Hydrogen kinetics in plasma chemistry

HYDROGEN KINETICS IN PLASMA CHEMISTRY

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Introduction

A special interest arises nowadays in the development of effective sources of reactive hydrogen radicals: vibrationally-excited molecules, atoms and ions. The beams of hydrogen radicals are of principal importance in the various schemes for deposition of hydrocarbon coatings, for selective etching of the surfaces, in the passivation of amorphous silicon and polysilicon films [1]. The kinetics of hydrogen molecules, atoms and ions in plasmas and on surfaces are of great interest in understanding the process of negative hydrogen ion formation in volume- and surface production negative ion sources [2]. In fusion experiments the kinetics of hydrogen species determine the heat losses in the plasma. Therefore a traditional and new theoretical and experimental methods have to be employed in order to make a correct study and optimization of the non-equilibrium properties of hydrogen radicals in plasmas.

Modelling

It is obvious that any progress in the characterization of the plasma properties is impossible without theoretical analysis and correct mathematical modelling of physical and chemical phenomena. Two theoretical approaches have been used to simulate the properties of thermal and low-pressure hydrogen plasmas.

1. The flow of wall stabilized plasmas in a cylindrical channel with axial gas flow is considered. The MHD conservation equations of energy and momentum, equation of continuity, the Maxwell equations and Ohm's law have been treated by the method described in detail elsewhere [3]. It was shown [5], that in contrast to the argon arc, near the axis of the hydrogen arc a strongly constricted high-temperature axial channel is realized. Near the channel walls the hydrogen plasma ionization and dissociation degrees are sharply lower in comparison with the corresponding axial values. In the hydrogen arc the conductive heat flux on the walls of the channel exceeds the conductive heat flux in the argon arc by more than an order of magnitude [5].

2. Detailed kinetic scheme for the calculation of the rates of elementary collisional processes in non-equilibrium hydrogen plasma have been developed in [6]. In the local balance approximation the kinetic scheme includes the processes of electron-heavy particle interactions, VV-exchange and VT-relaxation of the vibrationally excited H_2, radiative transtitions of hydrogen atoms, chemical and ion-molecular reactions, electron attachment and detachment, electron-ion and ion-ion recombination. In the calculation of the electron energy distribution function (EEDF) the processes of elastic scattering by neutrals and ions, and rotational, vibrational and electronic excitation (deexcitation) of the molecules have been taken into account. Besides, the processes of the ionization of hydrogen atoms and molecules, and dissociative attachment of electrons to the molecules have been used in the calculation scheme. It is essential, that the model includes complete sets of electron-impact bound-bound and bound-free transitions between the quantum states of H_2. Franck-Condon factors and

densities were obtained by means of a numerical solution of Schrödinger equation for vibrational degrees of freedom of H_2 [6]. The numerical code obtained provides a solid basis for the accurate simulation of strongly non-equilibrium hydrogen plasma properties.

Diagnostics

1. A hydrogen wall stabilized cascaded arc plasma is a promising candidate as a high enthalpy source of hydrogen radicals for surface modification and for the creation of the intense atomic and ion (H^+ or H^-) beams. A comparative study of hydrogen and argon cascaded arc plasma have been experimentally carried out [7]. The results show, that the efficiency and the pressure gradients of the hydrogen arc was lower, than the same characteristics of the argon arc, whereas the electric field strength was higher. The experimental data were in a good agreement with the results of numerical modelling of the hydrogen and argon cascaded arc plasma [5,7].

2. A recombining plasma, expanding from the cascaded arc plasma source into a low background pressure vessel is used for high rate deposition of amorphous hydrogenated carbon or silicon layers, when the monomers as CH_4 or SiH_4 are injected to the beginning of the expanding argon plasma [8]. In the case that the plasma is used as a hydrogen atom or ion source, H_2 is injected in the argon plasma jet or the cascaded arc is operated in H_2. In the expanding plasma direct electron excitation and ionization are absent due to the low T_e [9,10] and the kinetics are controlled by heavy particle interactions as non-resonant charge exchange, dissociative recombination and attachment [11]. Optical absorption spectroscopy has been applied to measure the absolute population densities of the first excited levels of atomic hydrogen H^*(n=2) and argon Ar^*(4s) in hydrogen-argon mixture [12,13]. It has been shown, that the density of hydrogen excited atoms H^*(n=2) serves as an indicator of the presence of argon ions and hydrogen molecules in the expanding plasma. The atomic density of hydrogen and argon in the first excited state, and a simple kinetic model are used to determine the atomic ground state density and estimate dissociation degree of hydrogen plasma. The kinetic scheme used does not require information on the electron energy distribution function in the plasma [13].

