THE EFFECTS OF HELIUM ON DEUTERIUM RETENTION IN TUNGSTEN UNDER SIMULTANEOUS IRRADIATION

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science

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ABSTRACT

The trapping behavior of deuterium and helium in polycrystalline tungsten (PCW) under D⁺-only, He⁺-only, sequential and simultaneous irradiation was studied as a function of incident ion fluences and irradiation temperature. Deuterium implanted at 300 and 500 K gets trapped at surface adsorption sites, vacancy-related traps, or extended defects. No deuterium was trapped for 700 K implantations. Results were affected by tungsten-carbide impurities in PCW specimens. It is suggested that He trapping occurs via the formation of He clusters, at impurity sites, or as part of He-vacancy complexes. For sequential implantations, D and He were found to de-trap each other, with He impeding the trapping of D when implanted first at 300 K. Under simultaneous irradiation a decrease in D inventories was observed for all cases, and a re-distribution of He to higher energy traps (associated with He-vacancy complex formation) was observed for higher fluences and temperatures.
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Chapter 1  Introduction

1.1 Fusion Energy

Nuclear fusion is the physical process in which two light nuclei combine to form a heavier nucleus, resulting in the release of energy. The resulting nucleus must have greater binding energy per nucleon; subsequently, this process is energetically favorable for only the elements with atomic mass (A) lower than iron (Fe), which has the greatest binding energy per nucleon among all elements. In all cases there is a disparity in mass between the reactants and products of a fusion reaction. This “missing” mass accounts for the energy released by the reaction according to Einstein’s mass-energy equivalence relation \( E = \Delta mc^2 \) [1].

Fusion is the process of energy production for all stars in the Universe. Our Sun, more specifically, relies on the fusion of hydrogen atoms yielding helium via the proton-proton chain (see [2]). However, despite its natural abundance, and the relatively small repulsive electromagnetic forces between interacting nuclei, hydrogen is simply not practical for energy production on Earth because of its relatively low reaction cross-section. Alternatively, deuterium, which constitutes 0.0153% of natural hydrogen, has significantly larger reaction cross-section for fusion-type nuclear interactions; while reactions between deuterium (D) and tritium (T) have the largest cross-section. It is therefore anticipated that fusion reactors will operate with the DT reaction (deuterium-tritium) [1]:

\[
\begin{align*}
\frac{3}{2}D + \frac{3}{2}T & \rightarrow \frac{3}{2}He(3.54\text{MeV}) + \frac{1}{0}n(14.05\text{MeV})
\end{align*}
\]

However, this is not the ultimate goal of fusion research. The above reaction has many disadvantages that make it less than ideal for long term sustainability. Tritium for instance is a radioactive isotope of hydrogen that is negligible in nature, therefore, it is necessary to breed tritium from lithium (Li), which is in significantly shorter supply than water (which is our source for D). Furthermore, there is a highly energetic neutron produced that causes radiation damage and makes the walls radioactive; meanwhile leaving only 1/5 of the reaction energy to be directly converted into electricity via the charged particle [1]. The eventual goal of fusion research is to design reactors that operate via DD reactions, however, this process requires higher temperatures, and has a lower relative power density [2].
From the construction point of view, there are two main requirements in designing a fusion reactor; the first is to heat the fuel to achieve ignition, and the second is to confine the heated fuel particles [1]. Since the positively charged fusing nuclei must overcome the repulsive electromagnetic forces between them a large amount of kinetic energy must be supplied, typically requiring temperatures on the order of \(10^8\) K (for DT fusion). As a consequence of these intense temperatures the fuel particles must be confined to prevent contact with the inner-walls of the reactor. At \(10^8\) K fuel particles are in a plasma state, and subsequently magnetic fields can be applied to confine the particles. The most probable magnetic configuration for the commercial fusion reactor of the future is the tokamak. The tokamak design is characterized by a toroidal-shaped vacuum chamber that utilizes both toroidal and poloidal magnetic fields to confine the plasma. The plasma is heated resistively by the electric current flowing through it (Ohmic heating), with additional heating via neutral beam injection, and radio-frequency (RF) induction [3].

While the tokamak has proven to be scientifically feasible, it has yet to demonstrate engineering feasibility. Essentially, all experimental reactors consume more energy than they produce. Among the most successful experimental tokamaks, the Joint European Torus (JET) has produced 16.1 MW of energy via DT fusion while achieving a Q value of 0.64 (power produced by DT fusion/power input) [4], and the Tokamak Fusion Test Reactor (TFTR) has produced \(~11\) MW while achieving \(Q = 0.27\) [5]. The primary focus of the fusion research community at the present time is the development of ITER, the International Thermonuclear Experimental Reactor. The technical objectives of ITER are to achieve extended burn in inductive operation with \(Q \geq 10\), not precluding ignition, for a period of 300-500s, and to demonstrate steady state operation using non-inductive current drive with \(Q \geq 5\). The device is projected to produce 500MW from DT fusion and has the ultimate goal of achieving ignition conditions [6].

### 1.2 Plasma-Facing Materials

A key consideration for the design of ITER is the selection of plasma-facing materials (PFM). Candidate materials are selected with the purpose of protecting the vessel structure and other sub-wall components from the negative effects of plasma-surface interactions. Therefore,
Some attractive properties for candidate materials include low erosion yield (to extend material lifetimes), high thermal conductivity, high thermal stress resistance/high melting point, low atomic number (Z) to limit radiation losses and low hydrogen retention (more specifically tritium). The allowable inventory of retained tritium in a fusion reactor is limited for three main reasons, all of which stem from the radioactive nature of tritium. First, the tritium inventory must be controlled to ensure that the tritium released in a worst case incident would not exceed the no-evacuation limit at the site boundary. Second, due to its negligible abundance in nature, tritium is expensive and obviously in short supply. Finally, the low margin for tritium breeding from lithium further limits allowable losses [7].

While there are no candidate materials with ideal PFM properties for the entire plasma-facing area of ITER, there are suitable materials for different applications in the device. Figure 1 illustrates a cross-section of the reactor showing the major plasma-facing components [8]. Heat loads and particle fluxes are anticipated to be on the order of $10$-$20$ MW/m$^2$ and $\sim 10^{24}$ DT/m$^2$s for the divertor target; an average of $\sim 3$ MW/m$^2$ and $10^{20} - 10^{21}$ DT/m$^2$s for the lower baffle, divertor dome and divertor sidewall; and $\sim 1$ MW/m$^2$ and $10^{19} - 10^{20}$ DT/m$^2$s for the upper baffle and first wall [8]. The primary candidates for PFM in ITER are beryllium, tungsten and carbon. Although carbon is known to create issues with tritium codeposition and mixing of materials, it is the best candidate PFM for the divertor target region because of its ability to withstand the high heat loads with reasonable erosion lifetime. Despite known disadvantages of low melting point, and high sputtering yield, beryllium is considered a primary candidate PFM for the first wall of the reactor, although direct contact with the plasma is expected only during off-normal events. Beryllium does offer some advantages in the form of high thermal conductivity to protect the underlying first-wall structures, the ability to getter oxygen impurities from the plasma, and having a low atomic number (Z). This last characteristic is highly attractive for any PFM as the radiation losses in the plasma are proportional to the $2^{\text{nd}}$ (Bremsstrahlung radiation) and $4^{\text{th}}$ (line radiation) power of the atomic number. Tungsten, having the highest sputtering threshold of the three materials, is considered a primary candidate for the divertor dome, divertor sidewall and lower baffle to minimize the sputtering erosion from charge-exchange neutrals [8].
Initial results indicate that tungsten is the most attractive of the three candidate materials when it comes to hydrogen isotope retention. At first glance, beryllium appears to be an attractive material for hydrogen retention. Because of its low solubility for hydrogen, beryllium implanted with deuterium and tritium results in a saturated layer in the very-near surface with limited inventory. However, nuclear reactions created by neutrons lead to breeding of tritium and helium in the material bulk which adds to the tritium inventory in the bulk after long-term exposure. Carbon typically retains a small fraction of incident hydrogen isotopes, primarily on the internal porous surface. However, sputtered carbon and beryllium are expected to create codeposition layers with the tritium from the plasma in the cooler areas of the tokamak, potentially removing kilograms of tritium from the fuel cycle and depositing it in “hard-to-reach” areas of the reactor. It is the codeposited Be and C layers that are expected to dominate tritium retention in ITER [8].

Though tungsten continues to be studied for plasma facing applications, initial results indicate that relatively low tritium inventories could be expected with this material [8]. This
favorable characteristic, combined with its attractive thermo-mechanical properties have led to the speculation that tungsten could be used as a first wall material in future devices [9].

1.3 **Hydrogen and Helium Retention in Tungsten**

Controlling the tritium inventory in the reactor is of primary importance. However, the presence of helium, as a product of DT fusion reactions, must be taken into account when considering the hydrogen retention characteristics of tungsten. Because helium is a closed-shell inert gas, it interacts only repulsively with metal atoms. Future fusion reactors would produce sufficient quantities of helium to degrade the material properties of tungsten, which could in turn affect hydrogen trapping [10]. Considerable amount of information is available on the trapping behavior of hydrogen in tungsten, as well as on the effects of helium in metals (including tungsten); see Chapter 2.

1.4 **Thesis Objective**

The objective of this thesis is to further expand upon previous studies on deuterium and helium trapping in tungsten done by H.T.Lee [11] using improved measurement techniques (with a higher resolution quadrupole mass spectrometer) and investigating additional temperatures and particle fluences. Similar to Lee, this work aims to observe and report the trapping behavior of polycrystalline tungsten (PCW) under simultaneous and sequential implantation by deuterium (D\(^+\)) and helium (He\(^+\)) ion beams at 300K, 500K and 700K for fluences of ~ 10\(^{23}\) D\(^+\)/m\(^2\) with ~ 1-2 x 10\(^{21}\) He\(^+\)/m\(^2\) and ~ 10\(^{24}\) D\(^+\)/m\(^2\) with ~ 1-2 x 10\(^{22}\) He\(^+\)/m\(^2\). An Extrel MAX 60 quadrupole mass spectrometer (QMS), capable of resolving between molecular deuterium (D\(_2\)) and helium (He), was used to measure the independent release rates of deuterium and helium during “thermal desorption spectroscopy” (TDS). The release peaks observed in the TDS spectra, cross-referenced with depth profile experiments from the literature [11], will be used to elucidate trapping mechanisms. A phenomenological mechanism governing deuterium and helium trapping in polycrystalline tungsten that is consistent with the results of the above detailed experiments and the literature will then be presented.
Chapter 2  Background

This chapter will begin with a brief overview of the material properties of tungsten and its use in fusion reactors. Next, some key results of hydrogen trapping in tungsten for various types of tungsten and different irradiation conditions will be presented, along with some interpretations of the results. Following, there will be a section to detail the interactions of helium with metals, focusing eventually on tungsten. The final section will present key results from studies of hydrogen and helium trapping in tungsten, along with some of the conclusions drawn by other researchers.

2.1 Tungsten

Tungsten is a high-Z transition metal that is best known for its thermal properties. It has the highest melting point and lowest vapor pressure, with values of \[3410 \pm 20 \, ^\circ\text{C} \approx 3683 \, \text{K}\] and \[6.5 \times 10^{-7} \, \text{Pa}\] (at 2300 K) respectively, as well as the highest tensile strength of any pure metal. Tungsten also has good thermal conductivity with a value of \(~173 \, \text{W/mK}\) at 300 K, and a peak value of \(~195-200 \, \text{W/mK}\) at \(~100-150 \, \text{K}\) [12].

For fusion reactor applications, high melting temperature, good thermal conductivity, and low sputtering yield make tungsten an attractive candidate for plasma-facing applications. Tungsten is considered a primary candidate for the divertor region of the next-step fusion reactor, ITER. The divertor is the preferred location for tungsten use because the low plasma temperature leads to low sputtering [9]. Again, contamination of the plasma by high-Z materials must be minimized, or preferably avoided completely because the radiation losses depend so strongly on the atomic number (Z) (to the 2nd and 4th power of Z).

While there are limited areas of ITER where tungsten will be used for the initial phases of operation, tungsten could be used for all plasma-facing surfaces at some point in the future. Unfortunately, the high heat loads of disruptions anticipated in ITER are expected to damage the tungsten (and beryllium, though low-Z reduces the resulting radiation losses) surfaces and the spreading of vaporized/melted material to other surfaces would cause too much plasma cooling for fusion [9, 13]. For the time being, tungsten will only be used in areas of the divertor that are...
subject to lower heat fluxes, lower particle fluxes and lower energies (See section 1.2) until all plasma activities are well understood.

2.2 Retention of Hydrogen Isotopes in Tungsten

The topic of hydrogen retention in plasma facing materials is a key issue in determining a material’s suitability for fusion applications. As mentioned in Chapter 1, tritium management during the DT fusion phase is of utmost importance for future reactors. Since interest in tungsten as a plasma facing material has been renewed, a great deal of effort has gone into studying the retention of hydrogen in this high-Z material. Several review papers [7, 14, 15] have been published that deal with hydrogen in tungsten, and the subsequent implications of using tungsten as a plasma facing material. In the following, the fusion relevant properties of hydrogen in tungsten are discussed.

Diffusion is one of the fundamental properties affecting retention and migration of hydrogen in a material [7]. The most quoted value for diffusivity of hydrogen in tungsten was determined by Frauenfelder using a hot rolled 99.95% pure tungsten sheet for temperatures between 1200 and 2400K. Frauenfelder determined the value for diffusivity of hydrogen in tungsten to be \( D = 4.1 \times 10^{-7} \exp(-0.39 \text{ eV/kT}) \) [16]. This is considered to be the most reliable value for diffusivity of hydrogen in tungsten because of the large range of temperatures studied, coupled with the high temperatures that effectively rendered trapping of hydrogen negligible. In the same study, Frauenfelder also determined the solubility of hydrogen in tungsten for temperatures between 1100K and 2400K, using the same 99.95% pure tungsten. From his investigation, the solubility of hydrogen in tungsten was found to be \( S = 9.3 \times 10^{-3} \exp(-1.04 \text{ eV/kT}) \frac{\text{H}}{\text{W*atm}^{1/2}} \) [16]; considered by many as the most reliable value for solubility.

Ion beam implantation is a popular technique for studying hydrogen interactions in tungsten because of the ability to accurately control parameters such as ion doses (flux and fluence) and energy. However, it is impractical to simulate conditions that plasma-facing materials will be subjected to in the next step fusion reactors (i.e. fluences \( > 10^{26} \text{ ions/m}^2 \)) using ion-beams, particularly for tungsten which is planned for use in the divertor region where fluences are expected to be \( \sim 10^{28} – 10^{29} \text{ DT/m}^2 \) [17]. Furthermore, the plasma conditions in future fusion reactors will vary for different areas of the device, and for different experimental
reactors. As a result, most ion beam experiments focus on revealing patterns and mechanisms for
the trapping of hydrogen isotopes in tungsten to understand the underlying physics governing
these processes, and to allow for extrapolation of results to actual conditions within fusion
reactors. Fluence dependence studies have been done by Haasz et al. [18] and Poon et al. [19].
Haasz et al. [18] investigated deuterium retention in 99.95 wt% polycrystalline tungsten (PCW,
prepared by Rembar corp.) and W-1%La$_2$O$_3$ alloy (proposed alloy for use in ITER) as a function
of incident fluence. For 25µm thick Rembar samples irradiated at room temperature (300 K) it
was found that the total retained D fluence tended towards saturation at $\sim 6 \times 10^{20}$ D/m$^2$ for
incident fluences $> 10^{23}$ D$^+$/m$^2$. This behavior was consistent for all irradiation energies
investigated (300 eV/D, 500 eV/D, and 1 keV/D) and was independent of implantation history
and sample thickness (experiments with 25 and 250 µm thick Rembar samples). At 500 K,
however, the D retained appeared to follow a square root dependence (i.e. retained fluence is
proportional to the square root of incident fluence) with no sign of saturation up to incident
fluences of $3 \times 10^{24}$ D/m$^2$ for the 25 µm Rembar PCW; the amount retained appears to be
diffusion limited. The W-1%La$_2$O$_3$ alloy exhibited very similar behavior as the Rembar PCW for
room temperature implantations (300 K), however, when irradiated at 500 K, the W-1%La$_2$O$_3$
alloy appeared to tend toward saturation for incident fluences $> 10^{24}$ D$^+$/m$^2$ [18]. Poon et al. [19]
investigated deuterium retention in single crystal tungsten (SCW) as a function of fluence and
impurity levels using 500 eV/D. The high purity SCW, prepared by the State Institute of Rare
Metals in Moscow, behaved as the Rembar PCW did for 300 K irradiations. For 500 K
irradiations, D retention was not detected below fluences of $\sim 10^{23}$ D$^+$/m$^2$. Total D retention
appeared to increase linearly with incident fluence until $\sim 3 \times 10^{24}$ D$^+$/m$^2$, after which point the
relationship weakened. Despite this relation, the total D retained for high purity SCW was still an
order of magnitude lower than for Rembar PCW for incident fluences of $\sim 10^{25}$ D$^+$/m$^2$ at 500 K
[19]. Though results appear consistent for all materials when irradiated at room temperature (300
K), it is evident that D retention in tungsten at elevated temperatures is affected by diffusion,
which, in turn is dependent on impurity content, and material structure.

Fluence dependence experiments were extended to include different types of
polycrystalline tungsten to further investigate the effects of material structure. Tian et al. [20]
and Ogorodnikova et al. [21, 22] performed fluence dependence studies using pure (99.97 wt%)
polycrystalline tungsten manufactured by Plansee, observed to have mean grain size of 40 µm
using scanning electron microscopy (SEM) [21]. Among the more interesting results, Ogorodnikova et al. [21], using a 200 eV/D and 500 eV/D beam, discovered a completely different relation for fluence dependence compared to previous studies with pure PCW. At 500 K, it appears the D retention follows roughly a square root dependence with incident fluence for values up to $\sim 3 \times 10^{24} \text{D}^+/\text{m}^2$, similar to results in [18]. However, at room temperature (323 K for 200 eV/D, 300 K for 500 eV/D) there was an increasing trend as for the 500 K case, with no sign of saturation. The only other instance where this behavior was observed for room temperature irradiations was in rhenium-doped tungsten [23]. Tian et al. [20] sought to verify these results by repeating experiments using the same material. For room temperature irradiations (300 K), both at 200 eV/D and 500 eV/D, Tian et al. found that D retention tended toward saturation at $\sim 4 \times 10^{20} \text{D}^+/\text{m}^2$ for incident fluences above $5 \times 10^{23} \text{D}^+/\text{m}^2$. These results agree with most published results, raising questions about Plansee results in [21, 22]. In the same study, Tian et al. also sought to extend the range of incident fluences for Plansee PCW under 500 K irradiations. Similar to the cases presented above, the level of retained D increased with incident fluence up to a value of $\sim 5 \times 10^{20} \text{D}^+/\text{m}^2$ for an incident fluence of $8 \times 10^{25} \text{D}^+/\text{m}^2$ with a 200 eV/D beam, still showing no signs of saturation. These results are intriguing since these values are approaching fluences in plasma devices. The question remains whether this increasing trend will continue beyond fluences of $\sim 10^{26} \text{D}^+/\text{m}^2$ into the ITER fluence range [20].

