

Influence of vibrational kinetics in a low pressure capacitively coupled hydrogen discharge

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Abstract

In this paper we present the self consistent coupling of a 2D model of a parallel plate radio frequency discharge in pure hydrogen with a homogeneous chemical kinetics model including $H_2(X^1\Sigma_g^+, v=0..14)$ molecules and hydrogen atoms $H(n=1-5)$. The model can estimate the ground state atomic hydrogen density and it was found that the vibrational kinetics changes the H_3^+ ion density and coupled power to the discharge about 40% when comparing with previous estimates using a simplified kinetics.

1. Introduction

Parallel plate radio frequency (RF) capacitively coupled discharges driven at 13.56 MHz are of great interest in plasma assisted material processing applications, for example in plasma enhanced chemical vapour deposition (PECVD) of silicon and diamond thin films using hydrogen based mixtures. The optimisation and scale up of such reactors, requires the development of complete transport plasma models that couple the gas flow, multi component diffusion transport, gas phase and surface kinetic processes, with the electrical description of the RF discharge.

The present work is part of an effort to model and optimise an existing PECVD reactor for quality μ -Si:H deposition, using SiH_4 - H_2 mixtures under high dilution conditions for silane. The RF reactor is similar to the GEC reference cell, with 6.2 cm radius and 3 cm inter-electrode distance [2], operating at pressures between 0.1 – 1 Torr, frequencies in the 13.56 - 80 MHz range and RF voltages 50 – 250 V. The translational gas temperature is assumed to be 323.15 K.

The modelling started by studying a capacitively coupled discharge in pure hydrogen for various excitation frequencies, using a 2D time dependent fluid type model to describe the transport of electrons, H^+ , H_2^+ , H_3^+ and H in the reactor under study [2]. In a previous work [3], it was shown that the model predicts the correct trends of plasma density and self-bias voltage variation with driving frequency and RF voltage. However, model predictions were found to be systematically underestimated with respect to measurements, which was partially attributed to experimental uncertainties and to the simple hydrogen kinetics adopted in the model.

A realistic hydrogen chemistry must include the kinetics of vibrationally excited molecules and electronically excited atomic species. The hydrogen vibrational excited species can have an important role in RF discharges, as a significant part of the coupled power is lost in vibrational excitation, due to the fact of being easily excited. These species may constitute important channels of atomic hydrogen and charged particle production. In order to clarify the role of these species, we have self consistently coupled a homogeneous chemical kinetic model for hydrogen, including $H_2(X^1\Sigma_g^+, v=0..14)$ molecules and hydrogen atoms $H(n=1-5)$, to the previously developed charged particle transport model.

This paper analyses the effect of this improved kinetics of hydrogen in reactor operation.

2. Model

A rigorous description of low temperature non equilibrium plasma, must couple the electron transport to gas phase chemistry, because rate coefficients of processes involving electrons must be calculated using the EEDF, which on other hand depends on chemical composition. Due to the strong non thermal equilibrium that may exist between the different species, the chemistry of the plasmas must also take into account the possible deviation of the electron energy distribution function (EEDF) and vibrational distribution (VDF) of hydrogen molecules from the Maxwell-Boltzmann equilibrium distribution.

2.1 Hydrogen Kinetics

The hydrogen kinetics is well established in several works [1]. The kinetics used in the present work describes the dynamics of vibrationally excited molecules in ground state $H_2(X^1\Sigma_g^+, v=0..14)$, hydrogen atoms in ground and excited states $H(n=1-5)$, electrons, positive and negative ions (H_3^+, H_2^+, H^+, H^-). The kinetic processes considered are reported in table 1.

