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Deposition of hydrogenated amorphous silicon by photochemical decomposition of silane

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Deposition of hydrogenated amorphous silicon by photochemical decomposition of silane

Afstudeerverslag
A.J. Broekhuizen

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DEPOSITION OF HYDROGENATED AMORPHOUS SILICON BY PHOTOCHEMICAL DECOMPOSITION OF SILANE


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Summary

Hydrogenated amorphous silicon (a-Si:H) is an amorphous semiconductor, which is used more and more in thin film technology. The main application of a-Si:H is the production of p-i-n solar cells at low cost. a-Si:H is usually made by glow discharge deposition in a silane (SiH₄) plasma. The 254 nm mercury assisted photochemical vapour deposition is proposed as an alternative method.

Radiation at 254 nm is emitted by a low pressure mercury lamp and this radiation is absorbed in a reactor by traces of mercury. During a collision between a Hg(^3P₁) mercury atom and a silane molecule the primary reaction products SiH₃ and H are formed. It is believed that high quality a-Si:H films are made by depositing mainly SiH₃ radicals.

In this work much attention has been paid to the modeling of the dominant processes in a parallel plate photo-CVD reactor: radiative transfer, gaseous reactions and the surface phenomena. The efficiency of the radiative transfer depends on the lamp temperature and mercury density in the reactor, which can be determined simultaneously by an absorption cell of variable length. The deposition rate is limited by recombination of SiH₃ radicals with a recombination coefficient of 1.5 \times 10^{-10} \text{cm}^3 \text{s}^{-1}. The reaction probability of SiH₃ radicals on a-Si:H is low (between 0.10 at 40°C and 0.21 at 350°C) and more than 70% of these radicals recombine at the surface. Thus only a few per cent of the SiH₃, which arrive at the surface are incorporated into the film. With the present reactor deposition rates up to 3 to 5 Å/s are feasible, while window deposition remains low (40 Å after two hour).
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Summary

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CHAPTER 1 : INTRODUCTION

1.1 THE GROUP "SYNTHESE DE COUCHES MINCES POUR L'ENERGETIQUE" at the ECOLE POLYTECHNIQUE.

The group "Synthèse de couches minces pour l'énergétique" (SCME) has been founded 8 years ago by several physicists from high energy physics and consists actually of some 15 members.

The common subject of the group is the thin film technology of hydrogenated amorphous silicon (a-Si:H), the main application of which is the fabrication of solar cells at low cost. While the industrial production of solar cells has been exported to Solems, a private enterprise created by one of the members of SCME, the main interest of the group is oriented towards the characterization of thin films, new deposition techniques, deposition of other material than pure a-Si:H and fabrication of devices. In particular have to be mentioned real-time in-situ ellipsometry (visible and IR), which permits an accurate analysis of the film during the growth, and in-situ measurement of the surface potential by a Kelvin probe. As a new deposition technique, mercury assisted photo-CVD is proposed and other materials, that receive increasing interest are a-Ge:H and a-Si:Ge:H alloys, doped material (by introducing boron of phosphorus) and a-Si$_3$N$_4$. Devices of high quality are produced in the so called "ARCAM" reactor.

1.2 HYDROGENATED AMORPHOUS SILICON

Electronical and optical properties of crystalline semiconductors are assumed to be closely related to the periodicity of a single crystal. Thus it is amazing to discover that in the absence of such a periodicity many of
those properties, e.g. the band gap and optical absorption edge, are also encountered in amorphous semiconductors. It is believed that the short-range order is responsible for those properties. Amorphous semiconductors consist of a random network with correlations up to the third or fourth nearest neighbours and thus possess such a short-range order. The amorphous state can be determined empirically by a diffraction pattern, which must consist of diffuse rings.

Pure amorphous silicon appeared to be a bad semiconductor. This can be accounted for by the presence of a large number of dangling bonds. The unpaired electrons give rise to an ESR signal of about $5 \times 10^{19}$ spin/cm$^3$ and these electron energy states lie in between the valence and conduction band. These states act as fast nonradiative recombination centers, so that photoconductivity and photoluminescence are uninterestingly small in pure a-Si. Moreover these dangling bonds pin the Fermi level at the middle of the gap and introduction of impurities of donor or acceptor type into a-Si doesn’t move the Fermi-level significantly. Since normal annealing procedures reduce the ESR signal, it was assumed that ideal a-Si might be approached by annealing or by slow deposition onto substrates at elevated temperatures. More recently it was established that annealing effect are minimal and that a-Si will crystallize before all the dangling bonds are removed.

In 1975 Spear and Le Comber synthetized a new amorphous silicon material which could be doped both n-type and p-type [1]. This material contained a significant amount of bonded hydrogen and is called therefore hydrogenated amorphous silicon (a-Si:H). The main role of hydrogen is the bonding of the unpaired electrons and thus the passivation of the dangling bonds. The main features of a-Si and a-Si:H are compared in Table 1.1

Among the possible preparation techniques of a-Si:H the most popular nowadays is the plasma deposition in a glow discharge (DC, AC, RF) of silane (SiH$_4$) onto a substrate held at about 250°C. Other preparation techniques to be mentioned are reactive sputtering from a silicon target in a H$_2$/Ar plasma, thermal decomposition of silane (generally termed chemical vapour
deposition (CVD)), ionized cluster beam deposition (ICB) and more recently direct or mercury assisted photo-CVD and laser enhanced CVD.

<table>
<thead>
<tr>
<th></th>
<th>a-Si</th>
<th>a-Si:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen content</td>
<td>-</td>
<td>3-20%</td>
</tr>
<tr>
<td>Spins (ESR-signal)</td>
<td>$5 \times 10^{19}/\text{cm}^3$</td>
<td>$&lt; 10^{17}/\text{cm}^3$</td>
</tr>
<tr>
<td>doping</td>
<td>ineffective</td>
<td>possible</td>
</tr>
<tr>
<td>resistance</td>
<td>$10^{2}-10^{5} \ \Omega \ \text{cm}$</td>
<td>$10^{7}-10^{12} \ \Omega \ \text{cm}$</td>
</tr>
<tr>
<td>photoconductivity</td>
<td>&lt;&lt; dark conductivity</td>
<td>$10^{3}-10^{4} \times \text{dark conductivity}$</td>
</tr>
</tbody>
</table>
| devices        | -             | Schottky, p.i.n solar cells FET, etc..

Table 1.1: Properties of a-Si and a-Si:H

1.3 PHOTO CVD

In order to improve the optical and electronical properties of thin a-Si:H films prepared by Glow Discharge, other preparation techniques might be required.

Deposition of a-Si:H by photochemical decomposition of silane posesses some advantages compared to plasma deposition. The damages caused by high energetic ions and by high energy radiation are avoided in photo-CVD because of the absence of charged particles. The same could be said about impurity incorporation, caused by sputtering of the electrodes.

Photo-CVD comprehends both direct photo chemical deposition and mercury sensitized photochemical deposition using the resonant mercury lines at 185 nm (6.71 eV) and 254 nm (4.89 eV).

Let's focus here on 254 nm mercury sensitized photo-CVD. This process
is very selective and produces only the silyl (SiH₃) radical. One assumes that the best a-Si:H films are made by depositing SiH₃ radicals. SiH₃ possesses a great surface mobility, which might favour a homogeneous growth, in which stress and number of defects are minimized. It should be noted, that in glow discharge deposition, regimes known to produce the best optoelectronic quality a-Si:H, SiH₃ is also the main contributor to films growth as has been demonstrated recently by Gallagher et al. [35]: they used radical mass spectroscopy to analyse the flux of species incoming onto the walls. But there is yet another advantage of the selective character of 254 nm mercury assisted photo-CVD. The modeling of such a reactor is considerably simplified and this permits an accurate study of the processes in the gas phase and on the surface, during the growth of an a-Si:H film.

Although the first paper on mercury photosensitized CVD of a-Si:H appeared in 1964 [2], publications about electronical and optical properties of a-Si:H prepared by photochemical decomposition of silane [3, 4, 5] or disilane [4, 5, 7, 8] films have only been reported since 1983. The films are of good quality but the processes, which lead to the formation of a-Si:H films are not well understood. Nowadays photo-CVD is also used for the deposition of silicon nitride or silicon oxide in electronical devices [6] and even for epitaxial growth of silicon [9].
CHAPTER 2 : EXPERIMENTAL SET-UP

2.1 FORMATION OF a-Si:H BY MEANS OF PHOTO-CVD.

Before describing the UV-deposition reactor, the main steps leading to an a-Si:H film will be mentioned. The first step is the emission of resonant photons by the low pressure mercury lamp:

\[ \text{Hg}^{3\text{P}_1} \rightarrow \text{Hg}^{1\text{S}_0} + \nu \quad (\lambda = 253.7 \text{ nm}, \ E = 4.89 \text{ eV}) \]  \hspace{1cm} (2.1)

secondly, the absorption of these resonant photons by traces of mercury in the reactor:

\[ \text{Hg}^{1\text{S}_0} + \nu \rightarrow \text{Hg}^{3\text{P}_1} \]  \hspace{1cm} (2.2)

further the quenching of excited mercury atoms by silane molecules:

\[ \text{Hg}^{3\text{P}_1} + \text{SiH}_4 \rightarrow \text{Hg}^{1\text{S}_0} + \text{SiH}_2 + \text{H} \]  \hspace{1cm} (2.3)

finally the adsorption of SiH$_2$ radicals on the substrate, thus leading to the deposition of a-Si:H films.

\[ \text{SiH}_2(\text{gas}) \rightarrow \text{SiH}_2(\text{ads}) \downarrow \]  \hspace{1cm} (2.4)

Apart from these reactions secondary reactions take place, which are responsible for the formation of mainly H$_2$, Si$_2$H$_6$, and SiH$_2$. This will be discussed more in detail in the chapters 4 and 5.
2.2 THE PHOTO-CVD REACTOR

The photo-CVD reactor is schematically drawn in figure 2.1. The gas (SiH₄, H₂, Ar or a mixture) inlet is located on the right side and the gas passes through a mercury reservoir. Mercury atoms, which are evaporated above the liquid surface, are taken into the reactor by the gas flow. The mercury density can be varied independently from the gas flow, either by heating the mercury reservoir and thus increasing the mercury vapour pressure, or by using part of the bypass and thus diminishing the sweeping effect of the flowing gas. Then the gas passes through an absorption cell, which is used to measure the mercury density, and enters into the reaction chamber. The reaction chamber is delimited by a cylindrical shield to approximate a one-dimensional geometry (8.5 cm diameter, 4.2 cm length) with slits to pass the reflectometry beam and gas flow. Samples of 1 square cm can be mounted onto a substrate, the temperature of which can be varied between room temperature and 300°C. A low pressure mercury lamp emits resonant radiation at 254 nm and 185 nm. This lamp is the same as that used for the absorption cell and is described in chapter 3.

This lamp is separated from the vacuum system by a quartz window and a filter to absorb the 185 nm radiation. The window and shield are coated with Fomblin oil to prevent amorphous silicon deposition on them [4, 10].

The gas outlet consists of two identical mechanical rotary pumps. One is used to assure the initial vacuum after air exposure of the reactor. The other is used to pump silane during deposition. The aim of this is to avoid the contact between silane and air because of the explosive character of the former. Furthermore copper curls are introduced in the "silane pump" line, which serve as a mercury trap. This line is also equipped with a porous joint to assure, that the pressure is situated in the free molecular regime (i.e. the pumping speed is proportional to M⁻¹/₂, M being the molecular mass). The pumping speed can be varied by changing the orifice of a valve, situated just before the pump inlet.
The pressure inside the reactor is measured by a capacitance manometer. A quadrupole mass spectrometer is used to measure partial pressures ($\text{SiH}_4$, $\text{Si}_2\text{H}_6$, $\text{H}_2$) or contaminations. The deposition rate of $\text{a-Si:H}$ can be measured by a helium-neon laser reflectrometer. This reflectrometer can be replaced by an ellipsometer (visible or IR).

2.3 EXPERIMENTAL CONDITIONS

The density inside the vacuum system ($n = N/V$) satisfies the balance equation:

$$\frac{dN}{dt} = \Phi - \frac{nV}{\tau}$$  \hspace{1cm} (2.6)

with $\Phi$ the flux (particles/sec) and $\tau$ the average residence time. Thus in steady state the flux is proportional to the density (pressure) and inversely proportional to the average residence time

$$\Phi = nN/\tau$$ \hspace{1cm} (2.7)

When the gas inlet valve is closed, the density decreases exponentially as a function of the time:

$$n(t) = n_0 e^{-t/\tau}$$ \hspace{1cm} (2.8)

$$p(t) = p_0 e^{-t/\tau}$$ \hspace{1cm} (2.8a)

So $\tau$ can be calculated out of the slope of a logarithmic plot of the pressure against the time. Equation (2.8a) holds above 200 mTorr. This means, that above 200 mTorr $\tau$ is not pressure dependent and that the molecular flow $\Phi$ varies linearly with the pressure. Deviations below 200 mTorr may occur because of outgassing and the finite residual pressure related to the decreasing pumping speed at decreasing pressure. $\Phi$ can also be varied by changing $\tau$ and keeping $p_0$ constant. Starting from an initial
pressure $p_1, p_0$ can be obtained by diminishing the area of the orifice of the valve just before the pump inlet. Measurements revealed that $\Phi$ and thus $\tau$ are proportional to $(p_0/p_1)$ in the range 100 mTorr-1 Torr.

\[
\begin{align*}
V_{\text{vac}} &= 3.5 \text{ l} \\
V_{\text{react}} &= 0.25 \text{ l} \\
\Phi &= 20 \text{ sccm} \\
(t)_{\text{vac}} &= 13 \text{ s} \\
\Phi_{\text{leak, outgassing}} &= \sim 10^{-5} \text{ sccm}
\end{align*}
\]

Table 2.2 - Typical values in the vacuum system and the reactor (delimited by the cylindrical shield) at standard deposition conditions ($p_i = p_0 = 1$ Torr, gas $\text{SiH}_4$, $T_{\text{gas}} = 320-350$ K).

