

# Arrhenius-like behavior in plasma reactions

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An Arrhenius-like behavior of the silane dissociation rate constant as a function of the power actually fed in a rf discharge system is reported. The rate constant is calculated using mass-spectrometric measurements of silane consumption for 50 and 75 mTorr discharges, while the power consumed in the discharge is determined by using detailed voltage and current measurements. The slope of the natural logarithm of the dissociation rate constant as a function of the inverse of the discharge power increases with pressure. This is attributed to a change in the shape and/or the mean energy of the electron energy distribution function, while the linearity indicates an analogous increase of the active electron concentration with increasing discharge power, excluding a significant change in the shape of the electron energy distribution function. © 1997 American Institute of Physics. [S0003-6951(97)04731-1]

In plasma chemical reactors, the existence of a rf field, interacting with the various charged particles and surfaces, imposes several differences from classical chemical systems. From the kinetic point of view, the presence of highly excited species requires the use of state-specific data, while Arrhenius-type extrapolations, using the gas temperature, cannot describe the variation of the rate constant of electron–molecule reactions as a function of the energy of the system, since these systems decline from thermodynamic equilibrium. However, recent developments,<sup>1</sup> have permitted the accurate determination of the power actually consumed in reactive gas plasmas, such as the silane discharge, widely used in the microelectronic industry.<sup>2,3</sup> Thus, there is a possibility of correlating the dissociation rate constant to the energy content of the discharge environment.

In classical chemistry terms, only a tiny proportion of the molecular collisions among the reactants are sufficiently energetic to lead to reaction. This fraction of collisions, with a kinetic energy in excess of the activation energy, is given by the exponent of the Boltzmann distribution. In the same manner, from the numerous electron–molecule collisions in the plasma-induced decomposition of silane, only those with electrons having enough energy lead to silane dissociation. The number of effective collisions is proportional to the amount of electrons having energy higher than the dissociation threshold, i.e., the high-energy tail of the distribution. Although the electron energy distribution function in the plasma environment is not necessarily Maxwellian, (Bi-Maxwellian- or Druyvesteyn-like distributions, according to the conditions, have been reported in rare-gas or silane discharges),<sup>4–6</sup> there is still a relation between the energy content of such a process (i.e., the power dissipated in the discharge) and the effective or “active” electron density.

In this work, an Arrhenius-like behavior (i.e., the plot of  $\ln k$  versus the inverse of power consumption) is revealed in the plasma decomposition of pure silane. The dissociation rate constant is determined by using mass-spectrometric measurements of silane consumption, while the power actu-

ally consumed in the discharge is determined using voltage and current measurements.

The experimental setup is described in detail elsewhere.<sup>7</sup> The stainless-steel plasma chamber, 160 mm in diameter and 210 mm long, contains two cylindrically symmetric electrodes, 55 mm in diameter with a 25 mm distance. One of the electrodes is powered by a 13.56 MHz rf generator isolated with an *L*-type matching network, while the other electrode as well as the chamber walls are grounded, the rf electrode being surrounded by a grounded shield. The chamber is completely characterized from the electrical point of view.<sup>2</sup> The pressure is kept constant by a downstream throttle valve controller with the aid of a capacitance manometer, while the flow rate is independently adjusted [in this study at  $15.5 \text{ cm}^3 \text{ min}^{-1}$  at STP (sccm)], using a mass flow controller. Ultra-high-purity silane is used in all cases (Matheson). All the experiments were performed at room temperature in order to avoid interfering effects and in particle-free conditions as controlled by using a light-scattering technique.<sup>3</sup>

The measured voltage and current waveforms, used for the determination of the power actually consumed in the discharge, are corrected for the cell's stray impedance and transformed with the aid of an electrical circuit to equivalent waveforms at the surface of the powered electrode. Furthermore, an external shunt circuit, consisting of a coil and an air variable capacitor, is connected in parallel with the cell for increasing accuracy, while the resistive losses in the shunt and the cell are taken into account in the equivalent electrical circuit.<sup>2</sup> For the mass-spectrometric measurements, the gas from the plasma chamber is sampled through a variable leak valve positioned between the plasma chamber and the throttle valve. The partial pressure of  $\text{SiH}_4$  in the reaction chamber is determined by measuring the ion current at  $m/e = 32$ , for the ions generated in the source region of the mass spectrometer.<sup>8</sup>

Silane is dissociated by impact with electrons possessing sufficient energy, with a rate given by the equation:

$$\frac{dn_{\text{SiH}_4}}{dt} = -kn_{\text{SiH}_4}, \quad (1)$$

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where  $k$ , the dissociation rate constant is:

$$k = N_e \int f(E) v_e(E) \sigma(E) dE. \quad (2)$$

$N_e$  is the total electron density,  $f(E)dE$  is the fractional number of electrons having energies between  $E$  and  $E + dE$ ,  $v_e(E)$  is the electron velocity, and  $\sigma(E)$  is the dissociation cross section of silane. This equation gives explicitly the frequency of efficient collisions between silane molecules and electrons, per gas density, relating the rate constant to the effective or "active" electron density. However, in order to use Eq. (2) for determining the dissociation rate constant, the electron density, the electron energy distribution function, and their variation with the conditions used, have to be known. Otherwise, under certain conditions, the rate constant can also be deduced from silane consumption measurements employing classical chemical reactor principles. For this purpose, a continuous stirred tank reactor model, where the partial pressures of silane and its decomposition products are homogeneous in the reactor volume, is used and an overall (space averaged) rate constant is calculated.<sup>3</sup> Taking into account the additional dissociation of silane in secondary gas phase chemical reactions with radicals, the rate constant for low conversion, which in this case is less than 1%, becomes:<sup>3</sup>

$$k = \frac{f}{N_0 V_p} \frac{x}{3.66 - x}, \quad (3)$$

where  $f$  is the input silane flow rate in molecules/s,  $N_0$  is the silane density ( $\text{cm}^{-3}$ ) in the plasma-off condition,  $V_p$  is the plasma volume ( $\text{cm}^3$ ), and  $x$  is the conversion of silane.

Thus, in Fig. 1(a)  $\ln k$  is plotted as a function of the inverse discharge power,  $1/P$ , for silane pressures of 50 and 75 mTorr, error bars representing the standard deviation of several measurements at identical conditions. It is observed that the electron impact dissociation constant,  $k$ , is always greater for 50 mTorr than for 75 mTorr for a given power level, while in both pressures there is a linear dependence of  $\ln k$  on the inverse of the discharge power. The slope for 75 mTorr is larger in absolute value ( $-94 \text{ mW}$ ) than that for 50 mTorr ( $-48 \text{ mW}$ ), suggesting that the decomposition of silane in this pressure is a more power-sensitive reaction compared to the lower pressure. The linear dependence indicates an analogy to Arrhenius behavior, as in the case of classical chemical reactions, the energy term in the Boltzmann exponent being substituted by the power consumption. The difference is that, in classical chemistry terms, the variation of  $k$  with pressure is not usually expected, while in this case, besides the dissociation threshold, the analogy to the activation energy is also related to the effectiveness of the discharge at each pressure.<sup>3</sup> This last parameter is basically related to the stochastic-to-collisional rf power ratio.<sup>9</sup>

However, the different ratio of stochastic-to-collisional rf power for the two pressures cannot explain the different slopes for the two pressures. Stochastic electron heating refers to the heating of electrons by the successive contraction and expansion of the sheath accompanied by the movement of plasma electrons incoming from the plasma to the wall and receding to the plasma. During the sheath expansion, electrons at the sheath edge gain energy from the sheath

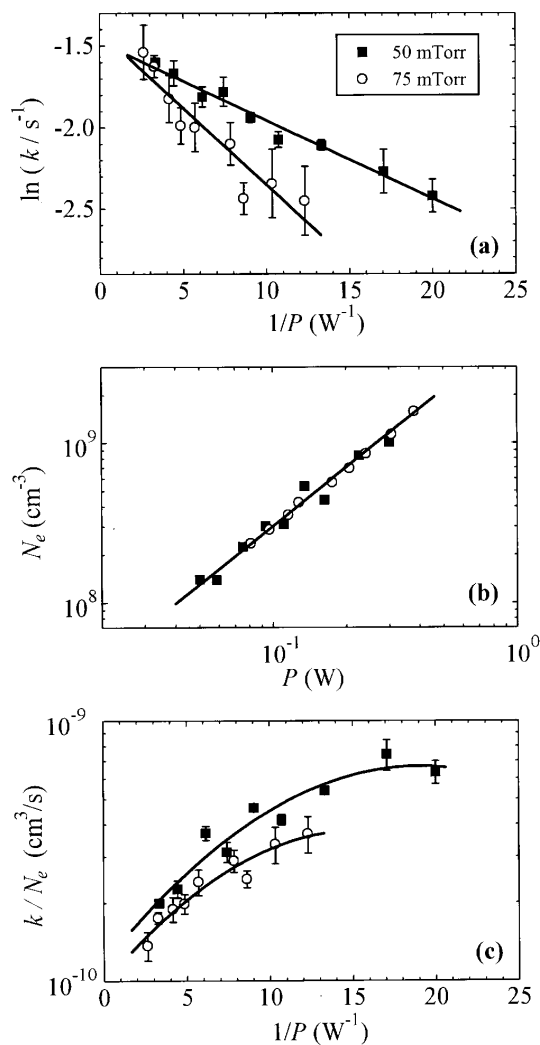


FIG. 1. (a) Plot of the  $\ln k$  ( $k$  is the rate constant for the silane decomposition) against the inverse of the discharge power,  $1/P$ , for two silane pressures of 50 and 75 mTorr. The best fitted straight lines are also shown. The slope for 75 mTorr ( $-94 \text{ mW}$ ) is almost twice the slope for 50 mTorr ( $-48 \text{ mW}$ ). (b) The electron density,  $N_e$ , as a function of the discharge power,  $P$ , for the two silane pressures. This plot has been created by using the present discharge current data ( $0.2\text{--}1.3 \text{ mA/cm}^2$ ) and the scaling law of Ref. 11 derived from microwave interferometry data in asymmetric argon discharges. (c) The ratio  $k/N_e$  as a function of the  $1/P$  for the two silane pressures.

electric field. On the other hand, collisional power dissipation refers to the power that is consumed in electron-silane molecule collisions. This ratio (stochastic to collisional) decreases as pressure increases<sup>9</sup> and would give an even larger slope (in absolute value) for the 75 mTorr pressure if the  $\ln k$  was plotted against the inverse of the collisional power term.

The observed behavior can be explained by a variation of the mean electron energy and/or the electron energy distribution with both power and pressure. More specifically, the discharge current in the present study varies between  $0.2$  and  $1.3 \text{ mA/cm}^2$ . In this range, a change in the electron heating mode, which would lead to a dramatic change of the mean electron energy, is not expected.<sup>10</sup> On the other hand, the electron density,  $N_e$ , increases with discharge power, with the same power law for both pressures, as revealed in Fig. 1(b). In this Fig. 1(b), the electron density,  $N_e$ , is plot-

ted as a function of the discharge power for the two silane pressures of 50 and 75 mTorr. This plot has been created by using the present discharge current data and the scaling law of Ref. 11 derived from microwave interferometry data in asymmetric argon discharges. Thus, although the actual electron density,  $N_e$ , is probably different in silane compared to argon glow discharges, no significant difference is expected between the two pressures for the same power consumption.

The change of the electron density,  $N_e$ , with the discharge power can explain the increase of the silane dissociation constant,  $k$ , as power increases, since the active electron density increases accordingly. However, as deduced by Fig. 1(b), this cannot explain the different slopes of  $\ln k$  between the two pressures.

Therefore, considering again Eq. (2), the rate constant for constant  $N_e$  will only depend on the electron energy distribution function,  $f(E)$ , since the dissociation cross section,  $\sigma(E)$ , of silane is independent of the electron energy distribution function or discharge conditions, being only a function of electron energy, and the same is true for the electron velocity,  $v_e(E) \propto \sqrt{E}$ .

Accordingly, the different slopes observed in Fig. 1(a) can only be due to a variation of the electron energy distribution function,  $f(E)$ , which induces a difference in the active electron density for the same increase of  $N_e$ . In order to disengage the influence of the change in electron density,  $N_e$ , with power to its contribution to the active electron density, the ratio  $k/N_e$  is plotted in Fig. 1(c) as a function of the inverse of the discharge power for the two pressures. This ratio is always smaller for the higher pressure and declines as power increases for both pressures. In fact, the change in this ratio is the direct effect of the discharge conditions on the modification of the energy distribution function,  $f(E)$ . If one assumes a simple Maxwell- or Druyvesteyn-type distribu-

tion, the modification of the rate of change of the active electron density with the increase of  $N_e$  can be achieved by a decrease of the mean electron energy and/or a deviation of the shape of the distribution and mainly a shortening of its high-energy tail as pressure increases.

On the other hand, the linear behavior of  $\ln k$  as a function of  $1/P$  indicates that in the case of power increase there is no significant modification of the shape of the electron energy distribution function in the range of conditions used. It results also from the intercept of the curves of Fig. 1(a) that, for high power levels, the value of  $k$  is almost the same, i.e., 0.23 and 0.24 s<sup>-1</sup> for 50 and 75 mTorr, respectively, indicating that the process is collision frequency limited.

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