Table 1

	Process	Reference
Vibrational species		
e - V	$e + H_2(v) \leftrightarrow e + H_2(v \pm i), i=1..3$	[4,5]
E - V	$e + H_2(v) \rightarrow e + H_2(B^1\Sigma_u^+, C^1\Pi_u) \rightarrow e + H_2(v')$	[4,5]
V - V	$H_2(v) + H_2(w) \leftrightarrow H_2(v-1) + H_2(w+1)$	[5]
V - T	$H_2(v) + H_2 \leftrightarrow H_2(v \pm 1) + H_2$	[5]
V - T	$H_2(v) + H \leftrightarrow H_2(v \pm i) + H, i=1..5$	[5,6]
Dissociation	$e + H_2(v) \rightarrow e + H_2(a^3\Sigma_g^+, b^3\Sigma_u^+, c^3\Pi_u, e^3\Sigma_u^+) \rightarrow e + 2H(1s)$	[4,5]
	$e + H_2(v) \rightarrow e + H(1s) + H(n=2,3)$	[4]
Ionisation	$e + H_2(v) \rightarrow e + e + H_2^+$ $\rightarrow e + e + H^+ + H$	[4,15]
Diss. Attachement	$e + H_2(v) \rightarrow e + H_2^- \rightarrow H + H^-$	[8]
Wall	$H_2(v>0) \rightarrow H_2(v=0)$	[7]
Dissociation by Vib. Pumping	$H_2(v=14) + H_2 \leftrightarrow 2H(1s) + H_2$ $H_2(v=14) + H \leftrightarrow 3H(1s)$	[9]
Atomic species		
Exc/De-exc.	$e + H(n) \leftrightarrow e + H(m), n,m=1..5$	[13]
Ionisation	$e + H(n) \rightarrow e + H^+$	[13]
Rad. De-exc.	$H(n) \rightarrow H(m) + h\nu$	[13]
Deactivation	$H(2s) + H_2 \rightarrow H(2p) + H_2$ $H(2p) + H_2 \rightarrow H(2s) + H_2$ $H(2s) + H_2 \rightarrow H_3^+ + H$ $H(2s) + H_2 \rightarrow 3H(1s)$	[11] [13] [11] [13]
Wall	$H(1s) \rightarrow \frac{1}{2}H_2(v=0)$ $H(n>1) \rightarrow H(1s)$	[12] [13]
Additional Processes		
electron – ion recombination	$e + H_3^+ \rightarrow 3 H$ $e + H_2^+ \rightarrow H(1s) + H(n), n>1$ $e + H^+ \rightarrow H(n) + h\nu$ $2e + H_3^+ \rightarrow H_2 + H + e$ $2e + H_2^+ \rightarrow 2H(1s) + e$ $2e + H^+ \rightarrow H(n) + e$ $e + H_3^+ + wall \rightarrow H_2 + H$ $e + H_2^+ + wall \rightarrow H_2$ $e + H^+ + wall \rightarrow H$	[10] [10] [10] [9] [9] [9] [9] [9] [9]
ion – ion neutralization	$H^- + H_3^+ \rightarrow 2 H_2$ $H^- + H_2^+ \rightarrow H_2 + H(n>2)$ $H^- + H^+ \rightarrow H(n=3) + H$	[9] [14] [9]
Ass. detachment	$H + H^- \rightarrow H_2 + e$	[9]
Ion conversion	$H_2^+ + H_2 \rightarrow H_3^+ + H$ $H_2^+ + H \rightarrow H^+ + H_2$ $H^+ + 2H_2 \rightarrow H_3^+ + H_2$ $H^+ + H_2(v>3) \rightarrow H_2^+ + H$	[9] [9] [9] [9]

2.2 Plasma Model

A 2D time dependent fluid type model was developed to describe the transport of electrons, H⁻, H⁺, H₂⁺ and H₃⁺ in the reactor under study [2]. The description, in space and time, of charged particle transport uses the corresponding continuity, momentum transfer and mean energy equations (the latter for electrons only), coupled with Poisson's equation.

We adopt the local electron mean energy approximation. The electron transport parameters are tabulated as a function of electron mean energy, by first solving the stationary, space-independent electron Boltzmann equation using the electron cross-sections compiled in references [4]. The ion mobilities are those of reference [15].

The system of equations is discretized in a grid of 16x32 points using finite differences, and is solved subject to appropriated boundary conditions. Typically, 1000 time steps are used within each RF period, and a few hundred RF cycles are needed to reach convergence. Convergence is assumed if relative changes of particle densities, mean electron energy, plasma potential and self-bias voltage, between two consecutive periods is less than 0.05%.

