On the Decomposition of Silane in Plasma Deposition Reactors

C. A. DeJOSEPH, Jr., P. D. HAALAND, AND A. GARSCADDEN, SENIOR MEMBER, IEEE

Abstract—In a low-pressure discharge, plasma-enhanced decomposition of silane proceeds by various channels including electron-impact, ion- and radical-induced, and heterogeneous reactions. The results of several experiments are presented to clarify the relative importance of the processes. The conclusions of these studies and associated analysis are that the dominant processes are strongly influenced by the gas residence time, the power density input, and the electronegative characteristics of the silane discharge.

I. INTRODUCTION

SINCE the discovery of plasma-enhanced deposition of amorphous silicon from silane by Spear and Le-Comber [1] in 1975, the semiconductor community has invested considerable resources in the characterization of the thin films. More recently, several groups have initiated studies of the plasma conditions and their influence on film deposition rate and film quality. This laboratory has concentrated on the first aspect by investigating some of the gaseous electronic and collisional phenomena that occur in deposition reactors. We will outline the present understanding of the first steps in the transformation of the gaseous silane molecule, which is fully saturated with hydrogen, to a film which has typically one-tenth equivalent atom of hydrogen per silicon atom.

The most popular commercial deposition reactors capacitively couple 13.6-MHz RF energy at modest power into a low-pressure dilute mixture of silane and argon or hydrogen (Table I). Definition of all of the possible reactions that occur in the RF discharge is not yet sufficiently precise to permit conclusive modeling in the complex molecular gas mixtures encountered in plasma reactors. The following discussion will therefore attempt to provide elements of the database for such modeling. Analytical and experimental results of dc discharges in silane and silane mixtures, for which physically reasonable and reproducible boundary conditions are available, will be stressed. In view of the different models of the RF discharge, it has been considered easier to establish unanimity and defined conditions for dc discharges. The conditions under which dc results can be extended to RF reactors will be discussed.

Plasma-enhanced deposition differs fundamentally from classical chemical vapor deposition because of the presence of energetic electrons, ions, and radicals in the low-pressure discharges. In order to bound the problem of plasma-enhanced decomposition of silane, one must assess the relative roles of these species. In addition, the nonequilibrium heterogeneous kinetics must be considered.

II. METHODS

A. Analytical Model

Electron collisions dissociate the original silane and also generate radicals, excited states, and ions according to the rate equation

\[ R = N_0 \int f(E)E^{1/2} Q(E) \, dE. \] (1)

The rate constant \( R \) must be calculated from the cross section \( Q(E) \) of the gas of interest, its density \( N_0 \), and the actual electron energy distribution function (EEDF), \( f(E) \), for the plasma conditions under consideration. For either dc or RF discharges, the EEDF is not expected to be Maxwellian. Since measurements of \( f(E) \) in the complex mixtures of gases are not available, our approach has been to calculate \( f(E) \) using cross sections derived from well-defined measurements of dissociative excitation [2], ultraviolet absorption [3], electron energy loss [4], electron drift velocity [5], and characteristic energy. Comparisons of the experimental results in different silane–rare-gas mixtures with computer experiments permit selection of, and reasonable bounds on, the momentum transfer, the total vibrational excitation, and the electron-impact dissociation cross sections. Very similar results have recently been obtained by Hayashi [6]. The set of cross sections used in the calculations is illustrated in Fig. 1. Due to the different electron drift velocities at

TABLE I

<table>
<thead>
<tr>
<th>OPERATING CONDITIONS</th>
<th>Typical Deposition Reactor Operating Conditions</th>
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<tbody>
<tr>
<td>Gas Pressure</td>
<td>10 - 1000 mtorr</td>
</tr>
<tr>
<td>SiH₄ Fraction</td>
<td>1 - 50%</td>
</tr>
<tr>
<td>Buffer Gas</td>
<td>Ar, H₂, He</td>
</tr>
<tr>
<td>Power Density</td>
<td>1-100 mW/cm³</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>to 280°C</td>
</tr>
<tr>
<td>Gas Temperature</td>
<td>30°C</td>
</tr>
<tr>
<td>Fractional Decomposition</td>
<td>5 - 25%</td>
</tr>
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</table>
different silane percentages and in different buffer gases, the electron density can vary considerably even when the discharge current is held constant. This effect must be allowed for when calculating the effective dissociation rate per electron.

