Particle-in-Cell Simulations of High-Pressure Hydrogen Plasmas Driven by Nano-second Pulsed High-Voltages

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Abstract. Particle-in-cell simulations have been performed to clarify the fundamental physical processes of hydrogen plasmas driven by a nano-second pulsed high voltage under a gas pressure near atmospheric pressure. The discharge is a capacitively-coupled plasma generated between metal electrodes whose gap length is about 1 mm. The simulation has shown details of electron and ion dynamics of the hydrogen plasmas during its formation and decay processes. Temporal evolution of the electron energy distribution function has revealed that, due to the fast dynamics, electrons are not in local thermal equilibrium at an early stage of the discharge.

1. Introduction

A hydrogen molecule is one of the simplest diatomic molecules and its atomic processes have been widely studied and generally considered to be well understood. A gas discharge based on pure hydrogen has been also widely studied partly because it is one of the simplest “molecular” gas discharges and also partly because discharges based on its isotopes, i.e., deuterium and tritium, have been considered as plasmas to be used in magnetically-confined thermonuclear fusion reactors such as tokamaks. Hydrogen plasmas are also chemically reactive. For example, hydrogen plasmas are used to clean surfaces of tokamak inner walls or microelectronic devices because highly reactive species in hydrogen plasmas can react with impurities deposited on those surfaces.

Conventionally, for processing applications, hydrogen plasmas are generated under low pressure conditions and therefore materials that can be treated by such hydrogen plasmas have been limited to those that can be placed in a vacuum chamber. On the other hand, for chemically reactive plasmas with little thermal load that can be operated in atmospheric-pressure conditions, the range of their process applications is much wider. For example, a material that contains sufficient amount of water (such as living tissues) can be treated by such plasmas.

In this work, in an attempt to develop plasma processing techniques in atmospheric pressure conditions, we study fundamental properties of atmospheric-pressure plasmas. Especially of interest here is to understand fundamental physical processes that take place during the formation and decay phases of a hydrogen discharge generated by a fast high-voltage pulse. Such pulsed discharges are commonly employed among almost most low-gas-temperature atmospheric-pressure plasmas such as dielectric barrier discharges.

In what follows, we study a (spatially) one-dimensional plasma generated between flat metal electrodes by nano-second pulsed high-voltages at a gas-pressure near atmospheric pressure¹, using numerical simulations. The discharge gas is hydrogen. Physical processes involved in the formation of
such plasma are very fast and transient. Therefore, although the pressure is high and the plasma can be very collisional, there is a possibility that the electrons may not be locally in thermal equilibrium. Therefore, as we shall explain more in detail in the following sections, we use a particle method for numerical simulations, from which temporal evolution of the electron energy distribution during the discharge can be obtained.

2. Particle-in-Cell simulation
In this work, a 1d2v (one dimensional in physical space and two dimensional in velocity space) electrostatic particle-in-cell (PIC)\(^2\)\(^-\)\(^4\) code with Monte Carlo Collisions (MCC)\(^2\)\(^,\)\(^5\) has been developed to simulate capacitively coupled plasma (CCP) discharges. The null collision operator\(^5\) has been employed to improve computational efficiency for collision calculations. This code has been fully tested and verified for sample simulations of several simple cases such as Langmuir oscillation, plasma sheath formation\(^7\), and low pressure radio-frequency (RF) argon discharges\(^8\)\(^,\)\(^9\).

3. The numerical model
In the simulation, a hydrogen plasma is generated between two parallel electrodes, i.e., a grounded anode and a cathode connected with an external voltage source. The applied voltage is a triangular pulse with a peak value of -2 kV, and its duration is 10 ns. Its temporal profile is shown in figure 1. The total process simulated in this study lasts for about 25 ns. The distance between the two parallel electrodes is 1.2 mm. The hydrogen gas pressure is set at 0.3 atm. These conditions are similar to those used for the experiments given in Ref. [1].

Initially a low-density plasma is uniformly distributed between the electrodes, which may be considered as a remnant of the previous pulsed discharge. As the initial conditions, the plasma is assumed to be in thermal equilibrium at 300 K. The secondary electron emission coefficient is assumed to be null for the sake of simplicity.

