molecular interaction to a radical–molecule type interaction for both monomer dissociation and polymerization processes.