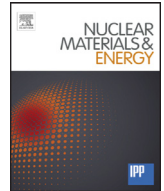




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Characteristic of a PdCu membrane as atomic hydrogen probe for QUEST

Masayuki Onaka^a, Ikuji Takagi^{a,*}, Taishi Kobayashi^a, Takayuki Sasaki^a, Arseniy Kuzmin^b, Hideki Zushi^b

^a Department of Nuclear Engineering, Kyoto University, Kyoto daigaku-Katsura, Nishikyo-ku, Kyoto 615-8540, Japan

^b RIAM, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka, 816-8580, Japan

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ABSTRACT

A permeation probe is a useful device for detecting the atomic hydrogen flux to plasma-facing walls. Recently, we developed a new type of probe using 60Pd-40Cu alloy (PdCu) as the permeation material. The deuterium behaviors in PdCu samples were investigated using nuclear reaction analysis (NRA) and permeation observations, and the diffusion coefficient and recombination coefficients were determined from these observations. It was found that the sensitivity of a 0.02-mm-thick probe was as high as 0.5 below 473 K and was independent of the incident flux. The response time at 473 K was 0.41 s and 1.3 s under an incident flux of $10^{20} \text{ m}^{-2} \text{ s}^{-1}$ and $10^{19} \text{ m}^{-2} \text{ s}^{-1}$, respectively. Thus, we concluded that the new PdCu probe can effectively detect the incident atomic hydrogen with high sensitivity and a suitable response time.

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1. Introduction

Hydrogen recycling from plasma-facing walls would directly affect the performance of fusion devices [1–3]. Thus, its control is an important issue for maintaining sufficiently stable fusion plasma over a long period of time [4]. However, little information is available on the atomic hydrogen flux to a wall, which is the main source of recycling, because of the difficulties in measuring neutral particles. In our previous works [5,6], a permeation probe with a metal membrane [7] was installed in the spherical tokamak QUEST at Kyusyu University to measure the atomic hydrogen flux. This probe can discriminate atomic hydrogen from hydrogen molecules based on the difference in permeation behaviors through the membrane. Atomic hydrogen such as neutral atoms and atomic hydrogen ions can easily enter and permeate the metal, which is known as the plasma-driven permeation. Thermal molecules of hydrogen, on the contrary, hardly permeate because they have to be dissociated into atoms before entering the metal and the probability of dissociation is generally very low. It was found that a Ni membrane probe operated for a long period of time (more than several thousand discharges), and provided data

on the wall pumping and fueling, which were attributed to hydrogen recycling [5,6].

There are two unique features of the permeation probe compared to other diagnostic systems such as H- α measurement. The first involves the position quality. The probe only detects atomic hydrogen impinging on a place where the membrane is located. The second is its movability. Because the probe size is very small, it can be installed inside the wall and moved by remote manipulation. A disadvantage of the probe is the time response due to hydrogen diffusion through the membrane. For the real-time measurement of the atomic hydrogen flux, it is essential to improve the time response. For this reason, we have developed a new probe with a membrane made of 60Pd-40Cu alloy (PdCu) [8]. The hydrogen diffusion coefficient in PdCu is very high [9]. PdCu has a higher mechanical strength than pure Pd, allowing a smaller membrane thickness. These characteristics would lead to an improvement in the time-response and sensitivity. A long operating period is also expected because no hydride is formed in PdCu.

The characteristics of the permeation probe, such as its response time and sensitivity, can be evaluated based on the diffusion coefficient and recombination coefficients. However, little information is available on the diffusion coefficient, and there are no data on the recombination coefficients. In the present work, these properties were experimentally determined, and the characteristics of the PdCu probe were evaluated and compared with those of the former Ni probe.

* Corresponding author. Fax: +81 75 383 3915.

E-mail address: takagi@nucleng.kyoto-u.ac.jp (I. Takagi).