The dominant product of electron impact ionization of a hydrogen molecule is an H\(_2^+\) ion\(^10\). However, typically the produced H\(_2^+\) ion readily collides with another hydrogen molecule and turns into an H\(_3^+\) ion\(^11\). Therefore, the only ionic species used in the simulations presented here is H\(_3^+\). The electron-neutral collision processes considered here are elastic collision, ionization to H\(_2^+\) (which is considered to turn to H\(_3^+\) immediately), vibrational excitation of \(v = 0 \rightarrow 1\), and electronic excitations to the \(b \ ^3\Sigma^+\), \(B \ ^1\Sigma^+_u\), and \(E,F \ ^1\Sigma^+_g\) states. The corresponding cross section data are adopted from Ref. [10] and summarized in figure 2. The ion-neutral elastic collision has been also taken into account and the cross section data for this process have been obtained from Ref. [11].

![Figure 1. The temporal profile of applied voltage on the cathode.](image1)

![Figure 2. Electron-H\(_2\) molecule collision cross sections adopted from Ref. [10].](image2)
4. Simulation results and discussion
Trajectories of charged particles and the time evolution of electric field profile have been evaluated under the condition that the voltage given in figure 1 is applied to the cathode. Details of behavior and statistical characteristics of the hydrogen plasmas obtained from the simulation are described below.

4.1. Electric field and potential profiles
The time evolution of electric field is shown in figure 3(a). At $t = 8$ ns (i.e., 3 ns after the onset of voltage application) when the magnitude of the applied voltage has risen to 1.2 kV, the electric field profile is fairly flat, which indicates that there is little space charge in the plasma. This is also seen in the electric field potential shown in figure 3(b), where the potential profile is linear. By the time the voltage peaks (at $t = 10$ ns), however, a thick cathode sheath is formed and the electric field in the bulk is shielded to the high degree. Since no secondary electron emission is taken into this simulation, few electrons remain near the cathode by this time and the plasma is located closer to the anode. After the applied voltage peaks, it is seen that the anode sheath is gradually formed since many electrons are absorbed by the anode until the ambipolar diffusion prevents electrons from further drifting toward the anode.

Figure 3. Snapshots of electric field (a) and potential (b) profiles at different time instances. Plasma starts to shield the applied voltage at 8 ns and leads to a plasma potential confining electrons inside the bulk plasma.

4.2. Dynamics of charged particles
Time evolutions of the electron and ion density profiles are given in figure 4. Before the onset of driving voltage application, electrons and ions remain uniform in space with little loss to the electrodes. After the voltage is applied and its magnitude increases, electrons move toward the anode, generating more charged particles through the ionization process along their way toward the anode whereas ions in the system hardly move in this fast time scale due to their large inertia. The number of charged particles thus greatly increases during the period from $t = 7$ ns to 9 ns as ionizations mostly are occurred in this period. By this time a plasma bulk is distinctly formed with a small peak at the edge close to cathode. The peak is likely to be created by electron impact ionization near the sheath edge where colliding electrons have high kinetic energies due to the acceleration by the strong sheath potential. Since the electrons drift toward the anode with high velocities near the sheath edge whereas ions are nearly immobile in this time scale, the peak in electron density profile is smaller and closer to the anode compared with that in the ion density profile. The cumulated charged particles will gradually diffuse outward after the peak period of ionization rate.
4.3. Electron energy probability function

The electron energy distribution function (EEPF) is defined as

$$f_e(E) = \rho_e f_e(E) / \sqrt{E}$$

where $E$ is the electron energy, $\rho_e$ is the electron number density, and $f_e(E)$ is the electron energy distribution function whose integration over the entire $E$ yields unity. The EEPF $f_e(E)$ is defined at each location. Note that if the electron velocity distribution function is Maxwellian, the logarithm of EEP, i.e., $\ln f_e(E)$ is a linear function of $E$. In this study, the EEPF was measured near the center of the discharge gap at some time instances, which are shown in Fig. 5. It is seen that, at an early stage of discharge, the EEPF deviates from a simple Maxwellian to a non-Maxwellian due to the electron acceleration by the strong electric field induced by the pulse voltage. Detail analysis of the EEPF time evolution is beyond the scope of present work and deferred to a future study.

5. Conclusions

The dynamics of a hydrogen plasma generated by a high voltage pulse applied to a pair of parallel electrodes has been investigated. It has been found that the formation of the plasma is essentially driven by fast electron dynamics whereas ions and neutral species hardly move in this time scale. Macroscopic dynamics of the discharge obtained from the simulations have been found similar to the recent experimental observations of pulsed hydrogen discharges performed under the conditions nearly identical to those of this study. The simulations have also shown that, despite the high collisionality, electrons in the bulk, measured at the center of the discharge region, can transiently exhibit non-Maxwellian energy distributions. In other words, in such a fast discharge process, the system is not necessarily in local thermal equilibrium.

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Figure 5. The EEPFs measured in the middle of the discharge at different time instances before (a) and after (b) the peak of the applied voltage.

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