The mercury density might be estimated from the following assumptions:

1) The mercury density is limited by the evaporation speed $v_e$ in the mercury vessel. $v_e$ equals the evaporation speed of liquid mercury in vacuum [11]:

\[
v_e (\text{kg m}^{-2} \text{s}^{-1}) = \left( \frac{m}{2\pi RT} \right)^{1/2} p_e
\]

with $p_e$ the vapour pressure of mercury [11]

\[
\log (p_e/\text{Pa}) = 10.15 - 3212.5/(T/\text{Kelvin})
\]

2) The residence time for mercury atoms equals the average residence time for silane atoms, multiplied by $(M_{Hg}/M_{\text{SiH}_4})^{1/2}$

\[
\tau_{\text{Hg}} = \tau_{\text{(SiH}_4)} \left( \frac{M_{Hg}}{M_{\text{SiH}_4}} \right)^{1/2}
\]
CHAPTER 3:

DETERMINATION OF LAMP EMISSION LINE PROFILE AND MERCURY DENSITY BY MEASURING THE ABSORPTION OF RADIATION AT 254 nm

This chapter contains a paper, which has been submitted to Revue de Physique Appliquée. The references refer to a list at the end of this chapter.

ABSTRACT:

A simple method, using a variable length cell to measure the absorption of the 253.7 nm resonant line, emitted by a low pressure mercury lamp, allows simultaneous determination of the mercury density in the cell and the actual lamp temperature, which controls the mercury vapour pressure in the lamp, hence its self-absorbed emission line profile. This technique is proposed as a convenient control diagnostic in a Hg-assisted photo-CVD reactor.

INTRODUCTION

The well known 253.7 nm spectral line of mercury corresponding to the \( ^3P_1 - ^1S_0 \) transition has been for a long time a favoured prototype in fundamental studies of resonant atomic transitions and resonant radiative transfer [1]. Moreover mercury photosensitization of molecules, using low pressure mercury discharge lamps, has been an active field of research in photochemistry [2, 3], which has been renewed recently as a method of decomposition of organic and inorganic molecules for thin film deposition in electronic device technology. The so-called mercury assisted photochemical
vapour deposition technique, referred hereafter as Hg-photo CVD, has been used to sensitize insulating or semiconducting films such as SiO₂[4], Si₃N₄[5] or hydrogenated amorphous silicon (a-Si:H) [6-9].

In an attempt to model the gas and surface processes involved in Hg-photo-CVD of a-Si:H from SiH₄ [10] we have paid particular attention to the problem of radiative energy transfer from the low pressure Hg-lamp to the flowing gas containing a small amount of mercury. The efficiency of this energy transfer is essentially determined by the mercury density N in the reactor and the lamp temperature T₀, which controls the mercury vapour pressure inside the lamp, hence its self absorbed emission line profile. We show here that both parameters N and T₀ can be determined simultaneously out of measurements of the absorption of the 254 nm line as a function of the optical path length, by connecting an absorption cell of variable length to the reactor.

EXPERIMENTAL

The Hg-photo CVD reactor has been described elsewhere [10] and we focus here on the absorption cell, schematically represented in Fig. 1. The lamp consists of an approximately 1 meter long. Suprasil quartz tube (1 mm quartz thickness, 5 mm internal diameter) in the form of a spiral with electrodes at each end. The tube contains natural mercury and 50 torr argon as a carrier gas. The discharge is established by applying a high voltage at 50 Hz, adjustable up to 10 KV peak to peak amplitude.

![Figure 1](image)

Figure 1: An overview of the absorption cell. (1): the low pressure mercury lamp, (2): the parallel light beam of 2 mm diameter, (3): the absorption cell of variable length 1, (4): the monochromator and photomultiplier tube.
The lamp temperature is controlled by air cooling and monitored by a thermocouple, touching the quartz tube. However the measured external lamp temperature $T^*$ cannot be taken as a reliable measurement of the gas temperature $T_0$, which controls the mercury vapour pressure inside the lamp. $T_0$ is primarily related to the internal quartz tube temperature, but may be affected by the presence of electrodes. We assume that at this low pressure the gas temperature $T_0$ is homogenous throughout the tube.

Only a small portion of the tube is used as a source for the absorption cell by selecting a parallel light beam (2 mm diameter), which intercepts perpendicularly the tube axis, so that the thickness of the source is taken equal to the internal tube diameter: $\varepsilon_0 = 5 \text{ mm}$.

The absorption path length $\varepsilon$ between quartz windows is varied between 4 mm and 50 mm by means of a stainless steel bellows. Finally the transmitted 253.7 nm radiation is filtered by a monochromator and detected by a photomultiplier tube. The PMT signals during a sequence of measurements are corrected for small fluctuations of the lamp intensity recorded by a 254 nm radiometer. Then the signals are normalized to the zero absorption signal obtained by purging out the cell from mercury. If any small residual absorption subsists, the zero absorption signal $V_{\text{pm}}(0)$ is obtained by a linear extrapolation to $x = 0$. Finally the measured absorbance $A_{\text{mes}}(\varepsilon)$ is calculated as:

$$A_{\text{mes}}(\varepsilon) = 1 - \frac{V_{\text{pm}}(\varepsilon)}{V_{\text{pm}}(0)}$$

When the so defined $A_{\text{mes}}(\varepsilon)$ is compared to the calculated absorbance $A_{\text{cal}}(\varepsilon)$ the former must be corrected for reflections at the quartz-gas interfaces to obtain the true absorbance $A_{\text{mes}}(\varepsilon)$ for a cell of length $\varepsilon$ without reflection (see appendix).
COMPUTATION OF ABSORBANCE $A(\xi)$

The absorbance $A(\xi)$ of a line passing through an absorbing medium satisfies the Lambert-Beer equation, which must be integrated over the reduced wavelength $y$ [11]:

$$A(\xi) = 1 - \int_{-\infty}^{\infty} s(y) \exp (-k(y) \xi) dy$$

(2)

where $y = 2(\xi n 2)^{1/2} ((\lambda - \lambda_o)/\Delta \lambda_d$ and $\Delta \lambda_d$ the Doppler line width in the mercury lamp:

$$\Delta \lambda_d = 2 (\xi n 2)^{1/2} (v_0/c) \lambda_o$$

(3)

with $v_0 = \sqrt{2kT/m}$ and $c$ the velocity of light. Further $s(y)$ equals the normalized source function of the lamp, $k(y) = k\sqrt{\pi}P(y)$ the absorption coefficient in the cell and $P(y)$ the normalized absorption spectrum in the cell.

The source function $s(y)$ can be derived from the transport equation of radiation into one direction $I(y, x)$ inside the lamp ($-\xi_o/2 < x < \xi_o/2$)

$$\frac{dI(y, x)}{dx} = -\sqrt{\pi} k_0 P_0(y) I(y, x) + \epsilon(y, x)$$

(4)

where the subscripts $o$ refer to the lamp and $\epsilon(y, x)$ describes the emission term: $\epsilon(y, x) = \epsilon_o(x) \sqrt{\pi} P_0(y)$. This equation can be solved by a proper choice of $\epsilon_o(x)$ and the boundary condition:

$$I(y, -\xi_o/2) = 0$$

(5)

At first we consider the lamp as a homogenous plasma: $\epsilon_o(x) = \epsilon_o$. The self absorbed emission spectrum $s(y)$, which is proportional to $I(y, \xi_o/2)$, satisfies the following equations according to reference[12]:

- 3.4 -
\[ s(y) = s_0(1 - \exp(-k_0 \ell_o \sqrt{\pi} P_0(y))) \]  
(6)

\[ \int_{-\infty}^{\infty} s(y) \, dy = 1 \]  
(6a)

A better approximation for \( s(y) \) may be obtained by considering the lamp as a positive column [13]. The relatively high pressure of the argon buffer gas allows the applicability of the Schottky ambipolar diffusion theory [14]. This theory predicts a Bessel function like electron density profile in a cylindrical theory and a cosine like electron density profile in a slab geometry. Because the difference between a zeroth order Bessel function and a cosine is not enormous, we take the latter for simplicity of calculation. If we assume, that excitation of mercury atoms to the \( ^3P_1 \) level is merely caused by electron impact, then \( \epsilon(y,x) = \epsilon_o \sqrt{\pi} P_0(y) \cos(\pi x/\ell_o) \) and the normalized source function \( s(y) \) is again proportional to \( I(y, \ell_o/2) \):

\[ s(y) = s_0 \frac{P_0(y)}{\pi^2 + \pi k_o \ell_o^2 P_0(y)} \left\{ 1 + \exp(-\sqrt{\pi} k_0 \ell_o \sqrt{\pi} P_0(y)) \right\} \]  
(7)

The absorption coefficient at the center of a Doppler broadered line is

\[ k_o = \lambda_o^3 N_o g_2/8 \pi^{3/2} g_1 \, v_o \, \tau \]  
(8)

\( \tau = 122 \, \text{ns} \), the natural lifetime of the \( ^3P_1 \)-level, according to [15], \( g_2 \) and \( g_1 \) the statistical weights of the \( ^3P_1 \) level and \( ^1S_0 \) level (\( g_2 = 3, g_1 = 1 \)) and \( N_o \) the mercury density inside the lamp, which is determined by the mercury vapour \( p_e \) of the lamp at a temperature \( T_o \) [16]

\[ \log (p_e/p_a) = 10.15 - 3212.5/(T_o/\text{Kelvin}) \]  
(9)
The absorption coefficient $k$ satisfies to the same equation (8), when the subscript 0 of the lamp is omitted. Several broadening mechanisms determine the emission and absorption spectra $P_0(y)$ and $P(y)$:

1) Doppler broadening (Gaussian profile)

$$P_d(y) = \frac{1}{\pi^{1/2}} \exp \left( -y^2 \right)$$

(10)

(2) Natural broadening (Lorentzian profile)

$$P_n(y) = \frac{1}{\pi} \frac{a_n}{y^2 + a_n^2}$$

(11)

where $a_n = \lambda_0/(4\pi v_0 \tau)$.

3) Pressure broadening also resulting in a Lorentzian profile. We consider here resonant broadening and broadening caused by a neutral foreign gas (van der Waals interaction). The same formalism, used for natural broadening can describe these broadening profiles, if $\tau$ is replaced by an effective collision time [11, 17, 18]

$$\tau_{res} = \tau/(1.8 \times 10^{22} N_{Hg})$$

(12)

$$\tau_L = 1/(\pi \sigma_L^2 N_L v_{rel})$$

(13)

with $\pi \sigma_L^2$ an effective mercury foreign atom cross-section, $N_L$ the foreign atom density and $v_{rel}$ the corresponding relative velocity $v_{rel} = (8k T/\pi \mu)^{1/2}$ with $\mu$ the reduced mass of colliding atoms.

Summation of the different Lorentzian profiles will result in again a Lorentzian profile with $a = a_n + a_{res} + a_L$. A combination of statistically
independent broadening mechanisms of Gaussian and Lorentzian form gives a 
Voigt profile [19]

\[ P_v(y) = \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-s^2)}{a^2 + (s-y)^2} \, ds \] (14)

In the case that \( a < 10^{-2} \) equation (14) can be simplified into the following 

\[ P_v(y) = \frac{1}{\sqrt{\pi}} \exp(-y^2) \] \[ |y| \leq 2 \] (14a)

\[ = \frac{1}{\sqrt{\pi}} \left( \exp(-y^2) + \frac{a}{\sqrt{\pi} \, y^2} \right) \] \[ |y| > 2 \] (14b)

Thus the wings of the line profile are determined by the dispersion formula 
as follows from equation (14b), even if \( a \ll 1 \). Although the intensity of 
the wings is small compared to that of the center, their form may strongly 
affect \( s(y) \) if \( k_0 \, \rho_0 \gg 1 \), as is illustrated in figure 3.3. In the 
absorption cell the Doppler profile is slightly modified by the difference 
in temperature between lamp and cell:

\[ P_d(y) = \frac{1}{\pi^{1/2}} \frac{1}{\alpha \, \pi^{1/2}} \exp(-y/\alpha)^2 \] (15)

with \( \alpha = (T/T_0)^{1/2} \).

Natural mercury has six stable isotopes (mass 196 is negligible), four 
of even mass having zero nuclear spin and hence showing only one hyperfine 
line, two of odd mass having nuclear spins 1/2 and 3/2 and therefore giving 
two and three hyperfine lines respectively. Thus the 253.7 nm line of 
mercury doesn't consist of one single line but is split into 9 components 
[2] and \( P(y) \) is a summation over these 9 components:
Figure 3.2: The hyperfine structure of the 254 nm mercury line and the volumetric emission spectrum $P_0(y)$ inside the lamp in the case of a Voigt profile.

Figure 3.3: The source function of the lamp $S(y)$ as a function of the reduced wavelength $y$ in the case of an inhomogeneous lamp model (positive column) at a lamp temperature of 310 K. The solid line corresponds to a Voigt profile and the dashed line to a Doppler profile.
\[ P_{\text{hfs}}(y) = \sum_{i=1}^{g} b_i P(y - \Delta y_i) \]  

(16)

where \( b_i \) is the relative intensity and \( \Delta y_i \) the shift of each component from the center of the mercury line of mass 200.

**RESULTS AND CONCLUSIONS**

Absorption measurements have been carried out, in which the two parameters, the lamp temperature \( T_0 \) and the mercury density \( N \), have been varied independently. These two parameters are calculated out of a least square fit by minimizing \( \chi^2 \):

\[ \chi^2 = \frac{1}{N_m - N_p} \sum_i \left( \frac{A_{\text{mes}}(\xi_i) - A_{\text{cal}}(\xi_i)}{\Delta A_{\text{mes}}(\xi_i)} \right)^2 \]  

(17)

where \( N_m \) and \( N_p \) are the numbers of measured points and number of parameters respectively. The error \( \Delta A_{\text{mes}}(\xi_i) \) is typically 1\%. Figure 3.4 is a characteristic example of the measured and fitted absorbance as a function of the length of the cell. Figure 3.5 shows the fitted mercury density as a function of the pressure in the case of a homogenous lamp and inhomogenous lamp (positive column). In both cases we have taken the approximated Voigt profile for the lamp and the Doppler profile for the cell. The corresponding lamp temperatures are nearly constant: 320 ± 1K for the homogenous lamp model and 315 ± 1K for the inhomogenous lamp model. This must be compared with an externally measured \( T_0^* = 313 \) K. The values of \( \chi^2 \) are in between 0.1 and 0.6.

Figure 3.6 summarizes the results of the absorption measurements as a function of the lamp temperature at constant mercury density. Three models have been compared. Model I corresponds to a homogenous lamp model with a Doppler broadened line profile. Model II to a homogenous lamp model and a Voigt profile and Model III to an inhomogenous lamp with a Voigt profile.
Figure 3.4: A typical example of a measured and calculated absorbance $A(1)$ as a function of the length of the absorption cell.