B. Silane Dissociation

The dissociation rates of silane diluted in various gases were measured by determining the change in silane concentration downstream of either an RF or a dc discharge under well-controlled pressure and mass flow conditions. With these controls, the residence time of the silane in the discharge can be accurately calculated. Thus a change in silane density measured downstream for a given residence time will give an effective decomposition or dissociation rate for chosen discharge conditions. The silane concentration was determined by measuring the infrared absorption of an isolated vibration–rotation line of silane using a tunable diode laser (TDL) spectrometer. The very narrow linewidth of the TDL (approximately $3 \times 10^{-4}$ cm$^{-1}$) compared to the Doppler width of a silane line makes determination of the concentration from the measured absorbance very straightforward. The vibrational band used was the $v_3$ centered near 911 cm$^{-1}$. It was chosen because lasers in that wavelength region were on hand and the band is very intense. A particular line was selected based on the criteria of being isolated, so that peak absorbances could be used, and of having a “convenient” intensity for the conditions (concentration, path length) of the experiment. Over the course of the investigation, six different convenient lines were used according to the initial concentration of silane and the amount of dissociation.

Specific experiments involved measurements on primarily two discharge configurations. A dc discharge was operated at constant current in a 2.2-cm-diameter pyrex tube with hollow cylindrical Kovar electrodes. The electrode spacing was 22 cm. Gas mixtures of 1-percent silane in argon, helium, or nitrogen were used. Infrared absorption measurements were made in a 41-cm absorption cell placed downstream of the discharge. In the second configuration, an RF discharge was operated at constant power into the matching network at a frequency of 13.56 MHz. A 9.5-cm-diameter pyrex discharge tube contained three circular stainless steel wire-mesh electrodes spaced 4 cm apart and perpendicular to the gas flow. The middle electrode was driven by the unbalanced RF while the two outer electrodes were grounded. This configuration gave very stable discharges and allowed for changes in RF power while maintaining a constant discharge volume. Parasitic discharges to the vacuum manifold or flanges were avoided. In this experiment, absorption measurements were made a few centimeters downstream of the last (grounded) electrode by double passing the TDL beam through the discharge tube transverse to the gas flow. In both experiments, pressure and flow were measured and regulated with a mass flow/pressure microprocessor-controlled system using a capacitance manometer and thermal conductivity mass flow meters.

C. Cation–Molecule Reactions

Measurements of silicon hydride cation ($SiH^+_n$, $n = 1, 2, 3$) reactions with silane were performed at very low pressure using Fourier-transform mass spectrometry (FTMS) [7]. The mixtures were 5-percent silane in helium or in argon (purchased from Scientific Gas Products Inc). The gas was introduced through a thoroughly purged manifold into a Nicolet FTMS-1000 instrument. At total pressures of roughly $5 \times 10^{-8}$ torr, as measured by a Bayard–Alpert-type ionization gauge, mixtures of $SiH^+_n$ and—depending on the electron energy—$Ar^+$ or $He^+$, were formed by a pulsed electron beam of several hundred nanoamperes for a duration of 5 ms. Ions of all but one chosen $m/e$ were ejected from the cell by irradiation at their characteristic cyclotron frequencies. The resulting sample of, for example, $SiH^+_2$ was collisionally thermalized by the buffer gas and allowed to react with the background $SiH_4$ (2.10$^{-10}$ torr) for programmed times. FTMS spectra were then recorded for a mass range of 18–150 which included $SiH^+_n$, $Si_2H^+_n$, and $Si_3H^+_n$.

D. Heterogeneous Pyrolysis Measurements

A 2 ½-in flanged six-way high vacuum cross served as the experimental chamber for pyrolysis measurements. The sample in this case, a 1.8-cm$^3$ piece of crystalline silicon was supported above a two-pin medium current feedthrough flange equipped with a thermocouple feed. Gas mixtures, prepared in a liquid $N_2$ trapped diffusion-pumped manifold fitted with a 1000-torr capacitance manometer, were injected into the chamber in 5 ms through a Lasertechnics pulsed valve. Partial pressures were measured by sampling gas through a Granville–Phillips precision leak valve into a differentially pumped modulated beam quadrupole mass spectrometer. The total pressure in the chamber was monitored with a 1-torr capacitance manometer which also permitted calibration of the mass spectrometer’s sensitivity for each gas species. The substrate temperature was monitored by the thermocouple and by infrared/visible pyrometry of the sample. The data from the mass spectrometer and capacitance manometer...
were read into a computer system for reduction and plotting.