Beyond determining fluence dependence, many studies included experiments to measure the influence of different D energy, flux, and implantation temperatures on D retention in tungsten. In [20], various beam energies were used in the fluence dependence studies with Plansee PCW, all below the threshold for damage formation ($\sim 960$ eV for D on W). For 300 K irradiations, increasing the beam energy from 100 to 500 eV/D, for incident fluences of $\sim 1 \times 10^{23} \text{D}^+/\text{m}^2$ and $\sim 1 \times 10^{24} \text{D}^+/\text{m}^2$, leads to a negligible increase in D retention. For 500 K irradiations, for an incident fluence of $\sim 1 \times 10^{23} \text{D}^+/\text{m}^2$, increasing the beam energy from 100 to 500 eV/D leads to a 3-fold increase in D retention. From these results, it appears that ion energy becomes a factor at elevated temperatures despite being below the damage threshold. There are two possible factors contributing to this phenomenon; the increased diffusion of D at 500 K, coupled with the possible damage creation by C and O impurities in the Plansee PCW. Because C and O atoms are relatively smaller than W, incident D$^+$ ions can impart more energy to these atoms. Similarly, because these impurities are considerably more massive than D, the threshold
for damage creation in tungsten is smaller (140 eV for O, and 175 eV for C, assuming a displacement threshold of 41 eV for W). Therefore, it is possible that 500 eV-D⁺ ions are creating damage in the Plansee PCW via recoil collisions with C and O, whereas the 100 and 200 eV-D⁺ ions have insufficient energy [20]. Similar conclusions were drawn in [18] where it was noted the D retention levels depended on ion energy for elevated temperatures between 300 and 550 K. Temperature dependence studies produced variable results based on different materials investigated. D retention in single crystal tungsten (SCW) irradiated with $10^{24}$ D⁺/m² appears to decrease linearly as temperature is increased from 300 to 700 K, with no retention observed for implants above 700 K [19]. Similarly, Plansee PCW irradiated with $10^{23}$ D⁺/m² exhibits a linearly decreasing trend as implant temperature is increased from 300 to 500 K [20]. The most interesting results came from Rembar PCW irradiated with $10^{23}$ D⁺/m²; in which D retention is enhanced for increasing temperatures up to 450 K, with a decreasing trend including a plateau at 500 to 550 K. Again, there is no retention for temperatures exceeding 700 K [18]. Though the dependence was weak, it was found that D retention was affected by beam flux. Poon et al. [24] discovered a significant variation in D retention for SCW at low D⁺ fluxes and low D⁺ fluences ($10^{21}$ D⁺/m²). For beam fluxes below $10^{18}$ D⁺/m² s, Poon et al. found a significant decrease in D retention, leading to the hypothesis that there is a flux threshold for deuterium retention in tungsten under certain conditions [24].

Depth analysis of implanted deuterium is useful as an additional means to measure the D retained in samples, to complement data obtained with thermal desorption spectroscopy (TDS, used in the studies discussed previously). Furthermore, depth profiles reveal diffusion characteristics of the implanted ions, helping to unravel the mechanisms governing the retention of deuterium in tungsten. Results will be presented for later comparison with depth analysis data for specimens irradiated with both deuterium and helium. Alimov et al. [25] measured the depth distribution of deuterium in single- and polycrystalline tungsten (SCW and PCW) up to 7µm deep using the D(³He,p)⁴He nuclear reaction in a resonance-like technique. The depth at which deuterium is retained for tungsten specimens irradiated with 200 – 1500eV D ions can be tentatively divided into three zones: (i) the near-surface layer (up to a depth of ~ 0.2-0.5µm, depending on ion energy); (ii) the sub-surface layer (from ~ 0.5 to ~ 3µm); and (iii) the bulk (> 6µm) [26]. In the case of SCW irradiated with 200-eV D⁺ at 300 K the near-surface D concentration increases from ~ 0.01 to ~ 5 at.% as the D⁺ fluence is increased from $5 \times 10^{22}$ to 1
x 10^{24} \, \text{D}^+/\text{m}^2$. The large increase of the D concentration can only be explained by a structural change in the SCW specimens during D$^+$ irradiation, leading to additional traps for D retention. The sub-surface D concentration is $\sim 0.01$ at.% for all ion fluences used, whereas the D concentration in the bulk lies in the range $10^{-4}$ to $3 \times 10^{-3}$ at.% [25, 26]. For PCW irradiated with 200-eV D$^+$ at 323 K, the near-surface D concentration ranges from 1 to 5 at.%. The D concentration in the sub-surface layer reaches a maximum value of 0.1 at.% as the fluence is increased to $1 \times 10^{24} \, \text{D}^+/\text{m}^2$, approximately ten times greater than was observed for SCW. Increasing the fluence beyond $10^{24} \, \text{D}^+/\text{m}^2$ leads to a decrease in the D concentration to a value of $\sim 0.03$ at.% for fluences $\geq 3 \times 10^{24} \, \text{D}^+/\text{m}^2$. The D concentration in the bulk increases with D$^+$ fluence and reaches a peak value of $\sim 6 \times 10^{-3}$ at.% for fluences $> 1 \times 10^{24} \, \text{D}^+/\text{m}^2$ [25, 26].

Haasz et al. [18] measured near-surface D concentrations for 25µm thick, 99.95 wt.% pure PCW specimens using D(3He,4He)p NRA. The depth profiles for specimens irradiated with 500-eV D$^+$ at a fluence of $10^{24} \, \text{D}^+/\text{m}^2$ and implant temperature of 300 K show the peak of the distribution at $\sim 80$nm, with a D concentration of $\sim 3$ at.% [18]; D was also observed to be trapped beyond 500nm into the bulk. For the same parameters at 500 K, NRA profiles show that a nearly uniform concentration of D exists throughout the specimen; $\sim 0.05$ - 0.1 at.% on both the front and back surfaces. The nearly uniform D concentration implies that nearly all of the traps in the bulk have been filled by diffusing D since one would expect near surface traps to preferentially fill before D would reach deeper traps. However, specimens irradiated at 500 K up to a fluence of $3 \times 10^{24} \, \text{D}^+/\text{m}^2$ show no signs of saturation [18]. Therefore, either higher fluences are needed to achieve bulk saturation, or there is a source of traps associated with the implantation process [18].

While TDS (thermal desorption spectroscopy) is used as a standard method for measuring total deuterium retention in most of the studies presented above, it can be used to obtain more detailed data for the purpose of studying the underlying trapping mechanics. Using TDS profiles, combined with SIMS measurements of implantation profiles and the multi-trap diffusion code TMAP7 [73], Poon et al. [27] were able to draw an approximate model of hydrogen trapping in single crystal tungsten. For 500 eV/D$^+$ irradiations of SCW at 500 K to a fluence of $10^{24} \, \text{D}^+/\text{m}^2$ TDS profiles yielded a dominant peak at $\sim 900$ K, with two very subtle peaks between 500 and 700 K. For 300 K irradiations under the same conditions the 900 K peak disappeared with two dominant, nearly equal-sized peaks at 520 and 640K. Using SIMS data coupled with SIMS/NRA
depth profiles extracted from a study by Alimov et. al. [25] to provide the known distributions, TMAP7 modeling yielded trap energies of 1.07 ± 0.03, 1.34 ± 0.03, and 2.1 ± 0.05 eV corresponding to the 520, 640 and 900 K peaks respectively. Experimental results and previous studies supported the idea of vacancy traps of 1.34 and 1.07 eV for the first and second deuterium trapped at a single vacancy, respectively, for a D₂V complex. The last peak was postulated as trapping of atomic deuterium on void walls with trap energy of 2.1 eV [27]. The above demonstrates an example in which TDS profiles are useful in the task of elucidating the trapping mechanisms of deuterium in tungsten; meanwhile it reveals the tools required to achieve this goal.

Another important aspect to consider for hydrogen inventories is the effects of surface modifications/damage on the trapping properties of tungsten. Studies have shown hydrogen ion irradiation on tungsten to cause blistering [28, 29, 30] that is typically linked with modified trapping behavior. Studies have found that tungsten surfaces exposed to low energy (below threshold for damage formation), high flux plasmas and ion beam bombardment exhibit blister formation [29, 31]. Furthermore, there appears to be a correlation between deuterium retention and blister formation in tungsten specimens exposed to D plasmas, which further depends on irradiation temperature [28, 29]. Exposure to ion beam bombardment over a range of energies, fluences, and temperatures led to the following conclusions: For 1 keV-D⁺ ions at room temperature blister formation is observed for fluences as low as 10²³ D⁺/m², where the size of the blisters increase with increasing fluence; blister formation is observed for ion energies as low as 100 eV/D at a fluence of 10²⁵ D⁺/m², where the size of the blisters increase with increasing energy; and there appears to be no blister formation for irradiation temperatures of 873 K and above [30]. Haasz et al. [31] performed a systematic study to investigate the effect of ion-induced damage (such as surface blisters and bubbles) on deuterium retention. For experiments with 500 eV-D⁺ ions they observed increased D retention on specimens previously exposed to high fluences (damage fluence) compared to the lower-fluence control samples. Additionally, there was evidence of surface blisters as a result of the higher fluences. However, there appears to be an exception to this trend for samples pre-irradiated with damage fluences of 10²⁵ and 3 x 10²⁵ D/m². This effect is consistent with blister formation and hydrogen recycling through fissures in the blisters. Furthermore, identical studies with 1 keV-D⁺ ions do not show any change in D retention as a function of prior implantations. It is postulated that the probe fluence
of $10^{23}$ D$^+$/m$^2$ is sufficient to saturate trap sites in the near surface at this energy, thus negating any effects of increasing damage fluences on D retention [31]. The issue of blister formation is important because it can affect the hydrogen inventories as well as lead to flaking of the plasma facing tungsten surfaces, leading to plasma contamination. The literature suggests that blisters are sensitive to combinations of ion flux, fluence, energy, and irradiation temperature, though there appears to be insufficient information to predict their formation.

### 2.3 Trapping of Helium in Metals

While hydrogen trapping in tungsten has been studied extensively in the fusion reactor materials community, most investigations include hydrogen irradiation/hydrogen plasma experiments only. In a fusion reactor, plasma facing materials will be bombarded by fusion reaction products, namely helium and energetic neutrons, as well as sputtered materials from other plasma facing surfaces. Including the irradiation effects of these additional species, therefore, offers a much more realistic assessment of the hydrogen trapping properties of tungsten, or any other plasma facing material. Helium, in particular, being a closed-shell inert gas, tends to interact only repulsively with metal atoms [10]. Furthermore, as a reaction product, it will be unconditionally present in tokamaks. Therefore, it is expected that helium will have a significant impact on the mechanical characteristics of tungsten, and the subsequent trapping of hydrogen. The following briefly describes some studies pertaining to the behavior of helium in metals, with a section dealing with helium behavior in tungsten to establish some fundamental behavior for comparison with hydrogen-helium studies.

#### 2.3.1 Behavior of Helium in Metals

Thomas [10] wrote a short review summarizing some experimental studies of helium in metals, emphasizing fundamental He behavior at low temperature, low He concentrations, and in the absence of radiation induced defects [10]. For the specific case of He in high purity Ni (99.999%), Al (99.999%), and stainless steel (solution treated), all metals annealed pre-implantation, it is postulated that pre-existing defects are not primarily responsible for the
trapping of He. Furthermore, experiments with single crystal Ni exhibited strong trapping of He, leading researchers to conclude that grain boundaries are not necessarily the major trapping sites either. A strong dependence of the He release fraction on the initial He concentration is indicative that He-He interactions increase trapping efficiency. Similar strong He trapping was also found in an amorphous metal alloy tritium charged and aged at 80K to approximately 1 ppm He concentration, and in zone refined Nb aged at room temperature to about 3000 atomic ppm He. This behavior suggests that He trapping occurs universally in metals and does not require pre-existing defects. The driving force of this process is the high energy of solution for interstitial He and ultimately leads to the precipitation of microscopic bubbles [10]. The review concluded that He is generally mobile at or below room temperature in metals. Point defects, such as vacancies and substitutional rare gas atoms behave as unsaturable traps and eventually, with large numbers of trapped He, become indistinguishable. Studies with other metals (Pd, V) led to the suggestion that implantation-induced vacancies inhibit bubble growth and increase the density of bubble nucleation sites by trapping He atoms. Bubble growth in both implanted samples and in tritiated metals, where He is produced via tritium decay, is likely to be by the same mechanism; absorption of migrating He atoms accompanied by emission of metal atoms, either by self-interstitial atom formation or by loop punching. It was also postulated that helium may be a strong embrittling agent because of preferential precipitation at dislocations (evident in studies with Nb and V in which helium bubbles were found at dislocations) [10]. There are more studies that investigate the behavior of helium in many different metals, however, for this purpose, a brief review is sufficient. Since this study deals with tungsten only, more data illustrating the behavior of helium in tungsten is presented in the next section.

### 2.3.2 Behavior of Helium in Tungsten

Fundamental studies were carried out by Erents et al. [32, 33] to determine the trapping mechanisms of helium and other inert gases in polycrystalline tungsten. The trapping and subsequent thermal re-emission of 100 eV – 2 keV He\(^+\) ions in polycrystalline tungsten targets was investigated with the use of an ion gun [32]. Thermal desorption spectroscopy (TDS) revealed two major peaks, with a third peak emerging from the splitting of the lower temperature peak for higher ion energies (1000 eV) and fluences. The first two peaks, which occur at 575 K
and 850 K, are associated with surface atom and vacancy migration at the surface. The activation energy for the 575 and 850 K peaks are determined to be 1.6 eV and 2.1 eV respectively, and they appear to be independent of ion energy. The higher temperature peak, located at ~ 2000 K, is associated with diffusion of helium from the bulk of the target material. The activation energy for this peak was determined to be 5.5 eV. The fact that an identical type of spectra are observed when no possible damage to the target could have occurred (similar TDS spectrum for many ion energies) illustrates that gas release is conditioned by migration processes in the tungsten [32]. In another study, it was found that Kr\(^+\) ion irradiation of tungsten greatly enhanced the probability of trapping He\(^+\) ions subsequently injected. It was concluded that the Kr\(^+\) ions produced damage centres which act as sites for He atom retention [33]. In the following, more proof will be presented that illustrates how damage centres act as trapping sites for implanted helium.

Iwakiri et al. [34] performed in-situ transmission electron microscopy (TEM) studies to investigate the microstructural changes in tungsten subject to low-energy He\(^+\) ion irradiation [34]. Experiments were carried out with 0.25 and 8 keV He\(^+\) ions at 293, 873, and 1073 K. For 8 keV He\(^+\) ion irradiation, helium vacancy complexes (between injected He and irradiation-induced vacancies) act as nucleation sites for dislocation loops and helium bubbles. This behavior was observed at all temperatures, though the density and size of the defects depend largely on temperature. In the case of 0.25 keV He\(^+\) ion irradiation, where the incident energy is insufficient for knock-on damage, He platelets, interstitial loops, and bubbles were formed. It is postulated that impurity atoms may act as trapping centres for He atoms, which form bubbles by ejecting W atoms from their lattice sites. Formation of He platelets leads to nucleation of interstitial loops by the punching-out process, and the loops grow by absorbing interstitials ejected from the bubbles [34]. These data suggest that plasma-facing materials for D-T tokamak devices may suffer serious radiation damage by He\(^+\) ions from the plasma at elevated temperatures, and even when the particle energy is below the threshold for knock-on damage [34].

Kornelsen [35] observed similar behavior when investigating the interaction of injected helium with lattice defects in a tungsten crystal. It was commonly known that helium injected into tungsten undergoes rapid interstitial diffusion at room temperature unless it encounters lattice defects. Kornelsen used this effect to study the lattice damage produced near a tungsten surface by the impact of small numbers of 5 keV heavy ions (Ne\(^+\), Ar\(^+\), Kr\(^+\), Xe\(^+\)). 250eV-He\(^+\)
ions, which do not produce any observable damage, were observed to be trapped in the damage created by the prior heavy ion bombardment. TDS results from varying the damage anneal temperature, the helium fluence, the helium irradiation temperature, and the mass of the damaging ions suggest that all of the entrapment occurs at defects of the vacancy type, and that the binding energy is modified by parameters that change the available vacancy volume [35]. More specifically, there is evidence that at least two and possibly three helium atoms can be trapped in a single vacancy, two types of divacancies exist, and that vacancies become trapped in the strain field of large impurity atoms. Furthermore, for sufficient helium fluences (> $10^{18}$ ions/m$^2$), any of the trapping sites can act as nuclei for the formation of helium bubbles [35].

Subsequent studies focused on the effects of low energy, high flux helium plasmas on target tungsten surfaces [36, 37]. Tokunaga et al. [36] observed changes in surface morphology of powder metallurgy tungsten and plasma sprayed tungsten coated CFC for 100 eV-He$^+$, high flux (up to $1.20 \times 10^{22}$ He$^+/m^2$s) helium irradiation up to a fluence of $10^{26}$ He$^+/m^2$. Nishijima et al. [37] similarly observed that holes are formed in powder metallurgy tungsten with incident ion energy above 5 eV, for particle fluxes above $10^{22}$ He$^+/m^2$s. This observation could be related to the surface barrier potential energy for He$^+$ penetrating into tungsten. Surface temperature strongly influences the number and size of the holes, with observations of several hundred nm diameter-sized holes/bubbles at temperatures above 1600 K. Nishijima et al. further reported there is no qualitative difference in the hole formation between powder metallurgy tungsten and single crystal, which has much fewer intrinsic defects. It is postulated that thermal vacancies, generated by high temperatures, are the dominating trap sites for He atoms for the bubble nucleation. Furthermore, the high temperature also relates to high mobility and coalescence of He bubbles and vacancies, which contributes to the growth of He bubbles [37]. Again, vacancies are observed as the predominant trapping sites for He implanted in tungsten. The fluence dependence of thermal desorption behavior of helium in tungsten was studied at different irradiation temperatures (RT or 873 K) and ion energies (250 eV, 1 keV, or 8 keV) [38]. It was found that total helium retention reached a saturation level of ~ $1-3 \times 10^{21}$ He$^+/m^2$ for high incident fluences greater than ~ $5 \times 10^{21}$ He$^+/m^2$. This behavior was observed for all irradiation temperatures and ion energies used in this study [38].

In a study very similar to the work presented here, Lee et al. [39] investigated the trapping of 500 eV-He$^+$ ions in polycrystalline tungsten for comparison with TDS data from
simultaneous and sequential He\textsuperscript{+}-D\textsuperscript{+} irradiations. TDS results at 300 K reveal three He release peaks in the vicinity of \(\sim 500\), \(\sim 1000\), and \(\sim 1200\) K. It was postulated that the \(\sim 500\) K TDS peak may be from He clusters at grain boundaries and within the crystal, possibly at dislocation loops near helium-vacancy (He\textsubscript{n}V\textsubscript{m}) complexes. The release peak at \(\sim 1000\) K is attributed to He released from He\textsubscript{n}V\textsubscript{m} complexes or He bubbles. However, post-irradiation imaging of the specimen surface was not performed in this study, so the possible existence of He bubbles could not be confirmed. For the case of 700 K irradiations, the \(\sim 500\) K peak was still observed despite the higher irradiation temperature. This phenomenon was observed in other studies in which tungsten was irradiated with He plasmas at 873-933 K [36], as well as 700 and 1600 K [40]. These results suggest there is some mechanism whereby He atoms in higher-energy traps are transferred to low-energy traps when specimens irradiated at elevated temperatures cool down [39]. Similar to the case of 300 K irradiation, there is a second peak that varies between 980 and 1020K, which is attributed to the same mechanism. Additional irradiation with 2 keV-He\textsuperscript{+} causes an increase in the magnitude of this \(\sim 1000\) K peak and an increase in the total amount of retained He. This result supports the earlier interpretation that He release at this peak is from He\textsubscript{n}V\textsubscript{m} complexes or He bubbles, since 2 keV-He\textsuperscript{+} is expected to increase vacancy creation from knock-on damage. The third He release peak, at \(\sim 1200\) K, is observed for select cases of 300 and 700 K irradiations. It is postulated that the appearance of this peak is an indicator that the He\textsubscript{n}V\textsubscript{m} complexes formed during irradiation were in transition to larger traps like bubbles [39]. Fluence dependence data was obtained by integrating the TDS data for 300 and 700 K irradiations. For 500 eV-He\textsuperscript{+} irradiation at 300 K, a 5-fold increase in retention over three orders of magnitude increase in incident fluence is observed; furthermore, a trend to saturation was observed at \(\sim 5 \times 10^{20}\) He/m\textsuperscript{2} for incident fluences above \(10^{24}\) He\textsuperscript{+}/m\textsuperscript{2} (where the implanted sample was baked at \(\sim 380\) K prior to desorption). Increasing the irradiation energy to 2 keV/He resulted in a 2.5-fold increase in He retention compared to the 500 eV/He case at the same fluence. Again, it is suggested that this may be due to additional vacancy trapping sites formed by knock-on damage. With a 1 h hold time, He retention amounts for 700 K irradiations were similar to 300 K irradiations for 500 eV-He\textsuperscript{+} ions. However, without the hold time, He retention was \(\sim 2.5\) times higher, with at least part of this increase attributed to enhanced He diffusion. The dominant trapping process is thought to be He trapping at vacancies, by punching out self-interstitial atoms [39].
Studies of helium behavior in tungsten reveal that implanted He traps preferentially at vacancy sites, which act as nucleation sites for dislocation loops and helium bubbles. The study by Lee et al. [39] confirms this behavior with studies varying irradiation energy, and suggests that higher irradiation temperatures lead to enhanced diffusion of He into the bulk. This latter study was performed for comparison with cases of simultaneous and sequential irradiations of tungsten by D\(^+\) and He\(^+\), which will be presented in the following section.

