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# Hydrogen incorporation into tungsten deposits growing under hydrogen and argon mixed plasma

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Tungsten deposits were produced by exposing a tungsten tube to hydrogen and argon mixed plasma in different deposition conditions. The erosion rate of the tungsten tube decreased with increasing hydrogen concentration in the working gas. This indicates that the erosion was mainly caused by argon ion incident. In order to release hydrogen incorporated into the tungsten deposit, the tungsten deposit has to be heated up to 600 $^{o}$C. While the tungsten deposition rate was promoted by the increase of negative target bias supplied to the tungsten tube, the influence of the target bias on hydrogen retention in the tungsten deposit was different in the deposition condition. However, it was found that hydrogen retention increases with the ratio of the energetic hydrogen flux reflected on the tungsten tube to the tungsten deposition flux. The flux ratio of hydrogen to tungsten toward the growing surface of the tungsten deposit is an important parameter to evaluate the amount of hydrogen incorporated into tungsten deposits growing under the plasma containing hydrogen ions.

Keywords: tungsten, deposition, hydrogen retention, sputtering

## 1. Introduction

It is important to understand the accumulation phenomena of hydrogen isotopes in a plasma confinement vessel of a fusion reactor from viewpoints of tritium economy and safety. Plasma-facing wall is eroded by energetic particle incident and sputtered atoms would form deposition layers. It has been known that carbon deposition layer can contain a large amount of hydrogen isotopes. Tungsten is a candidate material for plasma-facing wall because of low solubility and low sputtering yield for hydrogen isotopes. In a long time operation of a fusion reactor, a certain amount of tungsten deposits would be formed in the plasma confinement vessel. Erosion and deposition will be promoted if a noble gas such as argon is introduced around plasma-facing wall for a reduction of heat load. It has been reported by the present authors that a large amount of hydrogen isotopes are incorporated into tungsten deposition layer formed by hydrogen isotope plasma sputtering [1,2]. The empirical equation has been proposed from a systematic study of the influence of the deposition conditions on the deuterium retention by using magnetron sputtering and linear plasma devices [3]. The influence of oxygen on hydrogen isotope retention in tungsten deposition layers has been investigated [4,5]. Nevertheless, experimental data for hydrogen isotope retention in tungsten deposits are still insufficient. In this study, the influence of the deposition condition on hydrogen incorporation in tungsten deposits growing under hydrogen and argon mixed plasma was investigated.

## 2. Experimental

A schematic diagram of the experimental apparatus is shown in Fig.1. A cylindrical quartz tube, 13 mm in outer diameter, 10 mm in inner diameter and 400 mm in length, which has a horizontal branch tubule, 6 mm in outer diameter, 4 mm in inner diameter and 30 mm in length, was used as a plasma sputtering chamber. A tungsten tube, 1.4 mm in outer diameter, 0.2 mm in thickness and 99.95% in purity (Nilaco Co.), was inserted to the branch tubule as a sputtering target. A copper tube, 3 mm in outer diameter, was rolled on the outer surface of the quartz tube in the upstream side as an inductive coil. The distance from the edge of the coil to the tungsten tube was set to be 35 mm. In order to collect a part of sputtered tungsten, a quartz substrate, $10 \times 5$ mm$^2$ in size and 1 mm in thickness, was placed beneath the tungsten tube. The detail of the sputtering-deposition region is illustrated in Fig.2. The distance from the center of the quartz tube to the surface of the substrate was 3.3 mm. The angle $\theta$ is about 113$^{o}$ which is 31 % of the all circumferences. The length of the quartz substrate is 5 mm which is 50 % of the tungsten tube length in the longitudinal direction. Therefore the plasma-facing area of the quartz substrate views approximately 16 % of the plasma-facing area of the tungsten tube. The mixture gas of hydrogen and argon was introduced via a mass flow controller (SEC-E40, HORIBA