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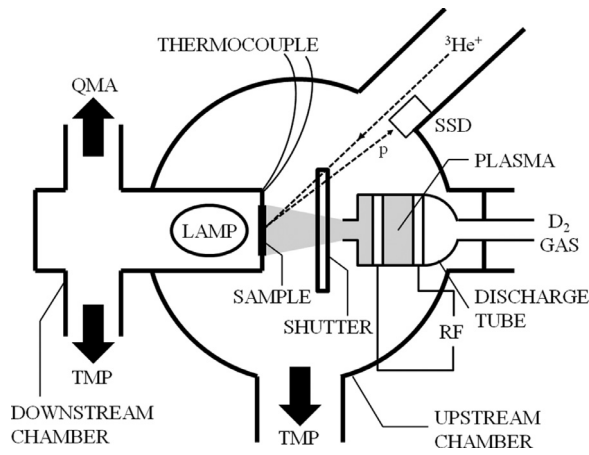


Fig. 1. Schematic view of experimental setup.

2. Diffusion coefficient

The sample material was the palladium-copper alloy 60Pd–40Cu (in wt%) prepared by Tanaka Kikinzoku Kogyo. A 0.2 mm-thick disk with an effective diameter of 18.5 mm was used as a sample specimen for diffusion coefficient measurements.

Fig. 1 shows a schematic view of an experimental setup. The sample was mounted between upstream and downstream chambers. The upstream side of the sample was exposed to deuterium RF plasma produced in a discharge tube, and the permeation flux to the downstream side was monitored by a quadrupole mass analyzer (QMA). After the permeation reached a steady state, a mechanical shutter [10] located between the sample and the plasma was quickly moved from one side to the other, and the time-dependent change in the permeation flux was monitored. The shutter had small holes at the initial position and a large hole at the end position. Thus, the operation of the shutter increased the deuterium incident flux to the sample. In this system with plasma and the shutter, the incident flux change had little effect on the sample temperature compared with a conventional system with a gas pressure change. The sample was heated by a lamp, and its temperature was 373–593 K.

In the analysis, permeation is first assumed to be limited by the recombination process, that is, the hydrogen (deuterium) concentration C is uniform over the sample. Since in the steady state, an incident flux F is the sum of a permeation flux J through the sample and a reemission flux R from the upstream surface, the flux balance is expressed as follows:

$$F = J + R \quad (1)$$

where,

$$J = K_d C^2 \quad (2)$$

$$R = K_u C^2 \quad (3)$$

K_u and K_d are the recombination coefficients of the upstream and downstream surfaces, respectively. From Eqs. (1)–(3),

$$F = \frac{K_u + K_d}{K_d} J \quad (4)$$

Eq. (4) shows that F is proportional to J . When the incident flux is changed from F_i to F_f at $t=0$, where F_i and F_f are values at the initial and the end positions of the shutter, respectively, the time evolution of the transient permeation flux $J(t)$ is expressed as [11],

$$J(t) = J_f \left[\frac{A(t) - 1}{A(t) + 1} \right]^2 \quad (5)$$

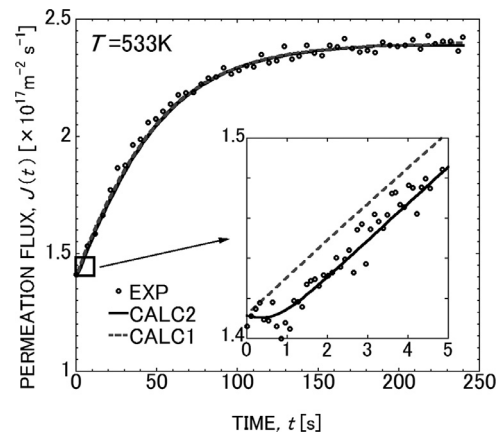


Fig. 2. Time evolution of permeation flux through 0.2 mm-thick PdCu sample at 533 K. The results of calculations with the recombination-limited analysis (CALC1) and diffusion analysis (CALC2) are also shown.