### 2.4 Hydrogen and Helium Trapping in Tungsten

This discussion begins with a brief assessment of some studies investigating effects of simultaneous He\(^+\)-D\(^+\) irradiation with plasma devices and ion beam experiments, as well as He\(^+\) pre-irradiation effects on D retention in tungsten [40, 41, 42, 43, 44]. The section will converge on the more relevant studies of systematic sequential and simultaneous irradiation of polycrystalline tungsten by helium and deuterium ion beams [39, 45].

In the following, details are presented from studies involving experiments with plasma devices (D and He plasmas). Nishijima et al. [40] investigated the suppression of blister formation and deuterium retention on tungsten surfaces due to mechanical polishing and helium pre-exposure. More specifically pertaining to helium pre-exposure, Nishijima et al. found that pre-exposing 99.95 % pure, 0.2 mm thick powder metallurgy tungsten (PM-W) samples to high flux (4.2 x 10\(^{21}\) He\(^+\)/m\(^2\)s) , 80 eV-He\(^+\) plasma ions at 700 K up to a fluence of 3 x 10\(^{25}\) He\(^+\)/m\(^2\) drastically reduced deuterium retention and suppressed blister formation. For post-implanted, 80 eV-D\(^+\) plasma ions at 500 K, at a flux of 2.5 x 10\(^{21}\) D\(^+\)/m\(^2\)s, and up to a fluence of 2.7 x 10\(^{25}\) D\(^+\)/m\(^2\), the total deuterium retention was reduced from 1.04 x 10\(^{21}\) D/m\(^2\) for the mirror finished PM-W sample, down to 6.6 x 10\(^{19}\) D/m\(^2\) for the sample pre-exposed to the He plasma [40]. TDS release profiles indicated that the trapping energies for the deuterium atoms are not drastically changed by He\(^+\) pre-exposure. It was deduced that the suppression of blister formation was the result of reduced deuterium gas retention in the PM-W sample. Furthermore, it was postulated that helium bubble formation in the pre-exposed sample could lead to cracks surrounding the He bubbles and nano-sized holes on the surface, thus leading to additional release pathways for implanted D. This hypothesis is supported by TEM analysis revealing nano-sized He bubbles (high gas pressure) on the surface of the pre-exposed sample. Another study by Nishijima et al.
[41], again using PM-W pre-exposed to He plasma with similar high flux, high fluence, low energy parameters, investigated the effects of He irradiation temperature on subsequent D retention (again similar parameters). It was found that He$^+$ pre-exposure at 1600 K led to increased D retention by a factor of 6 larger than for the virgin PM-W sample. Submicron-sized He bubble formation and secondary interstitial defects surrounding the He bubbles, which could act as D trapping sites, are thought to be the primary cause of increased D retention. Similar to the previous study, He$^+$ pre-exposure at 700 K led to a 5-fold decrease in D retention compared to the virgin sample. For this case, no additional traps were introduced because neither radiation-induced defects nor thermal vacancies are formed in this case. The annealing effect and/or the occupation of trap sites by He atoms would decrease the number of available trapping sites for D atoms [41].

Miyamoto et al. [42] investigated the effects of mixed deuterium-helium plasmas on deuterium retention and blister formation in tungsten. Experiments were carried out with low energy (~ 55 ± 15 eV), high flux (~ $10^{22}$ ions/m$^2$s), high fluence ($\leq 4.5 \times 10^{26}$ ions/m$^2$) ion irradiation at ~ 573 K in mixed species D + He plasmas in PISCES-A. Blister formation was observed to be suppressed (surface feature known to increase D retention) and D retention was also reduced in the D + He plasma exposed W samples. Similar to studies by Nishijima et al. presented above, nano-sized high density He bubbles were observed in the near surface and are thought to act as a diffusion barrier to implanted D atoms [42]. In all three plasma studies presented it appears that He$^+$ pre-exposure, or simultaneous exposure of mixed D + He plasmas leads to decreased D retention in tungsten samples exposed to moderate temperature plasmas (500 – 700 K). The only case in which D retention was increased was for the case of high temperature (1600 K) He$^+$ pre-exposure, which created D trapping sites in tungsten samples while no He remains. However, the moderate temperature results agree that He plasma exposure reduces D retention, likely by occupying trapping sites or blocking diffusion into tungsten samples.

Ion beam analysis of tungsten samples pre-irradiated by high energy He$^+$ ions was carried out to determine the effects on deuterium retention. Iwakiri et al. [43] investigated the effects of helium ion bombardment on deuterium behavior in tungsten. Pre-irradiation with 8 keV-He$^+$ ions (high enough energy to create damage) in PM-W samples led to a 3-fold increase in deuterium retention for $2.0 \times 10^{21}$ He$^+$/m$^2$ followed by $1.0 \times 10^{22}$ D$_2^+$/m$^2$ implanted at 4 keV/D.
Furthermore, D was predominantly released between 600 and 800 K in the TDS profiles compared to 400 to 600 K for the D\(^+\)-only case. It is postulated that the strong stress field around the high-pressure helium bubbles (likely dislocation loops) is acting as trapping sites for D desorption above 600 K [43]. Simultaneous effects of hydrogen and helium ions in tungsten were then investigated by Ueda et al. [44]. For tungsten samples irradiated with a mixed 1 keV beam of H\(_3^+\) (50 - 60 %) and C\(^+\) (0.8 - 1.0 %), forming a W and C layer on the target sample, and as little as 0.1 % He\(^+\) ions, blister formation was reduced (473 K) or completely suppressed (653 and 723 K). He bubbles, 2 nm in size, were formed near the surface and likely created a diffusion barrier of hydrogen into the bulk by reducing the number of diffusion channels or by excitation of stress fields. A 3-fold reduction in hydrogen diffusion rate was observed for simultaneous He\(^+\)-H\(^+\) irradiation [44]. Again, these results reinforce the theory that He\(^+\) irradiation leads to decreased D retention in tungsten, with the exception of high energy He\(^+\) implants, which likely create additional trapping sites for implanted deuterium.

Finally, Lee et al. [39, 45] performed systematic studies investigating the trapping of hydrogen and helium in polycrystalline tungsten under simultaneous and sequential irradiations. For these studies, the quadrupole mass spectrometer could not adequately resolve the individual release rates of He and D\(_2\), therefore, identical experiments were carried out with He and H to determine He release rates, which were subsequently subtracted from the mass-4 TDS data for He-D experiments. In the case of simultaneous (SIM) He\(^+\)-H\(^+\)/He\(^+\)-D\(^+\) irradiations at 300 and 700 K there is no observable effect of the presence of H or D on the trapping of He in tungsten. Elastic recoil detection (ERD) analysis reveals He trapping is confined to ~ 30 nm of the surface. He retention levels and TDS spectra for SIM experiments closely follow results for He\(^+\)-only irradiations. There are, however, changes to the D trapping behavior for SIM He\(^+\)-D\(^+\) irradiations. For 300 K SIM He\(^+\)-D\(^+\) irradiations, the D release profile differs from the D\(^+\)-only case by the reduction of the peak at ~ 650 K, however, the primary peak at 500 K was largely unchanged. Furthermore, ERD analysis revealed that D diffusion was limited by the presence of He (D contained within 35 nm of the surface, compared to 100’s of nm for the D\(^+\)-only case [18, 26]). However, the total D retention was equal to the retained amount for the D\(^+\)-only case, independent of incident He\(^+\) fluence. Since D retention is observed to be restricted within ~ 30 – 35 nm of the surface for SIM He\(^+\)-D\(^+\) irradiations, this implies there is a 30 % enhancement of D inventory which is attributed to D retention in the near surface. It is postulated that incident He\(^+\)
forms He-vacancy complexes that produce secondary defects surrounding them, subsequently acting as trapping sites for D in the near surface [45]. For 700 K irradiations, no D retention was observed [45]. For the case of sequential (SEQ) He\textsuperscript{+} - D\textsuperscript{+} irradiations at 300 K, both D and He were released in the range of 400 – 800 K in TDS profiles [39]. He is released in two peaks at 500 and 680 K, with the D\textsuperscript{+} post-irradiation apparently eliminating He release peaks above 800 K. D is released in one peak at 500 K only. Since the 680 K He peak has not been observed for He\textsuperscript{+}-only irradiations it is interpreted, along with the 500 K D release peak, to be due to a new trapping configuration involving interstitial deuterium and helium clusters in the near surface (within ~ 35 nm). Furthermore, the He pre-irradiation reduced D inventory by ~ 70 %, in part due to limited D diffusion into the bulk. Similar SEQ He\textsuperscript{+} - D\textsuperscript{+} irradiations at 700 K resulted in a reduced single He peak in the ~ 950 – 1050 K range, with very little release observed below 800 K. The post-implanted D is thought to de-trap and break apart the He-vacancy complexes, though elevated specimen temperatures desorbs all D from the specimen during irradiation. When the irradiation order is reversed, SEQ D\textsuperscript{+} - He\textsuperscript{+} irradiations at 300 K reveal that He trapping is similar to that observed for He\textsuperscript{+}-only. Only the D trapped in the near surface is affected with a ~ 40 % reduction in the D inventory when compared to the D\textsuperscript{+}-only case. The loss is observed in the 680 K D release peak, interpreted as D released from vacancies in the near surface. D trapped in the bulk appears to be unaffected by He post-irradiation and contributes ~ 30 % of the total D inventory for 500 eV D\textsuperscript{+} irradiations at 300 K. SEQ D\textsuperscript{+} - He\textsuperscript{+} irradiations at 700 K reveal that D\textsuperscript{+} pre-irradiation has little effect on the subsequent trapping behavior of He [39].

The studies detailed in this section are presented to improve the understanding and interpretation of the results for the experimental results presented in Chapter 5. Investigations by Lee et al. [39, 45] form a foundation for the work of this thesis, and for all intents and purposes, this study is an extension of Lee’s work.
Chapter 3 Experimental Apparatus

3.1 Polycrystalline Tungsten Specimens

To investigate the trapping behavior of deuterium and helium multiple specimens measuring 10 x 10 mm$^2$ were cut from 25µm thick, 99.96 wt% pure, polycrystalline (PCW) foil sheets. These sheets, provided by Rembar Corporation, were hot-reduction rolled to their final thickness. The elemental content (for certain elements) quoted by the manufacturer is listed in Table 3.1 [46]. Each specimen was annealed at high temperatures preceding all ion implantations; details are provided in Chapter 4.

<table>
<thead>
<tr>
<th>Elemental Content</th>
<th>Concentration (by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H)</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>&lt; 30 ppm</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>&lt; 30 ppm</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>&lt; 30 ppm</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>&lt; 15 ppm</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>Tungsten (W)</td>
<td>&gt; 99.96 wt%</td>
</tr>
</tbody>
</table>

Table 1 – Elemental impurity content for Rembar PCW foil specimens.

3.2 The Dual-Beam Ion Accelerator Facility

3.2.1 Dual-Beam Ion Accelerators
All ion implantations were performed using the dual beam ion accelerator facility at the University of Toronto Institute for Aerospace Studies (UTIAS). The system consists of two independently controlled, low-energy, high-flux, mass-selected ion beam accelerators that intersect in an ultra-high vacuum stainless steel target chamber at an angle of 42°. A full description of the facility and the operating procedures is available in Reference [47]. See Figure 2 for a schematic of the system.

![Dual beam ion accelerator facility](image)

**Figure 2 - Dual beam ion accelerator facility [47]**

Both accelerators are composed of essentially the same components, with the exception of the ion sources and mass analyzing magnets. The beam lines are referred to as the "light ion side" (LIS), characterized by a 30º bending magnet with a 1:7 mass resolution; and the "heavy ion side" (HIS), which is characterized by a 90º bending magnet with a 1:30 mass resolution.

The LIS operates with a hot-filament based duoplasmatron ion source and could be used to generate both deuterium (D$_3^+$) and helium (He$^+$). The plasma in the LIS is created within a cylindrical cavity by introducing high-purity deuterium (or helium) gas from a high-pressure reservoir that is controlled by a pressure regulator and variable leak valve. The hot filament, with an electron-emitting coating, is used as a cathode and the plasma is constricted by an axial magnetic field which directs it into a funnel-shaped anode. Plasma ions then exit the source through a 0.15mm diameter aperture via a 3.2mm diameter channel, accelerated by a 10kV
extraction gap. Ions are then focused by a double-gridded einzel lens and aligned by a pair of vertical steering plates before entering the 30° bending magnet for mass selection and neutral particle rejection. Following the magnet is a 10mm diameter aperture to aid in beam species selection, which is followed by a double-gridded deceleration gap to slow the 10keV ions to their selected energies. Downstream is another set of horizontal (x) and vertical (y) steering plates to position the beam. Finally, a large diameter single-grid einzel lens focuses the beam through a 3mm diameter aperture onto a target 10mm away.

The HIS operates with a hollow-cathode ion source and was used to generate He$^+$ ions. The hollow-cathode geometry traps electrons in a narrow tube, which subsequently undergo more ionizing collisions, creating denser plasma inside the tube. This dense plasma then releases the electrons required for the main discharge [48]. Similar to the LIS, a plasma is created in a cylindrical cavity by introducing high purity helium gas in the same manner. The plasma ions are then extracted through a 0.25mm pinhole aperture by a 10kV extraction gap. Ions are then focused with a single cylinder einzel lens before entering the 90° mass-selecting bending magnet; after which point they are vertically steered into a deceleration gap. The ions pass another set of x and y steerer plates and are focused through a second 3mm aperture with a single-grid einzel lens onto the target, as on the LIS.

The test specimen is placed at the point of beam intersection in the implantation chamber. The beam current is then measured with a stainless steel strip placed behind the test specimen and clamped in place by a ceramic heater (See section 3.3). The beam spots are slightly elliptical in shape due to off-normal incidence on the target and measure ~ 3mm and ~5 mm in diameter for the HIS and LIS respectively. A piece of oxidized copper was used to ensure beam overlap and proper alignment.

The facility is equipped with a total of four Leybold-Heraeus turbomolecular pumps, each coupled to a mechanical pump for the required backing line vacuum. The LIS and HIS beam lines are separately pumped by a turbomolecular/mechanical pump pairing up to the gate valves, which are upstream from the second einzel lenses in both beam lines, see Figure 2.

3.2.2 Target Chamber
The target chamber is a stainless steel cylinder that measures 0.19m high, and 0.35m in diameter. The cylindrical chamber, along with the components downstream from the gate valves all utilize metal seals, and are bakeable to ~500K, though none of the experiments required baking of the system. The two remaining turbomolecular pumps are on either side of the beam apertures and provide the ultra-high vacuum in the chamber. The nominal background pressure in the chamber was of the order 2.5-7.5 x 10^{-8} Torr, while the typical background pressure while running both beams was of the order 1 x 10^{-6} Torr.

3.2.3 Implantation Specimen Holder

The specimen holder, as illustrated in Figure 3, was very similar to the one used by Poon [49] and Lee [11]. It was designed to allow direct measurement of the beam current on the specimen, heating of the specimen, temperature measurement of the specimen, and to maintain a relatively uniform ion flux over the exposed area. To achieve these design requirements, the specimen holder was constructed as a series of layers [49]. The base of the holder consisted of a 26 x 45 mm², 0.25 mm thick stainless steel plate with a 6.2 mm diameter aperture at the centre. The next layer was a 10 x 15 mm² piece of Rembar PCW, the same material used for the specimens discussed in section 3.1. A 2 mm diameter aperture was drilled through this foil, which subsequently defined the size of the ion-exposed area of the specimen. The tungsten foil was then spot-welded onto the stainless steel plate, with the apertures concentric. Two layers of 50 μm thick mica with an aperture slightly larger than the aperture of the tungsten mask were then added on top of the tungsten layer. The mica layers provided electrical isolation between the tungsten foil mask and the specimen, allowing the ion flux on the specimen to be measured directly. Because of frequent electrical shorts between the specimen and the mask, thought to occur at the slightly larger aperture in the mica, two layers of mica were used in the design of the specimen holder. A 25 μm diameter nickel-chromium/nickel-aluminum (chromel-alumel, type K) thermocouple was inserted between the mica layer and the specimen, with the tip of the thermocouple placed within 1 mm of the edge of the tungsten mask aperture. The mica layers and the thermocouple were held in place using UHV compatible, high-temperature adhesive – carbon-based Graphi-Bond™. A small 10 mm ceramic heater, capable of heating the specimen to temperatures exceeding 700 K, was placed against the back surface of the specimen and was
held in place by bolts passing through the stainless steel base plate. An external power supply provided current to the ceramic heater via leads running to the stainless steel bolts that secure it to the base. A graphite washer was inserted between the ceramic heater and stainless steel washers to ensure good electrical contact, while specially machined ceramic washers were inserted into the bolt holes of the base plate to ensure electrical isolation between the heater and the base plate. A thin strip of stainless steel was inserted between the heater and the backside of the specimen; this was used to measure the ion flux on the specimen. This design was largely based on that of Poon with minor modifications. Additional information and theory on this general design can be found in [49].

![Diagram of Irradiation specimen holder used in dual beam ion accelerator.](image)

**Figure 3 - Irradiation specimen holder used in dual beam ion accelerator.**

### 3.3 Thermal Desorption Spectroscopy Chamber

High temperature annealing and TDS were performed in a vacuum system separate from the dual beam ion accelerator facility. A schematic is provided in Figure 4. Two calibrated leak bottles of D and He were installed to quantify the signals collected by an Extrel MAX 60 quadrupole mass spectrometer (QMS). A turbomolecular pump with a mechanical backing pump was used to obtain a background pressure of ~ $10^6$ – $10^8$ Torr (depending whether the system
was baked). Heating tapes covered the outside of the chamber and were subsequently used to outgas the inside surfaces prior to TDS measurements.

The specimen was resistively heated in a tungsten foil cradle which will be discussed in further detail in section 3.3.1. The current was provided by a Sorensen DCR 20-80B power supply, typically in the range of 25-30 A, resulting in specimen temperatures of up to 1500 K. The power supply was controlled by a LabWindows/CVI program written by Poon [49], which yielded linear temperature control by adjusting voltage parameters for temperature segments. Temperature measurements were carried out using a type C thermocouple spot-welded directly on the specimen, with platinum wire used as an interlayer to allow a strong weld between the thermocouple and the PCW specimen. The QMS then measured the release rate of desorbed atoms/molecules. Since the heating cradle and QMS differ from those used by Poon we will discuss these components in more detail in the following. For all other components of the TDS system, detailed discussions are provided in [49].

![Figure 4 - Thermal desorption spectroscopy facility at UTIAS.](image-url)
3.3.1 Heating Cradle

The heating cradle had the dual purpose of holding the specimen and heating it simultaneously. A 25 µm thick strip of pure (99.96 wt%) tungsten foil, cut from the same sheet used for specimens, was used for the cradle. The tungsten strip was cut and folded to hold the specimen in place as illustrated in Figure 5. The actual dimensions varied, but the fabrication generally began with a 60 x 15 mm² strip of tungsten. The heating cradle was then secured between two stainless steel jaws to which the current was supplied for resistive heating of the cradle. The specimen, in turn was heated by “contact” conduction radiation emitted from the tungsten cradle. Typically, cradles would last for approximately 10 “runs” of heating to 1500 K before needing replacement. The current required to heat the specimen would then vary between successive cradles, and depended on the amount of physical contact between the cradle and the specimen.

![Figure 5 - TDS heating cradle.](image)

3.3.2 Extrel MAX 60 Quadrupole Mass Spectrometer (QMS)

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Similar to Lee [11], a quadrupole mass spectrometer (QMS) was used to monitor the relative concentrations of various constituents in the background gas, namely D$_2$, He, and HD. Unlike Lee, however, the QMS used in this study has the resolution to differentiate between the mass 4 signals of He and D$_2$. The general operation of a quadrupole mass spectrometer is explained in [49]. In short, gas molecules are locally ionized using a hot filament in the ionizer zone; these ionized particles are then accelerated and focused through an electrostatic potential field; four parallel metal rods produce an electromagnetic field that then separates ions according to their mass-to-charge ratio before they strike the detector. Since the majority of ions are singly charged, the quadrupole basically acts as a mass filter for the detector, and so the QMS is ideal to identify and measure the quantity/concentration of a given atomic/molecular species.

