Modeling of The Atomic Hydrogen Production in the Reflective Discharge with Additional Self-Heating Cathode

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Abstract – This work is devoted to a theoretical simulation of atomic hydrogen production in self-maintained low-pressure discharge in crossed $E\times H$ fields (reflective-magnetron discharge) with an additional self-heated (hot) cathode in the form of a rod located in the system axis. The atomic hydrogen distribution in the discharge volume and the flux density of hydrogen atoms on the disk cathode are analytically calculated on basis of the theoretical model of the discharge and atomic hydrogen formation. Simulation results allow one to analyze in complex the operation of real atomic hydrogen sources based on this discharge type.

1. Introduction

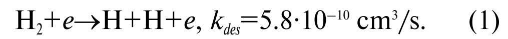
In recent years, the treatment of semiconductors structures by atomic hydrogen (AH) flows is wide applied due to a minimum of charges and defects bringing in. plasma sources based on high frequency and super-high frequency discharges [1, 2] and sources based on hydrogen molecules dissociation on a hot surface, in particular on a heated filament [3, 4] or a capillary [5, 6] were made for AH production.

In [7] a new AH source based on low-pressure discharge in crossed $E\times H$ fields was offered. It is distinguished among AH sources by the molecular hydrogen dissociation both in the discharge volume and on the heat-insulated rod which is situated in the axis of the system and heated to high temperatures by the energy released in the discharge. A method of self-consistent determination of discharge parameters based on a physical model of the discharge was proposed in [8]. The paper is a continuation of these works and it is devoted to a theoretical study of AH production in the reflective discharge with an additional self-heated cathode (SHC).

2. The model of AH production and recombination

Let us consider an axisymmetric discharge cell (of height h) consisting of a hollow cylindrical anode of radius R, two water-cooling plane-parallel disk cathodes biased by the same negative potential relative to the anode, and additional heat-insulated cathode (of radius R_0) in the form of a rod situated in the axis of the system and connected with one of cathodes. The discharge cell is in a uniform external magnetic field, whose field lines are parallel to the symmetry axis of the system. Both disk cathodes have small orifices (one for driving of the working gas, another for extraction of the hydrogen flow), but the effect of ones on discharge processes will be neglected in our calculations. It is possible to maintain a steady operating pressure of the gas in the discharge cell in the range $10–10^3$ Pa by forcing the gas to flow through these small orifices.

At first let us consider the basic channels of AH production and recombination. It is known [2, 9] that the AH production in low-temperature plasma occurs in the main due to the dissociation of hydrogen molecules by electron impact through the excitation of electronic states of molecules:

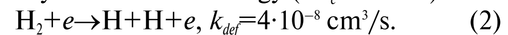


$$H_2+e\rightarrow H+H+e,\ k_{des}=5.8\cdot10^{-10}\ \text{cm}^3/\text{s}. \qquad (1)$$

The energy threshold for this reaction is rather high (8.7 eV), and, hence, the constant of dissociation by slow (plasma) electrons (kT_e~2 eV), k_{des}, is relatively small. The volume-averaged rate of AH production through molecules dissociation by plasma column electrons is determined by the concentration of molecular hydrogen, n_{H_2} (assumed here for estimations equal to $2\cdot10^{16}$ cm^{-3}), and the concentration of plasma electrons, n_{es} (assumed here for estimations equal to 10^{13} cm^{-3}), and the dissociation constant of hydrogen molecules by slow electrons, $k_{des}(T_e)$:

$$\Gamma_{es}=2k_{des}n_{H_2}n_{es}\sim2\cdot10^{20}\ \text{cm}^{-3}/\text{s}.$$

The dissociation of hydrogen molecules by means of impact excitation of molecules by fast electrons accelerated in the cathode drop occurs in the same way, but the corresponding constant, k_{def}, will be determined by the electrons energy (eU_c~100 eV):

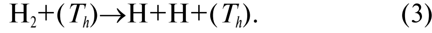


$$H_2+e\rightarrow H+H+e,\ k_{def}=4\cdot10^{-8}\ \text{cm}^3/\text{s}. \qquad (2)$$

The average rate of AH production through the dissociation of molecules by fast electrons is determined by the concentration of molecular hydrogen, n_{H_2}, and fast electrons, n_{ef}~$0.01n_{es}$, and by the constant of the dissociation of hydrogen molecules by fast electrons, $k_{def}(U_c)$:

$$\Gamma_{ef}(r)=2k_{des}n_{H_2}n_{ef}\sim1\cdot10^{20}\ \text{cm}^{-3}/\text{s}.$$

The rate of hydrogen atomization on the SHC surface heated to temperature T_h can be characterized by the probability of surface dissociation, P_d:



$$H_2+(T_h)\rightarrow H+H+(T_h). \qquad (3)$$

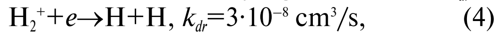
The average rate of AH production through the dissociation of hydrogen molecules on the hot surface of SHC can be written as:

$$\Gamma_s=1/2n_{H_2}v_{H_2}P_d\sim 1\cdot 10^{20}\ \text{cm}^{-2}/\text{s},$$

where v_{H_2} is the average velocity of hydrogen molecules and $P_d(T_h)$ is the probability of surface dissociation of hydrogen (here it is equal to 5 %). More correct calculations of P_d will be given below.

Rates of other reactions which can possible in the discharge cell are significantly lower; thereby they will not be consider in the calculations. We give for information quantitative data for characteristic rates of these reactions that are taking of [9, 10].

The dissociative recombination of hydrogen molecular ions is characterized by a great constant k_{dr}:

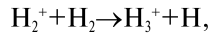


$$H_2^{+}+e\rightarrow H+H,\ k_{dr}=3\cdot 10^{-8}\ \text{cm}^3/\text{s}, \qquad (4)$$

but the concentration of hydrogen molecular ions in plasma is comparatively low ($n_{H_2^+}\sim n_{es}$). Therefore, the average rate of AH production through dissociative recombination of hydrogen molecular ions is estimated to be on the level:

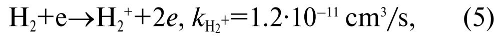
$$\Gamma_{dr}=k_{dr}n_{es}^2\sim 5\cdot 10^{17}\ \text{cm}^{-3}/\text{s}.$$

The fast ion-molecule reaction gives a rather more rate of AH production:



$$H_2^{+}+H_2\rightarrow H_3^{+}+H,$$

whose rate is limited by the rate of production of hydrogen molecular ions:

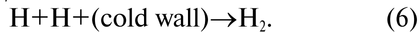


$$H_2+e\rightarrow H_2^{+}+2e,\ k_{H_2^+}=1.2\cdot 10^{-11}\ \text{cm}^3/\text{s}, \qquad (5)$$

$$\Gamma_{H_2^+}=k_{H_2^+}n_{es}n_{H_2}\approx 2\cdot 10^{18}\ \text{cm}^{-3}/\text{s}.$$

The processes of AH production, whose rates are proportional to square of charged particles concentrations (for example, electron-ion recombination of molecules), can be ignored.

Now we shall discuss the rates of possible channels of AH recombination. The recombination of hydrogen atoms on the cold walls of the discharge cell can be characterized by the probability of surface recombination, γ_r.



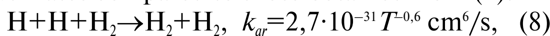
$$H+H+(\text{cold wall})\rightarrow H_2. \qquad (6)$$

The value of γ_r for an actual surface exposed to air is ~0.1 for the majority of metals [11]. In the case of a gas discharge in ultra-pure hydrogen, owing to ion sputtering and chemical etching, the surface of the metal electrode becomes atomically clean, and it can be assumed that $\gamma_r\cong 1$ [12]. Therefore, the effective rate of AH recombination on cold metal walls due to surface recombination, Rw, can be estimated to be

$$R_w\cong\gamma_r v_H n_H\approx 1\cdot 10^{20}\ \text{cm}^{-3}/\text{s}. \qquad (7)$$

Here $v_H=D_H/\Delta^2$ is the frequency of AH loosing on walls, where D_H is the AH diffusion coefficient and Δ is the mean path of an atom from the appearance place to electrodes surfaces.

Let us show that under conditions of a low-pressure discharge the triple recombination of hydrogen atoms in the discharge volume yield substantially lower rates compared to those obtained from (7):



$$H+H+H_2\rightarrow H_2+H_2,\ k_{ar}=2{,}7\cdot 10^{-31}T^{-0{,}6}\ \text{cm}^6/\text{s}, \qquad (8)$$

$$R_{ar}=k_{ar}n_{H_2}n_{H^2}\approx 1\cdot 10^{15}\ \text{cm}^{-3}/\text{s}. \qquad (9)$$

where k_{ar} is the coefficient of triple recombination of AH, T is the gas temperature in K [13].

In this work we consider the range of gas pressures that provide considerably greater rates of surface recombination in comparison with the rate of volume recombination of hydrogen. In this case, AH recombination only on cold walls of the discharge cell can be considered.

Thus, in our model AH production and recombination occur due to the processes (1–3) and (6), respectively. We also assume that the AH concentration is always low in comparison with the molecular hydrogen. For this case, it is possible to assume that the H2 concentration is a constant.

3. The model of AH production on a hot surface

Let us consider in more detail the AH production through the dissociation of molecules on the SHC surface. A hydrogen molecule flux $1/4n_{H_2}v_{H_2}$ falls on the surface of the heated metal; some part of these molecules will be reflected and other part will be adsorbed at the surface. The rate of adsorption of the H_2 molecule under impact with the surface is characterized by the coefficient of condensation, α_c, which is numerically equal to the probability of adsorption of the molecule under impact with the surface. In the literature the value of the coefficient is varied from 0.05 to 0.3. The bonding energy of a molecule H_2 with a surface is very low; therefore, the fact of molecule adsorption on the surface means its instant dissociation into two atoms H which have a rather high energy of bonding with the surface.

We will characterized desorption of atoms from the surface by the constant k_1 and recombination of atoms on the surface with their following desorption by the constant k_2. The approximate dependences of these constants on the temperature of the metal surface have the form [11]:

$$k_1(T_h)\cong 2.2\cdot 10^{13}\exp(-E_1/kT_h)\ \text{s}^{-1},$$

$$k_2(T_h)\cong 2.5\cdot 10^{-3}\exp(-E_2/kT_h)\ \text{cm}^2/\text{s}, \qquad (10)$$

where $E_1\approx 2.92$ eV is the bonding energy of a hydrogen atom with a tungsten surface, $E_2\approx 2E_1-E_D=1.35$ eV is the energy of formation of a hydrogen molecule on a tungsten surface, $E_D=4{,}48$ eV is the dissociation energy of a free hydrogen molecule.

A molecule adsorbed on the surface is dissociated instantly into two atoms which can thereafter either be desorbed from the surface in the form of AH or recombine back into a molecule and be rapidly desorbed from the surface in the form of molecular hydrogen. Then the balance of particles on the hot metal surface in the model can be written as:

$$\alpha_c n_{H_2}v_{H_2}/2=k_1n_s+k_2n_s^2, \qquad (11)$$

where n_s is the surface concentration of hydrogen atoms, $\alpha_c\cong 0.07$ is the coefficient of condensation of hydrogen molecules on the surface [11]. Solving (11), we can find n_s and determine the probability of

surface dissociation, P_d, as the ratio of the AH flux from the surface, $k_1 n_s$, to the double flux of falling molecules, $\alpha_c n_{H_2} v_{H_2}/2$:

$$P_d = \frac{k_1}{k_2 n_{H2} v_{H2}} (-k_1 + \sqrt{k_1^2 + 2k_2 \alpha_c n_{H2} v_{H2}}). \quad (12)$$

The dependence $P_d(T_h)$ is presented in Fig. 1. It can be seen that the probability of dissociation on the surface at a temperature of up to 1700 K is practically equal to zero. Further, the probability sharply increase with the temperature of the surface and tends to saturation, reaching its limiting value determined by the value of the coefficient of condensation, $\alpha_c \cong 0.07$. We shall use this dependence $P_d(T_h)$ in subsequent calculations.

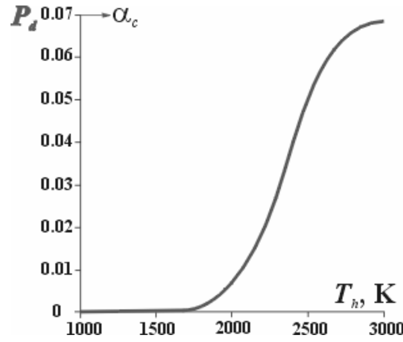


Fig. 1. The probability of surface dissociation of hydrogen molecules, P_d, as a function of the temperature of the surface T_h

4. Calculation of the AH concentration in the discharge volume

The time-independent continuity equation for hydrogen atoms can be written as:

$$-D_H \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial n_H(r,z)}{\partial r} \right) + \frac{\partial^2 n_H(r,z)}{\partial z^2} \right] = $$
$$= 2n_{H2}(k_{des} n_{es} + k_{def} n_{ef}(r)), \quad (13)$$

where r is the running radial coordinate, z is the running height coordinate, D_H is the diffusion coefficient of hydrogen atoms, n_{es} is the concentration of slow electrons (we assume it constant), $n_{ef}(\rho)=(2j_{fc}\tau_f/h)[1+C_K K_0(\rho)+C_I I_0(\rho)]$ is the concentration of fast electrons, C_K and C_I are constants calculated previously [8] from boundary conditions; $I_0(x)$, $K_0(x)$ are the modified Bessel functions; j_{fc} is the flux density of γ-electrons emitted from the cathode; τ_f is the effective life-time of a fast electron (the time for which a fast electron becomes a slow one); $\rho=R/l_d$ is the dimensionless radial coordinate; $l_d=(4m/3E_i)^{1/2}U_c/B$ is the characteristic diffusion length which determines the scale of movement of a fast electron across a magnetic field within its life-time; U_c is the cathode drop; E_i is the average energy of electron-ion pair formation; m is the electron mass; B is the magnetic field induction.

The boundary conditions for equation (13) can be written as:

$$n_H(r, \pm h/2)=0, \quad n_H(R, z)=0,$$

$$-D_H \left. \frac{\partial n_H(r,z)}{\partial r} \right|_{r=R_0} = \frac{1}{2} n_{H2} v_{H2} P_d - \frac{1}{4} n_H(R_0, z) v_H. \quad (14)$$

Taking into account boundary conditions (14), the solution of equation (13) will have the form:

$$\frac{n_H(\rho,\nu)}{n_{H2}} = \sum_{i=0}^{\infty} \frac{2(-1)^i}{L\lambda_i} \left(\frac{b}{\lambda_i^2} + \frac{a(C_I I_0(\rho) + C_K K_0(\rho))}{\lambda_i^2 - 1} \right) \cos(\lambda_i \nu) +$$
$$+ \sum_{i=0}^{\infty} [C_{1i} I_0(\lambda_i \rho) + C_{2i} K_0(\lambda_i \rho)] \cos(\lambda \gamma), \quad (15)$$

where $\nu=z/l_d$ is the dimensionless height coordinate; $L=h/2l_d$ is the normalized half-height of the discharge cell; $\lambda_i=\pi(2i+1)/2L$ are factors determined from the first boundary condition of (14); $a=4j_{fc}\tau_f k_{def} l_d^2/hD_H$ is a constant corresponding to the fast electrons contribution to the AH production; $b=2k_{des} n_{es} l_d^2/D_H$ is a constant corresponding to the slow electrons contribution to AH production; C_{1i} and C_{2i} are factors determined from boundary conditions (14).

Knowing the AH concentration (15), we can find an expression for AH flux onto the disk cathode:

$$q_H(r) = -D_H \left. \frac{\partial n_H(r,z)}{\partial z} \right|_{z=\frac{h}{2}}. \quad (16)$$

5. Results of calculation and discussion

We give examples of the dependences obtained with the use of the model described. For calculations we take following geometric dimensions for the discharge cell: h=1 cm, R=0.5 cm, R_0=0.1 cm, corresponding to the AH source described in [7]. Besides, we put γ=0.08, α_c=0.07 [11], the values characteristic of tungsten (the material of the SHC), and for the induction of an external magnetic field B=0.08 T.

The example of AH distribution in the volume is shown in Fig. 2, *a*. Calculation have shown that the main contribution to the AH concentration near the rod is from the thermal dissociation of hydrogen; the AH concentration in the bulk of the discharge is provided by plasma electrons; the contribution of fast electrons to AH production is insignificant. To support the aforesaid, we give a plot which illustrates the contribution of various channels of AH production to the flux on the disk cathode (Fig. 2, *b*). Contributions of channels of AH production through fast and slow electrons impact near the SHC become comparable between themselves in spite of the significantly smaller concentration of fast electrons, although their sum doesn't exceed a half of AH flux obtained by means of thermo-dissociation. But in the discharge volume the situation is changed: the contribution of thermo-dissociation becomes insignificant, while the main flux is given by AH produced through slow electrons impact dissociation.

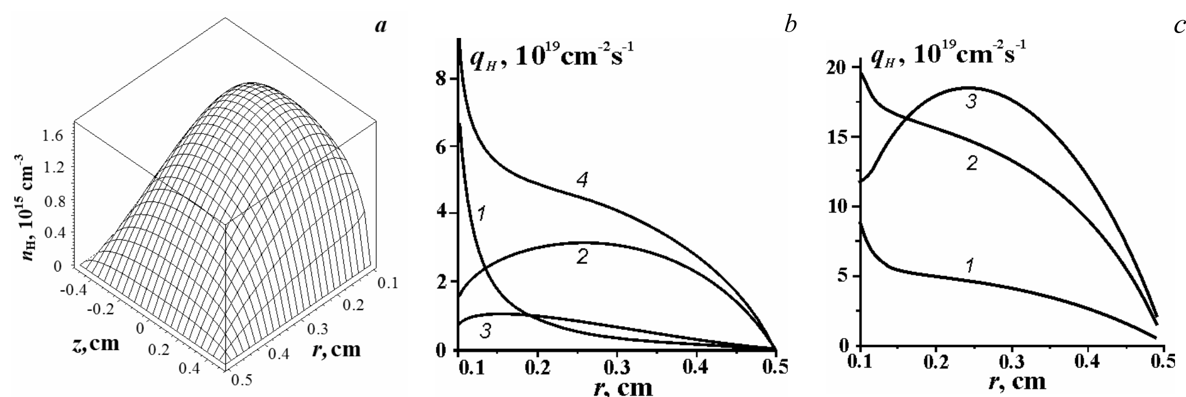


Fig. 2. The AH distribution in the discharge volume (*a*) and radial distribution of the AH flux on the disk cathode (*b*, *c*). In Fig. 2, *b*: curve 1 is the AH flux formed on the SHC surface; curve 2 is the AH flux formed due to slow electrons; curve 3 is the AH flux formed due to fast electrons; curve 4 is the total AH flux. In Fig. 2, *c*: curve 1: $n_{H_2} = 1.3 \cdot 10^{16}$ cm^{-3}, U_c=250 V, I=1 A, T_h=2400 K; curve 2: $1.3 \cdot 10^{16}$ cm^{-3}, 100 V, 4.4 A, 2700 K; curve 3: $6.4 \cdot 10^{16}$ cm^{-3}, 250 V, 1 A, 2400 K

Fig. 2, *c* shows how the radial distribution of the AH flux on the disk cathode varies with discharge operating conditions and molecular hydrogen concentration in the discharge cell. It is seen that variations in discharge operating conditions at the same pressure do not vary the form of the radial distribution. But the lower is the discharge operating voltage, and the higher current, the higher is the SHC temperature. And the higher is the temperature, the greater number of atoms which are formed on thermal dissociation of molecules on the SHC. The form of the radial AH flux distribution varies rather significantly with increasing of the molecular hydrogen concentration. Thus, increasing of the molecular hydrogen concentration, we can create conditions under which AH extraction will be effective not only near the SHC, but also at some distance from it. In the last case the fraction of metal impurities getting in the AH flux due to evaporation of the thermo-cathode material can be reduced significantly.

6. Conclusion

Based on the study performed, we can concluded that the model of AH production (based on the discharge operation model) allows one to calculate the AH concentration in the discharge volume and the radial distribution of AH flux taking into account contributions of different channels of AH production (knowing discharge parameters and the SHC temperature) in complex. Thus the model can be helpful in preliminary optimization of designs of AH sources based on reflective discharges with SHC.

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