Figure 3.5: Fitted mercury densities as a function of the silane pressure. The black spots correspond to calculations made by the inhomogeneous lamp model and the open spots to calculations made by the homogeneous lamp model.
\[
\begin{array}{|c|c|c|c|c|}
\hline
 & N(10^{19} \text{ m}^{-3}) & T_0 (\text{K}) & \chi^2 & T^* \\
\hline
\text{Model I} & & & & \\
1 & 2.86 \pm 0.09 & 320.2 \pm 0.4 & 0.66 & 299 \\
2 & 2.52 \pm 0.04 & 329.0 \pm 0.2 & 0.77 & 309 \\
3 & 2.43 \pm 0.08 & 337.4 \pm 0.1 & 0.47 & 317 \\
4 & 2.10 \pm 0.10 & 347.6 \pm 0.6 & 0.50 & 328 \\
\text{Model II} & & & & \\
1 & 2.51 \pm 0.03 & 305.5 \pm 1.5 & 0.07 & \\
2 & 2.42 \pm 0.07 & 314.9 \pm 0.1 & 0.46 & \\
3 & 2.27 \pm 0.14 & 319.3 \pm 1.0 & 0.23 & \\
4 & 2.00 \pm 0.11 & 325.5 \pm 0.3 & 0.28 & \\
\text{Model III} & & & & \\
1 & 2.70 \pm 0.04 & 304.0 \pm 0.1 & 0.07 & \\
2 & 2.68 \pm 0.09 & 310.4 \pm 0.5 & 0.20 & \\
3 & 2.81 \pm 0.08 & 314.6 \pm 0.4 & 0.23 & \\
4 & 2.80 \pm 0.09 & 319.2 \pm 0.1 & 0.46 & \\
\hline
\end{array}
\]

Table 3.6: Fitted mercury density \(N\) and lamp temperature \(T_0\), calculated \(\chi^2\) value and measured external lamp temperature \(T^*\).

Model I and II still show a dependence of the mercury density upon the lamp temperature, while the former ought to be constant. However the mercury density as calculated by model III doesn't show a significant variation with lamp temperature and is fairly constant within experimental error. Therefore we conclude that the radiation emitted by the lamp is adequately described by model III. The influence of some experimental errors has also been investigated. An offset of 1\% of \(V_{pm}(0)\) (equivalent to a residual absorption) doesn't change \(T_0\) but changes \(N\) by about 2\%. An error of 0.5 mm in \(l_0\) gives a variation of 5 K in \(T_0\) but doesn't affect \(N\). This can be accounted for by the fact that in reality the fitted parameter is not \(T_0\) but the optical thickness \(k_0\ell_0\), because the lamp emission profile \(s(y)\) in mainly determined by auto absorption. A random error of less then 0.2 mm in the length \(\ell_1\) of the cell only increases \(\chi^2\) without changing \(T_0\) or \(N\). Thus the random error in \(\ell_1\) is less than 0.2 mm. An error of 10 K degrees in the cell temperature changes \(N\) by about 2\%. The cell temperature is slightly above room temperature and has been measured by a thermocouple, thus the accuracy is larger than 2 degrees. A systematic error of \(\ell_1\) of 0.5 mm influences \(N\) by 10\%, while \(T_0\) remains approximately constant. Although the estimated error of \(\ell_1\) is less than 0.2 mm, this is probably the dominant experimental error in the determination of the mercury density.
Finally the necessity to take into account the hyperfine structure of the 253.7 nm line has been justified by calculations with 5 lines of equal intensity without overlap. This results in a fitted mercury density, which was some 20% lower than that calculated with the hyperfine structure.
APPENDIX

The measured absorbance $A_{\text{mes}}(\ell)$ must be corrected for the reflection at the air-quartz-gas interface of the absorption cell to obtain the true absorbance $A_{\text{mes}}(\ell)$ for a cell of length $\ell$ without reflection. If the interface is regarded optically as vacuum-quartz-vacuum, then a straightforward calculation of the reflectance $F$ yields:

$$F = \frac{1 - R^2}{1 + R^2} = \frac{2 n_q^2}{1 + n_q^2}$$

(A.1)

with $R$ the amplitude reflection coefficient for a vacuum-quartz interface and $n_q$ the index of quartz. We find $F = 0.08$ corresponding to $n_q = 1.5$. The PMT signal without absorption can be written as:

$$V_o(\ell) = V_o \left\{ (1-F)^2 + F^2(1-F)^2 + F^4(1-F)^2 + \ldots \right\} = V_o \frac{(1-F)^2}{1-F^2}$$

(A.2)

and with absorption as:

$$V(\ell) = V_o \left\{ (1-F)^2[1-A_{\text{mes}}(\ell)] + F^2(1-F)^2[1-A_{\text{mes}}(3\ell)] + F^4(1-F)^2[1-A_{\text{mes}}(5\ell)] \ldots \right\}$$

(A.3)

and this can be truncated after the second term because $F^2 \ll 1$. Finally

$$A^*_{\text{mes}}(\ell) = 1 - \frac{V(\ell)}{V_o(\ell)} \approx (1-F^2) A_{\text{mes}}(\ell) + F^2(1-F^2) A_{\text{mes}}(3\ell)$$

(A.4)
REFERENCES


CHAPTER 4: MODELING OF A PARALLEL PLATE PHOTO-CVD REACTOR

4.1 OVERVIEW OF THE DIFFERENT REACTIONS

In this paragraph the different reactions, which occur in a mercury sensitized photo-CVD reactor, will be outlined. This will be followed by a mathematical framework to calculate the radiative transfer, radical density profiles and deposition rate. Finally a numerical solution of the different equations will be given.

We focus here on 253.7 nm Hg assisted photochemical decomposition of silane. If available, data on 184.9 nm decomposition of silane or decomposition of hydrogen (H₂) and disilane (Si₂H₆) will be added.

The first step is the emission of resonant radiation by the mercury lamp:

\[ \text{Hg} \left( ^3P_{1/2,3/2} \right) \rightarrow \text{Hg} \left( ^1S_0 \right) + h\nu \ (\lambda = 253.7 \text{ nm}, \ E = 4.89 \text{ eV}) \]  \hspace{1cm} (4.1a)

\[ \text{Hg} \left( ^1P_{1/2,3/2} \right) \rightarrow \text{Hg} \left( ^1S_0 \right) + h\nu \ (\lambda = 184.9 \text{ nm}, \ E = 6.71 \text{ eV}) \]  \hspace{1cm} (4.1b)

The radiation can subsequently be absorbed by ground state mercury atoms in the reactor. This is the inverse reaction of (4.1) and the absorption coefficients depend on the transition time \( \tau \) (3.8). \( \tau \) equals 122
± 2 ns for the $^3P_1$ level [12] and 1.35 ± 0.13 ns for the $^1P_1$ level [13].

The next process is the quenching of these excited mercury atoms by silane. Experiments using NO as a scavenger gas for silyl (SiH$_3$) radicals revealed that the reaction decomposes silane into a silyl radical and atomic hydrogen [14]:

$$k_1, \quad \text{Hg}(^3P_1) + \text{SiH}_4 \rightarrow \text{Hg}(^1S_0) + \text{SiH}_3 + H \quad (4.2)$$

Alternative reactions, as reported by some authors [15, 16]

- \[ \text{Hg}(^3P_1) + \text{SiH}_4 \rightarrow \text{Hg}(^1S_0) + \text{SiH}_2 + 2H \quad (4.3\ a) \]
- \[ \rightarrow \text{Hg}(^1S_0) + \text{SiH}_2 + H_2 \quad (4.3\ b) \]
- \[ \text{Hg}(^3P_1) + \text{SiH}_4 \rightarrow \text{Hg}(^1S_0) + \text{Si} + 2H_2 \quad (4.3\ c) \]

are not probable and in contradiction with the former experiment. Moreover reaction (4.3 a) is endothermic (+ 1.3 eV/mol). Theoretical investigations on the decomposition mechanism of silane have been performed by Tsuda and coworkers [17]. They calculated the potential energy as a function of the molecular coordinates and investigated lowest energy paths on the so formed hypersurfaces. Excitation to the lowest triplet state of SiH$_4$ is followed spontaneously by decomposition into SiH$_3$ and to the lowest singlet state by decomposition into SiH$_2$. A vertical transition (photoabsorption, electron impact) from the silane ground state to the lowest triplet state needs 9.26 eV and some less for a transition to the lowest singlet state. Hg ($^3P_1$) only possesses 4.89 eV and cannot cause a vertical transitions in SiH$_4$. But the saddle point of the lowest triplet state lies below 4.89 eV on the hypersurface and therefore the Hg($^3P_1$) decomposition of silane is assumed to follow the lowest potential energy reaction path through the saddle point of the triplet state (conservation of spin), thus leading to the formation of SiH$_3$. However the Hg($^1P_1$) decomposition of silane presumably leads to excitation to the singlet state, followed by the formation of SiH$_2$. Measurement of the direct photolysis of silane [18] agree well with these conclusions:
\[
\text{SiH}_4 + \text{hv} \ (147 \text{ nm} = 8.45 \text{ eV}) \xrightarrow{\Phi_1} \text{SiH}_3 + \text{H} \quad (4.4 \text{ a})
\]

\[
\xrightarrow{\Phi_2} \text{SiH}_2 + 2\text{H} \quad (4.4 \text{ b})
\]

with \( \Phi_1 = 0.17 \) and \( \Phi_2 = 0.83 \) and the threshold value for direct photolysis is about 7.6 (160 nm).

Direct photolysis [19] and mercury assisted decomposition [20] of disilane has been measured:

\[
\text{hv} \ (147 \text{ nm}) + \text{Si}_2\text{H}_6 \xrightarrow{\Phi_1} \text{SiH}_2 + \text{SiH}_3 + \text{H} \quad (4.5 \text{ a})
\]

\[
\xrightarrow{\Phi_2} \text{Si}_2\text{H}_5 + \text{H} \quad (4.5 \text{ b})
\]

\[
\xrightarrow{\Phi_3} \text{SiH}_3\text{SiH} + 2\text{H} \quad (4.5 \text{ c})
\]

with \( \Phi_1 = 0.61 \), \( \Phi_2 = 0.21 \) and \( \Phi_3 = 0.18 \)

\[
\text{Hg}^{(3P_1)} + \text{Si}_2\text{H}_6 \rightarrow \text{Hg}^{(1S_0)} + \text{Si}_2\text{H}_5 + \text{H} \quad (4.6)
\]

\[
\text{Hg}^{(3P_1)} + \text{H}_2 \rightarrow \text{Hg}^{(1S_0)} + 2\text{H} \quad (4.7)
\]

The quenching of the \( 3P_1 \)-level also includes deexcitation to the metastable \( 3P_0 \)-level. In that case only 0.21 eV is transferred to silane, which should induce a vibrational excitation of silane. However the metastable \( \text{Hg}^{(3P_0)} \) atom might undergo a second collision leading to the complete quenching to the ground state

\[
\text{Hg}^{(3P_1)} + \text{SiH}_4 \rightarrow \text{Hg}^{(3P_0)} + \text{SiH}_4^* \quad (4.8 \text{ a})
\]

\[
\text{Hg}^{(3P_0)} + \text{SiH}_4 \rightarrow \text{Hg}^{(1S_0)} + \text{SiH}_3 + \text{H} \quad (4.8 \text{ b})
\]

The respective cross-sections for the three processes \( (3P_1 \rightarrow 1S_0, \ 3P_1 \rightarrow \)
$^3P_0$, $^3P_0 \rightarrow 'S_0$ have been measured by Horiguchi [21] for a large number of molecules including $H_2$ but not for silanes. However according to his classification of molecules, silanes should be classified in the first group. These molecules have quenching cross-sections close to the classical hard sphere cross-sections and deactivate $Hg(^3P_1)$ and $Hg(^3P_0)$ to form their triplet states. Their triplet states lie below the $Hg(^3P_1)$ level and for these molecules the ratio $\beta = \sigma_Q(^3P_1 \rightarrow Hg^3P_0)/\sigma_Q(^3P_1 - 'S_0)$ is smaller than 0.1 and the ratio $\alpha = \sigma_Q(^3P_0 \rightarrow 'S_0)/\sigma_Q(Hg^3P_1 - 'S_0)$ equals 1.2. In our model the presence of the $^3P_0$-level will simply be ignored, as is justified by the preceding discussion.

$$\Delta E(eV) \quad \sigma^2_Q(\AA^2) \quad \text{Ref.}$$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E(eV)$</th>
<th>$\sigma^2_Q(\AA^2)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Hg(^3P_1) + \text{SiH}_4 \rightarrow Hg(^1S_0) + \text{SiH}_3 + H$</td>
<td>0.97</td>
<td>40</td>
<td>[22]</td>
</tr>
<tr>
<td>$\rightarrow Hg(^1S_0) + \text{SiH}_2 + 2H$</td>
<td>-1.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rightarrow Hg(^1S_0) + \text{SiH}_2 + H_2$</td>
<td>2.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+ \text{Si}_2\text{H}_6 \rightarrow Hg(^1S_0) + \text{Si}_2\text{H}_5 + H$</td>
<td>1.15</td>
<td>60-100</td>
<td>[20]</td>
</tr>
<tr>
<td>$+ H_2 \rightarrow Hg(^1S_0) + 2H$</td>
<td>0.37</td>
<td>19±1</td>
<td>[22,23,24]</td>
</tr>
<tr>
<td>$\rightarrow Hg(^3P_0) + 2H$</td>
<td>0.21</td>
<td>&lt; 0.1</td>
<td>[21]</td>
</tr>
<tr>
<td>$Hg(^3P_0) + H_2 \rightarrow Hg(^1S_0) + 2H$</td>
<td>0.16</td>
<td>2.1</td>
<td>[21]</td>
</tr>
</tbody>
</table>

Table 4.1: Mercury sensitized decomposition of silanes and hydrogen.

No quantitative data on $Hg(^1P_1)$ are available.

