J. Phys. D: Appl. Phys. **29** (1996) 2452–2458. Printed in the UK

Dilution-enhanced radical generation in silane glow discharges

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Received 9 February 1996, in final form 7 May 1996

Abstract. The influence of dilution of silane with Ar, He and H_2 on the mechanism of radical generation in radio frequency discharges used for the deposition of a-Si:H has been examined. The density of SiH radicals in the discharge volume and near the deposition surface was examined by laser-induced fluorescence. The observed phenomena were attributed to the enhancement of the contribution of sheath-related electrons under certain dilution conditions. This explanation was confirmed by numerical simulation using Monte Carlo and probabilistic models that permitted the calculation of the total collision cross section of silane.

1. Introduction

It is well known that the process of a-Si:H deposition by plasma-enhanced CVD is not completely described by the current scientific knowledge concerning several aspects of the plasma–electric field and plasma–surface interaction mechanisms. The complex interaction between the microscopic quantities therein involved and the process parameters or the film properties is a subject of continuous studies aiming at a better controllability of film properties like microstructure, hydrogen content and, ultimately, improved and stable optoelectronic characteristics. Low-power, low-pressure conditions are widely used in order to obtain low-defect-density films. However, those films are highly stressed and are deposited at very low deposition rates. Other alternatives have been considered in order to address this problem. Among other methods, deposition from silane diluted with helium or under slight ion bombardment, which can be obtained under certain dilution conditions [1], has given some encouraging results. Dilution of silane with other gases modifies drastically all the aspects of plasma–field and plasma–surface interaction. This is because of the different ionization potential, collision cross sections, ion energy and ion current of the dilution gas compared to silane. Early studies were focused on the influence of dilution on the enhancement of silane decomposition, the deposition rate and the properties of the films. Thus, Knights *et al* [2] reported an enhancement of the deposition rate, but also a deterioration of the film quality. On the other hand, Vanier *et al* [3] observed an exponential decrease in the dissociation frequency of silane with silane fraction. Silane dilution has been used also for the growth of microcrystalline silicon thin films [4]. Thus, it was clear by then that silane dilution affects all the aspects of the process, by modifying silane decomposition, mass transfer to the deposition surface and consequently film growth, because of the modification of the composition of the flux of precursors and the possible effects of ion bombardment. In fact, ion bombardment studies have revealed spectacular increases in ion energy and current with dilution [5].

This group has studied in the past the influence of dilution on the radical generation mechanisms [6, 7] by using spatially resolved laser-induced fluorescence (LIF) and emission spectroscopy simultaneously [8]. These studies have shown that, besides the general enhancement of the radical generation rate caused by the increase in the electron temperature, there are also local phenomena near the electrodes that are influenced by the dilution percentage and the nature of the buffer gas. These phenomena gain more importance, given that most of the energy gained by electrons in these plasmas comes from the interaction of electrons with the oscillating sheath [9]. Moreover, an increase in radical generation near the deposition surface enriches the film precursor flux with high-sticking-coefficient radicals, like SiH and SiH_2, and consequently affects the film growth mechanism [10]. Therefore, the origins of these local phenomena as well as the general influence of dilution continue to be of interest not only for the evaluation of the influence of plasma-phase chemistry on the a-Si:H deposition process but also for the elucidation of the electron-heating mechanisms under these conditions.

For this purpose additional experiments, involving the recording of the ground state SiH radical concentration by LIF, were performed. Moreover, a Monte Carlo simulation and a simpler probabilistic model were proposed in order to explain the experimental observations. In the following we will present the results obtained from LIF measurements of the concentration of ground state SiH radicals at certain positions of the discharge space, as a function of the dilution percentage, the total pressure and the nature of the buffer gas, together with the results of Monte Carlo and probabilistic simulations.