2.3 Chemical model

In this model we solve the coupled set of species continuity equations. This equations need to be solved in two dimensions for coherence with the plasma model, but that's a time consuming task due to the number of species and kinetic processes involved. Instead we use zero dimensional versions of the continuity equations, by averaging them in space, resulting in a volume averaged balance equation for each specie

$$\frac{\partial \bar{n}_i}{\partial t} = \left(\frac{\partial \bar{n}_i}{\partial t} \right)_{coll} + \left(\frac{\partial \bar{n}_i}{\partial t} \right)_{transport}$$

where $\bar{n}_i = \frac{\iint n_i r dr dz}{\iint r dr dz}$ is the averaged density, $\left(\frac{\partial \bar{n}_i}{\partial t} \right)_{coll}$ the volume average sum of gains

and losses of specie i and $\left(\frac{\partial \bar{n}_i}{\partial t} \right)_{transport}$ is the total loss of specie i at the wall.

In the integration process we distinguished two regions in the plasma, a spatially homogeneous one corresponding to the plasma bulk and a boundary layer of the size of plasma sheath, where densities of neutral are assumed to vary linearly. This assumption should be accurate enough to analyse the importance of the neutral chemistry in reactor operation. The resulting set of coupled non linear equations was solved semi implicitly using a Gauss Seidel relaxation technique. The procedure converges in several thousands of iterations for relative variation of 10^{-12} in the density of any neutral specie.

The coupling between the two models is made by passing to the chemical model the average frequencies (in space and time) of gain and loss of each neutral specie with electrons. The system of balance equations is solved up to the steady state several times during charged species transport, typically every 5 RF periods, until overall convergence achieved. The new chemical composition, obtained after each run of the chemical model, is used to update the electron transport parameters and rate coefficients by solving the homogeneous time independent Boltzmann equation, before running again the plasma transport model. This self consistent coupling between plasma transport and chemical kinetics was used successfully in other works [16].

3. Results

We began by solving the problem without atomic hydrogen excited species and negative ions, for an applied RF voltage of 100V, pressure of 300 mTorr and excitation frequency of 13.56MHz. The densities of charged species, H atoms and the vibrational distribution of molecular species is shown in figures 1 and 2.

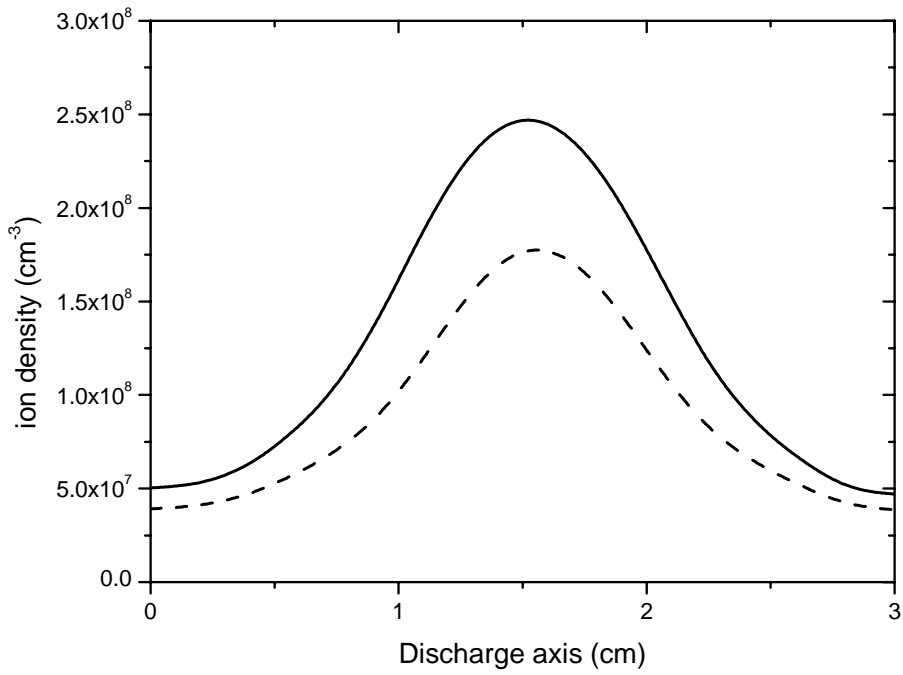


Figure 1 New (—) and previous (-----) H_3^+ ion density model estimates.

