Journal of Optoelectronics and Advanced Materials Vol. 7, No. 5, October 2005, p. 2363 - 2369

PARTICLE MODELLING OF PARALLEL PLATE RADIO FREQUENCY DISCHARGE PLASMAS IN HYDROGEN: INFLUENCE OF PRESSURE

P. Diomede[a*], S. Longo[a,b], M. Capitelli[a,b]

[a]Dipartimento di Chimica dell'Universita' di Bari, Via Orabona 4, 70126 Bari, Italy
[b]IMIP/CNR, Via Orabona 4, 70126 Bari, Italy

We present a 1.5D particle code for the modelling of parallel plate, capacitively coupled radio frequency discharge plasmas in hydrogen, which includes a rigorous kinetic modelling of ion transport and several solutions to speed up the convergence. In a test case the effect of pressure on the kinetics of charged particles and the plasma potential is analyzed. The relevance of the results of this kind of studies for material science is discussed.

(Received January 10, 2005; accepted September 22, 2005)

Keywords: Radio frequency discharge plasma, Pressure effect

1. Introduction

Plasmas produced by electric discharge ionization of hydrogen are of great interest as a test case for material science because of the high reactivity of hydrogen atoms that can be produced in this nonequilibrium plasma at low gas temperatures. For example, in the production of silicon and diamond films, the hydrogen atoms present in the plasma react with covalently bound H on the film surface speeding up the deposition process [1-3]. Fast H atom beams, resulting from detachment of accelerated H^- ions produced in hydrogen plasmas, are also considered for applications in material processing [4-5].

In order to perform numerical simulations of the deposition process, it is first necessary to model the RF discharge in pure hydrogen in detail.

In particular, the modelling of the capacitively coupled RF (Radio Frequency) discharge in pure hydrogen represents an important research topic for the plasma discharge community [6-9] for two main reasons: first, this kind of discharge is relatively easy and cheap to set up and it is able to produce a large volume of uniform plasma. Second, from an academic point of view, the discharge pumping mechanism is not trivial and requires a careful theoretical modelling.

This particular discharge plasma belongs to a class of strongly 'non local' situations where the electrons behave like a rarefied gas. Under such conditions, only kinetic methods, based on numerical solutions of kinetic equations for the translational distribution function f(r,v,t) of the charged particles, can be applied in order to get accurate values for the rate coefficients. The most well known technique of this kind is the so-called 'PIC/MC' i.e. Particle In Cell/Monte Carlo method [8,10,11]. In the PIC/MC approach the Newton equation for a large ensemble (10^4-10^5 particles) of mathematical point particles, assumed to describe a statistically representative sample of electrons and positive ions, is solved taking into account the local electric field as it results from local interpolation within a cell of a mathematical mesh (from which follows the name 'Particle in Cell'). The electric charge is determined by sampling the particles on the mesh.

Several kinds of PIC/MC models have already appeared in the literature, but there is not yet a comprehensive model which includes at the same time a kinetic level description of the electron/ion transport and the charge balance, as well as a vibrational/chemical kinetics of hydrogen molecules (left aside the so-called zero dimensional case in which all space dependences of the physical quantities are lost).

---

[*] Corresponding author: dmpl01ch@uniba.it

The coupling of the neutral gas and plasma phase kinetics should always be taken into account since, on one side, the rate coefficients for electron/molecule reactions depend on the local electron energy distribution function (eedf), on the other side, the charged particle motion is affected by the gas composition, in particular by the vibrational distribution and the atomic fraction.

Based on these ideas, a class of PIC/MC models including the kinetics of vibrationally excited molecules was considered in the past few years. These models include a kinetic description of the transport of charged particles and a state-to-state chemical kinetics for molecules, this last term meaning that molecules in different vibrational levels are treated as separate species. Another important problem not yet addressed for this system is an accurate, kinetic-level description of the several kinds of ions existing in the discharge, which should take into account also the thermal distribution of neutral particles in the bulk region of the plasma, where it cannot be neglected because of the thermal energy of ions. In this paper we present an up to date self-consistent 1D model of the hydrogen discharge plasma based on improvements of a previous version [12,13].

