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DEGREE OF DISSOCIATION MEASURED BY FTIR ABSORPTION SPECTROSCOPY APPLIED TO VHF SILANE PLASMAS

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Degree of dissociation measured by FTIR absorption spectroscopy applied to VHF silane plasmas

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Abstract. *In situ* Fourier transform infrared (FTIR) absorption spectroscopy has been used to determine the fractional depletion of silane in a radio-frequency (rf) glow discharge. The technique used a simple single pass arrangement and was implemented in a large area industrial reactor for deposition of amorphous silicon. Measurements were made on silane plasmas for a range of excitation frequencies. It was observed that at constant plasma power, the fractional depletion increased from 35% at 13.56 MHz to 70% at 70 MHz. With a simple model based on the density continuity equations in the gas phase, it was shown that this increase is due to a higher dissociation rate and is largely responsible for the observed increase in the deposition rate with the frequency.

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1. Introduction

Plasma enhanced chemical vapour deposition (PECVD) of amorphous silicon thin films has widespread applications, especially in the field of photovoltaic solar cells and thin film transistors for flat screen production. The most commonly used PECVD technique uses silane as working gas in a parallel plate reactor with 13.56 MHz excitation frequency. This configuration permits uniform deposition over the large surfaces required for industrial applications. The frequency choice is dictated by convention and the consequent availability of rf technology suited to this frequency, rather than by optimization of the physical processes in the discharge.

At 13.56 MHz, the deposition rate for good film quality remains relatively low (about 1-3 Å/s), and any attempt to increase this deposition rate tends to decrease film quality. Since the work of Curtins *et al* [1], it has been demonstrated that frequencies in the VHF (Very High Frequency: 30 - 300 MHz) range can be used to advantage, primarily

to obtain good quality films at high deposition rates [2, 3]. VHF plasmas are now the subject of a growing body of theoretical [4, 5, 6, 7] and experimental [5, 8, 9, 10, 11, 12] studies, but the observed increase of the amorphous and microcrystalline deposition rate with the frequency at constant power is still not well understood. Two alternatives are generally proposed to explain this increase: one is based on an enhancement of the silane dissociation into active radicals for the deposition (gas phase effects) due to an increase of the electron density and/or a change in the electron energy distribution function with the frequency [3]; and the other is based on an enhancement of the surface reactivity (plasma-film surface interaction) due to an increase of the ion flux with the frequency [9, 13].

The first step in the control of plasma deposition is an understanding of the phenomena in the gas phase. In particular the efficiency of the dissociation of the working gas into active radicals for the deposition will be a crucial point to obtain a rapid deposition process. The SiH_4 dissociation has previously been measured using a mass-spectrometric technique [9, 14] or using a tunable diode laser to measure the infrared absorption of a single SiH_4 ro-vibrational line [15]. However, mass-spectrometric measurements are difficult to interpret due to the complex cracking patterns when several molecules are present. On the other hand, the diode laser IR absorption measurement gives precise results but is technically complex.

In this paper, we present a simple practical technique using *in situ* Fourier transform infrared (FTIR) absorption spectroscopy to measure the silane gas concentration and degree of dissociation in a low pressure rf plasma deposition. This non-perturbative method was implemented on an industrial large area deposition reactor to study the effect of the excitation frequency on the gas phase reactions. Previously, FTIR absorption spectroscopy has been used as a plasma diagnostic to determine neutral gas temperatures [16, 17], radical composition [18, 19], to measure the dissociation of injected gases [20] and to study particles formed during the plasma [21]. In silane plasmas, FTIR has been used for *in situ* film and gas phase characterization [22], and for *in situ* study of particles formed during the plasma [23].