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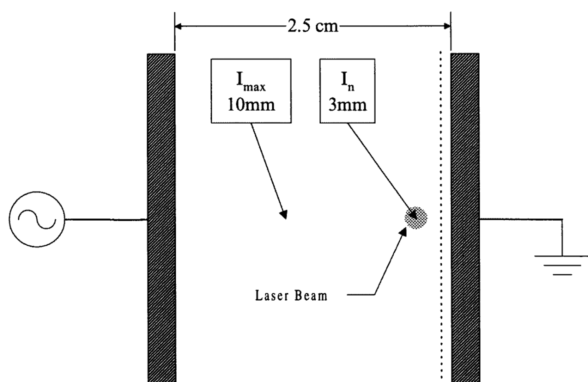


Figure 1. A schematic representation of the experimental dimensions. The dotted line represents the time-averaged plasma–sheath boundary.

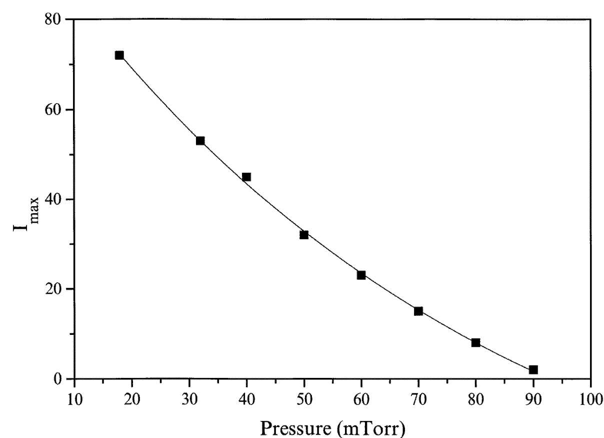


Figure 2. The LIF intensity (arbitrary units) as a function of pressure in a pure silane discharge. I_{max} is at 10 mm from the RF electrode. The line drawn is the result of a first-order exponential decay fitting function.

2. Experimental

The experimental apparatus, described in detail elsewhere [11], consists of a cylindrical stainless steel chamber equipped with four quartz windows for optical diagnostics. The collimated 2 mm beam of the tunable dye laser traverses the chamber in parallel to the two electrodes, exactly along the symmetry axis. Two positions of the laser beam were chosen: I_n, 3 mm from the earthed electrode surface, and I_{max} 10 mm from the RF electrode surface, as shown in figure 1. The first one is the closest position to the deposition surface that can be achieved by our experimental system, whereas the second position gave the maximum LIF intensity under a wide variety of conditions in this chamber [6].

The fluorescence light, from the $J = 2.5$ transition of the R_1 branch of the $A^2\Delta$–$X^2\Pi$ band of SiH at around 412 nm, is collected at right angles, by collimating and focusing lenses to a PMT equipped with a suitable interference filter. LIF signals are recorded on a Lecroy 9400 digital storage oscilloscope, by integrating in time the average of a large number of fluorescence waveforms. The recorded LIF intensity is directly proportional to the concentration of ground state SiH radicals in the sampled area. More details on the experimental procedure followed for recording LIF signals are given in [6]. During these experiments, neither the electrodes nor the chamber were heated since this would modify the molecular density for a given pressure. Gas flow rates and pressure were independently controlled by means of mass flow ratio controllers and a capacitance manometer together with a downstream throttling valve controller. For all the experiments, the parallel stainless steel electrodes (6 cm in diameter) of equal area had an interelectrode distance of 2.5 cm, the powered electrode being surrounded by an earthed shield. Mild plasma conditions were maintained by keeping the total power, as measured by a low-power SWR bridge, at 6 W. Except for one case, in which the pressure was varied by adding dilution gas while maintaining a constant silane flow, the flow rate was kept constant at 20 sccm, for variation of composition or variation of pressure experiments. In the case of constant pressure measurements the total pressure was 65 mTorr. All measurements were performed under particle-free conditions, as guaranteed by the absence of any additional laser scattering during the discharge operation [12], while at the same time spatially resolved emission profiles were used for determining the approximate time-averaged sheath thicknesses.