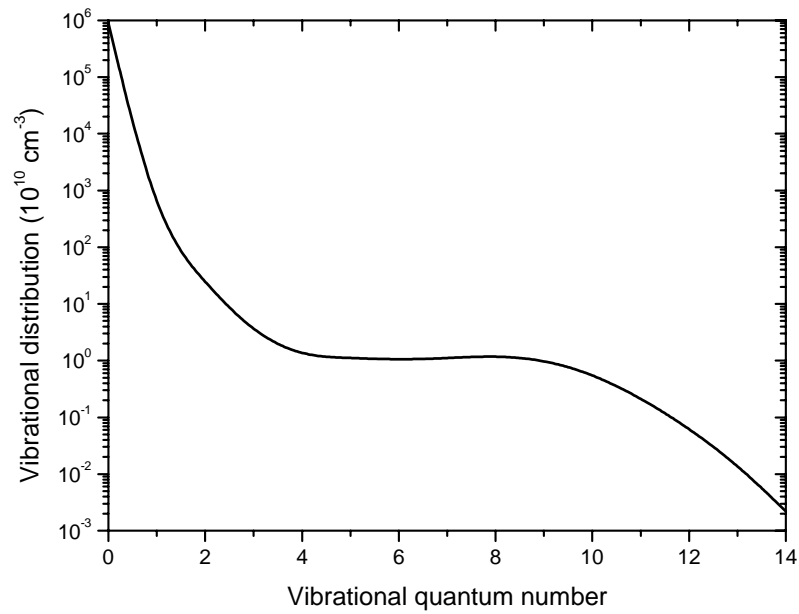


Figure 2 Vibrational distribution of hydrogen molecules.

The adoption of this new kinetics changed the model estimations of H_3^+ ion density and coupled power coupled to the discharge about 40 %, when comparing with previous results using a simplified hydrogen kinetics [2,3]. The bias voltage was only slightly affected. The increased ion density is due to the lower of ionisation potential of vibrationally excited species, which contributes to enhance the ionisation coefficient. The power coupled to the discharge increases, because more power is lost in vibrational excitation, ionisation and dissociation of hydrogen.

Introduction of negative ions in the kinetics, results in a significant slow down of model convergence. The H^- ion concentrates at discharge centre and its density is comparable to that of H_2^+ and H^+ , while the main plasma parameters are only marginally affected.

Finally we have considered atomic excited species. The associative ionisation becomes the most important channel of electrons and H_3^+ ions and contributes to increase significantly the densities of these species. We expect that it will bring the model estimates close to the experimental results available. Unfortunately, the introduction of this channel deteriorates plasma model convergence, due to the strong ionisation everywhere in the reactor. Probably the spatial profile of the atomic excited species needs to be calculated more accurately. Studies are in progress to correctly solve this problem.

4. Conclusion

We have successfully coupled self consistently the vibrational kinetics to a fluid type plasma transport model. The absence of vibrational kinetics explains in part why previous model predictions underestimate experimental measurements. Associative ionisation with participation of atomic excited hydrogen species seems to be an important process to consider, but the population of these species must be accurately calculated.

References

- [1] O. Leroy et al, Plasma Sources Sci. Technol. **7**, 348 (1998).
- [2] A. Salabas, G. Gousset and L. L. Alves, Plasma Sources Sci. Technol. **11**, 448 (2002).
- [3] L. Marques et al, Proceedings of Escampig **XVI**, Vol 2, 69 (2002).
- [4] H. Tawara et al, J. Phys. Chem. Ref. Data **19**, 617 (1990).
- [5] J. Loureiro et al, J. Phys. D: Appl. Phys. **22**, 1680 (1989).
- [6] Gorse et al, J. Chem. Phys. **117**, 177 (1987).
- [7] Gorse et al, Chem. Phys. **93**, 1 (1985).
- [8] Hickman, Phys. Rev. A **43**, 3495 (1991).
- [9] Matveyev A., V. Silakov, Plasma Sources Sci. Technol. **4**, 606 (1995).
- [10] R. Janev et al, Elementary processes in Hydrogen –Helium plasmas ed G. Ecker, P. Lambropoulos, and H Wlather (Berlin Springer) (1987).
- [11] M Glass - Maujean, Phys. Rev. Lett. **62**, 144 (1989).
- [12] P Kae-Nune, J Perrin, J Jolly, Surf. Sci. Lett, L495 (1996).
- [13] G. Gousset, Private communication.
- [14] M Eerden et al, Phys. Rev. A **51**, 3362 (1995).
- [15] T. Simko et al, Phys. Rev. E **56**, 5908 (1997).
- [16] S Longo, I Boyd, Chem. Phys. **238**, 445 (1998).