Modeling of microwave induced deposition plasmas

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The purpose of this study is to understand microwave plasmas in relation to solar cells deposition processes. The plasmas under investigation are surface wave induced plasmas, in particular, coaxial microwave plasmas. The coaxial configuration acts as microwave transmission line, in which plasma acts as an outer conductor. A metal rod antenna forms the axis of the symmetry. The antenna is surrounded by air at atmospheric pressure and a quartz tube. The configuration of coaxial microwave discharges permits large area surface treatments, especially if a set of such coaxial lines are used. Coaxial plasmaline is a part of ECN roll-to-roll PECVD reactor used for surface passivation of solar cells.

In the present work, a two-dimensional plasma model is used to describe the coaxial microwave discharge waves under different working conditions as a two-temperature non-equilibrium fluid sustained by electromagnetic surface waves. The model is applied to a microwave coaxial discharge. For argon and hydrogen the model is validated by experimental data obtained from Thomson scattering and line ratios of atomic and molecular emission. Model results are in a good agreement with experimental measurements.

Several parametric studies have been performed for hydrogen-silane mixtures, which can be used for understanding, predicting and optimizing the plasma deposition.
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Chapter 1

Introduction
1. Introduction

1.1 Plasmas

A plasma is an ionized gas in which, next to neutral particles also charged particles are present. Due to the presence of charged particles, plasmas are conductive and can be manipulated by electromagnetic fields.

Because of their low mass and high temperature, the electrons consume most of the electromagnetic energy in a low-temperature plasma. Part of this kinetic energy is transferred to heavy particles by elastic collisions. This energy transfer is very inefficient because of the large mass difference between electrons and other particles. As a result, a temperature difference between the electrons and the heavy particles can be sustained, in which case we speak of a two-temperature or non-local thermal equilibrium (non-LTE) plasma. In such plasmas, the electrons are the primary producers of reactive (excited or ionized) species.

Because of their ability to create reactive species at low gas temperatures, non-LTE plasmas are extensively used in application such as deposition or etching. Various reactor types have been developed for the plasma-enhanced chemical vapour deposition (PECVD) process. Based on the excitation electric field frequency, we can distinguish between direct current (DC), radio frequency (RF) or microwave discharges. Microwave plasmas are very efficient plasma sources for the creation of large fluxes of radical species. Microwave Induced plasma (MIP) are used for deposition of different layers such as SiO$_2$ for optical fibers [1], deposition of diamond like films [2], deposition of graphene [3] and the deposition of amorphous silicon for solar cells [4].

The aim of this study is to better understand a microwave plasma that is used for the deposition of solar cells.

1.2 Modeling of coaxial microwave discharge

With respect to the way in which electromagnetic field is applied to the plasma, we can classify the MIPs as microwave plasma torches, resonant cavities and traveling wave MIPs. A particular class of traveling wave discharges are surface wave discharges (SWDs). In surface wave produced plasmas the electromagnetic wave propagates along the interface between the plasma column and the surrounding dielectric tube and the plasma column is sustained by electromagnetic energy. The plasma as a propagating medium allows to transport the electromagnetic energy to regions further away from the field applicator (launcher) to create and sustain plasma there. The plasma produced by MIPs is electrodeless. These two characters makes SWDs a good choice for homogenous plasma in large area deposition.

A large and homogeneous deposition area can be realised by a coaxial plasma waveguide, a microwave surface wave discharge. In this configuration, a metal rod antenna is located around the axis of symmetry. It furthermore consists of
a dielectric tube which is separated from the antenna by an air region at atmospheric pressure. The microwave energy penetrates radially through the dielectric tube and ignites a plasma in a region at the outside of the dielectric tube, which is kept at a low pressure. This Plasmaline setup is shown in figure 1.1.

The coaxial discharge described here is inspired by the coaxial discharge of a so called (Duo-) Plasmaline [5]. Based on the Plasmaline, the company Roth & Rau developed a linear microwave plasma source for mass production of solar cells. This source was successfully used in [6] for surface passivation of solar cells.

The quality and growth rate of the layers produced by this kind of discharge is strongly affected by discharge parameters. At present, finding optimum discharge parameters is mostly a matter of trial and error. Numerical modeling can be a powerful tool to find the optimum discharge parameter. Moreover, it can be used to get a better understanding of the different aspects of this microwave discharge. One modeling approach for understanding such systems with complex chemistry is global modeling, which describes volume-averaged plasma quantities. Using global models, sensitivity studies for complex chemistry like silane-hydrogen are possible in a short time. This approach is useful for finding the relevant set of species and reactions to consider later on in a higher-dimensional model.

For complex systems, like the Plasmaline, a higher-dimensional model is needed to describe the plasma-wave coupling, the spatial distribution of species, the power density and the deposition rate. Such models require a simultaneous treatment of the electromagnetic, transport, chemistry and surface process. Because of the complexity of such models, they are usually simplified in various ways, for example by assuming a Maxwellian distribution function for the electrons.

In this thesis a self-consistent two dimensional steady state electromagnetic-fluid model is used to describe microwave induced plasmas in the coaxial plasma waveguide. The numerical model is constructed on the modeling platform Plasimo [7], which has been developed in the group Elementary Processes in Gas Discharges of the department of Applied Physics at Eindhoven University. The core of the physical model are a set of fluid equations for the plasma species and Maxwell’s equations for the electromagnetic field. The fluid equations are the particle, momentum and energy balance equations that are obtained as ‘moments’ of the Boltzmann equation. The Plasimo electromagnetic module for microwave modeling which is based on [8] developed for different geometries and materials.

This study has been done in the framework of project 10497 of the Dutch “Stichting Technische Wetenschappen” (STW), titled “Guiding the self-organization of high-tech plasmas: Modeling, experiments and in-depth monitoring of magnetized plasmas”. The main participant in the project’s user committee is the organization Energy Centrum Nederland (ECN). Parallel to the numerical study, at TU/e the coaxial plasma was investigated experimentally by Thomson scattering, optical emission and Langmuir probe measurements [9]. The experimental data
1. Introduction

![Image of an argon plasma in the Plasmaline.](image)

Figure 1.1. An argon plasma in the Plasmaline.

have been used to validate the modeling results.

1.3 Outline of this Thesis

This thesis has been structured as follows. In chapter 2, the relevant electromagnetic theory and the Plasimo module for the calculation of the electromagnetic field in the Plasmaline are presented. That module was developed partly in the framework of the present project, and care was taken to properly validate this model. The results of a comparison of numerical and analytical solutions for coaxial and circular waveguides is presented.

The fluid model will be discussed in the context of the application studies, which are covered by chapters 3, 4 and 5:

- In chapter 3 the investigation of the coaxial plasma waveguide is started by a simulation of the Plasmaline in argon and comparing the results with experimental data in order to validate the model. Models of coaxial discharges has also been reported by [10–12]. In chapter 3 we will discuss our model and the differences with previous works extensively.
1.3. Outline of this Thesis

- The interest for solar cells is in silane hydrogen with very high percentage of hydrogen. In chapter 4 we will therefore study the Plasmaline in (pure) hydrogen. The hydrogen model is used as a starting point for studying the complex mixture of $\text{H}_2/\text{SiH}_4$, which will be reported on in chapter 5. One of the main difficulties is the complexity of the silane-hydrogen discharge chemistry including volume reactions and plasma-wall interactions. Most studies for silane-hydrogen mixture were done in RF plasmas [13–15]. In [16], a global model was used to study the silane/hydrogen chemistry.

An important element in all these studies is the model for the species’ particle flux densities. In Plasimo, the diffusive fluxes can be obtained from Fick’s model or from a self-consistent multicomponent diffusion model. In chapters 3, 4 and 5, the Fick model is used. That is valid in case the plasma is ruled by a dominant background gas and a single ionic species. For more complex conditions, a more sophisticated diffusion model is needed. In chapter 6, the results of a multi-component diffusion model based on the Stefan-Maxwell equations, which was recently implemented by Peerenboom [17], are compared with results of the Fick model.

The main conclusions that can be drawn from the project have been summarized in chapter 7.
Chapter 2

Electromagnetic Model

This is a joint work with E H Kemaneci [18]
2. Electromagnetic Model

2.1 Introduction

In this section, we describe a model that computes the spatially resolved electromagnetic fields. The model forms one of the electromagnetic modules in Plasimo and it is employed in the plasma simulations of next chapters in this thesis. It is based on the Maxwell curl equations [19] with the assumption that the fields are time-harmonic in a homogeneous linear and isotropic media. The equations are discretised by finite difference approximations in the frequency domain by the help of the Yee algorithm [20]. Furthermore, we consider example cases of cylindrical waveguides including circular and coaxial waveguides. In these cases, the analytic descriptions are available and we compare them with the numerical solutions.

2.2 The Maxwell equations

The macroscopic electromagnetic phenomena are described by the Maxwell equations, which determine the spatial and temporal behaviour of the electric and magnetic fields. Inside a dissipative, neutral and non-magnetic linear medium, the Maxwell equations are

\[ \nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t}, \]  
\[ \nabla \times \mathbf{H} = \mathbf{J} + \epsilon_0 \epsilon_r \frac{\partial \mathbf{E}}{\partial t}, \]  
\[ \nabla \cdot (\epsilon_0 \epsilon_r \mathbf{E}) = \rho, \]  
\[ \nabla \cdot \mathbf{H} = 0, \]  

where \( \mathbf{E} \) is the electric field intensity, \( \mathbf{H} \) is the magnetic field intensity, \( \mathbf{J} \) is the electric current density, \( \rho \) is the electrical charge density, \( \mu = \mu_0 \) is the permeability of free space, \( \epsilon_0 \) is the permittivity of free space and \( \epsilon_r \) is the relative permittivity of the medium.

2.2.1 Harmonic fields: Complex notation

We assume that these fields are harmonic, i.e., the time dependence is given by a common term \( e^{i\omega t} \). For such fields, it is convenient to use the complex (also known as phasor) notation, so that a physical field \( \mathcal{F} \) is given by

\[ \mathcal{F} = \text{Re} \left( Fe^{i\omega t} \right), \]

where \( F \) is the complex amplitude.
Due to the common term, the notation transforms the instantaneous vector fields $E, H$ and $J$ into the corresponding complex amplitudes $\hat{E}, \hat{H}$ and $\hat{J}$, respectively. In this notation, the Maxwell equations are expressed as

\begin{align}
\nabla \times \mathbf{E} &= -i\omega \mu_0 \mathbf{H}, \quad (2.6) \\
\nabla \times \mathbf{H} &= \mathbf{J} + i\omega \varepsilon_0 \varepsilon_r \mathbf{E}, \quad (2.7) \\
\n\nabla \cdot (\varepsilon_0 \varepsilon_r \mathbf{E}) &= \rho, \quad (2.8) \\
\n\nabla \cdot \mathbf{H} &= 0. \quad (2.9)
\end{align}

Furthermore, assuming Ohm’s law, that is in the same notation $\mathbf{J} = \hat{\sigma} \mathbf{E}$ with a complex conductivity $\hat{\sigma}$, equation (2.7) reduces to

\begin{align}
\nabla \times \mathbf{H} &= i\omega \varepsilon_0 \left( \varepsilon_r + \frac{\sigma}{i\omega \varepsilon_0} \right) \mathbf{E} \equiv i\omega \varepsilon_0 \hat{\varepsilon}_r \mathbf{E}, \quad (2.10)
\end{align}

where a complex relative permittivity is also introduced

\begin{align}
\hat{\varepsilon}_r \equiv \varepsilon_r + \frac{\sigma}{i\omega \varepsilon_0}. \quad (2.11)
\end{align}

**2.2.2 Maxwell curl equations**

The equations (2.6 and 2.7) are also known as Maxwell curl equations and they describe the electromagnetic waves propagating in a medium. For the sake of simplicity, we introduce a scaled magnetic field $\tilde{H}$

\begin{align}
\tilde{H} = iZ_0 \mathbf{H}, \quad (2.12)
\end{align}

where $Z_0 = \sqrt{\mu_0 / \varepsilon_0}$ is the impedance of free space, and the vacuum wave number $k_0 = \omega / c_0 = \omega \sqrt{\varepsilon_0 \mu_0}$. In terms of these, the equations (2.6) and (2.10) satisfy

\begin{align}
\nabla \times \mathbf{E} + k_0 \tilde{H} &= 0, \quad (2.13) \\
\n\nabla \times \tilde{H} + k_0 \hat{\varepsilon}_r \mathbf{E} &= 0. \quad (2.14)
\end{align}

Equations (2.13, 2.14) are the governing equations in the electromagnetic model and numerically integrated over the spatial grids.

**2.2.3 Helmholtz wave equation**

The Maxwell curl equations (2.13,2.14) can be put into a single wave equation for the magnetic field intensity. Taking the curl of equation (2.10) and substituting in equation (2.6), we acquire

\begin{align}
\nabla \times \nabla \times \mathbf{H} - k_0^2 \hat{\varepsilon}_r \mathbf{H} + k_0 \frac{\nabla \hat{\varepsilon}_r}{\hat{\varepsilon}_r} \times \nabla \times \mathbf{H} &= 0. \quad (2.15)
\end{align}
The last term on the left-hand side vanishes for a medium with a piecewise uniform complex permittivity:

$$\nabla \times \nabla \times \mathbf{H} = k^2 \mathbf{H},$$

(2.16)

where the wave number $k$ has been defined as

$$k = k_0 \sqrt{\hat{\epsilon}_r}.$$  

(2.17)

Equation (2.16) is called the Helmholtz equation and can be used in plasma models [21]. It is employed in this chapter to obtain the analytic solutions.

2.3 Boundary conditions

The boundary conditions are divided into four distinct types: (1) material interfaces, (2) symmetry axis, (3) excitation and (4) propagation boundary conditions.

The interface between two materials with distinct dielectric permittivities forms a discontinuity in the media and defines a boundary condition of type (1) (for details see [22]). There are different materials in a system and the boundary conditions are specific to each material. The boundary conditions between two dielectric media is given by the continuity of the parallel electric field. We assume that a metal is a perfect conductor and that the electric field vanishes inside a metal. In this respect, if one of the materials is a metal, then the tangential electric field vanishes.

The boundary between a conductor and a dielectric is of special importance since it allows a wave propagation along their interface, which is known as surface-guided waves [23]. If the conductor is a plasma, the surface wave feeds it and at the same time the plasma itself sustains the wave propagation. Such configuration, where a dielectric tube, i.e., quartz, and a plasma meet, is known as a surface wave discharge and it is discussed in detail by various authors [24–26]. In some cases, air may also serve as a dielectric, which will allow surface propagation along its boundary with the plasma [27]. For this boundary condition, we also assume that the net surface charge is zero. In a plasma model, for example presented in next chapters, we neglect the plasma sheath next to a dielectric wall. This region is generally characterised with a net space charge and the zero surface charge assumption may seem unrealistic. On the other hand, if a net surface charge is present at the interface, this gives rise to various higher order hybrid microwave modes that break the axial symmetry. Such modes are outside the scope of this work, and their investigation is left for 3-D electromagnetic models.

A symmetry axis is the boundary condition of type (2) and states that the derivative that is normal to the symmetry axis is zero. The excitation boundary condition (type (3)) has a different characteristic compared to the aforementioned conditions since it specifies the incoming electromagnetic field configuration through a waveguide. We assume that this configuration in the waveguide
2.4 Discretisation

is known and that there is no reflection from the setup back into this boundary. The scale of the incoming electric field is arbitrary and it is iteratively re-scaled to match the input and the absorbed power.

All these boundary conditions describe physical phenomenon, for which the propagation boundary condition differs from them. It does not reflect a physical situation, but it is an artificial one only to restrict the computational domain bound to a finite region. In this respect, this boundary condition lets the waves propagate through the boundary without any reflection. It is imposed by assigning an analytic form to the wave at the boundary [28].

2.4 Discretisation

The time-harmonic fields are discretised via so called Finite Difference Frequency Domain (FDFD) method [29]. The method is based on the finite difference approximations of the spatial derivatives of the Maxwell curl equations given in the form (2.13, 2.14).

For the sake of simplicity, the discretisation procedure is generalised to an ortho-curvilinear coordinate system. Then the coordinate system can be easily converted by specifying its characteristics. An ortho-curvilinear coordinate system is described by a diagonal metric, in which the coordinates are orthogonal to each other [30]. The best known examples are the cartesian, cylindrical and spherical coordinate systems. In the discretisation procedure, a general ortho-curvilinear coordinate description is employed and the coordinate system is defined by identifying its metric. This greatly simplifies the implementation of distinct ortho-curvilinear coordinates in the models.

In the discretisation, the field vector components are differently positioned on the grid cells according to the Yee algorithm [20] (see Figure(2.1)). Similar to the control volume approach, the Maxwell curl equations are integrated over each grid cell and together with Stokes’ theorem of integration the components are placed accordingly. The electric field components are located on the cell walls and they overlap with the material interfaces parallel to them. A Yee grid cell and the smart positioning of the field components are shown in Figure 2.1 (a). The material interfaces are associated with the discontinuities in the medium and form a mutual boundary condition for both materials. As a consequence of the smart positioning, the Yee algorithm provides an easy implementation of the boundary conditions for the material interfaces. The neighbouring Yee cells for the boundary condition implementation are shown in Figure 2.1 (b).

2.5 The TM\(_{01}\) mode in cylindrical coordinates

In the remainder of this chapter, we are concerned with a cylindrical setup with axially symmetric field profiles. Furthermore, we consider TM\(_{01}\) mode of the elec-
2. Electromagnetic Model

\textbf{Figure 2.1.} (a) A 2-D grid cell and positions of the discrete field components in the cylindrical coordinate system for a TM_{001} mode. (b) Grid cells and boundaries for different materials.

An electromagnetic wave that propagates along the \( z \) direction of a cylindrical coordinate system \((z, r, \phi)\). This mode is composed of the field components \( \mathbf{E} = (E_z, E_r, 0) \) and \( \mathbf{H} = (0, 0, \hat{H}_\phi) \). The field \( \mathbf{H} \) is governed by equation (2.16), for the field component \( \hat{H}_\phi(z, r) \) this yields

\[
\frac{\partial^2 \hat{H}_\phi}{\partial z^2} + \frac{1}{r} \frac{\partial \hat{H}_\phi}{\partial r} - \frac{1}{r^2} \hat{H}_\phi + k_z^2 \hat{H}_\phi = 0. \tag{2.18}
\]

Using the method of separation of variables for \( \hat{H}_\phi = R(r)Z(z) \), we find that

\[
\frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} + \frac{1}{R(r)} \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} \right] - \frac{1}{r^2} + k_z^2 = 0. \tag{2.19}
\]

The first term is independent of \( r \) and \( \phi \). As a consequence, it must be also independent of \( z \) if the sum of all terms equals zero

\[
\frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = -k_z^2, \tag{2.20}
\]

where \( k_z \) is the complex axial wavenumber. The solutions to \( Z(z) \) are the harmonic functions \( h(k_z z) \)

\[
h(k_z z) \propto \exp(\pm ik_z z), \sin(k_z z), \cos(k_z z) \tag{2.21}
\]
By including the definition of the axial wavenumber, $k_z$ of equation (2.20) into equation (2.19) we get
\[
\frac{1}{R(r)} \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} \right] \frac{1}{r^2} + k^2 - k_z^2 = 0. \tag{2.22}
\]
We introduce the complex radial wavenumber as
\[
k_r^2 = k^2 - k_z^2. \tag{2.23}
\]
Substitution of equation (2.23) into equation (2.22) yields
\[
\frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} + \left( k_r^2 - \frac{1}{r^2} \right) R(r) = 0. \tag{2.24}
\]
This is the Bessel differential equation and the solutions to $R(r)$ are the Bessel functions $B_n(k_r r)$
\[
B_1(k_r r) \propto J_1(k_r r), Y_1(k_r r), H_1^{(1)}(k_r r), H_1^{(2)}(k_r r) \tag{2.25}
\]
with $n = 1$.

The Bessel functions of first and second kind, $J(k_r r)$ and $Y(k_r r)$, are analogous, respectively, to $\cos(k_r r)$ and $\sin(k_r r)$ both describing a standing wave for real arguments and an evanescent field for imaginary arguments. Similarly, the Hankel functions or Bessel functions of third kind, $H_1^{(1)}(k_r r)$ and $H_1^{(2)}(k_r r)$, are equivalent to $\exp(i k_r r)$ and $\exp(-i k_r r)$, describing a propagating solution in negative or positive direction for real argument and an evanescent field for imaginary argument. Therefore, the general solution for $H_\phi$ in a TM mode with rotational symmetry is
\[
\tilde{H}_\phi \propto B_1(k_r r) h(k_z z). \tag{2.26}
\]
Depending on the boundary conditions the corresponding Bessel and harmonic functions are used. Note that a linear combination of the solutions will also be solution of the wave equation. It is also important that when $k_r = 0$, the degenerated Bessel functions are
\[
B_0(k_r r)|_{k_r=0} = 1, \log(r) \tag{2.27}
\]
\[
B_n(k_r r)|_{k_r=0} = r^n, r^{-n}. \tag{2.28}
\]

In the following sections, we apply the electromagnetic module to a circular and a coaxial waveguide filled with air. We acquire the analytic solutions via the Helmholtz equation and compare with the simulation results. In order to investigate the accuracy of the method, we define a relative local error of the solution
\[
\epsilon \equiv \text{Max} \frac{\tilde{H}_\phi^N - \tilde{H}_\phi}{\text{Max}(\tilde{H}_\phi)}, \tag{2.29}
\]
where Max represents the maximum value of different spatial positions and $\tilde{H}^N_{\phi}$ represents the numerical solution.

In the discretisation scheme finite difference approximations are used, which are provided by Taylor series expansion [29,31].

Let $L$ be a differential operator, $u(x)$ an analytic function and $x$ the spatial coordinate. For a constant grid size $\delta x$, let $\bar{u}$ be the numerical solution and $\bar{L}$ be a numerical operator. The absolute local error is defined as the difference between the analytic and numerical solution and it is position dependent $e(x_n) = |u(x_n) - \bar{u}(x_n)|$, which is in general normalised to the function $\epsilon = e(x_n)/\bar{u}(x_n)$ (see equation 2.29). The consistent error is defined as $e_c(x_n) = |Lu(x_n) - \bar{L}\bar{u}(x_n)|$.

According to the Taylor series, the consistent error is equal to the remainder terms of the Taylor series expansion and its is related with the absolute local error with $Le = e_c$. If the numerical operator is invertible, the relation takes the form $e = \bar{L}^{-1}e_c$. The consistent error can be given by the relation

$$e_c = A(\delta x)^n,$$  \hspace{1cm} (2.30)

where $n$ is the order of the approximation and $A$ is the proportionality constant. The order and the constant are defined by the finite difference approximation, for example $n = 2$ in our case. The grid size is given by the relation $\delta x = l/N$, where $l$ is the length of the computation domain and $N$ is the number of grids. Therefore, the relation between the absolute local error and the number of grid points is

$$\ln e \approx \ln(\bar{L}^{-1}A\ln(N)^{-n}),$$  \hspace{1cm} (2.31)

which can be approximately stated by

$$\ln e \approx -\alpha \ln N,$$  \hspace{1cm} (2.32)

where $\alpha$ is defined by the previous parameters defining the differential equation and order of the finite difference approximation.

### 2.5.1 Circular waveguide

The geometry of a circular waveguide short-cut at one end ($z = L$) is shown in Figure (2.2). As $\tilde{H}_{\phi}$ must be defined at $r = 0$, the Bessel function of first kind $J_1$ is
used. Due to the short cut at \( z = L \), a combination of propagating waves appear

\[
\tilde{H}_\phi = J_1(k r) [A \exp(-i k z) + B \exp(i k z)].
\]

(2.33)

The boundary conditions are

\[
\frac{\partial \tilde{H}_\phi}{\partial z} \bigg|_{z=L} = 0,
\]

(2.34)

and

\[
\frac{1}{r} \frac{\partial r \tilde{H}_\phi}{\partial r} \bigg|_{r=a} = 0.
\]

(2.35)

From the first boundary condition

\[
-A \exp(-i k z L) + B \exp(i k z L) = 0,
\]

(2.36)

so that

\[
A \exp(-i k z L) = B \exp(i k z L) = C.
\]

(2.37)

Let’s introduce \( L \) into equation (2.33) via multiplying each exponential with the identity

\[
\exp(i k z L) \exp(-i k z L) = 1:
\]

\[
\tilde{H}_\phi = J_1(k r) [A \exp(-i k z L) \exp(-i k z (z - L)) + B \exp(i k z L) \exp(i k z (z - L))]
\]

(2.38)

Inserting equation (2.37) into equation (2.38) and dividing by 2

\[
\tilde{H}_\phi = J_1(k r) \frac{C}{2} \{ \exp(-i k z (z - L)) + \exp(i k z (z - L)) \}
\]

(2.39)

\[
= C J_1(k r) \cos(k z (z - L)).
\]

(2.40)

From the second boundary condition, using the formula for the derivative of Bessel functions (see equation 9.1.30 in [32]) we get

\[
\frac{k_r}{k_r} \frac{\partial k_r r J_1(k r)}{\partial k_r r} \bigg|_{r=a} = J_0(k ra) = \frac{1}{2} \cos(k z L) = 0.
\]

(2.41)

Therefore, the boundary condition at \( r = a \) implies that

\[
k_ra = x_{01},
\]

(2.42)

where \( x_{01} \) is the first zero of \( J_0 \). Remember that the boundary condition at \( r = 0 \), where the field must be finite, requires using \( J \) as \( Y \) is infinite at \( r = 0 \).

From the above condition the complex axial wave number is obtained as

\[
k_z = \sqrt{k^2 - \left( \frac{x_{01}}{a} \right)^2}.
\]

(2.43)
For $k_z$ real, we will use

$$\tilde{H}_\phi = C J_1 \left( \frac{x_{01}}{a} r \right) \cos [k_z (z - L)]. \quad (2.44)$$

However, when $k_z = i \gamma$ with $\gamma > 0$, i.e., $k_z$ becomes imaginary, we have an evanescent field

$$\tilde{H}_\phi = D J_1 \left( \frac{x_{01}}{a} r \right) \exp (-\gamma z). \quad (2.45)$$

**Error analysis**

The circular waveguide of length $L = 0.1226$ m and radius $a = 0.06$ m is numerically solved by the EM module and compared with the analytic solution obtained above. The normalised magnetic field pattern is shown in Figure (2.3). The analytic and numerical results show good agreement in the order of 0.7 % maximum difference. The error $\epsilon$ is shown as a function of the number of grid points in Figure (2.4). We use the expression (2.32), which relates the number of grids to the error $\epsilon$ and find the slope $\alpha = 0.97$. The scheme is first-order accurate that is in agreement with [33]. The behaviour of the error for radial and axial directions differ (see Figure (2.4)). Such an anisotropy is probably caused by the distinct governing equations in these directions and further investigation is required for a definite answer.
2.5. The TM$_{01}$ mode in cylindrical coordinates

Figure 2.4. Circular waveguide: Logarithm of the scaled absolute maximum error $\epsilon$ (equation 2.29) as a function of the logarithm of the number of grid points $N$. (1) $N$ is increased axially keeping the radial number fixed. (2) $N$ is increased radially keeping axial number of grids fixed and (3) $N$ is increased in both directions.

Figure 2.5. The coaxial waveguide with an inner radius $a$, an outer radius $b$ and a short-cut at $z = L$.

2.5.2 Coaxial waveguide

A schematic of the coaxial waveguide with an inner radius $a$ and outer radius $b$ is given in Figure 2.5. The waveguide is short-cut at axial position $z = L$. In the coaxial waveguide, as $a < r < b$ the plane $r = 0$ and $r = \infty$ are not part of the solution domain, therefore, the J and Y Bessel solutions are used.

$$\hat{H}_\phi = [AJ_1(k_r r) + BY_1(k_r r)] [C \exp(-ik_z z) + D \exp(i k_z z)].$$ (2.46)
Using the boundary condition at \( z = L \),

\[
\left. \frac{\partial \tilde{H}_\phi}{\partial z} \right|_{z=L} = 0 \tag{2.47}
\]

we obtain

\[
\tilde{H}_\phi = [A J_1(kr) + B Y_1(kr)] \cos [k_z(z - L)]. \tag{2.48}
\]

From the boundary condition at \( r = a \) and \( r = b \)

\[
\left. \frac{1}{r} \frac{\partial \tilde{H}_\phi}{\partial r} \right|_{r=a,b} = 0. \tag{2.49}
\]

and using the property for the derivative of the Bessel function

\[
\frac{k_r \partial}{k_r \partial r} \frac{B_1(kr)}{r} \bigg|_{r=a} = B_0(k,a) \tag{2.50}
\]

we obtain

\[
Ak_r J_0(k_r a) + Bk_r Y_0(k_r a) = 0, \tag{2.51}
\]
\[
Ak_r J_0(k_r b) + Bk_r Y_0(k_r b) = 0. \tag{2.52}
\]

The propagation of \((TM_{0m})\) modes is given by the characteristic relation

\[
J_0(k_r a)Y_0(k_r b) - J_0(k_r b)Y_0(k_r a) = 0 \tag{2.54}
\]

When \( k_r = 0 \), a combination of TEM and TM\(_{00}\) modes is obtained. In that case the boundary condition

\[
\left. \frac{1}{r} \frac{\partial B_1(k, r)}{\partial r} \right|_{r=a,b} = 0 \tag{2.55}
\]

is fulfilled if \( B_1(k, r) = 1/r \). For vacuum the TM\(_{00}\) mode is mostly suppressed when \( b < 2.3a \). Finally the magnetic field for the TEM mode is given by the relation

\[
\tilde{H}_\phi = \frac{C}{r} \cos [k_z(z - L)]. \tag{2.56}
\]

**Error analysis**

The circular waveguide with an inner radius of \( a = 0.0005 \) m, an outer radius of \( b = 0.045 \) m and a short-cut length of \( L = 0.2 \) m is numerically solved and results are shown in Figure 2.6. The solution agrees with the analytic data in the order of 0.5 % at maximum. The error \( \epsilon \) as a function of the total number of grid cells is shown in Figure 2.7. In this case, the error data does not produce a straight line as in the circular waveguide but slightly scattered. We provide a fit line and using the expression (2.32) we find a slope of \( \alpha = 1.3 \). This is larger than the slope of the circular waveguide; however, the scheme is approximately first-order accurate.
2.6 Conclusion

We introduced the electromagnetic module of Plasimo and applied it to circular and coaxial waveguides. The numerical simulations show good agreement with
2. Electromagnetic Model

the analytic results. An error is defined from these two distinct solutions and it is analysed with respect to the total grid numbers. It should be emphasised that the discretisation of a wave equation does not only cause an error in the finite difference approximations. It also alters the dispersion relation and leads to a phase difference with the exact wave. The dispersion relation is generally derived from the wave equation itself and it basically relates the wavenumber and the frequency with the phase velocity. On the other hand, the discretised wave equation causes a slight difference in the dispersion relation. This relation is called numerical dispersion [29], [30] and causes a grid length dependent phase difference between the analytic and numerical wave solutions. In this respect, as the waves propagate the error term increases.
Chapter 3

A modeling study of low-pressure coaxial plasma waveguide: Argon

2. AN ARGON PLASMA IN A COAXIAL WAVEGUIDE

Abstract

We present a two-dimensional plasma model for a coaxial microwave discharge. The microwave energy at driving frequency of 2.45 GHz is fed into a coaxial configuration in which the plasma acts as an outer conductor in such a way that a spatially extended surface wave is created. This geometry permits large surface treatment, especially if a set of such coaxial lines are used. The 2D model describes the plasma as a two-temperature non-chemical equilibrium fluid sustained by electromagnetic surface waves. We present results for argon as a working gas. Discussed is the importance of wave-plasma power coupling and electron heat transport. The radial localization of electron density in coaxial plasma waveguide is observed and compared to experimental results. Moreover, a parameter study allows to investigate the dependency of radial contraction of the electron density as function of pressure in the range of 2 to 8 mbar, and also the dependency of electron density on the power input in the range of 120 to 1200 W. In order to verify the model, the modeling results are compared with experimental results for the electron density and temperature and a good agreement is found.

3.1 Introduction

Microwave induced plasmas (MIP) are successfully and widely applied for spectrochemical analysis and surface treatments such as deposition, etching and coating [34]. A special type of MIPs is formed by the class of surface wave discharges (SWD). Since they cover a broad range of operating conditions, stability and reproducibility [25,35–45], SWDs are employed in many technological applications. Examples are the production of optical fibers [21], surface passivation of solar cells [6], graphene deposition [3] and biomedical applications [46].

In SWDs, the plasma is sustained by electromagnetic waves propagating along a plasma-dielectric interface. The plasma dimension in the wave propagation direction can be larger than the microwave wavelength; it depends mainly on the input power and the gas properties [34].

Well-known configurations are the cylindrical plasma columns generated by surfatron [35] or surfaguide launchers [47]. Typical for these cylindrical structures is that the axis of symmetry coincides with the axis of the plasma; the plasma is created inside a dielectric tube and thus inside the cylindrical mantle along which the surface wave propagates.

This study, however, is devoted to the coaxial structure in which not the plasma but a metal rod antenna is located at the axis of symmetry. This wave launching antenna is surrounded by air at atmospheric pressure and a quartz tube. This rod-in-a-tube device can be inserted in a low pressure vessel where it creates, under appropriate conditions, a plasma at the periphery. Thus, in contrast with the surfatron and surfaguide, the plasma is not located inside but outside the dielectric
3.1. Introduction

The key feature of the coaxial discharge, that the plasma is positioned at the outside, opens up the possibility that large plasma volume or areas can be treated. In fact, the coaxial discharge here described is inspired by the coaxial discharge of a so called (Duo-) Plasmaline [5], successfully used in [6] for surface passivation of solar cells and in [3] for graphene film deposition.

The modelling of coaxial discharges has been reported in the past. In [48] the propagation properties of a Plasmaline are investigated. A radial description of microwave coaxial discharge is given in [10], in which the momentum equation for ions is included. Self-consistent two-dimensional models have been discussed in Refs. [49–53]. For the coaxial discharge, [11] discusses a time-dependent electromagnetic model that is coupled with a hydrodynamic model. However, in that work the gas temperature is assumed to be constant, whereas in the present work the gas temperature is calculated from the corresponding energy balance. Furthermore in [11] a comparison with experimental work is missing. A 2D model of a low pressure (1 mbar) coaxial discharge is given in [12].

In this paper, a 2D model for the self-consistent description of the plasma-electromagnetic interaction in a coaxial microwave discharge is described. The aim of the model is to study

- the plasma-wave coupling and the effect of electron heat transport;
- the impact of changing the gas pressure and input power;
- features shown by experimental data such as the radial distribution of the electron density.

The model constructed for the coaxial discharge in two dimensions is compared with experimental results of the electron density and temperature obtained by Thomson scattering [9].

Despite the differences between the plasma and wave properties of coaxial surface waves with respect to those created by other cylindrical structures, the main characteristic remains the same: the plasma is created by an electromagnetic wave propagating along a plasma-dielectric interface. This implies that the method and model employed in [52] created to investigate a surfatron generated plasma can be used here, albeit in modified form.

We solve the specific mass balance equations for several species and two energy balances, one for electrons and one for heavy particles. The specific momentum balances are used in a simplified way to get an expression for the diffusion. In fact this gives a Fick diffusion description, which is justified since there is a single dominant species: atomic argon. Furthermore, the ion momentum
is described using the approximation of ambipolar diffusion. Despite its limitations, the ambipolar diffusion approach is still widely used in microwave induced plasma modelling [49, 51, 54].

The set of fluid equations is coupled to the electromagnetic module that delivers the two dimensional energy input to the plasma via ohmic dissipation. The numerical model is constructed in the modeling platform Plasimo. More information about Plasimo can be found in [55].

This paper has been organized as follows. In section 3.2, we discuss the physical model in more detail, the numerical methods are outlined in section 3.3. In section 3.4, we present the simulation results and compare those with results from Thomson scattering experiments. Conclusions are presented in section 3.5.

3.2 Physical Model

The core of the physical model is composed of fluid and EM equations. These require as input the geometry of the setup, the input power, the boundary conditions, the chemical reaction rates and the transport coefficients.

3.2.1 Governing equations

The governing equations of the coaxial Plasmaline are divided into the Maxwell equations for the electromagnetic part and a system of fluid equations (particle and energy balances) for the plasma [52].

Fluid equations

The fluid model assumes a steady state description and consists of the following equations [56]:

1. Specific species balance

\[ \nabla \cdot \Gamma_s = S_s \]  \hspace{1cm} (3.1)

with \( \Gamma_s \) the corresponding flux density and \( S_s \) the net production of the species due to inelastic processes. The flux density equals \( \Gamma_s = n_s v_s \), where \( n_s \) is the number density of species \( s \) and \( v_s \) is the velocity of species \( s \). Since we neglect the bulk flow velocity of the plasma, we rewrite the flux density as \( \Gamma_s = -D_s \nabla n_s \). Here \( D_s \) denotes the diffusion coefficients. With this assumption, the species balance becomes

\[ -\nabla \cdot (D_s \nabla n_s) = S_s. \]  \hspace{1cm} (3.2)

This equation is solved for \( s \) corresponding to species \( \text{Ar}^r, \text{Ar}^p, \text{Ar}(4p), \text{Ar}^+ \) and \( \text{Ar}_2^+ \). For neutral species, i.e., \( \text{Ar}^r, \text{Ar}^p \) and \( \text{Ar}(4p) \), we keep \( D_s \) as the
effective diffusion coefficient (see table 3.4 in section 3.2.5), whereas for ions, i.e., Ar\(^{+}\) and Ar\(_{2}\)^{+}, \(D_s\) is modified to become the corresponding ambipolar diffusion coefficient \(D_s^{+}\) (see again table 3.4). The processes that give shape to sources \(S_s\) are treated in section 3.2.4.

The electron density is obtained from quasi-neutrality and the argon density is obtained from the ideal gas law.

2. For the energy balance of the heavy particles we use the expression

\[
\nabla \cdot q_h = Q_{eh}^{\text{elas}} + Q_{eh}^{\text{in}}.
\]

(3.3)

Here the heavy particle heat flux is defined as \(q_h = -\lambda_h \nabla T_h\), with \(\lambda_h\) the heavy particle thermal conductivity obtained from the mixture rules [57]. The term \(Q_{eh}\) denotes the energy gain through elastic collisions with electrons and can be written as

\[
Q_{eh}^{\text{elas}} = \sum_s \frac{3}{2} n_e \nu_{es} \frac{2m_e}{m_s} k_B (T_e - T_h).
\]

(3.4)

Here \(T_e\) is the electron temperature, \(T_h\) is the heavy particle temperature, \(\nu_{es}\) is the frequency of elastic momentum transfer between electrons and species \(s\), \(m_e\) is the electron mass, \(m_s\) is the mass of species \(s\) and \(k_B\) is the Boltzmann constant. The term \(Q_{hh}\) refers to the energy gain or loss through inelastic collisions in which heavy particles are involved. We have assumed that the value of the ion temperature is equal to that of the gas temperature.

3. The energy balance for electrons reads

\[
\nabla \cdot q_e = Q_{ohm} - Q_{eh}^{\text{elas}} - Q_{eh}^{\text{in}} - Q_{rad}.
\]

(3.5)

Here the conductive heat flux is defined as \(q_e = -\lambda_e \nabla T_e\), with the electron thermal conductivity \(\lambda_e\) obtained from the Frost mixture rules [58]. The term \(Q_{eh}^{\text{in}}\) refers to the energy gain or loss through inelastic collisions, which can be expressed as

\[
Q_{eh}^{\text{in}} = \sum_i R_i \Delta \varepsilon_i
\]

(3.6)

where \(R_i\) is the reaction rate of process \(i\) and \(\Delta \varepsilon_i\) is the average energy exchange per event.

The time-averaged absorbed power is given by

\[
Q_{ohm} = \frac{1}{2} \text{Re}(J^*E) = \frac{1}{2} \text{Re}(\hat{\sigma}||E|^2)
\]

(3.7)

where Ohm’s law \(J = \hat{\sigma}E\) is used to relate the electron current density \(J\) to the harmonic electric field. \(J^*\) represents the complex conjugate of electron current density. The complex conductivity \(\hat{\sigma}\) of the plasma is obtained
3. An argon plasma in a coaxial waveguide

from the current density \( J = \partial_t \mathbf{E} = -e n_e \mathbf{v}_e \) and the cold collisional electron approximation of the electron momentum balance equation for harmonic fields [11,52,59].

Electromagnetic Equations

The model is based on the Maxwell-Faraday and Maxwell-Ampere equations for harmonic fields in the form \( \exp(i \omega t) \). Following the approach given in [52] this gives rise to two coupled equations

\[
\nabla \times \mathbf{E} + k_0 \mathbf{H} = 0, \\
\nabla \times \mathbf{H} + k_0 \hat{\varepsilon}_r \mathbf{E} = 0,
\]

(3.8)

(3.9)

where \( k_0 = \omega \sqrt{\mu_0 \varepsilon_0} \) is the vacuum wavenumber and \( \hat{\varepsilon}_r = \varepsilon_r - \frac{i \sigma}{\omega \varepsilon_0} \) is the complex relative permittivity, with \( \mu_0 \) the permeability of free space (H/m) and \( \varepsilon_0 \) the permittivity of free space in (F/m). These equations are based on the assumption that the medium is isotropic, so the permeability and the permittivity are scalars. \( \mathbf{H} \) (in V/m) is linked to the magnetic field component \( \mathbf{H} \) via \( \mathbf{H} = i \sqrt{\mu_0 / \varepsilon_0} \mathbf{H} \). We will further assume that the modes are Transverse Magnetic, TM, so that only \( E_z \), \( E_r \) and \( H_{\phi} \) are non-null. For the quartz tube \( \hat{\varepsilon}_r = 4 \), while for air \( \hat{\varepsilon}_r = 1 \).

3.2.2 Geometry

The computational domain of the coaxial linear microwave discharge is shown in Fig. 3.1b. It simulates the real set-up given in Fig. 3.1a. A metal rod is placed in the center of the setup surrounded by a quartz tube and air at atmospheric pressure which separates the plasma from the metal. In fact the plasma acts as an outer (non-perfect) conductor. The coaxial discharge is placed inside (along the axis of) a cylindrical metal chamber with windows, which can be set at different pressures. In the computational domain only metal walls are included.

An electromagnetic wave at a frequency of 2.45 GHz is directed into the setup carrying a power of \( P_{in} \) and then propagates as surface wave along the interface between the plasma and the quartz tube. The modeling domain is \( R_T = 100 \text{ mm} \) in radius and \( Z_T = 500 \text{ mm} \) long. The inner conductor radius is \( R_i = 3.65 \text{ mm} \). The inner radius of the quartz tube is \( R_o = 13 \text{ mm} \) and outer radius is \( R_q = 15 \text{ mm} \). The length of the quartz tube is \( Z_q = 420 \text{ mm} \) is equals to plasma one \( Z_p = 420 \text{ mm} \) and part of the inner conductor is injected into chamber until \( Z_m = 40 \text{ mm} \). All metallic boundaries (walls and rod antenna) are treated as perfectly conducting material. Dimensions of setup are given in table 3.1.
3.2. Physical Model

Figure 3.1. a) Picture of the Plasmaline. b) Schematic of the computational domain for the Plasmaline. The excitation boundary condition is imposed at the left side of the coaxial waveguide ($z = 0, R_i < r < R_o$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_T$</td>
<td>100 mm</td>
<td>$Z_T$</td>
<td>500 mm</td>
</tr>
<tr>
<td>$R_q$</td>
<td>15 mm</td>
<td>$Z_P$</td>
<td>420 mm</td>
</tr>
<tr>
<td>$R_o$</td>
<td>13 mm</td>
<td>$Z_q$</td>
<td>420 mm</td>
</tr>
<tr>
<td>$R_i$</td>
<td>3.65 mm</td>
<td>$Z_m$</td>
<td>40 mm</td>
</tr>
</tbody>
</table>

Table 3.1. Dimensions of the geometry in Plasmaline source.
3.2.3 Boundary conditions

**Fluid model:**

The gas temperature is set to prescribed values at the quartz and metal wall boundaries. For the electron temperature homogeneous Neumann boundary conditions are applied at each wall, as suggested in [52]. This means we assume no exchange of electron energy with the sheath.

The flux of atomic and molecular ions, $s$, at the wall is set as

$$-D^+_s \left( \frac{\partial n_s}{\partial r} \right) \bigg|_{r=R_p} = \gamma n_s v_B s,$$

(3.10)

where $v_{B,s} = \sqrt{k_B T_e / m_s}$ is the Bohm velocity of ion $s$ [54]. Here $D^+_s$ is the ambipolar diffusion coefficient, and $\gamma$ is a correction factor set at 5% for atomic ions and 100% for molecular ions. The reason for the low factor for atomic ions is to prevent low electron density values next to quartz wall. This avoids the appearance of the resonance region (see [10]) and is consistent with neglecting the sheath region (see [52]), while obtaining a reasonable value for ion density next to the ‘wall’, as judged by comparing modelling and experimental results. The effect of this boundary condition on the plasma is limited to a small region next to the quartz wall, as long as it avoids the minimum values related with the resonance region and the maximum value expected in the volume. The effect of the boundary condition at the wall has been observed for the case of a coaxial positive column in [60], where for a ratio of 0.3 between the electron density at the wall to the maximum value, a maximum variation of 10% in $n_e$ is observed in the region next to the wall.

**EM model:**

At the metal walls, the perfect electrical conductor (PEC) boundary condition is used [61], so that the component of the electric field tangential to the metallic surface is zero.

The excitation boundary condition is used at the left side of the coaxial waveguide ($z = 0, R_i < r < R_o$). It consists of two boundary conditions, one applied to the incident wave that set the power entering in the domain and a propagation boundary condition (PBC) for the reflected wave [61, 62]. We assume that the incident power is carried by a TEM mode so that the corresponding E-field component reads

$$E_r^+ (r,z) = \frac{C_{\text{TEM}}}{r} \exp(-i\beta z),$$

(3.11)

with $C_{\text{TEM}} = \sqrt{Z_0 |P_i| / \pi / \ln(R_o/R_i)}$, where $|P_i|$ is the (imposed) incident power and $\beta$ the wave numbers of the TEM mode in the coaxial waveguide.
3.2. Physical Model

Due to the discontinuity present in the domain the incident wave will generate a wave that is reflected back to the entrance. For the corresponding component $E_r^-$ we apply a PBC such that

$$\frac{\partial E_r^-}{\partial z} - i k E_r^- = 0. \quad (3.12)$$

In this case the wavenumber for the TEM mode coincides with the medium wavenumber, $k$. Note that this BC imposes at the entrance a plane wave propagating in the negative $z$-direction i.e. $E_r^- \propto \exp(+i\beta z)$. As the BC should be applied to the total $E_r$ field, we substitute the relation $E_r^- = E_r - E_r^+$ into (3.12), which, using equation (3.11), gives

$$\frac{\partial E_r}{\partial z} - \beta E_r = -2i\beta \frac{C_{TEM}}{r} \exp(-i\beta z). \quad (3.13)$$

At the right side of the coaxial waveguide ($z = Z_T, R_i < r < R_o$) a propagation boundary condition (PBC) [61] is used. As we impose this boundary condition for the wave propagation in the direction outwards of the computational domain, we rewrite Eq. 3.12 as

$$\frac{\partial E_r}{\partial z} + i\beta E_r = 0, \quad (3.14)$$

with the E-field given by $E_r \propto \exp(-i\beta z)$.

3.2.4 Chemistry

We consider the four $3p^24s$ levels as two blocks: the metastable levels $1s_3$ and $1s_5$ are grouped as species $Ar^{m}$, whereas the resonant levels $1s_2$ and $1s_4$ are grouped as species $Ar^{r}$. The $3p^54p$ levels are included as species $Ar^{4p}$.

For the ions we consider $Ar^+$ and molecular ions $Ar_{2}^{+}$. All these species, except electrons and ground state Ar atoms, are treated as transport sensitive species meaning that their densities are described by the corresponding particle balance equation [Eq. 3.1], i.e., the non-chemical equilibrium.

The electron density follows from charge neutrality, whereas the Ar density follows from the ideal gas law. An overview of the included reactions is given in tables 3.2 and 3.3 together with the rate coefficients formulas and the corresponding references. The transitions induced by these reactions are illustrated in Figs. 3.2a and 3.2b.

3.2.5 Transport Coefficients

Basically we use the same transport coefficients as those given in [52], although improved cross-sections for elastic interactions, provided as look-up tables at var-
### An argon plasma in a coaxial waveguide

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Excitation From Ground State</strong></td>
<td></td>
</tr>
<tr>
<td>(1) $\text{Ar} + e \rightarrow \text{Ar}^m + e$</td>
<td>$2.5 \times 10^{-15} T_e^{0.74} \exp(-11.56/T_e)$ [63]</td>
</tr>
<tr>
<td>(2) $\text{Ar} + e \rightarrow \text{Ar}^r + e$</td>
<td>$2.5 \times 10^{-15} T_e^{0.74} \exp(-11.56/T_e)$ [63]</td>
</tr>
<tr>
<td>(3) $\text{Ar} + e \rightarrow \text{Ar}(4p) + e$</td>
<td>$1.4 \times 10^{-14} T_e^{0.71} \exp(-13.2/T_e)$ [64]</td>
</tr>
<tr>
<td><strong>Deexcitation</strong></td>
<td></td>
</tr>
<tr>
<td>(4) $\text{Ar}^r + e \rightarrow \text{Ar} + e$</td>
<td>$4.3 \times 10^{-16} T_e^{0.74}$ [63]</td>
</tr>
<tr>
<td>(5) $\text{Ar}^m + e \rightarrow \text{Ar} + e$</td>
<td>$4.3 \times 10^{-16} T_e^{0.74}$ [63]</td>
</tr>
<tr>
<td>(6) $\text{Ar}(4p) + e \rightarrow \text{Ar} + e$</td>
<td>$3.9 \times 10^{-16} T_e^{0.71}$ [64]</td>
</tr>
<tr>
<td><strong>Stepwise Excitation and Deexcitation</strong></td>
<td></td>
</tr>
<tr>
<td>(7) $\text{Ar}^r + e \rightarrow \text{Ar}(4p) + e$</td>
<td>$8.9 \times 10^{-13} T_e^{0.51} \exp(-1.59/T_e)$ [63]</td>
</tr>
<tr>
<td>(8) $\text{Ar}^m + e \rightarrow \text{Ar}(4p) + e$</td>
<td>$8.9 \times 10^{-13} T_e^{0.51} \exp(-1.59/T_e)$ [63]</td>
</tr>
<tr>
<td>(9) $\text{Ar}^m + e \rightarrow \text{Ar}^r + e$</td>
<td>$2 \times 10^{-13}$ [63]</td>
</tr>
<tr>
<td>(10) $\text{Ar}^r + e \rightarrow \text{Ar}^m + e$</td>
<td>$3 \times 10^{-13}$ [63]</td>
</tr>
<tr>
<td>(11) $\text{Ar}(4p) + e \rightarrow \text{Ar}^r + e$</td>
<td>$1.5 \times 10^{-13} T_e^{0.51}$ [63]</td>
</tr>
<tr>
<td>(12) $\text{Ar}(4p) + e \rightarrow \text{Ar}^m + e$</td>
<td>$1.5 \times 10^{-13} T_e^{0.51}$ [63]</td>
</tr>
<tr>
<td><strong>Direct ionization</strong></td>
<td></td>
</tr>
<tr>
<td>(13) $\text{Ar} + e \rightarrow \text{Ar}^+ + 2e$</td>
<td>$2.3 \times 10^{-14} T_e^{0.68} \exp(-15.76/T_e)$ [64]</td>
</tr>
<tr>
<td><strong>Stepwise ionization</strong></td>
<td></td>
</tr>
<tr>
<td>(14) $\text{Ar}^m + e \rightarrow \text{Ar}^+ + 2e$</td>
<td>$6.8 \times 10^{-15} T_e^{0.67} \exp(-4.2/T_e)$ [63]</td>
</tr>
<tr>
<td>(15) $\text{Ar}^r + e \rightarrow \text{Ar}^+ + 2e$</td>
<td>$6.8 \times 10^{-15} T_e^{0.67} \exp(-4.2/T_e)$ [63]</td>
</tr>
<tr>
<td>(16) $\text{Ar}(4p) + e \rightarrow \text{Ar}^+ + 2e$</td>
<td>$1.8 \times 10^{-13} T_e^{0.61} \times \exp(-2.61/T_e)$ [64]</td>
</tr>
</tbody>
</table>

### Table 3.2. Electron induced reactions included in the model. All rate coefficients $k$ are expressed in $(m^3s^{-1})$. The temperature $T_e$ is in eV.

Various energies have been used [67]. For elastic collisions between charged particles, the cross sections are calculated from standard Coulomb theory. The interaction between two argon atoms is modeled with the variable hard sphere model of Bird [68]. The cross-section data for the charge transfer collisions of argon atoms with argon ions is taken from [69]. For cross-section data for elastic interaction between electrons and argon atoms is obtained from [70] and [71], for the energy range of 0.02 - 19 eV and 19 - 54 eV, respectively. Interpolation is performed when the cross section as a function of energy is needed. For transport properties of the electrons (thermal conductivity and electrical conductivity) the Frost mixture rules [58] are used, whereas for heavy particle transport properties the mixture rules of Mitchner and Kruger [57] are used. We refer to table 3.4 for the corresponding references.
3.2. Physical Model

Dissociative Recombination

\[
\text{(17)} \quad \text{Ar}_2^+ + e \rightarrow \text{Ar}^+ + \text{Ar} \quad 0.6 \times 10^{-12} \times \left(\frac{T_e (K)}{300}\right)^{0.66}
\]

\[
\text{(18)} \quad \text{Ar}_2^+ + e \rightarrow \text{Ar}^m + \text{Ar} \quad 0.6 \times 10^{-12} \times \left(\frac{T_e (K)}{300}\right)^{0.66}
\]

Three Body Recombination

\[
\text{(19)} \quad \text{Ar}^+ + 2e \rightarrow \text{Ar} + e \quad 8.75 \times 10^{-39} T_e (eV)^{-4.5}
\]

Ion Conversion

\[
\text{(20)} \quad \text{Ar}^+ + \text{Ar} \rightarrow \text{Ar}^m + \text{Ar} \quad 2.25 \times 10^{-43} \left[\frac{T_h (K)}{300}\right]^{-0.4}
\]

Electron Impact Dissociation

\[
\text{(21)} \quad \text{Ar}_2^+ + e \rightarrow \text{Ar}^+ + \text{Ar} + e \quad 1.11 \times 10^{-6} \exp \left\{- \frac{2.94 - 3\left[\frac{T_h (eV)}{0.026}\right]}{T_e (eV)}\right\}
\]

Atom Impact Dissociation

\[
\text{(22)} \quad \text{Ar}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + 2\text{Ar} \quad 5.22 \times 10^{-16} \exp \left[- \frac{1.304}{T_h (eV)}\right]
\]

Radiation

\[
\text{(23)} \quad \text{Ar}^r \rightarrow \text{Ar} + h\nu \quad 1 \times 10^5 \text{ s}^{-1}
\]

\[
\text{(24)} \quad \text{Ar} (4p) \rightarrow \text{Ar}^r + h\nu \quad 3.2 \times 10^7 \text{ s}^{-1}
\]

\[
\text{(25)} \quad \text{Ar} (4p) \rightarrow \text{Ar}^m + h\nu \quad 3 \times 10^7 \text{ s}^{-1}
\]

Table 3.3. Reactions involving molecular ions and radiative transitions that are implemented in the model. All rate coefficients are expressed in (m^3 s^{-1}) except \(k_{19}, k_{20}\) (m^6 s^{-1}) and radiative transitions (s^{-1})

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Binary Diffusion</td>
<td>(D_{ij}) (m^2 s^{-1})</td>
<td>{e, h}</td>
<td>(\frac{3}{16} \frac{f_{ij} k_T^2 T_i T_j}{\eta m_{ij} \Omega_{ij}^{(1,1)} (T_{ij})})</td>
<td>[56], [72], [73]</td>
</tr>
<tr>
<td>Effective Diffusion</td>
<td>(D_s) (m^2 s^{-1})</td>
<td>{e, h}</td>
<td>(D_s = p \left(\sum_{j \neq s} p_s / D_{sj}\right)^{-1})</td>
<td>[72]</td>
</tr>
<tr>
<td>Ambipolar Flow as Diffusion</td>
<td>(D_s^+) (m^2 s^{-1})</td>
<td>{h^+}</td>
<td>(D_s (1 + T_e / T_h))</td>
<td>[74]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>(\lambda_h) (WK^{-1} m^{-1})</td>
<td>{h}</td>
<td>Mitchner-Kruger</td>
<td>[57]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>(\lambda_e) (WK^{-1} m^{-1})</td>
<td>e</td>
<td>Frost</td>
<td>[57]</td>
</tr>
</tbody>
</table>

Table 3.4. Transport coefficients in the model. Here, \(f_{ij}\) is a correction factor of order unity, \(m_{ij}\) the reduced mass, \(T_i, T_j\) the temperature of the corresponding species, \(\Omega_{ij}^{(1,1)}\), a collision integral (cf [73]), \(T_{ij}\) an effective temperature, \(E_{tr,s}\) translational energy per particle of species \(s\), such that \(E_{tr,s} n_s\) is the sensible/translational internal energy per unit volume, \(p_s\) is the partial pressure of species \(s\).
Figure 3.2. Energy level diagram for species included in the model. The relevant conversion reactions are labelled with rate coefficients that can be found in tables 3.2 and 3.3. For low pressure the main competition is that between direct ionization ($k_e$) and diffusion. For increasing pressure the stepwise ionization (excitation) processes this schematic drawing becomes more and more important.

3.3 Numerical Methods

In section 3.3.1 we describe the general equation used to rewrite each of the fluid balance equations. This will facilitate the discretization, explained in section 3.3.2. Finally, in section 3.3.3, we describe the iterative scheme.
3.3. Numerical Methods

Figure 3.3. Grid cells for the fluid electromagnetic model, a) control volume, b) Yee cell, respectively. The Yee cell is used across all the c) EM region, e.g. dielectric and plasma, whereas the control volume is only used in the plasma region.

3.3.1 The $\phi$ Equation

In Plasimo, Equations (3.1), (3.3) and (3.5) are written in the general form

$$\nabla \cdot \Gamma_\phi = S_\phi,$$

with

$$\Gamma_\phi = f_\phi \rho_b \phi v_b - \lambda_\phi \nabla \phi$$

which is known as the canonical fluid equation or the $\phi$-equation. Here $\phi$ is the corresponding fluid variable, (e.g., $n_s, T_e, \ldots$), where $S_\phi$ is the source and $\Gamma_\phi$ is the fluxes, which are separated into convective and diffusive parts.

3.3.2 Discretization

The Control Volume method is used to discretize the fluid equations (3.1), (3.3) and (3.5). As shown in Fig. 3.3.(a), the sources and $\phi$-variables are defined at the grid points at the center of the cell, i.e. at the nodal grid points, whereas the fluxes and velocities are defined at the corresponding faces, i.e. at the flux grid points. For the electrodynamic part of the model, the Yee grid cell [20] is used to discretize the electromagnetic equations, (3.8) and (3.9).

3.3.3 The iterative scheme

An iterative scheme deals with the coupling between the mathematical equations. The first step in the initialization consists of generating the computational domain and the corresponding grid for the geometry given in the input [see (3.2.2)]. Subsequently, the initial values for the main plasma parameters (temperatures, densities, flow) and the boundary conditions are obtained. The main loop starts with the data for elastic and inelastic particle interactions, given in the chemistry part, which are used to update the transport coefficients and the source terms. The conductivity is required by the EM model to obtain the Ohmic dissipation,
the most important contribution to the source term of the electron energy equa-
tion. Next, once the diffusion coefficients and the sources are known, we solve the
species balance equations. Finally, the energy balance equations are solved, first
for the heavy particles and then for the electrons. For the first 100 iterations, EM
module called for each iteration. After that, EM module is called once for every
50 iterations. The loop is repeated until the convergence criterion is met, meaning
that the residues for the plasma parameters are below the requested values.

3.4 Results and Discussion

In section 3.4.1, we present the results in two dimensions and use them to discuss
the wave-plasma power coupling. We continue with section 3.4.2, where the effect
of changing the pressure and input power on the plasma quantities is studied.
Finally, we compare the model results with experimental results in section 3.4.3.

3.4.1 Description of the wave-plasma interaction

Figure 3.4 shows the radial and axial distribution of the electromagnetic field (har-
monic) components. The radial behaviour of $|E_r|$ is similar to that of a coaxial
waveguide with a TEM mode. From the inner metal conductor until the plasma,
$(R_i < r < R_q), \ |E_r|$ is the dominant electric field component; the $|E_z|$ values are
much smaller. In other words, the coaxial plasma configuration acts as a coax-
ial waveguide in which the metal acts as inner conductor and the plasma acts as
outer conductor. However, outside the quartz tube the the modes present in the
plasma feature a decay in radial direction, strongly increased by the shielding of
the wave by the high density plasma.

Moreover $|E_z|$, is much higher than $|E_r|$, and therefore $|E_z|$ is the EM field
component responsible for the plasma-wave coupling. Consequently the surface
wave is mainly in a TM mode. Note that there is no second surface wave at the
outer wall, which differentiates this plasma from those studied in [75].

Figure 3.5 shows the axial and radial distribution of the absorbed power den-
sity. In axial direction the power density is damped linearly, as it is known for
surface wave discharges, especially at low pressures [34]. The oscillations are cre-
ated by standing waves in the plasma due to reflections of the harmonic wave
on the power outlet on the right-hand side. Figure 3.5b demonstrates the local-
ization of the absorbed power density close to the quartz wall. This is expected
as surface waves are known for carrying the energy very close to the dielectric
interface [10,34].

Now we look at the electron properties. In Fig. 3.6 the electron temperature
and density are shown. Both are apparently localized at the quartz-plasma in-
terface, but distributed differently into the plasma domain. Although the ab-
sorbed power density is even more localized close to interface, Fig. 3.6a shows
Figure 3.4. a) Axial \((r = 15.2 \text{ mm, inside plasma})\) and b) radial \((z = 76 \text{ mm})\) distributions for \(|E_r|, |E_z|\) and \(|\tilde{H}_\phi|\). The pressure is set at \(p = 3 \text{ mbar}\) and the power input \(P_{in} = 300\) W. In the radial profile, the first rectangle demonstrates the metal rod radial position, and the second one the quartz position.

that the electron temperature profile is quite extended over the whole domain due to energy transport. To understand this behaviour, we have to look at the different terms in the electron energy equation [Eq. (3.5)]. To improve readability we defined the transport term \(T = -\nabla \cdot \lambda_e \nabla T_e\), and the lost power density \(Q_L = Q_{elas} - Q_{inel} - Q_{rad}\), such that Eq. (3.5) reads now \(T = Q_{ohm} - Q_L\).

Figure 3.7a shows in detail the terms of the energy balance, i.e. transport \((T)\) power density \((Q_{ohm})\) as the source term, and the loss term \((Q_L)\) that consists of elastic and inelastic collisions. At \(r = R_l\) the transport term changes from positive to negative. In the region \(R_{th} < r < R_l\), where the transport term value is positive, the required energy for creating electrons is obtained locally. That is different in the region \(R_l < r < R_T\), where the transport term is negative. Here, the value for the locally absorbed power density is lower than that required to sustain the plasma and the energy is required to sustain the plasma is provided via transport.
Figure 3.5. (a) Axial \((r = 15.2 \text{ mm, inside plasma})\) and (b) radial \((z = 76 \text{ mm})\) distributions for the power density. The conditions are the same as in Fig. 3.4.

Figure 3.8b shows the radial distribution of the electron density. To better understand the structure of the electron density profile, we examine the electron particle balance equation [Eq. (3.1)]. Based on this equation we define the electron diffusion frequency as \(-\nabla \cdot D_{\text{amb}} \nabla n_e\). The electron chemical source \(S_e\) consists of production and destruction parts. The production terms are related to ionization processes including direct and stepwise ionization. Destruction originates from electron volume recombination that consists of two-electron recombination and molecular assisted recombination (MAR). The latter one is the recombination due to formation and subsequent destruction of molecular ions. Formation and loss frequencies are shown in Fig. 3.8a.

The location of the maximum in the ionization frequency in our results is close to the quartz wall, as discussed previously, since the power density is much higher and the local power coupling is stronger. For this reason, we can conclude that the maximum of the power density distribution explains the maximum of ionization frequency next to the quartz wall. Because of this, a maximum of electron density
3.4. Results and Discussion

Electron Temperature [K]  

<table>
<thead>
<tr>
<th>ax1al position, z [mm]</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>radial position, r [mm]</td>
<td>0</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
</tr>
</tbody>
</table>

Gas Temperature [K]  

<table>
<thead>
<tr>
<th>ax1al position, z [mm]</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>radial position, r [mm]</td>
<td>0</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
</tr>
</tbody>
</table>

Electron Density \([n_e \text{ m}^{-3}]\) \([10^{18} \text{ m}^{-3}]\)  

<table>
<thead>
<tr>
<th>ax1al position, z [mm]</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>radial position, r [mm]</td>
<td>0</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
</tr>
</tbody>
</table>

Figure 3.6. (a) The electron temperature and (b) the electron density. (c) The gas temperature. The same conditions as Fig. 3.4.

is expected close to the wall, although to fully explain the radial profile an analysis of the loss mechanisms is needed. For the electron density losses, there are two main mechanisms responsible, diffusion and volume recombination. For these mechanisms we distinguish two regions: one where diffusion is more important than recombination and one where recombination is the main loss mechanism.

Based on loss mechanisms and without considering the strong inhomogeneity of the ionization frequency it is possible to show that:

1. in the first region where diffusion is dominant, the electron density has a concave character, i.e. second derivative of electron density is negative, which resembles the Bessel profile;

2. at the region where recombination is of the same order as diffusion, there is
Figure 3.7. (a) Different terms of electron energy balance equation are shown, inner graph zoom is on the region where power density is smaller than $4 \times 10^5$ W/m$^3$, and (b) the radial profile of electron temperature. The same conditions as Fig. 3.4.

a transition from concave to convex character i.e. from negative to positive second derivative of electron density, which features a guassian-like profile.

Figure 3.6c shows the spatial distribution of the gas temperature. Elastic collisions are the main process responsible for gas heating. The maximum of the gas temperature is around 700 K.

3.4.2 Parametric study

Dependence on Gas Pressure

We did a set of simulations for different values of pressure, namely $p = 2, 3, 4, 6$ and 8 mbar with a microwave input power of 300 W. In Fig. 3.9, the radial distribution of the electron density at axial position of $z = 70$ mm is shown. By increasing the pressure, the maximum of the electron density is increased. Concerning the radial distribution: at lower pressure values the main transport mechanism is diffusion, but for higher pressure values, recombination effects are more important and dominate the radial contraction in the discharge.

In Fig. 3.10, we see that the electron temperature decreases for increasing pressure. The explanation is summarized in the dependency of the diffusion losses on the pressure. As diffusion increases at lower pressure, there is a greater demand for ionization, which lead to higher electron temperature.

Dependence on Power input and Power response.

Simulations have also been performed at a constant background pressure of $p = 3$ mbar for different input microwave power values of $P_{in} = 120, 300, 400, 800$ and
3.4. Results and Discussion

![Graph showing diffusion, ionization, and recombination frequencies against radial profile.]

Figure 3.8. (a) Generation and loss (diffusion and recombination frequency) of electron-ion pairs (b) the radial profile of electron density. The same conditions as Fig. 3.4 are used.

![Graph showing radial distribution for electron density at different pressure values.]

Figure 3.9. Radial distribution for the electron density at different pressure values.

1200 W, corresponding to the total power deposited in the plasma of $P_{dep} = 68, 142, 179, 296$ and 421 W, respectively. Figure 3.12 shows the electron density as
3. An argon plasma in a coaxial waveguide

![Graph](image1)

**Figure 3.10.** Radial distribution for the electron temperature at different pressure values.

A function of the input power. As the power increases from 120 to 1200 W, the electron density increases from \(2.3 \times 10^{18}\) to \(1.1 \times 10^{19}\) \((m^{-3})\). The higher input power leads to a higher power density and higher electron density values.

Note that the relative absorbed power, the ratio of absorbed power to input power is decreasing as shown in Fig. 3.11. That means the power coupling becomes less effective. This can be understood from the fact that when the electron density is enhanced, the length of penetration of microwave power in radial direction, will be diminished. The plasma becomes a better conductor.

![Graph](image2)

**Figure 3.11.** The relative absorbed power \(\frac{P_{\text{abs}}}{P_{\text{in}}}\) as a function of the input power \(P_{\text{in}}\).

As given in Fig. 3.13, we observe almost linear relation between deposited power and the maximum of electron density. This is consistent with [34,39,52].
3.4. Results and Discussion

Figure 3.12. Profile of electron density for different power input is shown.

Figure 3.13. The maximum electron density is linear with the absorbed power.

3.4.3 Comparison with Experiments

In order to validate the model, we have compared the numerical results with measurements. Thomson scattering was carried out by Hübner et al. [9] on a setup with the same geometry in order to measure the electron density and electron temperature. This active laser scattering technique provides local values of $n_e$ and $T_e$.

The difference between the experimental setup with the model setup is that the power supply used in experiment is self-modulated, whereas in the model continuous power is used. Moreover, the measurements reveal that the temporal power profile affects the $T_e$ profile, even though the electron density is almost constant at the pressure of 8 mbar. For more details we refer to [76–78].
In Fig. 3.14, we compare the calculated electron density in radial direction with experimental results, both at axial position of $z = 200 \text{ mm}$, 8 mbar and the same input power 400 W. We observe a similar contraction in the numerical results as in the measurements. However, there is a difference between the absolute values. The explanation is that the value of deposited power in the real system is unknown and most likely lower than in the simulation. Probably because of losses and reflections of the power before entering the plasma domain (e.g. the coupling into the coaxial structure). The linear relation of total deposited power with the maximum electron density in Fig. 3.13 predicts that a much smaller fraction of the power must be absorbed in reality.

![Graph showing modeled and experimental electron density comparison](image.png)

**Figure 3.14.** The calculated radial distribution of the electron density compared to experimental results, both at $z = 200 \text{ mm}$, 8 mbar and 400 W input power.

The second quantity measured by Thomson scattering is the electron temperature. In Fig. 3.15 values of the electron temperature at $z = 200 \text{ mm}$ for 8 mbar are shown of the measured and simulated profiles.

Although the agreement is fairly good, we clearly note an absolute difference. In order to explain this difference, we must take into account that in the experiment the power is always modulated due to uncontrollable self-pulsing of power supply and the discharge, whereas the model is limited to constant power. In this case, we should find the corresponding steady state situation from experimental outputs. We therefore propose to compare the effective production. So we define an effective continuous wave electron temperature along the pulse, $T_{e}^{cw}$ such that

$$\left\langle k_{\text{ion}}[T_{e}^{cw}] \right\rangle = \frac{1}{t_0} \int_0^{t_0} k_{\text{ion}}[T_e(t)]dt$$

(3.16)

where $t_0$ is the pulse duration, $k$ is the effective ionization rate coefficient, and $T_e(t)$ is the electron temperature measured along the pulse by TS and triggering.
3.4. Results and Discussion

Figure 3.15. The calculated and experimental radial distribution of the electron temperature. Same conditions as Fig. 3.14. The absolute difference can be explained by the power modulation in the experiment.

In the conditions described in this article, direct ionization is the dominant reaction for plasma production. Thus, this rate coefficient is used in Eq. (3.16) to obtain $T_{cw}$ at $r = 18 \text{ mm}$. This result is given in Fig. 3.15.

To make clear the procedure behind the calculation of $T_{cw}$, we refer to Fig. 3.16. In here, the time evolution of the electron temperature, $T_e(t)$, is shown as measured in the experimental setup. Its average value, $<T_e(t)>$, is also presented. Next, we define the temporal ionization frequency as $v_i(t) = N k_{ion}[T_e(t)]$, i.e. the gas density times the direct rate coefficient (i.e. R13 in Table 3.2) using $T_e(t)$ as input argument. Therefore, the average of $v_i(t)$, i.e., $<v_i(t)>$ is the effective plasma production frequency, which using Eq. (3.16) is related to $T_{cw}$ as

$<k_{ion}[T_{cw}]> = <v_i(t)> / N$.  \hspace{1cm} (3.17)

Then the value of $T_{cw}$ is derived from $<v_i(t)>$ for $r = 18 \text{ mm}$. We now see a good agreement between $T_e(cw)$ from experimental data and simulation.

### 3.4.4 Validity of the Model

**Flow**

The flow is neglected in agreement with the very low flow found in the real setup. Therefore, convection fluxes can be ignored with respect to diffusion fluxes. This assumption is valid if the temperature gradient is small enough to avoid any free convection phenomena.
Figure 3.16. Thomson scattering measurements of electron temperature during pulse duration, $T_e(t)$, and its average, $\langle T_e(t) \rangle$, calculated ionization frequency during pulse duration, $\nu_i(t) = \nu_i[T_e(t)]$, its average $\langle \nu_i(t) \rangle$, and the corresponding effective continuous wave electron temperature $T_{e\text{cw}}$.

Wall Temperature

It was not possible to determine the wall temperature $T_w$ experimentally due to the geometry of the set-up. Therefore we estimated the value of $T_w$ imposed at each wall. The most important value is at the quartz wall because next to it the plasma is more intense and more influenced by the value of $T_w$.

TM azimuthal symmetric

We assume TM azimuthal symmetry, because it is the minimum description needed to model a TM surface wave along the plasma and the TEM mode in the coaxial waveguide. A larger distance between the inner and outer conductor would be needed to excite non-symmetric higher order modes. Although this distance is different when plasma is considered, we restricted the model to TM modes.

Sheath and Resonance regions

The sheath region is neglected from our model (apart from using it implicitly in the definition of ambipolar diffusion). To include a sheath model would require modifications of the electromagnetic model and momentum equations for ions, e.g. by adding the Poisson equation (and corresponding ambipolar field); the description for the electromagnetic resonances; extend the electron momentum equation such that in can describe the sheath, thermal effects and a description of (quasi)electrostatic waves [79].
3.5. Conclusions

We computed the ratio of the ion-neutral mean free path $\lambda_{in}$ to the collisionless DC sheath thickness, $s$, obtaining maximum values along the wall of $\lambda_{in}/s \approx 4$. This shows that the sheath is mainly collisionless. To obtain $\lambda_{in}$, we used the averaged ion-neutral cross-section as obtained from [69]. The Child law is used when deriving the sheath thickness [80] as $s = (2\sqrt{2}/3)\lambda_d(V_p/T_e)^{4/3}$ with the Debye length $\lambda_d = \sqrt{\epsilon_0 k_B T_e/q_e n_e}$, and the plasma potential estimated as $V_p = 10\,V$. We found values of $10^{-5}\,m$ next to the quartz wall.

The boundary condition for the electron temperature at the wall is adiabatic i.e., $\frac{\partial T_e}{\partial r} = 0$, meaning we do not consider energy exchange of electrons with the sheath. The boundary condition for atomic and molecular ion densities is obtained from the speed of sound with a correction factor $\gamma$ [54]. We chose this factor such that a reasonable value for ion densities is obtained next to the wall (in agreement with experiment as shown in Fig.(3.14). As discussed in 3.4, the effect of the boundary condition for ions is limited to a region nearby the wall and does not propagate further into the volume. There the radial profile of ion density is ruled by the strong radial variation in production of ions and the recombination of them in the volume.

The value of $\gamma$ was also estimated to avoid the resonance region. In [10], a description of the resonance region was added to a 1D fluid model, showing already the difficulties of treating such a region.

Furthermore, a description of the sheath and resonance regions would require a finer grid for these regions, resulting in an increase of the computational cost of each simulation.

EEDF

The (effective) electron temperature is not defined as $2/3$ of the electron mean energy, but as the effective parameter that fulfill equations (3.2) and (3.5), in which a Maxwellian EEDF has been used to obtain the transport coefficients and rate coefficients. We are aware that the EEDF is not Maxwellian but most probably depleted in its tail as shown in [81] for pressure range of 6-20 mbar. This is more important with respect to the transport coefficients, such as the ambipolar diffusion, as they would depend mostly on the bulk of the EEDF, which is underestimated in the Maxwellian description [34].

The ratio $\omega/[(2m_e/m_i)\nu_{th}]$ is in the range $10^6 - 10^4$ which ensures that the EEDF is stationary with respect to the EM field modulation [82].

3.5 Conclusions

This paper presents and discuss a two dimensional model of a coaxial plasma waveguide. The model allows the study of wave plasma interaction and electron heat transport. It was found that electron heat transport in the coaxial discharge
is an important phenomena and much more important than in the surfatron; the reason is that the plasma radius is much larger.

Also a very strong inhomogeneity for ionization frequency is shown. This is an important characteristic that demonstrates a strong difference with the surfatron case in [52], where the electron temperature and the ionization frequency was approximately constant in the radial direction. The radial localization of electron density in coaxial plasma waveguides has been observed and compared to experimental data.

Moreover we found that these discharges show a self-protection against high energy coupling; for higher power levels the penetration of EM fields is more limited caused by the increasing conducting character of the plasma which obstructs further power absorption.

A parametric study revealed that the model can reproduce the trends that have been found experimentally. The results obtained with the model were compared with experimental values from Thomson scattering measurements, demonstrating a good agreement for electron density e.g. reproducing the radial localization toward the quart wall. For the electron temperature, the differences in absolute values were explained by the fact that the model uses continuous power whereas the experiment is in pulsing regime.
Chapter 4

A modeling study of low-pressure coaxial plasma waveguide: Hydrogen

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S Rahimi, M Jimenez-Diaz, S Hübner and J van Dijk. A two-dimensional model for coaxial hydrogen plasma waveguides. to be submitted
Abstract

A self-consistent two-dimensional model of the electromagnetic field and the non-LTE plasma for a hydrogen coaxial microwave plasma configuration has been developed. We demonstrate that the model prediction of plasma properties is strongly correlated to the estimation of atomic hydrogen wall recombination. Parametric studies of input power, pressure and H wall recombination probability give additional insight into ion/radical densities. The results are compared to experimental measurements that were done by means of optical emission spectroscopy, more specifically by the line ratios of atomic and molecular emission. Similar trends in model results and experimental outputs was found.

4.1 Introduction

Hydrogen plasmas are found in the universe in space plasmas such as planetary ionospheres, interstellar media, solar and stellar atmospheres and the solar wind. Moreover, hydrogen plasmas are widely used in technological applications such as material treatments and fusion research [83]. Hydrogen mixtures are extensively used in plasma-enhanced chemical vapor deposition (PECVD). For instance, it is common to use CH$_4$/H$_2$ or SiH$_4$/H$_2$ for production of diamond film or amorphous silicon films. As a more recent application for hydrogen mixtures, for deposition of graphene film, a mixture of C$_2$F$_6$/H$_2$ is used [84]. Another example is the production of crystallized germanium thin-films obtained from the deposition of germanium from a GeH$_4$/H$_2$ mixture [85]. In these deposition systems, atomic hydrogen is a key parameter in the growth of these materials [86,87]. Understanding of hydrogen plasmas is crucial for all of these applications.

The relative importance of the chemical reactions in hydrogen mixtures depends on the particular plasma conditions. Theoretical and experimental investigations have been done for H$_2$ plasmas but still many thing remain uncertain regarding the coupling between the plasma chemistry and the discharge dynamics, especially in the high frequency (HF) regime.

Discharges produced in different configurations have been investigated numerically. For example, in [88–90] the numerical description of radio frequency discharges is given. In [91] a low pressure hydrogen dc in a hollow cathode discharges studied by measurements and a zero-order kinetic model. The key physicochemical process in the plasma composition was determined.

Some numerical works already have been done for H$_2$ in microwave discharge [50,92,93]. In [50], a two dimensional fluid model for a microwave hydrogen discharge was developed. The model was used for the study of a microwave cavity reactor. Agreement with experimental measurements was obtained. A traveling wave discharge is modelled by a self consistent model in [93].
High plasma densities and deposition rates can be achieved by microwave plasmas. One configuration is the Plasmaline, that has been successfully used for surface passivation of solar cells [6] and for graphene film deposition [3]. This configuration in argon is investigated numerically in [10–12]. From the experimental point of view, the coaxial waveguide is studied extensively in [9].

The objective of this article is to produce a self-consistent model of microwave fields and the plasma discharge in a coaxial microwave hydrogen discharge.

To verify the model a comparison is made with experimental data. The numerical frame is based on a previous model of an argon coaxial microwave discharge Chapter 3 of this thesis. The aim of this work is to analyze the influence of the operating conditions on the plasma properties. This understanding can be used to improve the control of deposition in SiH$_4$/H$_2$ plasmaline. In Section 4.2 a short description of the model is presented. This is followed by a description of the plasma chemistry, the plasma-wall interaction, and the calculation of the transport coefficients. Results of the simulation are given and explained in Section 4.3. In Section 4.4, the modeling results are compared with experimental data and differences are discussed.

4.2 Model

The numerical model of the hydrogen coaxial plasma waveguide is constructed in the modeling platform Plasimo. The core of the physical model is composed of fluid and EM equations. These require as input the geometry of the setup, the input power, the boundary conditions, the chemical reaction rates and the transport coefficients.

The fluid model assumes a steady state description and consists of the reactions of positive and negative halogen ions following equations:

- The particle balance equations

$$\nabla \cdot \Gamma_s = S_s$$  \hspace{1cm} (4.1)

with $\Gamma_s$ the corresponding flux density and $S_s$ the net production of the species due to inelastic processes. The flux density equals $\Gamma_s = n_s v_s$, where $n_s$ is the number density of species $s$ and $v_s$ is the velocity of species $s$. Since we neglect the bulk flow velocity of the plasma, we rewrite the flux density as $\Gamma_s = -D_s \nabla n_s$. $D_s$ denotes the diffusion coefficients. By this assumption, the species balance becomes

$$-\nabla \cdot D_s \nabla n_s = S_s.$$  \hspace{1cm} (4.2)

This equation is solved for $s$ corresponding to species H, H$^+$, H$_2^+$, H$_3^+$ and H$_2$(v = 4). For neutral species i.e. H, and H$_2$(v = 4), we keep $D_s$ as the
effective diffusion coefficient (see Table 4.3 in Section 4.2.4), whereas for the ions i.e. H\(^{+}\), H\(_2\)^{+} and H\(_3\)^{+}, \(D_s\) is modified to become the corresponding ambipolar diffusion coefficients \(D_s^{+}\) (see again Table 4.3). The processes that give shape to sources \(S_s\) are treated in Section 4.2.2. The electron density is obtained from quasi-neutrality and the molecular hydrogen density is obtained from the ideal gas law.

• The energy balance for the heavy particles

\[
\nabla \cdot q_h = Q_{eh}^{\text{elas}} + Q_{hh}^{\text{inel}}.\tag{4.3}
\]

Here the heavy particle heat flux is defined as \(q_h = -\lambda_h \nabla T_h\), with \(\lambda_h\) the heavy particle thermal conductivity obtained from the mixture rules [57]. The term \(Q_{eh}\) denotes the energy loss through elastic collisions with electrons and can be written as

\[
Q_{eh}^{\text{elas}} = \sum_s \frac{2m_e}{m_s} n_e \nu_{es} \frac{3}{2} k_B (T_e - T_h).\tag{4.4}
\]

Here \(T_e\) is the electron temperature, \(T_h\) is the heavy particle temperature, \(nu_{es}\) is the frequency of elastic momentum transfer between electrons and species \(s\), \(m_e\) is the electron mass, \(m_s\) is the mass of species \(s\) and \(k_B\) is the Boltzmann constant. The term \(Q_{hh}\) refers to the energy gain or loss through inelastic collisions in which heavy particles are involved. We have assumed that the value of the ion temperature is equal to that of the gas temperature.

• The energy balance for the electrons

\[
\nabla \cdot q_e = Q_{ohm} - Q_{eh}^{\text{elas}} - Q_{eh}^{\text{inel}} - Q_{rad}.\tag{4.5}
\]

Here the conductive heat flux is defined as \(q_e = -\lambda_e \nabla T_e\), with the electron thermal conductivity \(\lambda_e\) obtained from the Frost mixture rules [58]. The term \(Q_{eh}^{\text{inel}}\) refers to the energy exchange between electrons and heavy particles through inelastic collisions, which can be expressed as

\[
Q_{eh}^{\text{inel}} = \sum_i R_i \Delta \epsilon_i\tag{4.6}
\]

where \(R_i\) is the reaction rate of process \(i\) and \(\Delta \epsilon_i\) is the average energy exchange per event.

The time-averaged absorbed power is given by

\[
Q_{ohm} = \frac{1}{2} \text{Re}(J^*E) = \frac{1}{2} \text{Re}(\delta |E|^2)\tag{4.7}
\]
4.2. Model

where Ohm’s law $\mathbf{J} = \sigma \mathbf{E}$ is used to relate the electron current density $\mathbf{J}$ to the harmonic electric field. $\mathbf{J}^*$ represents the complex conjugate of electron current density. The complex conductivity $\hat{\sigma}$ of the plasma is obtained from the current density $\mathbf{J} = \hat{\sigma} \mathbf{E} = -en_e \mathbf{v}_e$ and the cold collisional electron approximation of the electron momentum balance equation for harmonic fields [52, 59]. The Control Volume method is used to discretize the fluid equations.

The electromagnetic model is based on the Maxwell-Faraday and Maxwell-Ampere equations for harmonic fields.

\[
\nabla \times \mathbf{E} + k_0 \hat{\mathbf{H}} = 0, \quad (4.8)
\]

\[
\nabla \times \hat{\mathbf{H}} + k_0 \hat{\epsilon}_r \mathbf{E} = 0, \quad (4.9)
\]

where $k_0 = \omega \sqrt{\mu_0/\epsilon_0}$ is the vacuum wavenumber and $\hat{\epsilon}_r = \epsilon_r - i \frac{\omega}{\omega \epsilon_0}$ is the complex relative permittivity, with $\mu_0$ the permeability of free space (H/m) and $\epsilon_0$ the permittivity of free space (F/m). These equations are based on the assumption that the medium is isotropic, so the permeability and the permittivity are scalars. $\hat{\mathbf{H}}$ (in V/m) is linked to the magnetic field component $\mathbf{H}$ via $\hat{\mathbf{H}} = i \frac{1}{\sqrt{\mu_0/\epsilon_0}} \mathbf{H}$. We will further assume that the modes are Transverse Magnetic, TM, so that only $E_z$, $E_r$ and $H_\phi$ are non-null. For the quartz tube $\hat{\epsilon}_r = 4$, while for air $\hat{\epsilon}_r = 1$. For the discretization of Maxwell equations, Yee’s method is used [20].

4.2.1 Geometry

The computational domain of the coaxial linear microwave discharge is shown in Figure 4.1b. It simulates the real set-up given in Figure 4.1a. A metal rod is located in the center of the setup surrounded by a quartz tube filled with air at atmospheric pressure, which separates the plasma from the metal. In fact the plasma acts as an outer (non-perfect) conductor of a coaxial cable. The coaxial discharge is placed inside (along the axis of) a cylindrical metal vacuum chamber with windows.

In the computational domain only outer metal walls are included. An electromagnetic wave at a frequency of 2.45 GHz is directed into the setup carrying a power of $P_\text{in}$ and then propagates as surface wave along the interface between the plasma and the quartz tube. The azimuthally symmetric computational domain is $R_T = 100$ mm in radius and $Z_T = 500$ mm long. The inner conductor radius is $R_i = 3.65$ mm. The inner radius of the quartz tube is $R_o = 13$ mm and outer radius is $R_q = 15$ mm. The length of the quartz tube which is not shielded by any metal equals $Z_q = Z_p - Z_m = 420$ mm, where $Z_p$ is the plasma length. All metallic boundaries (walls and rod antenna) are treated as perfectly conducting material. Dimensions of the setup are given in Table 4.1.
Figure 4.1. a) Picture of the coaxial plasma line. b) Schematic of the computational domain for the coaxial plasma line. The excitation boundary condition is imposed at the left side of the coaxial waveguide \((z = 0, R_i < r < R_o)\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_T)</td>
<td>100 mm</td>
<td>(Z_T)</td>
<td>500 mm</td>
</tr>
<tr>
<td>(R_q)</td>
<td>15 mm</td>
<td>(Z_p)</td>
<td>420 mm</td>
</tr>
<tr>
<td>(R_o)</td>
<td>13 mm</td>
<td>(Z_q)</td>
<td>420 mm</td>
</tr>
<tr>
<td>(R_i)</td>
<td>3.65 mm</td>
<td>(Z_m)</td>
<td>40 mm</td>
</tr>
</tbody>
</table>

Table 4.1. Dimensions of the geometry in Plasmaline source.
4.2. Model

4.2.2 Chemistry

We assume that the hydrogen plasma consists of species H₂, H, H⁺, H₂⁺, H₃⁺, Hν=4. Vibrationally excited molecules are important for charge exchange. Since the energy difference of H⁺ and H₂⁺ is almost the same as the energy of vibrationally excited molecules in levels 4, the charge transfer is most likely occur with Hν=4. In the model Hν=4 are included. For this plasma, we assumed that we can neglect the higher vibrational state. Dissociative attachment of higher vibrational excited stated is the main process for creation of negative ion.

All these species, except electrons and H₂, are treated as transport sensitive species meaning that their densities are described by the corresponding particle balance equation. The electron density is obtained from quasi-neutrality and the H₂ density is obtained from the ideal gas law.

An overview of reactions is given in Table 4.2 together with the rate coefficients formulas and the corresponding references.

<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>H₂ + e ↔ H⁺ + 2e</td>
<td>1.58 × 10⁻¹⁴Tₑ⁻⁰·⁵ exp(−15.378/Tₑ) [94]</td>
</tr>
<tr>
<td>(2)</td>
<td>H₂ + e ↔ 2H + e</td>
<td>1.413 × 10⁻¹⁵Tₑ⁻⁰·⁷⁵ exp(−4.48/Tₑ) [94]</td>
</tr>
<tr>
<td>(3)</td>
<td>H + e → H⁺ + 2e</td>
<td>1.914 × 10⁻¹⁴Tₑ⁻⁰·⁷⁵ exp(−9.56/Tₑ) [94]</td>
</tr>
<tr>
<td>(4)</td>
<td>H⁺ + e → H⁺ + H + e</td>
<td>6.8 × 10⁻¹⁵Tₑ⁻¹·⁵ exp(−2.7/Tₑ) [94]</td>
</tr>
<tr>
<td>(5)</td>
<td>H₃⁺ + e → H₂ + H</td>
<td>9.7 × 10⁻¹⁴Tₑ⁻⁰·⁵ [13]</td>
</tr>
<tr>
<td>(6)</td>
<td>H₂⁺ + e → H⁺ + H</td>
<td>5.66 × 10⁻¹⁴Tₑ⁻⁰·⁵ [13]</td>
</tr>
<tr>
<td>(7)</td>
<td>H⁺ + e → H</td>
<td>2.62 × 10⁻¹⁹Tₑ⁻¹·⁵ [13]</td>
</tr>
<tr>
<td>(8)</td>
<td>H₂⁺ + H₂ → H₃⁺ + H</td>
<td>2.1 × 10⁻¹⁵ [95]</td>
</tr>
<tr>
<td>(9)</td>
<td>H₂ + H ↔ 3H</td>
<td>5.6 × 10⁻¹⁵Tₑ⁻⁰·⁴¹⁹ exp(−4.478/TₑH₂) [95]</td>
</tr>
<tr>
<td>(10)</td>
<td>H₂ + H₂ ↔ 2H + H₂</td>
<td>5.6 × 10⁻¹⁵Tₑ⁻⁰·⁴¹⁹ exp(−4.478/TₑH₂) [95]</td>
</tr>
<tr>
<td>(11)</td>
<td>H₂ + e ↔ Hν=⁴ + e</td>
<td>4.69 × 10⁻¹⁶Tₑ⁻¹·⁸²⁰² exp(−1.89/Tₑ) [95]</td>
</tr>
<tr>
<td>(12)</td>
<td>Hν=⁴ + H⁺ → H₃⁺ + H</td>
<td>2.5 × 10⁻¹⁵ [95]</td>
</tr>
</tbody>
</table>

Table 4.2. Reactions used for the hydrogen model. All rate coefficients k are expresses in (m³s⁻¹). The temperature Tₑ is in eV.

For the conditions of the present setup, wall recombination is found to be one of the main loss mechanisms of atomic hydrogen. Many measurements have been
carried out for hydrogen atom recombination on quartz [96–99]. It is worth noting that there is a great disparity in the literature values for the recombination probability of H on quartz walls. For $T_h = 500$ K, based on [99], $\gamma \approx 10^{-4}$ whereas according to [96] $\gamma \approx 10^{-3}$. Also for steel walls different values were reported. In [100] the value of $\gamma$ is estimated as function of wall temperature. From wall temperature of 1200 K to 400 K the H recombination probability is decreasing from 0.14 to 0.004. A much higher value of $\gamma = 0.2$ was reported in [101]. Tserepi and Miller [102] determined the the H recombination probability to be around 0.03-0.045. Because of this uncertainty in the H recombination probability in Section 4.3.2 we have performed several numerical tests to analyze the sensitivity of the H molar fraction with variation of recombination probability.

For $H_j^2 = 4$ wall recombination probability of 1 is chosen. For other wall reactions a probability of 1 is used supposing all ionic species are neutralized at the wall

\[
\begin{align*}
H^+ & \text{ wall } \rightarrow H, \\
H_2^+ & \text{ wall } \rightarrow H_2, \\
H_3^+ & \text{ wall } \rightarrow H_2 + H.
\end{align*}
\]

### 4.2.3 Boundary conditions

**In the fluid model**

For solving the plasma transport equations appropriate boundary conditions are needed. The gas temperature is set to prescribed values at the quartz and metal wall boundaries. For the electron temperature homogeneous Neumann boundary conditions are applied at each wall, as suggested in [52]. This means we assume no exchange of electron energy (i.e. adiabatic) with the sheath.

The flux of atomic and molecular ions, $s$, at the wall is modeled as [54]

\[
-D_s^+ \left( \frac{\partial n_s}{\partial r} \right) \bigg|_{r=R_p} = n_s v_{B,s}
\]

where $v_{B,s} = \sqrt{k_B T_e/m_s}$ is the Bohm velocity of ion $s$ [54]. Here $D_s^+$ is the ambipolar diffusion coefficient. As discussed in Chapter 3, the effect of this boundary condition on the plasma is limited to a small region next to the quartz wall, as long as it avoids the minimum values related with the resonance region and the maximum value expected in the volume. The effect of the boundary condition at the wall has been observed for the case of a coaxial positive column in [60], where for a ratio of 0.3 between the electron density at the wall to the maximum value, a maximum variation of 10% in $n_e$ is observed in the region next to the wall. This is valid until the electron density at the quartz wall is higher than critical density for resonance condition. The sheath region and resonance region are
neglected in this model. To include a sheath model would require modifications of the electromagnetic model and momentum equations for ions, e.g. by adding the Poisson equation (and corresponding ambipolar field); the description for the electromagnetic resonances; extend the electron momentum equation such that it can describe the sheath, thermal effects and a description of (quasi)electrostatic waves [79].

The boundary condition of neutrals which reacts at the surface is given by [54]:

$$-D_s \frac{\partial n_s}{\partial r} \Big|_{r=R_p} = \frac{1}{4} \gamma v_{th,s} n_s \Big|_{r=R_p} - R$$  \hspace{1cm} (4.11)

The first term here is responsible for loss of species $s$ due to surface recombination or deexcitation and second term $R$ shows possible production in recombination or deexcitation of the other species. In first term $v_{th,s} = \sqrt{8k_B T_e/m_s}$ is thermal velocity of neutral $s$ and $\gamma$ is defined as the wall recombination probability of neutral $s$. In this study for hydrogen atom the effect of changing $\gamma$ is investigated and for $\text{H}_2 (\nu = 4)$, it is set to 1. Here $D_s$ is the effective diffusion coefficient.

In the EM model

At the metal walls, the perfect electrical conductor (PEC) boundary condition is used [61], so that the component of the electric field tangential to the metallic surface is zero. The exciting boundary condition is used at the left side of the coaxial waveguide ($z = 0, R_i < r < R_o$). It consists of two boundary conditions, one applied to the incident wave that set the power entering in the domain and a propagation boundary condition (PBC) for the reflected wave [61,62].

At the right side of the coaxial waveguide ($z = Z_T, R_i < r < R_o$) an absorbing boundary condition [61,103] is used.

4.2.4 Transport Coefficients

For transport properties of the electrons (thermal conductivity and electrical conductivity) the Frost mixture rules [58] are used, whereas for heavy particle transport properties mixture rules of Mitchner and Kruger [57] are used. We refer to Table 4.3 for the corresponding references.

For the calculation of the transport coefficients, the following cross-section data are used. For elastic collisions between charged particles, the cross-sections are calculated with standard Coulomb theory. The interaction between neutral particles is modeled with the variable hard sphere model of Bird [68]. The interaction between ions and neutrals is described by the Langevin cross-section. Cross-section data for elastic interaction between electrons and neutrals, provided as look-up tables at various energies obtained from [104].
4. A hydrogen plasma in a coaxial waveguide

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Binary Diffusion</td>
<td>$D_{ij}$ ($m^2 s^{-1}$)</td>
<td>${e, h}$</td>
<td>$\frac{3}{16} \frac{f_{ij} k_B T_i T_j}{pm_{ij} \Omega_{ij}^{(1,1)}(T_{ij})}$</td>
<td>[56], [72], [73]</td>
</tr>
<tr>
<td>Effective Diffusion</td>
<td>$D_s$ ($m^2 s^{-1}$)</td>
<td>${e, h}$</td>
<td>$D_s = p \left( \frac{\sum_{j \neq s} p_s}{D_{sj}} \right)^{-1}$</td>
<td>[72]</td>
</tr>
<tr>
<td>Ambipolar Flow as Diffusion</td>
<td>$D_s^+$ ($m^2 s^{-1}$)</td>
<td>${h^+}$</td>
<td>$D_s (1 + T_e/T_h)$</td>
<td>[74]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$\lambda_h$ ($W K^{-1} m^{-1}$)</td>
<td>${e}$</td>
<td>Mitchner-Kruger</td>
<td>[57]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$\lambda_e$ ($W K^{-1} m^{-1}$)</td>
<td>$e$</td>
<td>Frost</td>
<td>[57]</td>
</tr>
</tbody>
</table>

Table 4.3. Transport coefficients in the model. Here, $f_{ij}$ is a correction factor of order unity, $m_{ij}$ the reduced mass, $T_i$, $T_j$, the temperature of the corresponding species, $\Omega_{ij}^{(1,1)}$, a collision integral (cf [73]), $T_{ij}$ an effective temperature, $E_{tr,s}$ translational energy per particle of species $s$, such that $E_{tr,s} n_s$ is the translational internal energy per unit volume, $p_s$ is the partial pressure of species $s$.

4.3 Results and Discussion

In Section 4.3.1 we present the two-dimensional simulation results. We continue with Section 4.3.2 where the effects of changing the pressure, input power and hydrogen recombination probability on the discharge properties studied.

4.3.1 Plasma Properties

The two dimensional distribution of absorbed power density and electron temperature, electron density and hydrogen atom molar fraction for the hydrogen discharges are shown in Figure 4.2. The gas pressure is 0.8 mbar and the input power for this simulation is 1500 W. Hydrogen recombination probability is set to $\gamma = 0.0001$ on quartz wall and fixed to $\gamma = 0.1$ on steel walls. Although power density as main source for plasma production is localized close to the quartz-plasma interface, the electron temperature profile is quite extended over the whole domain due to transport. The most important reactions for production of ions is electron impact ionization [see Table 4.2 Reactions (1) and (3)]. The corresponding primary ions are $H_2^+$ and $H^+$. Because of its strong dependency on the electron temperature we can find the maximum of ionization frequency close to the quartz wall. For the electron density loss there are two mechanism responsible, diffusion and wall recombination.

Hydrogen atoms are produced basically by electron impact dissociation of $H_2$ i.e. Reaction (2) in Table 4.2. Because of the strong dependency of dissociation rate on the electron temperature, the concentration of hydrogen atoms is higher
4.3. Results and Discussion

Figure 4.2. 2D distribution of the a) Power density, b) Hydrogen atom molar fraction, c) Electron density, d) Electron Temperature

close to the quartz-plasma interface. The loss mechanism for hydrogen atoms is the chain of diffusion and consecutive wall recombination.

4.3.2 Parametric Study

Dependence on Gas Pressure

We did a set of simulations for different values of the pressure, namely $p = 0.1$, $0.2$, $0.8$, $1.4$ and $2$ mbar with a fixed microwave input power of 1500 W. In Figure 4.3
the radial and axial distribution of electron density is shown. By increasing the pressure, the maximum of electron density is increased. Figure 4.3a shows a decrease of the axial gradient of electron density in lower pressure. This is a well known consequence of the dependency of the electron-neutral collision frequency on the pressure.

In Figure 4.4, we see that the electron temperature decreases for increasing pressure because of dependency of the diffusion losses on pressure. In higher pressure, the lower hydrogen atoms and electron losses lead to a lower electron temperature and consequently to a smaller production of ions and hydrogen atoms.

Figure 4.5 and Figure 4.6 show the absolute and relative concentrations of each ionic species along the discharge length for different pressures. In Figure 4.5 the axial distribution of the density of the different ionic species at a radial position of $r = 17$ mm is shown. The most important reactions for production of ions are electron impact ionization reactions. The positive ion $H_3^+$ is produced from $H_2^+$ by the interchange reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$, and not by electron collisions,
4.3. Results and Discussion

[see Reaction (8) in Table (4.2)]. This process has a very large rate coefficients and transforms the primary $H_2^+$ ions into $H_3^+$ with great efficiency through collisions with the $H_2$ molecules. Through this mechanism, $H_3^+$ builds up to a relatively high concentration. At higher pressure, because of the smaller mean free path, this reaction is more efficient. The loss of $H_3^+$ is mainly due to diffusion and recombination at the wall. As shown in Figure 4.5 $H_3^+$ is the dominant ion in the 0.1 - 2 mbar [see Section (4.3.2)]. The other major ion is $H^+$ which is mainly produced by electron impact of hydrogen atoms and it is lost by diffusion and wall recombination. $H^+$ becomes the dominant ion when there is a relatively high concentration of H atoms in the setup.

The last ionic species is $H_2^+$. It has a very low density because of its destruction by collisions with hydrogen molecules.

Figure 4.6 shows the relative density of the $H^+$ and $H_2^+$ decreases along the discharge length. This is a result of lower ionization efficiency due to the decrease of the electron density. At the other side, as can be seen in Figure 4.6, the relative
4. A hydrogen plasma in a coaxial waveguide

Concentration of $H_3^+$ is increasing. As it is mentioned before, $H_3^+$ is produced through the collisions of $H_2^+$ and $H_2$. With the decrease of the electron density along the discharge length, the efficiency of the dissociation decreases, leading to a decrease of the atom density and an increase of the density of molecular hydrogen.

Hydrogen atoms are produced basically by electron impact dissociation of $H_2$ and are lost in wall collisions where they recombine to $H_2$. For the same deposited power, the largest H atoms molar fraction appears at the lowest pressure. Figure 4.7 shows the H molar fraction for different pressures and the same input power $P_{\text{in}} = 1500W$. In this condition the deposited power decreased from 1227 W at 0.8 mbar to 965 W at 0.20 mbar. But as is shown in Figure 4.8, when the absorbed power is the same, the H atoms molar fraction increases by decreasing the pressure. For higher pressures, the decrease of $T_e$ causes a reduction in the dissociation rate coefficient, partially compensated by the increase in electron density. The main loss mechanisms for hydrogen atoms are wall recombination of hydrogen atoms in the wall and H atom diffusion. For this set of simulations values of $\gamma = 0.001$ for quartz and $\gamma = 0.1$ for steel are used for the recombination coefficients of H on quartz walls and on the steel wall.

![Figure 4.5](image-url)
4.3. Results and Discussion

Figure 4.6. Relative concentration of the ions species to total electron density in H₂ plasmas for different pressure a) 0.8 mbar b) 2 mbar.

Dependence on Input Power

Simulations have also been performed at a constant background pressure of \( p = 0.8 \) mbar for different input microwave power values of \( P_{in} = 1000, 1500, \) and 2400 W. Figure 4.9b shows the electron density as a function of the input power. As the power increases from 1000 to 2400 W, the electron density increases from \( 4 \times 10^{17} \) to \( 1.2 \times 10^{18} \) m\(^{-3} \). A higher input power leads to a higher power density and higher electron density values.

Due to the higher electron density the electron impact dissociation is more effective and the H molar fraction is increased by increasing the power.

We observe an almost linear relation between deposited power and both the maximum of electron density and the hydrogen molar fraction. This is consistent with [105].

As shown in Figure 4.10b by increasing the input power the ratio of absorbed power to input power is decreased. That means the power coupling becomes less
effective and the plasma becomes a better conductor [105]. As given also in Figure 4.10a, we observe an almost linear relation between the deposited power and the maximum of the electron and atomic hydrogen densities.

**Dependence on the hydrogen wall recombination probability**

This section analyses the influence of the H recombination probability on the dissociation degree and the ionization degree in the Plasmaline. As it is mentioned, we found different values for the H recombination probability at the quartz wall in literature. We did a set of simulations to study the effect of it on plasma properties. The pressure is set to 0.8 mbar and a microwave input power of 1500 W is used. When the recombination probability is changed from $\gamma = 0$ to $\gamma = 10^{-2}$ the value of H molar fraction decreases from around 9% to 7%. Moreover, as can be seen in Figure 4.11b maximum of electron density increased around 6%, be-
cause electron impact ionization of hydrogen atoms is more efficient than hydrogen molecules. Analysing these results shows that by changing \( \gamma \) from 0 to \( 10^{-2} \) for quartz walls the molar fraction and ion density vary around 2%.

We also investigated the effect of the H atom recombination probability on steel walls. Figure 4.12 shows the molar fraction at 0.8 mbar when the H recombination probability is varied from \( \gamma = 0 \) to \( \gamma = 0.1 \). The value of the H molar fraction is decreased from 20% up to 7% and the maximum of electron density is increased by about 30%.

The next results demonstrate the effect of H atom recombination on steel walls for a pressure of 0.1 mbar. As can be seen in Figure 4.13 the value of molar fraction in the absence of recombination on the wall increases up to more than 50%. The drastic changes that happen in lower pressure mainly arises from the fact that electron impact dissociation is less inhomogeneous compared to the case of higher pressure and even though the maximum of H atoms production takes place in the quartz-plasma interface, in the other part of setup it is still high.

Figure 4.8. Axial and radial distribution of H molar fraction for different pressure and same absorbed power \( P_{\text{abs}} \approx 1200\text{W} \)
The higher dissociation degree results in an increase in density of H⁺ compared to the other ion densities. Figure 4.14 shows the relative concentration of H⁺ for different γ for pressures of 0.80 mbar and 0.10 mbar. For both of these conditions (0.80 mbar and 0.10 mbar) the H⁺ ion fraction is increased significantly by
the lower recombination probability. For 0.80 mbar H$_3^+$ is still the dominant ion except in the absence of wall recombination. For the case of a pressure of 10 mbar, the density H$^+$ and H$_3^+$ are in the same order for the recombination probability of $\gamma = 0.5$, for smaller H wall recombination probability H$^+$ is the major ion.

In this section, the effect of recombination probability was studied for pressures of 0.80 mbar and 0.10 mbar. The change of $\gamma$ has a stronger impact on the H molar fraction and electron density at lower pressure than at higher pressures and for relatively small $\gamma$ at lower pressures H$^+$ is the dominant ion.

Overall, the outcome of this section emphasizes that the predict of the model depends strongly on the wall recombination probability. A comparatively high concentration of H atoms that was found in the experimental setup [see Section 4.4] is representative of a small wall recombination probability.
4. A HYDROGEN PLASMA IN A COAXIAL WAVEGUIDE

Figure 4.11. Axial and radial distribution of H molar fraction and electron density versus quartz wall recombination probability

4.4 Comparison with Experiments

Combined theoretical and experimental studies are needed in order to validate models and to identify key processes. To provide a first experimental validation of the hydrogen plasma, optical emission spectroscopy, more specifically line ratios of atomic and molecular emission such as $H\alpha$, $H\beta$ and $H_2(d)$ (Fulcher) are used [9]. With a combination of line ratios the electron temperature and density and the dissociation degree of hydrogen are estimated by a rate equation. The three unknown plasma quantities require at least three line ratios. Emission arising from the molecular versus emission from the atomic system provides the dissociation degree via the excitation cross sections. The electron density enters the rate balance via depopulation of the atomic $n = 4$ or higher states. This method is similar to the one described in [106] except that we introduce quenching of the atomic hydrogen states. It was found that in our high electron density conditions this is of importance.
The following rate balance for H($n > 2$) are used

$$\frac{\partial n_{H(n=x)}}{\partial t} = n_e n_H k_{1,x}(T_e) + n_e n_{H_2} k_{\text{diss}(x)}(T_e) - A_{x,2} n_{H(n=x)} - n_e n_{H(n=x)} k_{x,x+1}(T_e),$$

where the first term on the rhs is the electron excitation from ground state to state $x$ with the rate $k_{1,x}$, the second is molecular dissociation by electron impact creating H($n = x$) with the rate $k_{\text{diss}(x)}$, the third term is radiative loss and the last electron quenching. The latter can be best described by electron excitation to H($n = x + 1$). A similar balance can be written for the molecular excited state H$_2$(d)

$$\frac{\partial n_{H_2(d)}}{\partial t} = n_e n_{H_2} k_{X,d}(T_e) - A_{d,d} n_{H_2(d)},$$

where the first term on the rhs is the electron excitation from ground state X to state d with the rate $k_{X,d}$ and the second term is the radiative loss via the Fulcher
system. The electron quenching is neglected as no accurate rate coefficients are known. All other rates can be found in [94, 106]. Now, using these balances and the line intensities of $H_{n=3,4}$ and $H_2(d)$ results in a system of linear equations with three unknowns, i.e., electron temperature, density and the ratio of $H/H_2$. In Figure 4.15a, the comparison between experimental results and modelling outputs is made. In the model we used a value of $\gamma = 0.001$ for the quartz wall and $\gamma = 0.004$ for the steel wall. In Figure 4.15a we compare the calculated electron density in axial direction with the experimental results for different pressures. The simulation agrees within a factor of two with the measurements. Also the electron temperature in Figure 4.15b is in the right order, although the simulation at low pressure predicts higher values than the experiments. That might have two reasons, firstly the simulation describes a continuous wave(CW)-plasma, while a high-frequency modulation was found in the experiment. The power modulation leads to a lower average temperature, also seen in [105]. In addition, not all de-population mechanisms of the excited states are taken into account. For instance

**Figure 4.13.** Axial distribution of $H$ molar fraction and radial distribution of electron density versus steel wall recombination probability for $p = 10$ Pa
4.4. Comparison with Experiments

Figure 4.14. Axial and radial distribution of the relative density of H\(^+\) to the total ion density versus steel wall recombination probability for pressure of a) 0.8 mbar and b) 0.1 mbar

electron excitation from H\((n = 4)\) to \(n = 6\) and higher states might account in total to a similar quantity as excitation to H\((n = 5)\). As these collisional (de)excitation processes are more efficient for energetically higher states, an underestimation of the respective densities is the consequence. That can be generalized by stating that in a collisional plasma the line and the line-continuum ratios have the tendency to underestimate the electron temperature. Here, collisional depends on the respective state.

In contrast to the electron parameters, the atomic hydrogen molar fraction differs substantially. A discrepancy by a factor of 5 can be seen in Figure 4.15c. It was found that the fraction of power that is absorbed in the plasma is a function of the pressure. At a constant absorbed power the H-atom molar fraction is decreasing with higher pressure. However, that effect is compensated when the power density is also increased with the pressure and a more or less constant molar fraction of atomic hydrogen is found in the model. In addition, as it is found in [107, 108], the H dissociation degree is changed drastically by changes of wall temperature
that is found when comparing CW-plasma and pulsed power plasma. That influences H wall recombination probability. As was shown in Section 4.3.2 the model prediction is a strong function of the rather uncertain atomic hydrogen wall recombination. When a rather low recombination probability is applied on steel, a better agreement is obtained, especially, for lower pressure.

To summarize; in case the absorbed power is the same, experiments and model show very similar trends. The largest relative concentration of H atoms appears at the lowest pressure with the highest absorbed power. However, the absolute values between experiment and model have systematic differences. It is unclear to what extent this is due to issues in the experimental method, such that results are obtained via line-of-sight measurements and a simplified rate balance is used. Also the cross sections are usually not very well defined for the low electron energy range present in our plasma. In addition, from modeling point of view the following topics should be discussed:

• The model exhibits an uncertainty related to limited knowledge of the input parameters and rates, for instance the atomic hydrogen wall recombination probability.

• Moreover, in the model a simplification was made in the chemistry. The only vibrational excited state which was included in the model is H$_2$($\nu = 4$). This species is important for charge transfer. Also negative ions are neglected which are mainly produced in the dissociative attachment of molecular hydrogen.

• Fick diffusion description is used in this model. This description is valid in the case of a plasma ruled by a dominating background gas. In the hydrogen discharge when the H molar fraction is high a more sophisticated diffusion model is needed.

• Others restrictions and assumptions of this model are discussed in [105].

In order to verify the assumption of the model and to have a good estimation for H atoms wall recombination, further comparison of the model with other techniques is required. For instance by implementing mass spectroscopy. If the values of ionic species would be measured it would be possible to determine which value is more realistic. With the high density of atomic hydrogen and considering the high efficiency of electron impact of hydrogen atoms compared to molecules the dominant ion would be H$^+$. However model predicts H$_3^+$ as dominant ionic species in pressure higher than 0.2 mbar and comparatively high H wall recombination. If mass spectroscopy shows the same dominant ion species it would be clear that the experimental measurements overestimate the molar fractions. In spite of these assumptions and uncertainty in the data, the fact that the relative trends in model and experiment are in fair agreement, approves the described comparison.
4.5 Conclusions

A hydrogen coaxial microwave plasma configuration is investigated numerically by a 2D self-consistent electromagnetic model. $H_3^+$ is the dominant ion in the

Figure 4.15. Comparison of results from a 2D Plasimo simulation with experimental results from the line ratio method on the coaxial plasma line as function of axial position for different pressures at the radial distance of about 1 mm from the quartz tube.
ionic composition of the plasma for pressure higher than 0.20 mbar. For pressures below 0.1 mbar with a very small H atom wall recombination, $H^+$ was the major ion.

In this chapter, simulations of the coaxial plasma line in hydrogen were compared to optical emission spectroscopy measurements. Simulated values show a good agreement with experimental measurements. Using parametric study, it was shown that the model can reproduce the same trends as experimental measurements. The absolute values of electron temperature and electron density are in the same order. For the molar fraction we see similar trends, although there is a difference between absolute values. Comparison between modeling results with experimental output shows the important role played by the atomic wall recombination mechanism in plasma description.
CHAPTER 5

Silane-Hydrogen in Plasmaline: Towards a deposition reactor model
A self-consistent two-dimensional model of the electromagnetic field and the non-LTE plasma is used for investigation of a mixture of silane-hydrogen in coaxial microwave plasma configuration. A parametric studies is used to investigate the dependency of deposition rates and radicals densities as function of pressure. Also the dependency of deposition rate with power input is studied. Several numerical tests have been performed to analyze the sensitivity of deposition rate and radical densities with H wall recombination probability, branching ratio of dissociation of silane and the coefficients rate of SiH$_3$ H-abstraction.

5.1 Introduction

The deposition of hydrogenated amorphous silicon thin films has many applications such as solar cells, thin film transistor image sensors and printing arrays [109]. A typical method to deposit thin films of amorphous silicon (a-Si:H) is plasma enhanced chemical vapor deposition (PECVD). The first plasma deposition system for amorphous silicon was reported by Chittick et al. [110]. It was a radio-frequency discharge. The first solar cell based on hydrogenated amorphous silicon was developed in 1976 by Carlson et al. [111]. Although the principles of deposition has been studied extensively, the physical and chemical processes which take place during the deposition are exceedingly complicated. A lot of studies have been done for silane hydrogen deposition reactors where most carried out on rf and dc deposition systems. For instance in [13], a one dimensional model is developed for a mixture of silane-hydrogen-argon. Fluid models were used to study H$_2$/SiH$_4$ in [14,15].

In this chapter a self consistent model is used to study a coaxial microwave plasmaline which is applied for the deposition of solar cells. For example, it can be used in the deposition of amorphous silicon nitride passivation layers on crystalline silicon solar cells or a mixture of SiH$_4$/H$_2$ can be implemented for deposition of layers of amorphous silicon for solar cell. The quality of layers could be benefited from understanding the deposition process. The difficulty in optimizing material properties is the complexity of the silane-hydrogen discharge chemistry including volume reactions and plasma-wall interactions. Plasma models give insights into the physics, the chemistry and the deposition process and they can be used to provide a way to optimize the deposition process and the material properties.

The model is used to investigate the external parameters such as pressure and power and the discharge properties.
5.2 The Model

The numerical model of the hydrogen-silane coaxial plasma waveguide is constructed in the modeling platform, Plasimo. The core of the physical model is composed of fluid and EM equations. These require as input the geometry of the setup, the input power, the boundary conditions, the chemical reaction rates, and the transport coefficients.

The fluid model assumes a steady state description and consists of the following equations:

- The particle balance equations;
- the energy balance for the heavy particles;
- the energy balance for the electrons.

The Control Volume method is used to discretize the fluid equations. The electromagnetic model is based on the Maxwell-Faraday and Maxwell-Ampere equations for harmonic fields. For the discretization of Maxwell equations, Yee’s method has been applied. The configuration is identical to the one in chapter 4.

5.2.1 Chemistry

The model includes 40 reactions to account for the collisions between electrons, ions, molecules and radicals. Hydrogen and silane in this model were assumed as background gases. It is known that higher order silanes are formed. Disilane and Trisilane are included in plasma chemistry. Dissociation by electron impact of neutrals will create radicals. Dissociation of SiH$_4$ can create different radicals, the model includes SiH$_3$ and SiH$_2$. For dissociation of higher order silane, only Si$_2$H$_5$ is included in the plasma chemistry. For silane and hydrogen mixtures we consider the presence of H$^+$, H$_2^+$, H$_3^+$, SiH$_3^+$, SiH$_2^+$ for positive ions and SiH$_3^-$ for negative ions.

An overview of reactions is given in tables 5.1 and 5.2 together with the rate coefficients formulas and the corresponding references.

For ionic wall reactions a probability of 1 is used supposing all ionic species are neutralized at the wall.

\[
\begin{align*}
H^+ + \text{wall} & \rightarrow H \\
H_2^+ + \text{wall} & \rightarrow H_2 \\
H_3^+ + \text{wall} & \rightarrow H_2 + H \\
\text{SiH}_3^+ + \text{wall} & \rightarrow \text{SiH}_3 \\
\text{SiH}_2^+ + \text{wall} & \rightarrow \text{SiH}_2 \\
\text{SiH}_3^- + \text{wall} & \rightarrow \text{SiH}_3 + e
\end{align*}
\]
which has a large impact on the results. In this study, we have performed a set
chapter4, there is a large uncertainty for the hydrogen recombination probability
of $\beta$ of 0.26 for recombination probability of $\gamma$.

The surface sticking coefficient of $\text{SiH}_3$ is applied. Therefore, a loss probability
of 0.26 for $\text{SiH}_3$ is applied.

Because the structure of $\text{Si}_2\text{H}_5$ is similar to $\text{SiH}_3$ we have used the same values
of $\beta, \gamma$ and $s$.

We have taken the value of $s = \beta = 0.80$ for $\text{SiH}_2$. As we discussed in
chapter 4, there is a large uncertainty for the hydrogen recombination probability
which has a large impact on the results. In this study, we have performed a set

<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$\text{H}_2 + e \leftrightarrow \text{H}_2^* + 2e$</td>
<td>$1.58 \times 10^{-14} T_e^{0.5} \exp(-15.378/T_e)$       [94]</td>
</tr>
<tr>
<td>(2)</td>
<td>$\text{H}_2 + e \leftrightarrow 2\text{H} + e$</td>
<td>$1.413 \times 10^{-15} T_e^2 \exp(-4.48/T_e)$           [94]</td>
</tr>
<tr>
<td>(3)</td>
<td>$\text{H} + e \rightarrow \text{H}^* + 2e$</td>
<td>$1.914 \times 10^{-14} T_e^{0.758} \exp(-9.56/T_e)$     [94]</td>
</tr>
<tr>
<td>(4)</td>
<td>$\text{H}_2 + e \leftrightarrow \text{H}_2^*=4 + e$</td>
<td>$4.69 \times 10^{-16} T_e^{1.8202} \exp(-1.89/T_e)$     [95]</td>
</tr>
<tr>
<td>(5)</td>
<td>$\text{SiH}_4 + e \rightarrow e + \text{SiH}_3 + \text{H}$</td>
<td>$7.7 \times 10^{-13} T_e^{-1} \exp(-10.6/T_e)$       [112]</td>
</tr>
<tr>
<td>(6)</td>
<td>$\text{SiH}_4 + e \rightarrow e + \text{SiH}_2 + \text{H}_2$</td>
<td>$1.6 \times 10^{-13} T_e^{-1} \exp(-10.6/T_e)$       [112]</td>
</tr>
<tr>
<td>(7)</td>
<td>$\text{SiH}_4 + e \rightarrow 2e + \text{SiH}_3^+ + \text{H}$</td>
<td>$1.6 \times 10^{-13} T_e^{-1.3} \exp(-15.9/T_e)$      [112]</td>
</tr>
<tr>
<td>(8)</td>
<td>$\text{SiH}_4 + e \rightarrow 2e + \text{SiH}_2^+ + \text{H}_2$</td>
<td>$3.56 \times 10^{-13} T_e^{-1.2} \exp(-15.5/T_e)$      [112]</td>
</tr>
<tr>
<td>(9)</td>
<td>$\text{SiH}_4 + e \rightarrow 2e + \text{SiH}_3^-$</td>
<td>$2.5 \times 10^{-13}$                                  [13]</td>
</tr>
<tr>
<td>(10)</td>
<td>$\text{Si}_2\text{H}_6 + e \rightarrow \text{SiH}_3 + \text{SiH}_2 + \text{H} + e$</td>
<td>$3.72 \times 10^{-10}$                                  [13]</td>
</tr>
</tbody>
</table>

| Electron induced reactions included in the model. All rate coefficients $k$ are expresses in $(m^3 s^{-1})$. The temperature $T_e$ is in $eV$. |

The flux of atomic and molecular ions, $s$, at the wall is set as [54] to

$$-D_s^+ \left( \frac{\partial n_s}{\partial r} \right) \bigg|_{r=R_p} = n_s v_{B,s}$$  \hspace{1cm} (5.1)\

where $v_{B,s} = \sqrt{k_B T_e/m_s}$ is the Bohm velocity of ion $s$ [54] and $D_s^+$ is the ambipolar diffusion coefficient.

Plasma wall interaction of neutral particles is described by taking into account
the loss probability of a radical on the surface, which is the sum of sticking probability and the recombination probability. The loss probabilities of $\text{SiH}_3$ were measured by Perrin [113]. The surface sticking coefficient of $\text{SiH}_3$ is $s = 0.09$ and recombination probability of $\gamma = 0.17$ is calculated. Therefore, a loss probability of 0.26 for $\text{SiH}_3$ is applied.

Because the structure of $\text{Si}_2\text{H}_5$ is similar to $\text{SiH}_3$ we have used the same values
of $\beta, \gamma$ and $s$. 

We have taken the value of $s = \beta = 0.80$ for $\text{SiH}_2$. As we discussed in
chapter 4, there is a large uncertainty for the hydrogen recombination probability
which has a large impact on the results. In this study, we have performed a set
of simulations to analyse the sensitivity of the deposition rate with variation of hydrogen recombination probability. For $H_2(v = 4)$, recombination probability is set to 1.

The quality of the growing films depends on the percentage of different species contributing to the growth.

To implement the deposition model the following boundary condition is implemented on radicals:

<table>
<thead>
<tr>
<th>#</th>
<th>Process</th>
<th>Rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>$H_2 + H \leftrightarrow 3H$</td>
<td>$5.6 \times 10^{-15} T_{H_2}^{0.419} \exp(-4.478/T_{H_2})$ [95]</td>
</tr>
<tr>
<td>18</td>
<td>$H_2 + H_2 \leftrightarrow 2H + H_2$</td>
<td>$5.6 \times 10^{-15} T_{H_2}^{0.419} \exp(-4.478/T_{H_2})$ [95]</td>
</tr>
<tr>
<td>19</td>
<td>$SiH_4 + H \rightarrow H_2 + SiH_3$</td>
<td>$2.8 \times 10^{-17} \exp(-1250/T_h)$ [113]</td>
</tr>
<tr>
<td>20</td>
<td>$Si_2H_6 + H \rightarrow Si_2H_5 + H_2$</td>
<td>$1.6 \times 10^{-16} \exp(-1250/T_h)$ [113]</td>
</tr>
<tr>
<td>21</td>
<td>$Si_2H_6 + H \rightarrow SiH_3 + SiH_4$</td>
<td>$0.8 \times 10^{-16} \exp(-1250/T_h)$ [113]</td>
</tr>
<tr>
<td>22</td>
<td>$H_2 + SiH_2 \rightarrow SiH_4$</td>
<td>$3.0 \times 10^{-18} (1 - (1 + 2.3 \times 10^{-2} p_0)^{-1})$ [113]</td>
</tr>
<tr>
<td>23</td>
<td>$SiH_3 + H \rightarrow SiH_2 + H_2$</td>
<td>$5.0 \times 10^{-16}$ [114]</td>
</tr>
<tr>
<td>24</td>
<td>$SiH_3 + SiH_3 \rightarrow SiH_4 + SiH_2$</td>
<td>$1.0 \times 10^{-17}$ [113]</td>
</tr>
<tr>
<td>25</td>
<td>$SiH_4 + SiH_2 \rightarrow Si_2H_6$</td>
<td>$2.0 \times 10^{-16} (1 - (1 + 0.32 p_0)^{-1})$ [113]</td>
</tr>
<tr>
<td>26</td>
<td>$Si_2H_6 + SiH_2 \rightarrow Si_3H_8$</td>
<td>$4.2 \times 10^{-16} (1 - (1 + 0.33 p_0)^{-1})$ [113]</td>
</tr>
<tr>
<td>27</td>
<td>$Si_2H_5 + SiH_3 \rightarrow SiH_5 + SiH_2$</td>
<td>$1.5 \times 10^{-16}$ [113]</td>
</tr>
<tr>
<td>28</td>
<td>$Si_3H_8 + H \rightarrow Si_2H_5 + SiH_4$</td>
<td>$2.4 \times 10^{-17} \exp(-1250/T_h)$ [113]</td>
</tr>
<tr>
<td>29</td>
<td>$H_2^=^+ + H^+ \rightarrow H_2^+ + H$</td>
<td>$2.5 \times 10^{-15}$ [95]</td>
</tr>
<tr>
<td>30</td>
<td>$H_2^+ + H_2 \rightarrow H_3^+ + H$</td>
<td>$2.1 \times 10^{-15}$ [95]</td>
</tr>
<tr>
<td>31</td>
<td>$SiH_2^+ + SiH_4 \rightarrow SiH_3^+ + SiH_3$</td>
<td>$1.1 \times 10^{-15}$ [15]</td>
</tr>
<tr>
<td>32</td>
<td>$SiH_2^+ + H_2 \rightarrow SiH_3^+ + H$</td>
<td>$1.1 \times 10^{-15}$ [15]</td>
</tr>
<tr>
<td>33</td>
<td>$SiH_4 + H_3^+ \rightarrow SiH_3^+ + H_2 + H_2$</td>
<td>$5.16 \times 10^{-16}$ [15]</td>
</tr>
<tr>
<td>34</td>
<td>$SiH_4 + H_2^+ \rightarrow SiH_3^+ + H_2 + H$</td>
<td>$6.2 \times 10^{-16}$ [15]</td>
</tr>
<tr>
<td>35</td>
<td>$SiH_4 + H^+ \rightarrow SiH_3^+ + H_2$</td>
<td>$5 \times 10^{-16}$ [15]</td>
</tr>
<tr>
<td>36</td>
<td>$SiH_3^+ + SiH_3^+ \rightarrow SiH_3 + SiH_3$</td>
<td>$7.22 \times 10^{-12} (T_h/300)^{-0.5}$ [113]</td>
</tr>
<tr>
<td>37</td>
<td>$SiH_2^+ + SiH_3^- \rightarrow SiH_2 + SiH_3$</td>
<td>$7.10 \times 10^{-12} (T_h/300)^{-0.5}$ [113]</td>
</tr>
<tr>
<td>38</td>
<td>$H_3^+ + SiH_3^- \rightarrow H_2 + SiH_4$</td>
<td>$1.27 \times 10^{-12} (T_h/300)^{-0.5}$ [113]</td>
</tr>
<tr>
<td>39</td>
<td>$H_2^+ + SiH_3^- \rightarrow H_2 + SiH_3$</td>
<td>$8.76 \times 10^{-13} (T_h/300)^{-0.5}$ [113]</td>
</tr>
<tr>
<td>40</td>
<td>$H^+ + SiH_3^- \rightarrow SiH_4$</td>
<td>$4.51 \times 10^{-13} (T_h/300)^{-0.5}$ [113]</td>
</tr>
</tbody>
</table>

Table 5.2. Reactions involving heavy particles included in the model. All rate coefficients are express in ($m^3 s^{-1}$) and the pressure $p_0$ is in mbar.
5. The silane-hydrogen in a coaxial waveguide

<table>
<thead>
<tr>
<th>Species</th>
<th>$\gamma$</th>
<th>$s$</th>
<th>$\beta$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.004</td>
<td>0.1</td>
<td>0.004</td>
<td>[14,113]</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>0.17</td>
<td>0.09</td>
<td>0.26</td>
<td>[14,113]</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>0</td>
<td>0.8</td>
<td>0.8</td>
<td>[14,113]</td>
</tr>
<tr>
<td>Si$_2$H$_5$</td>
<td>0.17</td>
<td>0.09</td>
<td>0.26</td>
<td>[14,113]</td>
</tr>
</tbody>
</table>

Table 5.3. Wall reactions for neutrals which included in the model

$$\Gamma = -D_s \left( \frac{\partial n_s}{\partial r} \right) \bigg|_{r=R_p} = + \frac{1}{4} \beta v_{th,s} n_s \bigg|_{r=R_p} - R$$  \hspace{1cm} (5.2)

where $\Gamma$ is the flux of reactive species incident on the surface. The first term on the right-hand side is responsible for the loss of species $s$ due to surface recombination, deexcitation and sticking process and second term $R$ shows possible production by recombination or deexcitation of other species. In the first term $v_{th,s} = \sqrt{\frac{8k_B T_e}{m_s}}$ is thermal velocity of neutral $s$ and $\beta$ is defined as the wall loss probability of neutral $s$ which is equal to summation of $\gamma$ and $s$. In this study, we do not model the sticking process and the sticking coefficients are also treated as recombination probability. This adds more fluxes of neutrals into the plasma as the value of SiH$_4$ is significantly higher than the other silane product, we expect that this simplification would not cause a significant error in the results.

5.2.2 Deposition rate

The flux of the radical $j$ toward the surface, which leads to sticking of silicon atoms can be written as [14,114]:

$$\Gamma_j = s \Gamma = s n_j \left( \frac{v_{th_j}}{4} \right) \beta_j$$

and the deposition rate for radical $j$ can be expressed as,

$$\left( V_d \right)_j = \frac{\alpha_j \Gamma_j}{n_s}$$

where $n_s$ is the surface density of the film, and $\alpha_j$ is the stoichiometry of the radical $j$ in Si atoms ($\alpha_j = 1$ is for SiH$_3$ and SiH$_2$ and $\alpha_j = 2$ for Si$_2$H$_5$).

5.3 Results and Discussion

In section 5.3.1 we will present the results in two dimensions. We will continue with studying the effect of changing the pressure, input power and hydrogen recombination probability on plasma properties.
5.3. Results and Discussion

![Graph](image)

5.3.1 Plasma Properties

The background gases in this study are hydrogen, silane (around 1%) and disilane (around 0.01%). Figure 5.1a shows the distribution of \( \text{SiH}_4 \) density. Main channels for losing silane are electron dissociation and H abstraction. It also consumed in the electron impact ionization, \( \text{SiH}_2 \) insertion and some other reactions but the rate of them is much smaller. The electron dissociation creates figure 5.1b shows the distribution of \( \text{Si}_2\text{H}_6 \) density. \( \text{Si}_2\text{H}_6 \) is mainly formed by the \( \text{SiH}_2 \) insertion reaction with \( \text{SiH}_4 \).

The electron dissociation and H-abstraction creates the \( \text{SiH}_2 \), \( \text{SiH}_3 \) and \( \text{Si}_2\text{H}_5 \) radicals. In Figure 5.2a the density of \( \text{SiH}_3 \) in 2D for pressure of 0.20 mbar is shown. The density of \( \text{SiH}_3 \) has a maximum on the plasma-quartz interface where in this pressure most of the \( \text{SiH}_3 \) is formed by electron dissociation of \( \text{SiH}_3 \).

In figure 5.3 the density of \( \text{SiH}_3 \) in 2D for a pressure of 0.20 mbar and 0.8 mbar are compared. For pressure of 0.8 mbar, it can be seen that apart from the maximum next to the quartz-plasma interface, there is also a peak in the middle \( \text{SiH}_3 \) of the plasma volume. This peak is formed by the H-abstraction of \( \text{SiH}_4 \). The electron temperature and gas temperature profiles (Figure 5.4) show why H abstraction plays a more important role in higher pressures. The electron temperature at
0.20 mbar is more homogenous, which demonstrating that the SiH₃ production is relatively high in places further from the quartz tube. Hence, in the plasma volume even at the maximum of the gas temperature profile (where H abstraction has the highest rate coefficient) the SiH₃ production through electron impact dominates the SiH₃ production from H abstraction. But for 80 mbar and higher pressures, because of the very inhomogeneous electron temperature profile and also because of a higher gas temperature value, H abstraction starts to be important. The destruction of SiH₃ occurring through reaction with itself and reaction with H atoms.

In figure 5.4a, we see that the electron temperature decreases for increasing pressure. The explanation is that due to lower electron-neutral collision frequency, the energy transfer between electrons and neutrals is very ineffective. Therefore, electrons absorb a large amount of power but lose a low amount, resulting in high electron temperature. For higher pressures, the larger electron-neutral collision frequency increases elastic and inelastic collisions and leads to a lower electron temperature. Figure 5.4b shows that the gas temperature increases for increasing
5.3. Results and Discussion

Figure 5.3. 2D distribution of the a) SiH\textsubscript{3} density, b) SiH\textsubscript{2} density, c) Si\textsubscript{2}H\textsubscript{5} density for the pressure of 0.80 mbar.

pressure. Higher electron density in higher pressure lead to higher gas heating which results in the higher gas temperature.

In figures 5.5a and 5.5b the densities of SiH\textsubscript{3} and SiH\textsubscript{2} in radial direction for different pressures are shown. SiH\textsubscript{2} decreases with increasing pressure due to heavy particle collisions with silane and disilane producing higher order silane. At higher pressure because of the smaller mean free path, insertion of SiH\textsubscript{2} which, is leading to creation of higher order silanes, is more likely. This is the reason that figure 5.5c shows that Si\textsubscript{2}H\textsubscript{5} is increasing by increasing the pressure.

Figure 5.6 shows the density of ionic species for pressures of 0.2 mbar and 0.8 mbar. Silane ion (SiH\textsubscript{2}\textsuperscript{+} and SiH\textsubscript{3}\textsuperscript{+}) production with a threshold energy of 11.9 eV are more efficient compared to ionization of molecular hydrogen with threshold energy of 15.4 eV and of atomic hydrogen with a threshold energy of 13.6 eV. The dominant positive ion appears to be SiH\textsubscript{3}\textsuperscript{+} ions. H\textsuperscript{3}\textsuperscript{+} also has a high density because of a very low silane concentration and SiH\textsubscript{2}\textsuperscript{+}, H\textsuperscript{+}, H\textsuperscript{+} have negligible densities compared to SiH\textsubscript{3}\textsuperscript{+} and H\textsuperscript{3}\textsuperscript{+}.

The effect of pressure on the deposition rate

The first parameter to be studied in the deposition is the pressure. The influ-
5. The silane-hydrogen in a coaxial waveguide

The influence of the pressure on the deposition rate and contribution of each radical in the deposition process is demonstrated in figure 5.7. By increasing the pressure, the deposition rate is decreased. This is consistent with the measurements in [6].

The effect of H recombination probability on the deposition rate

Atomic hydrogen plays a fundamental role in the hydrogen-silane mixture, because the H-abstraction processes are important for the creation of radicals. Furthermore, atomic hydrogen is produced in many electron impact reactions. As was shown in the previous chapter, plasma properties correlated to the estimation of atomic hydrogen in wall recombination. In this section, we will check

Figure 5.4. Radial distribution electron temperature and gas temperature for different pressure.
5.3. Results and Discussion

![Graphs showing radial distribution of radical species densities for different pressures.](image)

**Figure 5.5.** Radial distribution of radical species densities for different pressures.
the effect of the H recombination probability on the steel walls on the deposition rate. Figure 5.8 shows that the deposition rate for 20 mbar and 80 mbar for a recombination probability decrease of 0.004. We can see the changes that happen in deposition rate and in contribution of each radical in deposition rate by comparing Figure 5.8b with Figure 5.7d and Figure 5.8a with Figure 5.7c. For both pressures the deposition rates are increase significantly and contribution of all radicals, especially SiH\textsubscript{3} and SiH\textsubscript{2} also increase. As we have shown in chapter 4 the atomic hydrogen density depends strongly on the wall recombination probability. By increasing the hydrogen atom density the rate of H-abstraction reactions increases which it will result in a higher production of reactive species SiH\textsubscript{3} and Si2H\textsubscript{5}. Especially because of a higher density of SiH\textsubscript{4} the production rate of SiH\textsubscript{3} is increased. The SiH\textsubscript{3} radicals destructed to SiH\textsubscript{2} through two channels (i.e, SiH\textsubscript{3} + SiH\textsubscript{3} → SiH\textsubscript{4} + SiH\textsubscript{2} and SiH\textsubscript{3} + H → H\textsubscript{2} + SiH\textsubscript{2}). for the latter
5.3. Results and Discussion

Figure 5.7. The contribution of different radicals in deposition rate for pressures of a)2 mbar, b)1.5 mbar, c)0.8 mbar and d)0.2 mbar is shown.

we choose the rate coefficient of \( k = 5 \times 10^{-10} \) which is relatively high and we will discuss the rate of this reaction in the section 5.3.1. Moreover, the change of deposition rate is higher at 0.2 mbar rather than 0.8 mbar. As we show in chapter 4 the change of \( \gamma \) has a stronger impact on the H molar fraction and electron density for lower pressure than for higher pressure.

In summary, modeling shows that the hydrogen-wall recombination probability plays an important role for achieving high deposition rates. This can be used for optimizing the deposited layer but requires further investigation about surface processes. We bring your attention to the fact that, in [115], it was shown that H wall recombination is a function of operating condition.

The sensitivity study of the rate of \( \text{SiH}_3 + \text{H} \) on the deposition rate
In figures 5.7 and 5.8 we observe that the SiH$_3$ has small and almost constant contribution to the growth rate. As the production of SiH$_3$ has a high rate in electron dissociation of silane and H abstraction it shows as that the chosen rate of loss mechanism for this radical is so high. Two loss processes for SiH$_3$ are present through collisions of this radical with itself (i.e, SiH$_3$ + SiH$_3$) and with hydrogen (i.e, SiH$_3$ + H). As the silane mixture is strongly diluted with hydrogen the second reaction is very important for destruction of this radical. For this reaction like most of the other reactions in silane mixtures, there are significant discrepancies in data from different literature sources. For instance, in [114] the value of $k = 5 \times 10^{-10}$ cm$^3$s$^{-1}$ is used and in [13] the value of $k = 1 \times 10^{-10}$ cm$^3$s$^{-1}$, while in [113] rate coefficient of this reaction is introduced as $k = 2 \times 10^{-10}$ cm$^3$s$^{-1}$. For the results of previous sections the value of $k = 5 \times 10^{-10}$ cm$^3$s$^{-1}$ is used which is
5.3. Results and Discussion

![Graph](image)

**Figure 5.9.** Densities of different radicals versus different rate coefficients for reaction between SiH$_3$ and atomic hydrogen.

relatively high value and based on the densities of the radicals we can see that most of the produced SiH$_3$ are transformed to SiH$_2$. Increasing the density of SiH$_2$ leads to higher production of higher order silane and consequently higher order radicals which is in our case Si$_2$H$_5$. In order to see the effect of this rate coefficient on the distribution of different radicals and deposition rates we start a new simulation for pressures of 0.8 mbar and 0.2 mbar with a rate coefficient of $k = 1 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$ for the reaction SiH$_3$ + H. Figure 5.9 shows the densities of the different radicals for the new chemistry condition. By comparing the radical density for equivalent pressure in Figure 5.5 we can see the significant increase of SiH$_3$, however, the density of SiH$_2$ is decreased slightly.
The effect of deposited power on the deposition rate

The increase of power is combined by an increase of the deposition rate. The contribution of each radical remains almost constant. As we have shown for argon and hydrogen, by increasing the power the maximum of electron density is increased and this increases the rate of electron impact reaction of background gas which leads to more production of reactive species, including atomic hydrogen. Increase of atomic hydrogen also make H-abstraction of SiH$_4$ and Si$_2$H$_6$ more efficient so the total growth rate has an almost linear relation with the deposited power.

Figure 5.10. Deposition rate and contribution of each particles for different input power: a) input power 1500 W, b) input power 2400 W, c) input power 3000 W. d) shows the total deposition rate for $P_{in} = 1500, 2400, 3000$ W.

Although the growth rate and production of radicals have been increased by increasing the power, we should keep in mind that by increasing the power which means increasing of electron density, the energy coupling between plasma and microwave becomes less efficient.
The effect of branching ratio

One of the important uncertainty in silane chemistry is related to the branching ratio for electron-impact dissociation of $\text{SiH}_4$ into radicals. In [116], based on modeling results, it is concluded that the branching ratio of dissociation of $\text{SiH}_4$ into $\text{SiH}_3$ must exceed 80%. A ratio of 83:17 for $\text{SiH}_2 : \text{SiH}_3$ was reported in [117]. Janev [118] suggested the branching ratio of 46:26:15:13 for $\text{SiH}_3 : \text{SiH}_2 : \text{SiH} : \text{Si}$. In figure 5.11 we present the effect of variation of branching ratio from 83:17 to 17:83 for $\text{SiH}_2 : \text{SiH}_3$ on the radical densities and deposition rate. Changing the branching ratio results in an increase in $\text{SiH}_2$ density and a reduction in $\text{SiH}_3$ density. As we discussed in section 5.3.1, a higher value of $\text{SiH}_2$ lead to more production of higher order silane and decreased amount of reactive species. Because $\text{SiH}_2$ has a very high sticking coefficients, its density does not affect much the deposited substrate by changing the branching ratio of electron impact dissociation.

Based on this figure 5.11, we can say that changing the branching ratio does not affect the deposition rates strongly.

5.4 Conclusion

A self-consistent model has been used to describe hydrogen silane mixture in Plasmaline. Using the model, the relation between external parameters and plasma properties and deposited layer was investigated. The results of this study can be used as a useful tool for optimizing the deposition parameters. The model predicts a reduction in the deposition rate with increasing pressure. The model shows that there is a strong dependency between deposition rate and hydrogen wall recombination. It emphasis on the importance of surface process on the deposition layer and quality of the layer. The input power leads to an increase of deposition rate.
Figure 5.11. Radical densities study for different branching ratio for silane dissociation. The value of a) 17% and b) 83% for SiH$_3$ is used. c) the total deposition rate is compared for conditions (a) and (b).
Chapter 6

A Comparison of Stefan-Maxwell’s and Fick’s Diffusion Models
Abstract

In this chapter, a comparison between Fick’s and Stefan-Maxwell’s diffusion models is presented. It is demonstrated analytically and numerically, that in the plasma which is ruled by dominant background gas, dominant ion species and with the small temperature gradients, the multicomponent diffusion model based on Stefan-Maxwell equations reduces to the Fick’s diffusion model.

6.1 Introduction

A very important part for modeling of plasma is diffusion. One of the commonly used description is Fick diffusion model. This description is valid in the case of binary and dilute mixtures when the plasma ruled by a dominating background gas.

In order to describe more complex mixtures, without dominating background species, multi-ion mixtures or with significant temperature gradients, a more complete description of diffusion is necessary. For instance a Stefan-Maxwell diffusion model presented in [17, 119]. In this model, the diffusive flux of species depends not only on its concentration gradient but also on the concentration gradients of other species. The model solves a coupled set of continuity equations for all species in which the diffusive fluxes are described by matrix. In one recent work [17] the finite volume discretization schemes is used.

This chapter is devoted to comparison of Fick and Stefan-Maxwell diffusion model in case of a very simple chemistry. It is shown analytically and it is confirmed numerically that for a dominant background gas when the gradient of temperature is small the multicomponent diffusion model gives the same results as Fick’s model.

6.2 Multi component diffusion model

6.2.1 Multi component diffusion model in neutral mixtures

The theory and implementation of this model is explained in detail in [17]. The multi-component mixture model is based on the continuity equation for the different species. The continuity equation for species $i$, expressed in terms of the species mass fraction $(y_i)$, can be written as:

$$\frac{\partial}{\partial t} (\rho y_i) + \nabla . (\rho \mathbf{v} y_i) + \nabla . (\rho \mathbf{v}_i y_i) = m_i \omega_i, \quad (6.1)$$

where $\rho$ is the mass density $\mathbf{v}$ the mass average velocity of the plasma, $\mathbf{v}_i$ the diffusion velocity and $m_i \omega_i$ is the mass production rate per unit volume. The
diffusion velocity \( v_i \) is defined as the velocity of species \( i \) with respect to the mass average velocity.

\[
v_i = u_i - v.
\] (6.2)

Mass conservation constraint implies that:

\[
\sum_i y_i = 1.
\] (6.3)

As a result of these definitions no net mass is transported by the sum of diffusive fluxes:

\[
\sum_i y_i v_i = 0.
\] (6.4)

Since no net mass is produced in reactions:

\[
\sum_i m_i \omega_i = 0.
\] (6.5)

To close equation 6.1 calculation for diffusion velocities of the species are required and to solve it for the species mass fraction, an expression for diffusive mass fluxes in terms of the gradients of the mass fraction is needed. Starting from the Stefan-Maxwell equations, the diffusion flux will be expressed in terms of the gradients of the mass fractions.

\[
\frac{\partial}{\partial t} (\rho y_i) + \nabla \cdot (\rho v y_i) + \nabla \cdot \left( \sum_j \Gamma_{ij} \nabla y_j \right) = 0.
\] (6.6)

Where the coefficients \( \Gamma_{ij} \) denote the elements of the flux diffusion matrix \( \Gamma \), which express the diffusive mass fluxes in terms of the gradients of the mass fractions.

The diffusion velocities are described by Stefan-Maxwell equations, i.e.,

\[
\sum_j F_{ij} v_j = -d_i \quad \Leftrightarrow \quad Fv = -d;
\] (6.7)

where \( F = F_{ij} \) is the friction matrix, \( v \) is the vector of diffusive velocities and \( d = d_i \) is the driving force for species \( i \). In order to keep the discussion as simple as possible only concentration force is taken into account:

\[
d_i = \nabla z_i,
\] (6.8)

where \( z_i = \frac{p_i}{p} \) is the partial pressure with \( p \) as the total pressure. \( f_{ij} \) is the mutual friction coefficient between species \( i \) and \( j \), which can be expressed as:

\[
f_{ij} = \frac{z_i z_j}{D_{ij}} \quad f_{ii} = 0,
\] (6.9)
6. A Comparison of Stefan-Maxwell’s and Fick’s Diffusion Models

with $D_{ij}$ the usual binary diffusion coefficients. Elements of $F_{ij}$ is given by

$$F_{ij} = \begin{cases} \sum_k f_{ik} & \text{if } i = j \\ -f_{ij} & \text{if } i \neq j \end{cases}$$

The matrix $\mathbf{F}$ is singular and does not have an inverse. We can calculate regularized matrices by adding a matrix $\alpha \mathbf{y} \otimes \mathbf{y}$. $\mathbf{y} \otimes \mathbf{y} = \mathbf{yy}^T$ is the dyadic product.

$$\tilde{\mathbf{F}} = \mathbf{F} + \alpha \mathbf{y} \otimes \mathbf{y},$$

where $\alpha$ is a free, positive parameter. In order to invert $\tilde{\mathbf{F}}$, $\alpha$ has to be chosen appropriately. An appropriate choice for $\alpha$ is

$$\alpha = \frac{1}{\max(D_{ij})},$$

(6.10)

since it guarantees that the elements of the matrices $\mathbf{F}$ and $\alpha \mathbf{y} \otimes \mathbf{y}$ have the same order of magnitude. After regularization of $\mathbf{F}$ and based on mass fraction constraint the Stefan-Maxwell equations become

$$\tilde{\mathbf{F}} \mathbf{v} = -\mathbf{d} \quad \Leftrightarrow \quad \sum_j \tilde{F}_{ij}v_j = -d_i;$$

(6.11)

where $\tilde{F}_{ij}$ are elements of $\tilde{\mathbf{F}} = \mathbf{F} + \alpha \mathbf{y} \otimes \mathbf{y}$.

Since the continuity equations are solved for the mass fraction $y_i$ of the species, the driving force $d_i$ will be calculated in terms of the mass fraction.

The relation between the partial pressure and mass fraction is given by

$$z_i = \frac{p_i}{p} = \frac{n_i k T_i}{\sum_j n_j k T_j} = \frac{y_i T_i / m_i}{\sum_j y_j T_j / m_j},$$

(6.12)

where $m_i$ is the mass of species $i$ and $T_i$ is the temperature of species $i$.

By taking the gradient of expression 6.12, the gradients of the partial pressure and mass fraction are related by matrix $\mathbf{M}$:

$$\nabla z_i = \sum_j M_{ij} \nabla y_i,$$

(6.13)

where

$$\mathbf{M} = \text{diag}(\mathbf{z}) \ (\mathbf{I} - \mathbf{u} \otimes \mathbf{z}) \ \text{diag}^{-1}(\mathbf{y}),$$

(6.14)

where $\mathbf{u} = (1, \cdots, 1)^T$. Determining $\nabla z_i$ from this expression will give a singular result. Regularization can be achieved similar to the strategy presented in [17] for molar fraction to mass fraction conversion.

To eliminate the singularity of $\mathbf{M}$, we adopt a relation between partial pressure and mass fraction similar to [17,119]:
6.2. Multi component diffusion model

\[ z_i = \frac{\sigma^m y_i T_i}{m_i} \sum_j y_j T_j / m_j = \sigma^m w y_i T_i / m_i, \quad 1/w = \sum_j y_j T_j / m_j. \] (6.15)

we used \( \sigma^m = \sum_i y_i \).

Determining \( \nabla z_i \) now gives:

\[
\nabla z_i = \frac{\sigma^m w T_i}{m_i} \nabla y_i + \frac{w T_i y_i}{m_i} \nabla \sigma + \frac{\sigma^m w y_i}{m_i} \nabla T_i + \frac{\sigma^m T_i y_i}{m_i} \nabla w. \] (6.16)

Substituting the expressions for \( \nabla \sigma \) and \( \nabla w \) results in:

\[
\nabla z_i = \frac{\sigma^m w T_i}{m_i} \nabla y_i + \frac{w T_i y_i}{m_i} \sum_j \nabla y_j + \frac{\sigma^m T_i y_i}{m_i} \nabla \sigma + \frac{\sigma^m w y_i}{m_i} \nabla T_i - \frac{\sigma^m T_i y_i w^2}{m_i} \sum_j y_j / m_j \nabla T_j. \] (6.17)

When temperature gradients are ignored, the expressions for the conversion matrix \( \tilde{M} \) become:

\[ \tilde{M} = \text{diag}(z) + \frac{z \otimes (y-z)}{\langle z, u \rangle} \text{diag}^{-1}(y). \] (6.18)

The new matrix elements \( \tilde{M}_{ij} \) are given by

\[
\tilde{M}_{ij} = \begin{cases} \sigma u T_i / m_i + u (y_i T_i / m_i - z_i T_j / m_j) & \text{if } i = j, \\ u (y_i T_i / m_i - z_i T_j / m_j) & \text{if } i \neq j. \end{cases} \] (6.19)

Then we introduce matrix \( \tilde{D} = \tilde{F}^{-1} \). Based on calculation of \( \tilde{F}^{-1} \) the diffusion velocities can be expressed as:

\[ v_i = \sum_j \tilde{D}_{ij} \sum_k \tilde{M}_{jk} \nabla y_k, \] (6.20)

in final step diffusive flux defined as:

\[ J_i = \rho y_i v_i = \rho y_i \sum_j \tilde{D}_{ij} \sum_k \tilde{M}_{jk} \nabla y_k, \] (6.21)

\[ J_i = -\sum_j \Gamma_{ij} \nabla y_j, \] (6.22)

if we define \( R = \text{diag}(\rho y_i) \) then the flux diffusion matrix can be expressed as:

\[ \Gamma = R \tilde{D} \tilde{M}. \] (6.23)
6. A Comparison of Stefan-Maxwell’s and Fick’s Diffusion Models

6.2.2 Ambipolar Diffusion

In this part diffusion model is extended to a mixture of electrons and ions. In the presence of charged particles, the interaction among charged particles affects their diffusion flux, enhancing the diffusion of heavier and slower ions while slowing the lighter and faster electrons.

The assumption of an ambipolar plasma puts an extra constraint which is the current constraint.

\[ j = \sum_i n_i q_i v_i = 0 \iff <s, v> = 0, \quad (6.24) \]

where \( s = (n_1 q_1, \ldots, n_n q_n)^T \). Because of that, besides the pressure gradients, ambipolar electric field is also taken into account. In the presence of the ambipolar electric field, the diffusion driving force is given by:

\[ \mathbf{d}_i = -\nabla z_i + s \mathbf{E}_{amb} / p, \quad (6.25) \]

substitution of the driving force in 6.11 yields:

\[ \mathbf{v} = -D(\nabla z_i - s \mathbf{E}_{amb} / p), \quad (6.26) \]

where \( <a, b> = \sum_i a_i b_i \) defines as inner product. By taking the inner product of 6.26 with \( s \), the ambipolar field is obtained as:

\[ <s, v> = 0 \iff \mathbf{E}_{amb} / p = <s, D\partial z>, \quad (6.27) \]

by substitution of 6.27 in 6.26 we can get an expression for the ambipolar diffusion matrix \( \hat{D} \):

\[ \mathbf{v} = -\left( D - \frac{Ds \otimes Ds}{<s, Ds>} \right) \frac{\nabla p}{p} = -\hat{D} \partial z, \quad (6.28) \]

\( s \) and \( y \) are in the nullspace of this matrix which means that \( \hat{D} \) is a singular matrix. As it is mentioned before, a way to remove non-singularity is to add diffusive terms. A strategy for regularization of this matrix was presented in [17]:

\[ \overline{\hat{D}} = \left( D - \frac{Ds \otimes Ds}{<s, Ds>} - \beta \mathbf{u} \otimes \mathbf{u} + \gamma \mathbf{r} \otimes \mathbf{r} \right), \quad (6.29) \]

with \( \mathbf{r} = (q_1 / m_1, \ldots, q_n / m_n)^T \). The coefficient \( \gamma \) similar to \( \beta \) is a positive parameter. In order to keep the elements in the same order of \( \hat{D} \), \( \gamma \) is chosen as:

\[ \gamma = \frac{<\mathbf{Dr}, \mathbf{r}>^2}{<\mathbf{r}, \mathbf{r}>^2}. \quad (6.30) \]
6.2. Multi component diffusion model

For simplicity we assume that \( \tilde{M} \) is equal to the case in the absence of ambipolar electric field [see equation 6.18]. Then we can define the flux diffusion matrix in the presence of ambipolar field as:

\[
\Gamma = R \left( D - \frac{Ds \otimes Dz}{<s, Ds>} - \beta u \otimes u + \gamma r \otimes r \right) \tilde{M}. \tag{6.31}
\]

6.2.3 Fick and Stefan-Maxwell

Now, we will show that in binary and dilute mixtures when plasma ruled by dominant ions, the multicomponent diffusion formalism will reduce to the ambipolar case in Fick’s law. For showing this we consider a plasma mixture with three species: neutral, ions and electrons. The neutrals form the dominant background. The first species is the neutral one and there are three friction coefficients, \( f_{1+}, f_{1e}, f_{+e} \). As the density of neutral is much higher than charged particle we can neglect the \( f_{+e} \). Friction coefficients are given by

\[
f_{1+} = z_{1+} z_{+} D_{1+} \quad \text{and} \quad f_{1e} = \frac{z_{1e} z_{e} D_{1e}}{f_{1e}}.
\]

\[
\tilde{F} = \begin{pmatrix}
    f_{1+} + f_{1e} + a y_{1} y_{1} & -f_{1+} + a y_{1} y_{+} & -f_{1e} + a y_{1} y_{e} \\
    -f_{1+} + a y_{1} y_{+} & f_{1+} + a y_{+} y_{+} & a y_{+} y_{e} \\
    -f_{1e} + a y_{1} y_{e} & a y_{+} y_{e} & f_{1e} + a y_{e} y_{e}
\end{pmatrix}.
\]

Inversion of this matrix by neglecting of quadratic terms in \( y_{+} \) and \( y_{e} \) yields to:

\[
D = \tilde{F}^{-1} - \frac{1}{\alpha} u \otimes u = \begin{pmatrix}
    0 & -\frac{y_{1} y_{+}}{f_{1+}} & -\frac{y_{1} y_{e}}{f_{1e}} \\
    0 & -\frac{y_{1}^{2}}{f_{1+}} & 0 \\
    0 & 0 & -\frac{y_{e}^{2}}{f_{1e}}
\end{pmatrix}.
\]

If we calculate the second species mass fluxes without considering ambipolar field based on \( J = RD\partial z \):

\[
J_{2} = -\frac{\rho y_{1}^{2}}{f_{1+}} y_{+} \partial z_{+}.
\]

The mass fluxes in presence of ambipolar field are given by:

\[
J = RD \left( I - \frac{s \otimes Ds}{<s, Ds>} \right) \partial z, \quad \tag{6.32}
\]

\[
\left( I - \frac{s \otimes Ds}{<s, Ds>} \right) = \begin{pmatrix}
    1 & 0 & 0 \\
    0 & \frac{f_{1+}}{f_{1+} + f_{1e}} & \frac{f_{1e}}{f_{1+} + f_{1e}} \\
    0 & \frac{f_{1+} + f_{1e}}{f_{1+} + f_{1e}} & \frac{f_{1+} + f_{1e}}{f_{1+} + f_{1e}}
\end{pmatrix}.
\]
6. A Comparison of Stefan-Maxwell’s and Fick’s Diffusion Models

The matrix $R$ is equal to $R = \text{diag}(\rho y)$. As the mobility of electrons is much higher than ions, friction coefficients of electrons is negligible in comparison with ions which results for $J$ in:

$$J \approx -\frac{\rho y_1^2}{f_1+} \begin{pmatrix} 0 & -(y_+ + y_e) & -(y_+ + y_e) \\ 0 & y_+ & y_+ \\ 0 & y_- & y_- \end{pmatrix} \partial z.$$

From that we obtain ion diffusive fluxes as:

$$J_+ = -\frac{\rho y_1^2}{f_1+} y_+ (\partial z_+ + \partial z_e),$$

we assume that the plasma is quasi-neutral $n_e = n_i$ and the ion temperature equals to gas temperature $T_h$. If we compare $J_+$ with $J_2$ we have:

$$\frac{J_+}{J_2} = \frac{(\nabla z_+ + \nabla z_e)}{\nabla z_+},$$

$$\frac{J_+}{J_2} = \frac{(\nabla k_b n_+ T_h + \nabla k_b n_e T_e)}{\nabla k_b n_+ T_h},$$

By ignoring the gradients of electron and gas temperature we can rewrite this to:

$$\frac{J_+}{J_2} = 1 + \frac{T_e}{T_h}.$$

It shows that ion diffusion due to the ambipolar electric field has the effect of multiplying $D_2$ by the factor of $1 + \frac{T_e}{T_h}$, which is equals to the classical ambipolar condition in Fick’s law.

6.2.4 Fick and Stefan-Maxwell in presence of multi-ions

We consider a plasma in which four species are considered: neutrals, electrons, one positive ion and one negative ion. We assume the neutral is the dominant species: $y_1 \approx 1, y_+ \approx 0, y_- \approx 0, y_e \approx 0$. then we can neglect the friction between charged particles. The friction matrix is given by:

$$\tilde{F} = \begin{pmatrix} f_1+ + f_1e + f_1- + ay_1y_1 & -f_1+ + ay_1y_+ & -f_1+ + ay_1y_e & -f_1- + ay_1y_- \\ -f_1+ + ay_1y_+ & f_1+ + ay+y_+ & ay+y_+ & ay+y_- \\ -f_1e + ay_1y_e & ay+y_e & f_1e + ay_e y_e & ay_e y_- \\ -f_1- + ay_1y_- & ay+y_- & ay_e y_- & f_1- + ay_1y_- \end{pmatrix}.$$

$$D = \tilde{F}^{-1} - \frac{1}{\alpha} u \otimes u,$$
Calculation of matrix $\mathbf{RD}$ and neglect of quadratic terms in, $y_+, y_e, y_-$ gives:

$$\mathbf{RD} = \rho \begin{pmatrix} 0 & -\frac{y_+ y_1}{f_{1+}} & -\frac{y_e y_1}{f_{1e}} & -\frac{y_- y_1}{f_{1-}} \\ 0 & \frac{y_+ y_1}{f_{1+}} & 0 & 0 \\ 0 & 0 & \frac{y_e y_1}{f_{1e}} & 0 \\ 0 & 0 & 0 & \frac{y_- y_1}{f_{1-}} \end{pmatrix}.$$ 

Then for calculation of the $\left( \mathbf{I} - \frac{s \otimes \mathbf{D}_s}{<s, \mathbf{D}_s>} \right)$, $s$ is defined as:

$$s = n_e [0, 1 + \delta, -1, -\delta]^T,$$

with $\delta = \frac{n_e}{n_-}$ defined as the ratio of electron density to the density of negative ions. If we substitute the values of $y_1 = 1, y_+ = 0, y_e = 0, y_- = 0$ in matrix $D, \mathbf{D}_s$ become:

$$\mathbf{D}_s = n_e [0, \frac{1 + \delta}{f_{1+}}, -\frac{1}{f_{1e}}, -\frac{\delta}{f_{1-}}]^T,$$

we compute the value of $<s, \mathbf{D}_s>$;

$$<s, \mathbf{D}_s> = n_e^2 \left[ \frac{(1 + \delta)^2}{f_{1e}} + \frac{1}{f_{1e}} + \frac{\delta^2}{f_{1-}} \right],$$

$$\left( \mathbf{I} - \frac{s \otimes \mathbf{D}_s}{<s, \mathbf{D}_s>} \right) = \frac{1}{(1 + \delta)^2 f_{1e} f_{1-} + f_{1+} f_{1-} + \delta^2 f_{1+} f_{1e}} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & f_{1+} f_{1-} + \delta^2 f_{1+} f_{1e} & (1 + \delta) f_{1+} f_{1e} & \delta (1 + \delta) f_{1+} f_{1e} \\ 0 & (1 + \delta) f_{1e} f_{1-} & (1 + \delta)^2 f_{1-} f_{1e} + \delta^2 f_{1+} f_{1e} & -\delta f_{1+} f_{1e} \\ 0 & \delta (1 + \delta) f_{1-} f_{1e} & -\delta f_{1+} f_{1e} & (\delta + 1)^2 f_{1-} f_{1e} + f_{1+} f_{1-} \end{pmatrix}. $$

Calculation of the mass fluxes and neglect of quadratic terms in $y_-$ and $y_e$ gives:

$$\mathbf{J} = -\mathbf{RD} \left( \mathbf{I} - \frac{s \otimes \mathbf{D}_s}{<s, \mathbf{D}_s>} \right) \partial \mathbf{z} = \frac{\rho}{C} \begin{pmatrix} 0 & -\frac{y_+ y_1}{f_{1+}} & -\frac{y_e y_1}{f_{1e}} & -\frac{y_- y_1}{f_{1-}} \\ 0 & \frac{y_+ y_1}{f_{1+}} & 0 & 0 \\ 0 & 0 & \frac{y_e y_1}{f_{1e}} & 0 \\ 0 & 0 & 0 & \frac{y_- y_1}{f_{1-}} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & f_{1+} f_{1-} + \delta^2 f_{1+} f_{1e} & (1 + \delta) f_{1+} f_{1e} & \delta (1 + \delta) f_{1+} f_{1e} \\ 0 & (1 + \delta) f_{1e} f_{1-} & (1 + \delta)^2 f_{1-} f_{1e} + \delta^2 f_{1+} f_{1e} & -\delta f_{1+} f_{1e} \\ 0 & \delta (1 + \delta) f_{1-} f_{1e} & -\delta f_{1+} f_{1e} & (\delta + 1)^2 f_{1-} f_{1e} + f_{1+} f_{1-} \end{pmatrix}. $$

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C is defined as \((1 + \delta)^2 f_{1e} f_{1-} + f_{1+} f_{1-} + \delta^2 f_{1-} f_{1e}\). Then mass fluxes of positive ions, electrons and negative ions can be computed as:

\[
J_+ = \frac{\rho y_1^2 y_+ (f_{1-} + \delta^2 f_{1e})}{C} \nabla z_+ + \frac{\rho y_1^2 y_+ (\delta + 1) f_{1-}}{C} \nabla z_e + \frac{\rho y_1^2 y_+ \delta (\delta + 1) f_{1e}}{C} \nabla z_-
\]

\[
J_e = \frac{\rho y_1^2 y_+ (1 + \delta) f_{1-}}{C} \nabla z_+ + \frac{\rho y_1^2 y_+ (1 + \delta)^2 f_{1-} + \delta^2 f_{1e}}{C} \nabla z_e - \frac{\rho y_1^2 y_e \delta f_{1e}}{C} \nabla z_-
\]

\[
J_+ = \frac{\rho y_1^2 y_+ f_{1e} \delta (\delta + 1)}{C} \nabla z_+ - \frac{\rho y_1^2 y_+ \delta f_{1e}}{C} \nabla z_e + \frac{\rho y_1^2 y_+ [f_{1e} (\delta + 1)^2 f_{1e} + f_{1+}]}{C} \nabla z_-
\]

We implement these terms for two different limits of \(\delta\):

- When \(\delta \ll 1\), the electron density is comparable to the positive ion density \(n_e \approx n_+\), then the mass fluxes of positive ions and electrons computed as:

\[
J_+ = \frac{\rho y_1^2 y_+}{f_{1e} + f_{1+}} \nabla z_+ + \frac{\rho y_1^2 y_+}{f_{1e} + f_{1+}} \nabla z_e;
\]

\[
J_e = \frac{\rho y_1^2 y_e}{f_{1e} + f_{1+}} \nabla z_+ + \frac{\rho y_1^2 y_e}{f_{1e} + f_{1+}} \nabla z_e.
\]

Based on expressions for \(J_+\) and \(J_e\) one can conclude that the diffusion of this species is approximately equal to ambipolar diffusion without negative ions. For the mass flux of negative ions, using the fact that \(f_{1+} \gg f_{1e}\) leads to:

\[
J_+ = \frac{\rho y_1^2 y_{-f_{1e} \delta}}{f_{1e} + f_{1+}} \nabla z_+ - \frac{\rho y_1^2 y_{-(\delta)}}{f_{1+}} \nabla z_e + \frac{\rho y_1^2 y_{-(\delta)}}{f_{1+}} \nabla z_+ \approx -\frac{\rho y_1^2 y_{-(\delta)}}{f_{1+}} \nabla z_e + \frac{\rho y_1^2 y_{-(\delta)}}{f_{1+}} \nabla z_+.
\]

When \(\delta \gg 1\), the negative ion density is comparable to the positive ion density \(n_- \approx n_+\):

\[
J_+ = \frac{\rho y_1^2 y_+}{f_{1e} + f_{1+}} \nabla z_+ + \frac{\rho y_1^2 y_+ f_{1e}}{\delta f_{1e} (f_{1e} + f_{1+})} \nabla z_e + \frac{\rho y_1^2 y_+}{f_{1e} + f_{1+}} \nabla z_-
\]

\[
J_e = \frac{\rho y_1^2 y_e f_{1e}}{\delta f_{1e} (f_{1+} + f_{1e})} \nabla z_+ + \frac{\rho y_1^2 y_e f_{1e}}{f_{1e} (f_{1+} + f_{1e})} \nabla z_e - \frac{\rho y_1^2 y_e f_{1+}}{\delta f_{1e} (f_{1e} + f_{1+})} \nabla z_-
\]

\[
J_+ = \frac{\rho y_1^2 y_{-f_{1e} \delta}}{f_{1e} + f_{1+}} \nabla z_+ - \frac{\rho y_1^2 y_{-f_{1e} \delta}}{\delta f_{1e} (f_{1e} + f_{1+})} \nabla z_e + \frac{\rho y_1^2 y_{-f_{1e} \delta}}{f_{1e} + f_{1+}} \nabla z_+.
\]
6.3 Results

In this section the results from Fick and Stefan-Maxwell model for some cases will be compared. Since the aim is to compare the diffusion model, we restricted ourselves to simple case of chemistry for argon and hydrogen. However, this makes the models unrealistic, it should not affect the comparison of the diffusion behavior. A comparison is done for coaxial plasma line for very simple argon chemistry for Fick and multicomponent Stefan-Maxwell diffusion. The model consists of three types of particles, neutral argon, atomic ions and electron.

\[
\text{Ar} + e \rightarrow \text{Ar}^+ + 2e \quad 2.3 \times 10^{-14} T_e^{0.68} \exp(-15.76/T_e) \quad [64]
\]

\[
\text{Ar}^+ + 2e \rightarrow \text{Ar} + e \quad 8.75 \times 10^{-39} T_e (eV)^{-4.5} \quad [66]
\]

In the figure 6.1 the electron density and temperature calculated from Fick and Stefan-Maxwell equation are shown. There is a small differences in the results of Fick’s and Stefan-Maxwell’s model. These differences can be explained by the fact that in the ambipolar diffusion in Fick’s model the gradient of electron and gas temperatures is ignored and only the density gradient is considered. However in the other model as the gradient of partial pressure \( \nabla z_i = \nabla p_i / p \) is in driving force, the effect of temperature gradient is also taken into the account.

In order to study the effect of temperature gradient on the diffusion we also simulate the same setup for the fixed values of electron temperature \( T_e = 13500 \, K \) and gas temperature \( T_h = 500 \, K \). The results are shown in Figure 6.2 which presents that if there is no temperature gradient the results from two methods are exactly the same, and this confirms that Stefan-Maxwell and Fick diffusion model are identical in this case.

In other test for making the effect of temperature gradients on diffusion more clear, was done using a profile function for gas temperature \( T_h = 600 \left(1 - 16 \left( r - R_T / 2 \right)^4 / R_T^4 \right) \, K \) and constant electron temperature \( T_e = 13500 \, K \). \( R_T \) is the total length of the setup. The results are shown in figure 6.3. As can be seen, the differences in electron densities are more significant where \( \nabla T_h \) is higher.

To study the difference between Fick’s and Stefan-Maxwell’s model when there is no dominant background gas, we simulate a mixture of \( \text{H}, \text{H}_2 \) and \( \text{H}_2^+ \). The dissociation and ionization reactions are taken into account.

\[
\text{H}_2 + e \leftrightarrow \text{H}_2^+ + 2e
\]

\[
\text{H}_2 + e \leftrightarrow 2\text{H} + e
\]

Electron temperature values are set to constant value of \( T_e = 17400 \, K \) and gas temperature values remain constant in \( T_h = 600 \, K \). The results of the simulations, from Fick’s and Stefan-Maxwell’s model, are presented in figure 6.4. As
can be seen, the results are different. This was to be expected since the densities of atomic hydrogen and molecular hydrogen are comparable.

A 1D plasma model as a test case is used to study the differences between Fick’s
6.4. Conclusion

The aim of this chapter is to compare the Fick’s diffusion model and self-consistent multi-component diffusion model, which is based on Stefan-Maxwell equations. It was shown that for the case that when there is a dominant background gas and single ions with uniform electron temperature and gas temperature, Fick’s diffusion model is equivalent to Stefan-Maxwell’s model. Otherwise, the two models give quite different results for plasma properties.

As Figure 6.5 shows, the prediction of Fick’s model and Stefan-Maxwell model are different in the presence of negative ions. Fick model in Plasimo treats the flux of negative ions as neutrals, which is not a bad approximation when the density of negative ions are so small, according to Section 6.2.4, but it is not correct when the density of negative ions are comparable to the densities of other charged particles.

\[
H + e \rightarrow H^+ + 2e \quad 1.914 \times 10^{-14} T_e^{0.758} \exp(-9.56/T_e) \quad [94]
\]

Figure 6.2. Comparison of electron density and electron temperature as calculated by Fick’s model and Stefan-Maxwell method. Gas temperature and electron temperature are constant.

and Stefan-Maxwell’s model in presence of multi-ions. The hydrogen model is included species of H, H\(^+\), H\(^-\) and electrons. At the left of the setup the mass fraction of H\(^+\) and H\(^-\) is set to 0.01 and at the right side the mass fraction of H\(^+\) is equal 0.01 and H\(^-\) is set to 0.001. The H and electron mass fraction at the boundary were determined from the mass and charge constraint. The H atom ionization is considered in the model.
Figure 6.3. Comparison of electron density and electron temperature as calculated by Fick model and Stefan-Maxwell method in the case there is a gradient in the gas temperature profile.
Figure 6.4. Comparison of electron density, atomic and molecular hydrogen and as calculated by Fick model and Stefan-Maxwell method when there is not a dominant background gas.
Figure 6.5. Comparison of (a) electron density, (b) H\textsuperscript{−} and (c) H\textsuperscript{+} as calculated by Fick model and Stefan-Maxwell method.
Chapter 7

Conclusions
7.1 Conclusions

The purpose of this thesis was to investigate the plasma behavior in microwave induced plasmas. Understanding such a system is important for many applications like deposition processes in solar cells. This type of plasma is surface wave induced plasma. More specifically, the application of microwave plasma source in a coaxial microwave reactor was studied in this work. We approach to this problem using mathematical modeling and simulation of the plasma system, including fluid and electromagnetic equations. The simulation of this complex system provides us a powerful tool for understanding processes happening during deposition in the plasma. We have used the experimental data resulted from the equivalent experimental setup to validate our model.

The model was applied to an argon, a hydrogen plasma and also to a mixture of hydrogen-silane plasma for several different working conditions.

• The results obtained with the model for argon plasma were compared to the experimental values from Thomson scattering measurements and it results to a good agreement for the electron density. For electron temperature, there was a differences in absolute values between model and the experiment. This can be explained by the fact that the model uses a continuous power whereas in the experimental setup a pulsing regime for power has been used. It was shown that the model can reproduce the same trends as experimental measurements.

• Electron heat transport in the coaxial discharge is an important phenomena and more important than in the surfatron. This is due much larger plasma radius in the coaxial discharge plasmas.

• Moreover a strong inhomogeneity for ionization frequency was shown. This is an important characteristic that demonstrates a strong difference with the surfatron case, where the electron temperature and the ionization frequency was approximately constant in the radial direction.

• A radial localization of electron density in coaxial plasma waveguides has been observed and explained as a consequence of the coaxial geometry and the strong inhomogeneity of the EM field, and electron temperature. This has been confirmed by experimental data.

• We found that these discharges show a self-limitation against high energy coupling; for higher power levels the penetration of EM fields is more limited caused by the increasing the conducting character of the plasma which obstructs further power absorption.
• Simulation of the coaxial plasma line in hydrogen were compared to optical emission spectroscopy measurements. Simulated values show a good agreement with experimental measurements in general trends.

• Comparison between modeling results with experimental output shows the important role of the atomic wall recombination mechanism in plasma description.

• The model was used to describe the silane-hydrogen mixture. In order to study the relation between plasma properties, deposition rate and some external parameters, some parametric studies were perform.

• The model predicts a reduction in the deposition rate with increasing pressure.

• It, moreover, shows that there is a strong dependency between deposition rate and hydrogen wall recombination. It emphasis on the importance of surface process on the deposition layer and quality of the layer.

• Increasing input power leads to increase in deposition rate. Although increasing the power means increasing of electron density which makes the power coupling less effective.

• There are many uncertainties about hydrogen-silane chemistry. The model was used for sensitivity studies of branching ratio of SiH4 and H-abstraction of SiH3. These two examples presented here shows how crucial it is to create a valid and stable chemistry for different conditions. However, a 2D model is not the most efficient way for sensitivity studies. Using a global model can help to analyze the importance of the production and destruction of each species. The results can be used to optimize the 2D model.

• Rates of electron impact reactions taken from literature with a Maxwellian distribution function. To increase the accuracy of the model the plasma-electromagnetic models should be coupled with a Boltzmann solver.

• The surface processes in this model are a simplification of the reality. We consider the sticking process as part of recombination process which adds unrealistic but insignificant flow of SiH4 to the plasma. Constant sticking coefficients have been used. Based on this we can estimate the deposition rate. A more complicated surface-plasma interaction should be taken into account to describe the sticking process and the influence of hydrogen in the deposited layer.

• For modeling of argon, hydrogen and silane-hydrogen mixtures the Fick’s description was used which is not completely correct in the case, where
plasma is not ruled by a single dominant species, when there is more than one major ion and in the case of gradients in the temperature profile. A more sophisticated diffusion model is needed for more reliable results. A multicomponent diffusion model based on the Stefan-Maxwell equation is compared with Fick’s description. It was shown that for the case where we there is a dominant background gas and single ions with uniform electron temperature and gas temperature, Fick and Stefan-Maxwell models are identical. But the results from multicomponent diffusion model and fick model are different in the case of a gradient in temperature and there is one dominant background species in the plasma.

- The description of the sheath is simplified by means of ambipolar diffusion and boundary condition. A more complex sheath model would bring insight and improve the simulation results.

- In the model plasma resonances are not included, thus limiting the coupling of energy from the em wave to the plasma depending on the plasma conditions.
Bibliography


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