3. Results and discussion

The LIF intensity is proportional to the concentration of SiH in the sampled discharge volume, bearing in mind that the plasma can be considered optically thin and that non-radiative de-excitation is not observed under these pressure conditions. This is a result of the mass balance between generation through electron impact dissociation of silane, reaction of SiH with silane and diffusion of SiH molecules in the discharge gas according, for one dimension, to the equation

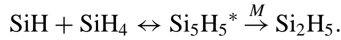
$$\frac{\partial N_{[SiH]}}{\partial t} = k_d N_{[e^-]} N_{[SiH_4]} - k_r N_{[SiH]} N_{[SiH_4]} + D \frac{\partial^2 N_{[SiH]}}{\partial x^2} \quad (1)$$

where N refers to the number density of the species, k_d is the silane dissociation constant, k_r the SiH–SiH_4 reaction constant and D the SiH diffusion coefficient in the specific discharge gas. k_d is a function of electron energy which varies in space, as well as with power and pressure. Thus, the SiH production frequency is

$$k_d N_{[e^-]} = \sigma \bar{\nu}_e N^*_{[e^-]} \quad (2)$$

where σ is the cross section of SiH_4 electron collisional dissociation towards SiH, $\bar{\nu}_e$ the mean electron velocity and $N^*_{[e^-]}$ the efficient electron density (the density of electrons having enough energy to dissociate silane). k_r is a function of the gas temperature. Nomura *et al* [13] have claimed that the dominant reaction channel is a three-body process

requiring a collisional stabilization by a third body and thus it is also a function of pressure:



$$\mathrm{SiH} + \mathrm{SiH_4} \leftrightarrow \mathrm{Si_5H_5}^* \xrightarrow{M} \mathrm{Si_2H_5}.$$

On the other hand, both electron impact dissociation and SiH insertion constants can be influenced by thermalization of silane through low-energy electron impact [14]. Therefore the intensity measured is expected to be influenced by those macroscopic parameters that can influence at least one of the above-described processes.

Pressure and dilution can influence all of these processes either directly, by modifying the mean free path or the diffusion coefficient of the species, or indirectly, by modifying microscopic plasma quantities like the electron density or temperature which in turn can modify the production rate of the species. Thus, in the case of pure silane, if one ignores for simplicity the diffusive terms since the regime is dominated by the fast SiH insertion reaction [13, 15–17], the steady-state mass balance equation of SiH is

$$k_d N_{[e^-]} N_{[SiH_4]} = k_r N_{[SiH]} N_{[SiH_4]} \tag{3}$$

and thus

$$N_{[SiH]} = \frac{k_d}{k_r} N_{[e^-]}. \tag{4}$$

Therefore, the measured LIF intensity will depend mainly on the electron temperature and density, or, taking into account equation (2), on the efficient electron density and on the influence of pressure on k_r under the specific plasma conditions.

In this context the expected general effect of a pressure increase is a decrease in the electron temperature and an increase in k_r, both resulting in a decrease in the measured SiH density. In fact, as one can observe in figure 2, which presents the variation of LIF intensity with pressure for a pure silane discharge, the fluorescence intensity shows a first-order exponential decay with increasing pressure.

In the case that silane flow is kept constant and pressure is increased by adjusting the flow of the dilution agent, $N_{[SiH_4]}$ remains constant with pressure. Thus, although the pressure rises there is no increase in the number of SiH–SiH_4 collisions. Therefore, as can be seen in figure 3, the use of dilution leads to a very different behaviour. Namely, there is a linear increase in LIF intensity with increasing pressure. This increase is also attributed to an increase in the efficient electron density; however, the factors that will influence $N^*_{[e^-]}$ must be discussed further.

The electron temperature should increase in general when diluting with a gas of higher ionization potential [18] or lower collision cross section, under constant total pressure. In fact, Perrin [19] has used the empirical relationship $k_B T_e(\mathrm{eV}) = 3.7 + 2.22\theta$, where θ is the hydrogen fraction, to calculate the electron temperature in hydrogen-diluted silane. However, previous experiments under constant total pressure showed no significant increase as a function of the dilution gas percentage for I_{max} [6]. Additionally, there is an electron density increase, whereas a relative decrease in the electron temperature and an increase in k_r are expected because of the pressure increase.