The Extrel MAX 60 QMS used in this study is designed for high resolution filtration of low mass particles (1 – 60 amu). Using the supplied Extrel software it was possible to calibrate the resolution of the QMS to separate the mass signals of D$_2$ and He which differ by ~ 0.026 amu, sacrificing sensitivity to other mass signals in the process. It was thus possible to conduct a study of D and He trapping behavior in tungsten with both species simultaneously present in the sample. Figure 6 illustrates the software output of the QMS (Merlin). The top left corner illustrates a Real Time Profile over the specified range of 3.9 – 4.1 amu; this feature compares instantaneous mass signals over a given mass range. The bottom right corner illustrates a Chromatogram which provides time dependent plots of the QMS signal for selected masses. The corresponding instantaneous profile is illustrated in the top right corner for a selected time point on the Chromatogram. For this study, mass 3.030 (HD), 4.000 (He), and 4.026 amu (D$_2$) were monitored with the Chromatogram feature to investigate the trapping behavior of D and He.

The primary concern prior to commencing experiments was the relative “spill over” of signals between mass locations that were very close together. To resolve this issue a brief study was conducted to quantitatively characterize the relative change in mass signal when one species was present in significantly larger concentrations than the other. The general procedure was to introduce an amount of D$_2$ using the respective leak bottle that produced a QMS signal that was ~ 100 times greater than that for He, which was the largest D$_2$/He ratio possible with the given background levels. The leak bottle was then shut off, and the mass 4.000 (He) signal was recorded both before and after. This procedure was also followed with the D$_2$ leak bottle off to begin, followed by turning it on and recording the before and after He mass signals. The
difference in the He mass signal was then used to calculate the relative “spill over” of the 4.026 amu ($D_2$) signal into the 4.000 amu (He) signal. Both experiments yielded an approximate 3% leaking of the $D_2$ mass signal into the He mass signal, thereby giving us a quantitative measure of the potential error inherent in the QMS data. Figure 7 illustrates the results of this experiment with the $D_2$ leak bottle on to begin on the left and off to begin on the right. The Chromatogram view illustrates the changes in He mass signal in response to the $D_2$ mass signal.

Figure 6 - Software output of Extrel QMS (Merlin) illustrating the separation between He and $D_2$ mass signals - top left: Real time profile; top right: Spec view; bottom right: Chromatogram.
Figure 7 - Calibration experiment to determine the "spill over" of D$_2$ mass signal to the He mass signal with (left) D$_2$ leak bottle on to begin; and (right) D$_2$ leak bottle off to begin.
Chapter 4  Experimental Procedure

Each specimen underwent a three stage process for this study. First, each specimen was annealed at 1473 K using the TDS facility. Next, the specimen was implanted with either deuterium, helium, or both using the dual-beam ion accelerator facility. And finally, each specimen underwent thermal desorption in the TDS facility. Detailed descriptions of each stage are provided in the following.

4.1  Specimen Anneal

All polycrystalline samples were annealed at 1473 K for 30 minutes using the thermal desorption system. In some cases, poor contact with the thermocouple or the heating cradle caused samples to be heated to > 1473 K, with an upper limit of ~ 1900 K measured with a pyrometer. The chamber pressure was pumped down to better than $5 \times 10^{-6}$ Torr before heating commenced. In general, four specimens were annealed simultaneously by loading them all on the heating cradle, with the thermocouple spot-welded to a fifth specimen to monitor temperature. This fifth specimen was never used for implantation because of damage caused by spot-welding. The specimens were then allowed to cool slowly to avoid quenching and they were only removed from the system when they reached temperatures of ~ 300 K. The process from loading samples to taking them out of the chamber typically took 4-6 hours. Annealed specimens were left in air for as little as 30 minutes in some cases, but more typically for weeks, prior to actual implantation.

The high temperature treatment was expected to desorb hydrogen and any other trapped gases produced during the manufacturing process. Thermal annealing studies have shown vacancy annihilation to occur at ~ 800 K, depending on temperature ramping rates [50]. Therefore, a very small population of vacancies is expected following the annealing procedure. It is also expected to reduce the number of voids as shown by Eleveld [51] in which voids (high density vacancy clusters) were removed when PCW specimens were annealed above 1700 K. We anticipate similar defect reduction for specimens annealed in the present study.
4.2 Specimen Irradiations

It was shown by Haasz et al. [18, 31] that implantation history has a major impact on D retention in PCW despite prior implantations with ion energies below the damage threshold (500 eV/D). For this study, virgin samples were used for all implantations to avoid any such effects.

The annealed specimens were placed in the dual beam particle accelerator for implantation. The system was pumped down to pressures in the range of ~ 10^{-7} Torr. All specimens were labeled according to the order in which they were irradiated with the convention AL##, using the author’s initials as a prefix so as not to confuse specimens with other researchers’. The D^+ only implants were performed using the LIS accelerator. Most He^+ only implants were performed using the HIS accelerator (AL24, 29, 35, 42, 43), and due to complications generating He^+ ions with the HIS, one He^+ only implant was performed using the LIS accelerator (AL48). The simultaneous implantations (SIM), and half of the sequential implantations (SEQ) (AL25, 26, 31, 32, 36, 37) were carried out with D_3^+ generated with the LIS, and He^+ generated with the HIS. The other half of the SEQ implantations (AL53, 54, 55, 56, 57, 58) were carried out with both D_3^+ and He^+ ions generated with the LIS accelerator, again due to complications with the HIS.

For the case of D^+ only, and the generation of D^+ ions in dual bombardment experiments (SIM and SEQ), implantations were carried out using 3.03 keV D_3^+ ions with the specimen biased to 1530 V in every case, resulting in energies of 500 eV/D atom. For all cases in which He^+ ions were generated with the HIS, implantations were carried out with 2.03 keV He^+ ions with the specimen biased to 1530 V in every case, resulting in energies of 500 eV/He atom. For the cases in which He^+ ions were generated with the LIS, some were performed with 2.03 keV He^+ ions and 1530 V specimen bias (AL53, 54), while others were performed with 3.03 keV He^+ ions and 2530 V specimen bias (AL48, 55, 56, 57, 58). In every case, specimens were irradiated with energies of 500 eV/He atom. Typical fluxes ranged from ~ 2.4 – 4.8 x 10^{19} D^+/m^2s and from ~ 5.0 – 9.9 x 10^{17} He^+/m^2s for HIS generated He^+ ions, or from ~ 9.9 x 10^{17} – 8.3 x 10^{18} He^+/m^2s for LIS generated He^+ ions. Unlike in the experiments carried out by Lee [11], the beam stop used to adjust ion fluxes prior to specimen irradiation was not available. Subsequently, fluxes were adjusted during the initial stage of specimen irradiation, using the average flux over a given span of adjustment time to calculate total incident fluence. For simultaneous irradiations,
therefore, it was necessary to irradiate the specimen with D\(^+\) and He\(^+\) ions individually to adjust, and stabilize beam fluxes prior to SIM implantation. The exposure to individual ions was minimized as best as possible, with “single ion” irradiation times of less than 1 minute (AL27, 30, 33), less than 5 minutes (AL39, 40), and less than 10 minutes (AL41). In the case of sequential irradiations, typical delays between implants ranged from \(~ 10 – 60\) minutes for HIS generated He\(^+\) ion-experiments, and \(~ 120 – 150\) minutes for LIS generated He\(^+\) ion-experiments, with one special case requiring a delay of \(~ 17.5\) hours (AL57). At the end of implantation for all cases, the beam (D\(^+\) ion, He\(^+\) ion, or both) was turned off instantly by switching off the acceleration voltage. For 500 K and 700 K irradiations, the power supply for the specimen heater was switched off immediately following all implantations to preserve any additional retention that might have otherwise desorbed in the implantation chamber. The specimens cooled at a rate of \(~ 100\) K/min. Though the heater power supply was never switched on, for 300 K irradiations, temperature data from the thermocouple was still recorded to monitor any substantial irradiation induced temperature changes. Finally, it is worth noting that for 500 K and 700 K SEQ irradiations the specimen’s temperature was maintained between implantations, with the exception of AL57 due to the long delay. With delay periods ranging from 10 to 150 minutes some desorption of either deuterium or helium between implantations cannot be ruled out.

4.3 Thermal Desorption Spectroscopy (TDS)

Comparing values published in literature, experimental measurements of hydrogen retention in PCW has been shown to vary by up to a factor of five [14, 18, 22]; and though differences in material properties are largely responsible, some of these discrepancies can be attributed to variations in the TDS procedure. Parameters such as in-situ vs. ex-situ TDS, post-implantation wait time, and pre-baking of the system have all been shown to affect the measured desorption profiles, and subsequent retention levels. Quastel et al. [52] found that for SCW irradiated to \(10^{23}\) D\(^+\)/m\(^2\) with 500 eV/D, D retention was found to decrease by as much as a factor of 2 with increasing the time delay between D\(^+\) irradiation and TDS from \(< 1\) h to \(> 8\) weeks, and mild baking of the test chamber to \(~ 360\) K prior to TDS resulted in the escape of \(~ 40\) % of the trapped deuterium. Due to equipment scheduling conflicts, it was not possible to consistently control the delay between D\(^+\) irradiation and TDS. However, comparing data from
[19], [52] and [53], there does not appear to be much change in D\(^+\) retention for ex-situ TDS performed anywhere from 8 hours to 11 weeks. Since specimen loading and chamber baking require at least 4-6 hours we do not expect significant discrepancies in results due to inconsistent delay periods prior to TDS. Regardless, Lee [11] reported up to 40% reduction in solute and surface adsorbed D due to extended (12 hours to 15 days) post-implantation wait times, with a similar reduction observed when the TDS chamber was baked to ~ 380 K; therefore, we expect that chamber baking will overshadow any delay effects.

Following irradiation, tungsten-rhenium thermocouple wires were spot-welded to the specimen, typically within 3 mm of the beam spot. The specimen was then installed in the heating cradle and the system was pumped to a base pressure of ~ 5 x 10\(^{-6}\) Torr. In all cases the system was baked following the procedures of Poon [49]. High temperature heating tapes were used to bake the TDS system walls, reaching specimen temperatures of up to ~ 360 K, with typical bake times of ~ 2.5 to 4 hours.

The first step for TDS measurements was to calibrate the Extrel MAX 60 QMS using calibrated D\(_2\) and He leak bottles. Steady-state signals from both leak bottles were measured with both leaks on and off; the difference was then equated with the known gas flow rate (calculated from calibrated signal at a given date and decay rate) to give an absolute measure of the number of D\(_2\) and He atoms detected. Data were recorded for ~ 400 scans with the leak bottles on and ~ 200 – 300 scans with the bottles off to calibrate the QMS. The second step was to initiate the CVI code that controls the heating rate, taking note of the QMS scan number for analysis when heating was initiated. The heating program controlled the voltage profile of the power supply according to pre-programmed temperature segments which were determined by trial and error. All specimens were heating approximately linearly to 1473 K and held at this temperature for 3 minutes. Typical ramping rates ranged from ~ 2 – 5 K/s. During the ramp the Extrel QMS was used to monitor the mass signals at 3.030 (HD), 4.000 (He), and 4.026 (D\(_2\)) amu. The CVI program recorded specimen temperature at a rate of 120 measurements per minute (2 per second), with the QMS recording mass data at a rate of 118 scans per minute. After holding at 1473 K for ~ 3 minutes the specimen was cooled at a rate of 5 K/s. For later reference when interpreting TDS results, it should be noted that samples AL23, 24, 25, 26, 27, 28 and 29 were cut from “old” batch PCW, while all subsequent samples were cut from “new” batch PCW. Details as to the implications of new- vs. old-batch PCW will be discussed in section 5.1.2.
4.4 TDS Analysis

TDS data were then analyzed to obtain temperature desorption profiles and total trapped inventories of implanted D\(^+\) and/or He\(^+\) ions. Unlike the studies published by Lee et al. [39, 45] the task of analyzing TDS data in the present study was relatively simple for single and double ion implantations. Since the QMS data and CVI temperature data were recorded at about the same rate, data points were aligned with one another starting from the QMS scan number noted in section 4.3. The QMS data were then multiplied by the leak calibration factor (He leak for the 4.000 amu signal (He), and D\(_2\) leak for the 4.026 amu signal (D\(_2\))), the background level was subtracted, and the remaining data were divided by the beam spot area to obtain the atomic (multiplied by 2 for deuterium) release rate per unit area. This information was then plotted as a function of temperature yielding desorption spectra for the interpretation of our retention experiments. To calculate the total retention, the area under the desorption curve was integrated minus the background level. Essentially, every pair of adjacent data points for atomic release rate per unit area were averaged, and then multiplied by the elapsed time between these points, yielding the total retention for that given time interval. Adding all these contributions together we obtained the total D/He retention in the specimen.

4.5 Irradiation Experiments

A total of 30 experiments were performed for the purpose of investigating the trapping behavior of D and He in PCW, varying parameters such as temperature, incident fluence, and order of implantation. Additional implantations were performed to understand discrepancies from expected behavior, although these are not part of the scope of this study. We present in Table 4.1 the irradiations performed with their respective experimental parameters.
### Table 2 – Ion sequence and incident fluences used for experiments; note that specimens are labeled with the author’s initials (to avoid confusion with other researchers’ specimens) followed by a number indicating the relative order in which specimens were irradiated.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>D(^+)-only</th>
<th>He(^+)-only</th>
<th>SEQ He(^+)-D(^+)</th>
<th>SEQ D(^+)-He(^+)</th>
<th>SIM D(^+)-He(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>AL23 1.00x10(^{23})</td>
<td>AL24 1.00x10(^{21})</td>
<td>AL25 1.00x10(^{24})</td>
<td>AL26 1.00x10(^{23})</td>
<td>AL27 1.00x10(^{23})</td>
</tr>
<tr>
<td></td>
<td>AL28 1.00x10(^{24})</td>
<td>AL29 1.00x10(^{23})</td>
<td>AL31 2.54x10(^{21})</td>
<td>AL32 1.00x10(^{24})</td>
<td>AL33 2.55x10(^{21})</td>
</tr>
<tr>
<td>500 K</td>
<td>AL45 1.00x10(^{24})</td>
<td>AL43 1.81x10(^{22})</td>
<td>AL56 1.82x10(^{22})</td>
<td>AL55 1.00x10(^{24})</td>
<td>AL54 1.79x10(^{22})</td>
</tr>
<tr>
<td>700 K</td>
<td>AL46 1.00x10(^{24})</td>
<td>AL48 1.42x10(^{22})</td>
<td>AL58 1.40x10(^{22})</td>
<td>AL57 1.00x10(^{24})</td>
<td>AL41 1.39x10(^{22})</td>
</tr>
</tbody>
</table>
Chapter 5  Experimental Results and Discussion

The following sections of this chapter present, systematically, experimental results of D+-only, He+-only, sequential and simultaneous irradiations at 300, 500, and 700 K. Qualitative interpretations will be included based on experimental results and logical deductions from conclusions drawn in the existing literature. Furthermore, the analysis of TDS profiles presented herein will assume that each peak is representative of a single trap energy. For most cases a single-step desorption process is assumed whereby atoms dissociate from a defect in a single, thermally activated jump process and are released from the surface after rapid diffusion.

5.1  D+-Only Irradiations

5.1.1  D+-Only Irradiations at 300 K

Deuterium was implanted into polycrystalline tungsten (PCW) at 300 K for fluences of 1 x 10^{23} (old-batch) and 1 x 10^{24} D+/m^2 (new-batch) with 1.5 keV D_3^+ (500 eV/D) ions at a flux of approximately 2.4 x 10^{19} to 4.8 x 10^{19} D+/m^2/s. These implantations were carried out for comparison with results from the double ion irradiation experiments. The TDS profiles for these irradiations are presented in Figure 8. For the lower fluence case there appears to be one dominant release peak at ~ 610 K with a minor shoulder on the low energy edge of the peak around ~ 500 K; for the higher fluence case the dominant release peak is observed at ~ 660 K with a more pronounced shoulder at ~ 500 K. Lee reported similar peaks for deuterium implanted in PCW at 300 K with 1.5 keV D_3^+ (500 eV/D) ions to fluences of 1.0 x 10^{23} D+/m^2 and 5.5 x 10^{23} D+/m^2, with slight differences. He found two dominant release peaks at 500 K and 630-680 K with a relatively small peak found at 900 K for the higher fluence case [11]. It should be noted, however, that when the TDS system was baked to 380 K, similar to the procedure followed for this study, the 500 K peak appeared as a shoulder in the higher temperature peak. Therefore, these results agree quite well with those obtained by Lee, with the exception of the 900 K peak. We will attempt in the following to interpret the physical origins of the two release peaks (500 K, and 610-660 K) observed in TDS profiles for D+-only irradiations. The assignment
of a specific trapping process to the 500 K desorption peak, however, is difficult due to the many trapping configurations that can lead to a release peak at this temperature. The following is an interpretation of the trapping process that is most consistent with the results presented.

![Graph](image)

**Figure 8 - TDS profile for D\(^{+}\)-only irradiations at 300K for fluences of 10\(^{23}\) D\(^{+}/m^{2}\) (old-batch PCW; red) and 10\(^{24}\) D\(^{+}/m^{2}\) (new-batch PCW; blue).**

The D release peak at 500 K is thought to be the result of contributions from three different processes. Studies have shown that solute D atoms mobile at 300 K desorb between 400 K and 700 K [11, 52, 54], though most of these contributions have been reduced by baking of the TDS system. The above noted studies also reported that surface adsorbed D is observed to desorb at 500 K. For this particular study the 500 K peak is evidently lower, relatively speaking, than results presented by Lee [11]. Furthermore, in Lee’s efforts to establish the effects of baking the TDS system prior to heating he reported a large reduction in the 500 K peak for specimens subject to pre-TDS baking, similar to single crystal tungsten (SCW) results where surface
adsorbed D was released following TDS chamber baking [52]. These results further reinforce the hypothesis that D released at the 500 K peak may come from surface-bound D. Finally, there are studies that have reported D release from a vacancy accounting for a release peak at 500 K [49].

Considering specimens are annealed at 1473 K, vacancy population is not expected to be significant. Furthermore, the displacement damage threshold in tungsten is reported as 38-44 eV [55], and calculations \( E_D = \frac{1}{4} E_w \frac{m_D}{m_w} (\frac{m_w}{m_D} + 1)^2 \) taking into account conservation of energy and momentum yield a threshold of ~ 888-1029 eV for D\(^+\) impact on tungsten. Clearly, the 500 eV-D\(^+\) ions used in this study are below this threshold, and are thus not expected to generate vacancies. However, Picraux [56] showed that incident particles with energies below the damage threshold can transfer their momentum to heavier impurity atoms, which have a lower threshold for damage creation (also mentioned by Tian et al. [20]). A similar mechanism was proposed by Poon et al. [57] in which D retention levels were shown to decrease with reduced impurity concentrations in SCW. This mechanism was proposed to explain the large reduction in the 500 K peak for D implanted to a fluence of \( 3 \times 10^{23} \) D\(^+\)/m\(^2\); in which case the pre-TDS baking did not affect the 500 K release peak. These results tend to suggest that D release at 500 K depends very little on surface adsorbed or solute D for fluences greater than \( 1 \times 10^{23} \) D\(^+\)/m\(^2\). For fluences \( \leq 1 \times 10^{23} \) D\(^+\)/m\(^2\), it is proposed that the majority of the trapped amount of D contributing to the 500 K peak is adsorbed D with contributions from solute D, with comparatively smaller contributions from vacancies. This hypothesis is supported by Lee’s results [11], as well as the results reported herein that show a clear decrease in the 500 K peak for the lower fluence case with pre-TDS bake (when compared to Lee’s results without bake). All information considered, it is proposed there is a fluence dependent release of D at 500 K from vacancies.

Poon [49] and Fransens et al. [58] have both proposed that a second D atom traps at a deuterium-vacancy (DV) complex for fluences \( > 1 \times 10^{23} \) D\(^+\)/m\(^2\) and is released at ~ 500 K. Poon [49] reported a five-fold increase in the amount of D retained within 6 nm of the SCW specimens for the case of \( 3 \times 10^{23} \) D\(^+\)/m\(^2\) compared to a \( 1 \times 10^{23} \) D\(^+\)/m\(^2\) implant with SIMS measurement. The corresponding increase was noted in the 500 K release peak which indicates that the second D along with the first D is being trapped at near-surface vacancies.

The proposed binding energies for trapped D associated with the 500 K peak are 0.85 eV [22], associated with D trapped at intrinsic defects throughout the specimen with a corresponding
release at 450 K; 0.4 - 0.8 eV, associated with surface adsorbed D [54]; and 0.99 eV [58], 1.03 eV [54], or 1.07 eV [27] associated with the dissociation of a second D atom from a DV complex.