$$A(t) = \frac{\sqrt{J_f} + \sqrt{J_i}}{\sqrt{J_f} - \sqrt{J_i}} \exp(\lambda t) \quad (6)$$

$$\lambda = \frac{2(K_u + K_d)\sqrt{J_f}}{L\sqrt{K_d}} \quad (7)$$

where L is the sample thickness, and J_i and J_f are the permeation flux at the initial ($t=0$) and final ($t \rightarrow \infty$) states, respectively. Eq. (5) can be fitted to almost all of the experimental data, as shown by the dashed line (CALC1) in Fig. 2 with one fitting parameter of λ . K_u and K_d are estimated from λ in Eq. (7) and J_f in Eq. (4), where F_f is assumed to be $5.0 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$. In the calculation, the initial rise of the permeation curve around $t=0$ cannot be fitted, as shown in the inner frame of the figure, as the result of a time-lag caused by the diffusion process. This indicates that the permeation is limited by the recombination process at all times except for the initial rise.

In order to analyze the experimental data at the initial rise, a one-dimensional diffusion equation is numerically solved under the boundary conditions for recombinative desorption [6],

$$F_f = [K_u C^2 - D(\partial C/\partial x)]_{x=0} \quad (8)$$

$$0 = [K_d C^2 + D(\partial C/\partial x)]_{x=L} \quad (9)$$

and an initial condition of

$$C(x, 0) = C_i \quad (10)$$

C_i is the steady-state deuterium concentration at $t \leq 0$. It is not zero because the sample is exposed to deuterium plasma through the small holes in the shutter. In the analysis, K_u and K_d are taken from the above results of CALC1. These values might include some small errors but they do not affect the initial rise of the permeation curve. The value of C_i is estimated from J_f and K_d with Eq. (2). The result of the calculation with a fitting parameter of diffusion coefficient D agrees well with the experimental data, as shown in a solid line (CALC2) in Fig. 2. The values of D at several sample temperatures are plotted in Fig. 3, from which D is expressed as

$$D = 2.9_{-0.7}^{+0.9} \times 10^{-8} \exp(-0.048 \pm 0.012 \text{ eV}/kT) \text{ m}^2/\text{s} \quad (11)$$

This agrees well with the results of Völkl's work on hydrogen diffusion [9], as shown in Fig. 3, considering that the data are somewhat scattered as a result of experimental errors, and the pre-exponential factor of the diffusion coefficient is smaller for D than for H , typically by the inverse of the square root of the mass ratio [12].

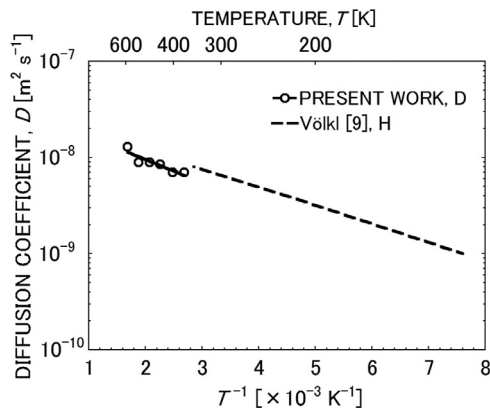


Fig. 3. Temperature dependence of deuterium diffusion coefficient in PdCu.

3. Recombination coefficients

In the above diffusion measurement, a 0.2-mm-thick sample was used to emphasize the lag-time by the diffusion process, while the thickness of the probe membrane was only 0.02 mm for the purpose of improving the time response. Because the recombination process is greatly affected by surface impurities [13], the recombination coefficients in the 0.2 mm sample might be different from those in the 0.02 mm probe membrane. Moreover, the recombination coefficients could not be exactly estimated in the diffusion experiment because the exact value of the incident flux was unknown. Hence, another series of experiments on the recombination coefficient was performed, in which the deuterium concentration and permeation flux in a 0.02 mm-thick sample were observed at the same time.

