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Journal of Nuclear Materials 266–269 (1999) 1212–1218

Journal of
nuclear
materials

Growth of redeposited carbon and its impact on isotope retention properties on tungsten in a high flux deuterium plasma

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Abstract

Experiments were performed in a linear magnetized plasma facility (PISCES-B) to simulate carbon re-deposition in the divertor of a fusion reactor such as the International Thermonuclear Experimental Reactor (ITER). The average ion energies are about 100 eV and the ion flux is $2 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$. Tungsten discs and foils were exposed to deuterium plasma for a period of 45–120 min at various substrate temperatures. Carbon impurities were introduced either using graphite sample holder or downstream CD_4 puffing near the targets. In-situ XPS measurements showed a shifting of the binding energy of the carbon in the interlayer between the carbon film and the tungsten surface. Based on AES depth profile, the ratio of tungsten to carbon in the interlayer is about 1.9 : 1. Scanning electron microscopy of plasma-exposed tungsten revealed bubble and pits formation on uncontaminated surfaces. Raman measurements on deposited carbon films were also performed. Deuterium retention measurements were done using Thermal Desorption Spectrometry (TDS). The dominant factor that influences the hydrogen isotope retention is substrate temperature. Measurements indicated a transition from D_2 dominant retention at low temperature exposure to D dominant retention at high temperature exposure. Carbon-contaminated tungsten substrates also showed similar, but a moderate, transition. Total deuterium retention decreases as the exposed temperature increases. The threshold of the carbon impurity concentration in the plasma, under which carbon starts to be deposited on the tungsten surface, is about 0.75% at 850 K. Keeping the impurity concentration at 1%, the temperature threshold is about 750 K. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carbon deposition; Deuterium; PISCES-B; Tungsten; ITER

1. Introduction

The issue of carbon contamination to the plasma facing material such as beryllium [1–3] in a fusion environment has generated interest to study carbon contamination in tungsten. Such studies are pertinent to the International Thermonuclear Experimental Reactor (ITER) [4,5]. Carbon composite materials and tungsten are the candidate materials in the divertor region in ITER where the armors will be subjected to $10^{22} \text{ m}^{-2} \text{ s}^{-1}$, or higher, ion flux bombardment. Because of high

sputtering yield and chemical erosion of the carbon composite material, the sputtered particles and hydrocarbon species can migrate into the plasma. They will be ionized by the energetic electrons, and will be re-deposited onto the tungsten armor. During this process, hydrogen fuel such as deuterium and tritium will be co-deposited with the carbon, leading to issues such as fuel inventory on the reactor wall. The retention of radioactive tritium presents safety concerns during accident scenarios as well as periodical maintenance.

Retention measurements and understanding the outgassing characteristics of the isotopes are therefore important. Study of carbon re-deposition on tungsten in a controlled carbon-contaminated plasma environment is needed. This paper addresses these issues by

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performing a series of carbon–tungsten experiments that are pertinent to the ITER operation parameters, particularly isotope retention characteristics, bubble formation, carbon impurity simulation and deposition, surface and carbon film characterization, and interlayer investigations between the deposited carbon films and the tungsten substrates. Such information has not been available for the ITER operation conditions.

2. Experiments

2.1. Experimental setup

According to Federici, tungsten armors will be subject to an ion flux of $10^{22} \text{ m}^{-2} \text{ s}^{-1}$ bombardment at two different temperatures: 850 K in the lower baffle and 520 K in the divertor with average ion energy of 100 eV [5]. These plasma conditions are achievable in the linear magnetized plasma facility, PISCES-B, which is used to simulate plasma–wall interactions in fusion reactor. Operation and performance of the facility has been described in a previous publication [1] and thus is not repeated here. Initial experiments using a graphite sample holder resulted in carbon films formation at temperatures above 850 K. The tungsten samples were floating in the plasma with a potential of $-100 \pm 5 \text{ V}$. The graphite holder generated a local high concentration of carbon near the targets. Although successfully simulating carbon re-deposition process, there was a lack of control of the carbon impurity concentration. A downstream CD_4 gas inlet with a high precision mass flow controller was therefore implemented. Partial pressure of the hydrocarbon was monitored by a high-pressure gas analyzer (Ferran Scientific MPA-565C). An earlier publication [6] has indicated that the measurements of the carbon impurities from the gas analyzer agree with the results using emission spectroscopy techniques. Plasma conditions used in this study were kept about the same with ion flux in the range of 7×10^{21} – $2 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$. At this level of ion bombardment, the substrate surfaces were saturated [7], a condition that ITER needs to assess tritium inventory on wall materials. An essential difference in isotope retention measurements between this study and previous studies [7–12] is that previous studies used ion energies at or above 500 eV. This study used low ion energies at 100 eV, under which ion-induced substrate damage would not take place. The purity of the plasma was about 99.5% deuterium. Typical oxygen content is about 0.02%. Based on an earlier publication [13], the deuterium plasma contained approximately 85% D^+ , 13% D_2^+ and 5% D_3^+ .

Substrate temperatures were controlled by varying the heat-removing rate in the sample manipulators and by varying the plasma parameters. Two water-cooling

sample manipulators were used: one with a copper head for low temperature experiments ($<880 \text{ K}$) and the other with an Inconel head for high temperature experiments ($>880 \text{ K}$). A molybdenum sample cap, about 1.5 inches in diameter, was used to hold the one-inch samples. Typically, the diameters of the plasmas were about two inches. The temperatures of the samples were primarily measured by the attached K-type thermocouple wires at the backside of each substrate. A remote infrared pyrometer was also used to monitor the surface emissivity of the tungsten substrate. If carbon is deposited on the surface, the pyrometer reading will increase even though the TC reading stays the same as described earlier [6].

Three type of tungsten samples were used: (1) PLANSEE's $\text{W1\%La}_2\text{O}_3$ tungsten disc, 2 mm thick; (2) ÆSAR's tungsten disc, 99%W, 2 mm thick, and (3) ÆSAR's tungsten foil, 99.95%W, 100 μm thick. All samples were one inch in diameter. They were sealed in plastic bags when shipped. Although the second type of samples was specified as 99% pure, Auger spectroscopy of the samples indicated that the surface concentration of oxygen could be as high as 10%. However, the average value was about 5%. The tungsten foil showed no oxygen content or below the detection limit of the analyzer. All three kinds of samples showed no carbon on their surfaces as received. They were stored in a desiccator before being exposed to the deuterium plasmas. The duration of plasma exposure was mostly 1 h, with a few exceptions running to 45, 90 and 120 min.

2.2. Post-exposure analyses

2.2.1. Surface microanalyses

Before being taken out of the vacuum, each plasma-exposed sample was transported to the surface analysis station for Auger spectroscopy (AES) and X-ray photoemission spectroscopy (XPS). The surface station is equipped with a PHI model 15-255GAR CMA, a dual-anode (PHI 04-548) 15 kV X-ray source, and a 4-keV argon sputtering gun for depth profiling. Each sample was also examined before and after exposure under a scanning electron microscope, JEOL T330A. A KEVEX quantum detector is also coupled to the SEM for Energy dispersive X-ray (EDX) analyses.

2.2.2. Thermal desorption spectrometry (TDS)

After being taken out of the PISCES-B facility, each sample was immediately transferred to a TDS station for retention measurement, to minimize exposure to the air. The TDS station is equipped with a programmable controller to maintain a linear temperature ramp. Two different rates were used: 0.32 and 0.52 K/s. The maximum temperature attained was 1273 K for all TDS measurements.

Calibration of the TDS system was done using a constant leak deuterium (D_2) vessel supplied by Vacuum

Technology Inc. It has a leak rate of 3.46×10^{-13} Pascal-L/s. The percentage error is about 2%. A BALZERS QMG 064 gas analyzer is used to measure the partial pressure of the desorbed species. The calibration factor for HD molecules is set to be the same as D_2 . Since there is no accurate way to calibrate HDO and D_2O , it is therefore assumed that the two species have the same calibration factor as D_2 . Because the combined amount of HDO and D_2O detected in all TDS measurements represents not more than 10% of the total deuterium desorption, such an assumption should not affect the validity of the measurements. The reason for including HDO and D_2O is that these two species are detected from substrates exposed at low temperatures. At substrate temperatures above 880 K, they are not always detected.

3. Results and discussions

3.1. Transition from non-carbon and carbon deposition

Downstream CD_4 puffing was used to simulate carbon impurities in a deuterium plasma at various substrate temperatures. Fig. 1 shows the distribution of experiments performed at various carbon concentrations and substrate temperatures. At the impurity level of about 1% CD_4 , measured by the gas analyzer, no carbon deposition was observed in the plasma exposed substrates at temperatures below 700 K. When the substrate temperature was increased to 850 K, carbon particles started to form on the tungsten surface, mostly along sharp edges which serve as the nucleation sites. Although the original surface roughness of the tungsten

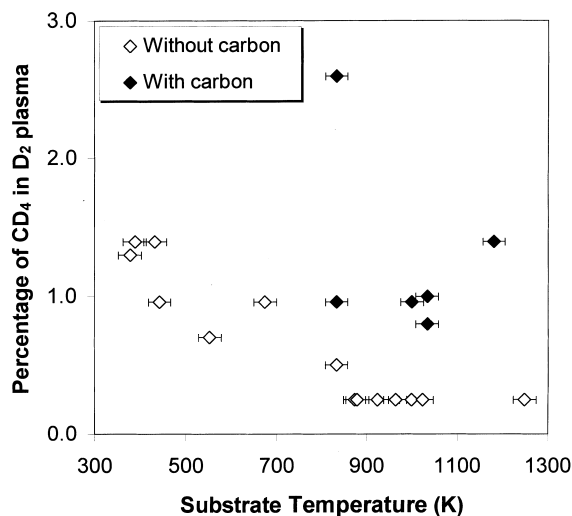


Fig. 1. Distribution of no-carbon and carbon deposition at various concentration and substrate temperatures.

foil is very smooth, about 100 \AA measured by a DEKTAK profilometer, an increase of impurity concentration to 2.6% at 850 K results in a smooth carbon film deposition as shown in Fig. 2. It is believed that during plasma exposure, the surface of the foil is roughened by pit formations – described in a later section – which facilitates the carbon deposition.

Raman signatures of the plasma-deposited carbon films indicate that the films were mainly glassy carbon [14] with double peaks at 1350 and 1600 cm^{-1} . The 1350 cm^{-1} peak is known as poly-graphite, and the 1600 cm^{-1} peak represents crystal-graphite. The signature is compared with a CVD diamond film and POCO graphite as shown in Fig. 3. At 1180 K, a preferential growth of carbon was observed as shown in Fig. 4. The CD_4 content in the D_2 plasma was 1.4%.

At 850 K, the temperature at which tungsten armor is operated in the lower baffle in ITER, no carbon deposition was detected at 0.5% CD_4 . This amount is about twice as much as the intrinsic carbon impurity concentration measured in the PISCES-B facility. Without CD_4 puffing, carbon was not observed on the exposed tungsten surface even when the substrate temperature reached 1230 K. Since carbon composites will be used in the divertor, it is very likely that the carbon species will reach the lower baffle and get re-deposited. An in-situ RF or microwave carbon ashing system can be used to remove the re-deposited carbon.

To study the transition from the carbon layer to the tungsten substrate, a depth profile of Auger spectroscopy was taken. As shown in Fig. 5, the surface carbon was almost completely removed during the first 22 min of ion sputtering. Four sets of XPS data were taken to study the chemical state of the carbon: (1) before the ion milling process, (2) after 22 min of ion sputtering, (3) after 120 min of ion sputtering, and (4) a standard

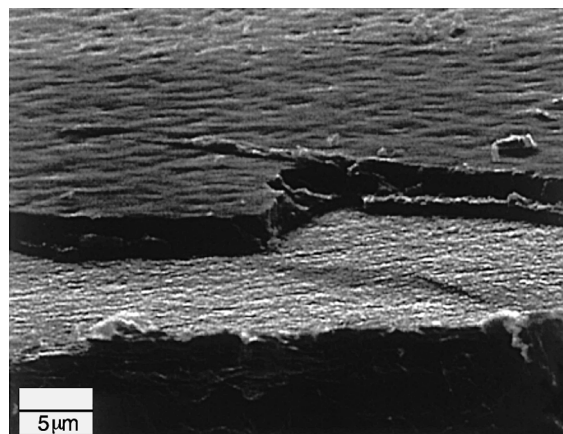


Fig. 2. SEM picture of the carbon film deposited on a tungsten foil at 2.6% carbon impurity and 850 K substrate temperature.

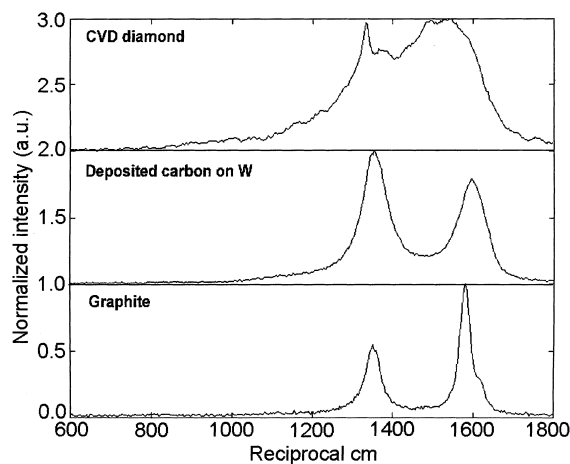


Fig. 3. Raman signatures of CVD diamond, re-deposited carbon in a deuterium plasma, and graphite. The re-deposited carbon film is mainly glassy carbon [14].

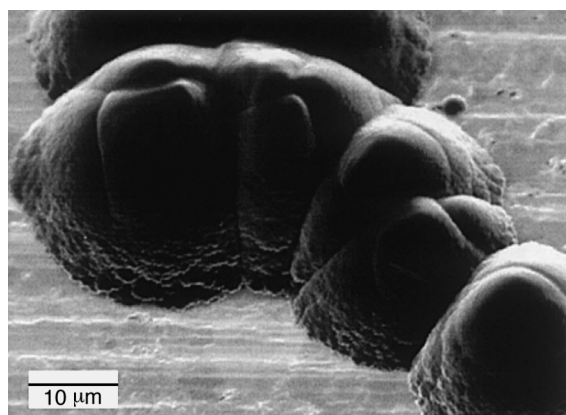


Fig. 4. Preferential carbon growth at 1180 K on a W-1%La₂O₃ tungsten substrate with 1.4% CD₄ downstream puffing in a deuterium plasma.

tungsten carbide, WC, material as reference. The results are depicted in Fig. 6, showing the shifting of the binding energies of carbon at the surface ($t=0$ min), a mixed layer ($t=22$ min), and the interlayer ($t=120$ min). The binding energy for the carbon peak (C 1s) in graphite is 284 eV. The shifting of the carbon peak to 283.3 eV in the interlayer seems almost completed at $t=120$ min. Compared with the binding energy of the tungsten carbide standard, which shows a carbon peak at 282.6 eV, it is therefore believed that the interlayer contains other forms in the carbon–tungsten system. The AES profile in Fig. 5 offers a clue to determine the composition of the interlayer, although not impeccable. At $t=0$ min, the amount of tungsten, as shown, is about 28%. Assuming that this represents the percentage of

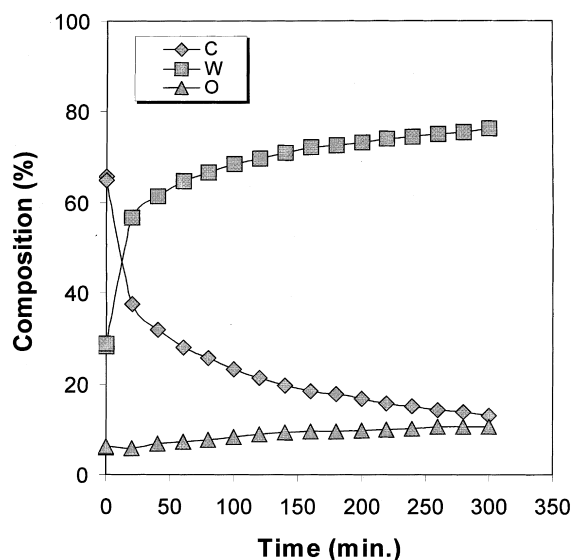


Fig. 5. AES depth profile showing transition from carbon to carbon–tungsten interlayer. At $t=120$ min as in Fig. 6, the ratio of tungsten to carbon is 1.9 : 1.

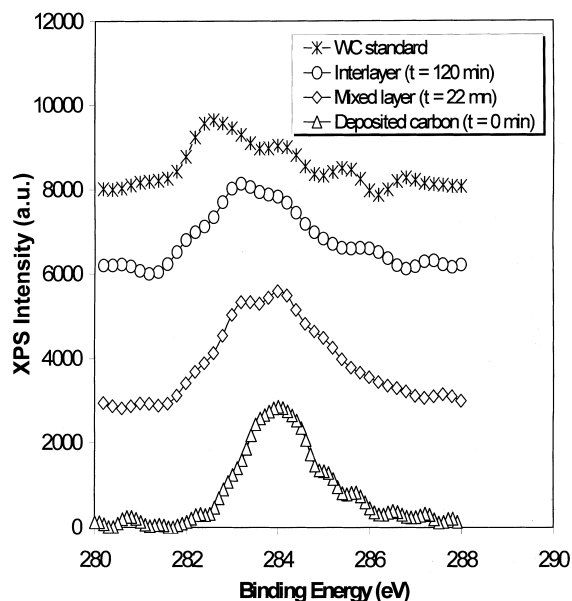


Fig. 6. XPS data showing the shifting of the C 1s carbon peak in the surface carbon film ($t=0$ min), the mixed layer ($t=22$ min) and the interlayer ($t=120$ min). The reference tungsten carbide material shows a binding energy of 282.7 eV. The total shift of the binding energy of the carbon in the surface film to the interlayer is 0.6 eV.

area on tungsten which is free of carbon, the composition of the interlayer can be determined at $t=120$ min, which shows 70% tungsten and 22% carbon. Subtracting

the initial 28%, the ratio of tungsten to carbon at $t = 120$ min is 1.9 : 1, which is very close to the 2 : 1 ratio for tungsten carbide (W_2C). After an additional 20 min of ion sputtering, the ratio only increases slightly to 2.2 : 1 at $t = 140$ min. The ratio continues to increase as the interlayer is gradually depleted by the ion sputtering process.

3.2. Bubble formation

Bubble formation in tungsten using the PISCES-B facility has recently been reported [6]. Pits were observed on the surface of PLANSEE tungsten samples after exposure to deuterium plasma at temperatures above 800 K. In summary, the size of pits decreased as the surface temperature increased. When the tungsten foil was exposed to the high ion flux plasma at temperatures between 400 and 500 K, bubbles were observed as shown in Fig. 7. This is the result of deuterium gas formed underneath the foil. Although Subrahmanyam [15] used implanted He ions (2–30 MeV) in tungsten to study helium bubbles, he pointed out that the helium bubbles which were formed within the substrate were overpressurized. For the same reason, such pressure buildup creates the macroscopic blisters (light color) on the surface of a tungsten foil after deuterium exposure. As shown in Fig. 7(a), the diameters of the blister vary from hundreds of micrometers to 0.5 mm in diameter. At high resolution, the center of the erupted blister, near the lower left corner in Fig. 7(a), is shown in Fig. 7(b). The pattern looks like a showerhead, which consists of holes with sizes varying from submicron to ten microns. These large holes cannot be formed as a result of ion sputtering by the deuterium ions because of the negligible sputtering rate of tungsten by the deuterium ions. Instead, as stated in Ref. [6], it is believed that the sudden release of deuterium gas within the substrate widens the pits. Impurities such as carbon in this case are also not responsible for such surface damage because the pit formation is not uniformly distributed throughout the substrate surface. When using tungsten discs from AESAR, instead of forming blisters, clusters of submicron pits were found on the tungsten surface. Fig. 8(a) shows the surface before exposure, and Fig. 8(b) after plasma exposure. The microscopic pits are believed to be the vent channels for the deuterium molecules. Although the CD_4 impurity was 1.4%, no carbon was formed on the tungsten surface whose exposure temperature was 440 K.

The difference between AESAR's tungsten discs and tungsten foils shows that substrate preparation makes a difference in bubble formation, which leads to surface damage. The exposed surface has to be annealed. Otherwise the pits will be the ideal nucleation sites for carbon deposition. Although rapid thermal process can be used to recrystallize the damaged surface [16], it is still

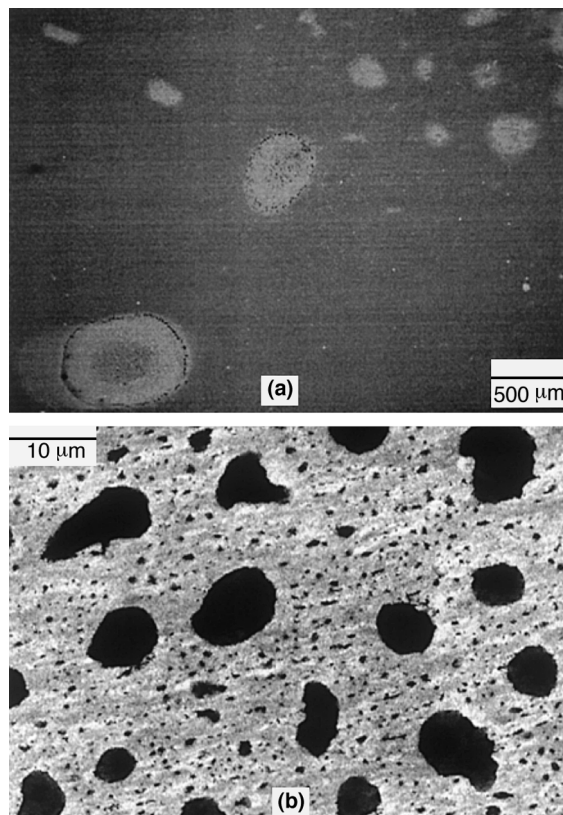


Fig. 7. (a) Blister formation on tungsten foil at 400–500 K. The other areas are smooth and have no pits. (b) High resolution of the pits on the erupted blister near the lower left hand corner of the picture in (a).

unclear whether such a process can heal the defects formed below the surface as observed in the previous study [6].

3.3. TDS analyses

Fig. 9 shows the total amount of deuterium atoms desorbed from carbon-contaminated and uncontaminated tungsten samples. In general, results show that there is no significant difference in hydrogen retention between the three kinds of tungsten samples after plasma exposure. The dominant factors, which influence the hydrogen isotope retention in plasma exposed tungsten, are (i) the substrate temperature and (ii) whether carbon is deposited on the tungsten surface.

Uncontaminated tungsten substrates: For uncontaminated tungsten substrate, the total isotope retention during low temperature exposure is higher than those exposed at high temperatures (>700 K). A possible reason is that deuterium bubbles formed within the substrates are retained inside the substrates when the exposure temperature is low. As the substrate tempera-

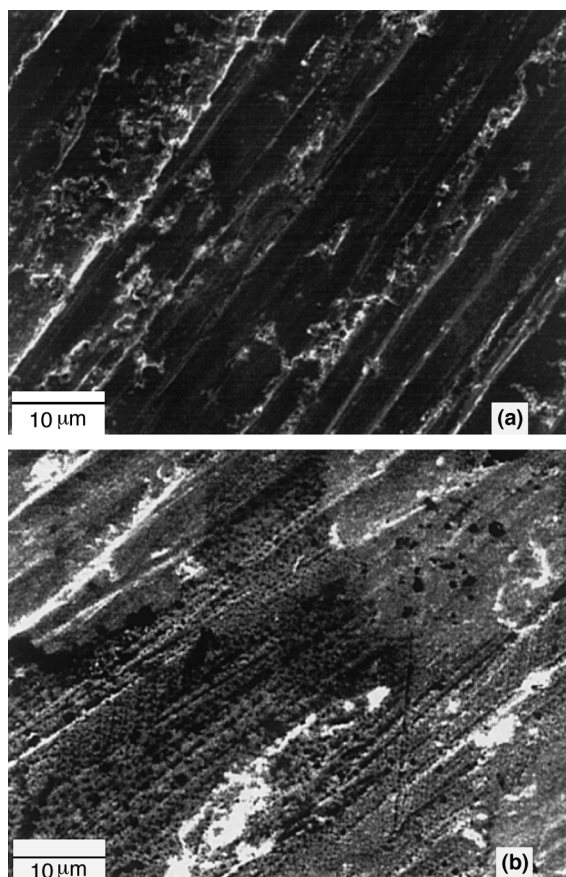


Fig. 8. (a) Tungsten (AESAR) surface before and (b) after plasma exposure, showing a cluster of microscopic pits, which are believed to be the channels of the erupted deuterium gas.

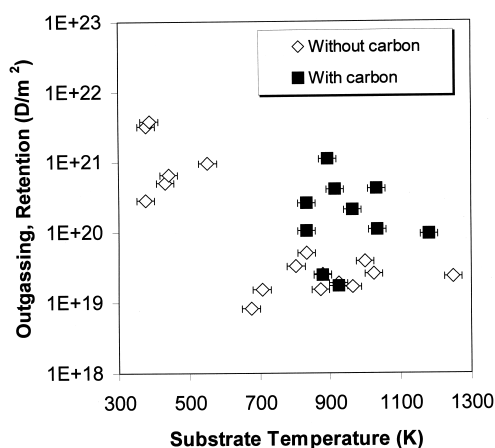


Fig. 9. Total deuterium retention versus substrate temperature in plasma exposed tungsten.

ture increases, these molecules are released in situ. The percentage of deuterium molecules (D_2) in the total deuterium (D) released during each TDS measurement is

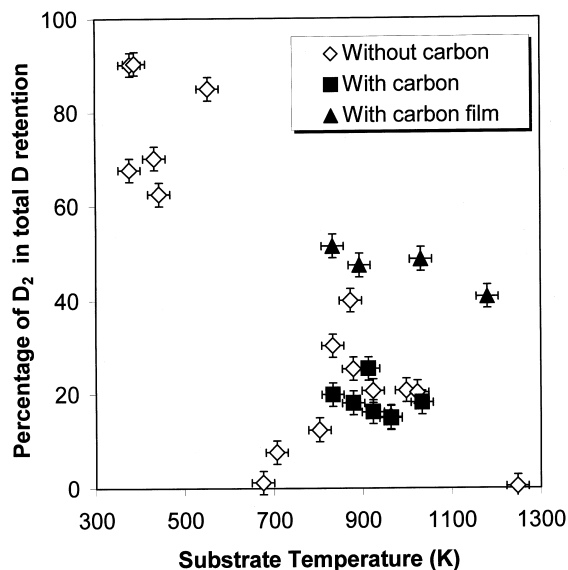


Fig. 10. Percentage of D_2 molecules in total deuterium retention in plasma exposed tungsten.

plotted against the substrate temperature in Fig. 10. There appears to be a transition around 700–800 K where D_2 dominant retention is shifted to D dominant retention, which combines with atomic hydrogen atom to form HD during outgassing.

Carbon-contaminated tungsten samples: The impact of carbon on deuterium retention is shown in Fig. 9. Compared with the retention in uncontaminated tungsten substrate under a similar exposure temperature, the carbon-contaminated substrates retain more hydrogen isotope than uncontaminated tungsten samples. This shows that most of the deuterium species are residing in the carbon film. In Fig. 10, the solid triangles represent surface coverage of carbon larger than 50%. The figure indicates that the carbon films tend to trap more D_2 molecules than tungsten under similar substrate temperatures. Secondly, 850 K seems to be the breakeven point when 50% of trapped deuterium are in the form of D_2 molecules. As the temperature increases, D atoms become the dominant species trapped in the carbon film.

3.4. Summary and discussions

Simulations of carbon re-deposition have been performed using PISCES-B. Tungsten substrates are exposed to a high ion flux ($10^{22} \text{ m}^{-2} \text{ s}^{-1}$) deuterium plasma for a total fluence of the order of 10^{26} D/m^2 . At 850 K, a 0.5% carbon impurity concentration in the plasma will not cause carbon film formation on the tungsten surface. Keeping the impurity level at 1%, substrates exposed at temperature at or below 700 K do not result in carbon deposition. Deuterium molecules recombined in

substrates are trapped at low-temperature plasma exposure, leading to pit formation on surface. A transition from D₂ dominant trapping to D dominant trapping takes place around 700–800 K. Pit formation presents two problems. One is the surface damage; the other is increasing the population of nucleation site for carbon deposition.

The deposited carbon on the tungsten substrates increases the retention of hydrogen species, which are mainly residing in the carbon film. At temperatures above 850 K, the D atoms become the dominant species trapped in the carbon films. Because of these findings, removal of carbon, such as in-situ oxygen plasma ashing, is needed to reduce tritium inventory in the tungsten armor used in the lower baffle.

Since the temperature of the tungsten armor in the divertor is only around 500 K, carbon contamination is of less concern. The high ion flux will constantly clean up the surface. Pit formation or surface damage will be the major issue. Periodic surface annealing seems to be a conceivable solution to this problem, but remains to be explored.

Acknowledgements

The first author would like to express gratitude to the supporting staff in the PISCES Lab, who did a good job in

this investigation. This work is funded by the Department of Energy, contract no. DE-FG03-95ER-54301.

References

- [1] F.C. Sze et al., *J. Nucl. Mater.* 246 (1997) 165.
- [2] J. Won et al., *J. Nucl. Mater.* 241–243 (1997) 1110.
- [3] R.P. Doerner et al., these Proceedings.
- [4] International Thermonuclear Experimental Reactor, DOE/ER-ITER-0004, 1993.
- [5] G. Federici, R.A. Anderl et al., these Proceedings.
- [6] F.C. Sze et al., *J. Nucl. Mater.* 264 (1998) 89.
- [7] A.A. Haasz, J.W. Davis, *J. Nucl. Mater.* 241–243 (1997) 1076.
- [8] P. Franzen et al., *J. Nucl. Mater.* 241–243 (1997) 1082.
- [9] C. Garcia-Rosales et al., *J. Nucl. Mater.* 233–237 (1996) 803.
- [10] R. Frauenfelder, *J. Vac. Sci. Technol.* 6 (1969) 388.
- [11] R.A. Anderl et al., *Fusion Technol.* 21 (1992) 745.
- [12] A.A. Haasz et al., these Proceedings.
- [13] Y. Hirooka et al., *J. Nucl. Mater.* 196–198 (1992) 149.
- [14] R.E. Shroder et al., Raman analysis of the composite structures in diamond thin films, SPIE, vol. 969, *Diamond Optics*, 1988, p. 79.
- [15] V.S. Subrahmanyam et al., *Solid State Commun.* 89 (1994) 523.
- [16] V.N. Podíyachev, M.I. Gavriluk, Translation from *Problemy Prochnosti* (in Russian), No. 12 (1975) 81.