The higher temperature peak at 610 – 660 K is very likely the result of D release from near surface vacancies - the first atom of the DV complex - with contributions from extended defects like dislocations and grain boundaries beyond the near-surface, as suggested by Lee [11]. In his thesis, Lee reported that waiting 15 days prior to desorption led to a 40 % reduction of solute D in the specimen, similar to the results reported by Quastel et al. [52]. However, it was found that the reduction corresponds to a greater drop in magnitude for the 680 K desorption peak compared to the 500 K peak. This led to the hypothesis that the 500 K desorption peak may in part be due to D released from surface adsorption sites (as suggested above), since D released from the bulk would continually refill the surface sites following recombination. The next logical hypothesis is that the 680 K peak is associated with D trapped beyond the near-surface region. Therefore, it is proposed that the higher temperature 610 – 660 K peak is associated with D trapped at surface vacancies, with a binding energy of 1.34 eV [27], and dislocations and grain boundaries beyond the near-surface region.

A few studies have reported a 900 K peak for D implanted in tungsten. Poon et al. [27], as well as Haasz et al. [31], Alimov et al. [59], and Lee [11] have interpreted this release peak to be associated with D adsorbed on void walls, with Poon et al. associating to it a binding energy of 2.1 eV [27]. We do not observe this peak in the results presented herein, although a ~ 900 K shoulder was observed in a $5.5 \times 10^{23} \text{D}^+/\text{m}^2$ implanted PCW specimen in preliminary experiments not included in this thesis. The discrepancy in results is thought to be the consequence of inconsistencies in PCW material between batches. There will be more discussion on this topic in section 5.1.2.

The total D retention was calculated by integrating the TDS release profiles over all time to be $3.43 \times 10^{20} \text{D}^+/\text{m}^2 \pm 20\%$ for an incident fluence of $1 \times 10^{23} \text{D}^+/\text{m}^2$, and $3.14 \times 10^{20} \text{D}^+/\text{m}^2 \pm 20\%$ for an incident fluence of $1 \times 10^{24} \text{D}^+/\text{m}^2$. These results are consistent, within experimental uncertainties, with Haasz et al. [18] who found that D retention for 500 eV D$^+$ implanted in PCW tends toward saturation at $\sim 6.0 \times 10^{20} \text{D}^+/\text{m}^2$ for incident fluences $\geq 10^{23} \text{D}^+/\text{m}^2$. One must take into account the additional $\sim 40\%$ reduction in D retention due to pre-TDS chamber baking; a procedure that was not used in [18].
5.1.2 \textit{D\textsuperscript{+}-Only Irradiations at 500 K}

Similar to the 300 K irradiation case, deuterium was implanted into PCW at 500 K for fluences of $1 \times 10^{23}$ (old-batch) and $1 \times 10^{24}$ D\textsuperscript{+}/m\textsuperscript{2} (new-batch) with 1.5 keV D\textsubscript{3}\textsuperscript{+} (500 eV/D) ions at a flux of approximately $3.3 \times 10^{19}$ to $4.65 \times 10^{19}$ D\textsuperscript{+}/m\textsuperscript{2}s. The TDS profiles for these irradiations are presented in Figure 9. For the lower fluence case D is released in one peak at ~700 K; similarly, for the higher fluence case D is released in one peak at ~660 K. Lee [11, 39, 45] did not perform any measurements of D retention for irradiations at 500 K, so there are no data for comparison. There are, however, multiple studies investigating the effects of temperature on D retention in tungsten, with some reporting data for 500 K irradiations [18, 19, 31, 53].

In the previous section it was postulated that the higher temperature release peak, observed at 610 – 660 K, was associated with D trapped at near surface vacancies, as well as dislocations and grain boundaries beyond the near-surface region. For PCW irradiated at 500 K, we observe a single peak at ~700 K, which is interpreted as resulting from the same process as the 610 – 660 K peak observed for 300 K irradiations. We find further support from 500 K irradiation studies that this peak arises from bulk trapping of D at dislocations and grain boundaries. Haasz et al. [18] observed that D retention did not tend toward saturation for 500 K implantation (500 eV/D) in PCW up to a fluence of $3 \times 10^{24}$ D\textsuperscript{+}/m\textsuperscript{2}, whereas saturation was observed for fluences $> 10^{23}$ D\textsuperscript{+}/m\textsuperscript{2} for 300 K implants. The slope of the relationship also suggests a diffusion-limited trapping mechanism for D at 500 K. Furthermore, nuclear reaction analysis (NRA) reveals that D concentration was nearly uniform throughout the specimen, with ~0.05 - 0.1 at.\% at the front and back surfaces [18]. These results indicate that D trapping beyond the near-surface is largely responsible for the observed D retention at 500 K, further supporting our interpretation of the single 700 K peak. In [31], Haasz et al. investigated the effects of damage on D retention in PCW at 500 K. Damaged specimens exhibited a larger inventory of D compared with virgin specimens. Furthermore, blisters were observed for damaged specimens, leading to the speculation that bubbles are formed in the bulk. The increased D retention is then postulated to be resulting from trapping in swelling-induced stresses such as dislocations [31]. Studies with SCW [19, 53] lend further insight into the role of grain boundaries in the trapping of
D at 500 K. For high purity SCW the D retention for 500 K implants was significantly lower for fluences < 10^{24} \text{D}^+/{\text{m}^2} when compared to retention values for 300 K implants [19]. This discrepancy was highlighted by decreased retention in the 700 K peak which accounts for the majority of trapping at 500 K. For lower purity SCW, Haasz et al. [53] reported that D retention at 500 K was relatively constant for all fluences, with greater retention than 300 K implants at fluences <10^{22} \text{D}^+/{\text{m}^2}. Later studies [49], however, revealed that this behavior was caused by repeated prior irradiation of the specimens. D retention for lower purity virgin specimens at 500 K was subsequently found to be significantly lower for fluences < 10^{24} \text{D}^+/{\text{m}^2} when compared to the 300 K case, as was reported for the high purity specimens [49]. Compared with trends in PCW, it is likely that increased diffusion of D along grain boundaries and dislocations to trapping sites beyond the near-surface region accounts for the larger inventories in PCW. These results all support our earlier interpretation that the 700 K release peak (610 – 660 K for 300 K) in PCW arises from D trapped along grain boundaries and dislocations in the bulk, as well as nano-voids as suggested by Poon et al. [27] for SCW where grain boundaries do not exist.

There are some discrepancies, however, when comparing the results in this study to results published in the literature. First, it was noted in [18] that the primary D release peak for 500 K implants was observed at ~ 900 K. As detailed in Chapter 4, relatively similar temperature and QMS mass scanning rates allow for us to determine a direct relationship of D release as a function of temperature. In an alternative approach, the temperature can be approximated as a linear function of time, and this relationship can be subsequently applied to D release data. In one experiment (not included in this chapter), it was observed that applying this approximation method led to a shift of the single D release peak to ~ 850 – 900 K, whereas the original peak was located at ~ 700 K when drawing a direct relationship of D release as a function of temperature. However, since we observed this temperature shift in release peak for only one experiment, and TDS profiles reported in [18] were also obtained by drawing a direct relationship between temperature and QMS data recorded at the same rate, there is insufficient evidence to conclude different processing techniques as the cause for these discrepancies. An alternative suggestion is to consider the effects of TDS heating rates on peak positions as detailed by Lee in [11]. Lee explains how higher heating rates cause TDS peaks to shift to higher temperatures by as much as 50 K, however, this effect does not encompass the magnitude of the shift we observe in this study (on the order of ~ 200 K). These discrepancies remain unresolved.
Another significant discrepancy observed for results of the 500 K irradiation experiments was found in comparing total D retention between different batches of PCW. The total D retention for the higher fluence ($1 \times 10^{24} \text{ D}^+/\text{m}^2$) case was found to be a factor of $\sim 10 – 20$ lower than inventories reported in [18] for similar irradiation conditions. Further investigation revealed a clear discrepancy in D retention between different batches of PCW, indicating the possibility of differences in composition and/or purity. Experiments were carried out to characterize the retention behavior of the “newer” batch of PCW from Rembar Corp. as a function of incident D$^+$ fluence for 500 K irradiations. D retention for 300 K irradiations did not show any significant discrepancies compared with the literature. Figure 10 shows D retention for the “new” batch of PCW, as well as results for the “old” batch PCW for comparison. It was found that D retention

Figure 9 - TDS profile for D$^+$-only irradiations at 500K for fluences of $10^{23} \text{ D}^+/\text{m}^2$ (old-batch PCW; red) and $10^{24} \text{ D}^+/\text{m}^2$ (new-batch PCW; blue).
for this new batch of PCW was reduced for all fluences, with the most drastic discrepancies for
$10^{24}$ D$^+/m^2$ implantations, though there was generally similar behavior as a function of fluence.
No sign of saturation was seen for fluences up to $10^{24}$ D$^+/m^2$, though the slope of the curve was
smaller. Upon further investigation of the TDS profiles, as shown in Figure 11, D release is still
characterized by a release peak at $\sim 650 – 700$ K, though a lower temperature shoulder is evident
for all fluences. Returning to our previous discussion of D release behavior, it is likely that the
lower temperature shoulder corresponds to D retention at near surface vacancies, whereas the
primary peak is associated with D release from bulk traps. Lee [11] had suggested near surface
vacancies as a potential trapping mechanism contributing to the higher temperature 680 K peak
observed for 300 K irradiated specimens. Furthermore, Poon et al. [27] associated a single D
trapped at vacancies to the 640 K TDS peak. Since deeper deuterium will take a longer time to
diffuse to the surface of the specimen before being released, it is logical to assume the lower
temperature shoulder on the primary TDS release peak to be associated with D bound at the
surface. This interpretation is further supported by the fact that the higher temperature peak
becomes progressively more dominant as the fluence increases. It is logical to assume that the
near surface vacancies will trap D first, with D trapping beyond the near-surface as these traps
become filled with increasing incident fluence. From comparisons of TDS profiles for the old-
and new-batch PCW specimens (Figures 11 and 12) it appears that the significant decrease in D
inventory for the newer batch results from a reduction of the primary $\sim 700$K peak associated
with D trapped beyond the near-surface. The logical conclusion is that some difference in
composition or structure is reducing the diffusion of D into the bulk of the specimens, or
alternatively, leads to the release of deeply bound D prior to TDS.

In a separate study investigating the mechanisms of blister formation in PCW irradiated
with D$^+$ ions, He$^+$ ions, and both D$^+$ and He$^+$ sequentially and simultaneously, SEM images were
obtained illustrating a clear difference in grain structure between batches [60]. Figure 13 (a)
illustrates the grain structures of the original batch of Rembar PCW subsequent to 500 eV-D$^+$
irradiation at 500 K up to a fluence of $10^{24}$ D$^+/m^2$ with a flux of $2 \times 10^{18}$ D$^+/m^2$ s. Figure 13 (b) is
for the new batch of Rembar PCW following irradiation under similar conditions though at a
higher flux of $1.8 \times 10^{19}$ D$^+/m^2$ s. The SEM images illustrate a large difference in grain structure
and blister formation for two specimens of supposedly identical material, under similar
irradiation conditions. It should be noted that the new-batch-PCW exhibited a reduction in blister
formation, which has been correlated with reduced D retention [28, 29]. While this information is insufficient to draw any solid conclusions as to the cause for discrepancies in D retention at 500 K, some possibilities have been suggested following X-ray Photospectroscopy (XPS) analyses of the two types of PCW specimens. In preliminary results, XPS measurements have revealed a tungsten-carbide (WC) layer on the surface of the new-batch-PCW, with increased carbon impurity content throughout the bulk [74]. In the following, we consider how this additional layer might affect D retention at 500 K.

Poon et al. [61] investigated the effects of C\textsuperscript{+} pre-irradiation on D retention in Rembar PCW. Poon found in some cases that pre-irradiation with C\textsuperscript{+}-ions led to the formation of tungsten-carbide (WC), which subsequently led to decreased D retention. It was suggested that the presence of WC reduced D retention either by occupation of trapping sites by C atoms which subsequently formed carbides, or by altering surface recombination of D atoms. The most intriguing result was that D retention at an incident fluence of $10^{24}$ D\textsuperscript{+}/m\textsuperscript{2} was lower for 500 K implantations compared to the pure PCW case, while results were relatively similar between C\textsuperscript{+} pre-irradiated samples and PCW at 300 K [61]. Furthermore, it was observed that C concentration at the surface was reduced for higher temperature (500 K) C\textsuperscript{+} implantations, leading to the suggestion that C diffusion into the bulk is enhanced at higher temperature. With further results from XPS analysis indicating that the WC layer in the surface survives the annealing process at 1473 K for ~ 2 hours [74], then we propose that WC is blocking the diffusion of D into beyond the near-surface, thereby significantly reducing the inventories of D trapped along dislocations and grain boundaries in the bulk. Considering our proposed model in which D retention beyond the near-surface is the primary trapping mechanism at 500 K, we could then account for the large discrepancies in D retention between new- and old-batch PCW. As further evidence that new-batch PCW is somehow modified, Figure 14 illustrates the temperature dependence of D retention for an incident fluence of $10^{24}$ D\textsuperscript{+}/m\textsuperscript{2}, which is significantly different from the temperature dependence plot with the same material from [18].

In conclusion, we observe that D retention in the new-batch PCW is significantly lower than in the old one for the 500 K case, whereas there is good agreement for new- and old-batch PCW at 300 K. Comparing the new- and old-batch results at 500 K in Figure 10 we find that the discrepancies between old and new batches are less pronounced at lower incident fluences. These
observations support the hypothesis that discrepancies between batches are related to a tungsten-carbide layer on the new Rembar PCW specimens.

![Total Deuterium Retention in PCW (by batch)](chart.png)

*Figure 10 - Deuterium retention as a function of incident fluence for new- and old-batch PCW at 500K.*

5.1.3 \textit{D}^+\textit{-Only Irradiations at 700 K}

In agreement with D retention results in [11, 18], we also found no significant D retention for PCW (new-batch) specimens irradiated at 700 K. In [18] it is suggested that diffusion becomes more important as irradiation temperature is increased, supported by the observation that D concentration is uniform throughout the specimen for 500 K irradiation of 500 eV-\textit{D}^+ ions [18]. One could only expect the diffusion to be even more important at 700 K, and coupled with the deactivation of major trapping sites at this temperature, no D retention is observed. In a single case of sequential D^+-\textit{He}^+ irradiation at high fluence, however, a slight amount of D was observed to release from the PCW specimen during TDS. More details on this will be provided in section 5.4.3.
Figure 11 - TDS profiles for $D^+$-only implantations corresponding to the total retention results for new-batch PCW at 500K presented in Figure 10.

Figure 12 - TDS profiles for $D^+$-only implantations corresponding to the total retention results for old-batch PCW at 500K presented in Figure 10.
Figure 13 - SEM images of (a) old-batch PCW and (b) new-batch PCW irradiated with a fluence of $10^{24} \text{D}^+/\text{m}^2$ at 500K.

Figure 14 - Temperature dependence of D retention in new-batch PCW for $10^{24} \text{D}^+/\text{m}^2$ implantations compared with results from [18] for $10^{23} \text{D}^+/\text{m}^2$. 
5.2 *He*⁺-Only Irradiations

5.2.1 *He*⁺-Only Irradiations at 300 K

Helium was implanted into PCW at 300 K for fluences of $1 \times 10^{21}$ (old-batch) and $1.35 \times 10^{22}$ He⁺/m² (new-batch) with 500 eV-He⁺ ions at a flux of approximately $5 \times 10^{17}$ to $9 \times 10^{17}$ He⁺/m²/s to provide reference results for comparison with results of the double ion irradiation experiments. The TDS profiles for these irradiations are presented in Figure 15. For the lower fluence case there appears to be two dominant peaks at ~ 500 K and ~ 1060 K with a pronounced shoulder on the 1060 K peak at ~ 950 K. For the higher fluence implant it appears as though the lower temperature peak has shifted to ~ 580 K, and there is now a dominant peak at ~ 960 K, this time with a less discernable shoulder at ~ 1050 K. These observations are somewhat consistent with results presented by Lee [11] in which he reported desorption at 500 K, 950 K and 1150 K for one case of 300 K irradiation. In the following we will attempt to provide an interpretation of the mechanisms responsible for the 500 – 580 K, 950 – 960 K, and 1060 K TDS release peaks.

It is worth noting that Lee [11] interpreted the desorption peaks he observed as being associated with He released from sites very near the surface. This was initially based on conclusions drawn by Kornelsen for thermal release of inert gases from SCW [62], where He is expected to trap in the near surface. This was later confirmed by elastic recoil detection (ERD) analysis that indicated He was only trapped within 30 nm of the PCW surface for 300 K irradiations [11].

The 500 – 580 K desorption peak is thought to be associated with He atoms released from surface-bound defects, traps beyond the near-surface, or from impurities and grain boundary sites. However, the ERD results from [11] essentially rule out the possibility that traps beyond the near-surface region contribute to the 500 – 580 K desorption peak.
In another study, Kornelsen [63], associated the release of He between 300 – 900 K with surface-related trapping sites because it was found that the amplitude and peak substructure both depend on the crystal face bombarded, and the amplitude was largely affected by the amount of gas adsorbed on the crystal surface [63]. Erents and Carter [64] also observed He release at ~ 575 K from PCW implanted with 290, 540 and 1000 eV-He$^+$ ions. The higher energy case reveals a separation between the 575 K release peak and a peak at 850 K. Both peaks, which appear to be independent of ion energy and compared to Kornelsen’s work, the fluence as well, are suggested to be due to the target surface properties [64].

Similar to Lee [11], the results presented in Figure 15 show that the 500 – 580 K peak is largely dependent on incident fluence, and increases in magnitude with increasing fluence. However, unlike Lee, and similar to results presented by Erents and Carter [32] who observed the removal of this lower temperature peak following post-implantation with heavier inert gases, the present sequential implantation experiments clearly show that post-implantation with

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**Figure 15 - TDS profiles for He$^+$-only irradiations at 300K for fluences of 1.00 x 10$^{21}$ He$^+$/m$^2$ (old-batch PCW; red) and 1.35 x 10$^{22}$ He$^+$/m$^2$ (new-batch PCW; blue).**
deuterium reduces this peak, with nearly complete removal at higher D post-implantation fluences (see section 5.3). However, it should be noted that Lee reported little effect on this peak due to hydrogen post-implantation, suggesting perhaps that deuterium has different effects on the trapping of helium in PCW.

An alternative interpretation is that He interstitially trapped at impurities is responsible for the 500 – 580 K release peak. Kornelsen [65] found that substitutional Xe (1.5 keV/Xe) impurity atoms introduced into SCW trapped He atoms and released them at temperatures below 1000 K. For the case of a single He atom trapped by a Xe atom, desorption is calculated to occur at ~ 500 K. At higher He$^{+}$ fluences, the binding energy of He atoms was found to increase monotonically with the number of atoms trapped at the substitutional noble gas atom sites from 1.2 eV for a single atom to 2.1 eV for 7 to 10 atoms. This process leads to progressively higher He release temperatures ranging from 506 K to 902 K [65]. Similar results were observed for He interaction with substitutional metallic impurities such as Ag, Al, or Cu [66]. For identical materials, Lee observed enhanced AlO content in the first 10 nm of the PCW specimen surface from SIMS [11]; so He trapping at metallic impurities cannot be ruled out for this case. The main discrepancy between results presented in Figure 15 and results supporting the hypothesis of He trapping at impurities is the lack of discernable desorption peaks in the temperature range of 600 – 800 K, as calculated in [65]. However, despite the lack of peaks, He desorption is still observed at 600 – 800 K, with increasing magnitude for greater incident fluence of He$^{+}$ ions. This could be due to He desorption from a multiply occupied impurity site.

Modeling work by Wilson et al. [67] proposed that He atoms in a metal lattice are able to cluster together, producing vacancies and nearby self-interstitial defects. The minimum number of interstitial He atoms needed for the creation of these vacancies/defects is 5. While the results presented appear inconsistent in some form with the interpretations presented in the literature, there are still some possibilities that have been presented. Lee et al. [39] postulated that the release of He at ~ 500 K (representing the 500 – 580 K peak in this case) may be from He clusters at grain boundaries and within the crystal, possibly at dislocation loops near helium-vacancy complexes ($\text{He}_n\text{V}_m$).