III. RESULTS AND DISCUSSION

In order to bound the importance of the various rates, the EEDF was calculated, as outlined in Section II-A above, assuming a homogeneous plasma and a constant $E/N$ (where $E$ is the applied electric field and $N$ is the total gas density). Typical calculated rates for dissociation vibrational excitation, ionization, and attachment in silane–argon mixtures using the silane cross sections of Fig. 1 are displayed in Fig. 2. The rate of one-step dissociation is exceeded only by the vibrational excitation rate over the range of reduced electric field ($E/N$ in units of $10^{-17} \text{ V \cdot cm}^2$ or Townsend, Td) considered. Due to the dissociation cross section's lower threshold of 7.8 eV, dissociation by electron impact is roughly two orders of magnitude faster than dissociative ionization, which onsets at 12.5 eV. Note that this calculation assumes that dissociation is caused by the higher energy "tail" of the electron energy distribution relevant to a homogeneous positive column discharge. If there are beam electrons such as occur in the negative glow, then their dissociation rate must be added to these rates to obtain the total rate of dissociation by electron impact.

Experimental comparisons for these calculations were provided by measurements of the total dissociation of silane in dilute gas mixtures. Data from a typical experiment using a dc discharge are shown in Fig. 3. From the measured dissociation, discharge current, and the drift velocity calculated from the Boltzmann transport (BT) equation, one can derive the electron density and thus estimate the total rate constant for electron dissociation of silane by the discharge. For 1-percent silane in argon at $E/N = 87$ Td, this rate is $2.8 \times 10^{-8} \text{ cm}^3/\text{s}$. Shown as a delta in Fig. 2(a), this measured rate is within a factor of two of that calculated for simple electron-impact dissociation, agreement which is considered reasonable in light of the nonlinear effects of cross-section uncertainties on calculated rates. Cross sections inferred from detailed specific literature rates permitted extension of the BT analytical approach which could be probed experimentally. Reasonable agreement both for dissociation rates and their scaling with $E/N$ in argon:silane and helium:silane dc discharges have been obtained. However, the measured dissociation rate in nitrogen:silane dc discharges was much higher than the calculated rate. The results implying additional heavy particle-induced dissociation will be treated in a separate publication.

Similar measurements have also been made down-
stream of a low-power RF discharge (Fig. 4). Starkly contrasting the dc data, there is no clear scaling of dissociation rate with discharge power in the RF configuration. Even when great care is taken to define the discharge volume, the power into the matching network is apparently not sufficient to characterize the discharge. Also, the dissociation is not a simple exponential function of residence time as one might anticipate in a dilute mixture of non-attaching gases. It is therefore necessary to closely define the experimental configuration and other operational parameters (residence times, gas composition, current and voltage waveforms, phase angles, etc.) to permit reliable comparison of results from diverse experimental systems. Further, these data illustrate the difficulty of correlating experimental results to RF reactor models.

While the above data suggest that electron-impact dissociation is sufficient to account for the observed depletion of silane in a low-current short gas residence time dc discharge, the role of ion–molecule reactions has been considered to dominate that of electron impact in silane dissociation [8]. There has also been considerable work examining the electron-impact dissociative ionization channels [9]. The sampling of ions from low-pressure discharges by conventional mass spectrometry is difficult, and the sequence of ion reactions is not accessible. In order to bound the role of ion–molecule decomposition of silane in plasma-enhanced deposition, we have probed these dynamics at very low pressure by FTMS. Typical results for the interaction of SiH₄⁺ with silane in argon are illustrated in Fig. 5. Complete results for each of the ions formed by electron impact on silane have been presented elsewhere [7]. In addition, substantial data on the reactions of silicon hydride and noble gas cations with silane are in the open literature [10], [11].

