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Journal of Nuclear Materials 258–263 (1998) 1066–1072

journal of nuclear materials

Estimation of incident flux rate in PDP experiments by calculating plasma composition

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Abstract

To evaluate the incident flux rate in PDP experiments by the electron cyclotron resonance (ECR) discharge device, the plasma composition was investigated by measurement and calculation. Electron temperature, electron density, plasma potential, and H_α emission intensity were measured and the atomic/ionic hydrogen densities in the plasma were calculated. The incident flux rate could be evaluated from the view point that atomic/ionic hydrogen particles go toward the membrane via inter-diffusion or ambipolar-diffusion in the sheath. Good agreement was achieved between the measured PDP rate and the calculated one which was based on the evaluated incident flux rate. Quantitative investigation of PDP behavior by means of plasma discharge devices has come to be possible thanks to this incident flux evaluation.

1. Introduction

It is well-known that atomizing or ionizing hydrogen molecules brings about large hydrogen permeation rate through a metal membrane, which is called plasma driven permeation (PDP) [1]. This phenomenon is very important for developing fusion reactors because it may cause tritium leakage from the plasma fusion reactors. It is one of the most serious problem of plasma wall interaction (PWI). On the other hand, it can be applied to the tritium separation system by means of a superpermeable membrane pump [2–4]. A lot of PDP experiments have been carried out by employing atomizers, ion guns, plasma discharge devices etc. and they have given us valuable knowledge of the PDP mechanism ([5–7] etc.). To study PWI, the circumstance of the scrape-off plasma layer has to be taken into consideration. There are low energy atoms, ions, and electrons in this layer. We have carried out PDP experiments with electron cyclotron resonance (ECR) discharge plasma to deal with these particles together. The incident flux rate has to be evaluated to investigate permeation behavior quantitatively, e.g. recombination coefficients, permeation probability, etc. But it is difficult to grasp the rate in the PDP experiment using a plasma discharge device. In this work, the densities of atomic/ionic hydrogen were calculated and the incident flux rate was evaluated. The plasma characters, that is, electron temperature; T_e, electron density; $[e^-]$, and plasma potential; V_p, in addition to PDP rate were measured. The relation between PDP rates and the calculated densities was investigated to know the incident flux rate.

2. Experimental

The arrangement of ECR discharge device for PDP experiments is shown in Fig. 1. A test membrane is placed in the middle of the plasma chamber and isolated electrically from the device body. Hydrogen in the plasma impinges upon the membrane surface and the permeation rate through it is measured by the mass spectrometer [8]. The Langmuir Probe is inserted into the plasma and T_e, $[e^-]$ and V_p are diagnosed [9]. H_α emission intensity, which gives the information of the excited state atomic hydrogen density, was measured by

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PII: S0022-3115(98)00086-5

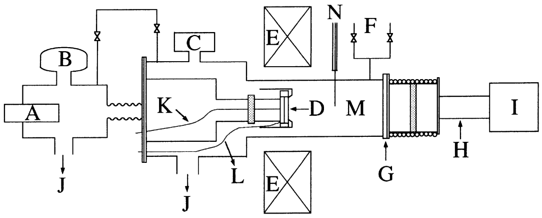

Fig. 1. Arrangement of the experimental apparatus A: Quadrupole mass spectrometer; B: ionization vacuum gauge; C: capacitance manometer; D: test membrane; E: magnet (0.0875 T); F: hydrogen isotope gas feedinlet; G: ceramic window; H: micro-wave guide; I: micro-wave generator; J: turbo molecular pump; K: thermo couple; L: lead-wire for bias; M: plasma chamber; N: langmuir probe.

a spectrum analyzer. In this work, the experiment was carried out with introducing H_2 gas into the plasma chamber at the pressure of 0.1–10 Pa and discharging by 2.45 GHz microwaves and 875 gauss magnetic field.

3. Calculation analysis

The calculation of atomic and ionic hydrogen densities in the ECR discharge plasma is executed in this work, because the incident flux rate into the membrane surface is considered to be greatly related to the densities and it is difficult to measure them experimentally.

