Transient depletion of source gases during materials processing: a case study on the plasma deposition of microcrystalline silicon

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Abstract. Transient depletion of source gases can play an important role in materials processing, particularly during the initial phase of thin film synthesis in which nucleation takes place and the interface is formed. In this paper, we present a zero-order analytical model that allows an estimation of the magnitude and timescale of transient depletion. The model is based on a lumped particle balance for a processing region and reactor volume that are coupled via a directive feed gas flow and diffusive transport. To illustrate the model, an experimental case study is presented on transient depletion during the parallel plate radio-frequency SiH\textsubscript{4} + H\textsubscript{2} plasma deposition of microcrystalline silicon for solar cells. The SiH\textsubscript{4} steady-state depletion was experimentally determined by mass spectrometry, deposition rate and optical emission spectroscopy measurements. The transient depletion of the SiH\textsubscript{4} was monitored by time-resolved optical emission spectroscopy measurements. Model and experiment are in good agreement. The implications for materials processing and thin film synthesis, as well as methods to control transient depletion, are discussed.

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1. Introduction

The vapor-phase processing of materials, such as thin film deposition, etching, grafting and modification of surfaces is extremely important to present day industrial manufacturing. The ability to realize precisely defined material properties, morphology or structures relies on the reproducibility and stability of the conditions under which the processing takes place. Many devices rely on the precise control of the initial processing stage particularly.

One aspect of the initial processing stage is interface formation. Especially in micro- and nanotechnology, where device structures are ultra thin, a good control of the interface properties is essential. A good example is the hetero-junction solar cell technology, in which a ~5 nm thick amorphous silicon film is deposited on top of a crystalline silicon wafer \[1, 2\]. The properties of the crystalline silicon–amorphous silicon interface are decisive to the eventual solar cell performance in terms of e.g. the efficiency of the conversion of light into electric energy.

A second aspect of the initial processing stage is nucleation. Examples in which this nucleation plays an essential role are plasma-deposited nanofibers \[3\] and plasma-deposited nanotubes \[4, 5\], in which both the form and size of the nanostructures are critically determined by the initial processing conditions under which these structures nucleate. Another example is the deposition of microcrystalline silicon, which finds applications in devices like thin film silicon solar cells and thin film silicon transistors. Because of the crucial importance to device performance the incubation, nucleation and subsequent evolution of nanometre sized crystallites embedded in the micrometre sized columns of microcrystalline silicon is an extensively studied subject \[6\].

For this latter example of micro-crystalline silicon deposition, we recently reported on an inherent drift during the initial processing conditions \[7, 8\]. Namely, we found the SiH₄ density in the reactor to decrease dramatically during roughly the first minute of processing. This transient depletion of the SiH₄ source gas induced the formation of an additional incubation layer with a thickness of the order of 10–100 nm. By designing a dedicated plasma ignition
procedure involving an H\textsubscript{2} purging step prior to ignition, we succeeded in eliminating the influence of the transient depletion induced incubation layer. As a result, we were able to demonstrate for the first time that highly efficient micro-crystalline silicon solar cells can be deposited from a source gas consisting solely of SiH\textsubscript{4} without the typical strong dilution in H\textsubscript{2}.

In our previous work [7, 8] we concentrated mostly on the film properties and solar cell performance and provided only a preliminary qualitative explanation for the occurrence of transient depletion. The purpose of the current paper is to understand the physics of transient depletion with the help of a simple zero-dimensional model that is described in section 2. Analytical results from this model can be used to estimate the importance of transient depletion for arbitrary processing techniques and in arbitrary materials processing reactors. In section 3, we compare these analytical expressions with an experimental case study on the plasma deposition of microcrystalline silicon.

2. Model

2.1. General formulation

In this paper, we do not have the intention to make a full-scale model of all aspects of transient depletion. Instead, the aim is to develop a simple model that captures all the relevant physics. To this end the vapor-phase materials processing reactor is divided into a processing region and a reactor volume. The processing region is defined as the active region in which the depletion of the source gases and the corresponding materials processing or thin film synthesis takes place. The reactor volume is defined as a ‘dead’ region in which no processing takes place.

The model on transient depletion is based on the parallel plate plasma reactor illustrated in figure 1. However, it is presented without loss of generality which means that it can be applied easily to other reactor configurations. The processing region with volume \( V_p \) and local source gas density \( n_p \) is located within the reactor volume with volume \( V_r \) and source gas density \( n_r \).
The vapor-phase processing leads to a consumption and consequent depletion of the source gas in this processing region, with the corresponding loss term given by $L_{\text{depl}}$. The source gas is supplied through a feed gas line, which is connected either to the reactor volume (source term $S_{\text{r-feed}}$) or directly to the processing region (source term $S_{\text{p-feed}}$). The coupling between processing region and reactor volume takes place via a directive flow ($S_{\text{flow}} = L_{\text{flow}}$) and via diffusive transport ($S_{\text{diff}} = L_{\text{diff}}$). Source gas may leave the reactor volume via a connected pump line (loss term $L_{\text{pump}}$).

We assume a uniform source gas density in the processing region and a uniform source gas density in the reactor volume (valid for a Peclet number $Pe \ll 1$). Within this description, a discontinuity in source gas density may take place at the boundary between the processing region and reactor volume. Diffusive transport from reactor volume to processing region can be described by introducing a typical length scale over which the discontinuity in source gas density occurs. The directive flow from the gas inlet towards the pumps can be modelled using a typical gas residence time. These descriptions used for the diffusive transport and directive flow assume a sub-sonic flow (valid for a Mach number $M \ll 1$) of continuous gas (valid for a Knudsen number $Kn \ll 1$) in the laminar regime (valid for a Reynolds number $Re \ll \sim 2300$).

A particle balance can be formulated that keeps track of the source gas density as a function of the various source and loss terms. Such particle balances are commonly used in numerical models using a finite element approach, as e.g. the model on a parallel plate SiH$_4$ + H$_2$ plasma by Nienhuis et al [9]. As we assume uniform source gas densities our model consists of two coupled particle balances: one for the processing region

$$V_p \frac{\partial n_p}{\partial t} = S_{\text{p-feed}} + S_{\text{diff}} - L_{\text{depl}} - L_{\text{flow}}, \quad (1)$$

and one for the reactor volume

$$V_r \frac{\partial n_r}{\partial t} = S_{\text{r-feed}} + S_{\text{flow}} - L_{\text{diff}} - L_{\text{pump}}. \quad (2)$$

The model of equations (1) and (2) could easily be extended for multiple gas species. Chemically inactive dilution gases can be included indirectly through their effect on the initial source gas density, directive flow and diffusive transport. We later include the H$_2$ dilution gas in the SiH$_4$ + H$_2$ plasma in this indirect way. Additional source gases of interest could be included by extending the model with two particle balance equations, one for the processing region and one for the reactor volume, for each additional source gas species. Gas species that are generated rather than depleted in the processing, such as the rest gas in figure 1, could be included by a negative depletion loss term. In the remainder of this section, equations (1) and (2) are used to describe the density of one specific source gas species that is consumed in the vapor phase materials processing. The processing starts at time $t = 0$ and is characterized by an instantaneous increase of $L_{\text{depl}}$.

To derive explicit analytical solutions for different initial values and parameters, we need expressions for the source and loss terms. The first two straightforward terms are the feed gas flows of the source gas into the reactor volume ($S_{\text{r-feed}}$) and into the processing region ($S_{\text{p-feed}}$). For nonzero $S_{\text{p-feed}}$ a directive flow towards the reactor volume is present, denoted by $L_{\text{flow}}$ and equaling $S_{\text{flow}}$ by definition. This directive flow term can be expressed as a linear function of $n_p$ using a characteristic residence time of the source gas in the processing region $\tau_{\text{p-res}}$

$$S_{\text{flow}} = \frac{n_p V_p}{\tau_{\text{p-res}}}. \quad (3)$$
The gas residence time can be expressed in terms of the initial equilibrium source gas density \( n_0 \), i.e.

\[
\tau_{p \text{-res}} = \frac{n_0 V_p}{S_{p\text{-feed}}}. \tag{4}
\]

Here, we neglect possible residence time changes that might arise if more than one rest gas molecule is created upon the depletion of one source gas molecule. Source gas is lost from the reactor volume to the pump via the loss term \( L_{\text{pump}} \). This loss term can be calculated in a similar way as \( L_{\text{flow}} \), substituting \( V_r, n_r, \tau_{r\text{-res}} \) and \( (S_{p\text{-feed}} + S_{r\text{-feed}}) \) for \( V_p, n_p, \tau_{p\text{-res}}, \) and \( S_{p\text{-feed}} \), respectively, yielding

\[
L_{\text{pump}} = \frac{n_r V_r}{\tau_{r\text{-res}}}, \tag{5}
\]

in which

\[
\tau_{r\text{-res}} = \frac{n_0 V_r}{(S_{p\text{-feed}} + S_{r\text{-feed}})}. \tag{6}
\]

An important loss term, being the underlying mechanism of both the materials processing and the transient depletion effect, is given by \( L_{\text{depl}} \). Similar to the other source and loss terms, we express the loss of source gas in the processing region by means of a characteristic timescale, i.e

\[
L_{\text{depl}} = \begin{cases} 
0, & t < 0 \\
\frac{n_p V_p}{\tau_{\text{depl}}}, & t \geq 0 
\end{cases} \tag{7}
\]

A general empirical way to deal with \( \tau_{\text{depl}} \) is to use it as fit parameter that allows tuning of the materials processing reactions (i.e. deposition rate or etch rate) to the experimentally obtained value. However, by considering the rate-limiting step of the vapor-phase materials processing \( \tau_{\text{depl}} \) can be approximated in a more fundamental way. For example, thermal dissociation of the source gas might be the rate-limiting step in applications like chemical vapor deposition (CVD) or hot-wire CVD, where a hot substrate or hot filament is used to dissociate the source gas. In this case, the timescale for depletion might be governed by

\[
\tau_{\text{depl}} \propto \tau_{\text{coll}} \exp \left[ -\frac{E_A}{k_B T_{\text{diss}}} \right], \tag{8}
\]

in which \( 1/\tau_{\text{coll}} \) is the collision frequency of the source gas with the hot filament or substrate, \( E_A \) is the activation energy for the thermal dissociation, \( k_B \) is Boltzmann’s constant and \( T_{\text{diss}} \) is the temperature at which the thermal dissociation takes place (equation taken from [10] in slightly modified form). In plasma enhanced chemical vapor deposition (PECVD) applications the depletion of the source gas might be dominated by electron kinetics. Consequently, in these applications the timescale for depletion can be described by

\[
\tau_{\text{depl}} = (n_e k_{\text{diss}})^{-1}, \tag{9}
\]

where \( n_e \) is the electron density in the processing region and \( k_{\text{diss}} \) is an effective dissociation rate of the source gas. As a last example, if diffusion towards the substrate is the rate-limiting step, \( \tau_{\text{depl}} \) could be described by the linearized Fick’s second law of diffusion

\[
\tau_{\text{depl}} = \frac{d^2}{D}, \tag{10}
\]
where \(d\) is a characteristic processing region dimension along which the diffusion takes place (i.e. normal to the substrate) and \(D\) is the diffusion coefficient of the source gas. This description of the timescale could make sense in applications where the source gas is effectively lost at the surface, e.g. in some CVD applications or in plasma deposition processes with a fast source gas dissociation but slow diffusion and slow gas-phase recombination.

The last source term we take into account is the diffusive transport of source gas from the reactor volume back into the processing region \(S_{\text{diff}}\), by definition acting as a loss term for the reactor volume \(L_{\text{diff}}\). The diffusive transport is described by Fick’s first law of diffusion. Using a characteristic length scale over which the source gas density difference between the reactor volume and the processing region develops, Fick’s law can be linearized to yield

\[
L_{\text{diff}} = \frac{AD(n_r - n_p)}{R} = \frac{V_r}{\tau_{\text{diff}}}(n_r - n_p),
\]

(11)

where \(R\) is a characteristic dimension of the processing region along which diffusion takes place (i.e., normal to the boundary between reactor volume and processing region, cf figure 1(b) the direction lateral to the electrode), \(A\) is the area of the boundary between processing region and reactor volume, and \(\tau_{\text{diff}}\) is defined as

\[
\tau_{\text{diff}} = \frac{RV_r}{AD}.
\]

(12)

The diffusion coefficient \(D\) can be approximated in various ways. The most straightforward approximation is the product of thermal velocity \(v_{\text{th}}\) and mean free path \(\lambda\)

\[
D \approx v_{\text{th}} \lambda \approx \frac{2(k_B T)^{3/2}}{p\sigma \sqrt{\pi m}},
\]

(13)

where \(p\) is the gas pressure, \(T\) is the gas temperature and \(\sigma\) the collision cross-section. More sophisticated data are available for many specific much-used gases and gas mixtures. In particular, binary diffusion in a multiple gas species mixture requires a more advanced description of the diffusion coefficient. Other potential situations that would require a more sophisticated description would be e.g. the occurrence of turbulence near the boundary between the processing region and reactor volume or a large directive flow in which the diffusive transport has to work up-stream.

To complete the set of time-dependent linear differential equations, we need initial values. We want to discuss the case of transient depletion in a standard process and the case in which we actively control the initial (i.e. at \(t = 0\)) source gas density in order to avoid transient depletion. The first case is characterized by an equilibrium initial source gas density

\[
n_p(t = 0) = n_r(t = 0) = n_0.
\]

(14)

This initial equilibrium source gas density is given by

\[
n_0 = \frac{S_{\text{feed}} + S_{\text{r-fe}}}{Q} \frac{p}{k_B T},
\]

(15)

where \(Q\) is the total flow in the reactor (the source gas of study plus additional source or diluting gases). The corresponding analytical solutions to (1) and (2) using (14) as initial value are discussed in section 2.3. The second case is characterized by an initial source gas density that is zero at a certain time \(t_{\text{delay}}\) before the processing starts

\[
n_p(t = -t_{\text{delay}}) = n_r(t = -t_{\text{delay}}) = 0.
\]

(16)

As we show in section 2.4, this initial value enables the source gas density at \(t = 0\) to be controlled in a predictive manner.
2.2. Steady-state

The steady-state solution of the coupled differential equations (1) and (2), i.e. \( n_p(t \to \infty) \) and \( n_r(t \to \infty) \), is obtained by putting \( \partial n_p / \partial t = \partial n_r / \partial t = 0 \) which yields

\[
n_p(t \to \infty) = n_0 \frac{\tau_{depl}(V_p \tau_{diff} + V_r \tau_{res})}{V_p(\tau_{p-res} \tau_{diff} + \tau_{p-res} \tau_{r-res} + \tau_{depl} \tau_{diff}) + V_r \tau_{depl} \tau_{p-res}} \tag{17}
\]

and

\[
n_r(t \to \infty) = n_0 \frac{V_r V_p \tau_{res} \tau_{diff} + V_r^2 \tau_{p-res} \tau_{res} - V_p^2 \tau_{r-res} \tau_{diff} + V_r V_p \tau_{diff} \tau_{depl}}{V_r V_p(\tau_{p-res} \tau_{diff} + \tau_{p-res} \tau_{r-res} + \tau_{depl} \tau_{diff}) + V_r^2 \tau_{depl} \tau_{p-res}}. \tag{18}
\]

Insightful quantities related to the steady-state source gas densities are the steady-state depletion \( f_{depl} \)

\[
f_{depl} = 1 - \frac{n_p(t \to \infty)}{n_0}, \tag{19}
\]

and the steady-state source gas utilization efficiency \( \eta_{gas} \)

\[
\eta_{gas} = \frac{L_{depl}(t \to \infty)}{S_{p-feed} + S_{r-feed}} = \frac{V_p \tau_{res} n_p(t \to \infty)}{V_r \tau_{depl} n_0}. \tag{20}
\]

In parallel plate plasma technology, the special assumption of \( S_{r-feed} = 0 \) corresponds to a ‘showerhead electrode’ by which the source gas fed directly to the plasma. Recently, two papers appeared in which this ‘showerhead’ assumption was used to develop a similar analytical model to ours [11, 12]. The general solution of (17) can be rewritten to this special case by inserting \( S_{p-feed} = 0 \) into (15), yielding

\[
n_p(t \to \infty) = n_r(t \to \infty) = n_0 \times \frac{\tau_{depl}}{(\tau_{p-res} + \tau_{depl})}, \tag{21}
\]

and

\[
\eta_{gas} = f_{depl} = \frac{\tau_{p-res}}{(\tau_{p-res} + \tau_{depl})}, \tag{22}
\]

in agreement with [11, 12].

2.3. Transient depletion

In this subsection, we investigate the time-dependent solutions to (1) and (2) using as an initial value a source gas density that follows directly from the partial flow, as given in (15). The initial processing stage is defined as the time after processing has started but before a steady-state gas composition is reached. We consider three limiting cases of the transient depletion in the initial processing stage, all for significant steady state depletion \( f_{depl} > 0 \).

1. The ‘local depletion’ limit for \( \tau_{r-res} \ll \tau_{diff} \) and \( \tau_{depl} \ll \tau_{diff} \). In this limit, the diffusive transport is a relatively slow process. The slow diffusive ‘cross-talk’ means that the processing region (described by (1)) can be treated independently from the reactor volume (described by (2)). The transient depletion relevant to the materials processing thus occurs locally in the processing region only. Mathematically, this limit means that \( L_{depl} \) is the dominant term and (1) can be written as

\[
V_p \frac{\partial n_p}{\partial t} = -L_{depl} = -\frac{V_0}{\tau_{depl}} n_p(t), \tag{23}
\]
with the solution

\[ n_p(t) = n_0 \exp[-t/\tau_{\text{depl}}], \quad 0 < t \leq \tau_{\text{depl}}. \]  \hspace{1cm} (24)

Note that for \( t \gg \tau_{\text{depl}} \), the steady-state is obtained and \( n_p \) is given by (17).

2. The ‘complete mixing’ limit for \( \tau_{\text{diff}} \ll \tau_{\text{depl}} \ll \tau_{\text{res}} \). In this limit, the diffusive transport is very fast and realizes almost equal source gas density in the processing region and the reactor volume, i.e. \( n_p = n_r \equiv n \). Consequently, the depletion reaction in the processing region is limiting the transient depletion of the reactor volume

\[ V_r \frac{\partial n}{\partial t} = -L_{\text{depl}} = -\frac{V_p}{\tau_{\text{depl}}} n(t), \]  \hspace{1cm} (25)

with the solution

\[ n(t) = n_0 \exp[-V_p t / V_r \tau_{\text{depl}}], \quad 0 < t \leq \sim V_t \tau_{\text{depl}} / V_p. \]  \hspace{1cm} (26)

Note again that for \( t \gg V_r \tau_{\text{depl}} / V_p \), the steady-state is obtained with \( n_p \) given by (17) and \( n_r \) by (18). Furthermore, note in this respect that (17) and (18) actually yield the same result in this complete mixing limit.

3. The ‘back diffusion’ limit for \( \tau_{\text{depl}} \ll \tau_{\text{diff}} \ll \tau_{\text{res}} \). In this limit, the processing region gets initially \( (t < \tau_{\text{depl}}) \) locally depleted according to (24). After local depletion has created a density difference between processing region and reactor volume \( (n_p < n_r) \), the diffusive transport from reactor volume into processing region starts and slowly depletes the reactor volume of initially present source gas. Since generally the reactor volume is much larger than the processing region, this slow reactor volume depletion has a higher impact on the materials processing than the fast initial local depletion. During this back diffusive transport phase \( (t \gg \tau_{\text{depl}}) \), a quasi steady-state balance will establish itself in the processing region, in which the source gas diffusing into the processing region is quickly depleted. Mathematically, the back diffusion limit converts (1) to \( S_{\text{diff}} \approx L_{\text{depl}} \), or

\[ n_p(t) = \frac{V_r \tau_{\text{depl}}}{V_r \tau_{\text{depl}} + V_p \tau_{\text{diff}}} n_r(t), \quad t \gg \tau_{\text{depl}}, \]  \hspace{1cm} (27)

whereas it converts (2) to

\[ V_r \frac{\partial n_r}{\partial t} = -L_{\text{diff}} = \frac{V_p V_r}{V_p \tau_{\text{diff}} + V_r \tau_{\text{depl}}} n_r(t). \]  \hspace{1cm} (28)

Equation (28) can be solved analytically leading to

\[ n_r(t) = n_0 \exp[-V_p t / (V_p \tau_{\text{diff}} + V_r \tau_{\text{depl}})], \quad 0 < t \leq \sim (V_p \tau_{\text{diff}} + V_r \tau_{\text{depl}}) / V_p. \]  \hspace{1cm} (29)

Again, note that for \( t \gg (V_p \tau_{\text{diff}} + V_r \tau_{\text{depl}}) / V_p \) the steady-state solution is obtained with \( n_p \) given by (17) and \( n_r \) by (18).

2.4. Tailored initial source gas density

The reason for the occurrence of transient depletion is that the initial source gas density \( n_r(t = 0) = n_p(t = 0) = n_0 \) is higher than the steady-state source gas densities \( n_r(t \to \infty) \), \( n_p(t \to \infty) \). Thus, it should be possible to minimize the effect of transient depletion by realizing an initial source gas density close to the steady-state value, i.e. \( n_p(t = 0) \approx n_p(t \to \infty) \).
and \( n_r(t = 0) \approx n_r(t \rightarrow \infty) \). By definition, the former requirement is crucial for preventing transient depletion in the ‘local depletion’ limit, whereas the latter requirement is crucial for preventing transient depletion in the ‘back diffusion’ limit. In the ‘complete mixing’ limit the two requirements are indistinguishable and consequently can only be fulfilled simultaneously.

In our previous work \([7]\), we developed an experimental procedure that can fulfill the latter requirement of \( n_r(t = 0) \approx n_r(t \rightarrow \infty) \). This procedure, which we refer to as the procedure of tailored initial source gas density, is based on a delayed source gas injection that realizes zero source gas density at a certain time \( t_{\text{delay}} \) before processing starts. For this initial value of \( n_r(t = -t_{\text{delay}}) = 0 \), and using \( V_r \gg V_p \) and \( L_{\text{depl}}(t < 0) = 0 \) one obtains from (2) an increasing source gas density in the reactor volume according to

\[
n_r(t) = n_0 \left( 1 - \exp \left[ -\left( t + t_{\text{delay}} \right)/\tau_{\text{r-res}} \right] \right), \quad -t_{\text{delay}} < t < 0. \tag{30}
\]

Equation (30) describes how the initial source gas density in the reactor volume \( n_r(t = 0) \) can be varied between \( 0 < n_r(t = 0) < n_0 \) by tuning \( t_{\text{delay}} \). For the optimized \( t_{\text{delay}} \) it holds that \( n_r(t = 0) = n_r(t \rightarrow \infty) \). This value for \( t_{\text{delay}} \) follows simply from (30) and is given by

\[
t_{\text{delay}} = \tau_{\text{r-res}} \ln \left( \frac{1}{1 - n_r(t \rightarrow \infty)/n_0} \right), \tag{31}
\]

in which \( n_r(t \rightarrow \infty)/n_0 \) can be calculated using (18).

2.5. Summary

In this section, we developed an engineering model by which the source gas density is described as it decreases from the situation before processing starts \( (n_p = n_0) \) to the steady-state situation during processing \( (n_p = n_0(1 - f_{\text{depl}})) \). Characteristic timescales for the various processes \( (\tau_{p-res}, \tau_{r-res}, \tau_{\text{depl}} \text{ and } \tau_{\text{diff}}) \) were derived. Analytical solutions for the steady-state depletion and source gas utilization were given. Moreover, analytical solutions for the limiting cases for transient depletion were obtained. These limiting cases were labeled ‘local depletion’, ‘complete mixing’, and ‘back diffusion’. The developed engineering model can be used to judge the significance of transient depletion to an arbitrary vapor-phase materials processing application. Moreover, it assists in the control over transient depletion using the procedure of tailored initial source gas density.

3. Experiments in an SiH\(_4\) + H\(_2\) plasma

This section illustrates the use of the engineering model presented in section 2 by means of a comparison with experimental data obtained in a parallel plate plasma reactor that is used for deposition of microcrystalline silicon.

3.1. Experimental

Figure 2 provides a sketch of the used plasma source. The plasma was ignited between two parallel electrodes positioned in a cylindrical reactor with a volume of \( V_r = 13 \) litres. The radius of the powered electrode was \( R = 7 \) cm. The gap between the electrodes was \( d = 1.0 \) cm. The upper electrode could be mounted with a \( 10 \times 10 \text{ cm}^2 \) substrate. The volume of the processing region can thus be approximated by \( V_p = \pi R^2 d = 0.15 \) litres. The area of the boundary...
between processing region and reactor volume can be approximated by \( A = 2\pi R d = 43 \text{ cm}^2 \). The substrate was elevated to a temperature of \( T = 200^\circ \text{C} \) using a resistive heater installed in the vacuum. The pressure in the reactor volume was kept at \( p = 1330 \text{ Pa} \) using a butterfly valve. The showerhead holes in the lower electrode realized a gas injection directly into the plasma (i.e. \( S_{\text{r-feed}} = 0 \)). The SiH\(_4\) + H\(_2\) source gas flow was regulated via mass flow controllers with a response time of a few seconds. Unless specifically stated otherwise, the used SiH\(_4\) flow was \( S_{\text{p-feed}} = 2 \text{ sccm} \) and the used H\(_2\) flow was 20 sccm, in which 1 sccm or standard cm\(^3\) min\(^{-1}\) equals \( 4.5 \times 10^{17} \) particles s\(^{-1}\). An applied power of 60 W was used at a driving frequency of 13.56 MHz. The corresponding rf amplitude was 150 V and the dc-bias was \(-5 \text{ V}\). This reactor configuration and these operating conditions followed from successive optimization steps presented in previous work \([7, 8, 13-15]\) and have been shown to allow high-rate (\( \sim 0.5 \text{ nm s}^{-1} \)) deposition of highly efficient (\( \sim 9\% \)) micro-crystalline silicon solar cells.

A differentially pumped mass spectrometer (UTI, type 100c) was connected to the reactor in order to measure the steady-state depletion of SiH\(_4\) in a way similar to \([16-18]\). The peak at 30 amu was used as a measure for SiH\(_4\) density. The depletion in the reactor volume was obtained from the signal ratio with plasma on (\( I_{\text{on}} \)) to that with the plasma off (\( I_{\text{off}} \)). Note that we applied a feed gas flow into the processing region only, \( n_i(t \to \infty) = n_p(t \to \infty) \) from section 2.2, equation (21). This means that the mass spectrometry measurements yielded \( f_{\text{depl}} \) according to

\[
f_{\text{depl}} = 1 - \frac{n_p(t \to \infty)}{n_0} = 1 - \frac{I_{\text{on}}}{I_{\text{off}}}.
\]

The deposition rate \( r_d \) was used correlated to the source gas utilization efficiency \( \eta_{\text{gas}} \). Here, \( r_d \) was calculated from the film thickness measured using an ex situ step-profiler. Assuming uniform deposition on both electrodes, the gas utilization efficiency is given by

\[
\eta_{\text{gas}} = f_{\text{depl}} = \frac{2\pi R^2 r_d n_{\mu c}}{S_{\text{p-feed}}},
\]

where \( n_{\mu c} \sim 5 \times 10^{22} \text{ cm}^{-3} \) \([19]\) is the Si atom density in the deposited silicon film.

Optical emission spectroscopy performed on the SiH(A\(^2\Delta \rightarrow X^2\Pi\)) spectral line at 414.3 nm was used to follow the transient SiH\(_4\) density. The plasma was imaged on to the
entrance slit of an Oriel MS257 spectrometer, equipped with a 24001 mm\(^{-1}\) grating blazed at 500 nm and an air cooled Andor DU420-OE CCD camera. The window through which the plasma was monitored was shielded from deposition by a 10 cm long 1.5 \times 1.5 cm\(^2\) wide tube. An integration time of 1 s was used in the experiments, which will turn out to be well suited to follow the transient depletion in the ‘back diffusion’ limit. The method of recording transient SiH emission was similar to [7], [20]–[22]. A new aspect in the current investigation was the calibration of emission intensity in terms of absolute SiH\(_4\) density (cf appendix A).

3.2. Application of the model

In this subsection, we use the analytical expressions derived in section 2 to describe the transient depletion under the experimental conditions discussed in section 3.1. We calculate the relevant timescales \(\tau_{\text{depl}}, \tau_{\text{diff}}, \tau_{\text{p-res}}\) and \(\tau_{\text{r-res}}\) in order to evaluate steady-state depletion and to characterize which limiting case of section 2.3 applies.

For the given pressure and gas flow, the Reynolds number is of the order of \(Re = 10^{-2}\), the Knudsen number of the order of \(Kn = 10^{-3}\), the Mach number of the order of \(M = 10^{-5}\), and the Peclet number of the order of \(Pe = 10^{-1}\) for the processing region and \(Pe = 10^{-2}\) for the reactor volume. These numbers indicate that no turbulence, shock waves or molecular flow needs to be considered and that the source gas densities in the processing region and reactor volume can be considered to be uniform, respectively.

The depletion timescale \(\tau_{\text{depl}}\) can be calculated using (9), in which we assumed the electron density to be \(n_e = 10^{10} \text{ cm}^{-3}\), which is a typical value for medium pressure H\(_2\) plasmas [23], and calculated \(k_{\text{diss}}\) from the integral over the electron energy \(E\)

\[
k_{\text{diss}} = \int \sigma_{\text{diss}} \sqrt{\frac{2E}{m_e}} f_e \, dE.
\] (34)

For the calculation of \(k_{\text{diss}}\), we took the total dissociation cross-section \(\sigma_{\text{diss}}\) from [24] and a Maxwellian electron energy distribution function with an electron temperature of about \(2 \times 10^4 \text{ K}\) typical to medium pressure H\(_2\) plasmas [25]. We arrive at \(\tau_{\text{depl}} \approx 0.1 \text{ s}\). Because of the uncertainties in electron temperature, electron density, and cross-section, we expect the uncertainty in \(\tau_{\text{depl}}\) to be a factor of two. Our estimate of \(\tau_{\text{depl}}\) is consistent with numerical simulations by Amanatides et al [26], who arrive at values between 0.03 and 0.3 s under similar conditions as we used.

The diffusive transport from reactor volume into the processing region takes place through the boundary that surrounds the cylindrical parallel plate plasma and is approximated by \(A = 2\pi Rd\). Substituting in (12) yields the electrode radius independent relation

\[
\tau_{\text{diff}} = \frac{V_r}{2\pi D}.
\] (35)

We calculated the diffusion constant \(D\) according to the Chapman–Enskog formalism for which the data for SiH\(_4\) + H\(_2\) gas mixtures is given in [24]. For SiH\(_4\) diffusing in a pure H\(_2\) background gas at 1330 Pa and 200°C, this gives a diffusion constant of \(D = 1 \times 10^4 \text{ cm}^2 \text{ s}^{-1}\) and a timescale for diffusion of \(\tau_{\text{diff}} = 20 \text{ s}\). The assumed pure H\(_2\) background is applicable because under the high depletion conditions the partial SiH\(_4\) pressure is low (<10% initially, <1% in the steady-state). Considering the uncertainties in temperature distribution, diffusion constant and reactor volume, the uncertainty in the timescale for diffusive transport is estimated to be about a factor of two.
Table 1. Input and output quantities of the model of section 2 applied to the conditions of section 3.1.

| Input quantity                        | Symbol | Value  | Unit  |
|---------------------------------------|--------|--------|-------|
| Reactor volume                        | $V_r$  | $1.3 \times 10^4$ | cm$^3$ |
| Processing region                     | $V_p$  | $1.5 \times 10^2$ | cm$^3$ |
| Electrode radius                      | $R$    | 7.0    | cm    |
| Electrode gap                         | $d$    | 1.0    | cm    |
| SiH$_4$ flow (showerhead)             | $S_{p-feed}$ | 2.0   | sccm  |
| Total flow                            | $Q$    | 22     | sccm  |
| Electron density                      | $n_e$  | $1.0 \times 10^{10}$ | cm$^{-3}$ |
| Electron temperature                  | $T_e$  | $2.0 \times 10^4$ | K     |
| Pressure                              | $p$    | $1.3 \times 10^3$ | Pa    |
| Temperature                           | $T$    | $4.7 \times 10^2$ | K     |

| Output quantity                       | Symbol | Value  | Unit  | Equation / reference |
|---------------------------------------|--------|--------|-------|----------------------|
| Equilibrium SiH$_4$ density           | $n_0$  | $2 \times 10^{16}$ | cm$^{-3}$ | (15) |
| Diffusion constant                    | $D$    | $1 \times 10^{4}$ | cm$^2$ s$^{-1}$ | [24] |
| Residence time in processing region   | $\tau_{p-res}$ | 3      | s     | (4) |
| Residence time in reactor volume      | $\tau_{r-res}$ | $3 \times 10^2$ | s     | (6) |
| Depletion timescale                   | $\tau_{depl}$ | 0.1    | s     | (9) |
| Diffusion time scale                  | $\tau_{diff}$ | $2 \times 10^1$ | s     | (35) |
| Steady-state SiH$_4$ depletion        | $f_{depl}$ | 96     | %     | (19) |
| Optimum delay                         | $t_{delay}$ | 10     | s     | (31) |

Equations (4) and (6) can be used directly and yield $\tau_{p-res} = 3$ s and $\tau_{r-res} = 300$ s. Considering the uncertainties in reactor volume, temperature distribution, and mass flow controller calibration the uncertainty in these gas residence times is expected to be about 50%. Table 1 lists all relevant input values and the results of the calculations.

From table 1 it follows that under the conditions of section 3.1 almost full depletion is expected ($f_{depl} \approx 96\%$). Since the calculated timescales obey $\tau_{depl} \ll \tau_{diff} \ll \tau_{r-res}$ the ‘back diffusion’ limiting case should apply. In the ‘back diffusion’ limit, it should be possible to prevent transient depletion by adopting the procedure of tailored initial source gas density. To do so the SiH$_4$ flow should be switched on $t_{delay} = 10$ s before plasma ignition.

3.3. Results and discussion

Figure 3 shows the steady-state depletion $f_{depl}$ as a function of the H$_2$ flow. The steady-state depletion was experimentally determined from mass spectroscopy (using (32)), from the deposition rate (using (33)) and from the calibrated optical emission spectroscopy measurements (using (A.3), appendix). The analytical result of (22) is also shown. The comparison shows that the model predictions and experimental data agree well, and that for the condition of 20 sccm H$_2$ flow the steady-state depletion is about 95%.

As a next step, we investigate the transient depletion after plasma ignition, thereby keeping the H$_2$ flow fixed at 20 sccm. Figure 4 presents the results of the time dependent calibrated SiH emission intensity measurements. Additionally, figure 4 shows the numerically obtained...
Figure 3. The steady-state SiH$_4$ depletion $f_{\text{depl}}$ versus the H$_2$ flow at fixed SiH$_4$ flow of 2 sccm, determined using mass spectrometry, optical emission spectroscopy and deposition rate. The dashed line shows the outcome of (22).

Figure 4. SiH$_4$ density in the processing region $n_p$, normalized to its initial value $n_0$, as obtained from calibrated SiH emission intensity measurements (open circles), numerical solving of the model (dashed line), and analytical solving of the model in the local depletion and back diffusion limits (solid lines), versus the time after plasma ignition. The inset shows the SiH$_4$ density after subtraction of the steady-state value to facilitate a comparison of experimental and modeled timescales.

exact solution to (1) and (2) and the analytic solutions for the local depletion and back diffusion limiting cases (cf section 2). Here, the numerical solution was obtained using a finite element approach with adaptive discrete time steps $\Delta t$ that realized a 0.1% change in $n_p$ or $n_t$ per step. Recall from table 1 that the experimental condition was expected to fall within the back diffusion limit, for which it should obey the local depletion behaviour of (24) for $t < \tau_{\text{depl}}$ and the back diffusion behavior of (27) for $t \gg \tau_{\text{depl}}$. A good correspondence between measurement,
Figure 5. Measured time-resolved SiH$_4$ density in the processing region for an equilibrium initial SiH$_4$ density (open circles) and tailored initial SiH$_4$ density using $t_{\text{delay}} = 0$ s (open stars), $t_{\text{delay}} = 12$ s (closed circles) and $t_{\text{delay}} = 20$ s (open triangles).

A numerical solution, and analytical model is obtained, demonstrating the suitability of the model to describe the transient depletion. Moreover, the comparison of the numerically obtained solution to the analytical limits of local depletion and back diffusion illustrates the validity of the analytical descriptions: the local depletion description is valid for $t < t_{\text{depl}} = 0.1$ s, whereas the back diffusion description is valid for $t_{\text{depl}} = 0.1$ s $< t < \sim (V_p \tau_{\text{diff}} + V_r \tau_{\text{depl}})/V_p = 30$ s.

Finally, we investigate the suitability of the procedure of tailored initial source gas density to prevent the transient depletion from occurring. To do so, the plasma was ignited at a time $t_{\text{delay}}$ after switching on the SiH$_4$ flow. Figure 5 shows the normalized SiH$_4$ density as a function of time for varying delay time $t_{\text{delay}}$ as obtained from the calibrated SiH emission intensity measurements. An empirically optimized value of 12 s was found. For this optimum $t_{\text{delay}}$ the transient depletion was successfully prevented and a stable SiH$_4$ density was obtained directly after plasma ignition. The experimentally found 12 s lies close to the 10 s predicted by the model (cf table 1).

4. Conclusions and outlook

Transient depletion of source gases affects the initial processing stage of materials processing applications. A zero-dimensional model was developed and exact analytical solutions describing three limiting cases of transient depletion, labelled ‘local depletion’, ‘complete mixing’, and ‘back diffusion’, were discussed. This perspective on transient depletion was illustrated by experiments on the deposition of micromcrystalline silicon using a parallel plate SiH$_4$ + H$_2$ plasma. It was shown both analytically and experimentally that in the case of back diffusion, the transient depletion of the source gas in the entire reactor volume, i.e. not only in the processing region, affects the materials processing in the initial processing stage. The occurrence of SiH$_4$ back diffusion could be prevented using a newly developed procedure of tailored initial SiH$_4$ density, in which the SiH$_4$ flow is switched on only shortly before plasma ignition.
General requirements for transient depletion to be of importance for a materials processing application can be formulated as (i) a high gas utilization and (ii) a narrow process window. The first requirement means that there is a significant source gas depletion (cf (33)), which is an essential prerequisite for transient depletion to occur at all. The second requirement means that the transient depletion can easily cause a drift outside the targeted process window, and thus have a significant effect on the materials processing application. In general the requirement of high gas utilization will be met by cost-effective and low-waste materials processing applications, whereas the requirement of a narrow process window will be met by applications in which complex structures with precise and tailor-made properties are processed. We therefore expect that, as the materials processing field advances, the two requirements will be met by an increasing number of applications. Consequently, the control over the processing stability, including the control over transient depletion, will be of increasing significance to the materials processing field.

The procedure of tailored initial source gas density allows sufficient control over transient depletion as long as the mass flow controller response time is faster than the typical timescale on which the transient depletion takes place. An alternative method to prevent transient depletion from affecting the materials processing could be to shield the substrate from deposition during the initial processing stage using a shutter. However, a shutter is difficult to realize experimentally in the large area deposition reactors frequently used in industry. Additional methods to control transient depletion in large-area reactors with short time scales for transient depletion may therefore still have to be developed.

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Appendix. SiH$_4$ density calibration

This appendix provides background information on the procedures to obtain the SiH$_4$ density from the various diagnostics. The basis for these diagnostics is demonstrated in figure A.1, recorded using a fixed H$_2$ flow of 20 sccm: The 30 amu signal from the mass spectrometer, the deposition rate, the Si($4s^11P^0 \rightarrow 3p^21S$) emission intensity at 390.5 nm and the SiH ($A^2\Delta \rightarrow X^2\Pi$) emission intensity at 414.3 nm all linearly increase as a function of the applied SiH$_4$ flow.

The observed linear relation for the emission intensity as a function of SiH$_4$ flow was found before by Heintze et al [27]. It can be understood by considering that excited Si and SiH (denoted as Si$^*$ and SiH$^*$, respectively) originate predominantly from electron-impact dissociative excitation of SiH$_4$ [28, 29],

\[ e^- + \text{SiH}_4 \rightarrow e^- + \text{Si}^* + 2\text{H} + \text{H}_2, \quad (A.1) \]

\[ e^- + \text{SiH}_4 \rightarrow e^- + \text{SiH}^* + \text{H} + \text{H}_2, \quad (A.2) \]
Figure A.1. Measured current at 30 amu (open stars), deposition rate (solid squares), and steady-state emission intensity of SiH (triangles) and Si (circles) as a function of the applied SiH\textsubscript{4} flow.

which means that the emission intensity should be linear with the SiH\textsubscript{4} density as long as the electron density, the reaction rate and the non-radiative quenching ratio remain constant. In this respect, studying plasmas that are highly H\textsubscript{2} diluted and/or highly depleted of SiH\textsubscript{4} has the advantage that the plasma (electron temperature, reaction rates, etc) can be considered to be dominated by H\textsubscript{2} and thus unaffected by the applied SiH\textsubscript{4} flow. Monitoring the Si emission has the advantage that the short Si\textsuperscript{*} lifetime of only 5 ns prevents non-radiative collisional quenching from playing a significant role. On the other hand, quenching of SiH\textsuperscript{*} is not expected to be important for partial SiH\textsubscript{4} pressures below 250 Pa \cite{30}, and monitoring the SiH emission has the inherent advantage that the intensity is about ten times higher than the Si emission. Because of this intensity advantage we used the SiH emission in all experiments.

As the relation between SiH\textsubscript{4} density and SiH emission is linear it suffices for the absolute calibration to measure the origin (i.e. the emission at 414 nm with the SiH\textsubscript{4} flow switched off) and one additional data point. The additional data point is obtained by making use of the procedure of tailored initial source gas density and supporting model of section 2.4. The reactor
volume was first filled with $H_2$. Then, the SiH$_4$ flow was switched on. A time $t_{\text{delay}}$ later, the plasma was ignited. This $t_{\text{delay}}$ was empirically tuned to realize a situation in which the SiH emission was stable directly after plasma ignition, as for example shown in figure 5 for 20 sccm $H_2$ and $t_{\text{delay}} = 12$ s. For this $t_{\text{delay}}$, equation (30) dictates the source gas density corresponding to the measured SiH emission. This straightforward and fast calibration procedure was performed separately before each presented measurement series.

Note that by a substitution of (22) in (31), one obtains a straightforward direct relation between the obtained $t_{\text{delay}}$ and the steady-state source gas depletion

$$f_{\text{depl}} = \exp [-t_{\text{delay}}/\tau_{\text{res}}].$$  \hspace{1cm} (A.3)

which was used in the construction of figure 3. Considering the mass flow controller response time of $\sim 1$–2 s, this method of steady-state SiH$_4$ depletion determination becomes inaccurate for $t_{\text{delay}}$ shorter than $\sim 4$ s.

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