2. PECVD reactor experimental setup

The experimental setup in figure 1 is described in more detail elsewhere [24]. The plasma reactor is a modified version of the industrial KAI type reactor developed by Balzers for large area (substrate dimensions: 35 cm × 45 cm) thin film deposition. It consists of a rectangular grounded reactor box 57 cm long by 47 cm wide by 4 cm high installed inside a larger vacuum chamber. The rf electrode is suspended inside the reactor box above the floor with 2.5 cm electrode gap (d_{gap}). The rf generator is capacitively coupled via a π-type matching network at the input of which the forward

and reflected power are measured. To prevent problems of non-uniform plasma at high frequencies due to variation in the rf voltage amplitude across the electrode area, the rf and ground connections are centrally located on the top of the rf electrode and reactor box respectively [24, 25]. The process gas is introduced through a uniform showerhead in the rf electrode and the residual gases are pumped out from one side of the reactor through a coarse grid. To reduce contamination, the reactor box and vacuum chamber are differentially pumped: low pressure is maintained in the vacuum chamber while the process pressure in the reactor is regulated by a throttle valve. Plasma parameters relevant to the deposition of amorphous silicon were chosen, namely, a 100 sccm flow of silane with a pressure of 0.2 Torr and a uniform reactor temperature of 200 °C. The excitation frequency was varied from 13.56 MHz to 70 MHz and the power dissipated in the plasma, estimated with the subtractive method, was kept constant at 80 W (30 mW/cm^2).

3. FTIR experimental arangement and method

IR absorption spectroscopy was performed with a commercial Bruker FTIR apparatus. In the simple single-pass geometry shown in figure 1, the parallel beam leaving the spectrometer was directed through the plasma and focussed by an off-axis paraboloid gold mirror onto an external detector (Graseby type FTIR-W24). For optical access, ZnSe windows were mounted on the vacuum chamber, and sapphire windows on the plasma reactor. The sapphire windows were placed at the end of 10 cm long tubes to reduce problems of deposition; metal grids placed at the tube entrance preserved the electrical continuity of the reactor wall. Due to the differential pumping, the IR silane absorption is due only to the silane present in the reactor itself. The Fourier transform of the detector signal yields the spectrum in the 1600-4000 cm^{-1} range (the lower limit is due to the sapphire cutoff) with an instrumental spectral resolution of 0.5 cm^{-1}. To obtain a reasonable signal-to-noise ratio, the measurements were performed by averaging over 50 spectral scans.

Figure 2 shows the measured transmittance spectra of the SiH_4 ν_3 band centred at 2189 cm^{-1} for 0.2 Torr reactor pressure with plasma off and plasma on. The difference in transmittance, most clearly visible in the Q branch, is due to SiH_4 gas dissociation by the plasma. Although the spectra show the rotational structure of the P and R branches of the ν_3 band, the 0.5 cm^{-1} resolution was not sufficient to completely resolve the individual gas lines. As shown by Cleland *et al* [16], this lack of resolution results in a non-linear relation between the measured transmittance T and the true transmittance of the lines and consequently, the Beer and Bouguer law could not be used to calculate directly the SiH_4 density from the measured transmittance spectra.

Instead, to determine the SiH_4 density, a calibration curve for the integral of the Q

branch ($\int_Q(1 - T(\nu))d\nu$) versus the SiH_4 pressure, shown in figure 3, was first obtained from SiH_4 gas spectra at different reactor pressures and a reactor temperature of 200°C. The integral limits were chosen to be from 2174 to 2190 cm^{-1}. This calibration curve is valid only for our optical path length (67 cm), gas temperature (200°C) and FTIR resolution (0.5 cm^{-1}); any change in these parameters necessitates a new calibration curve. The SiH_4 density for the different plasma conditions was then obtained from the Q branch area using this calibration curve.

To correctly interpret the reduced Q branch area as due to dissociation of the SiH_4, we first checked if any plasma-induced change in rotational and vibrational temperature of the neutral gas can modify the form of the transmittance spectrum. In our case, careful comparisons of spectra obtained at 200°C with the plasma on, with spectra of the same absorbance obtained with gas only by suitable choice of the gas pressure show no change in the P Q R rotational branch form and no appearance of hot bands. This was not the case if we compared the shape of a gas spectrum at 200°C with the shape of a gas spectrum at 25°C for the same Q branch amplitude. We conclude that, in our case, any changes in the rotational and vibrational temperature due to plasma heating remain small and therefore the temperature effects on the Q branch area could be neglected. This was in agreement with temperature studies in other plasmas with comparable power densities [26, 17, 22]. A high vibrational temperature due to plasma heating was observed by Knight *et al* [27] but in their case, the rf power density was 5 times higher than for our experiments. Calculations for SiH_4-H_2 rf plasmas made by Perrin [28] confirm that high vibrational temperatures could be obtained at high power density, but otherwise, this temperature remains in equilibrium with the gas translational temperature.