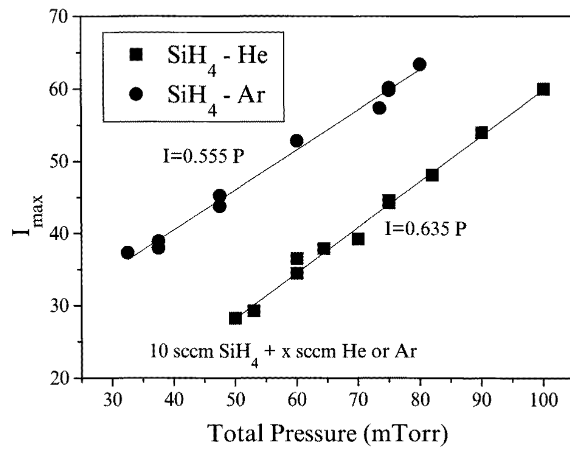


Figure 3. The LIF intensity (arbitrary units) as a function of total pressure in silane–helium and silane–argon discharges. I_{max} is at 10 mm from the RF electrode. The lines drawn are the result of least squares fitting.

The different behaviour of Ar and He as diluants gives further insight into this phenomenon. Helium, the gas of smaller collision cross section and higher ionization potential, gives a higher rate of increase with increasing dilution than does Ar which gives higher LIF intensities in general due to the fact that it contributes to the decomposition of silane through high-energy metastable states [20, 21]. In fact, the production frequency of SiH radicals has been shown to increase from 0.03 s^{-1} [22] for pure silane to 0.3 s^{-1} for 10% silane in argon [13].

Therefore, according to the previous discussion, the increase in the measured LIF intensity can be attributed to the increase both in the electron temperature and in electron density under these conditions: however, one must consider the fact that, under the given conditions, a decrease in the discharge impedance is also expected. The latter effect would lead to an increase in the power dissipated in the discharge and thus to an additional increase in the electron temperature.

Furthermore, in the case of silane dilution the ion bombardment and the ion energy increase significantly, depending on the diluent gas [5]. The ion flux and ion energies are higher for the case of He than they are for the case of H_2, whereas Ar makes an even smaller contribution. Given the fact that γ, the secondary electron emission coefficient, for a-Si:H is only 0.033 [23], the addition of fast secondary electrons would not lead to a modification of the primary electron heating mechanism, which is related to sheath heating [9]. However, it is expected that the addition of fast secondary electrons would be observable, at least near the sheaths.

Since the increase in the observed LIF intensity is related to the energy and population distributions of fast electrons in space, an earlier observation of this group can be used for further examination of its microscopic nature. Namely, it was observed that the LIF intensity near the deposition electrode surface, at constant total pressure, increases with dilution, presenting a maximum

for a certain dilution percentage, while at the same time the LIF intensity in the bulk plasma does not show the same behaviour [7]. The exact percentage corresponding to the maximum LIF intensity was found to depend on the nature of the dilution gas used. The origin of this phenomenon was wrongly attributed to the increase in SiH diffusion due to the existing concentration gradients [6]. However, it was proven that the observed SiH concentration profiles under these conditions are reaction rather than diffusion-dominated and thus they represent the spatial generation profiles of these radicals [11]. In fact, our effort to reproduce the phenomenon by increasing the SiH diffusion coefficient, through modelling, failed since diffusion cannot account for the local increase in SiH density near the electrodes.

This phenomenon was further investigated experimentally by varying the total pressure for certain silane percentages. Thus, in figure 4 is presented the variation in LIF intensity at I_n and I_{max} as a function of pressure for dilutions of 10 and 20% in hydrogen. In the upper graph one can observe that there is a maximum in the LIF intensity at a specific pressure for each percentage. Namely, this maximum moves towards lower pressures for higher silane percentages. The same is true for the LIF intensity at I_{max} (lower graph) although the maximum is present at much higher pressures compared with I_n. Since the silane density is almost the same in both regions of interest, independent of total pressure and diffusion coefficient, this difference depicts well the spatial dependence of the electron energy distribution function. This phenomenon can only be attributed to an enhancement of the density of electrons which have enough energy to dissociate silane in the sampled region.

In order to reveal the relation of the observed phenomena to the density of sheath-related electrons, either wave-riding or secondary, two models were constructed. The first one was a Monte Carlo simulation taking into consideration the collision sequence of a large number of mono-energetic electrons entering the bulk from the bulk–sheath boundary, taking into account the total collision cross sections of silane and of the respective dilution gas atoms. The model assumes that these electrons are fast enough to dissociate silane into radicals and that the electron energy distribution function does not change significantly over a distance of 2 mm from the earthed electrode, time-averaged plasma–sheath boundary. Thus, the number of dissociating collisions leading to SiH is proportional to the total number of collisions in the sampled volume.