Let's consider now the gas phase reactions. The primary radicals are $\text{SiH}_3$ and $H$. The following sequence of reactions is proposed:

$$k_2 \quad H + \text{SiH}_4 \rightarrow H_2 + \text{SiH}_3 \quad (4.9)$$
\[ k_{31} \]
\[
\text{SiH}_3 + \text{SiH}_3 \rightarrow \text{Si}_2\text{H}_6^{**} \tag{4.10 \text{ a}}
\]

\[ k_{32} \]
\[
\rightarrow \text{SiH}_4 + \text{SiH}_2 \tag{4.10 \text{ b}}
\]

\[ k_{51} \]
\[
\text{Si}_2\text{H}_6^{**} \rightarrow \text{Si}_2\text{H}_6 \tag{4.11 \text{ a}}
\]

\[ k_{52} \]
\[
\rightarrow \text{Si}_2\text{H}_4 + \text{H}_2 \tag{4.11 \text{ b}}
\]

\[ k_{53} \]
\[
\rightarrow \text{SiH}_4 + \text{SiH}_2 \tag{4.11 \text{ c}}
\]

\[ k_a \]
\[
\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6^{*} \tag{4.12}
\]

\[ k_{41} \]
\[
\text{Si}_2\text{H}_6^{*} \rightarrow \text{Si}_2\text{H}_6 \tag{4.13 \text{ a}}
\]

\[ k_{42} \]
\[
\rightarrow \text{Si}_2\text{H}_4 + \text{H}_2 \tag{4.13 \text{ b}}
\]

\[ k_b \]
\[
\text{Si}_2\text{H}_4 + \text{SiH}_2 \rightarrow \text{Si}_3\text{H}_8^{*} \tag{4.14}
\]

So one absorbed photon produces two silyl radicals and one hydrogen molecule. H reacts directly on SiH\textsubscript{4} and there is no doubt about reaction (4.9). SiH\textsubscript{3} doesn't react on silane, therefore the only reaction, which can occur is with another radical. Only SiH\textsubscript{3} is present at a sufficient concentration. The initial step in the reaction of SiH\textsubscript{3} with itself is disproportionation (4.10 b) or recombination (4.10 a) and the ratio \( k_{32}/k_{31} \) is pressure independant. But the vibrationally highly excited Si\textsubscript{2}H\textsubscript{6}**
molecule has a lifetime of about $10^{-9}$s [34] and must be stabilized by collisions. Otherwise it will undergo the disproportionation reaction (4.11 c). Thus the ratio $k_{51}/k_{53}$ is pressure dependant and the final ratio of disproportionation to recombination also. But at infinite pressure each $\text{Si}_2\text{H}_6^{**}$ molecule will stabilize and from extrapolations the pressure independent ratio $k_{32}/k_{31}$ was found to be $0.7 \pm 0.1$ [34]. At common pressures in the reactor the recombination via reaction (4.11 a) can be neglected. Perkins [18] also mentions the formation of $\text{Si}_2\text{H}_4$ followed by reaction (4.14), but his measurements are indirect and his conclusions are not very reliable. Silylene ($\text{SiH}_2$) will insert rapidly into silane to form $\text{Si}_2\text{H}_6^*$. The stabilization of $\text{Si}_2\text{H}_6^*$ takes place via collisions but may be incomplete at pressures below several hundred millitorrs.

Decomposition of disilane is very similar to that of silane, because it yields initially $\text{H}$ and $\text{Si}_2\text{H}_5$ a radical, which behaves like $\text{SiH}_3$;

$$k_{71}$$

$$\text{H} + \text{Si}_2\text{H}_6 \rightarrow \text{H}_2 + \text{Si}_2\text{H}_5 \quad (4.15 \text{ a})$$

$$k_{72}$$

$$\rightarrow \text{SiH}_3 + \text{Si}_2\text{H}_4 \quad (4.15 \text{ b})$$

$$\text{Si}_2\text{H}_5 + \text{Si}_2\text{H}_5 \rightarrow \text{Si}_2\text{H}_6 + \text{Si}_2\text{H}_4 \quad (4.16)$$
<table>
<thead>
<tr>
<th>Species</th>
<th>$E_f$(eV)</th>
<th>Bond</th>
<th>$E_{dis}$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_4$</td>
<td>0.36</td>
<td>D(SiH$_3$-H)</td>
<td>3.91</td>
</tr>
<tr>
<td>Si$_2$H$_6$</td>
<td>0.83</td>
<td>D(Si$_2$H$_5$-H)</td>
<td>3.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D(H$_3$Si-)</td>
<td>3.22</td>
</tr>
<tr>
<td>Si$_3$H$_8$</td>
<td>1.26</td>
<td>D(H$_3$SiH$_2$Si-SiH$_3$)</td>
<td>3.08</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>D(H-H)</td>
<td>4.53</td>
</tr>
<tr>
<td>H</td>
<td>2.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>2.02</td>
<td>D(SiH$_2$-H)</td>
<td>2.78</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>2.55</td>
<td>D(SiH-H)</td>
<td>3.35</td>
</tr>
<tr>
<td>SiH</td>
<td>3.6</td>
<td>D(Si-H)</td>
<td>3.34</td>
</tr>
<tr>
<td>Si</td>
<td>4.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$_2$H$_5$</td>
<td>2.31</td>
<td>D(Si$_2$H$_4$-H)</td>
<td>2.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D(H$_3$Si-SiH$_2$)</td>
<td>2.26</td>
</tr>
<tr>
<td>Si$_2$H$_4$</td>
<td>3.62</td>
<td>D(Si$_2$H$_3$-H)</td>
<td>3.08</td>
</tr>
</tbody>
</table>

Table 4.2: Formation energy for silanes and hydrogen out of gaseous H$_2$ and crystalline silicon. Dissociation energy and corresponding bonds.

The dissociation energy of a bond is the difference between the formation energy $E_{fo}$ of the species before and $E_{f1}$ and $E_{f2}$ of the species after bond cleavage.

These values are derived from the thesis of J. Perrin at the University Paris VII (1983): Physico-Chimie d'un plasma multipolaire de silane et processus de déposition du silicium amorphe hydrogéné.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E$</th>
<th>$k$ at 300 K</th>
<th>$E_A$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H + \text{SiH}_4 \rightarrow H_2 + \text{SiH}_3$</td>
<td>-0.61</td>
<td>0.43 ± 0.05</td>
<td>0.10</td>
<td>[25-27]</td>
</tr>
<tr>
<td>$H + \text{Si}_2\text{H}_6 \rightarrow H_2 + \text{Si}_2\text{H}_5$</td>
<td>-0.78</td>
<td>3.5 ± 0.3</td>
<td></td>
<td>[20][27]</td>
</tr>
<tr>
<td>$\text{SiH}_4 + \text{SiH}_3$</td>
<td>-0.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiH}_3 + \text{SiH}_3 \rightarrow \text{SiH}_4 + \text{SiH}_2$</td>
<td>-1.13</td>
<td>(1.5 ± 0.2) $\times 10^2$</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>$\rightarrow \text{Si}_2\text{H}_4 + H_2$</td>
<td>-0.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rightarrow \text{Si}_2\text{H}_6$</td>
<td>-3.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiH}_2 + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_6$</td>
<td>- 2.08</td>
<td>0.95</td>
<td>0.05</td>
<td>[28]</td>
</tr>
</tbody>
</table>

Table 4.3: Dominant gas phase reactions with energy balance, reactions constant and activation energy.

Finally possible reactions at the surfaces will be discussed. There is an exchange of species between surface and the gas phase. That means that not only particles arriving from the gas phase may cause a chemical reaction at the surface, but also that these particles may return in the gas phase in another composition. This may be an important source or loss for some specific particles. An extensive discussion on the surface reactions on a-Si:H and Fomblin oil is given in Chapter 5 and here only the conventions, necessary for the mathematical model of the reactor, are outlined. We take the silyl radical to illustrate this.

\[
\begin{align*}
\text{SiH}_3(\text{gas}) & \xrightarrow{\beta} \text{Si}_2(\text{surface}) \\
\alpha &= \text{incorporation} \\
\gamma &= \text{recombination} \\
\epsilon &= \text{etching}
\end{align*}
\]

A fraction $\beta$ of the $\text{SiH}_3$ flux will be adsorbed of the surface. This will be followed by incorporation into the film ($\alpha$), recombination of the surface and subsequent return to the gas phase but not as silyl ($\gamma$) or etching ($\epsilon$).
Thus

\[
\beta = \alpha + \gamma + \epsilon \quad (4.17)
\]

4.2 RADIATIVE TRANSFER

The transfer of resonant radiation from a low pressure mercury lamp to a parallel plate reactor containing mercury atoms and a quenching gas is a complex problem. This is a consequence of the imprisonment, a phenomenon adequately described by Holstein [29, 30] and Biberman [31], which makes a numerical computation of this radiative transfer necessary. Another complication is the hyperfine structure of the 253.7 nm line and the line broadening mechanisms.

Two possible configurations are taken into account. First the radiation from the lamp is considered as a parallel light beam of infinite radius. This results in a fully onedimensional treatment of the problem. Secondly the case of a diffuse beam emitted by a lamp of finite radius and a reactor of finite radius is treated. Although this requires a two dimensional approach (in cylindrical coordinates) we follow a quasi-1-dimensional approximation. Because the lamp used for absorption measurement is the same as the deposition lamp, the results from the preceding chapter can be used.

The balance equation for the excited mercury density \( n(x) \) contains four terms. The two creation terms depend on the type of beam and the two loss terms are independent of it [32]:

\[
B(x) + \Delta n = \frac{n(x)}{\tau} + Z_Q n(x) \quad (4.18)
\]

\( B(x) \) represents the absorption and \( \Delta n \) the imprisonment. \( n(x)/\tau \) equals the loss by spontaneous emission and \( Z_Q n(x) \) by quenching

\[
Z_Q = (\pi \sigma^2) v_{rel} N \quad (4.19)
\]
where $N$ stands for the silane density, $\pi \sigma^2$ the quenching cross-section and $v_{rel} = (8kT/\pi \mu)^{1/2}$ the relative velocity of mercury and silane atoms.

**PARALLEL BEAM**

We assume the lamp at $x = 0$ and the substrate on $x = L$. In the absence of absorbing molecules the photons flux $I_{ph}$ is constant, thus the creation of excited mercury atoms $B(x)dx$ between $x$ and $x + dx$ equals the loss of photons between $x$ and $x + dx$:

$$B(x)dx = - \int_{-\infty}^{\infty} \frac{\partial I_{ph}(x,y)}{\partial x} dy~dx = - \frac{\partial}{\partial x} \int_{-\infty}^{\infty} I_{ph}(0,y) e^{-\sqrt{\pi}kx} P(y) dy~dx$$

(4.20)

in which the photon flux $I_{ph}(0,y)$ is proportional to the source function $s(y)$ of the lamp

$$I_{ph}(0,y) = \frac{w_0}{hv} s(y)$$

(4.21)

with $w_0$ the intensity of the lamp (Watt/m²). $s(y)$ has been calculated for a homogeneous plasma (3.6) and a positive column (3.7). Substitution of (4.21) into (4.20) and differentiation of the latter gives the final expression for $B(x)$:

$$B(x) = \frac{w_0}{hv} \int_{-\infty}^{\infty} s(y) \sqrt{\pi}k P(y) e^{-\sqrt{\pi}kx} P(y) dy$$

(4.22)

Imprisonment of resonant radiation is the phenomenon that radiation reemitted at one place can be reabsorbed elsewhere. This process increases the effective lifetime of resonant radiation.

$$\Delta n(x) = \int_{0}^{L} \frac{n(\xi)}{\tau} K(\xi, x) d\xi$$

(4.23)

where $n(\xi)/\tau$ is the number of photons emitted per unit of time and volume at
ξ and $K(ξ, x)dx$ the probability that a photon reemitted at $ξ$ will be reabsorbed between $x$ and $x+dx$:

$$K(ξ, x) = \frac{1}{2} \int_{-∞}^{∞} P(y) \sqrt{π} e^{-y^2} P(y) \int_{1}^{∞} \frac{e^{-k\sqrt{π}|ξ-x|u} P(y)}{u} du dy \quad (4.24)$$

This is essentially the same equation as (4.22) apart from a geometrical factor. $s(y)$ in equation (4.22) is the equivalent of $P(y)$ in eq. (4.24). The factor $1/2$ appears, because only half of the randomly reemitted radiation can reach a plane $x>ξ$.

**DIFFUSE BEAM**

A more sophisticated and realistic model for the propagation of light emitted by the lamp is a model, in which the lamp is situated at a distance $s$ from the window and has a finite radius $r$ (see figure 4.4). The emission is considered to be diffuse and the photon flux decreases as a function of $x$ even without absorption. To avoid a fully two-dimensional treatment $I_{ph}(x)$ and $B(x)$ are computed only on the lamp axis:

$$I_{ph}(x) = \frac{W_o}{hν} \frac{F(x+s)}{F(s)} \quad (4.25)$$

with

$$F(z) = \int_{-∞}^{∞} \int_{1}^{∞} \frac{u_m(z)}{u^2} s(y) dy = \int_{-∞}^{∞} s(y)(1-1/u_m(z))dy \quad (4.26)$$

and $u_m(z) = \sqrt{r^2 + z^2}/z$. \quad (4.27)

In the case of absorption (4.25) becomes:
To find the absorption $B(x)$ eq. 4.28) must be differentiated towards $x$. The term proportional to $\sqrt{\pi k} P(y)$ represents the absorption, the term corresponding to the upper boundary of the integral equals the geometrical loss. Thus:

$$B(x) = \frac{w_0}{h v F(s)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} s(y) u^{-1} e^{-\sqrt{\pi k} P(y) u x} \, du \, dy$$  (4.29)

The imprisonment must be corrected for the finite radius. Thus the upper boundary of the integral (4.24) must be modified:

$$K(\xi, x) = \frac{1}{2} \int_{-\infty}^{\infty} P(y) \sqrt{\pi k} P(y) \int_{-\infty}^{\infty} \frac{u_m(|x-\xi|)}{1 - \exp[-k \sqrt{\pi} |\xi-x|] u P(y)] \, du \, dy$$  (4.30)

**Reflection**

Reflection from the substrate plate also influences the photon absorption efficiency. We assume that the reflectance at any angle of incidence $R_{\phi}$ is determined by the complex refractive index $\tilde{n}$ of a-Si:H at 254 nm.

In the case of a parallel beam irradiation the contribution of the reflection to $B(x)$ is simply obtained by computing $B(2\ell-x)$ from eq. (4.22) multiplied by the reflectance at normal incidence $R_0 = |(\tilde{n}+1)|^2$.

In the case of diffuse irradiation, one has to take into account the angular dependence of the reflectance $R_{\phi} = |r_s^2(\phi) + r_p^2(\phi)|/2$ where $r_s$ and $r_p$ are the complex Fresnel reflection coefficients for a wave electric field respectively perpendicular and parallel to the plane of incidence. By taking $I_{ph}(\ell)$ constant inside the cylinder $\rho < r$ and zero outside, $B(x)$ can be
approximated by eq. (4.29) in which \( s(y) \) is replaced by \( s(y)R_\varphi (u = 1/\cos \varphi) \)
and \( x \) by \( 2\ell - x \).

The contribution of the reflection to \( K(z,x) \) can be taken into account in the same way as for \( B(x) \) in the case of a diffuse lamp.

4.3 BALANCE EQUATIONS FOR THE RADICALS

Once the \( Hg (^3P_1) \) density profile \( n(x) \) is known, the radical density profiles \( n_H(x) \) for atomic hydrogen, \( n_{s3}(x) \) for silyl and \( n_{s2}(x) \) for silene can be calculated. Because an hydrogen atom produces a silyl radical, \( n_H(x) \) must be calculated first.

HYDROGEN DENSITY PROFILE

As initial gas pure silane is used. If the mean molecular hydrogen density \([H_2]\) is small compared to \([\text{SiH}_4]\), then quenching by \( H_2 \) can be neglected, and the only reactions in which \( H \) is involved are (4.2) and (4.9). The balance equation for \( H \) is a diffusion equation with two boundary conditions.

\[
-D_H \frac{d^2 n_H(x)}{dx^2} = k_1 N_s n(x) - k_2 N_s n_H(x) \tag{4.31}
\]

\[
-D_H \left[ \frac{\partial n_H(x)}{\partial x} \right]_{x_1} = \frac{1}{4} \left[ n_H m_H n_H(x) \right]_{x_1} \tag{4.32}
\]

\( k_1 \) and \( k_2 \) are the reactions coefficients as defined in paragraph 4.1, \( N_s \) is the silane density (which is assumed to be constant), \( D_H \) is the diffusion coefficient of atomic hydrogen in silane and \( 1-n_H \) is the radical reflection probability for atomic hydrogen on the Fomblin oil \( (x_1 = 0) \) or on a-Si:H \( (x_2 = \ell) \). The positive sign refers to \( x_2 = \ell \), the negative to \( x_1 = 0 \).

The diffusion constant depends on the temperature, pressure and the
cross-section for elastic collisions:

\[ D = \frac{3}{8} \frac{\pi kT}{2\mu} (N_s \sigma_{el})^{-1} \]  \hspace{1cm} (4.33)

This has been measured for SiH in silane [32] and a value of 400 cm²/s has been derived at \( p = 1 \) torr and \( T = 500K \). Thus:

\[ D_{s1} = \frac{400}{(T/500 \text{ K})^{1/2}} \text{ cm}^2/\text{s} \]  \hspace{1cm} (4.34)

The elastic cross-section \( \sigma_{el} \) is determined by the internuclear distance \( d_{12} \) between a silane atom and the radical:

\[ \sigma_{el} = \pi d_{12}^2 \]  \hspace{1cm} (4.35)

The internuclear distance \( r_{SiH} = 1.5 \pm 0.03 \, \text{Å} \), the classical hydrogen radius \( r_H = 0.8 \, \text{Å} \) and the value of \( d_{12} \) derived from (4.34) between SiH₄ and SiH equals 3.2 Å = 2.14 \( r_{SiH} \). That's why a radius of 1.07 \( r_{SiH} \) is attributed to both SiH₄ and the SiHₐ radicals (m=1,2,3), from which the values of \( d_{12} \) can calculated:

\[
\begin{align*}
\text{H + SiH₄ :} & \quad d_{12} = r_H + 1.07 \, r_{SiH} = 2.4 \, \text{Å} \\
\text{SiHₐ + SiH₄ :} & \quad d_{12} = 2.14 \, r_{SiH} = 3.2 \, \text{Å}
\end{align*}
\]  \hspace{1cm} (4.36)

By inserting \( d_{12} \) in equation (4.33) an expression similar to (4.34) can be derived for \( D_H \):

\[ D_H = \frac{2900}{p/\text{torr}} \frac{(T/500 \text{ K})^{1/2}}{\text{ cm}^2/\text{s}} \]  \hspace{1cm} (4.37)

A fundamental ambiguity is encountered when the boundary conditions must be set up for equation (4.31). This is a diffusion equation and describes a macroscopic phenomenon. But the boundary conditions describe phenomena on molecular scale. Therefore the solution of the diffusion equation cannot reproduce sudden changes in the densities within some mean free path length \( \lambda \) from the surface.
According to the diffusion theory the net particle flux $\Phi$ equals:

$$\Phi = -D \frac{dn}{dx} \hspace{1cm} (4.38)$$

The molecular theory predicts a flux in one direction $\Phi^+ = 1/4 \, n v$. Thus near the surface with a radical reflection probability $1-\beta$ the net flux $\Phi$ according to the molecular theory equals:

$$\Phi = \Phi^+ - \Phi^- = \frac{1}{4} n v - \frac{1}{4} n v (1-\beta) = \frac{1}{4} \beta n v \hspace{1cm} (4.39)$$

Equalizing those two results yields the boundary condition (4.32). Consider now two cases:

1) $\beta=0$: $\partial n / \partial x = 0$ at the surface and the density profile is flat.

2) $\beta=1$: $n(x_1) = (4D/v)[dn/dx]_{x_1}$. Although no radicals return from the surface, the density is non zero. A zero density can be obtained by adapting slightly (4.32):

$$-D_H \left[ \frac{dn_H}{dx} \right]_{x_1} = \frac{1}{4} \left[ \frac{\beta_H}{1-\beta_H} \right] v_H n_H \hspace{1cm} (4.40)$$

but then $dn_H/dx$ is not defined at the surface.

Assuming a linear density profile near the surface, the location $\Delta X$ behind the surface $x_2 = \ell$ where the density is zero, can be calculated:

$$n(\ell+\Delta X) : n(\ell) + \frac{\partial n(x)}{dx} \bigg|_{\ell} \Delta X = 0 \hspace{1cm} (4.41)$$

$$\Delta X = -\frac{n(\ell)}{dn(x)/dx} = \frac{4D}{v} = \frac{4(\lambda^2/2v_c)}{v} = 2 \lambda \hspace{1cm} (4.42)$$
H. Wise and B.J. Wood [32] propose the following boundary conditions:

\[
- \left. D_H \left( \frac{dn_H}{dx} \right) \right|_{x_1} = \pm \frac{1}{4} \left[ \frac{\beta_H}{1-\beta_H/2} v_H n_H \right]_{x_1}
\]

This assumes a linearly decreasing density profile near the surface in stead of a constant density profile, from which (4.39) has been derived.

\[
\psi = \frac{1}{4} \beta \left( \frac{n(\ell) + n(\ell-\lambda)}{2} \right) n = \frac{1}{4} \beta n(\ell) n - \frac{1}{4} \beta n \frac{\partial n}{\partial x} \bigg|_{x=\ell}
\]

In that case \( \Delta x = \lambda \). The differences between these boundary conditions occur only on molecular scale, thus eq. (4.32) is considered to be sufficiently accurate.

**Silyl and Silene Density Profile**

The equation governing the silyl and silene densities are essentially the same as the equations for atomic hydrogen:

\[
\begin{align*}
- D_{s3} \frac{d^2 n_{s3}^2(x)}{dx^2} &= k_1 N_s n(x) + k_2 N_s n_H(x) - k_3 n_{s3}^2(x) \\
- D_{s3} \frac{dn_{s3}^2(x_i)}{dx} &= \pm \frac{1}{4} \beta_{s3}(x_i) v_{s3} n_{s3}(x_i)
\end{align*}
\]

where \( k_3 \) takes into account destruction of \( \text{SiH}_3 \) by recombination and disproportionation

\[
\begin{align*}
- D_{s2} \frac{d^2 n_{s2}^2(x)}{dx^2} &= k_3 n_{s2}^2(x) - k_4 N_s n_{s2}(x) \\
- D_{s2} \frac{dn_{s2}^2(x_i)}{dx} &= \pm \frac{1}{4} \beta_{s2} (x_i) v_{s2} n_{s2} (x_i)
\end{align*}
\]
according to the reactions (4.10 b), (4.12) and (4.13 a).

The mean density \([n_i]\) of a species can be calculated in this one dimensional problem:

\[
[n_i] = \frac{1}{\xi} \int_0^\xi n_i(x) \, dx
\]  

(4.49)

The production (particles/sec), or depletion in the case of silane, of stable products can be calculated, if the contribution for surface reactions is neglected:

\[
\Phi_{H_2} = k_2 [H] N_S V_1
\]  

(4.50)

\[
\Phi_{Si_2H_6} = k_4 [SiH_2] N_S V_1
\]  

(4.51)

\[
\Phi_{SiH_4} = (-k_1 [Hg(3P_1)]) N_S - k_2 [H] N_S + k_3 [SiH_3^2] - k_4 [SiH_2] N_S) V_1
\]  

(4.52)

with \(V_1\) the reactor volume.

To calculate the partial pressures these expressions must be multiplied by a mass-dependent factor.

\[
P_i = \Phi_i \frac{kT}{V_2} \tau_i
\]  

(4.53)

with \(V_2\) the volume of the vacuum system and \(\tau_i = \sqrt{N_i/32} \tau_{SiH_4}\) the residence time of each product.

If the film growth is only a consequence of deposition by \(SiH_3\) or \(SiH_2\) (no etching by \(H\)), then the deposition rate (Å/s) can easily be obtained from the \(SiH_2\) and \(SiH_3\) fluxes on to the substrate:
\[
\frac{\nu_d (A/s)}{n(a-Si:H)} = \frac{10^{10}}{n(a-Si:H)} \left( -D_{s3} a_{s3} \frac{dn_{s3}}{dx} - D_{s2} a_{s2} \frac{dn_{s2}}{dx} \right)_{x=e} \tag{4.54}
\]

\[
= \frac{10^{10}}{4} a_{s3} n_{s3}(x) v_{s3} + a_{s2} n_{s2}(x) v_{s2} \frac{1}{n(a-Si:H)} \bigg|_{x=e} \tag{4.55}
\]

with \( n(a-Si:H) = 5 \times 10^{28} \text{ at. m}^{-3} \), the silicon density in solid a-Si:H. Eq. (4.55) corresponds to the boundary condition (4.32).

4.4 NUMERICAL SOLUTIONS

Density profile of \( \text{Hg}(^3P_1) \)

By defining \( \lambda \) as the fractional loss by spontaneous deexcitation

\[
\lambda = \frac{1/\tau}{1/\tau + Z_Q} = \frac{1}{1 + \tau Z_Q} \tag{4.56}
\]

the steady state density equation of \( \text{Hg}(^3P_1) \) atoms can be written in the form:

\[
n(x) - \lambda \int_{0}^{e} n(\xi) K(\xi, x) d\xi = \lambda \tau B(x) \tag{4.57}
\]

This is a Fredholm integral equation of the second kind where the kernel \( K(\xi, x) \) is not symmetric, if the reflection is included. Moreover \( K(\xi, x) \) has a singularity at \( \xi = x \). Therefore we use an approximate method, similar to that used by Biberman [31], to solve the equation. The interval \([0, e]\) is divided into \( m \) subintervals. This reduces the problem to the solution of a system of linear equations

\[
n(x_i) - \lambda \sum_{j=1}^{m} n(x_j) \sigma_{ij} = \lambda \tau B(x_i) \tag{4.58}
\]
for \( x_i = 2\Delta(i-1) \), \( i = 1 \) to \( m+1 \), \( \Delta = \varepsilon/2m \) and

\[
t_{ij} = \int_{x_j-\Delta}^{x_j+\Delta} K(\xi, x_i) \, d\xi \\
\theta_i = \int_0^\Delta K(\xi, x_i) \, d\xi \\
\theta_{i,m+1} = \int_{\varepsilon-\Delta}^{\varepsilon} K(\xi, x_i) \, d\xi
\]

(4.59)

(4.59 a)

(4.59 b)

This suggests that

\[
\int_{x_j-\Delta}^{x_j+\Delta} n(\xi) K(\xi, x_i) \, d\xi \approx n(x_j) \theta_{ij}
\]

(4.60)

In matrix formulation eq. (4.58) becomes:

\[
n - \lambda \Theta n = \lambda \tau B
\]

(4.61)

where \( n \) and \( B \) are the \((m+1)\) vectors \([n(x_i)]\) and \([B(x_i)]\) and \( \Theta \) the \((m+1)\) \( x(m+1) \) matrix \([\theta_{ij}]\).

Equation (4.61) has been solved by an iterative method:

\[
n_{p+1} = \lambda \tau B + \lambda \Theta n_p
\]

(4.62)

\[
n_0 = \lambda \tau B
\]

(4.62 a)

The following convergence criterion has been used:

\[
\text{Max} \left\{ \frac{|n_p(x_i) - n_{p-1}(x_i)|}{n_p(x_i)} \right\} \leq 10^{-3}
\]

(4.63)
Finally a continuous function \( n(x) \) was obtained by a cubic spline interpolation between the \( m+1 \) points \( n(x_i) \). Due to the approximation made in eq. (4.60), the accuracy of the method depends on the grid resolution \( 1/m \) compared to the optical thickness \( k' \). It has been verified for the highest optical thickness considered here: \( k'=20 \), that

\[
\max \left\{ 1 - \frac{n(x_i)\text{me=20}}{n(x_i)\text{me=40}} \right\} \leq 10^{-2} \tag{4.64}
\]

which is considered to be satisfactory.

The Hg\((^3P_1)\) density profile has been computed in the case of a parallel beam and a diffuse lamp (see fig. 4.5 and 4.6 respectively). The absorption profile is a Doppler broadened profile (eq. 3.11), the lamp emission profile is a Voigt profile (eq. 3.10) and the source function \( s(y) \) corresponds to the case of a positive column (eq. 3.14).

Finally the 253.7 nm hyperfine structure has been approximated by 5 lines of equal intensity with an average line separation \( \Delta \lambda_0=11.7 \text{ Å} \).

Density profile of H

Once the Hg\((^3P_1)\) density profile has been computed, the atomic hydrogen density profile \( n_H(x) \) can be calculated analytically. Therefore we write the set of equations (4.31-4.32) in the form:

\[
\frac{d^2 n_H(x)}{dx^2} = a^2 \left\{ n_H(x) - \left( k_1/k_2 \right) n(x) \right\} \tag{4.65}
\]

\[
\frac{dn_H(x)}{dx} \bigg|_{0, \ell} = -a_1 n_H(x) \bigg|_{0, \ell} \tag{4.66}
\]

where \( a^2 = k_2 N_s/D_H \), \( a_o = -\beta_H(0) v_H/4D_H \) and \( a_\ell = \beta_H(\ell) v_H/4D_H \). The analytical
solution can be obtained by a double integration of eq. (4.65). The remaining constants can be determined with the boundary conditions at \( x=0 \) and \( x=e \). This gives the final result:

\[
n_H(x) = \alpha(k_1/k_2) \int_0^X n(t) \sinh \left( \alpha(t-x) \right) \, dt + \frac{v_1 w_2}{u_1 v_2 - u_2 v_1} \sinh \alpha x - \frac{u_1 w_2}{u_1 v_2 - u_2 v_1} \cosh \alpha x
\]

where

\[
u_1 = a_0
\]

\[
u_2 = a \sinh \alpha \epsilon + a_1 \cosh \alpha \epsilon
\]

\[
u_3 = a \cosh \alpha \epsilon + a_1 \sinh \alpha \epsilon
\]

\[
\omega_2 = \alpha(k_1/k_2) \sinh \alpha(0) \left( \left( k_1 \frac{N}{D_H} \right) \cosh \alpha(0) \right)
\]

From the differential equation (4.65) we see that an approximated solution of \( n_H(x) \) far away from the boundaries yields:

\[
n_H(x) \approx (k_1/k_2) n(x) \approx 10^3 n(x)
\]

In the analytical solution (4.67) \( n_H(x) \) is expressed as a sum of three separate terms, which are large compared to \( n_H(x) \) itself. At 1 Torr \( \alpha = 10^3 \text{cm}^{-1} \) and increases with \( p^{3/4} \). The integrals in expression (4.67) must be calculated numerically and contain factors like \( \exp(\alpha x) \). Therefore a slight error in the calculation of the integrals can affect \( n_H(x) \) dramatically. This problem has been solved in two different manners.

First the differential equation might be solved numerically. By
applying a shooting method this boundary value problem can be reduced to an initial value problem. But his method fails, because of numerical instability. Starting at $x=0$, the solution rapidly diverges because the large positive value of $a^2$. Therefore this boundary value problem must be solved by a finite-difference method. As initial approximate solution has been used:

$$n_H(x) = \left\{ 1 - 4\left( \frac{1}{2} \frac{E-x}{\ell^2} \right)^2 \right\} \left( \frac{k_1}{k_2} \right) n(x) \quad (4.69)$$

By applying the latter technique the solution for $n_H(x)$ converges up to $p = 3$ torr, which lies above pressures used during the experiments. An approximate analytical solution can be obtained by dividing the interval $[0, \ell]$ into a large number of subintervals, in which $n(x)$ is supposed to be constant. In that case the integrals can be replaced by analytical expressions, thus avoiding the influence of rounding errors. If whole the solution is calculated in quadruple precision (16 significant numbers), then $n_H(x)$ can be calculated up to $p = 5$ torr.

Finally the complete solution $n_H(x)$ is obtained by a cubic spline interpolation between the points in which $n_H(x)$ has been calculated by either of the two procedures described above.

**Density profile of SiH$_3$**

Now that the $\text{Hg}(^{3}p_1)$ and H density profiles are known, the density profile $n_{s3}(x)$ of SiH$_3$ can be calculated. Eq. 4.45-4.46 are rewritten as:

$$\frac{d^2n_{s3}(x)}{dx^2} = - \alpha_{s3} \left\{ n(x) + (k_2/k_1)n_H(x) \right\} + D_{s3} k_3 n_{s3}^2(x) \quad (4.70)$$

$$\frac{dn_{s3}(x)}{dx} \bigg|_{o, \ell} = - b_i n_{s3} \bigg|_{o, \ell} \quad (4.71)$$

where $\alpha_{s3} = k_1 N_s/D_{s3}$, $b_o = - \beta_{s3}(0) v_s^3/4 D_{s3}$ and $b_t = \beta_{s3}(\ell) v_s^3/4 D_{s3}$. At
first the recombination/disproportionation term is neglected \((k_3 = 0)\). Then again the solution can be determined analytically by a double integration of the differential equation, in which the unknown constants are determined by the boundary conditions. Because of the positive sign in eq. (4.70) there are no problem of rounding errors

\[
\begin{align*}
    n_{s3}^t(x) &= \int_0^x \int_0^t \eta_{s3} \left[ n(\xi) + \left( k_2/k_1 \right) n_H^t(\xi) \right] d\xi \, dt \\
    &= - \frac{q_1 r_2}{p_1 q_2 - p_2 q_1} x + \frac{p_1 r_2}{p_1 q_2 - p_2 q_1} \tag{4.72}
\end{align*}
\]

with:

\[
\begin{align*}
    p_1 &= 1 \\
    p_2 &= 1 + b_1 \epsilon \\
    q_1 &= b_0 \\
    q_2 &= b_1 \\
    r_2 &= \int_0^\epsilon \eta_{s3} \left[ n(t) + \left( k_2/k_1 \right) n_H(t) \right] dt + \int_0^\epsilon \int_0^t b_1 \eta_{s3} \left[ n(\zeta) + \left( k_2/k_1 \right) n_s(\zeta) \right] d\zeta \, dt
\end{align*}
\]

This solution now serves as initial approximate solution of eq. (4.70) with recombination. This is a non linear differential equation, which has been solved by the same finite difference method, as has been used for \(n_H(x)\). Finally the complete solution \(n_{s3}(x)\) again is obtained by a cubic spline interpolation between the mesh of points from the finite difference method.

- 4.23 -
Density profile of SiH$_2$

This is exactly the same differential equation and the same boundary value condition as for atomic hydrogen:

\[
\frac{d^2n_{s3}(x)}{dx^2} + \sigma_{s2} \frac{n_{s2}(x)}{D_{s2}} - \frac{k_\infty}{D_{s3}} n_{s3}(x) = 0 \tag{4.73}
\]

\[
\frac{dn_{s2}(x)}{dx} \bigg|_{o, \ell} = -c_1 n_{s2}(x) \bigg|_{o, \ell} \tag{4.74}
\]

where \( \sigma_{s2} = k_4 N_s/D_{s2}, \ c_0 = \beta_{s2}(0) v_{s2}/4 D_{s2} \) and \( c_\ell = \beta_{s2}(\ell) v_{s2}/4 D_{s2} \).

Therefore the equation has been solved in the same way as the atomic hydrogen equation. Especially problems concerned with rounding errors or instability have been solved by taking the approximated analytic solution.

RESULTS

The results of these calculations are shown in figures 4.7-4.12. The surface reaction probabilities \( \beta \) have been chosen corresponding to measurements or assumptions discussed in Chapter 5: \( \beta_H(0) = 0, \ \beta_H(\ell) = 1, \ \beta_{s3}(0) = 0, \ \beta_{s3}(\ell) = 0.1, \ \beta_{s2}(0) = 0, \ \beta_{s3}(\ell) = 0.5 \). Figure 4.7 shows the mean densities as a function of the pressure, figures 4.8-4.9 the radical density profiles at different experimental conditions. Finally figure 4.10 shows the calculated deposition rate, according to eq. 4.54 as a function of the pressure and mercury density. All calculations have been performed for the diffuse lamp model with reflection at the a-Si:H surface.
Figure 4.1 from [17]: Illustration of the dissociation of SiH₄ according to two different set of basic functions.
Figure 4.4: Illustration of the different radiation processes for the diffuse lamp model and definition of the used parameters. (1): direct absorption, (2): absorption after reflection on the substrate, (3) imprisonment of radiation from a plane $\xi$, (4) imprisonment after reflection on the substrate.

$$u = \frac{1}{\cos \varphi_m}$$
figure 4.5: Spatial distribution of the Hg(3P1) atom density under parallel beam irradiation without reflection on the substrate for several lamp emission profiles \( P_0(y) \) and source functions \( s(y) \). (a): Doppler profile, (b): self-absorbed Doppler profile, (c) self-absorbed Voigt profile (\( P_{Ar} = 5 \) torr), (d) as c with 50 torr argon pressure, (e) as d without hyperfine overlap. The dashed lines correspond to the density \( n_0(x) = \lambda \tau B(x) \) when imprisonment is neglected.
Figure 4.6: Hg($^2P_1$) density profile for a diffuse lamp model for different mercury densities inside the reactor ($k_1 = 10$ corresponds to a mercury density of $2 \times 10^{13}$ cm$^{-3}$). The dashed lines are calculated without reflection and the solid with reflection on the substrate.
Figure 4.7: Mean densities as a function of the silane pressure. This situation corresponds to a mercury density, which varies as a function of the pressure as has been verified experimentally by the absorption measurements.
Figure 4.8: Normalized radical density profiles of Hg($^3P_1$), H and SiH$_3$ for a mercury density of $2 \times 10^{12}$ cm$^{-3}$. The solid lines correspond to a pressure of 1 torr, the dashed lines to a pressure of 0.1 torr.
Figure 4.9: Normalized radical density profiles of Hg(3P₁), H and SiH₃ for a mercury density of 2 \times 10^{13} \text{ cm}^{-3}. The solid lines correspond to a pressure of 1 torr, the dashed lines to a pressure of 0.1 torr.
Figure 4.10: Deposition rate as a function of the silane pressure for two different values of the mercury density.
Chapter 5: Gas and surface processes

5.1 Introduction

This chapter deals with the gaseous and surface processes in the mercury sensitized photo-CVD reactor. Because of the interaction between species in the gas phase and on the surface, a complete separation of these two processes is not possible and might lead to erroneous conclusions.

Apart from some reaction coefficients, the gas phase reactions themselves are well known and described adequately in the previous chapter. Therefore the aim of the experiments, as far as the gaseous reactions are concerned, is the verification of these reactions and the determination of the unknown reaction coefficients.

On the contrary there is a great uncertainty on the surface processes, both on a-Si:H and on the Fomblin oil, and there are not many reliable data. So the aim of this work has also been the execution of reliable measurements of the surface phenomena, both qualitatively and quantitatively. To explain these observed phenomena, possible reaction mechanisms are proposed.

The model presented in the previous chapter allows a intelligent choice for the values of the parameters during the experiments: silane pressure, mercury density, lamp intensity and temperature, gas flow, geometry and substrate temperature. Thus there is an important feedback between model and experiments.

5.2 Spatial distribution of the lamp intensity

The lamp intensity on the axis has been measured as a function of the
distance from the window with a radiometer, which detects only radiation at 254 nm. The results of this measurement are shown in figure 5.1 and the solid curve represents calculations based on the diffuse lamp model. The

![Diagram](image)

- Figure 5.1: Normalized measured (dots) and calculated (solid line) light intensity of the lamp on the axis. Lamp radius $r=4.2$ cm, lamp-window spacing $s=1.5$ cm.

lamp radius is 4.2 cm, the lamp temperature is 315 K and the distance from the window equals 1.5 cm. For large distances there is a good agreement between the measured light intensity variation and the calculation made with the diffuse lamp model. The parallel beam model predicts a constant light intensity as a function of the distance from the window and must therefore be rejected. Yet because of the finite angular acceptance of 37° of the radiometer only part of the incoming light intensity can be measured close to the lamp. Therefore the light intensity at $x=0$ must be extrapolated from the diffuse lamp model. The maximum light intensity equals 300 W/m², but this has been measured without the 185 nm filter. As a matter of fact this filter also absorbs 70% of the 254 nm radiation, so that the actual light intensity at 254 nm is about 100 W/m².
5.3 Experimental verifications of gas phase and surface reactions

First we recapitulate the sequence of reactions in the gas phase, which have been proposed in chapter 4:

\[
\begin{align*}
\text{Hg}^3P_1 + \text{SiH}_4 & \rightarrow \text{Hg}^1S_0 + \text{SiH}_3 + \text{H} \quad , \quad k_1 = 5.9 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \\
\text{H} + \text{SiH}_4 & \rightarrow \text{H}_2 + \text{SiH}_3 \quad , \quad k_2 = 4.3 \times 10^{-13} \text{ cm}^3\text{s}^{-1} \\
\text{SiH}_3 + \text{SiH}_3 & \rightarrow \text{SiH}_4 + \text{SiH}_2 \quad , \quad k_3 = ? \\
\text{SiH}_2 + \text{SiH}_4 & \rightarrow \text{Si}_2\text{H}_6 \quad , \quad k_4 = 9.5 \times 10^{-13} \text{ cm}^3\text{s}^{-1}
\end{align*}
\]

The only unknown reaction coefficient is the coefficient of the recombination/disproportionation reaction \(k_3\). To determine this coefficient two kind of experiments have been performed.

1) The first experiment consists of measuring the deposition rate of \(a\)-Si:H on the substrate as a function of the silane pressure. The deposition rate is measured in situ with the Helium-Neon reflectometer. The distance between two fringes equals 830 Å and can be calculated with equation (5.1):

\[
d_{\text{interfringe}} = \frac{1}{2\lambda} (1 - \sin^2\varphi/n^2)^{1/2}
\]

where \(\lambda = 632.8 \text{ nm}\) is the wavelength of the helium-neon laser, \(\varphi = 70^\circ\) is the angle between the laser beam and the normal on the substrate and \(n = 3.7\) is the index at 632.8 nm of \(a\)-Si:H deposited at 100 °C. To obtain a good contrast between the fringes a aluminium layer has been evaporated onto the glass substrate.

Two series of measurements have been done; one serie at a high mercury density of \(2-5 \times 10^{12} \text{ cm}^{-3}\) and one serie at a relatively low mercury density of \(1-3 \times 10^{12} \text{ cm}^{-3}\) by leading part of the silane flow through the bypass. The
mercury density has been measured with the absorption cell and varies as a function of the silane pressure. All the other experimental parameters have been kept constant. The light intensity is 100 W/m², the lamp temperature is 42°C, the substrate is held at 100°C, the window-substrate spacing is 4.2 cm and the gas temperature is about 50°C. For deposition rates of 0.25 - 1.0 Å/s the deposition of 1000 Å requires between 15 and 60 minutes. After such a period no substantial deposition has been observed on the Fomblin oil. The results of these measurements are shown in figure 5.2.

A mercury density of \(2 \times 10^{13} \text{ cm}^{-3}\) corresponds to an optical thickness \(\kappa l = 10\), thus in that case the deposition process is not limited by the light absorption and does not depend strongly upon the mercury density. The \(\text{SiH}_3\) production increases with the silane pressure, so we expect an increasing deposition rate at increasing silane pressure, if recombination is not important. However we observe that the deposition rate diminishes at increasing pressure, especially at high mercury concentration. This indicates that recombination of silyl radicals in an important process.

Simulations have been made to fit the computed deposition rate with these measurements by varying the recombination coefficient. Because the computed deposition rate also depends on the unknown surface reaction probabilities as will be defined in paragraph 5.4, one have to make a choice for these surface reaction probabilities. We assume no incorporation, recombination or etching on the Fomblin, thus all the \(\beta\)'s are zero on the Fomblin. On a-Si:H we take \(\beta_\text{H}(1) = 1, \beta_\text{SiH}_3(1) = 0.1, \beta_\text{SiH}_2(1) = 0.5\). This will be justified further in this chapter. The results of these computations are shown together with the measurements in figure 5.2. A value of \(1.3 \pm 0.3 \times 10^{-10} \text{ cm}^3\text{s}^{-1}\) is obtained from this comparison. At low pressure (100 mtorr) the reactions of \(\text{SiH}_2\) and \(\text{H}\) on the surfaces are important, while at high pressure (1 torr) most of the \(\text{SiH}_2\) and \(\text{H}\) radicals react in the gas phase before arriving at the walls. Therefore the interpretation at high pressures is less speculative and nearly whole the contribution to the deposition...
Figure 5.2: Deposition rate as a function of the silane pressure for a mercury density of 2 to $5 \times 10^{13}$ cm$^{-3}$ (a) and 1 to $3 \times 10^{12}$ cm$^{-3}$ (b). The striped part represents the contribution of SiH$_2$. $k_3 = 1.3 \times 10^{-10}$ cm$^{-3}$
comes from SiH₃. The deposition rate computed from the flux of radicals arriving at the a-Si:H surface according to eq. (4.53) is between five and ten times the measured deposition rate. So far we have made no difference between adsorption and incorporation, because this doesn't intervene in the balance equations of the radicals. But the deposition rate is proportional to the incorporation probability \( \alpha_{\text{SiH₃}}(1) \). Therefore we conclude that a large number of adsorbed silyl radicals (between 60% and 90%) are not incorporated in the film: \( \alpha_{\text{SiH₃}}(1) \ll \beta_{\text{SiH₃}}(1) \). On the contrary most of the adsorbed silyl radicals recombine at the surface. It seems likely that they recombine rather as silane than disilane, because preliminary partial pressure measurements neither reveal a significant disilane formation nor a substantial silane depletion.

It should be noted too that diffusion of radicals out of the reaction chamber is not responsible for the discrepancy between measured and computed deposition rate. To justify this statement the deposition rate has been measured in the absence of the cylindrical shield. In that case the deposition rate diminished less than 15% compared to measurements with shield. Thus we remain at the conclusion that most of the adsorbed silyl radicals recombine at the a-Si:H surface in stead of incorporating.

2) The second experiment is the measurement of the deposition rate as a function of the window-substrate spacing \( l \) by superposing 6 mm thick aluminium rings onto the substrate holder. The spacing can now be varied between 6 and 42 mm. Because of the geometry of the reactor is not possible to measure the deposition rate with the reflectometer, if the window-substrate spacing is not fixed at 42 mm. Therefore the thickness of the film has been measured by a Talystep after two hour deposition onto a glass substrate. To avoid a competition between silyl and silylene radicals the pressure has been kept fixed at 1 torr. Again two series of measurements have been performed, one
Figure 5.3: Deposition rate as a function of the window substrate spacing \( l \). a: \([\text{Hg}] = 2.8 \times 10^{13} \text{ cm}^{-3}\), b: \([\text{Hg}] = 3.2 \times 10^{12} \text{ cm}^{-3}\); \( k_3 = 1.5 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}\). The left hand scale refers to measured deposition rates, the right hand to computed deposition rates.
for a high mercury density of $2.5 \times 10^{13}$ cm$^{-3}$ and one for a low mercury density of $1.4 \times 10^{12}$ cm$^{-3}$. All the other parameters have been kept constant at the same value of the previous experiment.

The results of these measurements and the belonging computed deposition rates are shown in figure 5.3. Keeping in mind the discussion about adsorption, incorporation and recombination at the a-Si:H surface there exists a good agreement with the previous experiment. However the results at 1 torr are more reliable than at lower pressure and therefore the determination of the recombination coefficient of silyl radicals in the gas phase $k_3$ is more precise and this yields $1.5 \pm 0.1 \times 10^{-10}$ cm$^3$s$^{-1}$. Out of a surface reaction or destruction probability $\beta_{\text{SiH}_3}(1)$ of 0.1 a value of 0.08 for the recombination probability $\gamma_{\text{SiH}_3}(1)$ and 0.02 for the incorporation probability $\alpha_{\text{SiH}_3}(1)$ on the a-Si:H surface can be retained.

In the case of the experiment at high mercury concentration, the light intensity decreased at half of its initial value after two hour deposition. This is due to a-Si:H deposition at the Fomblin oil, because a-Si:H absorbs strongly radiation at 254 nm. The absorption coefficient equals $6 \times 10^{-7}$ cm$^{-1}$, thus 50% absorption corresponds to 40 Å deposition. At a SiH$_3$ density of $8 \times 10^{12}$ cm$^{-3}$ near the window it means that $\alpha_{\text{SiH}_3}(0)$ equals $10^{-4}$.

These two measurements correspond well to those reported lately by Delahoy and coworkers [10] on mercury assited decomposition of disilane. They measured a decreasing deposition rate at increasing window–substrate spacing. However their conclusion that this is the consequence of a competition between deposition onto the substrate and onto the window is erroneous. The latter is nearly negligible and the decreasing deposition rate is due to recombination of Si$_2$H$_5$ or SiH$_3$ in the gas phase.

The destruction probability of SiH$_3$ on a-Si:H $\beta_{\text{SiH}_3}(1)$ can be measured directly. To this aim the following experiment has been performed. A thin grid has been stretched onto the substrate. The dimensions of this grid are given in figure 5.4. The spacing between the grid and the surface of the
substrate equals 35 µm, i.e. larger than the mean free path at 1 torr (70 µm). This distance is imposed by a copper foil of the same thickness.

After 1 hour deposition the thicknesses of the deposited layers on the substrate and on both sides of the grid are measured with a scanning electron microscope (SEM). At 1 torr deposition by silylene radicals can be neglected and if no collisions between grid and substrate take place the following equations for the deposited thicknesses can be written down.

\[
e_0 = \phi_0 \alpha \tag{5.2}
\]

\[
e_1 = \phi_0 \alpha \left( \frac{1}{1-(1-\tau)(1-\beta)} \right) \tag{5.3}
\]

\[
e_2 = \phi_0 \alpha \left( \frac{1-\beta}{1-(1-\tau)(1-\beta)} \right) \tag{5.4}
\]

Thus a comparison between the deposited thicknesses yields directly \( \beta_{\text{SiH}_3}(1) \). Table 5.5 summarizes the results of these measurements as a function of the substrate temperature \( T_s \).
Because of the bad adherence of the a-Si:H film on different metallic films the thickness $e_1$ could not be measured. So $\beta_{SiH_3}(l) \approx 0.10$ at room temperature and increases with the temperature. This will be discussed in the next paragraph.

The adsorption coefficient $\beta_{SiH_3}(l)$ can also be measured by an indirect method. This method consists of SEM measurements of a-Si:H thicknesses deposited on thin tungsten wires of 50 $\mu$m diameter, which are stretched at several distances between window and substrate. If the contribution of silylene radicals to the deposition is neglected and the wires don't disturb the plasma, then this thickness is proportional to the local silyl density. So this experiment measures the relative SiH$_3$ density profile. This profile is a good check of the overall validity of the model. The form of this profile near the substrate is sensitive to the destruction probability $\beta_{SiH_3}(l)$, especially at low mercury density.

This measurement has been performed at 1 torr pressure, room temperature and a mercury density of $1.4 \times 10^{12}$ cm$^{-1}$ as measured by the absorption cell.

\[
\begin{array}{cccc}
T_s (^\circ C) & e_0 (nm) & e_2 (nm) & \beta_{SiH_3}(l) \\
40 & 380 & 220 & 0.10 \\
125 & 300 & 170 & 0.105 \\
200 & 405 & 220 & 0.12 \\
290 & 395 & 170 & 0.18 \\
350 & 800 & 330 & 0.21 \\
\end{array}
\]

Table 5.5: SEM measurements of deposited thicknesses on both sides of the grid and destruction probability $\beta$ of silyl radicals on a-Si:H as a function of the substrate temperature $T_s$. 
Figure 5.6: The wire experiment

Figure 5.7: Calculated normalized density profiles ($[\text{Hg}] = 1.4 \times 10^{12} \text{ cm}^{-3}$, $W = 100 \text{ W cm}^{-2}$, compared to the measured SiH$_3$ density profile with $k_3 = 1.5 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$.
The results of these measurements are shown in figure 5.7 together with simulated density profiles for various $\beta_{\text{SiH}_3(1)}$. This measurement confirms the global validity of the model and the value of $\beta_{\text{SiH}_3(1)} \approx 0.10$ at room temperature. This experiment requires a uniform temperature, therefore it couldn't be repeated at higher temperatures.

5.4 Surface reaction probabilities

$$\begin{align*}
\beta & \quad \text{incorporation} \\
R(\text{gas}) & \quad \left\{ \begin{array}{c}
\alpha \rightarrow \\
\gamma \rightarrow \\
\epsilon \rightarrow
\end{array} \right. \\
1-\beta & \quad \text{recombination} \\
\text{R(\text{surface})} & \quad \text{etching}
\end{align*}$$

The initial steps of a radical arriving at a surface are adsorption or reflection on that surface. Adsorption can consist of direct chemisorption, if a covalent bond is established with an atom of the solid surface or physisorption on already saturated sites. For example on a silicon surface partially saturated with hydrogen, the radical $\text{SiH}_3$ can undergo direct chemisorption on a Si dangling bond, but cannot insert in a Si-H surface bond and remains weakly physisorbed on such a Si-H site. In the case of $\text{SiH}_2$ however direct chemisorption is likely on both Si dangling bonds and on Si-H saturated sites, since $\text{SiH}_2$ can insert in a SiH bond as illustrated by the reactivity of $\text{SiH}_2$ with $\text{SiH}_4$ in the gas phase.

Once in a physisorbed state the radical can either desorb from the surface in its original form or hop from the physisorbed sites to a neighbouring site, until it finds a chemisorption site, and recombine with another radical to form a stable molecule, which subsequently desorbs in the gas phase.

To summarize this discussion on the detailed microscopic processes, which are more or less speculative, we use macroscopic concepts in terms of an effective reaction or destruction probability $\beta$, incorporation
probability $\alpha$, recombination probability $\gamma$ and possible etching probability $\varepsilon$.

$\beta$ is in fact the probability for a radical to be destroyed on the surface either by incorporation ($\alpha$), recombination ($\gamma$) or etching ($\varepsilon$), instead of being reflected or desorbed as a radical in the gas phase. Thus we write:

$$\beta = 1 - \frac{\psi_i}{\psi_r}$$  \hspace{1cm} (5.5)

where $\psi_i$ is the incident flux and $\psi_r$ the reflected or desorbed flux of the radical under consideration. For simplicity we assume that a given physisorbed radical cannot desorb under another radical form. Consequently all the radicals, which are not reflected or desorbed, are lost at the surfaces either by recombination with another radical to form a stable molecules, which subsequently desorbs ($\gamma$) or by finding a chemisorption state hence becoming part of the growing film ($\alpha$). The case of etching ($\varepsilon$) is a particular case of recombination, specifically for hydrogen atoms, which can establish successive Si–H bonds with silicon atoms of the surface, until a SiH$_4$ or a weakly adsorbed species (SiH$_3$) is formed, and subsequently desorb. These various reactions channels for a radical are all involved in $\beta$ and we can write:

$$\beta = \alpha + \gamma + \varepsilon$$  \hspace{1cm} (5.6)

5.5 Surface reaction probabilities on the Fomblin oil

We will now discuss the value of $\beta$, $\alpha$, $\gamma$ and $\varepsilon$ for H, SiH$_2$ and SiH$_3$ radicals on the Fomblin oil.

The Fomblin oil is a fluorinated inert pump oil. Therefore we expect the surface reaction probabilities to be small. The quality of the Fomblin oil remained good after 2 hour deposition apart from a thin film of a-Si:H. Thus
the etching probabilities of the three radicals are negligible and incorporation of SiH₃ radicals is small (α_{SiH₃}(0) ≈ 10^{-4}). The density profile as has been measured by the wire experiment did not reveal a maximum near the window. This means that β_{SiH₃}(0) << 0.1 and thus γ_{SiH₃}(0) too. The same could be said about SiH₂, but the chemisorption probability may be somewhat greater due to the more reactive character of SiH₂ radicals. The determination of these probabilities for H is a bit speculative. Because of the inert nature of the Fomblin oil etching and incorporation will be small. The most probable reaction of H radicals seems recombination with other adsorbed H radicals.

<table>
<thead>
<tr>
<th></th>
<th>β</th>
<th>α</th>
<th>γ</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₃</td>
<td>&lt;&lt; 0.1</td>
<td>10^{-4}</td>
<td>&lt;&lt; 0.1</td>
<td>0</td>
</tr>
<tr>
<td>SiH₂</td>
<td>&lt; 0.1</td>
<td>10^{-3}</td>
<td>&lt; 0.1</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>&lt; 0.3</td>
<td>0</td>
<td>&lt; 0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

*Table 5.8: Surface reaction probabilities on the Fomblin oil*

5.6 Growth mechanism of an a-Si:H film

This paragraph deals with the growth mechanism of an a-Si:H film and more specifically by means of mercury assisted photo-CVD. We will follow the theory developed by Gallagher et al [35,36], based upon mass spectroscopic measurements of stable fragments, ions and radicals near a growing a-Si:H surface in a silane RF plasma. Their theory and conclusions will be completed and adapted from our own observations.

At deposition conditions of 0.1 to 1 torr of silane nearly all the dangling silicon bonds on the surface are saturated with hydrogen atoms and for the surface monolayer the atomic ratio H/Si is 2 to 3. A silicon atom is supposed to be part of the film if at least one of its bonds is connected with
another silicon atom of the film.

At first we do not consider the morphology of the surface and look at the unstructured surface. Single radical reactions are schematically drawn in figure 5.9. A SiH\textsubscript{x} radical (x \leq 2) possesses at least two dangling bonds and can insert directly into the film. This reaction is analogous to the SiH\textsubscript{x} insertion reaction into silane in the gas phase and these reaction are exothermic by about 2 to 3 eV. Therefore we expect a high chemisorption probability so that β should be about 0.5, 0.8 and 1 for SiH\textsubscript{2}, SiH and Si respectively, i.e. substantially greater than for SiH\textsubscript{3}.

![Single Radical Reactions](image)

**Figure 5.9: Single radical reactions on an unstructured a-Si:H surface; A is a adsorbed silicon radical, b is a surface SiH bond and \( \delta \) is a dangling bond.**

On the contrary SiH\textsubscript{3} possesses only one dangling bond and cannot insert directly into the film but forms a weakly bounded state A. From this state it can recombine as SiH\textsubscript{4} or incorporate into the film with the release of H or H\textsubscript{2}. However based upon pyrolysis studies [37] these incorporation reactions are supposed to be slow. Another possibility is the migration of such a
weakly bonded state along the surface until an unsaturated dangling bond has been found followed by incorporation into the film. Evidence for this surface migration was measured by Knights [38]. Under deposition conditions that favour silyl radicals he observed a conformal coverage in trenches of several microns in depth and of 1 micron in width. Two radical reactions may also lead to the incorporation of one SiH₃ radical. This is drawn in figure 5.10 and such a two radical reactions can account for a possible source of Si₂H₆ or Si₂H₄.

\begin{figure}
\centering
\includegraphics{fig5.10.png}
\caption{two silyl radical reactions on the unstructured a-Si:H surface}
\end{figure}

A reaction of an hydrogen atom on the a-Si:H surface will nearly always lead to the formation of molecular hydrogen and the creation of a dangling silicon bond, because the bonding energy of an H-H bond is 1 to 1.5 eV larger than that of a Si-Si bond.

The silane surface pyrolysis is based upon the H₂ release from the surface. But this reaction has an activation energy of 2.4 eV and is unimportant below 350°C [37]. The reverse reaction can occur by H₂ molecules built up in the gas at two adjacent dangling silicon bond, although such a configuration is not very probable.
We now consider the structural character of the a-Si:H surface. The silicon atoms in a-Si:H fit a four-fold coordinated structure and the short range order of c-Si is conserved in the amorphous state. Therefore we take the morphology of c-Si.

*figure 5.11: H₂ release from the unstructured surface followed by the pyrolytic silane insertion reaction*

*figure 5.12: The morphology of c-Si. This can be seen as two FCC structures, one of which is shifted a quarter of the cubic diagonal from the other.*
The adsorbed SiH$_3$ radical reaction with a dangling bond to attach the SiH$_3$ with a single Si-Si bond is shown in two different configurations and seems feasible in almost all crystallographic directions. The same can be said

\[
\begin{align*}
  \text{Si-H} + \text{Si} & \rightarrow \text{Si-Si} + \text{H}_2 \\
  1 & \rightarrow 2 \\
  1 & \rightarrow 3 \\
  1 & \rightarrow 3 \\
  \text{Si-H} & \rightarrow \text{Si-Si} + \text{H}_2 \\
  1 & \rightarrow 2 \\
  1 & \rightarrow 3 \\
  1 & \rightarrow 3 \\
\end{align*}
\]

*figure 5.13: Primary insertion reaction of silyl radicals on a structured a-Si:H surface. silyl and dangling bond on adjacent surface silicon atoms (a) and on the same surface silicon atom (b)*

about the pyrolysis H$_2$ release. So generally the morphology of a-Si:H does not affect the primary reactions on the surface. However it permits a more detailed description of further reactions. This is the transformation of the H-rich surface to the H-poor film. The reaction that eliminates most of the hydrogen atoms involves the rupture of two neighboring Si-H bonds and the formation of one Si-Si bond and molecular hydrogen. This conversion is energetically allowed, but only if two silicon atoms can approximately attain the crystal spacing and coordination. To achieve this it is necessary to alternatively add an Si-Si bond to a single (S) and a double (D) bonded silicon and to two single bonded silicon atoms. Such a sequence of reactions is not possible on the 111 surface (right side of figure 5.12). However the A→S→D steps can occur quickly at surface voids or dislocations, thus favouring a more homogeneous and crystallographic growth. This growth mechanism fits well with the observations by Gallagher et al. that the
transition of a H-rich surface to an H-poor film occurs within one monolayer.

The insertion of silicon radicals with two or more dangling bonds can occur at whatever location and favours a growth with a large number of dislocations, leading to a columnar growth [38].

This is consistent with the ability to grow microcrystals in an H rich deposition discharge. The H atoms favour SiH₃ radicals in the plasma and remove H atoms from the surface, thus increasing in particular the ability of SiH₃ radicals to attach to the surface. H atoms can also etch silicon atoms in poorly configurated states.

Good a-Si:H films are believed to have a structure close to that of c-Si. Therefore our overall conclusion is that a-Si:H with good electrical and optical properties is fabricated by depositing silyl radicals.

The substrate temperature $T_s$ is an important parameter during the deposition:
1) Good a-Si:H films are made at a substrate temperature of 250 °C.
2) $\beta_{\text{SiH}_3}$ increases with increasing $T_s$.
3) The disilane production at the surface decreases with increasing $T_s$.

A possible explanation of these phenomena is that an increasing temperature may enhance surface migration, but also diminish the surface coverage by hydrogen atoms hence the dangling silicon bond sites. The latter effect may be caused by the activation of recombination of an hydrogen atom from the gas with an hydrogen atom from the surface or by the hydrogen elimination reaction on the surface (the transformation of two Si-H bonds into one Si-Si bond and H₂ ) and is consistent with the increase of $\beta_{\text{SiH}_3}$.

On another hand an enhanced surface migration may favour a better homogeneity of the growth process consistent with the improvement of optoelectronic properties up to 250 °C. Going to higher temperatures will however lead to a deterioration of these properties due to a lack of hydrogen to saturate bulk defects in the film.

The decrease of disilane production at the surface may result from the disproportionation of excited Si₂H₆ molecules formed by SiH₃ recombination and preferential desorption as monosilane SiH₄ molecules.

Finally we summarize these results in terms of reaction probabilities for a surface temperature between room temperature and 100 °C.

<table>
<thead>
<tr>
<th></th>
<th>$\beta$</th>
<th>$\alpha$</th>
<th>$\gamma$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₃</td>
<td>0.10</td>
<td>0.02</td>
<td>0.08</td>
<td>0</td>
</tr>
<tr>
<td>SiH₂</td>
<td>~0.5</td>
<td>~0.4</td>
<td>~0.1</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>≤1</td>
<td>small</td>
<td>small</td>
</tr>
</tbody>
</table>

Table 5.15: Surface reaction probabilities on a-Si:H
Chapter 6: Conclusions and Discussion

6.1 Modeling of a photo CVD-reactor

The 254 nm mercury assisted photochemical decomposition of silane, leading to the deposition of a-Si:H comprehends a number of processes, all of which have been studied with more or less precision during this work. The comprehensive model, which has been presented in chapter 4, shows a good agreement with the experiments and accounts for several observations reported by other authors.

First we discuss the radiative transfer from the low pressure mercury lamp to the mercury atoms in the reactor, followed by the decomposition of silane. The relevant parameters of this process are the lamp intensity and temperature and the mercury density in the reactor. The efficiency of this process depends strongly upon the lamp temperature, which controls the mercury vapour pressure and hence its self absorbed emission profile. Therefore it is essential to control the lamp temperature and to use a low pressure mercury lamp. The assumptions, that the lamp can be regarded as a positive column of a plasma and that the profile is given by a Voigt profile are consistent with the absorption measurements. The spatial propagation of the intensity of the radiation is described adequately by the diffuse lamp model. The Hg(3P1) density profile can be calculated based upon the theory of Biberman about the imprisonment of resonant radiation.

The dominant gaseous reactions and reactions coefficients are now well known, including the recombination/disproportionation coefficient of silyl radicals. Although the disproportionation reaction, which forms silane and silylene, is the most probable, other reactions cannot be totally excluded. The calculated density profiles of H, SiH3 and SiH2 depend also on the surface reaction probabilities, which are set a bit arbitrary in some cases. However at a pressure of 1 torr SiH3 is by far the dominant radical and most
of the H and SiH₂ radicals react before arriving at the surface.

The model proposed by Gallagher to describe the growth at an a-Si:H surface accounts for the observed low reaction probability and important surface migration of SiH₃. The most important surface reactions of silyl are presumably the one radical recombination reaction to form silane and the one radical incorporation reaction.

6.2 Production and quality of a-Si:H films fabricated by mercury assisted photo-CVD

With the present apparatus it must be possible to deposit a-Si:H at conditions, that produce good optoelectronic material (λ = 254 nm, p = 1 torr, T = 250 °C), with a deposition rate of 3 to 5 Å/s. In that case the production of a-Si:H films of 5000 Å thickness (this corresponds to the thickness of the i-layer in a p-i-n solar cell) requires about 20 minutes and this is largely acceptable for industrial applications. Therefore the use of the 185 nm line with an 100 times greater absorption coefficient, as has been proposed by Tarui et al. [40], with a deposition rate of 7 Å/s is not necessary. Moreover this seems likely to form SiH₂ as primary radical, so it might deteriorate the optoelectronic qualities of the film.

A more important drawback of the photo-CVD method is the use of the Fomblin oil to prevent deposition onto the window. This layer must be renewed every two hours, which is tedious and might introduce additional contamination, because of the air exposure. The vapour pressure of the Fomblin oil itself is low and it has not been detected in the gas by the quadrupole mass spectrometer. So direct contamination of the Fomblin oil in the film does not seem to be important.

Mercury contamination has not been investigated, but SIMS measurements reported by Delahoy [8], did not reveal a detectable mercury concentration (<10¹⁸ cm⁻³).
Thin films of 1 micron have been deposited at a substrate temperature of 20 to 100 °C. As soon as we tried to deposit at 250 °C onto a Corning substrate in order to determine the density of state in the gap by PDS measurements (photon deflection spectroscopy), the 1 micron thick films peeled off after air exposure. Partial pressure measurements showed a small residual pump oil pressure, which forms a layer on the substrate. This diminishes the adherence of the a-Si:H film on the substrate. The adherence is important, because a-Si:H deposited at 250 °C always contains some stress. This problem can be solved by the use of a diffusion or turbomolecular pump to insure a lower residual pressure.

6.3 Suggestions for further research

The partial pressure measurements, which have been performed, did not reveal an important disilane production nor a significant silane depletion. However these measurements are not very accurate and no quantitative data can be obtained from it. It will be interesting to couple these measurements with a quartz microbalance. The microbalance permits an instantaneous measurement of the deposition rate, thus avoiding the long and tedious measurements with the reflectometer. Then it may also be possible to measure the initial deposition rate on the substrate.

The influence of hydrogen can be investigated by introducing the hydrogen together with the silane.

A more precise study of the reaction mechanisms on the a-Si:H surface will be performed with the aid of an infrared ellipsometer, which will be coupled to the reactor.

After the installation of a diffusion pump it will be possible to investigate the optoelectronic properties of the film and the correlation between these and the deposition conditions.
References

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[34] B. Reimann, A. Matteu, R. Laupert and P. Potzinger, Berichte der Bunsen-Gesellschaft, 81, (1977), 500
Appendix: electronic transitions in the mercury atom

Figure 2.10 from Pitts and Calvert [3.3] shows the energy level diagram and electronic transitions of the mercury atom.

The utmost shell consists of two s-electrons in the ground state. Therefore mercury has singlet and triplet states. The significance of the levels can be explained by taking the 6 (\(\text{^3P}_1\)) level as an example:

\[
\begin{align*}
6 & \quad : \text{principal quantum number of the utmost electron} \\
\text{^3P}_1 & \quad : \text{the so-called spectroscopic term represents} \, 2S + 1L_J, \text{ in which these letters stand for the total spin quantum number, the total orbital angular momentum number and the total momentum number respectively.}
\end{align*}
\]

The degeneracy of a level is given by \(2J + 1\), because \(m_J\) can vary between \(-|J|\) and \(+|J|\) with unit step width.

**Hyperfine structure**

The nuclear spin \(I\) and the total angular momentum \(J\) combine to a grand total angular momentum \(F\):

\[
F = I + J \\
F = |I - J|, \, |I - J + 1|, \, \ldots, \, |I + J|
\]

Let's consider the \(\text{^3P}_1 \rightarrow \text{^1S}_0\) transition:

The even mass isotopes have zero nuclear spin: \(I = 0\) and thus \(F = J\). So the degeneracy of these isotopes are \(g_2 = 3\) and \(g_1 = 1\) for the \(\text{^3P}_1\) and \(\text{^1S}_0\) levels respectively.

\(\text{Hg}^{199}\) has \(I = 1/2\) and the \(\text{^3P}_1\) level is splitted into two levels with \(F = -a.1-\)
3/2 and $F = 1/2$ and $g_2 = 4$ and $g_2 = 2$ respectively. The $^1S_0$ level has $F = 1/2$ and thus $g_1 = 2$.

$\text{Hg}^{201}$ has $I = 3/2$, thus the upper level consists of three separate levels with $F = 5/2$, $F = 3/2$ and $F = 1/2$ with $g_2 = 6$, 4 and 2 respectively. The lower level has $F = 3/2$ thus $g_1 = 2$.

![Greenman energy-level diagram for mercury, showing origin of the lines most important in photochemistry (many others are omitted for clarity). The "forbidden" triplet-singlet transitions are dashed. Actually they are strong because the selection rule $\Delta S = 0$ breaks down for heavy atoms. Only two transitions are possible in absorption at ordinary temperature, the allowed one at 1849 Å and the "forbidden" one at 2537 Å. The "forbidden" 2654 line appears only in emission from the metastable $6(3P_0)$ state. No absorption is possible because in addition to the rule $\Delta S = 0$ the more rigid rule, $J = 0 \leftrightarrow J = 0$, would be violated (see text). Adapted from Rollefson and Burton, p. 15.](image-url)