The TDS desorption peak observed at 950 – 960 K peak is interpreted, for nearly identical experimental parameters, as He released from $\text{He}_n\text{V}_m$ complexes or He bubbles [39]. This hypothesis is supported by multiple sources reporting that He release from a vacancy site
filled with 5 – 10 He atoms is observed at ~ 950 K in thermal helium desorption studies [35, 62, 63, 65, 68, 69]; as well as the observation that implantations at higher ion energy appear to enhance this peak [11]. Kornelsen [35] found that a single helium atom trapped at a vacancy is released at 1560 K. Further He atoms trapped at the same site results in lower release temperatures of ~ 1220 K and ~ 1100 K for He filling of 2 and 3-4 atoms respectively. Five to ten He atoms is projected as the upper limit for He filling at a vacancy in W before “trap-mutation” occurs [35]. In our study He release peaks are observed between ~ 950 K and ~ 1100 K; therefore it is possible that the 950 – 960 K desorption peak is a result of He filling at a pre-existing vacancy. However, desorption being limited to temperatures below 1200 K does not support this hypothesis since we would expect higher temperature desorption peaks for lower populated vacancies. Another possibility is that the 950 – 960 K peak is the result of a He$_6$ cluster punching out a self-interstitial atom (SIA) to form a He$_6$V complex. Again, however, there is an absence of expected desorption peaks from 950 to 1560 K for each He atom releasing from the He$_6$V complex. A possible solution is proposed by Lee [11] in which the attached SIA can relax into the vacancy following the release of the first He, resulting in the release of the remaining He cluster. This hypothesis is supported by the current study since there is only a small vacancy population expected in specimens following annealing, and implantation is performed with low energy ions. This is further supported by the observation that higher fluences lead to an increase in the magnitude of the 950 – 960 K peak; it is expected that with higher concentrations of He, more He clusters can form, leading to an increase in the number of He$_6$V complexes.

An interesting result that links bubble formation to the 950 – 960 K peak is found in [30, 70]. The TDS results from specimens containing micron-sized He bubbles formed during 4 keV-He$^+$ ion implantation to $10^{22}$ He$^+$/m$^2$ fluence [30, 70] indicate He release at ~ 770 K, similar to a case in which Lee [11] observed a ~ 780 – 840 K release peak for 5 keV He$^+$ at a fluence of 5.0 x $10^{22}$ He$^+$/m$^2$. Therefore, He bubbles cannot be ruled out as a possible source for release at 950 – 960 K.

The 1060 K peak appears to be the dominant higher temperature release peak for the lower fluence case in our study. Lee [11] observed this peak at temperatures ranging 1050 – 1250 K, and reported a sharp release peak for fluences of ~ 5 x $10^{22}$ He$^+$/m$^2$. This sharp release, being typically characteristic of sequential dissociation [71] whereby He atoms trapped at
vacancy clusters initially desorb, was interpreted as the dissociation of defect clusters. This hypothesis is further supported by experiments conducted by Lee with 500 eV He\(^+\) ions, where occasionally a peak is also observed at 1150 K [39]. Alternatively, Kornelsen [35] had interpreted a ~ 1100 K peak to be associated with a single He from a He\(_{3-4}\)V complex, although the dissociation of the remaining 2-3 He atoms should produce desorption peaks at > 1100 K.

As shown in Figure 15, however, there does not appear to be any peak at or above 1150 K for 300 K irradiations. While there is no clear interpretation for the 1060 K peak, it is safe to presume this peak is associated in some way with He\(_n\)V\(_m\) complexes. As an added note, pre- and post-implanted deuterium was found to reduce He released at ~ 1050 – 1060 K, while simultaneous irradiation with deuterium appears to enhance this peak at lower fluence, while extending He release to higher temperatures (~1300 K); see sections 5.3 – 5.5.

**5.2.2 He\(^+\)-Only Irradiations at 500 K**

Helium was implanted into PCW at 500 K for fluences of 1 x 10\(^{21}\) (old-batch) and 1.8 x 10\(^{22}\) He\(^+\)/m\(^2\) (new-batch) with 500 eV-He\(^+\) ions at a flux of approximately 6 x 10\(^{17}\) to 9 x 10\(^{17}\) He\(^+\)/m\(^2\)s again for comparison with results of double ion irradiation experiments. The TDS profiles for these irradiations are presented in Figure 16. The TDS profiles for He release at 500 K appear to have less defined peaks than those observed at 300 K. For the lower fluence implant, poorly distinguished He release peaks are observed at ~ 580 K and ~ 770 K, with a broad release peak spanning ~ 1100 – 1473 K exhibiting minor peaks at ~ 1250, ~1350, and ~1450 K. For the higher fluence case, the He release rate is observed to be relatively constant between ~ 600 and 1000 K, with minor peaks at ~ 620, ~ 850, and ~ 950 K. Again, Lee [11] did not perform any experiments at 500 K, and so there are no data for comparison.

For 500 K irradiations at both fluences we observe He to be released at ~ 580 – 620 K. In section 5.2.1 we discussed possible mechanisms for He desorbed in the range of 500 – 580 K, concluding that He is likely trapped at impurity sites, or in He clusters along grain boundaries, within the crystal, or possibly at dislocation loops near helium-vacancy complexes. In either case, evidence suggests that this peak arises from He release from near-surface trapping sites. When increasing the fluence by about an order of magnitude we observe an approximately 2-fold
increase in this peak, compared to an approximate 5-fold increase for 300 K irradiations. More discussion will follow on this finding in section 5.2.3.

We attribute the ~ 770 K and ~ 850 K peaks to arise either from He release from He-vacancy complexes, or to be associated with trapping at impurities as suggested in section 5.2.1. From [65], it was determined that release at ~ 800 K was associated with 4 He atoms bound at a single trap of unknown nature. Since we have associated the higher temperature ~ 950 K peak with He$_6$V complexes, it is counter-intuitive to associate He release at these lower temperatures with He$_4$V complexes. Therefore, we can safely assume that these “unknown” traps are not vacancies.

The mechanism associated with the release peak observed at ~ 950 K is detailed in section 5.2.1 in which the general conclusion was that this peak arose from He released from He$_6$V complexes or He bubbles. The higher temperature peaks observed for the lower fluence irradiation case can be characterized as individual He atoms released from multiply occupied vacancy sites in sequential fashion. Kornelsen [35] interpreted peaks at 1120, 1220, and 1560 K as the first, second and third He atoms released from a He$_3$V complex. Considering the poor resolution of the peaks, one could interpret the 1250, 1350, and 1450 K peaks observed in this study as the sequential release of three He atoms from a single vacancy site. Lee [11] also suggested that higher temperature peaks (1150 K in his case) result from He trapping at vacancy clusters, this being supported by experiments exhibiting increased retention for 2 keV He$^+$ ions. This is considered an alternative interpretation for these high temperature TDS release peaks, with the same assumption that He atoms are desorbed sequentially from multiply occupied vacancy clusters. The disappearance of these higher temperature release peaks for higher fluence implants can be thought as resulting from greater He occupation of vacancy sites, leading to an increase in He release at ~ 950 K (dissociation of He$_6$V complex, or He bubbles) and at ~ 600 K (He trapped in He clusters along grain boundaries, within the crystal, or at dislocation loops) to account for the difference.
5.2.3 \( \text{He}^+ \)-Only Irradiations at 700 K

Helium was implanted into new-batch PCW at 700 K for fluences of \( 2 \times 10^{21} \ \text{He}^+/\text{m}^2 \) and \( 1.4 \times 10^{22} \ \text{He}^+/\text{m}^2 \) with 500 eV-\( \text{He}^+ \) ions at a flux of approximately \( 9 \times 10^{17} \) to \( 2 \times 10^{18} \ \text{He}^+/\text{m}^2 \) s for comparison with results of the double ion irradiation experiments. We note that the high-fluence \( \text{He}^+ \) implantation was performed using the LIS leg of the dual-beam accelerator, while the low-fluence \( \text{He}^+ \) implantation was performed using the HIS for these experiments. The TDS profiles for these irradiations are presented in Figure 17. We observe in both cases a number of peaks with relatively poor distinction. For the lower fluence case, peaks are observed at \( \sim 550 \text{ K} \), \( \sim 850 \text{ K} \) and a broad peak from \( \sim 1000 \text{ – } 1300 \text{ K} \). For the higher fluence case, peaks are observed at \( \sim 550 \text{ K} \), \( \sim 800 \text{ K} \), \( \sim 900 \text{ K} \), and \( \sim 1300 \text{ K} \). These TDS profiles are in poor agreement with those published by Lee [39], possibly because of batch differences in PCW (see section 5.1.2).
Figure 17 - TDS profiles for He\textsuperscript{+}-only irradiations in new-batch PCW at 700K for fluences of 2.01 x 10\textsuperscript{21} He\textsuperscript{+}/m\textsuperscript{2} (red) and 1.42 x 10\textsuperscript{22} He\textsuperscript{+}/m\textsuperscript{2} (blue).

Again, from previous sections we have hypothesized the ~ 550 K peak to be associated with He released from He clusters along grain boundaries, within the crystal, or at dislocation loops; or possibly He released from He bubbles. The higher temperature peaks at ≥ 800 K are likely associated with He release from He\textsubscript{III}V\textsubscript{m} complexes in some capacity as detailed in 5.2.1 and 5.2.2. It is interesting to note that despite the elevated irradiation temperature of 700 K we still observe He release at ~ 550 K. The explanation suggested by Lee et al. [39] is that He atoms trapped at higher energy sites are able to relax into lower energy trapping centers when the specimen is allowed to cool post-irradiation. While we did not perform any experiments to investigate the mechanism responsible for this phenomenon, we propose that state transitions in PCW specimens lead to the transfer of He atoms to lower energy traps upon cooling.

The results presented in sections 5.2.1 and 5.2.3 are generally consistent with TDS profiles presented by Lee [11]. Similar to the present study, Lee [11] reported He release profiles that were characterized by two broad temperature “peaks” spanning ~ 400 – 700 K and ~ 800 –
1050 K for 300 K irradiations. In some cases, an additional peak was observed at 1100 – 1200 K. For 700 K irradiations, TDS profiles were dominated by He release in the higher temperature range > 800 K. These are where the discrepancies arise with the present study. It is thought that we observe different He trapping behavior at 700 K due to PCW batch variation (see section 5.1.2). While the effects of new-batch PCW on He retention were not characterized, judging from the effects on D retention at various temperatures, we would anticipate that batch variation becomes more important as the irradiation temperature is increased. As a result, we expect that the trapping behavior of He in new-batch PCW is modified at higher irradiation temperatures as compared to old-batch PCW.

5.3 Sequential He\(^+\)-D\(^+\) Irradiations

The results and interpretations of trapping mechanisms for single ion irradiations are presented above to form a basis from which trapping mechanisms and other ion influences can be deduced for double ion irradiations. In the following we will present and analyze results from experiments in which specimens were irradiated sequentially or simultaneously with He\(^+\) and D\(^+\) ions.

5.3.1 Sequential He\(^+\)-D\(^+\) Irradiations at 300 K

Experiments were performed in which PCW specimens were irradiated with He\(^+\) ions followed by D\(^+\) ions in a sequential fashion with similar fluences to those used in the single ion irradiation experiments; that is, with the He\(^+\) fluence being 1 – 2 % of the D\(^+\) fluence. For the 300 K case PCW specimens were first irradiated with He\(^+\) fluences of 1 x 10\(^{21}\) (old-batch) or 1.4 x 10\(^{22}\) He\(^+\)/m\(^2\) (new-batch) followed by D\(^+\) fluences of 1 x 10\(^{23}\) or 1 x 10\(^{24}\) D\(^+\)/m\(^2\), respectively. Fluxes ranged from 5 x 10\(^{17}\) to 8 x 10\(^{18}\) He\(^+\)/m\(^2\)s (using the LIS for the higher fluence case), and on the order of ~ 1 – 4 x 10\(^{19}\) D\(^+\)/m\(^2\)s. Results from the TDS analysis are presented in Figure 18. The general observations are that post-implanted D\(^+\) leads to a significant reduction in He inventory and also that the pre-implanted He\(^+\) leads to decreased trapping of post-implanted D\(^+\) ions.
He Trapping:

For lower fluence He$^+$ and D$^+$ SEQ implants the greatest reduction in He inventory over the He$^+$-only case is observed in the 950 K and 1060 K TDS release peaks, with a relatively smaller loss in the 500 K peak; see Figure 18 (a). These results are generally consistent with observations made by Lee [11], with the differences that Lee observed no change in the lower temperature 500 K and 680 K peaks, and the higher temperature peaks (950 K and 1150 K in his case) were completely eliminated. However, these discrepancies do not alter the interpretation of the underlying mechanisms leading to reduced He inventories. For the higher fluence He$^+$ and D$^+$ SEQ implants we observe very similar behavior wherein there is practically no He desorbed at higher temperatures (950 K and 1060 K peaks), with a barely observable amount desorbed at 500 K; see Figure 18 (b).

The reduction/elimination of the 950 K and 1060 K peaks indicate the de-trapping of helium at He-vacancy complexes. It should be noted that there is a larger reduction in the 1060 K peak, which would suggest that He de-trapped from vacancy clusters are re-trapped at lower energy sites (grain boundaries, He$_6$-vacancy complexes). This behavior is consistent with experimental results from [30] where He bubbles were removed following D$^+$ post-implantation, and [39], in which D$^+$ post-implantation led to an elimination of He desorption at higher temperature peaks (950 K and 1150 K in Lee’s case). While Lee had observed a complete elimination of these higher temperature TDS peaks for irradiation conditions similar to those in our low fluence case, Lee did postulate that perhaps the defects associated with these desorption peaks could survive for higher incident He fluences [11]. This hypothesis is somewhat supported by the present study since we do observe He release above 800 K under sequential He$^+$-D$^+$ irradiation, although the incident He$^+$ fluence is likely not a large contributing factor. In fact, we observe the opposite effect in which increasing He$^+$ and D$^+$ fluences by 10 times leads to reduced He inventories at ~ 950 - 1060 K. Recalling results for He$^+$-only irradiation at 300 K from section 5.2.1, increasing the He$^+$ fluence 10-fold has very little effect on He inventories at higher energy traps (desorbing above 800 K); therefore we cannot expect to observe additional He inventories desorbing at higher temperatures in the case of sequential He$^+$-D$^+$ irradiation. Coupled with a 10-fold increase in D$^+$ fluence, which would logically de-trap 10 times as much
He, we end up with even less He inventories at ~ 950 – 1060 K under high fluence sequential He⁺-D⁺ irradiation.

The reduction of He release in the lower temperature 500 K peak is inconsistent with results presented by Lee [11], however, this does not necessarily indicate that a radically different physical process is responsible. Taking into consideration ERD results from [11], He is trapped in the near surface, as is D (both within 30 – 35 nm for 300 K case) for sequential He⁺-D⁺ implantations. Considering the irradiation conditions in [11] are very nearly identical to our present lower-fluence case, it is safe to assume that a similar trapping pattern is occurring in this case with He trapping in the near surface. Therefore, returning to arguments presented in section 5.2.1, it is postulated that He nucleates within the lattice to form HeₙV complexes and He clusters at grain boundaries, and the implanted D⁺ breaks apart these He complexes, along with dissociation of He trapped at vacancy clusters. Since the binding energy is lower at the lower temperature peaks, and we observe a preferential elimination of higher energy peaks, it is quite likely that He trapped at He-vacancy complex-like defects are re-trapped in He clusters at grain boundaries, dislocations, and within the lattice. As a result, the 500 K peak is relatively less affected by D⁺ post-implantation, with larger reduction for higher energy peaks.

D Trapping:

From the alternative perspective, we observe a reduction in D inventory resulting from He⁺ pre-implantation, with relatively larger reductions in higher temperature 610 – 660 K peaks. Again, returning to Lee’s ERD depth results [39], D is observed to trap within ~ 35 nm of the specimen surface when implanted following He⁺ pre-implantation. These observations strongly support previous arguments that D trapped beyond the near-surface region contribute to the 610 – 660 K peak. The 500 K peak was postulated to correspond to a second D trapped at a DV complex. With this, we first postulate that He⁺ pre-implantation is preventing the diffusion of D into the bulk, hence the preferential reduction in the 610 – 660 K peak. Next, we observe a reduction in the 500 K peak and a slight shift to higher temperatures. It is postulated that He occupancy of vacancy sites leads to a reduction in the formation of DV complexes, thus reducing the contribution of first and second D release from vacancy sites to the 610 – 660 K and 500 K peaks respectively. To account for desorption at 500 K in the absence of any significant desorption at 650 K (since a reduction in DV complexes would inevitably indicate a decrease in
Lee [11] had suggested that D possibly traps at He$_n$V$_m$ complexes in a similar manner as a second D atom would be trapped at a DV complex, along with the alternative suggestion that post-implanted D$^+$ breaks apart He-vacancy complexes and He clusters and then traps interstitially with He atoms at various point and extended defects. However, considering the relatively small He inventories in this case, it is unlikely that D trapping with He is responsible for desorption at 500 K.

**Figure 18 - TDS profiles for SEQ He$^+$ followed by D$^+$ irradiations of PCW at 300 K:** for (a) SEQ: $1 \times 10^{21}$ He$^+/m^2 + 1 \times 10^{23}$ D$^+/m^2$ (old-batch PCW) and (b) SEQ: $1.37 \times 10^{22}$ He$^+/m^2 + 1 \times 10^{24}$ D$^+/m^2$ (new-batch PCW). In both (a) and (b) the single-species He$^+$-only and D$^+$-only fluences are the same as in the corresponding SEQ cases.
Calculating total retention from the TDS profiles presented in Figure 18, we find the total D retention decreases by approximately 60% when comparing inventories for sequential He\(^+\)-D\(^+\) to D\(^+\)-only irradiations; similar to results reported by Lee [11]. The reduction in retention is postulated to be caused by impeded diffusion of D into the bulk due to the presence of He in the near surface, impeded trapping of D at vacancies due to He occupancy of existing vacancy sites, and the loss of implantation energy to “break” apart He-vacancy complexes, rather than to form DV complexes in the lattice.

5.3.2 Sequential He\(^+\)-D\(^+\) Irradiations at 500 K

For the 500 K case, new-batch PCW specimens were again first irradiated with He\(^+\) fluences of 2.54 x 10\(^{21}\) or 1.8 x 10\(^{22}\) He\(^+\)/m\(^2\) followed by D\(^+\) fluences of 1 x 10\(^{23}\) or 1 x 10\(^{24}\) D\(^+\)/m\(^2\), respectively. Fluxes ranged from 8 x 10\(^{17}\) He\(^+\)/m\(^2\)s to 4 x 10\(^{18}\) He\(^+\)/m\(^2\)s (using the LIS for the higher fluence case), and on the order of ~ 1 – 4 x 10\(^{19}\) D\(^+\)/m\(^2\)s. Results from the TDS analysis are presented in Figure 19. With the higher irradiation temperature we observe slightly different behavior than that discussed in section 5.3.1. It is worth noting that for the higher-fluence implants the LIS was used for both He\(^+\) and D\(^+\) ions, thus necessitating a significant delay between successive irradiations, during which time the specimen was held at 500 K. The delay between irradiations was 10 minutes and 130 minutes for the lower and higher fluence cases respectively.

He-Trapping:

For sequential He\(^+\)-D\(^+\) implants, similar to the 300 K irradiation case, we observe that He inventory is significantly reduced following D\(^+\) post-irradiation, with larger relative drop for the higher D\(^+\) fluence; see Figure 19. For the lower-fluence case (see Figure 19 (a)), the reduction in the amount of trapped He is significant for all desorption temperatures, with a factor of 5 reduction in total He retention. The He desorption profile following D\(^+\) post irradiation shows a broad release between 600 and 1000 K, with a slightly larger hump at 800 – 1000 K, and broad release between 1100 and 1500 K. Similar to the 300 K case, we observe post implanted D\(^+\) ions de-trap He from the specimen at 500 K, but with less tendency to re-trap in the lower temperature traps. For the higher fluence case (see Figure 19 (b)), we observe a 10-fold reduction
in He inventory following D⁺ post irradiation, with the most prominent feature being a broad peak at 900 – 1100 K. Again, there appears to be a trend toward increased He de-trapping as the D⁺ fluence is increased. Unlike the 300 K case, there does not appear to be significant re-trapping of He in lower energy traps. Instead, the remaining He is observed to desorb at intermediate and higher temperatures. This is an interesting trend that is somewhat consistent with results reported by Lee [11] in which he observed a single He desorption peak at ~ 900 K for 700 K sequential He⁺-D⁺ irradiation, whereas for the 300 K case only the 500 and 680 K peaks survived. We will discuss this further in section 5.3.3.