In general, when two types of particles A and B exist and their velocities and densities are v_A, v_B and n_A, n_B respectively, the total reaction times per unit volume and unit time in collision process R is written as

$$R = K n_A n_B, \tag{1}$$

where K is a rate constant given by

$$K = \int\int F(v_A)F(v_B)|v_A - v_B|\sigma(|v_A - v_B|)\,dv_A\,dv_B. \tag{2}$$

$F(v)$ is Maxwell's velocity distribution function and σ is a reaction cross-section depending on the relative velocity. When the collision occurs between a molecule/atom and an electron, K is described as

$$K = \int |v_e|\sigma(|v_e|)F(v_e)\,dv_e, \tag{3}$$

because of the large velocity of electron v_e. The reactions considered here are as follows:

$$H_2 + e^- \rightarrow 2H^0 + e^-, \tag{4}$$

$$H_2 + e^- \rightarrow H_2^+ + 2e^-, \tag{5}$$

$$H_2 + e^- \rightarrow H^+ + H^0 + 2e^-, \tag{6}$$

$$H + e^- \rightarrow H^+ + 2e^-, \tag{7}$$

$$H_2^+ + e^- \rightarrow H^+ + H^0 + e^-, \tag{8}$$

$$H_2^+ + e^- \rightarrow H^0 + H^*(n \geqslant 2), \tag{9}$$

$$H_2^+ + e^- \rightarrow 2H^+ + 2e^-, \tag{10}$$

$$H_2^+ + e^- \rightarrow H^+ + H^*(n = 2) + e^-, \tag{11}$$

$$H_3^+ + e^- \rightarrow 3H^0 \quad \text{or} \quad H_2 + H^*(n = 2), \tag{12}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H^0. \tag{13}$$

The reactions of minus ions should be taken into consideration but they are negligible because of their small total amount in the steady state of the plasma considered here. Every atom/ion density is balanced in the steady state; that is, both generating and consuming speeds of it are equal. For example, H_3^+ is described as

$$K_{13}[H_2^+][H_2]V = 2K_{12}[H_3^+][e^-]V + SD_{H_3^+}[H_3^+]/L, \tag{14}$$

where K_{12}, K_{13} are rate constants of the reactions in Eqs. (12) and (13), respectively. $[X]$ means the density of X in the steady state plasma. V and S are the volume and the surface area of the plasma, L the sheath width and $D_{H_3^+}$ the ambipolar diffusion coefficient of H_3^+. $SD_{H_3^+}[H_3^+]/L$, means the consuming speed of H_3^+ by diffusing to the chamber wall. This generation/consumption balance equation is applied to H^0, H^+, H_2^+ and e^- in the same way. V and S of the experimental device shown in Fig. 1 are 3.5×10^{-4} m^3 and 5.0×10^{-2} m^2. L is estimated from the relation of Debye radius; λ_D, i.e.

$$L = \eta\lambda_D. \tag{15}$$

When a large monotonous conductor is inserted with the bias voltage of $-V_p$ against plasma potential, η is given by

$$0.97\eta^2 = \left(\frac{eV_p}{kT_e} - \frac{1}{2}\right)^{3/2}, \tag{16}$$

where e, k and T_e are elementary electric charge of electron, Boltzmann constant, and electron temperature, respectively. The values of $D_{H^+}P$, $D_{H_2^+}P$ and $D_{H_3^+}P$ used here are 9.31, 7.98 and 6.74 m^2 Pa/s [10–12], where P is gas pressure (Pa). The gradient of $[H^0]$ may exist in the sheath and interdiffusion is considered to occur. D_{H^0} (m^2/s) is given by

$$D_{H^0} = 1.14 \times 10^{-3}\frac{T^{1.728}}{P}, \tag{17}$$

where T and P are gas temperature (K) and gas pressure (Pa) [9]. The reaction cross-section data of Eqs. (4)–(13) have been reported [13] and K_2–K_{13} are calculated with Eq. (2) or Eq. (3). The total electric charge in the plasma is maintained neutral, that is,

$$[H^+] + [H_2^+] + [H_3^+] = [e^-]. \tag{18}$$

With Eq. (18) and the equations describing the generation/consumption balance of H^0, H^+, H_2^+ and H_3^+, each hydrogen atom/ion density in the steady state for a certain plasma condition can be calculated. The density of the exited state hydrogen ($n=2$); $[H^*]$ is estimated as

$$[H^*] = A[H]/B, \tag{19}$$

where A is the generation speed of H^* and B is that of atomic hydrogen including H^*, respectively.