The idea that stands behind this approach is that the increase in LIF intensity comes from the increase in penetration depth of sheath-related electrons in the bulk. Indifferent of their origin (secondary or wave-riding), these electrons have a longer penetration depth as the silane percentage or the dilution gas cross section is decreased. This is shown in figures 5 and 6 for various percentages of silane in helium and hydrogen respectively. It can be easily observed that, as expected, the penetration depth is higher for the case of He, whereas for a given x position, a

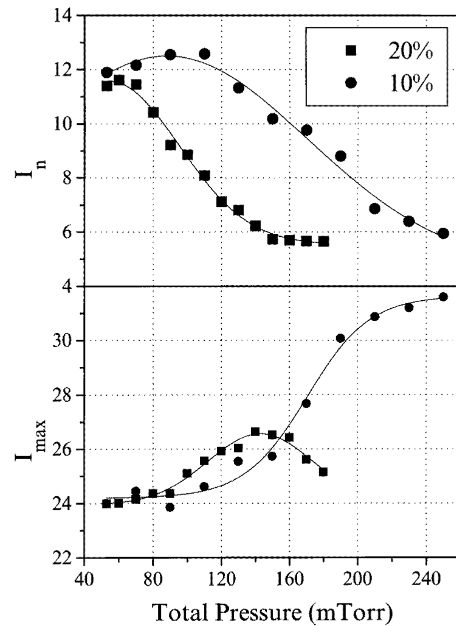


Figure 4. The LIF intensity (arbitrary units) as a function of total pressure in 10% and 20% silane–hydrogen discharges. I_{max} is at 10 mm from the RF electrode, I_n is at 3 mm from the earthed electrode.

maximum is observed at a specific silane percentage. This percentage is higher for smaller x. The first observation is compatible with the fact that higher penetration is possible with dilution gas atoms of smaller cross section. The second observation is due to the fact that, at higher dilution percentages, the electron penetration is too high, resulting in a higher spread of the number of collisions in space, whereas for low dilution percentages or no dilution most of the collisions happen in the immediate vicinity of the sheath boundary. This means that the position of the maximum will shift from short to longer x distances as the dilution percentage is increased.

The results of the model have been used for fitting experimentally observed LIF intensities at I_n for various silane percentages in helium and hydrogen at constant total pressure [6], by varying only the silane collision cross section. The LIF intensity for pure silane was used to convert the number of collisions to LIF intensity equivalent units. The results shown in figure 7 were obtained by using $\sigma_{SiH_4} = 4 \times 10^{-15}$ cm^2 for silane, $\sigma_{He} = 1.5 \times 10^{-16}$ cm^2 for He and $\sigma_{H_2} = 6 \times 10^{-16}$ cm^2 for hydrogen. One can observe a fairly good agreement with experimental data and data found in the literature, namely $(2\text{–}3) \times 10^{-16}$ cm^2 [24–26].

It is shown that the maximum number of collisions at a specific distance depends on the silane percentage and the dilution gas used. For lower percentages, or for a smaller cross section of the dilution gas atoms, the electrons are allowed to penetrate deeper into the bulk whereas in the opposite case most of the electrons collide before reaching the specified position.

These results were cross checked against experimental data concerning the variation in total pressure for certain

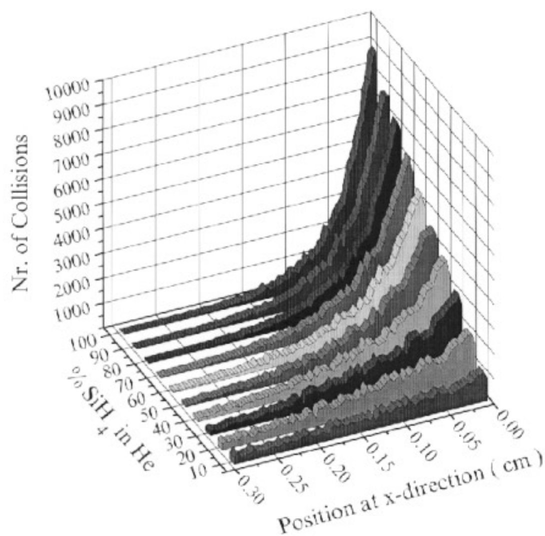


Figure 5. The total number of electron–silane collisions as a function of the distance (x) from the plasma–sheath boundary, for various percentages of silane in helium (results from Monte Carlo simulation).