The sample membrane, which was made of the same material as the permeation probe, was set between the two chambers in the experimental setup shown in Fig. 1. However, the mechanical shutter was removed, and the sample was set close to the discharge tube. Under continuous deuterium plasma exposure to the upstream side of the sample, that is, under a steady-state permeation, an analysis beam of 1.7 MeV $^3\text{He}^+$ from the 4 MV van de Graaff accelerator of Kyoto University was used to irradiate the plasma-exposure side, and the protons produced by a nuclear reaction $\text{D}(^3\text{He}, \text{p})^4\text{He}$ were detected using a solid-state detector (SSD). The deuterium depth profile near the surface was obtained from the energy spectrum of the protons. The probing depth was 1.5 μm . The details of this experiment have been described elsewhere [14]. The depth profile consisted of two parts; a peak at surface and a plateau in bulk, which were attributed to absorbed deuterium and dissolved deuterium, respectively. Here, the deuterium surface density S and deuterium concentration C were taken from the profile as an integral value between -0.2 and $0.2 \mu\text{m}$ and an averaged concentration between 0.2 and $1.5 \mu\text{m}$, respectively. The negative depth in the integration range was caused by the finite depth resolution of the NRA system ($0.2 \mu\text{m}$ for the full width at half maximum), and the deuterium atoms on the surface could be assigned at a negative depth. The temperature of the sample was 348–643 K. As C and S were measured under the constant permeation flux, these parameters were considered to represented values at steady state.

Fig. 4 shows the temperature dependences of J , C , and S . The recombination coefficient on the downstream surface K_d is directly obtained by substituting J and C into Eq. (2). Fig. 5 shows the temperature dependence of K_d , which is expressed as,

$$K_d = \begin{cases} 5.13^{+6.99}_{-2.96} \times 10^{-31} \exp(-0.0012 \pm 0.0410\text{eV}/kT) & \text{m}^4\text{s}^{-1} \text{ for } T > 483\text{K} \\ 4.32^{+8.98}_{-2.92} \times 10^{-27} \exp(-0.38 \pm 0.04\text{eV}/kT) & \text{m}^4\text{s}^{-1} \text{ for } T < 483\text{K} \end{cases} \quad (12)$$

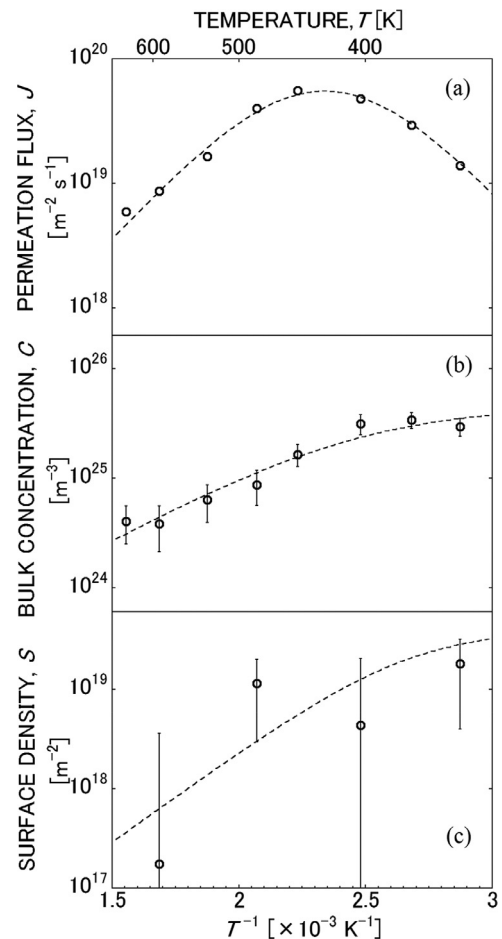


Fig. 4. Temperature dependence of (a) steady-state permeation flux J , (b) bulk concentration C , and (c) surface density S in 0.02 mm-thick sample exposed to deuterium plasma.