Under the assumption that all ion–molecule collisions which result in molecular dissociation also result in changes to the ion mass, one can bound the rates of ion-induced silane decomposition in a dc discharge. At any instant, the rate of ion–molecule decomposition is given by a weighted average of the individual rate over the ion composition:

\[ \frac{1}{[\text{SiH}_4]} \frac{d[\text{SiH}_4]}{dt} = k_{\text{Ar}}[\text{Ar}^+] + \sum_{i=0}^{3} k_i[\text{SiH}_i^+] \].

This expression is considerably simplified when one considers the rates of the reactions (Table II):

<table>
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<tr>
<th>TABLE II</th>
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<tr>
<td>SELECTED ION–MOLECULE REACTION RATES FOR SILANE MOLECULE</td>
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<tr>
<td>PARENT ION</td>
</tr>
<tr>
<td>SiH⁺</td>
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<tr>
<td>SiH⁺</td>
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<tr>
<td>Si⁺</td>
</tr>
<tr>
<td>SiH₂⁺</td>
</tr>
<tr>
<td>Ar⁺</td>
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<tr>
<td>He⁺</td>
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These reactions are sufficiently rapid to drive the silicon hydride cation composition to a preponderance of SiH⁺ since it alone is slowly depleted by the reaction

\[ \text{SiH}_n^+ + \text{SiH}_4 \rightarrow \text{SiH}_{n+1}^+ + (\text{SiH}_4)_n, \quad n = 0, 1, 2. \]

These conclusions are substantiated by Perrin et al., who, sampling by quadrupole mass spectrometry, found that
SiH$_3^+$ dominated the monosilicon hydride cation distribution in a multipole discharge when the collisional mean free path decreased below the reactor dimensions [12].

For argon:silane mixtures at modest residence times, (2) asymptotically approaches

\[
\frac{1}{[\text{SiH}_4]} \frac{d[\text{SiH}_4]}{dt} \rightarrow 0.1 M
\]

\[
= 1.7 \times 10^{-11} [\text{Ar}^+] + 2.4 \times 10^{-11} [\text{SiH}_3^+].
\]  

(5)

In Fig. 6, the rates of forming silicon hydride and noble gas cations by electron impact versus reduced electric field are plotted on the same scale as their ion–molecule losses. In the absence of negative ions, plasma neutrality requires that

\[
N_e = \sum N_i^+
\]

allowing direct comparison of the electron-impact and cation–molecule dissociation of silane. Note that electron-impact dissociation clearly dominates the ion-induced silane decomposition by roughly two orders of magnitude under these conditions.

In the absence of detailed information on the losses of negative silicon hydride ions, an assessment of their possible effect is necessarily more qualitative. The rates for formation of silicon hydride anions by electron impact were calculated using cross sections of Eböinghaus et al. [13] in the BT equation. The resulting rates (Fig. 7) are found to be rather large and do not justify the literature emphasis on cation chemistry alone. For a 5-percent mixture of silane in argon, the calculated attachment rate exceeds the positive ionization rate below 48 Td. Between 48 and 55 Td, the total ionization rate exceeds the attachment (negative ion formation) rate; however, the argon ionization exceeds the silicon hydride cation formation rate. If one postulates that the principal loss of anions is

\[
\text{SiH}_n^- + \text{SiH}_m^+ \rightarrow \text{SiH}_p^- + \text{SiH}_n^- + \text{Ar}
\]

(6)

while the reaction

\[
\text{SiH}_n^- + \text{Ar}^+ \rightarrow \text{SiH}_n + \text{Ar}
\]

(7)

is significantly slower, one infers that the ion composition converges to a mixture of SiH$_n^-$ and Ar$^+$ between 48 and 55 Td. Such conditions enter into the relationship of cation–molecule to electron-impact dissociation of silane by modifying the ratio of cations to electrons. Thus for a ratio of $N_e/N^-$ of 0.01 at 50 Td, the calculated rate for Ar$^+$ induced decomposition of silane is of the same order as that for direct electron-impact dissociation. Note that the calculated source of negative ions is here only from electron impact on the vibrational ground state of silane. Since one calculates large power depositions into silane and hydrogen vibrational excitations, the possible influence of
vibrationally enhanced dissociative attachment may merit consideration [14]. It should be stressed that these arguments are schematic and intended to illustrate boundary conditions under which ion–molecule depletion of silane might compete with electron-impact dissociation.