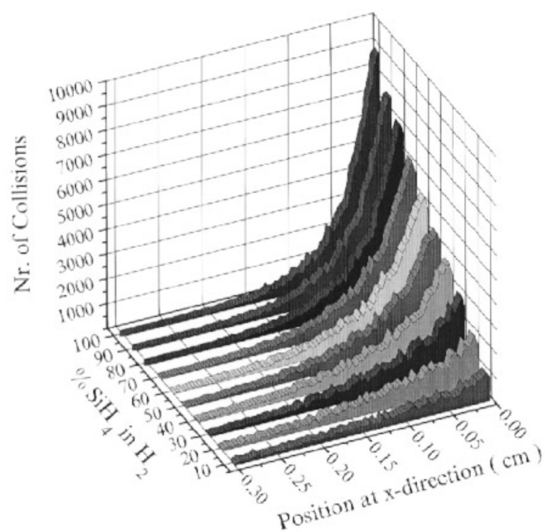


Figure 6. The total number of electron–silane collisions as a function of the distance (x) from the plasma–sheath boundary, for various percentages of silane in hydrogen (results from Monte Carlo simulation).

silane percentages in He and H_2 as shown in figure 8. The simulation results, shown by open symbols, almost coincide with the experimental observations, shown as full symbols. The lines drawn in figure 8 result from a probabilistic model that calculates the number of collisions according to the relation

$$N_L = N(1 - e^{-(\sigma_A N_A + \sigma_B N_B)L})$$

where N is the initial number of electrons, N_L is the number of electrons colliding in an area of 1 mm radius, at a distance L from the plasma–sheath boundary, σ_A and σ_B are the total collision cross sections of silane,

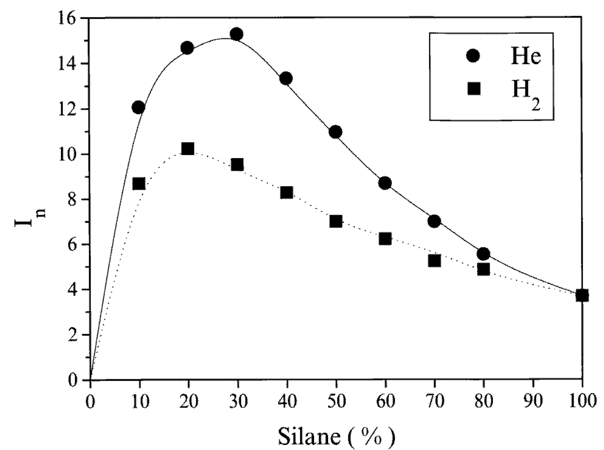


Figure 7. I_n at 3 mm from the earthed electrode (full symbols) as a function of silane percentage in helium and hydrogen. The lines drawn represent the result of Monte Carlo simulation.

as obtained from the Monte Carlo simulation, and the dilution gas respectively in cm^2; N_A and N_B are their number densities. This model's results are also, in most cases, in quite reasonable agreement with the experimental results, although the calculations are much faster than were those of the Monte Carlo simulation. Again in this case the maximum number of collisions depends on the density of silane and the cross section of the gas used for dilution. The pressure at which a maximum LIF intensity is achieved depends linearly on the silane percentage, as is shown in figure 9. The linear behaviour is compatible with the variation of the mean free path under these conditions.

These results, as well as the variation in total pressure at fixed silane percentage and the variation in silane percentage at constant total pressure validate the assumption that the positions of the observed maxima depend on the energetic electron density as this is modified by the electron penetration depth. This indicates that either the electron energy distribution is not significantly changed over the specified distance or the dissociation towards neutral radicals is not influenced too much by this change. If the increase in energy of the electron population with decreasing pressure could influence more the generation of SiH, the maxima observed in figure 8 would be harder to explain and they could not be reproduced by this model. In any case, the main electron-heating mechanism under the conditions used in this study is sheath heating, whereas the increase in energetic electron population comes also from the sheath boundary while Joule heating plays a minor role [9]. The same phenomenon of an increasing LIF intensity near the surface has been observed experimentally in the case of substrate heating, which induces a local heating of the gas and subsequently a decrease in local molecular density [27].