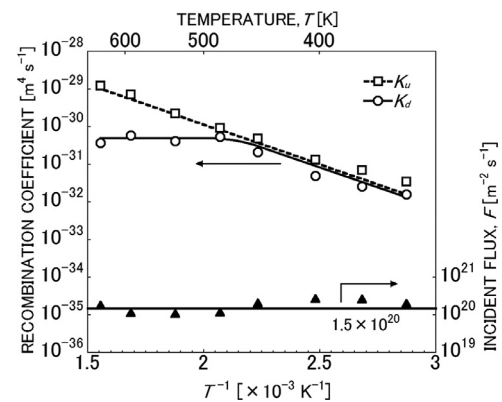


Fig. 5. Temperature dependences of deuterium recombination coefficients at upstream and downstream surfaces of PdCu.

In order to determine K_u , the time evolution of the permeation flux $J(t)$ was observed when the plasma was suddenly turned off. In this case with a thin membrane, the deuterium permeation is limited by the recombination process at any time, and $J(t)$ is given as follows:

$$J(t) = (\lambda' t + 1)^{-2} \quad (13)$$

$$\lambda' = \frac{(K_u + K_d)\sqrt{J_i}}{L\sqrt{K_d}} \quad (14)$$

by solving a particle balance equation [11]. The parameter λ' was estimated by fitting the experimental data with Eq. (13). Then, K_u was determined from Eq. (14) using the initial permeation flux J_i and recombination coefficient K_d . K_d was taken from the data shown in Fig. 5. The temperature dependence of K_u is shown in Fig. 5 and expressed as follows:

$$K_u = 1.43_{-0.41}^{+0.57} \times 10^{-26} \exp(-0.40 \pm 0.01 \text{ eV}/kT) \text{ m}^4 \text{ s}^{-1} \quad (15)$$

The recombination coefficient on the upstream surface K_u can be expressed as an Arrhenius equation, as shown in Eq. (15), which indicates that the recombination is limited by a single process. According to Pick's model under an equilibrium of hydrogen atoms between the surface and the bulk just beneath the surface [13], the pre-exponential factor of K_u , K_{u0} , is around $\nu N^{-4/3}/h^2$, where ν , N , and h are the attempt frequency, atomic density of PdCu, and number of solution sites per host atom, respectively [14]. K_{u0} is estimated to be $3.4 \times 10^{-27} \text{ m}^4 \text{ s}^{-1}$. Here, ν is taken as 10^{13} s^{-1} , N is $7.6 \times 10^{28} \text{ m}^{-3}$, and $h=3$. The value of h is based on the bcc structure of PdCu [15]. The estimated value of K_{u0} is smaller than the experimental one in Eq. (15) by a factor of four. However, K_{u0} can be explained by the model because the attempt frequency is a typical value, not an exact one for PdCu. The recombination coefficient of the downstream surface K_d below 483 K is essentially the same as K_u within the range of experimental errors. In contrast, over 483 K, K_d cannot be explained by the model. The pre-exponential factor is much smaller than the estimated value. This inconsistency has also been observed in pure Pd and D systems [16]. This could be because the surface and bulk cease to be in equilibrium, or the rate-determining process changes from surface recombination to another process such as bulk recombination [17].

The surface density S increases with a decrease in the sample temperature until it seems saturated, as shown in Fig. 4(c), although the data are scattered as the result of the low proton yield of the NRA. When the surface density is high, some incident particles are blocked by surface hydrogen atoms, and the particle balance in Eq. (1) should be rewritten as follows:

$$F(1 - \theta) = J + R \quad (16)$$

where θ is the deuterium surface coverage expressed as follows:

$$\theta = S/S_0 \quad (17)$$

S_0 is the saturation density and is estimated to be $4.0 \times 10^{19} \text{ m}^{-2}$ from Fig. 4. It is larger than the maximum value of the surface atomic density of PdCu, $1.8 \times 10^{19} \text{ m}^{-2}$ although these two values are expected to agree with each other. One reason is that the surface roughness increases the effective surface density [18]. From Eqs. (2), (3), and (16), F is expressed as,