In the spectra in presence of the plasma we did not observe any IR absorption peaks due to radicals such as SiH_x (with x = 1, 2 or 3), even for high degrees of dissociation. This difficulty of measuring the radical densities in silane plasmas by IR absorption measurements was also found by Knight *et al* [27]. The reasons are that, due to the surface reactivity of these radicals, their densities remain relatively low compared with the SiH_4 density, and also due to the dissociation mechanism, their rotational and vibrational temperatures are high which gives less absorption because of the reduced ground state population. Furthermore, due to the lack of symmetry of these molecules, the degenerancy of the lines is lifted and so the absorption is lower than for the SiH_4 symmetric molecule. Generally, measurements of the silane radical density are performed with the single line IR diode laser technique which has a better sensitivity and specificity than the simple FTIR technique used in this experiment.

4. Results and discussion

Using the FTIR SiH_4 density measurement technique, we can estimate the fractional depletion D at constant total pressure and temperature defined by:

$$D = (n^0_{SiH_4} - n_{SiH_4})/n^0_{SiH_4} \quad (1)$$

Where n_{SiH_4} and $n^0_{SiH_4}$ are the SiH_4 number density with and without plasma respectively. At constant total pressure, the decrease of the SiH_4 density due to dissociation is compensated by the increase in the radical and hydrogen densities which are the SiH_4 dissociation products. In these experiments, where the silane is consumed by electron impact dissociation, the fractional depletion is synonymous with the degree of dissociation.

Figure 4 shows the excitation frequency dependence at constant plasma power of the SiH_4 fractional depletion and of the a-Si:H deposition rate measured by laser interferometry. Clearly, VHF plasmas have a higher fractional depletion than 13.56 MHz plasma, ie. VHF operation is more efficient in dissociating the SiH_4. This directly measured increase of D with the frequency is in contradiction with the results obtained by Heintze *et al* [9] using the mass spectroscopy technique.

If all the dissociated SiH_4 were uniformly deposited in the reactor, this would give a linear relation between the fractional depletion and the deposition rate, with 16 Å/s the maximum value if all the 100 sccm of silane were deposited. The deposition rate axis range in figure 4 is chosen to correspond to the fractional depletion axis range so that the measured fractional depletion can be interpreted on the deposition rate axis as the upper limit for the deposition rate in this plasma condition. The difference in the measured deposition rate and this upper value is due the loss by pumping of the dissociated silane. From figure 4, it can be seen that the measured deposition rate obtained at 70 MHz is higher than the upper limit given by the fractional depletion at 13.56 MHz. This clearly shows that the increase of the deposition rate with the excitation frequency can not be explained only in terms of an increase of the surface reactivity, as proposed by Heintze [9, 13], but also necessitates an explaination in terms of an increase in the gas phase reaction rates.

A simple model based on the continuity equations in the gas phase, shows that the observed increase of the deposition rate with the frequency can be largely explained in terms of the measured increase of the fractional depletion as follows: The continuity equation of the SiH_4 density without plasma $n^0_{SiH_4}$ is locally described in the stationary state by the 1-D equation:

$$\phi - n^0_{SiH_4}\frac{dv^0}{dx} = 0 \quad (2)$$

where ϕ is the showerhead flux density (total flux divided by the reactor volume) and v^0 is the flow velocity in the direction of the pumping along the axis x. In the presence

of plasma, the continuity equation of the SiH_4 density n_{SiH_4} becomes:

$$\phi - Kn_{SiH_4} - n_{SiH_4}\frac{dv}{dx} = 0 \tag{3}$$

where $K = n_e k(T_e)$ is the dissociation rate given by the product of the electron density with the rate constant. For the radicals created by electron impact dissociation of SiH_4, the density continuity equation is:

$$Kn_{SiH_4} - Sn_{SiH_x} - n_{SiH_x}\frac{dv}{dx} = 0 \tag{4}$$

where $n_{SiH_x}(x = 0, 1, 2, 3)$ is the sum of the different radical densities, and S is a weighted average over the probability of depositing the different species. For the hydrogen the density continuity equation is:

$$K'n_{SiH_4} + S'n_{SiH_x} - n_{H_2}\frac{dv_{H_2}}{dx} = 0 \tag{5}$$

where $K'n_{SiH_4}$ is the hydrogen source term coming from the SiH_4 dissociation and $S'n_{SiH_x}$ is the source term coming from the hydrogen released during the film growth reactions. Any secondary reactions between neutral molecules or ions and neutral molecules have been neglected in this simple model.

At the pressure and flows used here, pressure variations along the reactor due to gas flow are negligible, and for uniform showerhead and plasma power (ie. ϕ, K, S, K' and S' independent of the position x), the gas composition in the plasma is constant [29, 30]. The silane, radical and hydrogen densities are then independent of the position and the derivative of the flux velocities are constant.

During the plasma, the SiH_4 dissociation and the hydrogen released from the film growth reactions give a net increase in the resulting total flux. But in our case where the pumping is limited by the conductance of the throttle valve, the hydrogen is more efficiently pumped than heavier molecules and it was observed that the throttle valve position remained practically unchanged with and without plasma. Then the derivative of the silane and radicals flux velocity in the plasma $\frac{dv}{dx}$ can be approximated by the value without plasma $\frac{dv^0}{dx}$ from equation (2) and was 1.64 s^{-1} for our conditions.

From equation (1) to equation (4) we can calculate the dissociation rate K and the deposition rate R in terms of the fractional depletion D:

$$K = \frac{dv^0}{dx}\left(\frac{D}{1-D}\right) \tag{6}$$

$$R = \frac{d_{gap}}{2}Sn_{SiH_x} = \frac{d_{gap}}{2}\frac{S\phi}{S + \frac{dv^0}{dx}}D \tag{7}$$

where the term $(d_{gap}/2)$ takes into account the fact that half of the volume contributes to deposition on the substrate and the other half contributes to the deposition on the rf electrode.

Equation (7) shows that the increase of D is responsible for an increase of R. But from figure 4, we can see that the deposition rate increases by a factor of three whereas the fractional depletion increases only by a factor of two. This means that the probability of deposition S must also increase with the frequency. This variation of S could be due to an increase of the surface reactivity (increase of the sticking probability) which could be caused by an increase of the ion bombardment flux, or to a change in the radical composition due to a change in the electron energy distribution function which could increase the ratio between the high- and low-sticking probability species. Secondary reactions which have been neglected in our model could also have an effect on S by changing the gas composition.

Figure 5 shows the frequency dependence of the dissociation rate K calculated from the measured depletion using equation (6). The measured increase of D is approximately a factor of two when the frequency increases from 13.56 MHz to 70 MHz, but due to the non-linearity of equation (6) this increase corresponds to a factor of four in K. We can then conclude that VHF plasmas are more efficient in dissociating the silane at constant plasma power (increase of the gas phase reactivity of the plasma). Since $K = n_e k(T_e)$, the increase of K could be the consequence of a higher electron density and/or a change in the electron energy distribution function with the excitation frequency.

5. Conclusions

The fractional depletion of silane has been measured by single pass FTIR absorption spectroscopy in a large area industrial reactor. The silane density was estimated, after calibration, by integration over the Q branch of the ν_3 transition. This non-perturbative measurement can be routinely performed with a standard commercial FTIR apparatus.

Measurements made on silane plasmas at constant power for a range of excitation frequencies have shown that the fractional depletion doubles on passing from 13.56 MHz to 70MHz. With a simple model based on gas phase density continuity equations, it was shown that this is due to a factor four increase in the dissociation rate, and is largely responsible for the observed increase in the deposition rate with the frequency in VHF plasmas.

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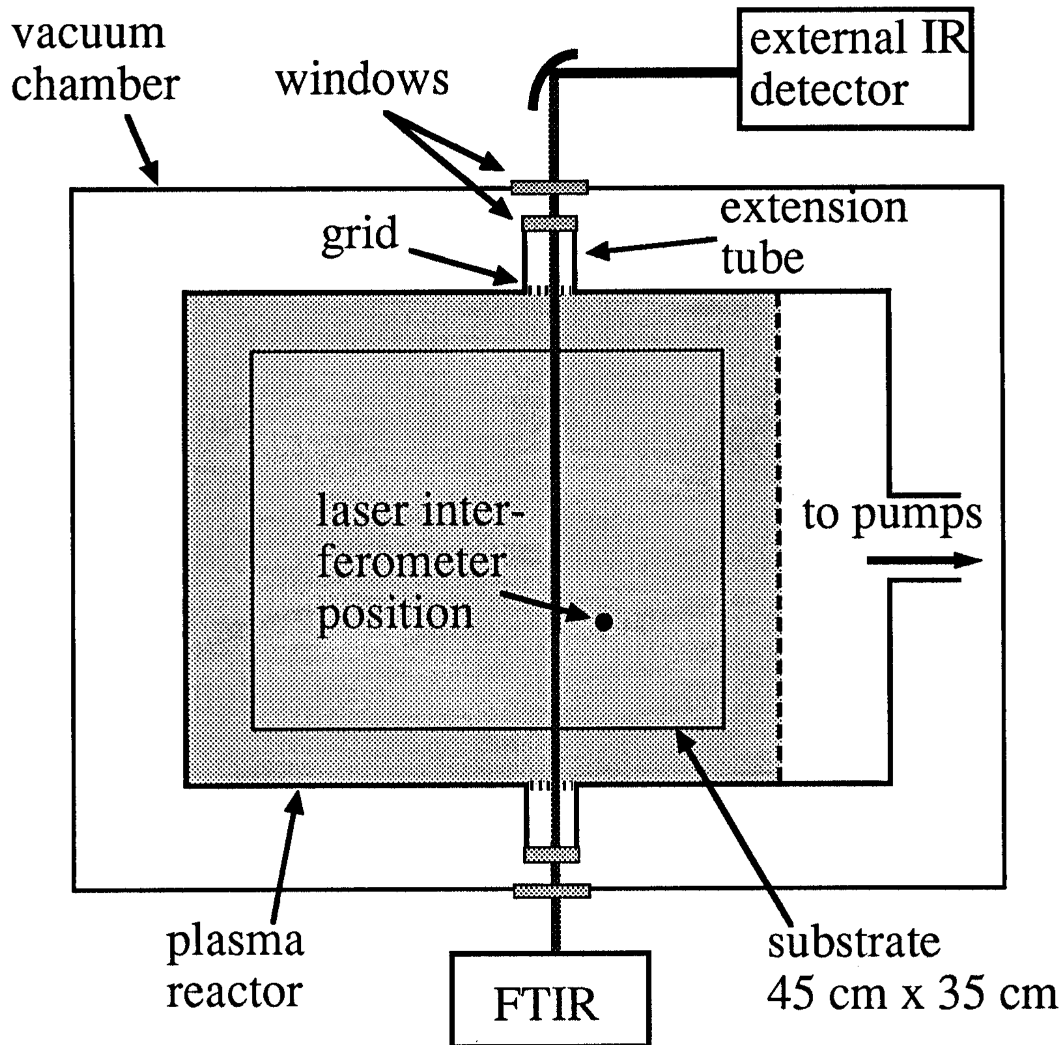

Figure 1: Schematic plan view of the plasma reactor and vacuum chamber showing the FTIR intrument and external detector used for single pass absorption spectroscopy measurements and the position of the laser interferometer used for deposition rate measurements.

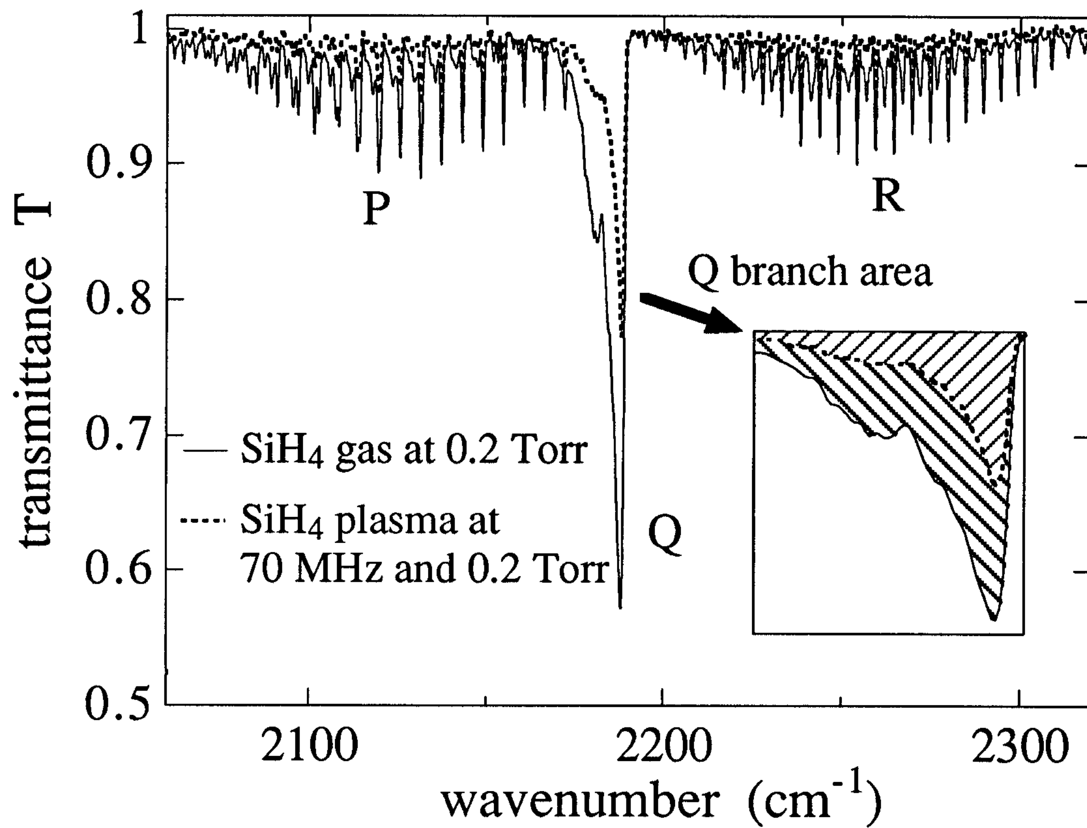

Figure 2: IR transmittance spectrum of the silane ν_3 transition in 0.2 Torr gas and plasma with 0.5 cm^{-1} resolution. The integral over the Q branch, shown in the inset, is used to calculate the silane density.

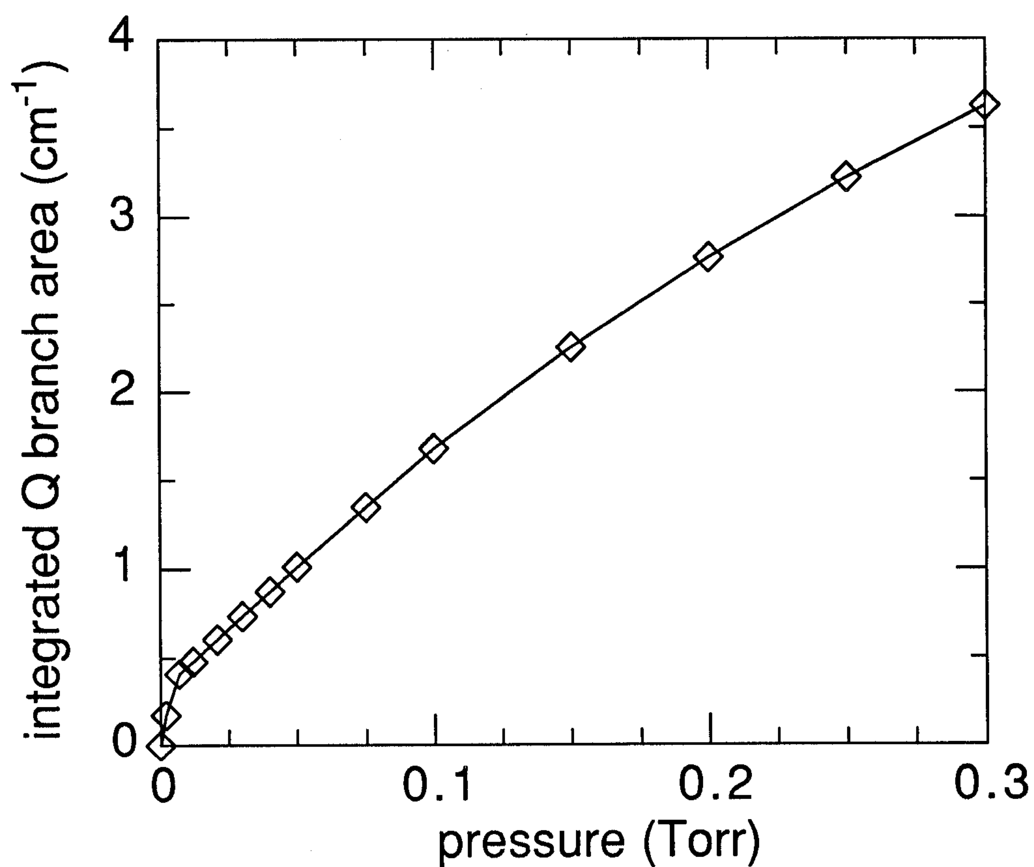

Figure 3: Measured pressure dependence of the Q branch transmittance integral. The line is simply the interpolation between the measured points. This curve was used as the calibration curve to determine the silane density in plasmas.

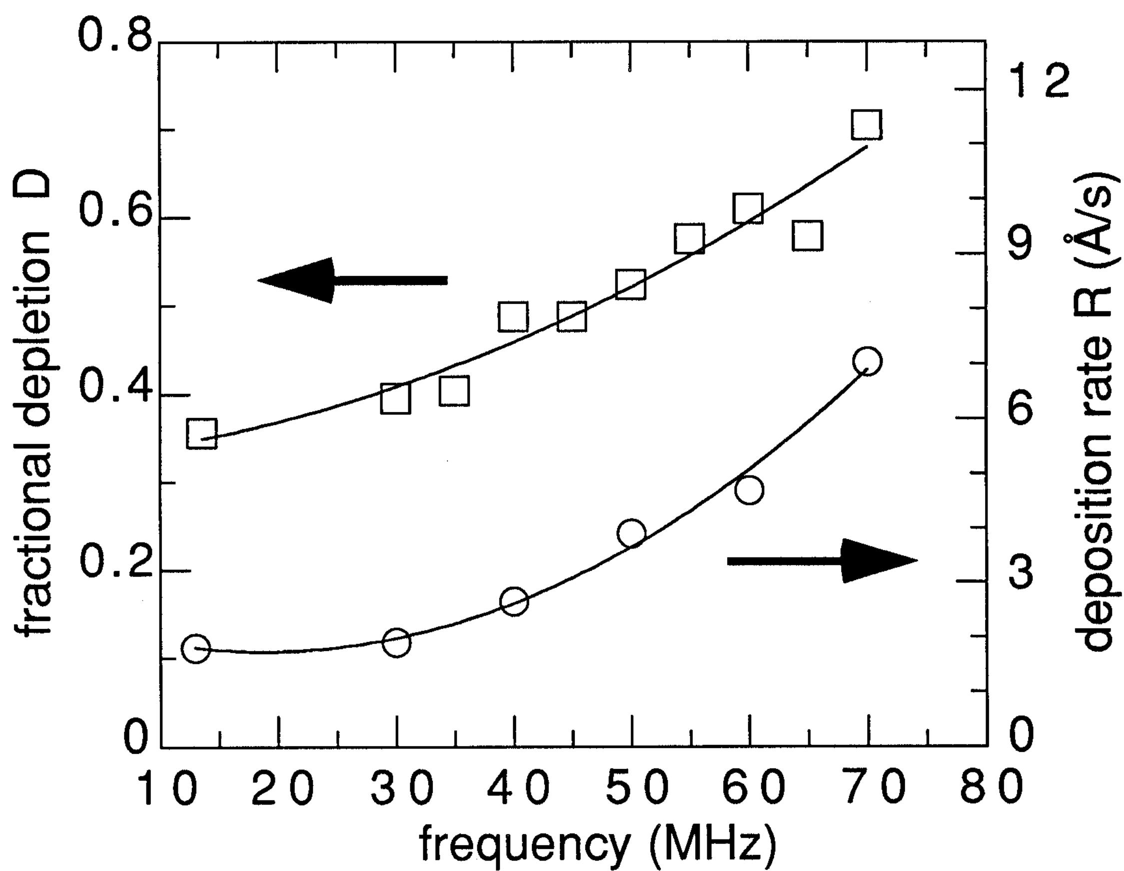

Figure 4: Dependence on the frequency of the silane fractional depletion and corresponding a-Si:H deposition rate for a pure silane plasma at 0.2 Torr, 100 sccm, 80 W and 200°C.

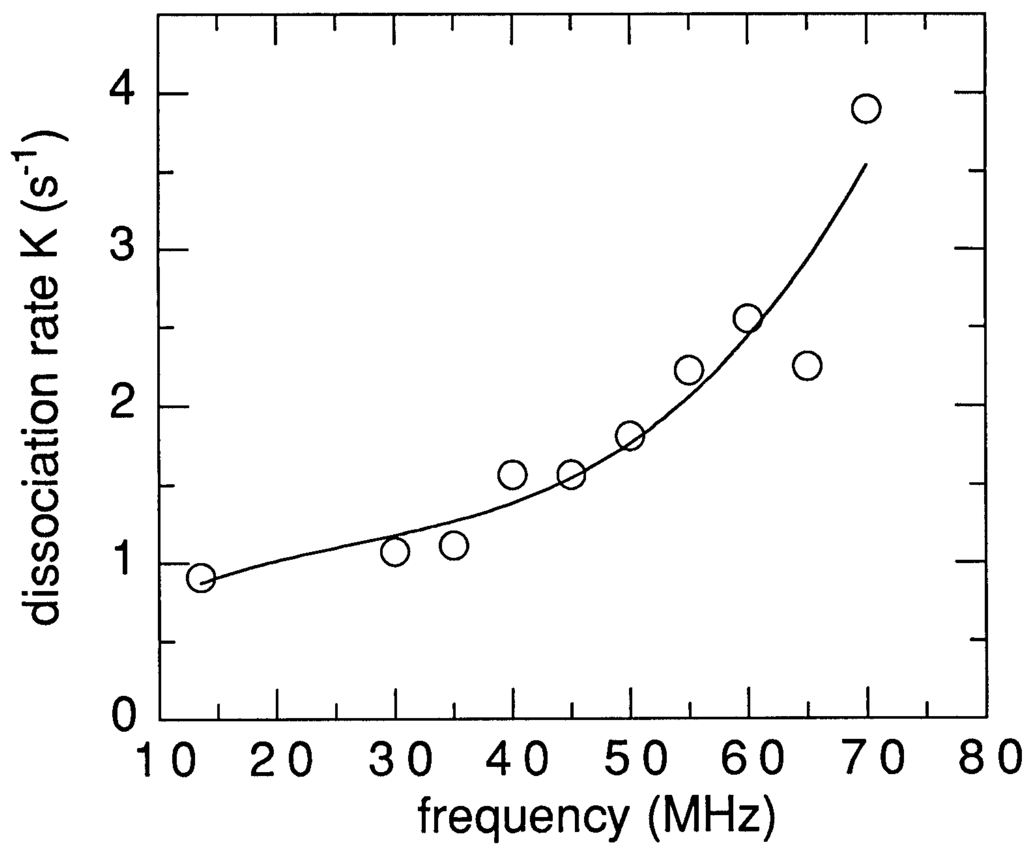

Figure 5: Dependence on the frequency of the dissociation rate calculated using equation (6) from the fractional depletion measurements in figure 4.