With the present model an analysis of the influence of pressure under constant voltage conditions on the discharge characteristics is performed.

2. Kinetic model and numerical method

In reactive plasmas usually the relaxation times of the chemical kinetics are by far higher than the corresponding ones for the electron kinetics, therefore adiabatic elimination of the time dependence of the neutral component densities can be applied. A self-consistent approach involving joint solution of the neutral and charged particle kinetics is necessary, for the reasons explained in the introduction.

Gas/surface reactions are included by setting appropriate boundary conditions [12]. The present model consists of a state-to-state, reaction diffusion model. The chemical kinetics includes eV processes (vibrational excitation due to electron impact):

$$e+H_2(X,v=0) \rightarrow e+H_2(X,v>0)$$

as well as EV processes (similar to eV, but with an electronically excited intermediate, therefore requiring electrons with energy > 10 eV), VV (collisional exchange of vibrational quanta) and VT (collisional quenching of vibrational quanta)

$$H_2(X,v) + H_2(X,w) \rightarrow H_2(X,v-1) + H_2(X,w+1)$$
$$H_2(X,v) + H_2/H \rightarrow H_2(X,v'<v) + H_2/H$$

Also we include several dissociation channels discussed in ref.[13], and attachment processes

$$e+H_2(X,v) \rightarrow H + H^-$$

over the vibrational ladder of the ground electronic state of H_2. A careful description of this last process is only possible if the vibrational distribution function (vdf) is known, since the cross section for the process above increases by several orders of magnitude in the range $0<v<5$. A 1.5D (meaning 1 space dimension and 2 velocity components) PIC/MC method is applied to electrons and four ionic species (H_3^+, H_2^+, H^+, and H^-). The electron/molecule process rates are calculated as a function of position taking into account the translational non equilibrium of electrons and the vibrational non equilibrium of molecules.

The improvements with respect to the previous version [12,13] of the code concern:

(1) the ion/molecule collision treatment, which has been attained by applying a thorough and rigorous Test Particle Monte Carlo technique, derived from the linear Boltzmann equation [14] taking into account the translational distribution of target molecules;

(2) ion kinetics in the treatment of negative ion production and loss, which is non trivial since the production of this ion is strongly affected by the vibrational kinetics, which in turn is affected by interaction with electrons, walls, and atoms.

The density for the neutral species is obtained by finding a stationary solution for the set of non-linear rate equations with a diffusion term that in one dimension reads as:

$$-D_c \frac{\partial n_c(x)}{\partial x^2} = \Sigma_r (\nu'_{rc} - \nu_{rc}) k_r\left(\langle f_e \rangle_t\right) \Pi_{c'} n_{c'}^{\nu_{rc}} \tag{1}$$

where D_c is the diffusion coefficient and ν_{rc} is the molecularity of the c-th species in the r-th elementary process.

After any calculation step of the motion equations, the electrical charge in any cell of the mesh is determined from the number of electrons and ions found in the cell itself, according to their statistical weight.

The electron-molecule process rate coefficients k_r in eq. (1) are calculated as a function of the position taking into account f_e, the electron energy distribution function (eedf):

$$k_r(x) = \sqrt{\frac{2}{m_e}} \int_0^\infty \varepsilon f_e(\varepsilon, x) \sigma(\varepsilon) d\varepsilon \tag{2}$$

where σ is the process related total cross section and ε is the electron energy.

The set of reaction-diffusion equations is numerically solved at the steady state on a mathematical grid by a Gauss/Seidel technique.

For the particle kinetics we use a modified time step technique [10,11], where the particle dynamics evolves in time with an appropriate time step Δt, while the time-to-next collision t_c is an independent variable for any particle, which decreases during the free-flight. The exact time when $t_c(i)=0$ marks a new collision event.

Recombination processes cannot fit the basic PIC/MC formalism since they involve two charged particles. We treat these processes as a combination of two first order ones, each including one of two particle species involved in the process, during a PIC time step .t. Charge neutrality is not enforced, but obtained on the average.

Negative ions reach a steady state density arising from the balance of pseudo zero order production channel (attachment, with rate α) and pseudo first-order consumption channels $\beta n(H^-)$ (detachment, recombination, where β is the loss frequency per H^- particle), i.e. $\alpha = \beta n(H^-)$. The relaxation time $1/\beta$ is often very long with respect to the other plasma time scales.

A special technique has been devised to speed up the convergence of the negative ion density: we scale both α and β to $k\alpha$ and $k\beta$ respectively, with $k > 1$, while keeping $n(H^-) = \alpha/\beta$ constant. This implies a scaling of the cross sections for attachment and detachment, and of the rate coefficients in the treatment of H^- recombination. This has been checked by direct comparison with code results with $k = 1$.

3. Results and discussion

All the quantities shown in the plots have been time averaged during a sampling time $\Delta t_{sampling}$, which is the time interval between two calls of the chemical kinetics module and is typically 2×10^5 time steps, while the time step value is 5×10^{-11} s. In order to save CPU time, any particle is selected for the sampling only with 10% probability.

The code was run for 10^6 PIC time steps with 6 PIC/kinetics iterations in order to reach a steady state solution. The main bottleneck is the (albeit scaled) negative ion density relaxation.

We consider as a test case the following physical conditions: gas temperature 300 K, voltage amplitude 300 V, discharge frequency 13.56 MHz, discharge gap 0.02 m, DC voltage (bias) 0 V. The hydrogen molecules vibrational deactivation probability on the walls is here $\gamma_V = 0.02$, while the atom recombination probability on the walls is $\gamma_H = 0.2$ and these values are obtained through a geometric average of the widely dispersed data found in literature [15-19].

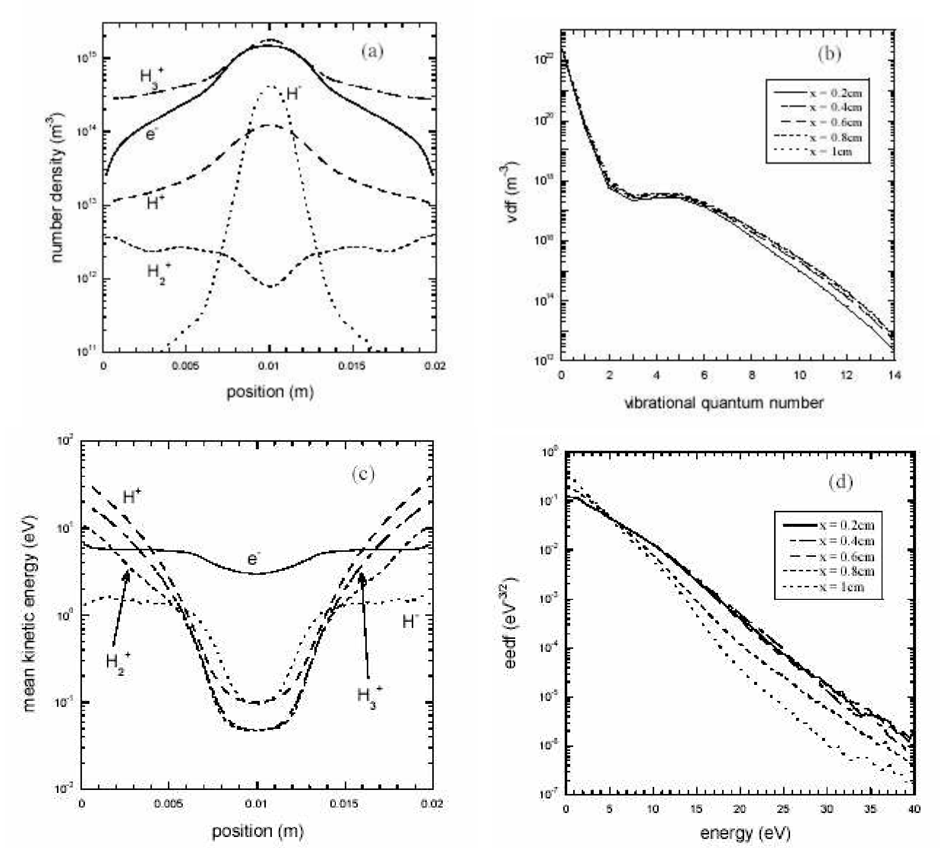

Fig. 1. Plasma quantities for a gas pressure of 1 Torr: (a) number density, (c) mean kinetic energy of charged species as a function of position, (b) vdf as a function of the vibrational quantum number and (d) eedf as a function of energy.

In Fig. 1 plasma quantities for a gas pressure of 1torr are shown. In particular Fig. 1(a) shows the space distribution of the time averaged densities of charged particles. The known phenomenology of discharge plasmas is retrieved: the plasma is neutral in the center (bulk) region while two positive regions (the sheaths) develop in contact with the electrode surface, following the absorption of a fraction of the electrons, which move considerably faster than ions in the plasma. Also it must be noted how negative ions accumulate in the very center of the discharge by dropping into the self-generated ambipolar potential well. The presence of negative ions in the center of the discharge produces a partially electronegative region in the center of the plasma, which affects the distributions of minoritary ions (especially H_2^+).

Fig. 1(c) shows the space distribution of the time averaged energy for charged particles: as expected positive ions are thermalized to the gas temperature in the bulk while they reach fairly high energies in the proximity of the electrode surfaces, while negative ions, which are confined in the center of the discharge, do not reach such high energies. Electrons, which are not effectively thermalized by collisions with the gas medium, have an energy of a few eV in the bulk plasma, and reach a higher energy in the sheath region. Anyway, the collisional kinetics of electrons cannot be determined, as known, from the average energy only, but an account of the full eedf is in order. This last is reported in fig.1(d), which shows that the eedf does not fit a Maxwell distribution (which would appear as a straight line in the kind of plot reported) and the most relevant feature is the long 'tail' at energy > 15 eV. This structure is due to the interaction of a small electron fraction with the high electric field in the sheath region, since only electrons above the ambipolar potential barrier can be accelerated by the sheath field [20]. The presence of this superthermal tail in the eedf favours the production of highly vibrationally excited molecules through the high threshold EV processes.

This results in a peculiar shape for the vibrational distribution function (vdf) as shown in Fig. 1(b), which is characterized by a plateau in the region of v = 4-7. This very long plateau contrasts with the shape of the vdf in the first levels, which can be approximately described by a Boltzmann distribution with a relatively low vibrational temperature T_{v01}.

As a result of this peculiar distribution, together with the strong increase of the dissociative attachment cross section with the vibrational quantum number for the first vibrational levels, the intermediate vibrational levels of the H_2 molecules play the most important role in the production of negative ions.

This result confirms the necessity of including a refined vibrational kinetics in chemical physical models for H_2 discharge plasmas, instead of just considering a single vibrational temperature.

In Fig. 2 the same quantities of Fig. 1 are shown for a gas pressure of 0.5torr. From Fig. 2(a) it can be noticed, in comparison with Fig. 1(a), that the pressure decreasing determines a decreasing of the plasma density, due to a lower ionization collision rate but specially to an higher ambipolar diffusion rate. The sheath thickness increases: it is in fact well known that the product between the pressure p and the sheath width l_{sh} is approximately constant if the RF voltage is not changed.

Decreasing the pressure leads to a lower disuniformity of the electron energy (Fig. 2(c)), because of the larger sheath length and the lower electron energy loss rate. The trend of the vdf does not change very much with the position (Fig.2(b)), since the faster diffusion smoothes the effect of the different pumping rates in different positions. Moreover, the diffusion of electrons to the sheath region and back is accelerated and collisional effects are less important, thereby producing a higher eedf tail in the plasma, as can be seen in Fig.2(d).

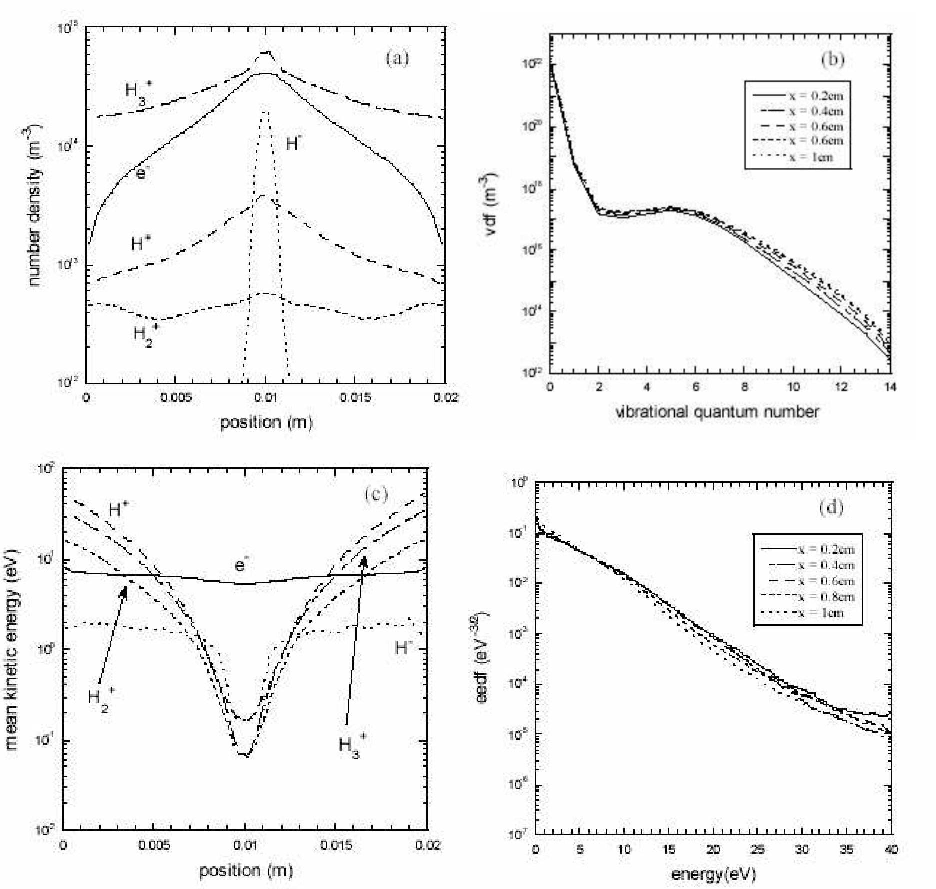

Fig. 2. Plasma quantities for a gas pressure of 0.5 Torr: (a) number density, (c) mean kinetic energy of charged species as a function of position, (b) vdf as a function of the vibrational quantum number and (d) eedf as a function of energy.

A plasma quantity which is very important for material science applications is the plasma potential, specially in the case of plasma etching, since it is the main factor determining the acceleration of positive ions towards the electrode surface. Moreover the plasma potential shape allows to visualize directly the electrostatic well which confines the electrons and the negative ions in the central region of the discharge gap. In Fig. 3 there is a comparison between the averaged plasma potential as a function of position for the test cases at 1torr and 0.5 torr: it can be noticed a slight decreasing in the bulk plasma with the pressure increasing. As it was already remarked in ref. [12] the origin of such a behaviour is not clear, but, since we attain the theoretical limit value for low pressure predicted by simplified analytical theories [21] it can be safely assumed that our simulations are consistent with the collisional plasma electrostatics, and that ion/neutral collisions are responsible for the reduction of the plasma potential when increasing the gas pressure.

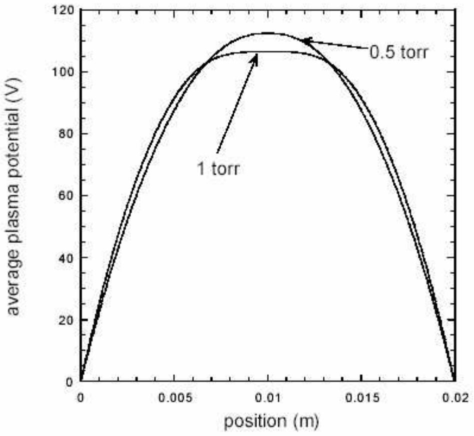

Fig. 3. Average plasma potential as a function of the position for the two test cases considered.

4. Conclusions

A one dimensional particle model for non equilibrium plasmas has been applied to simulate weakly ionized hydrogen plasmas produced in capacitively coupled parallel plate RF discharges. This work reports on the present status of the art; the main improvements with respect to the previous version are: a kinetic description of the interaction of charged particles with the thermal distribution of gas particles, a weighting method which enhances the statistics of minoritary ionic species and a scaling technique to speed up the negative ion stabilization. The method delivers a very detailed view of the plasma kinetics at a reasonable computational cost. As a test case, a study of the influence of hydrogen pressure at constant discharge voltage has been carried out, in order to discuss the complex interplay of phenomena which produce measurable change on plasma characteristics strongly connected to material processing, such as the plasma potential, the electron number density and mean energy.

Acknowledgments

This work was partially supported by MIUR (project no. 2003037912_010). The calculations were performed in the framework of the GRID-FIRB project.

References

[1] A. Gicquel, K. Hassouni, F. Silva, J. Achard, Current Applied Physics **1**, 479 (2001).
[2] R. B Jackman, J. Beckman, J. S. Foord, Diamond and Related Materials **4**, 735 (1995).
[3] P. Bruno, F. Bénédic, F. Mohasseb, G. Lombardi, F. Silva, K. Hassouni, Journal of Physics D: Applied Physics **37**, L35 (2004).
[4] A. von Keudell, Thin Solid Films **402**, 1 (2002).
[5] K. Tsutsumi, H. Terakado, M. Enami, M. Kobayashi, J. Vacuum Sci. Techn. **21**, 1959 (2003).
[6] M. Capitelli, C. M. Ferreira, F. Gordiets, A. I. Osipov, Plasma Kinetics in Atmospheric Gases, Springer-Verlag, Berlin Heidelberg (2000).

[7] M. A. Lieberman, A. J. Lichtemberg, Principles of Plasma Discharges and Materials Processing, Wiley, N.Y. (1994).
[8] V. Vahedi, G. DiPeso, C. K. Birdsall, M. A. Lieberman, T. D. Rognlien, Plasma Sour. Sci. Tech. **2**, 261 (1993).
[9] C. Gorse, R. Celiberto, M. Cacciatore, A. Laganà, M. Capitelli, Chem. Phys. **161**, 211 (1992).
[10] C. K. Birdsall, IEEE Trans. Plasma. Sci. **19**, 68 (1991).
[11] R. W. Hockney, and J. W. Eastwood, Computer Simulation Using Particles, Adam Hilger (1991).
[12] S. Longo, A. Milella, Chem. Phys. **274**, 219 (2001).
[13] S. Longo, I. D. Boyd, Chem. Phys. **238**, 445 (1998).
[14] S. Longo, P. Diomede, Eur. Phys. J. AP **26**, 177 (2004).
[15] A. M. Karo, J. R. Hiskes, R. J. Hardy, J. Vac. Sci. Technol. A **3**, 1222 (1985).
[16] V. L. Orkin, V. G. Fedotov, A. M. Chaikin, Kinet. Catal. **18**, 55 (1977).
[17] P. Kae-Nune, J. Perrin, J. Jolly, J. Guillon, Surf. Science **360**, L495 (1996).
[18] C. Gorse, M. Capitelli, J. Bretagne, M. Bacal, Chem. Phys. **93**, 1 (1985).
[19] B. J. Wood, H. Wise, J. Phys. Chem. **65**, 1976 (1961).
[20] I. D. Kaganovich, L .D. Tzendin, IEEE Trans. Plasma Science **20**, 66 (1992)
[21] K. Koler, J. W. Coburn, D. E. Horne, E. Kay, J. H. Keller, J. Appl. Phys. **57**, 56 (1985).