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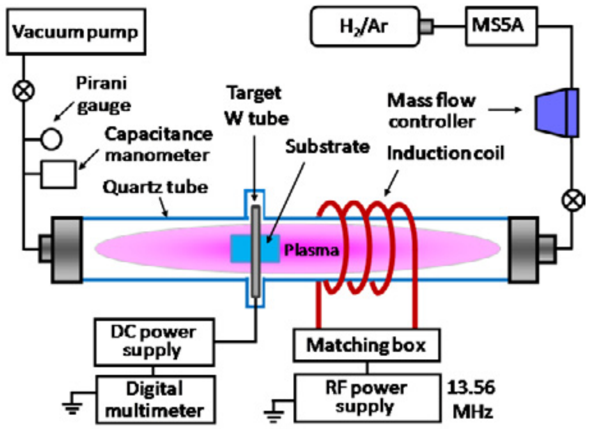

Fig.1 The schematic diagram of the experimental apparatus.

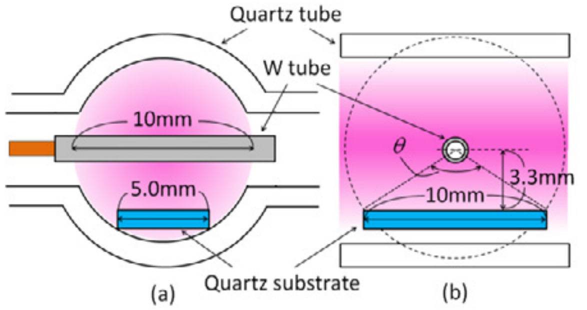

Fig.2 The illustration of the sputtering-deposition region. (a) : a view from the gas flow direction. (b) : a view from the cross-section direction of the W tube.

Ltd.) calibrated with pure hydrogen gas. Hydrogen concentrations in the mixture gas used in this study were 2, 20, 50 and 80 %. A packed bed of adsorbent, MS5A was installed between the gas cylinder and the mass flow controller to exclude a small amount of impurity water vapor in the gas cylinder. Plasma was inductively generated inside of the quartz tube by supplying the RF power of 40 W or 100 W with 13.56 MHz (NR05N-06, NRF Co.) to the copper coil via matching box (NM05AL-05, NRF Co.). In order to promote erosion of the tungsten tube, a negative bias of 200 V or 300V was supplied in the tungsten tube by a DC power supply (PWR400H, KIKUSUI Co.). The target current was measured by a digital multi-meter (PC520M, SANWA Inc.). Evacuation of the quartz tube was performed by a rotary pump (GLD-201B, ULVAC Inc.). The working gas pressure during sputtering-deposition process was monitored by a Pirani gauge (GP-1G, sencer:WPB-10-034, ULVAC Inc.). After the process, the absolute pressure was measured by a capacitance manometer (Baratron 626B, MKS Ltd.) in same deposition condition. The true flow rate of the mixture gas was obtained from the absolute pressure in the quartz tube and the exhaust velocity by the rotary pump. The temperature in the vicinity of the quartz substrate during sputtering-deposition process was measured by a thermocouple fixed on the outer surface of the quartz tube. In order to confirm the temperature inside the quartz tube, a thermocouple was inserted from the downstream side of the quartz tube to the position of the substrate. Both temperatures were almost same. The deposition conditions were summarized in Table 1. In cases that temperature is just 100 $^{o}$C, the temperature was controlled by a ribbon heater. The sputtering-deposition region was wrapped by the ribbon heater except in Ex.1 and Ex.2. The temperatures in Ex.1 and Ex.2 are lower than that in the others because there is no effect of heat retention by the ribbon heater.

The amount of deposited tungsten was obtained from the weight change of the substrate before and after sputtering-deposition process. The weight change was measured by an electric balance with sensitivity of 0.01 mg (CP225D, Sartorius Inc.), whereas the original weight of the substrate was about 100 mg. The cross section observation of the tungsten deposit was performed by the scanning electron microscopy (SEM:SU8000, HITACHI Co.). The weight percent of oxygen in the tungsten deposit was analyzed by energy dispersive X-ray equipment (EDX:Genesis2000, EDAX Inc.). SEM and EDX used in this study were installed at the Center of Advanced

Table 1 The summary of deposition conditions.