D Trapping:

The effects of He⁺ pre-implantation on D trapping are significantly more interesting. For the lower fluence case, D inventory is largely unchanged when irradiating the specimen following He⁺ pre-irradiation compared to a virgin specimen. This behavior is significantly different than what was observed for 300 K sequential He⁺-D⁺ irradiations, in which the D inventory was reduced to ~ 40% of that obtained for the single ion irradiation case, with slightly larger reduction for the higher-fluence case. Even more surprising, the D inventory in fact increased by a factor of ~ 1.5 for the higher-fluence case; we note that the observed increase is within the ±50 % of experimental variance, however. Nonetheless, specimens are at least retaining the same amount of D as in D⁺-only irradiations at 500 K. If we consider the behavior at 300 K, we suspect there is some form of modified trapping caused by He⁺ pre-irradiation. Similar behavior has been reported by Iwakiri et al. [41] in which D inventory was observed to increase, with an additional desorption peak at a higher temperature when the sample was pre-irradiated with 8 keV-He⁺ at room temperature. For this case [41] it was observed that He⁺ pre-irradiation led to the formation of He bubbles, which likely created D trapping sites in the specimen. For the current experiments we propose two possible mechanisms leading to increased D retention at 500 K. First, we propose that D is trapped at additional sites created by pre-implanted He⁺ ions. This would be consistent with Iwakiri et al. and would account for the additional, dominant desorption peak at ~ 750 K, likely resulting from a new trapping configuration. Alternatively, we observe that the increase in D inventory is associated with a larger desorption peak at higher temperatures (~ 750K for the high fluence case compared with ~600 K for D⁺-only), which, for D⁺-only implantation, was attributed to D trapping along grain
boundaries and dislocations beyond the near-surface region. Returning to our interpretation of reduced D retention in new-batch PCW at 500 K from section 5.1.2, we postulated WC impurities, detected in the near-surface with XPS analysis, were impeding the diffusion of D into the bulk. Considering the evidence that He\(^+\) pre-irradiation creates damage in the specimens that eventually lead to increased D retention, we postulate that He\(^+\) ions are interacting with these diffusion-impeding impurities in such a manner that their effect is reduced. As a result, we would expect increased D diffusion into the bulk, thereby increasing D inventory.

To summarize this discussion, we find that unlike the case for 300 K sequential He\(^+\)-D\(^+\) irradiation we observe that He\(^+\) pre-irradiation actually enhances D inventory at 500 K, with similar D retention at lower fluences, and \(\sim 1.5\) times greater D retention at higher fluences. Two possible mechanisms are proposed, one suggesting an increase in near-surface trapping sites created by the He\(^+\) pre-irradiation; the second related to D transport beyond the near-surface.

### 5.3.3 Sequential He\(^+\)-D\(^+\) Irradiations at 700 K

For the 700 K case, new-batch PCW specimens were first irradiated with He\(^+\) fluences of \(2 \times 10^{21}\) or \(1.4 \times 10^{22}\) He\(^+\)/m\(^2\) followed by D\(^+\) fluences of \(1.01 \times 10^{23}\) or \(1.00 \times 10^{24}\) D\(^+\)/m\(^2\), respectively. Fluxes were ranging from \(8 \times 10^{17}\) to \(8.4 \times 10^{18}\) He\(^+\)/m\(^2\)s (using the LIS accelerator for the higher-fluence case), and on the order of \(\sim 1 - 4 \times 10^{19}\) D\(^+\)/m\(^2\)s. Results from the TDS analysis are presented in Figure 20. As observed for D\(^+\)-only irradiation, there is no D retained at 700 K, so our discussion will focus on the effects of D\(^+\) post-implantation on the He trapping behavior.

**He Trapping:**

Again, there is a trend to larger reduction in the He inventory following higher fluence D\(^+\) post-implantation. As was observed for the 500 K case, the remaining He desorbs primarily at the high-temperature end of the profile. An interesting feature of the He\(^+\)-only implantations at 500 and 700 K is that the desorption spectrum still has release peaks at \(\sim 500\) K, see sections 5.2.2 and 5.2.3. This implies some mechanism during the cooling process which can transform a certain type of trap, which is capable of retaining He at 700 K during implantation, into traps which release He at \(\sim 500\) K during subsequent heating. We observe similar desorption of He
between 500 – 700 K in the case of sequential He\(^{+}\)-D\(^{+}\) at 700 K (as shown in Figure 20), implying that D\(^{+}\) post-irradiation has little effect on this mechanism.

Figure 19 - TDS profiles for SEQ He\(^{+}\) followed by D\(^{+}\) irradiations of new-batch PCW at 500 K: for (a) SEQ: \(2.54 \times 10^{21} \text{ He}^{+}/\text{m}^2 + 1 \times 10^{23} \text{ D}^{+}/\text{m}^2\) and (b) SEQ: \(1.82 \times 10^{22} \text{ He}^{+}/\text{m}^2 + 1 \times 10^{24} \text{ D}^{+}/\text{m}^2\). In both (a) and (b) the single-species He\(^{+}\)-only and D\(^{+}\)-only fluences are the same as in the corresponding SEQ cases.
Figure 20 - TDS profiles for SEQ He\(^{+}\) followed by D\(^{+}\) irradiations of new-batch PCW at 700 K: for (a) SEQ: \(2 \times 10^{21}\) He\(^{+}/m^2 + 1 \times 10^{23}\) D\(^{+}/m^2\) and (b) SEQ: \(1.4 \times 10^{22}\) He\(^{+}/m^2 + 1 \times 10^{24}\) D\(^{+}/m^2\). In both (a) and (b) the single-species He\(^{+}\)-only and D\(^{+}\)-only fluences are the same as in the corresponding SEQ cases.

5.4 Sequential D\(^{+}\)-He\(^{+}\) Irradiations

5.4.1 Sequential D\(^{+}\)-He\(^{+}\) at 300 K
We will now discuss results from experiments in which specimens were irradiated sequentially with He\(^+\) and D\(^+\) ions, but in reverse order. PCW specimens were irradiated with D\(^+\) ions followed by He\(^+\) ions in a sequential fashion with similar fluences to those used in single ion irradiation experiments and the He\(^+\)-D\(^+\) sequential experiments. For the 300 K case, PCW specimens were first irradiated with D\(^+\) fluences of \(1 \times 10^{23}\) (old-batch) or \(1 \times 10^{24}\) D\(^+\)/m\(^2\) (new-batch) followed by He\(^+\) fluences of \(1 \times 10^{21}\) or \(1.35 \times 10^{22}\) He\(^+\)/m\(^2\), respectively. Fluxes were on the order of \(\sim 2.5 – 4.5 \times 10^{19}\) D\(^+\)/m\(^2\)s and ranged from \(6 \times 10^{17}\) to \(5.6 \times 10^{18}\) He\(^+\)/m\(^2\)s (using the LIS accelerator for the higher-fluence case). Results from the TDS analysis are presented in Figure 21. We generally observed that He inventory was not significantly affected, while there was a noticeable reduction in D retention. These observations are qualitatively consistent with results reported by Hino [72] in which he observed a 50 % reduction in hydrogen inventory when sequentially irradiating a PCW specimen with 1.7 keV H\(^+\) ions to a fluence of \(5 \times 10^{22}\) H\(^+\)/m\(^2\) followed by 5 keV He\(^+\) ions to a fluence of \(5 \times 10^{21}\) He\(^+\)/m\(^2\). We will discuss possible mechanisms while drawing comparisons with Lee’s results [11].

**D Trapping:**

Similar to Lee [11], the greatest reduction in D inventory is observed in the higher temperature 610 – 660 K peak, with slightly different behavior for the higher-fluence case. Recall from previous discussions that the 610 – 660 K peak is associated with D trapped at vacancies in the near surface, as well as extended defects beyond the near-surface region. If we assume that He is trapped in the near surface, as was shown by Lee [11] using ERD for nearly identical experimental parameters and materials, then it follows that the observed reduction in the 610 – 660 K peak arises from the de-trapping of D from near-surface vacancy sites. For the lower-fluence case there is a \(\sim 22\%\) reduction in D inventory, and a \(\sim 35\%\) reduction for the higher-fluence case. Therefore, we can attribute at least 22 % of the D inventory for D\(^+\)-only implants to D trapped at surface vacancies for a fluence of \(10^{23}\) D\(^+\)/m\(^2\), and at least 35 % for a fluence of \(10^{24}\) D\(^+\)/m\(^2\).
Figure 21 - TDS profiles for SEQ D⁺ followed by He⁺ irradiations of PCW at 300 K: for (a) SEQ: $1 \times 10^{23}$ D⁺/m² + $1 \times 10^{21}$ He⁺/m² (old-batch PCW) and (b) SEQ: $1 \times 10^{24}$ D⁺/m² + $1.35 \times 10^{22}$ He⁺/m² (new-batch PCW). In both (a) and (b) the single-species D⁺-only and He⁺-only fluences are the same as in the corresponding SEQ cases.

He Trapping:

Helium retention for post-implanted He⁺ is largely unaffected by pre-implanted D⁺. There is an increase in He inventory for both low- and high-fluence sequential irradiations, however, it is not considered to be significant. The most interesting observation is the relative increase in He
desorption in the higher temperature region around \( \sim 900 \) K. Since we have already presumed a mechanism whereby post-implanted He\(^+\) de-traps D at near surface vacancies, and desorption of He in the \( \sim 900 \) K region has been attributed to He\(_n\)V\(_m\)-type traps, then we can assume that He trapping occurs at existing vacancies after de-trapping D from these locations. Whether or not these act as trapping sites for the remaining D would require further investigation. Therefore, for 300 K sequential D\(^+\)-He\(^+\) irradiation we note that D\(^+\) pre-irradiation has little impact on He trapping except for perhaps creating vacancy sites for the eventual formation of He-vacancy complexes, and that post-implanted He\(^+\) de-traps D at near surface vacancy sites and could provide trapping sites for the remaining D, as was proposed by Lee et al. [39].

5.4.2 Sequential D\(^+\)-He\(^+\) Irradiations at 500 K

We now direct our attention to experiments in which new-batch PCW was irradiated sequentially with D\(^+\) ions followed by He\(^+\) ions at 500 K. PCW specimens were first irradiated with D\(^+\) fluences of \(1 \times 10^{23}\) or \(1 \times 10^{24}\) D\(^+\)/m\(^2\) followed by He\(^+\) fluences of \(2.6 \times 10^{21}\) or \(1.8 \times 10^{22}\) He\(^+\)/m\(^2\), respectively. Fluxes were on the order of \(3 - 5 \times 10^{19}\) D\(^+\)/m\(^2\)s and ranged from \(9 \times 10^{17}\) to \(2 \times 10^{18}\) He\(^+\)/m\(^2\)s (using the LIS accelerator for the higher-fluence case). Results from the TDS analysis are presented in Figure 22. The behavior at 500 K is similar to that observed at 300 K, but with greatly enhanced de-trapping of D following He\(^+\) post-irradiation.

D Trapping:

For single ion irradiation at 500 K we find that D preferentially desorbs in one higher temperature peak (\(\sim 650 - 700\) K); interpreted as D trapped at surface vacancy sites and throughout the bulk beyond the near-surface region. Following He\(^+\) post-implantation, the D inventory is decreased by \(\sim 70\%\) in the lower-fluence case, and nearly an order of magnitude for the higher-fluence case. If we accept ERD results from [39] to be valid in this case, which would imply that post-implanted He\(^+\) can only de-trap D from near-surface sites, then these results confirm the trapping model proposed for D\(^+\)-only irradiation of new-batch PCW at 500 K. The large reduction in D retention confirms that surface vacancies are the dominant trapping mechanism for these specimens at 500 K in contrast to previous measurements which observed D uniformly trapped through the entire specimen [18]. Since D retention is observed to saturate
for incident fluences $> 10^{23}$ D$^+/m^2$, and the reduction in D retention is greater for the higher-fluence case, then we can logically assume that post-irradiation with $\sim 2.5 \times 10^{21}$ He$^+/m^2$ is insufficient to de-trap all D trapped at surface vacancies. Whether or not D is completely de-trapped from surface vacancies in the higher-fluence case is unknown, but we can safely assume that at least $\sim 90\%$ of the D inventory for $10^{24}$ D$^+/m^2$ in new-batch PCW at 500 K is due to trapping at surface vacancy sites. All this simply confirms that D trapping in the bulk, and therefore D diffusion, is largely impeded in the new-batch PCW at 500 K. It is worth noting that the $\sim 500$ K peak, discussed in the previous section, is no longer observed. This can simply be attributed to the specimen temperature during irradiation, which leads to the elimination of D re-trapped with He prior to TDS.

He Trapping:

As was observed for the 300 K case, He retention is slightly increased following D$^+$ pre-irradiation, predominantly in the higher temperature range ($900 – 1200$ K for the lower-fluence case, and $\sim 900$ K for the higher-fluence case). This supports our previously discussed model in which more vacancy sites are created, and thus He-vacancy complex formation is enhanced. Therefore, we find at 500 K that the effects of pre-implanted D$^+$ on He and post-implanted He$^+$ on D are largely the same as those observed at room temperature. The results presented in this section further served to improve our understanding of the mechanisms responsible for the discrepancies between new- and old-batch PCW for D$^+$ retention at 500 K.

5.4.3 Sequential D$^+$-He$^+$ Irradiations at 700 K

For the sequential irradiation of new-batch PCW with D$^+$ followed by He$^+$ at 700 K we found results that were largely consistent with the interpretations discussed thus far. PCW specimens were first irradiated with D$^+$ fluences of $1 \times 10^{23}$ and $1 \times 10^{24}$ D$^+/m^2$ followed by He$^+$ fluences of $2 \times 10^{21}$ and $1.4 \times 10^{22}$ He$^+/m^2$, respectively. Fluxes were on the order of $\sim 2.4 – 3.6 \times 10^{19}$ D$^+/m^2$s and ranged from $9 \times 10^{17}$ to $8.5 \times 10^{18}$ He$^+/m^2$s (using the LIS accelerator for the higher-fluence case). The TDS release profiles are presented in Figure 23. As expected, no D retention was observed, consistent with results from single species irradiations, and He retention was observed to increase significantly in the higher-fluence case.
Figure 22 - TDS profiles for SEQ D⁺ followed by He⁺ irradiations of new-batch PCW at 500 K: for (a) SEQ: $1 \times 10^{23} \text{D}^+/\text{m}^2 + 2.55 \times 10^{21} \text{He}^+/\text{m}^2$ and (b) SEQ: $1 \times 10^{24} \text{D}^+/\text{m}^2 + 1.82 \times 10^{22} \text{He}^+/\text{m}^2$. In both (a) and (b) the single-species D⁺-only and He⁺-only fluences are the same as in the corresponding SEQ cases.

First, it is worth noting that we do observe some QMS signals at 4.026 amu, normally attributed to D₂. However, the size and temperature dependence of these signals is consistent with them arising due to the limits of the QMS resolution as outlined in section 3.3.2.
He Trapping:

Similar to the results discussed in the 300 K and 500 K cases, the sequential D⁺-He⁺ irradiations lead to an increase in He retention, with greater retention for larger incident fluences. For the higher-fluence case, the increase in He retention is predominantly localized in the ~ 900 K and ~ 1050 K peaks, which have been associated with He desorption from He-vacancy type traps. This is indicative, again, that D⁺ pre-irradiation increases He-vacancy complex formation. Comparing results of D⁺-He⁺ sequentially irradiated PCW specimens for 300, 500, and 700 K, we recognize a recurring pattern of increased He trapping at vacancy-type defects, with increasing effect at higher temperatures. This leads us to conclude that D⁺ irradiation on PCW samples creates vacancy-type damage in the lattice, with greater density of vacancy creation with increasing temperature. As discussed previously, the D⁺ energy is insufficient for damage creation, although there could be some displacements created by recoil impurities. It is not clear how such a mechanism could be more effective at higher temperatures.

5.5 Simultaneous D⁺-He⁺ Irradiations

In the previous two subsections we presented and discussed results from experiments of single ion (D⁺-only and He⁺-only), and sequential D⁺-He⁺, He⁺-D⁺ irradiated PCW samples. These experiments were performed to improve our understanding of the underlying mechanisms of He and D retention in PCW, as well as the effect of these ions on one another. In the final section of this chapter we apply the knowledge from these previous sections to analyze the fusion-relevant case of simultaneous D⁺-He⁺ irradiation of PCW.

5.5.1 Simultaneous D⁺-He⁺ Irradiations at 300 K

For the 300 K case, PCW specimens were simultaneously irradiated with D⁺ fluences of $1 \times 10^{23}$ (old-batch) or $1 \times 10^{24}$ D⁺/m² (new-batch) coupled with He⁺ fluences of $1.9 \times 10^{21}$ or $1.3 \times 10^{22}$ He⁺/m², respectively. Fluxes were on the order of ~ $3.5 - 5 \times 10^{19}$ D⁺/m²s and ranged from $6 \times 10^{17}$ to $7 \times 10^{17}$ He⁺/m²s. Results from the TDS analysis are presented in Figure 24. For these
experiments we find a unique behavior that was not observed for either of the sequential implantations. Generally, He retention was found to be similar for the He$^+$-only and SIM D$^+$-He$^+$ cases for lower-fluence implantations; a slight increase was seen for release temperature $> 1000$ K. However, for the higher-fluence case the SIM profile was decreased by about a factor of 2. Deuterium retention, on the other hand, was found to decrease in both the low- and high-fluence cases, although the relative reduction in D inventory was found to be greater for the lower fluence case.

**He Trapping:**

For the lower-fluence case (see Figure 24 (a)), simultaneously bombarding the specimen with He$^+$ and D$^+$ ions has relatively little impact on He trapping in PCW. The only change noted for this case is the increase in the ~ 1080 K peak, and the appearance of a peak/shoulder at ~ 1250 K, although these discrepancies are not significant if we consider the large variance inherent in our experiments.

In the higher-fluence case (see Figure 24 (b)), we observe drastically different behavior of He trapping when the specimen is simultaneously implanted with He$^+$ and D$^+$ ions. Instead of leading to an enhancement of He trapping, simultaneous D$^+$ bombardment at higher fluences appears to reduce He retention at essentially all temperatures, though we still observe a new high temperature peak at ~ 1200 K. These results lead us to speculate there are competing processes affecting the trapping of He under simultaneous D$^+$-He$^+$ irradiation. As has been suggested for the sequential D$^+$-He$^+$ irradiation case, D$^+$ ion bombardment creates vacancy-type damage in the lattice, thereby creating additional trapping centers for He$\text{He}_nV_m$ complex formation for post-implanted He$^+$ ions, hence the appearance of the ~ 1200 – 1250 K peak for both low- and high-fluences. On the other hand, as was observed in the case of sequential He$^+$-D$^+$ irradiation, D$^+$ ion bombardment also tends to de-trap He from the PCW, in some cases leaving behind low temperature peaks that are populated by He atoms that de-trapped from higher energy traps. This de-trapping effect appears to become increasingly important as the D$^+$ fluence increases. The results for simultaneous D$^+$-He$^+$ irradiation at 300 K suggest that enhanced He$\text{He}_nV_m$ complex formation due to D$^+$ bombardment is the dominant mechanism affecting He retention at low fluences, whereas de-trapping of He due to D$^+$ bombardment becomes the dominant process at higher fluences.
Figure 23 - TDS profiles for SEQ D\textsuperscript{+} followed by He\textsuperscript{+} irradiations of new-batch PCW at 700 K: for (a) SEQ: $1 \times 10^{23} \text{D}^+/\text{m}^2 + 2.04 \times 10^{21} \text{He}^+/\text{m}^2$ and (b) SEQ: $1 \times 10^{24} \text{D}^+/\text{m}^2 + 1.44 \times 10^{22} \text{He}^+/\text{m}^2$. In both (a) and (b) the single-species D\textsuperscript{+}-only and He\textsuperscript{+}-only fluences are the same as in the corresponding SEQ cases.

D Trapping:

Unlike for He, D retention is observed to decrease in both the low- and high-fluence cases of simultaneous D\textsuperscript{+}-He\textsuperscript{+} irradiation. This behavior is expected since, regardless of the order
of irradiation, D retention was found to decrease when sequentially implanted with He at 300 K. Comparing results for sequential D⁺-He⁺ and sequential He⁺-D⁺ irradiations at 300 K, we observe the most significant reduction in D retention when D⁺ is implanted following He⁺ pre-irradiation. We can therefore assume that the suppression of D retention by He presence in PCW, either by blocking diffusion or occupying trapping sites, has a more significant impact on D retention than that of post-implanted He⁺ de-trapping of bound D. At low fluence, the effect of simultaneously implanted He⁺ on the TDS profile of D is most like that observed for the case of sequential He⁺-D⁺. Similar to that case, there appears to be greater suppression of D desorption at higher temperatures, which was associated with pre-implanted He blocking the diffusion of D into the bulk and occupying vacancy sites, thereby reducing the number of trapping centers for DV complex formation. The remaining peak was shifted as well, implying the possibility that D is trapped in some modified configuration, possibly with He, as was discussed in section 5.4. For the higher-fluence case, again, the D desorption profile for simultaneous irradiation is similar to that of sequential He⁺-D⁺, with the exception that retention is ~ 2.4 times greater. For this case D is found to desorb in a single ~ 500 K peak, consistent with the interpretation provided for the lower-fluence case. Since most desorption of D is found in the lower temperature peak, and assuming D is trapped within ~ 35 nm of the surface (as was reported in [45]), we propose that D is trapped in the near-surface, in some modified configuration with He.