4. Results of experiments and calculations

T_e, $[e^-]$, and V_p diagnosed by the Langmuir Probe and H_α emission intensity measured by a spectrum analyzer at the pressure of 0.1–10 Pa are shown in Fig. 2. All of them have different plasma pressure dependence. T_e tends to be higher at the lower pressure and is unchanged at $\sim$4.5 eV above 0.5 Pa. The reason why T_e at the lower pressure is higher is that the numbers of electrons and atoms are small and the energy supplied for an electron by ECR heating is large. $[e^-]$ has a peak around 0.9 Pa, which means this pressure region is the efficient condition for ionizing hydrogen due to ECR. To be qualitative, the number of electrons which are excited increases with the pressure being higher, but it decreases above a certain pressure because the collision of electrons with molecules or atoms increases and the electrons lose the energy not to excite molecules or atoms. Lower pressure gives longer mean free path of electrons. It results in increasing the number of electrons which diffuse toward the chamber wall and making the plasma potential higher at lower pressure. H_α emission intensity has a similar pressure dependence to $[e^-]$, which means the density of exited neutral atoms is affected by the electron density in the plasma.

The calculated plasma compositions are shown in Fig. 3. It is found that all of the hydrogen ion densities are greatly effected by $[e^-]$, and that H_2^+ is rich at the lower plasma pressure and H^+ and H_3^+ become richer at the higher pressure. This accords with the experimental result measured in the present device [14]. $[H^0]$ increases with the plasma pressure being higher in spite of $[e^-]$ being smaller. $[H^*]$ has a similar pressure dependence to

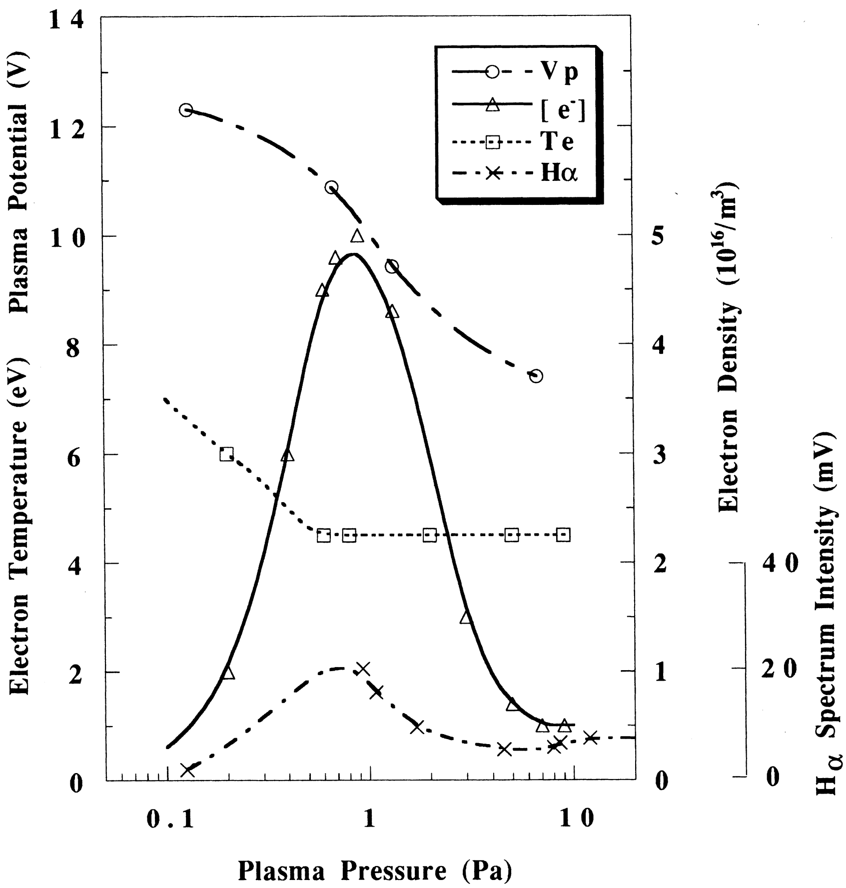

Fig. 2. The result of plasma parameter measurement.

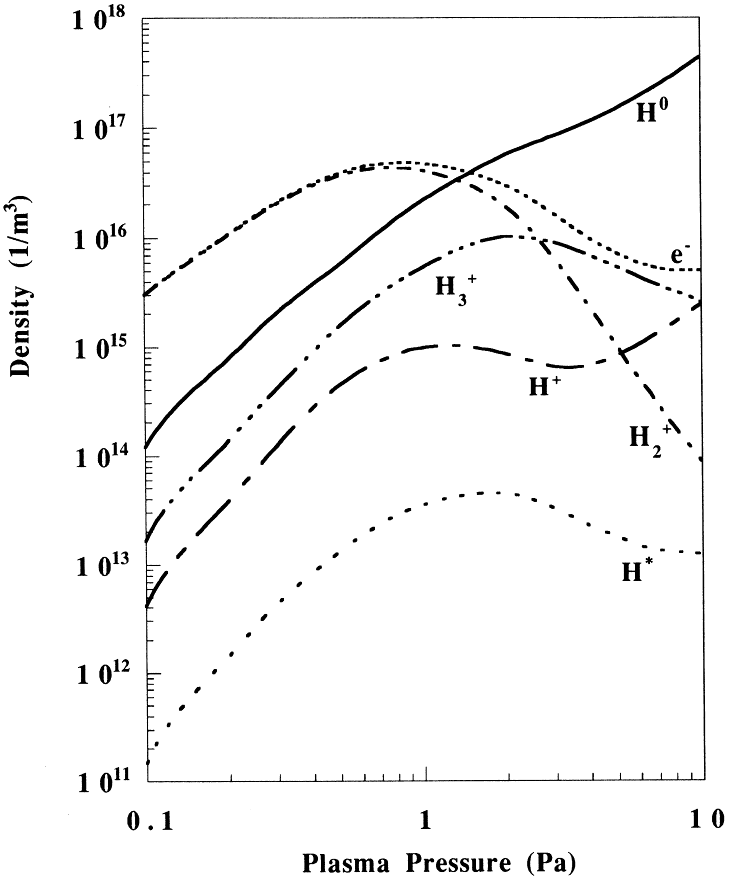

Fig. 3. The calculated plasma composition.

H_α emission intensity especially at the higher pressure, which affirms the fact that the intensity is proportional to the number of exited neutral hydrogen atoms ($n=2$) when T_e is constant. The accordance between the theoretical results and the experimental ones indicates that the plasma compositions in the device of Fig. 1 have been successfully estimated by the calculation executed here.

5. Discussion

It is important to know the incident hydrogen flux rate ϕ for the analysis of the data obtained in PDP experiments. ϕ is considered to be greatly influenced by plasma compositions. The reason why PDP rate is much larger than GDP rate is the existence of hydrogen atoms and ions in the plasma which have enough energy to dissolve into metal easily. The test membrane is located in the middle of the plasma chamber shown in Fig. 1 and isolated electrically from the device body. The floating potential of the membrane measure was around −7V against the plasma at the pressure of 1–7 Pa. If a sheath is formed in front of the membrane, the ions existing in the plasma are considered to diffuse to the membrane surface ambipolarly. The atoms may inter-diffuse to the surface when the density of H^0 has a gradient in the sheath. Here, ϕ was estimated from the terms of ambipolar/inter-diffusion of atoms/ions in the sheath in front of the membrane. ϕ is described as

$$\phi = (A_{H^0}D_{H^0}[H^0] + A_{H^+}D_{H^+}[H^+] + 2A_{H_2^+}D_{H_2^+}[H_2^+] + 3A_{H_3^+}D_{H_3^+}[H_3^+])/L_p, \quad (20)$$

where A_x is a constant representing the incident probability of each atomic/ionic hydrogen composition. D_x is the inter-diffusion or ambipolar-diffusion coefficient. L_p is the sheath width in front of the membrane. D_x and L_p should be changeable when the plasma pressure varies. To be qualitative, D_x becomes smaller as the plasma pressure becomes higher, and L_p is influenced by T_e, [e$^-$] and the floating potential of the membrane. When hydrogen gas is at the room temperature, $D_{H^0}:D_{H^+}:$

$D_{H_2^+}:D_{H_3^+}$ at unit pressure results in 3.28:1.38:1.18:1. If all of A_x's are equal, Eq. (20) is transformed into

$$\phi = \frac{kD_{H_3^+}[H_{eff}]}{L_p}, \tag{21}$$

$$[H_{eff}] = 3.28[H^0] + 1.38[H^+] + 2.36[H_2^+] + 3[H_3^+], \tag{22}$$

where k is a constant which compensates errors related to the incident probability.

It is difficult to estimate the sheath width exactly using Eqs. (15) and (16), because the area of the membrane is not large ($\sim$2 cm^2). In addition, the diffusion rate in the sheath cannot be evaluated exactly using $D_{H_3^+}$ which was determined under the higher pressure condition ($\sim 10^2$ Pa) because the pressure in the present case is low [10–12], i.e. 0.1–10 Pa. Here, it was assumed that the sheath width in front of the membrane could be estimated by these equations and that $D_{H_3^+}$ was available in this lower pressure. Fig. 4 shows the calculated incident flux rate using Eqs. (21) and (22) when k is 1. According to this calculation, $[H_2^+]$ mainly contributes to ϕ at lower pressure (<1 Pa) and $[H^0]$ does at higher pressure (>1 Pa).

The steady-state PDP is rate-determined by diffusion in bulk or recombination on surfaces [15]. In our previous work, when the plasma pressure was 1.33 Pa and the 200 μm Ni membrane was maintained at 523 K, PDP was proved to be rate-determined by recombination on the upstream surface and diffusion in the bulk, i.e. RD-Regime. In addition, the recombination coefficient of the upstream surface; K_1 was estimated at 8.7×10^{-29} m^4/s when K_1 is ten times as much as that of the downstream surface; K_2 and the diffusion coefficient of metal (Ni) for hydrogen; D_m at 6.3×10^{-11} m^2/s [16]. PDP rate, J in RD-Regime is given by

$$J = \frac{D_m}{2L_m}\sqrt{\frac{\phi}{2K_1}}, \tag{23}$$

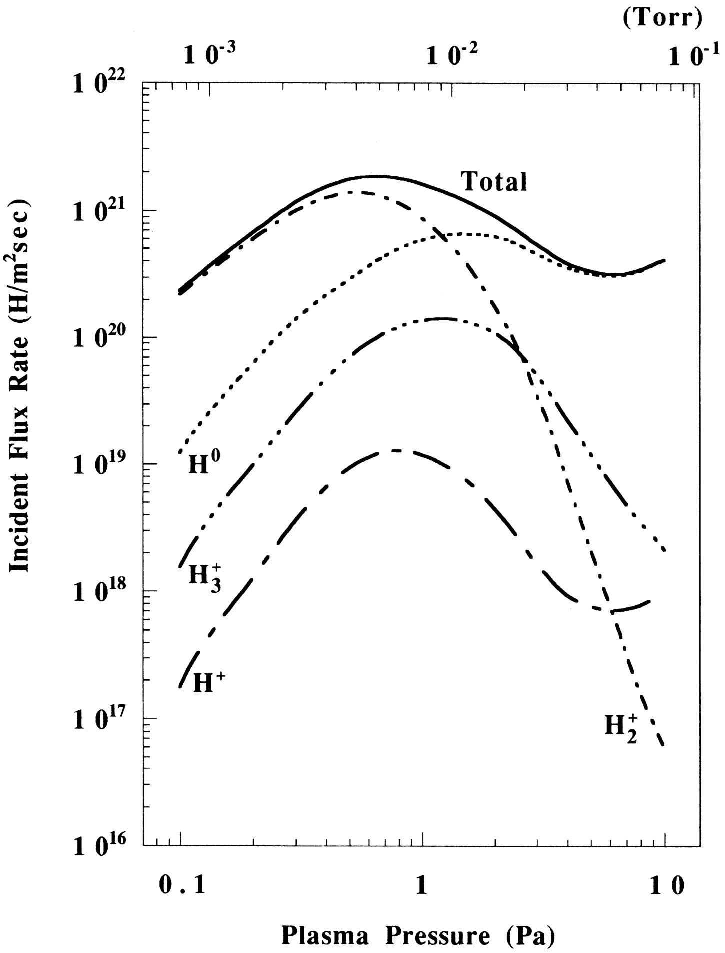

Fig. 4. The calculated incident flux rate for incident probability being 100%.

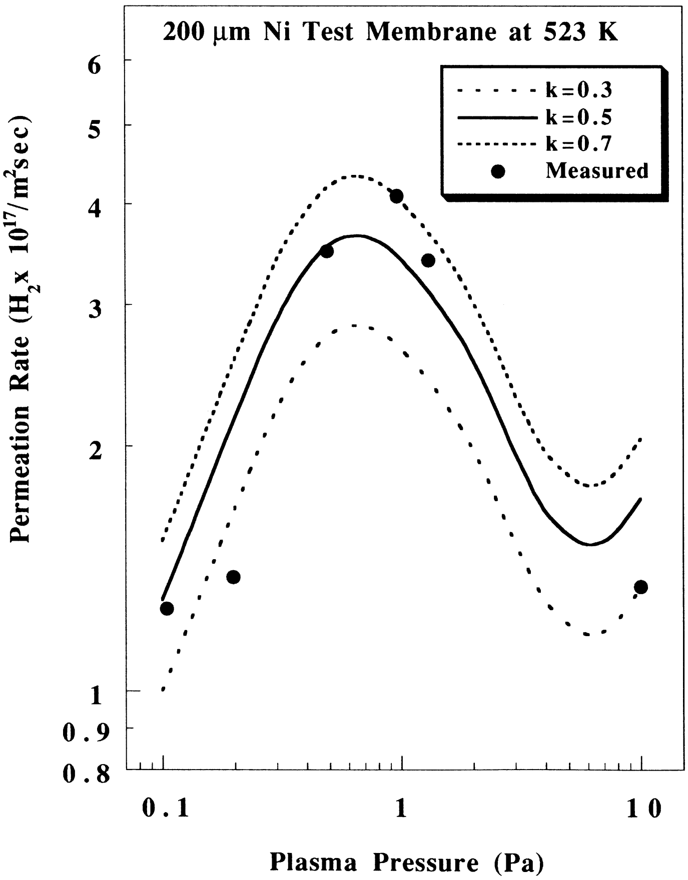

Fig. 5. The calculated PDP rates comparing with the measured ones.

where L_m is the thickness of a membrane [15]. With Eqs. (21)–(23), PDP rate in RD-Regime can be evaluated. Fig. 5 shows the calculated PDP rate through 200 μm Ni membrane maintained at 523 K for k being 0.3–0.7 in Eq. (21). In this figure, the experimental data measured at various plasma pressure are also shown all of which are considered to be in RD-Regime. Good agreement between the calculation and the experiment is achieved when the incident probability is around 50%, which means Eqs. (21) and (22) are available to evaluate the incident flux from the calculated plasma composition data. This result enables us to predict the incident flux rate when PDP experiments are carried out under the restricted discharge conditions in plasma devices.

6. Conclusion

The densities of plasma compositions, that is, atomic/ionic hydrogen composition in the ECR discharge plasma was formulated to obtain the incident flux rate in PDP experiments. For the numerical calculation, electron temperature; T_e, electron density; $[e^-]$, plasma potential; V_p were measured and each of them was found to have different plasma pressure dependence. They affected the plasma composition, e.g. the plasma pressure dependence of all atomic/ionic hydrogen densities was greatly influenced by $[e^-]$. The rate of incident flux ϕ was evaluated on the assumption that ϕ is caused by ambipolar-diffusion and inter-diffusion in the sheath. Good agreement was achieved between the measured PDP rate and the calculated one which was based on the evaluated ϕ. This has enabled us to investigate PDP behavior quantitatively which is experimented by means of plasma discharge devices.

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