| | $H_2$ [%] | Flow rate [sccm] | Pressure [Pa] | RF power [W] | Target bias [-V] | Flux to target [ions/m$^2$/s] | Temperature [$^o$C] | Deposition period [h] |
|---|---|---|---|---|---|---|---|---|
| Ex.1 | 2 | 3.8 | 7.6 | 40 | 200 | $1.30 \times 10^{20}$ | 58 | 20 |
| Ex.2 | 2 | 3.8 | 7.6 | 40 | 300 | $1.53 \times 10^{20}$ | 58 | 17 |
| Ex.3 | 20 | 6.7 | 7.1 | 100 | 200 | $1.31 \times 10^{20}$ | 104 | 20 |
| Ex.4 | 20 | 6.7 | 7.1 | 100 | 300 | $1.96 \times 10^{20}$ | 94 | 21 |
| Ex.5 | 20 | 3.1 | 4.6 | 100 | 300 | $1.62 \times 10^{20}$ | 100 | 14 |
| Ex.6 | 20 | 6.7 | 7.1 | 100 | 300 | $2.72 \times 10^{20}$ | 96 | 36.5 |
| Ex.7 | 20 | 3.1 | 4.6 | 40 | 200 | $1.23 \times 10^{20}$ | 100 | 24 |
| Ex.8 | 50 | 3.8 | 5.4 | 100 | 200 | $2.61 \times 10^{20}$ | 146 | 25 |
| Ex.9 | 50 | 3.8 | 5.4 | 100 | 300 | $2.77 \times 10^{20}$ | 106 | 46 |
| Ex.10 | 80 | 2.5 | 4.2 | 100 | 200 | $3.99 \times 10^{20}$ | 156 | 30 |

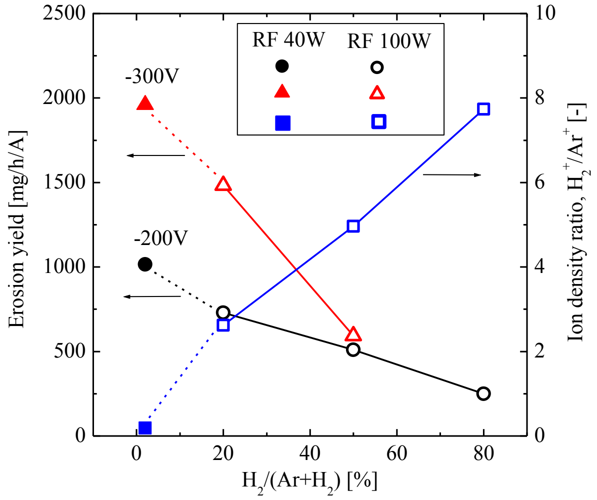

Fig.3 The dependence of hydrogen concentration in the working gas on the erosion yield of the tungsten tube and on the ratio of hydrogen ions to argon ions.

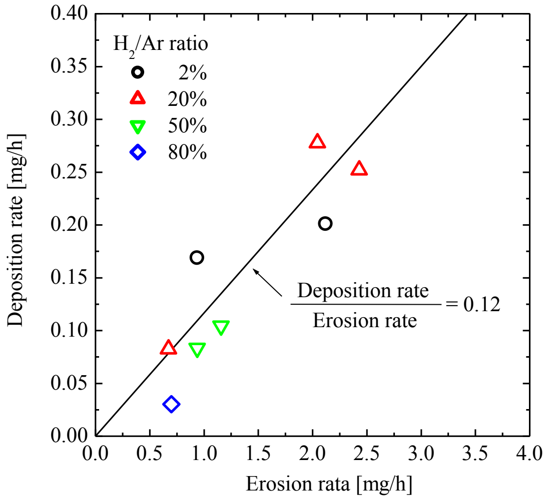

Fig.4 The deposition rate on the substrate with the erosion rate of the tungsten tube.

Instrumental Analysis, Kyushu University.

Ion densities at the vicinity of the substrate under pure hydrogen plasma and pure argon plasma were measured by the double probe method. The probes were inserted from the branch tubule to plasma without the target tube. Additionally, the emission intensities from $H_2^+$ and $Ar^+$ in plasma at the vicinity of the substrate were measured for pure hydrogen, pure argon and hydrogen-argon mixed plasma by a plasma process monitor (PlasCalc-2000, Mikropack). Ion densities of hydrogen and argon in the mixed plasma were estimated from the double probe measurement and the emission intensity measurement assuming the emission intensity is proportional to the ion density and $H_2^+$ is dominant in hydrogen ions.

After sputtering-deposition process, the substrates were placed into a separate quartz tube connected to a gas chromatograph (GC:GC-8A, SHIMAZU Co.). The quartz tube was filled with argon gas and heated from 200 °C to 800 °C in 200 °C step by an electric furnace. Argon gas was introduced into the reaction tube every 20 minutes in order to transport the released hydrogen into GC. Since the amount of hydrogen released at 800 °C was comparable to the background level, the hydrogen released by 600 °C was regarded as the hydrogen incorporated in the tungsten deposit.

## 3. Results and discussions

Fig.3 shows the dependence of hydrogen concentration in the working gas on erosion yield of the tungsten tube which was derived from dividing the erosion rate (mg/h) by the target current (A). The right axis indicates the ratio of hydrogen ion density and argon ion density under each deposition condition. The hydrogen ion ratio increased approximately proportionally to hydrogen concentration. It was observed that the erosion yield decreases with increasing hydrogen concentration. Additionally, the weight loss of the tungsten tube was undetectable in several-hour exposure under pure hydrogen plasma. These results indicate that the erosion of tungsten was caused by argon ion incident. Impinging energy of argon ions obtained from negative bias is mitigated by collisions with neutral molecules. Therefore the erosion yield is considered to decrease with decreasing the argon ion density. The erosion yield at a negative bias of 300 V was quite lager than that at a negative bias of 200 V in 2 % and 20 % of hydrogen concentration but these are close in 50 % of hydrogen concentration. This indicates that the negative bias effect on erosion is large when argon ion density is high.

The deposition rate against the erosion rate in each deposition condition is plotted to Fig.4. The ratio of the deposition rate to the erosion rate was 0.12 on the average. This value is smaller than 0.16 which is estimated geometrically. This difference is due to the erosion of the tungsten tube in the branch tubule, the slip of the substrate from the designed position and the scattering of sputtered tungsten atom by collision with neutral molecules.

SEM image of the cross-section of the tungsten deposit formed under hydrogen and argon mixed plasma, 20 % in hydrogen concentration, 7.1 Pa in working gas pressure, 100 W in RF power, 300 V in negative bias, 96 °C in temperature and 36.5 h in deposition period (Ex.6) is shown in Fig.5. The quartz substrate was broken in half and the surface was observed. It was found that the tungsten deposit has a columnar structure. The weight percent of oxygen in the tungsten deposit formed under hydrogen and argon mixed plasma, 20 % in hydrogen concentration, 4.8 Pa in working gas pressure, 40 W in RF power, 200 V in negative bias and 100 °C in temperature (Ex.7), is 2.0 wt%.

An example of hydrogen release behavior from tungsten

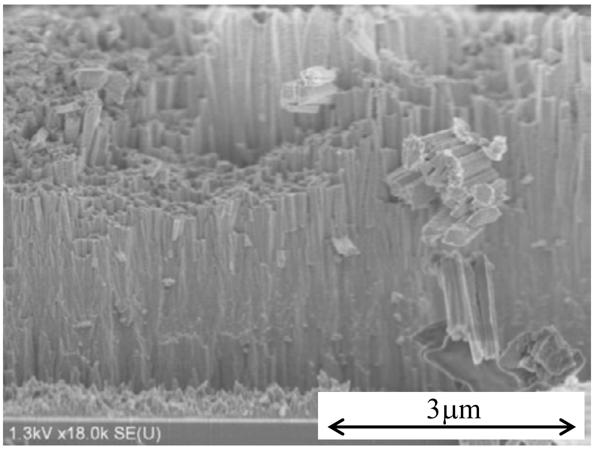

Fig.5 SEM image of the cross-section of the tungsten deposit formed in Ex.6.

deposits is shown in Fig.6. For all samples, the release behavior of hydrogen was similar. The hydrogen release began at 200 °C and continued until 600 °C. The highest release rate was observed at 400 °C. It was found that a high temperature of 600 °C is necessary to remove hydrogen incorporated in the tungsten deposit.

The dependence of negative bias on hydrogen retention (mol-$H_2$/g) and deposition rate (g/hour) are shown in Fig.7 for three deposition conditions. It was observed that the deposition rate at 300 V is obviously higher than that at 200 V. This means that the impinging energy of ions to the tungsten tube at 300 V is higher than that at 200 V. On the other hand, the change of hydrogen retention with negative bias was different in the deposition condition. A part of hydrogen and argon impinging to the target is considered to be reflected and implanted into the growing surface of the tungsten deposit. These reflected particles are considered to have relatively-high energy as compared with ions which impinge to the growing surface of the tungsten deposit with the sheath potential although its energy is reduced by the collision with neutral molecules

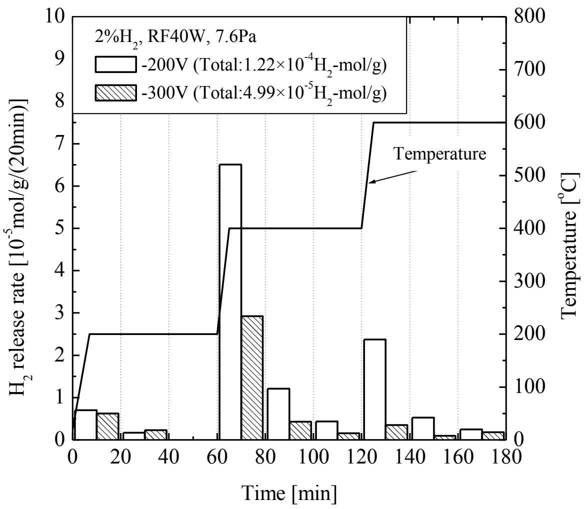

Fig.6 Hydrogen release behavior from the tungsten deposit formed in Ex.1 and Ex.2.

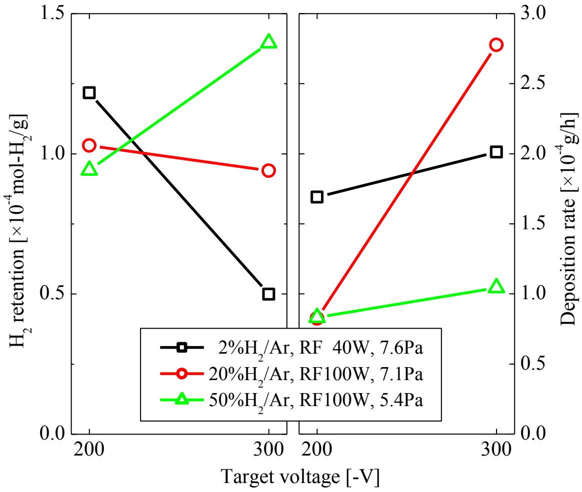

Fig.7 The dependence of target bias on hydrogen retention and deposition rate for three deposition conditions.

between the target and the substrate. Therefore, the bias of the target is considered to be one parameter that affects on hydrogen retention in tungsten deposits forming by sputtering method. However, the result shown in Fig.6 suggests that other parameter also contributes to hydrogen retention. The present authors considered that the ratio of hydrogen flux to tungsten flux from the target to the growing surface, $f_H/f_W$ contributes to hydrogen retention. The hydrogen flux reflected from the tungsten target was estimated from the hydrogen ion flux and the fraction of backscattered particles, $R_N$ [6]. The hydrogen ion flux was estimated from the target current and the ratio of hydrogen ion density to argon ion density. The tungsten flux was estimated from the deposition rate. The relationship between the ratio of hydrogen flux to tungsten flux and hydrogen retention as H/W is shown in Fig.8. The amount of tungsten deposited on the substrate was obtained from the deposition weight. Data from the parallel plate RF sputtering device [2,7] are also indicated. Although the tungsten deposit reported in [2] contained not only deuterium but also hydrogen, the reflected particle is assumed to be only deuterium because the working gas is pure deuterium. The expression obtained from fitting all of data is as follows:

$$\frac{H+D}{W}=6.9\times10^{-3}\left(f_{\mathrm{H}}/f_{\mathrm{W}}\right)^{0.42} , \qquad (1)$$

where $7.3 \leq f_H/f_W \leq 4780$, $65 \leq E_n \leq 652$ eV, $331 \leq$ Temperature $\leq 429$ K. $E_n$ is the average energy of the reflected particles on the target. The value of $E_n$ was estimated using the following formula [6]:

$$E_n(E_0)=E_0\frac{R_E(E_0)}{R_N(E_0)} , \qquad (2)$$

where $E_0$ is the energy of the ions impinging on the tungsten target, $R_E$ is the energy reflection coefficient. The

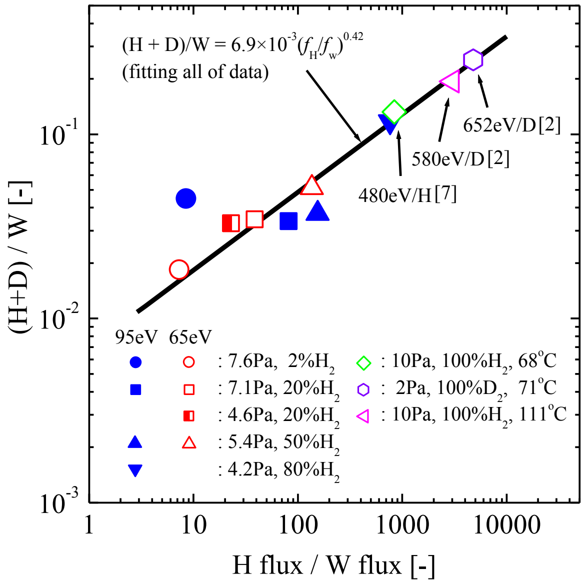

Fig.8 The dependence of the ratio of hydrogen flux to tungsten flux on hydrogen isotope retention.

obtained value, 0.42 is close to the value of 0.4±0.1 reported by De Temmerman and Doerner [3], where $2 \leq (f_H/f_W) \leq 500$, $60 \leq E_n \leq 280$eV, $293 \leq$ Temperature $\leq 600$ K. The dependence of $E_n$ on the retention was not observed in this work while they suggest in [3] that the retention is proportional to $E_n^{1.88}$. Strictly speaking, the impinging energy of reflected hydrogen to the growing surface of the tungsten deposit is abated by collisions with neutral molecules between the target to the substrate. That is to say, hydrogen retention depends on the working gas pressure as has been reported in [2]. Especially, the influence of the pressure would be large in the parallel plate RF sputtering device [7] because the distance from the target to the substrate is long. The impinging energy of hydrogen isotope to the growing surface in the parallel plate RF sputtering device might be comparable with that in the device used in this work. Hydrogen retention depends on temperature as has been reported in [3,4,8]. For the data summarized in Fig.8, these effects would be able to ignore because the temperatures are relatively low and the range is narrow.

## 4. Conclusions

The influence of deposition condition on hydrogen incorporation into tungsten deposits growing under hydrogen and argon mixed plasma was investigated by exposing a tungsten tube to the plasma. The erosion of the tungsten tube is mainly caused by the incident of argon ions. The tungsten deposit has a columnar structure. In order to remove the hydrogen incorporated into the tungsten deposit, a high temperature of 600 °C is necessary. While the tungsten deposition rate is promoted by the increase of negative target bias from 200 V to 300 V, the influence of the target bias on hydrogen retention is different in the deposition condition. Hydrogen concentration in the tungsten deposit increases with the ratio of the flux of the hydrogen reflecting from the tungsten target to tungsten deposition flux. The flux ratio of hydrogen and tungsten toward the growing surface of the tungsten deposit is an important parameter to evaluate hydrogen accumulation amounts.

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