From these results we can draw a few conclusions about the trapping of D and He under simultaneous irradiation at room temperature. First, despite observing similar He inventories at low fluence, we notice a decrease in He retention when He⁺ is implanted simultaneously with D⁺ at higher fluences, which suggests there are competing mechanisms governing the trapping of He, with de-trapping by D⁺ irradiation becoming dominant at higher fluences. Second, D retention is not enhanced by simultaneous irradiation with He⁺ ions, and shows little dependence on He inventory. Finally, D was found to desorb at lower temperatures, indicating that D diffusion and DV complex formation is limited by the presence of He. As a consequence it is postulated that D traps preferentially with He since there are relatively few DV complexes for a second D to trap. While He retention is observed to increase only slightly for higher-fluence simultaneous irradiation, D retention nearly doubles. Therefore, the trapping of D at defects associated with HeₙVₘ complexes is fluence dependent, though there is little enhancement of HeₙVₘ complex formation.
The lower-fluence results in the present study are generally consistent with those presented by Lee et al. [45] in which the He desorption profile was found to be unaffected by co-irradiation with D⁺. Furthermore, the ~ 650 K D desorption peak was found to decrease and ERD analysis revealed D to be limited to within ~ 30-35 nm of the surface [45], leading to the conclusion that He⁺ co-irradiation blocks the diffusion of D and likely creates traps for D at secondary defects surrounding He-vacancy complexes. While the total D retention is found to be similar between SIM D⁺-He⁺ and D⁺-only irradiations in [45], which is contrary to the results of the present study (in which D retention was found to decrease by ~ 55 % in the low-fluence case, and ~ 15 % in the high-fluence case), the underlying mechanisms at work appear to be similar under simultaneous irradiations.

5.5.2 *Simultaneous D⁺-He⁺ Irradiations at 500 K*

For the 500 K case, new-batch PCW specimens were simultaneously irradiated with D⁺ fluences of 1 x 10^{23} or 1 x 10^{24} D⁺/m² coupled with He⁺ fluences of 2.5 x 10^{21} or 1.8 x 10^{22} He⁺/m², respectively. Fluxes were on the order of ~ 3.6 – 4.9 x 10^{19} D⁺/m²s and ranged from 6 x 10^{17} to 9 x 10^{17} He⁺/m²s. Results from the TDS analysis are presented in Figure 25. With the increase in irradiation temperature we observe preferential desorption of He at higher temperature peaks, indicating an increased enhancement of HeₙVₘ complex formation, with similar observations of decreased D retention.

He Trapping:

As was noted in the case of sequential D⁺-He⁺ irradiation, vacancy creation due to ion bombardment appears to be temperature dependent. At 500 K we notice greater desorption of He in the vicinity of ~ 1000 K, suggesting that He-vacancy complex formation is increased as compared to the 300 K case of simultaneous irradiation. Again, the co-bombardment with D⁺ ions leads to increased vacancy-type damage formation, which in turn provides additional trapping centers for He-vacancy complex formation. For both the low- and higher-fluence irradiation cases the greatest enhancement in He retention is found at ~ 1000 K, associated with HeₙV complexes identified in section 5.2.1. While there is expected to be increased vacancy creation due to D⁺ ion bombardment, HeₙV complex formation appears to dominate. It is not
clear why there is a greater tendency for He$_6$V complex formation, but the enhancement of desorption at 1000 K is greater than for the case of sequential D$^+$/He$^+$ irradiation, suggesting there is some interaction under co-bombardment that leads to increased vacancy creation in the lattice.

![Figure 24 - TDS profiles for SIM D$^+$/He$^+$ irradiations of PCW at 300 K: for (a) SIM: 1 x 10$^{23}$ D$^+$/m$^2 + 1.85 x 10^{21}$ He$^+$/m$^2$ (old-batch PCW) and (b) SIM: 1 x 10$^{24}$ D$^+$/m$^2 + 1.32 x 10^{22}$ He$^+$/m$^2$ (new-batch PCW). In both (a) and (b) the single-species D$^+$-only and He$^+$-only fluences are the same as in the corresponding SIM cases.](image-url)
D Trapping:

Also similar to the case of sequential D\textsuperscript+-He\textsuperscript+ irradiation, DV complex formation is greatly impeded due to co-bombardment with He\textsuperscript+ ions. For the lower-fluence case we observe a shift in the D desorption peak from ~ 700 K to ~ 600 K, with a ~ 35% reduction in D retention. For the higher-fluence case we observe a significant reduction in D retention (~ 75%), with no shift in temperature for the TDS peak. Since diffusion is thought to be significantly impeded in the contaminated new-batch Rembar PCW, these results are an accurate reflection of the effects of He\textsuperscript+ co-bombardment on DV complex formation, similar to the case for sequential D\textsuperscript+-He\textsuperscript+ irradiation (though total D inventories are greater for SIM D\textsuperscript+-He\textsuperscript+ at 500 K as compared to SEQ D\textsuperscript+-He\textsuperscript+ irradiations). It is possible that co-bombardment has a less significant impact on de-trapping DV complexes compared with He\textsuperscript+ post-irradiation, though it is more likely that incident D\textsuperscript+ ions are simply repopulating DV complexes, thereby offsetting the impeding/destructive effects of He\textsuperscript+ co-irradiation.

To conclude, we observe enhanced He-vacancy complex formation, predominantly in the form of He\textsubscript{6}V complexes. Simultaneous irradiation has a greater impact on vacancy creation, with the higher irradiation temperature enhancing these effects. For deuterium, we propose that simultaneous irradiation with He\textsuperscript+ both impedes the formation of and destroys DV complexes, although the continuous irradiation with D\textsuperscript+ ions repopulates DV complexes thereby increasing D retention as compared to the case of SEQ D\textsuperscript+-He\textsuperscript+.

5.5.3 Simultaneous D\textsuperscript+-He\textsuperscript+ Irradiations at 700 K

For the 700 K case, new-batch PCW specimens were simultaneously irradiated with D\textsuperscript+ fluences of 1 x 10\textsuperscript{23} or 1 x 10\textsuperscript{24} D\textsuperscript+/m\textsuperscript{2} coupled with He\textsuperscript+ fluences of 2 x 10\textsuperscript{21} or 1.4 x 10\textsuperscript{22} He\textsuperscript+/m\textsuperscript{2}, respectively. Fluxes were on the order of ~ 3.6 – 4.9 x 10\textsuperscript{19} D\textsuperscript+/m\textsuperscript{2}s and ranged from 6 x 10\textsuperscript{17} to 9 x 10\textsuperscript{17} He\textsuperscript+/m\textsuperscript{2}s. Results from the TDS analysis are presented in Figure 26. As has been the case for all experiments at 700 K, there is no D retention observed, and so the following discussion will focus on the effects of D\textsuperscript+ co-bombardment on He retention.

He Trapping:
The TDS profile shape is strikingly similar to those obtained for simultaneous D\(^+\)-He\(^+\) irradiation at 300 K and 500 K. Again, we observe an increased relative effect on He retention at the higher temperature desorption peaks. Temperature distributions are consistent with the physical model proposed for enhancement of He-vacancy complex formation under simultaneous irradiation, though the relative increase is greater. These results, coupled with our observation for sequential D\(^+\)-He\(^+\) irradiation suggest that D\(^+\) ion-induced vacancy creation is temperature dependent, with increased effect as temperature increases. These results are inconsistent with those presented by Lee [11], which has been the case for the most part when considering He trapping. Since we observe significantly different trapping of He during He\(^+\)-only irradiation it is difficult to compare Lee’s [11] and our results. It is likely that the new-batch PCW has an effect on He trapping as well, and perhaps we would observe different behavior with the old-batch PCW.

5.6 Summary of Traps in Tungsten

To conclude this chapter on experimental results and discussion we will provide a brief summary of the “traps” in PCW accompanied by a table to classify them. From section 5.1 we observed that D generally desorbs in two TDS peaks, one at ~ 500 K and the other at ~ 650 K. The ~ 500 K peak was associated with surface adsorbed D, solute D, and a second D atom in a DV complex (in the near-surface region). The ~ 650 K peak was associated with the first D atom as part of the DV complex in the near surface, and D trapped at dislocations and grain boundaries beyond the near-surface region (in the bulk). When irradiation temperature is increased to 500 K contributions from surface adsorbed D, solute D and a second D atom in a DV complex become less significant, with predominant trapping beyond the near-surface (as shown by NRA [18]); although this is not observed for our new-batch PCW specimens.
Figure 25 - TDS profiles for SIM $D^+\text{-He}^+$ irradiations of new-batch PCW at 500 K: for (a) SEQ: $1 \times 10^{23} D^+/m^2 + 2.54 \times 10^{21} \text{He}^+/m^2$ and (b) SEQ: $1 \times 10^{24} D^+/m^2 + 1.79 \times 10^{22} \text{He}^+/m^2$. In both (a) and (b) the single-species $D^+$-only and $\text{He}^+$-only fluences are the same as in the corresponding SIM cases.
Figure 26 - TDS profiles for SIM D⁺-He⁺ irradiations of new-batch PCW at 700 K: for (a) SEQ: 1 x 10²³ D⁺/m² + 1.96 x 10²¹ He⁺/m² and (b) SEQ: 1 x 10²⁴ D⁺/m² + 1.39 x 10²² He⁺/m². In both (a) and (b) the single-species D⁺-only and He⁺-only fluences are the same as in the corresponding SIM cases.

From section 5.2 we observed that He generally desorbs in two or three broad TDS peaks, in the range of ~ 600 K, ~ 800 - 1000 K, and > 1050 K. Desorption at lower temperatures, ~ 600 K for this case, was interpreted to arise from He clusters at grain boundaries, at impurity sites, or along dislocation loops surrounding HeₜVₘ complexes. Desorption at > 950 K was associated with He trapping in some configuration with vacancies, with 950 K being associated
with HeₙV complexes formed by punching out a self-interstitial atom in the tungsten lattice, and higher temperature desorption (~ 1000 – 1400 K) either arising from He trapping at vacancy clusters, or lower occupancy (n < 6) HeₙV complexes. Lee et al. [39] determined that all He was trapped in the near-surface region of the PCW specimens for all irradiation experiments (~ 30 – 50 nm from the surface).

Under sequential He⁺-D⁺ irradiations, D was found to desorb at ~ 550 K (for 300 K irradiations) and at ~ 700 K with a shoulder at ~ 600 K (for 500 K irradiations). For 300 K irradiations it is postulated that the presence of He limits the diffusion of D into the bulk (as was shown with ERD for similar conditions [39]), meanwhile leading to a reduction in DV complex formation as incident D⁺ ion energy is preferentially lost in breaking apart HeₙVₘ complexes. The results for D inventory at 500 K are somewhat inconsistent with the trapping model that was proposed at 300 K. In this former case we observe similar and even increased D inventories under SEQ He⁺-D⁺ irradiation. It is postulated that pre-implanted He⁺ interacts with WC impurities (see section 5.1.2) in the near-surface in such a way that the diffusion-blocking effects of WC are reduced, or that more vacancy sites are available for DV complex formation due to He trapping with WC. He inventories were found to be significantly reduced following D⁺ post-irradiation, with relatively little He desorption observed in some cases (for 300 and 500 K irradiations) at ~ 550 K and 900 – 1100 K. It appears that D⁺ post-irradiation de-traps He from HeₙVₘ complexes and He clusters in the lattice with no discrimination. At 700 K, however, the de-trapping effects of D⁺ post-irradiation are less significant, leaving behind broad He desorption features at 800 – 1200 K, suggesting that some HeₙVₘ complexes survived.

Under sequential D⁺-He⁺ irradiations, He was generally found to desorb at ~ 600 K, ~ 800 – 1000 K, and in some cases at > 1050 K. He TDS profiles were found to be very similar under SEQ D⁺-He⁺ as in He⁺-only irradiations, and we expect these peaks are associated with the same processes discussed for the He⁺-only case. In some higher fluence experiments, however, peaks in the range of 900 – 1000 K were found to be larger than that observed in He⁺-only irradiations (implying there is increased HeₙVₘ complex formation). It was postulated that with increased fluence, D⁺ pre-bombardment is responsible for additional vacancy site creation, leading to an increase in HeₙVₘ complexes. D was found to desorb at ~ 550 – 600 K (at 300 K) and ~ 700 K (at 500 K). Post-implanted He⁺ was found to desorb surface bound D, providing an excellent measure of the relative amount of D atoms trapped in DV complexes. For our study,
these experiments helped in our interpretation of how D retention is different in new-batch PCW. At 500 K we essentially observed that > 90 % of D is de-trapped by He\(^+\) post-irradiation (for the high fluence case), which lead us to conclude D trapping beyond the near-surface is compromised in new-batch PCW, possibly due to the presence of WC detected on the surface [74].

Finally, under simultaneous irradiation we interpreted that competing mechanisms, discussed for sequential irradiation, are responsible for the trapping behavior of D and He. He was found to desorb at ~ 500 K, 900 – 1000 K, and > 1050 K, similar to that observed for SEQ D\(^+\)-He\(^+\). Similarly, desorption at 900 – 1000 K, and to a lesser extent at > 1050 K, was larger than that observed in the He\(^+\)-only case, suggesting that co-bombardment with D\(^+\) leads to an increase in He\(_n\)V\(_m\) complex formation, primarily in the form of He\(_6\)V complexes (associated with peaks at ~ 950 K). In fact, this enhancement was found to be greater for SIM D\(^+\)-He\(^+\) irradiations than for SEQ D\(^+\)-He\(^+\), suggesting that co-irradiation with D\(^+\) somehow leads to increased vacancy creation, or possibly has some alternative role in increasing He\(_n\)V\(_m\) complex formation. At 300 K, however, D\(^+\) co-irradiation was found to have opposing effects as a function of fluence. For the lower-fluence case, He inventories were found to be slightly enhanced, while at higher-fluence He inventories were lower than the He\(^+\)-only case. These results are suggestive of fluence-dependent competing processes of vacancy creation for enhanced He\(_n\)V\(_m\) complex formation and He de-trapping under co-irradiation with D\(^+\). D was found to desorb at ~ 550 – 600 K (at 300 K) and ~ 700 K (at 500 K). He\(^+\) co-irradiation was postulated to de-trap DV complexes as well as any additional D atoms in the DV complex, with D likely re-trapping in some new configuration with He (as suggested in [45]). Again, we find a significant decrease in D inventories for high fluence, 500 K irradiations, which likely results from the preferential de-trapping of DV complexes and the diffusion impeding effects of WC impurities and He\(^+\) co-irradiation. See Table 3 for a summary of traps in PCW.
<table>
<thead>
<tr>
<th>Irradiation</th>
<th>TDS peak</th>
<th>Nature of Trap</th>
<th>How Trap is Formed</th>
<th>Interpretation</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>D⁺-only</td>
<td>500 K</td>
<td>Surface adsorption; vacancy</td>
<td>Inherent; from D⁺ irradiation</td>
<td>D adsorbed at the surface or as a second D atom in a D₂V complex</td>
<td>[11] [27]</td>
</tr>
<tr>
<td>650 – 700 K</td>
<td>Vacancy; extended defects</td>
<td>D⁺ irradiation; inherent</td>
<td>D atom in a DV complex; at dislocations or along grain boundaries in the bulk</td>
<td>[27] [18] [53]</td>
<td></td>
</tr>
<tr>
<td>He⁺-only</td>
<td>600 K</td>
<td>Impurity; dislocation; vacancy</td>
<td>Inherent; inherent; He⁺-irradiation</td>
<td>He cluster trapped at impurities, along dislocations, or at secondary defects created by HeₙVₘ complex</td>
<td>[39]</td>
</tr>
<tr>
<td>800 – 1000 K</td>
<td>Vacancy</td>
<td>He⁺-irradiation</td>
<td>He⁺ cluster punching out SIA to form HeₙV complex</td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td>&gt; 1050 K</td>
<td>Vacancy</td>
<td>He⁺-irradiation</td>
<td>He trapped at vacancy cluster or HeₙVₘ complex formation where n &lt; 6 and m = 1</td>
<td></td>
<td>[39] [35]</td>
</tr>
<tr>
<td>SEQ He⁺-D⁺</td>
<td>D: ~ 500 K (RT)</td>
<td>Surface adsorption; vacancy</td>
<td>Inherent; D⁺/He⁺-irradiation</td>
<td>Surface adsorbed D or as a second D atom in a D₂V complex</td>
<td>[27] [39]</td>
</tr>
<tr>
<td>D: ~ 650 – 700 K (for 500 K irradiation)</td>
<td>Vacancy; extended defects</td>
<td>D⁺/He⁺-irradiation</td>
<td>DV complex and D trapping in the bulk along dislocations or grain boundaries (He impedes diffusion of D into bulk and blocks vacancy sites)</td>
<td>[27] [18] [39]</td>
<td></td>
</tr>
<tr>
<td>He: ~ 500 and 1000 K (RT)</td>
<td>Impurity; dislocation; vacancy</td>
<td>Inherent; inherent; He⁺-irradiation</td>
<td>Same interpretation as in He⁺-only case with He clusters impeding diffusion of D and HeₙVₘ complexes blocking DV formation</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>He: ~ 800 – 1200 K</td>
<td>Vacancy</td>
<td>He⁺-irradiation</td>
<td>Remaining HeₙVₘ complexes that survived D⁺ post-irradiation</td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td>SEQ D⁺-He⁺</td>
<td>D: ~ 500 – 600 K (RT)</td>
<td>HeₙVₘ complex; vacancy</td>
<td>D⁺/He⁺-irradiation</td>
<td>New trap configuration at defects created by HeₙVₘ complexes; second D atom in D₂V</td>
<td>[39] [27]</td>
</tr>
<tr>
<td>D: ~ 700 K (500 K)</td>
<td>Vacancy; extended defects</td>
<td>D⁺-irradiation; inherent</td>
<td>D atom from DV complex (de-trapped by He⁺); limited amount of D in bulk at extended defects</td>
<td>[27] [39]</td>
<td></td>
</tr>
<tr>
<td>He: 500 – 600 K</td>
<td>Impurity; extended defects; vacancy</td>
<td>Inherent; inherent; D⁺/He⁺-irradiation</td>
<td>He clusters trapped at extended defects, impurities or defects created by HeₙVₘ</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>He: 800 – 1200 K</td>
<td>Vacancy</td>
<td>D⁺/He⁺-irradiation</td>
<td>HeₙVₘ complex formation (enhanced by D⁺ pre-irradiation – creation of additional vacancies)</td>
<td></td>
<td></td>
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<tr>
<td>SIM D⁺-He⁺</td>
<td>D: 550 – 600 K</td>
<td>HeₙVm complex; vacancy</td>
<td>D⁺/He⁺-irradiation</td>
<td>New trap configuration at defects created by HeₙVm complexes; second D atom in D₂V</td>
<td>[39] [45] [27]</td>
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</tr>
<tr>
<td>D ~ 700 K</td>
<td>Vacancy; extended defects</td>
<td>D⁺/He⁺-irradiation</td>
<td>D atom from DV complex (de-trapped/impeded trapping by He⁺); limited amount of D in bulk at extended defects</td>
<td>[27] [45]</td>
<td></td>
</tr>
<tr>
<td>He: ~ 500 – 800 K</td>
<td>Impurity; extended defects; vacancy</td>
<td>Inherent; inherent; D⁺/He⁺-irradiation</td>
<td>He clusters trapped at extended defects, impurities or defects created by HeₙVm (reduced under D⁺ co-irradiation)</td>
<td>[39]</td>
<td></td>
</tr>
<tr>
<td>He: 800 – 1200 K</td>
<td>Vacancy</td>
<td>D⁺/He⁺-irradiation</td>
<td>HeₙVm complex formation (enhanced by D⁺ co-irradiation – creation of additional vacancies – greater effect than for SEQ D⁺-He⁺)</td>
<td></td>
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</tbody>
</table>

*Table 3 – