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Report on the Deuterium Retention in CVD Coated W on SiC in Support of the Ultramet Company's Small Business Innovation Research (SBIR) Project: SOW DE-FG02-07ER84941

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FINAL VERSION

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Summary:

A tungsten (W) coated (0.0005-inch thickness) silicon carbide (SiC) (1.0-inch diameter and 0.19-inch thickness) sample was exposed to a divertor relevant high-flux ($\sim 10^{22}$ $m^{-2}s^{-1}$) deuterium plasma at 200 and 400°C in the Idaho National Laboratory's (INL's) Tritium Plasma Experiment (TPE), and the total deuterium retention was subsequently measured via the thermal desorption spectroscopy (TDS) method. The deuterium retentions were 6.4×10^{19} m^{-2} and 1.7×10^{20} m^{-2}, for 200 and 400°C exposure, respectively. The Tritium Migration Analysis Program (TMAP) was used to analyze the measured TDS spectrum to investigate the deuterium behavior in the W coated SiC, and the results indicated that most of the deuterium was trapped in the W coated layer even at 400°C. This thin W layer (0.0005-inch ~ 13μm thickness) prevented deuterium ions from bombarding directly into the SiC substrate, minimizing erosion of SiC and damage creation via ion bombardment. The shift in the D desorption peak in the TDS spectra from 200 C to 400°C can be attributed to D migration to the bulk material. This unexpectedly low deuterium retention and short migration might be due to the porous nature of the tungsten coating, which can decrease the solution concentration of deuterium atoms.

Introduction:

Silicon carbide (SiC) is a candidate material for use in fusion reactors because of its very high melting point, low vapor pressure at most temperatures, and its very low tritium permeability [1-3]. It also can be used in extreme nuclear environments due to thermal, mechanical and chemical stability with exceptionally low radioactivity under neutron irradiation. Refractory armored materials such as W have been considered for the fusion applications to reduce the sputtering and erosion of SiC.

The original plan of this collaboration between INL and the Ultramet Company was to measure the gas-driven tritium permeation rate in low tritium partial pressure conditions (<10 ppm) from a tubular silicon carbide sample utilizing INL's tritium heat exchanger (THX) experiment. Unfortunately, Ultramet had difficulty jointing the tubular SiC sample to the supporting metal structure to test for gas-driven tritium permeation measurement. An alternative test plan was discussed, and it was decided to use instead the Tritium Plasma Experiment (TPE); the unique high-flux linear plasma facility that can handle tritium, beryllium and activated materials. The use of tritium in TPE can expand various capabilities including plasma-driven tritium permeation and tritium depth profiling up to milli-meter depths. Deuterium implantation and subsequent retention in SiC; however, was pursued in TPE due to the budget limitation for this collaboration.

Exposing SiC to a divertor-relevant high-flux plasma such as TPE requires precautions. Plasma can sputter carbon and silicon atoms from SiC and create ion-induced damage in the SiC sample. TPE is designed and devoted to study the hydrogen isotope behavior in tungsten, the leading plasma facing component (PFC) candidate material. The sputtering of carbon contaminates the TPE vacuum chamber because even a small (~0.1%) carbon impurity in the plasma significantly increases the hydrogen isotope retention in tungsten. In addition, increasing the tritium trapping sites will decrease the effective diffusivity and effective permeability, making it difficult to interpret the mass transport data. Therefore, refractory W armor on SiC was applied to reduce the sputtering and erosion of SiC and, a 0.0005-inch thick layer of tungsten was coated on the 1.0-inch diameter and 0.19-inch thick SiC sample. W has very similar coefficient of thermal expansion (CTE) (4.4×10^{-6}/K at RT) to that of SiC (4.0×10^{-6}/K at RT). This combination of W-coated SiC is one of the candidate methods of using SiC in a future fusion reactor. TPE has tested different types of coating (vacuum plasma spray W on F82H) in the past, and observed peculiar temperature behavior during the plasma exposure due to the mismatch of CTE between the coating and substrate materials. The compatibility of tungsten coating with SiC under intense plasma condition needs to be examined. Gas-driven tritium permeation is typically carried out at a very high temperature (>1000°C) for a long exposure time (10's of hours) whereas the TPE operation limits the maximum stable temperature of 500°C and plasma duration of approximately 2 hours.

Even at the TPE condition of 500°C, hydrogen isotopes will most likely not permeate the 0.19-inch (5 mm) thick SiC sample. The hydrogen isotopes would stay at near surface of SiC substrate due to the high diffusion activation energy of 1.89 eV reported [1-3]. The Tritium Migration Analysis Program (TMAP) analysis of the TDS spectrum will be used to determine deuterium behavior within the W coated SiC.

Objective:

The primary purpose of this initial testing is to investigate hydrogen isotope (deuteron) behavior in the W-coated SiC and the integrity/compatibility of refractory (W) armor on SiC under a divertor-relevant high-flux deuterium plasma for fusion applications.

Test condition:

A 0.0005-inch thick W layer was coated on the 1.0-inch diameter 0.19-inch thick SiC disc, and the disc was sent to the Safety and Tritium Applied Research (STAR) facility. The sample disc is shown in Figure 1. The plasma conditions for the deuterium plasma exposure in TPE are given in Table 1. The operating condition of the thermal desorption spectroscopy (TDS) system is the following; base pressure: 1×10^{-5} Pa, ramp rate: 10°C/min and maximum temperature: 1000°C. The plasma exposure requires the compression of the sample between the front W mask and the back Cu heat sink for temperature control. Unfortunately, cracking was observed on the edge of the W coating, and the integrity of the coating was lost after the 2nd plasma exposure as shown in Figure 1(b). This failure has nothing to do with the integrity of the W coating, and this failure can be overcome by modifying the target holder in TPE. Microscopic images of before and after plasma exposure are in Figure 2(a) and 2(b).

Experimental results:

Figure 3 shows thermal desorption spectra of the W coated SiC sample exposed to a high-flux deuterium plasma (ion flux: $(8\text{-}12) \times 10^{21}$ $m^{-2}s^{-1}$, ion fluence: $(2.3\text{-}3.5) \times 10^{25}$ m^{-2}, ion energy: 100 eV) at 200 and 400°C in INL's TPE.

Figure 3(a) shows two distinctive peaks, but the high temperature peak is attributed to only a mass 3 peak, indicating this is due to a large hydrogen retention (mass 2) in possibly the W coating layer; therefore, the only high temperature peak should be neglected for the actual deuterium retention estimate. The corrected deuterium retention for 200°C is 6.4×10^{19} m^{-2}.

Figure 3(b) shows only one peak, indicating hydrogen has been desorbed by the previous TDS; therefore, the contribution from both mass 3 and mass 4 should be included for the actual deuterium retention estimate. The deuterium retention for 400°C is 1.7×10^{20} m^{-2}, more than 2.5 times larger D retention than that at 200°C. This very low deuterium retention and short migration might be due to the porous nature of the tungsten coating, which can decrease the solute concentration of deuterium atoms. Underlying physics of hydrogen behavior in the porous coating layer is still not well known. Figure 4 shows the comparison with other types of tungsten coating and a reference TDS spectrum of deuterium exposed to silicon carbide. Different coating methods (vacuum plasma sprayed vs. chemical vapor deposition) exhibited different deuterium behavior, probably due to the difference in porosity. If the silicon carbide was not protected by high-energy ions, a significant amount of deuterium can be trapped in the silicon carbide.

The sample temperature was stable during two plasma exposures, indicating good integrity and compatibility of tungsten coating with SiC during divertor relevant high-flux deuterium plasma in TPE.

Sample temperature [°C]	Electron temperature [eV]	Electron density [m^{-3}]	Ion flux density [$m^{-2}s^{-1}$]	Plasma duration [s]	Ion fluence [m^{-2}]	Incident ion energy [eV]	Plasma potential [V]	Floating potential [V]
200	6.4	7.2e17	7.7e21	3600	2.3e25	100	-14.4	-37.9
400	5.8	1.1e18	1.2e22	3600	3.5e25	100	-10.3	-33.9

Table 1: Plasma conditions of deuterium plasma exposure.

Modeling:

The Tritium Migration Analysis Program version 7 (TMAP7) was used to simulate the obtained TDS spectra at 400°C and only thermal desorption was simulated in this report to avoid the difficulty of simulating the hydrogen isotope exposure process, which is a dynamic and non-equilibrium process. Significant hydrogen release (mass 2 and mass 3) was observed for the 200°C TDS spectrum indicating the modeling requires the initial trapped hydrogen concentration. This makes it difficult to simulate the TDS spectrum since it has to simulate deuterium isotope exchange with hydrogen. Meanwhile, the 400°C experiment was performed after the 200°C TDS experiment; therefore, we can neglect the background hydrogen effect on the TDS spectrum. The microscope image taken after plasma exposure (Figure 2(b)) shows 5-10 μm diameter blisters, indicating the deuterium migration can be significantly reduced by the presence of blisters that serve as a diffusion barrier.

In the simulation we introduce a 13 μm thick tungsten layer (segment 1) on top of a 5 mm thick tungsten target (segment 2). For the tungsten layer, we chose the hydrogen diffusivity formula of Frauenfelder [4] (corrected for deuterium) as suggested in the review paper by Causey [5] ($D = 2.9\times10^{-7} \exp(-0.39 \text{ eV}/kT)$ [m^2 s^{-1}]). Recombination coefficients vary by several orders of magnitude in the literature, but we chose to use the formula of Anderl et al [6] ($K_r = 3.2\times10^{-15} \exp(-1.16 \text{ eV}/kT)$ [m^4s^{-1}]). From the literature on detrapping energy in tungsten, the low-energy (0.8–1.1eV) trap is associated with deuterium atoms trapping with impurities or dislocations, the 1.3–1.5 eV trap is associated with deuterium atoms trapping at vacancies in tungsten and deuterium molecules desorbed from voids, and the high-energy (1.7–2.1 eV) trap is associated with dissociation and release of deuterium atoms decorating a void.

For silicon carbide, we have used the tritium diffusivity and solubility (corrected for deuterium) in vapor deposited silicon carbide measured by Causey et. al. [3] ($D = 9.8 \times 10^{-8} \exp(-1.89 \text{ eV}/kT)$ [m^2 s^{-1}] and $S = 8.2\times10^{-15} \exp(+0.61 \text{ eV}/kT)$ [atoms/cm^3 $atm^{0.5}$]). A trapping site in the silicon carbide was not considered for this simulation since the silicon carbide does not contact with energetic ions. Only deuterium in the solution site was considered. Causey et. al. measured the diffusivity and solubility in the

range of 1000 to 1600°C. The exothermic nature (e.g., negative heat of solution) of the measured solubility in silicon carbide exhibits a peculiar deuterium behavior (anomalous high solubility) at low temperature; therefore, the constant tritium solubility (corrected for deuterium) in vapor deposited silicon carbide ($S = 8.2\times10^{-15}$ [atoms/cm^3 atm$^{0.5}$]) was used in the simulation. The solubility at low temperature (< 1000°C) is required to simulate the hydrogen isotope behavior in silicon carbide accurately. Figure 5 shows the TMAP simulation along with the experimental TDS spectrum at 400°C. The trap energy and maximum depth were adjusted for the best fit to the experimental data.
The trap site uniformly distributed with $3.5\text{x}10^{-4}$ [T/W ratio], deuterium completely filled the traps up to 4 μm, and trapping energy of 1.25 eV gave a reasonable fit to the experimental data. The experimental TDS spectrum was able to fit with a low trap energy of 1.25 eV, indicating that all the deuterium is still trapped in the tungsten layer. The trap energy of 1.25 eV is thought to be associated with dissociation of deuterium bubbles. If the deuterium is trapped or absorbed in silicon carbide, the TDS spectrum should appear at a much higher temperature due to the high diffusion activation energy of 1.89 eV. This indicates that most of the deuterium was trapped in the W coated layer even at 400°C, and this thin W layer (0.0005 inch ~ 13μm thickness) prevented deuterium ion bombardment directly into the SiC substrate, minimizing the deuterium trapping created by ion bombardment. This suggests longer exposure times are needed to see the deuterium migration effects on silicon carbide.

Conclusion:

The W coated SiC (1.0-inch diameter 0.19-inch thick disc with 0.0005-inch thick W coating) was exposed to a divertor-relevant high-flux ($5\text{x}10^{21}$ m^{-2}s^{-1}) deuterium plasma at 200 and 400°C in TPE and total deuterium retention was subsequently measured via the thermal desorption spectroscopy (TDS) method. The deuterium retention was $6.4\text{x}10^{19}$ m^{-2} and $1.7\text{x}10^{20}$ m^{-2} under similar plasma conditions, for 200 C and 400°C exposure, respectively. The sample temperature was stable during two plasma exposures, indicating good integrity and compatibility of the tungsten coating on the SiC sample during exposure to the divertor relevant high-flux (~10^{22} m^{-2}s^{-1}) deuterium plasma in TPE. The experiment and TMAP simulation indicated that most of the deuterium was trapped in the W coated layer and this thin W layer (0.0005-inch ~ 13μm thickness) prevented deuterium ion bombardment directly into the SiC substrate, minimizing the deuterium trapping created by ion bombardment. Underlying physics of hydrogen behavior in the porous coating layer is not well known. Longer exposure times are needed to see the deuterium migration effects on silicon carbide. The shift in the D desorption peak in the TDS spectra from 200 to 400°C can be attributed to D migration to the bulk material. This very low deuterium retention and short migration might be due to the porous nature of the tungsten coating, which can decrease the solute concentration of deuterium atoms.

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[6] Anderl R A, Holland D F, Longhurst G R, Pawelko R J, Trybus C L and Sellers C H 1992 *Fusion Technol.* **21** 745

Figures:

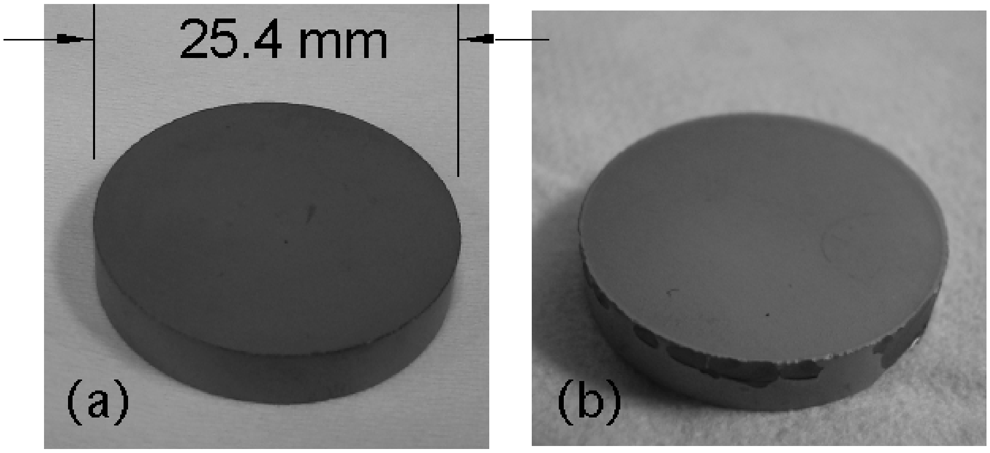

Figure 1: Photograph of the W coated SiC before (a) and after (b) plasma exposures.

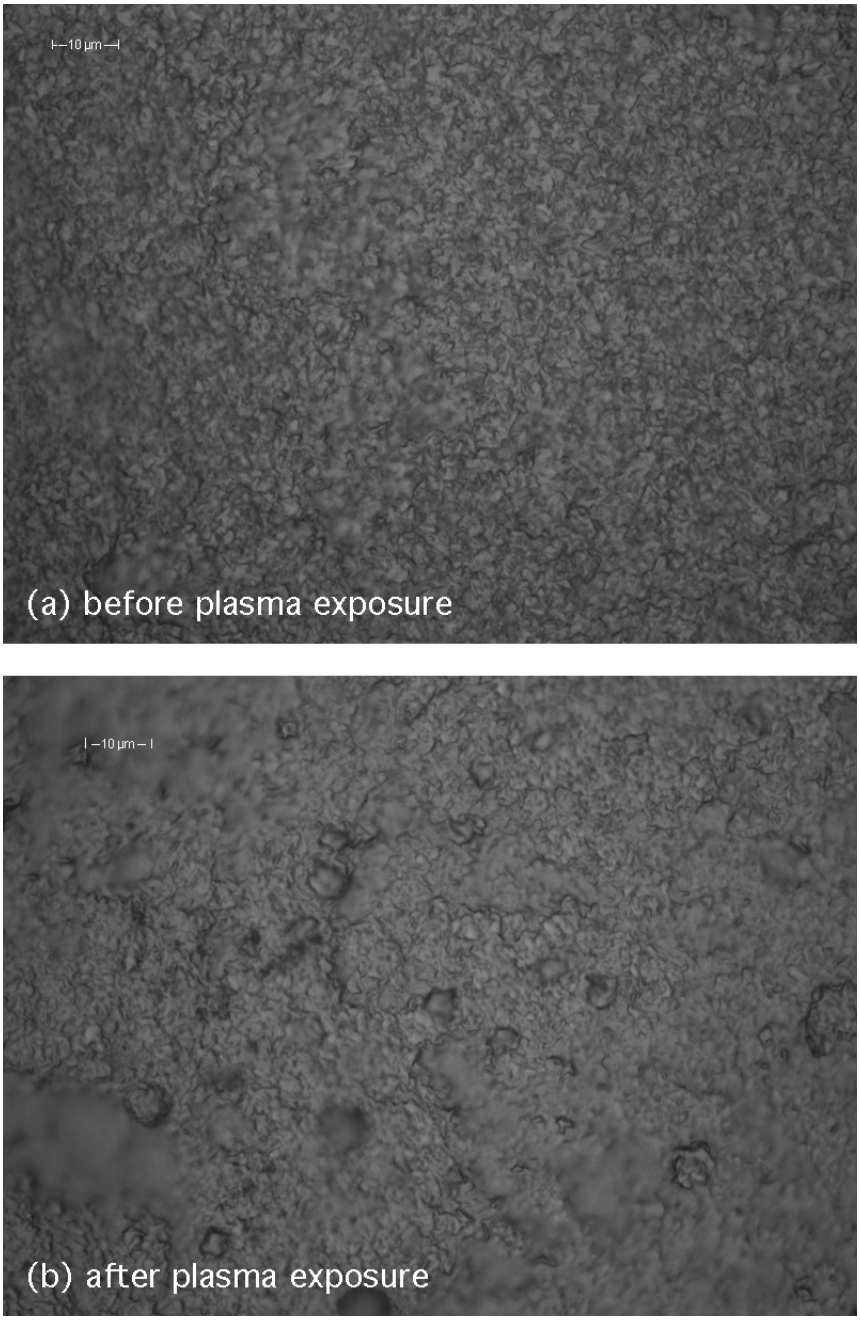

Figure 2: Microscope image of W coated SiC before (a) and after (b) plasma exposures.

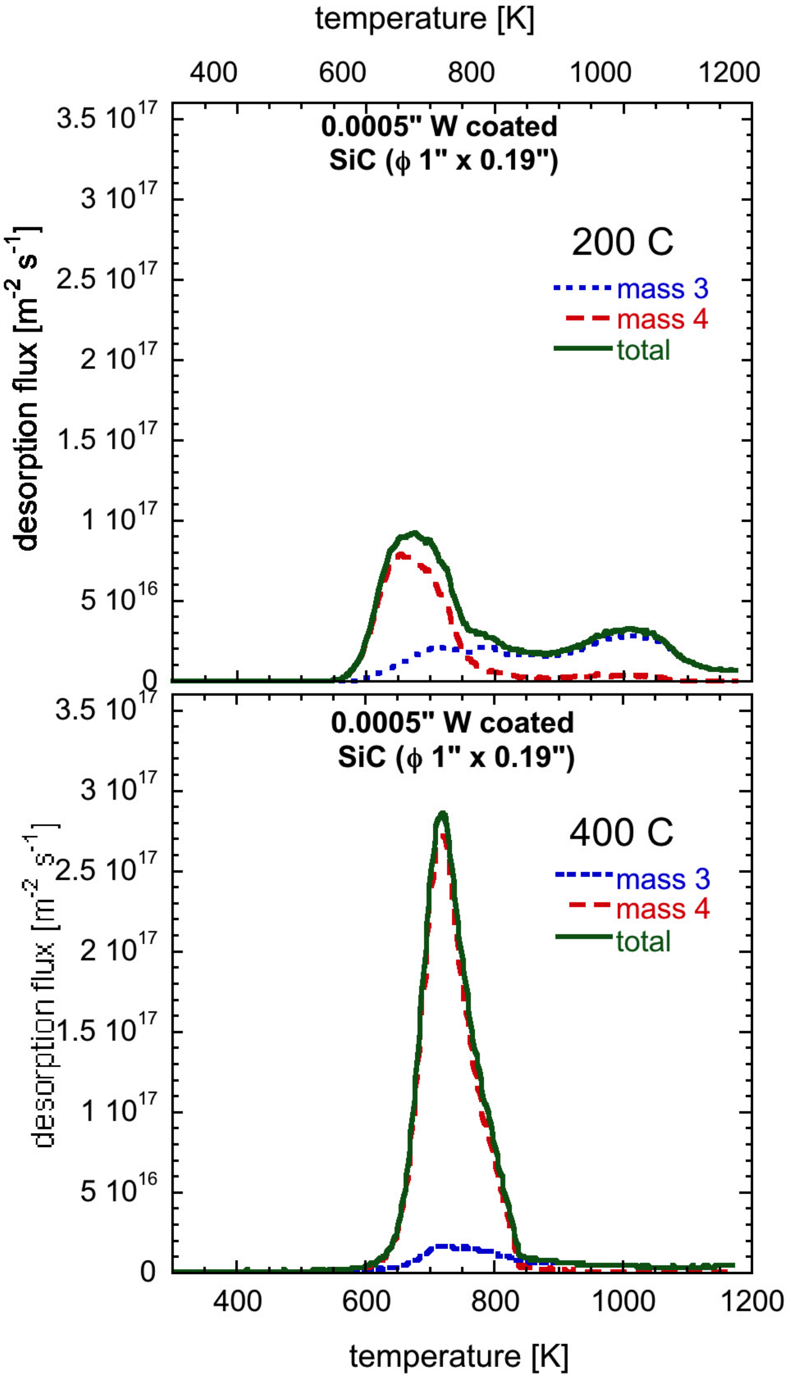

Figure 3: Thermal desorption spectra of W coated SiC sample exposed to high-flux deuterium plasma (ion flux: (8-12)x10^{21} $m^{-2}s^{-1}$, ion fluence: (2.3-3.5)x10^{25} m^{-2}, ion energy: 100 eV) at 200 and 400°C in INL's TPE.

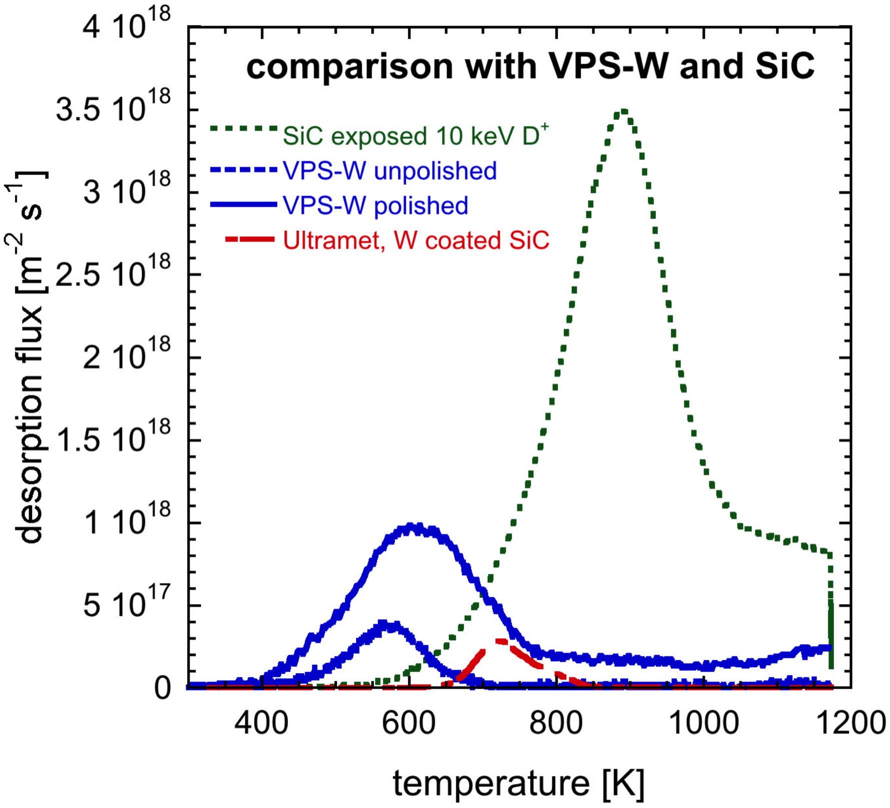

Figure 4: Comparison of thermal desorption spectra of W coated SiC sample exposed to high-flux deuterium plasma with VPS-W exposed to similar deuterium plasma in TPE and SiC exposed to high-energy deuterium ion in INL's TRIIX accelerator.

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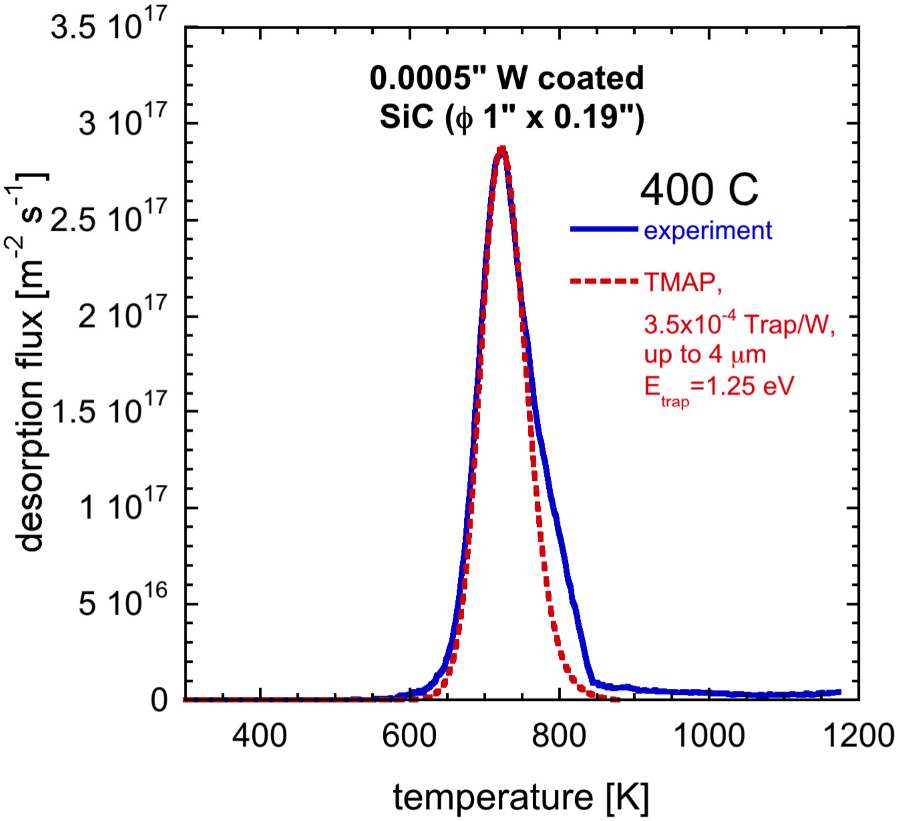

Figure 5: TMAP simulation of TDS spectrum at 400°C. The blue line denotes the experimental TDS spectrum exposed to deuterium plasma at 400°C, and the red dotted line denotes the TMAP simulation.