This phenomenon leads to a significant increase in the radical flux to the deposition surface. This is one of the reasons for the increase in deposition rate which

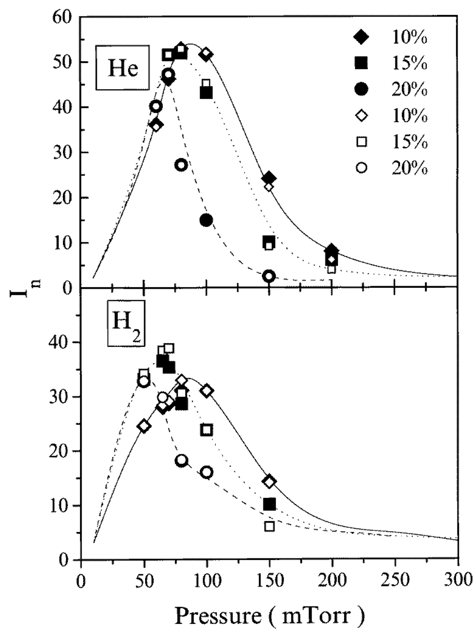


Figure 8. I_n at 3 mm from the earthed electrode (full symbols) as a function of total pressure for 10%, 15% and 20% silane in helium (upper graph) and hydrogen (lower graph), together with Monte Carlo simulation results (open symbols). The lines drawn represent the results of the probabilistic model.

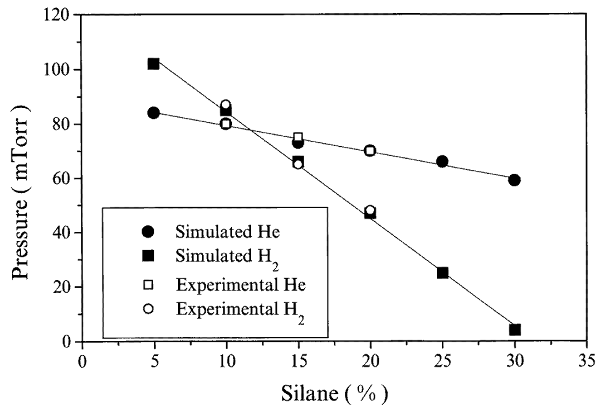


Figure 9. The pressure of maximum LIF intensity as a function of silane percentage in helium and hydrogen. Experimental points are represented by open symbols, Monte Carlo simulation by full symbols, whereas the lines result from the probabilistic model.

is observed in diluted silane. Therefore, high-sticking-coefficient radicals which otherwise have a low possibility of reaching the surface, since they react very fast with silane, participate more actively in the film growth under these conditions. This effect is of even geater importance, considering the fact that dilution will lead to an enhanced generation not only of SiH but also of the dominant radicals of silane decomposition like SiH_2 and SiH_3. This modifies directly the film growth rate and the deposition mechanism, the latter of which is also altered by the increased ion bombardment under these conditions.

4. Conclusion

The dilution of silane with gases of higher ionization potential and/or lower collision cross sections results in an enhancement of the generation of radicals in the gas phase. The local increase in silane decomposition and consequently in the concentration of radicals, observed by LIF near the deposition electrode, is attributed to the increase in penetration depth of fast electrons from the plasma–sheath boundary. According to the model described, the density of efficient electrons at the sampled volume will attain a maximum for a specific silane density for each dilution gas.

Both the general influence of dilution and the local increase cause an increase in the deposition rate, while the local increase can also alter the film growth mechanism because of the enrichment of the flux of precursors with high-sticking-coefficient radicals. The resulting film is expected to be influenced in terms of microstructure, hydrogen content and defect density, depending also on the efficiency of the ion bombardement. The simulation of this phenomenon has permitted us to calculate directly the total collision cross section of silane from experimental data.

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