$$F = \frac{(K_u + K_d)J}{K_d(1 - \theta)} \quad (18)$$

As the plasma condition is fixed in the whole experiment, F should be constant, which is confirmed by the data shown in Fig. 5. This indicates that the values of K_u and K_d are valid because these parameters are determined independently of F . The value of $F = 1.5 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}$ is much larger than $F_f = 5.0 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$ in the diffusion experiment because the sample is located very close to the outlet port of the discharge tube in this experiment while it is apart from the port due to the shutter in the diffusion experiment.

4. Discussion

The performances of the PdCu probe, including the response time, sensitivity, and measurement range will be evaluated using diffusion coefficient D and recombination coefficients K_u and K_d . The performance of the Ni probe will also be evaluated using D

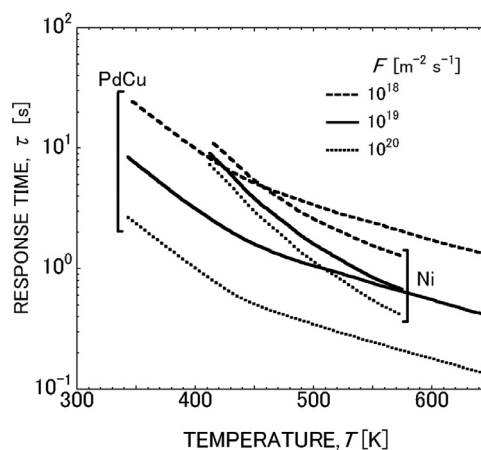


Fig. 6. Temperature dependences of response time τ in PdCu and Ni membranes with 0.02 mm thickness.

[9], K_u , and K_d [6]. The two membranes have the same thickness, 0.02 mm.

The response time τ is defined here as the intersection of the time axis with the tangent line at the inflection point of the permeation curve. The permeation curve is calculated from the diffusion equation [6] when the incident flux is changed from 0 to F at $t=0$. The result is shown as a function of the temperature dependence in Fig. 6. At an operating temperature of 575 K, the τ values of PdCu and Ni are nearly the same under an incident flux of $10^{19} \text{ m}^{-2} \text{ s}^{-1}$, which is a typical value in QUEST [6]. At a higher incident flux of $10^{20} \text{ m}^{-2} \text{ s}^{-1}$, PdCu shows a good response time of 0.21 s, which is superior to that of Ni.

Sensitivity p is defined as the ratio of the permeation flux to the incident flux, J/F . In the recombination-limited permeation, p is expressed as follows:

$$p = \frac{K_d}{K_u + K_d} \quad (19)$$

from Eq. (4). The sensitivity p does not depend on the incident flux. This is applicable to the PdCu probe. For the non-recombination limited permeation, such as in the Ni probe, p is given from Eqs. (1)–(3) and Fick's first law as follows:

$$p = \left(\frac{K_u L^2}{D^2} J + \frac{2K_u L}{D\sqrt{K_d}} \sqrt{J} + \frac{K_u + K_d}{K_d} \right)^{-1} \quad (20)$$

Eq. (20) indicates that p decreases with an increase in the permeation flux, and hence the incident flux. The temperature dependence of the sensitivity is shown in Fig. 7. It is clear that PdCu has the advantages of high sensitivity at lower temperatures and independence in relation to the incident flux.