In Refs. [11,14] an expanding argon cascaded arc plasma with different amounts of hydrogen added, was studied using the Thomson-Rayleigh scattering and optical emission spectroscopy. The electron density and temperature, neutral particle density and excited hydrogen atoms $H^*(n \geq 3)$ absolute population density have been determined as function of the axial position in the expansion. The admixture of a small amount of hydrogen to the argon flow leads to a dramatic - up to three orders of magnitude decrease of the charged particles density [11]. The explanation of this phenomena is the recirculation of H_2 in the vessel, which destructs the charged particle density by charge exchange to a molecular ion and subsequent dissociative recombination of the formed ArH^+ and H_2^+ molecular ions [11,14]:

$$H^+[Ar^+] + H_2^{v,j} \longrightarrow H_2^+[ArH^+] + H, \tag{1}$$

$$H_2^+[ArH^+] + e \longrightarrow H[Ar] + H^* \tag{2}$$

3. The absolute density of atomic hydrogen excited states in a magnetized expanding pure hydrogen plasma is measured using emission spectroscopy. In the experiments the cascaded arc has been operated under very low pressure of the order of 30 Torr, and very low hydrogen flow $\simeq 8$ scc/s. The motivation to apply magnetic field and to use low pressure

and gas flow is to avoid the observed strong recombination in a freely expanding plasma jet. Cascaded arc plasma under investigation should be far from the thermal equilibrium [3]. The generated plasma beam will contains the radicals and stable particles with the strong non-equilibrium characteristics of translational and internal degrees of freedom [5]. In the expansion a population inversion is observed between the quantum states $3 \leq p \leq 7$. The electron density n_e and temperature T_e are obtained by a double Langmuir probe diagnostics. Comparing the measured population densities with the densities calculated on basis of the measured n_e and T_e, using a purely atomic collisonal-radiative model, leads to the conclusion that purely atomic recombination processes can not account for the large population densities observed. It is argued that molecular induced recombination reactions in which the negative ion participates should be taken into account:

$$H_2^+[H^+] + H^- \longrightarrow H_2[H] + H^*(p). \qquad (3)$$

Hydrogen negative ions H^- and positive molecular ions H_2^+ either generated by the arc or formed in the reactions with the participation of rovibrationally excited $H_2^{v,j}$ molecules:

$$H_2^{v,j} + e \longrightarrow H^- + H, \qquad (4)$$

$$H_2^{v,j} + H^+ \longrightarrow H_2^+ + H. \qquad (5)$$

From the above discussion it is clear, that the crucial point of the kinetic schemes (1) - (5) is the presence in the recirculating plasma flow of rovibrationally excited hydrogen molecules. Such a molecules might be generated by volume, or by surface reactions. More experimental data is required to identify the source of $H_2^{v,j}$ molecules in the expanding plasma.

4. To avoid the influence of surface phenomena in the interpretation of charged particle recombination kinetics a hydrogen microwave pulsed discharge freely localized in a space has been specially designed and investigated [6]. The temporal evolution of the charged particle density has been measured by the technique of absorption of a diagnostic microwave beam. The results received show the fast exponential decay of electron density. It has been interpreted as a consequence of the fast dissociative recombination. Kinetic estimation show, that for this case the dissociative recombination of the complex molecular ions with the electrons are the main reasons for the plasma decay [6].

Discussion

Theoretical calculations and experimental methods have been used to analyse the properties both thermal and non-equilibrium hydrogen plasma. A good agreement between the calculated and experimental data on the macroscopic plasma properties have been obtained for the sub-atmospheric pressure arc discharges. At the same time several principal open questions remain about the properties of non-equlilibrium reduced pressure hydrogen plasma.

It was shown, that presence of rovibrationally-excited hydrogen molecules in the recombining plasma could strongly influence the mechanisms and even the directions of the chemical reactions. The formation mechanisms of these excited molecules are the subject of special interest. Both homo- and heterogeneous collisional processes should be analysed in that respect. For the volume production of $H_2^{v,j}$ reactions of stepwise electron excitation and mutual neutralization of the ions (3) have been analysed as possible candidates. For the expanding cascaded arc plasma the transport of rovibrationally-excited hydrogen molecules formed in the arc could be important as well.

The inelastic collisional processes of the plasma particles on the surfaces including absorption and desorption of the radicals could be interpreted as a catalytic action of the surfaces to the extent that it leads to changing of the particle excitation. For the non-equilibrium hydrogen plasma a special interest in that respect represent the heterogeneous reactions of catalytic atom recombination. In that case the desorbed molecules with the large probability leave the surface with a substantial rotational and/or vibrational energy, which depends on the recombination-desorption mechanisms. By the convective gas flows the desorbed rovibrationally-excited molecules can be transported into the plasma jet, strongly influence the plasma properties (see reactions (1) - (5)). In contrast to the ionizing plasma system, where the excitation phenomena in the volume determine practically all plasma properties, the recombining plasma with the cold electrons (where the excitation processes from the plasma volume are negligibly small), represents a special interest namely at analysis of the particle excitation phenomena on the surfaces.

Further evaluation of both theoretical and experimental diagnostic methods are required for a deeper understanding of the mechanisms of formation of non-equilibrium characteristics of hydrogen plasma.

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