Thermal Exchange Modelling on Hydrogen Plasma Reactor Walls

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Abstract: Discharge chemistry and transport in microwave plasmas are highly complex. All induced phenomena (electromagnetism, energy balance in the plasma bulk, reactive transport and surface kinetics) must be solved simultaneously. Sophisticated numerical models are needed to solve this strong coupling. A self-consistent model previously developed in our laboratory [1] has enabled us to determine that, at high power density, atomic hydrogen production is mainly controlled by gas temperature.

A reduced equivalent plasma model is proposed for thermal dissociation of molecular hydrogen which allows a detailed description of atomic hydrogen recombination. This model implemented through Comsol™ Multiphysics also account for surface temperature and thermal exchange on cavity walls, which was previously neglected.

Keywords: microwave plasmas, thermal exchange, surface catalytic recombination.

1. Introduction

Cold plasmas have many industrial applications, for example a CVD coating process (diamond deposition here), that require a detailed knowledge of physical phenomena involved. A complex model that solves strongly coupled physics simultaneously was previously developed at LIMHP [1]. This model accounts for up to nine species in hydrogen plasmas, with associated chemical reactions, energy equations for both gas and electrons and for the electric field, induced by microwave generator. In order to evaluate the influence of the plasma parameters, a simplified thermo-chemical model was developed. The main assumption of such a model is that, for high pressure, hydrogen is mainly thermally dissociated, which enables to neglect electrical phenomena [2].
Governing equations and specific boundary conditions of our thermo-chemical model are presented first. Reduction of the number of input parameters is proposed next. Then comparison with the self-consistent model mentioned above is done before conducting a parametric study on recombination rate on the quartz wall. Finally, before concluding, a recombination thermal dependence is introduced and discussed.

2. Physical model

2.1 Computational domain

For high pressure plasmas, a simplified equivalent plasma model can be proposed. In such a case, detailed knowledge of the electric field is not required: we can consider that microwave energy is converted into heat in the plasma domain, i.e. a zone of high electrical field near the substrate holder.
The plasma zone, where the power density is injected, is determined by experimental observation. We then assume that a homogeneous energy source term is applied in a hemispherical subdomain coincident within the plasma zone (see figure 1).

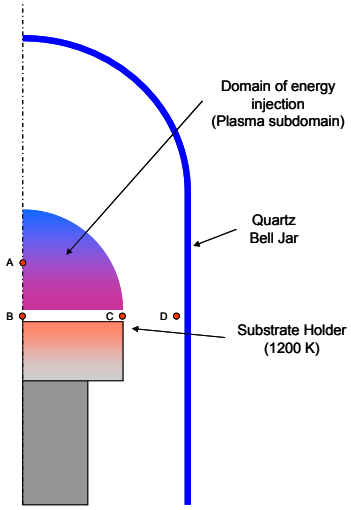

Figure 1: Computational domain of plasma Bell Jar reactor.

2.2 Governing Equations

The model describes only the conservation of the two main plasma species, molecular and atomic hydrogen, combined with an energy equation.
For the latter, we consider a gaseous mixture of molecular and atomic hydrogen, Equation (1) :

$$\nabla\left(-k\nabla T-\sum_i h_i N_i\right)=P_{MW} \qquad (1)$$

where k is the thermal conductivity of the gas mixture, P_{MW} represents the microwave energy transferred to the gas and the second term ($\sum h_i N_i$) is the enthalpic flux due to species diffusion. This term depends on the mass species flux. and must be implemented in the Comsol™ Equation System.

For both species, we compute the mole fraction, x_s, from the following continuity equation:

$$\nabla\left(-D_s\nabla x_s\right)=R_{chemistry} \qquad (2)$$

where D_s is the diffusion coefficient, strongly dependent on temperature, pressure and gas composition. $R_{chemistry}$ is the particle source term due to the following chemical mechanism:

$$2\ H_2 <\!\!-\!\!> 2\ H + H_2$$
$$H_2 + H <\!\!-\!\!> 3\ H$$

Energy and species conservation equations are then strongly coupled.

2.2 Boundary Conditions

We also consider atomic hydrogen losses by surface recombination on the wall:

$$H_{surf} -\!\!> 0.5\ H_2 \qquad (3)$$

This recombination takes place on the substrate holder and the quartz wall. The mass balance of this surface reaction can be expressed through F_H and F_{H2} fluxes:

$$F_H=-\frac{\gamma_H}{1-\gamma_H/2}.\frac{v_H}{4}.M_H.[H]$$
$$F_{H2}=-\frac{1}{2}F_H \qquad (4)$$

where γ_H is the recombination rate coefficient, v_H is the thermal velocity and M_H the molar mass of hydrogen.

This recombination leads to heat production on the reactor walls. This production induces a discontinuity in the energy equation on the internal quartz wall, given by the enthalpic flux, F_T:

$$F_T=-\alpha.F_H.\Delta H_{recombination} \qquad (5)$$

where $\Delta H_{recombination}$ is the enthalpy of reaction (3) and α the accommodation rate, that is to say the proportion of energy transmitted to the wall.
The recombination rate, γ_H, as well as the accommodation rate, α, are controlled by both wall temperature and surface state [4,5]. Leroy et al. have shown that, for a quartz surface, α can be considered as constant [4]. The parameter γ_H was first assumed constant to validate the model. We then illustrate the influence of this parameter value by means of a parametrical study. Finally, a physical variation law for γ_H was implemented to account for the reactor wall heating.

3. Methods

The model equations detailed in the previous section show that there are only two kinds of input data. On the one hand, species and thermal transport coefficients (D_s, k) for the gas mixture are computed using Hirschfelder relations, and are strongly dependant on pressure, temperature and gas composition. On the other hand, reaction rates are functions of temperature only.
The energy conservation equation (1) links input power and the induced temperature field. Then, the described model has two key input parameters: power density and pressure.

Experiments have shown [3,6] that microwave power and pressure in the cavity govern the plasma size. Then, for deposition processes,

which require a homogeneous plasma composition on the whole upper face of the substrate holder, pressure and power are strongly linked. In order to introduce this coupling, we first determine the power density needed for a given pressure to reproduce experimental results, in this case, atomic hydrogen mole fraction in the plasma bulk, as presented in figure 2.

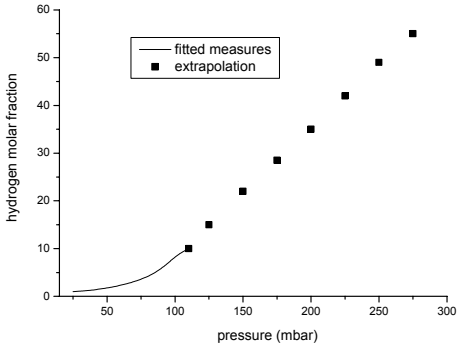

Figure 2 : Experimental results for hydrogen mole fraction in the plasma bulk as function of pressure (line: measured by optical spectroscopy; square: extrapolation of fitted data).

These experimental results show two different regions. At low pressure, mole fraction of atomic hydrogen increases slowly with increasing pressure. At higher pressures, the increase of hydrogen production becomes linear with pressure.

Regarding temperature, figure 3 compares the results obtained in the plasma bulk for the self-consistent model and for our simplified thermo-chemical model.

The self-consistent model solves precisely hydrogen discharge chemistry and transport. Our model described only chemistry governed by temperature.

Below 75 mbar, the self-consistent model predicts temperatures lower than 3000 K, whereas our thermo-chemical model needs higher temperatures in order to reach the experimental dissociation rate.

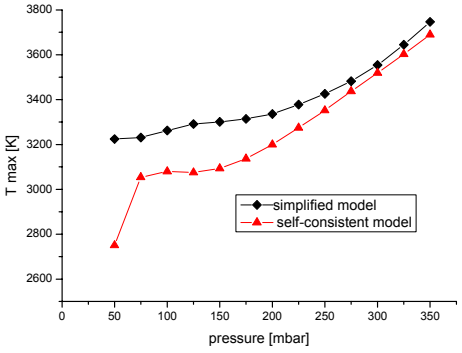

Figure 3 : Gas temperature obtained with simplified thermo-chemical model and with full self-consistent model (T_{quartz}= 400 K, γ_H=0.1).

The comparison shows clearly that, at low pressure (and power), atomic hydrogen is mainly produced by direct dissociation with electron collisions, which cannot be reproduced within our thermo-chemical model. When increasing pressure, differences between the two models decrease, indicating that thermal production of hydrogen becomes predominant compared with electronic dissociation. Above 200 mbar, both models tend to predict the same temperature in the plasma bulk.

4. Results and discussion

Catalytic recombination of hydrogen occurs at any surface. This recombination depends on atomic hydrogen concentration near the wall and on the recombination rate coefficient γ_H. This rate represents the fraction of particles coming on the wall that recombine. It strongly depends on surface temperature and wall material. In the previous section, the classical assumption [1-3] of a constant γ_H was made with a fixed quartz temperature.

However, it is well known that γ_H is not constant but strongly dependant of wall temperature [5].

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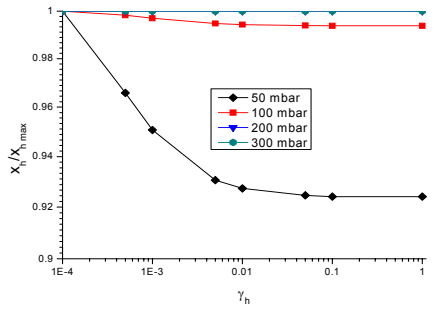

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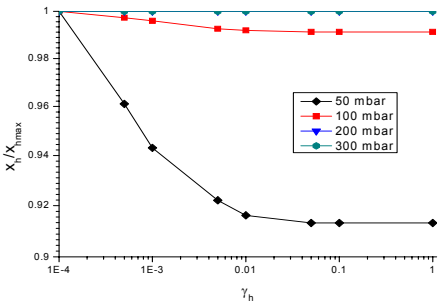

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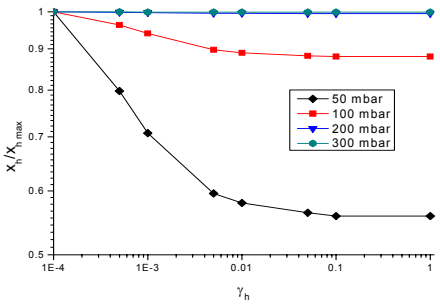

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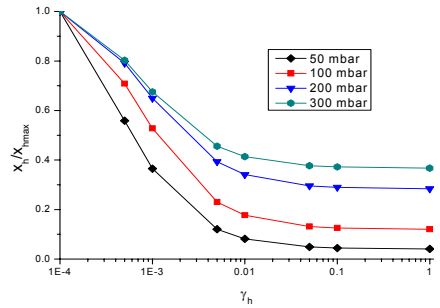
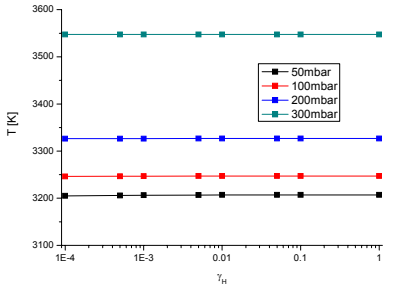


Figure 4 : Atomic hydrogen mole fraction normalized by the maximum value, i.e., $\gamma_H=10^{-4}$, **a)** in the plasma bulk., **b)** under the substrate holder in r=0, c) under the substrate holder at the right side, **d)** near the quartz wall.

a)



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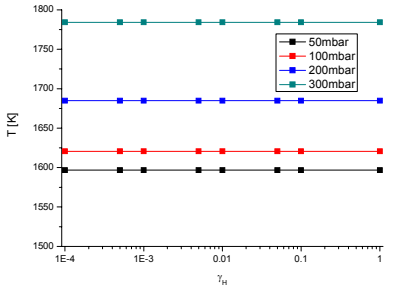

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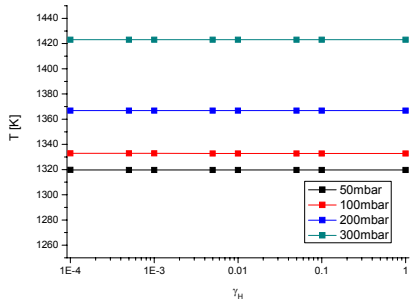

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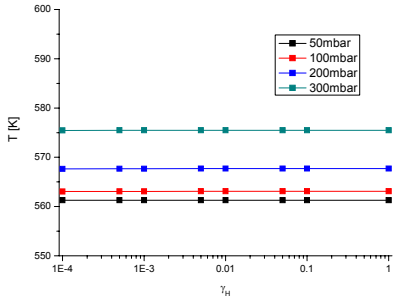

Figure 5 : Variation of gas temperature, **a)** in the plasma bulk. **b)** under the substrate holder in r=0, c) under the substrate holder at the right side, **d)** near the quartz wall.

Before going any further and introducing a physical variation law for γ_H , we investigate the influence of its value.

Figure 4 shows the results of the γ_H parametric study on atomic hydrogen distribution. At high pressure, the recombination rate has almost no influence on atomic hydrogen concentration in the entire reactor except near the wall.

A study of production and diffusion terms has shown that recombination losses at the wall are counterbalanced by production rate and diffusive flux toward the walls.

For lower pressures, recombination losses are no more counterbalanced by production and diffusion phenomena so that atomic hydrogen concentration is reduced along the substrate holder and even in the plasma bulk.

We also investigate the influence of recombination on the temperature field in the reactor. The results are presented in Figure 5. At any pressure, the increase of temperature is less than 2 K. A study of the different thermal fluxes has been done. It shows that conduction fluxes (F_D) are much larger that thermal fluxes due to recombination on the quartz ($F_D > 10^3.F_T$ for $\gamma_H=10^{-3}$). Quartz temperature is then controlled by conduction fluxes and thermal effects of recombination are then negligible.

In our experimental Bell Jar reactor the quartz wall is cooled by natural convection. Its temperature could be non uniform which implies a spatially dependent recombination rate, γ_H. Because one of the objectives of this work is to investigate the influence of the recombination on the temperature field and on the atomic hydrogen distribution in the reactor, it is important to consider a physical distribution for γ_H. We then implement the following relation, obtained from the work of Young et al [5] for the temperature range between 500 and 1000 K:

$$\gamma_H = 0.313 \exp\left(\frac{-4495}{T(K)}\right) \qquad (5)$$

Furthermore, instead of having a given temperature for the outside quartz face, a natural convective flux is specified. Temperature and thus recombination rate are then no more constant as shown in figure 6.

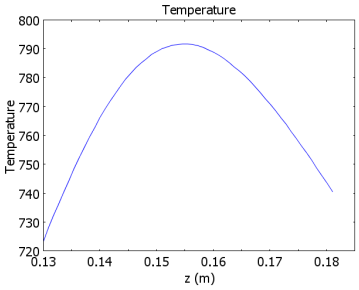

Figure 6 : Temperature on the quartz wall at 300 mbar. The maximum value is nearly located in the front of the hottest plasma point.

Figure 7 clearly shows that differences between a realistic configuration and a model with the assumption of constant quartz temperature can be important, especially at low pressure.

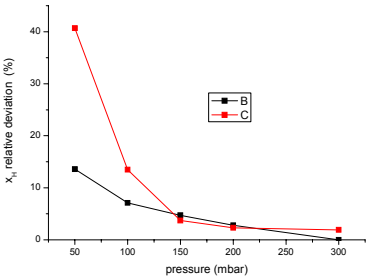

Figure 7 : deviation observed near the substrate holder (points B and C in Figure 1) in hydrogen mole fraction considering γ_H=0.1 and γ_H following equation 5.

The knowledge of the quartz temperature is one of the major aspects of this model. From the engineering point of view these data are very important to insure a good thermal management of the reactor, especially at high power density.

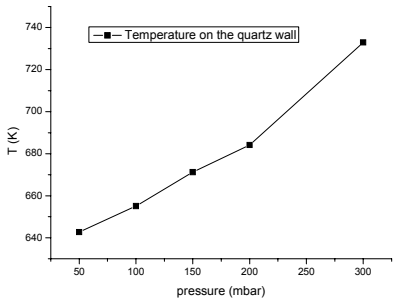

Figure 8: Temperature **on** the quartz wall of the Bell Jar reactor (at z_C = 0.132 mm).

Figure 8 indicates that it is necessary to cool the quartz wall efficiently near the substrate-holder at high pressure.

5. Conclusion

A simplified thermo-chemical model was first proposed for describing atomic concentration fields in a plasma reactor. Such a model enables fine treatment of surface phenomena.
After having validated the model with comparisons to experimental results, a parametric analysis was done on the recombination rate in order to establish its importance. The influence of the surface recombination rate on the atomic hydrogen concentration in the plasma was observed mainly at low pressure.
Next, an experimentally fitted law was introduced to take into account temperature variations along the wall for this quantity.
Contrary to atomic hydrogen concentration, the quartz wall temperature is not influenced by surface recombination.
This model can be very helpful for engineering development of high power density plasma reactors, since it can predict the elements having to be efficiently cooled.

6. Outlook

The results of our thermo-chemical simplified model can be compared with the self-consistent model. Axial profiles of both models at 300 mbar are given on figure 9.
This figure shows, first hat the maximum value and location of hydrogen mole fraction in the plasma is very well reproduced using our model. However, the width of the hydrogen profile is under-estimated. In our computations, we use a simplified law for energy deposition. Energy is only deposited homogeneously inside a hemispherical volume, which is not the case in a real plasma configuration. To be more accurate and improve the atomic hydrogen profile, a more realistic energy distribution will be introduced.

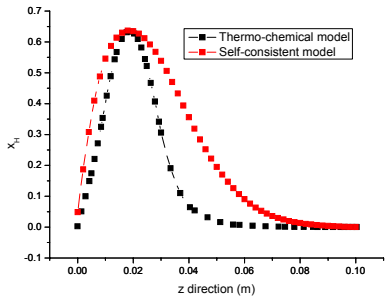

Figure 9 : Comparison of the axial distribution of atomic hydrogen for the thermo-chemical and self-consistent models. z=0 correspond to the surface holder and z=0.1m to the quartz bell jar

In a microwave cavity, the plasma ignition takes place in the highest electric field area. The use of electromagnetic solver of Comsol™ can be helpful to establish more accurately the energy distribution in a realistic plasma sub domain.

7. References

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