The rate-determining process of permeation at lower incident flux is generally not the diffusion process but the recombination process because the diffusion and recombination rates obey the first-order kinetics and the second-order kinetics of hydrogen concentration, respectively. This means that Eq. (19) could not be applied at higher incident flux and there should be the upper detection limit for F in the recombination-limited permeation. Here, the upper detection limit is obtained using a condition where the hydrogen concentration difference between the upstream and downstream sides becomes 10% of the upstream-side concentration. Above this limit, the permeation is no longer regarded as the recombination-limited permeation. The upper limit of PdCu between 348 and 643 K is found to be no less than $2 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$, which is much higher than the typical incident flux of $1 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$ in QUEST [6]. The upper limit in the Ni

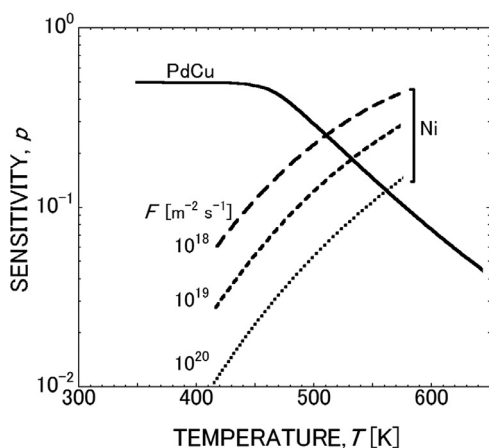


Fig. 7. Temperature dependences of sensitivity p in PdCu and Ni membranes with 0.02 mm thickness.

probe is only $9 \times 10^{16} \text{ m}^{-2} \text{ s}^{-1}$ at a maximum. It should be noted that, according to Eq. (16), J depends on not only F but also the surface coverage θ at high surface densities. The upper limit, however, does not take θ into account due to lack of information to estimate θ at any given temperature and F . The lower detection limit for F generally depends on the background level of a partial pressure of hydrogen. Therefore, the limit cannot be determined using the properties of the probe alone, but the vacuum system must also be considered. For the purpose of reference, the lower detection limit in the present work is listed as $5 \times 10^{15} \text{ m}^{-2} \text{ s}^{-1}$.

Based on the above discussion, PdCu is found to be a very suitable material for an atomic hydrogen probe. It is important to set an operating temperature for the probe because the response time τ improves with increasing temperature, whereas the sensitivity p decreases. When F is high, a high temperature such as 600 K is preferable. The response time is very good, and the low sensitivity is compensated by the high incident flux. When F is low, a low temperature such as 450 K is recommended. In this case, the sensitivity is very high, although the response time is somewhat longer.

For applying the probe to plasma devices, effects of incident energy on the permeation behavior will be discussed. As deuterium plasma is produced by RF discharge and not electrically biased, a kinetic energy of deuterium is very low, typically 1 eV [19]. So the deuterium atoms from the plasma land on the sample surface in the present work. In the plasma devices, higher energy hydrogen atoms also contribute to the incident flux. Eqs. (1) to (4) can still be applied to this case because these equations do not depend on whether the atoms impinge to the surface for a low energy case or

directly enter the bulk for a high energy case. There is an exception that Eq. (1) is replaced by Eq. (16) under such a condition of low incident energy and high surface coverage. The recombination coefficient is considered to be independent of the incident energy, which has been confirmed in our previous work [20].

5. Summary

To evaluate the performance of a new atomic hydrogen probe system with a PdCu membrane, the deuterium behaviors in PdCu samples were experimentally investigated using NRA and permeation observations. The diffusion coefficient and recombination coefficients on the upstream and downstream surfaces were determined as shown by Eqs. (11), (15), and (12), respectively, based on the concentration, surface density, steady-state permeation flux, and evolution of the permeation. It was found that the sensitivity of the probe with the 0.02 mm-thick membrane was very high at low temperatures and independent of the incident flux at a temperature range of 348–643 K. A typical response time was 0.21 s at a probe temperature of 575 K and an incident flux of $10^{20} \text{ m}^{-2} \text{ s}^{-1}$, which would allow the real-time measurement of the incident flux. The upper detection limit in the recombination-limited permeation was $2 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$, which was much higher than the incident flux in QUEST. It is concluded that the new PdCu probe has a good performance for detecting the incident atomic hydrogen with high sensitivity and a short response time.

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