The role of heterogeneous silane decomposition in plasmas has been hotly debated. Literature values for the activation energy required for pyrolysis span a wide range [15]. To aid in bounding the role of classical heterogeneous pyrolysis of silane, a pulsed-valve quadrupole mass spectrometer experiment was configured as described in Section II. A measure of silane or of a silane/hydrogen mixture was injected through a pulsed supersonic beam valve into a six-way high vacuum cross to interact with a resistively heated crystalline silicon substrate. A capacitance manometer was used both to calibrate the sensitivity of the quadrupole and to measure the total pressure during experimental runs. The partial pressure of silane and of hydrogen are monitored via the modulated beam mass spectrum of the gas sample which is leaked from the chamber. Under the experimental conditions, the silane collisional mean free path is significantly greater than the reactor dimensions. Thus molecules collide with the 1.8-cm$^3$ heated sample but have a high probability of thermalizing to 300 K on the reactor walls before colliding with another silane.

Typical experimental measurements of [SiH$_4$], [H$_2$], and the total pressure as a function of time are displayed in Fig. 8. On clean silicon, no decomposition is observed below 700°C. Above this temperature, the simple exponential decay of the silane increased beyond that caused by normal pumping through the leak. At the same time, hydrogen evolution is observed. (All traces contain an amount of H$_2$ to verify the QMS sensitivity.)

As one would expect, the evolution of hydrogen via the reaction

$$\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$$

(8)

causes an increase in the reactor pressure at early times. Since, by Graham’s law, hydrogen is pumped from the chamber at four times the rate of SiH$_4$, the total pressure decays more rapidly as the average fraction of H$_2$ in the mix increases. Specifically, this experiment measures the ratio of reactive to total gas–surface collisions when the surface is maintained at an equilibrated temperature. Since this ratio is unmeasurable ($< 10^{-7}$) below 700°C, we conclude that equilibrium power transfer from silicon to silane gas is insufficient to cause depletion of silane under plasma deposition conditions.

It should be stressed that nonequilibrium effects at the plasma boundaries may drive important heterogeneous decomposition. Thus ions accelerated by several tens to hundreds of volts in sheath fields may deposit energy leading to decomposition of absorbed silane. While we are not aware of any direct microscopic measurements, Zawojski [16] has inferred a significant correlation between deposition rates and sheath voltage. In any case, the thermal conductivity of silicon is too large to permit

**Fig. 8.** Results of the silane pyrolysis experiment. A mixture of 5-percent H$_2$ in SiH$_4$ was prepared and injected into the chamber in 5 ms leading to a total pressure maximum of 2.4 x 10$^{-3}$ torr. The bold traces (a) and (b) provided information on d[SiH$_4$]/dt and d[H$_2$]/dt in the absence of reactive sources and losses. Heating of the 1.8-cm$^3$ substrate to 735°C results in observable evolution of H$_2$ and more rapid depletion of SiH$_4$. These processes, which are unobserved below 700°C, increase as the temperature of the substrate is raised. Maxima in the total pressure curves (c) increase with increasing silane depletion as one expects from the stoichiometry: SiH$_4$ → Si(s) + 2H$_2$. Also, the rate of pumping through the mass spectrometer increases with increasing decomposition as the fraction of H$_2$, which effuses four times faster than silane by Graham’s law, increases.
maintenance of the required temperature gradient between the substrate thermocouple and the growing surface for classical pyrolysis to occur.

It appears that there is a critical difference between pyrolysis under plasma-assisted and classical chemical vapor deposition conditions. In the latter, energy is channeled into decomposition by multiple surface collisions and local thermodynamic equilibrium of silane near the boundary. The excited and/or dissociated fragments can react either with more silane or the surface itself leading to film growth. In plasma reactors, by contrast, the molecular mean free path is too long for frequent collisions and the substrate temperature is too low to provide the 50 or so kilocalories per mole required for decomposition in a single collision with the substrate. It is also not possible for a molecule which is partially activated by the 300°C substrate to transfer energy to another silane before being thermalized by collision with the buffer gas or a wall. We conclude that to the extent silane is decomposed on the growing silicon surface, it must result from nonequilibrium deposition of energy by the plasma to the absorbed gas–surface ensemble.

As in the case of negative ions, detailed rates for neutral fragment reactions with silane are sparse. One conspicuous feature of many of the possible reactions is the requirement for hydrogen atoms to balance the product equations. The rate for hydrogen atom reaction with silane has been measured [17] and confirmed to be of the order of the reaction rate for

\[
\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5
\]  

(9)

using pulsed-valve mass-spectrometric techniques in our laboratory. Based on the literature rate of 5 × 10^{-13} cm^3 s^{-1}, one requires [H]/N_e = 40 000 for the atom–molecule rate to equal electron-impact dissociation. Since glow discharges typically operate with a fractional ionization of 10^{-6}, one requires that [H]/N_TOT approach 0.04 for this radical channel to compete. While such a ratio is clearly not favored for 1-per cent silane mixtures, the influence of hydrogen-atom chemistry may become significant at higher silane fractions or in H_2:H_2Si mixtures. This may account, in part, for the varied rates of deposition measured with different gas mixtures. It should be noted that reaction of hydrogen atoms with silane is very much faster than three-body recombination under plasma deposition conditions. However, the competition between recombination at the reactor walls and reaction with silane may moderate the latter.

One key difference of the RF discharge is the presence of an ion sheath at each electrode. Transport of ions through this sheath causes secondary electron emission at the electrode. Secondary electrons are then accelerated through the full sheath potential into the body of the plasma. This fast beam component of the electron energy distribution is calculated to account for as much as 10^{-4} of the total electron density. While this is a small fraction, it must be remembered that over most of the RF cycle, all of these electrons are capable of causing dissociation and ionization of both silane and the buffer gas. In some cases, creation of long-lived excited states may also be important. In addition, these fast electrons perturb the selectivity of ionization in gas mixtures with different ionization thresholds. Thus for 1-, 5-, and 10-percent silane:helium mixtures, this beam can provide a source of very reactive [7], [11] helium cations which is absent in dc discharges due to the 13-eV difference in thresholds for formation of SiH_3^+ and He^+. The He^+ ion, which is two orders of magnitude more reactive than Ar^+ with silane [11], forms reactive Si^+ and SiH^+ in its first collision. To the extent that these ions (few of which are formed under dc excitation conditions) react to form higher order silanes, one may expect a nonlinear increase in ion–molecule depletion of silane with the He^+ formation in the RF discharge. Therefore we expect that the dissociation in the RF discharge will be influenced by the nature of the buffer gas because of the ion–molecule reaction rate differences. On the other hand, the differences in the dissociation rates in dc discharges due to the buffer gas are more probably due to the differences in electron transport and therefore different operating E/N for a selected current density.

The influence of RF excitation on sheath properties has been assessed by, for example, Pennebaker [18] and Kushner [19]. While details of the temporal sheath modulation, mapped at 10 kHz by Gottscho et al. [20], remain controversial at 13 MHz, it is clear that the RF sheaths provide significant anisotropic ion flux to the electrode surfaces. Thus RF excitation provides silane dissociation by nonequilibrium excitation of the (gas and) surfaces by ions as well as of the bulk gas by electrons.

IV. Conclusions

These notes deliberately do not advocate a particular detailed deposition mechanism. Rather, it is hoped that these experimental results and analytical models provide elements of the data base which permit reconciliation of the many varied deposition rates and film qualities that have been reported. From the experiments and calculations, it appears that the dominant dissociation mechanism will be different depending not only on the discharge excitation method but also on the selected gas mixture, residence times, and power loading. It is concluded that when the percentage of gas processed is low (also usually a condition for good quality of film), dissociation of silane proceeds principally by electron impact under dc-like excitation conditions. While the role of ion kinetics is less well defined, under most low-pressure conditions, cation molecule collisional decomposition proceeds about 100 times more slowly than direct electron-impact depletion. The presence of relatively large negative ion densities can increase the role of cation–molecule decomposition by driving down the ratio of electrons to positive ions. While much useful work remains to be done on negative ions of silane systems and the theoretical and experimental elaboration of 10^{-1}-Hz discharges, it is suggested that bounds on the relevant kinetics are best established from simpler dc or low-frequency discharge configurations. A very re-
cent paper [21] discusses the role of positive ion collisions in silane in detail and emphasizes the sheath regions.

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REFERENCES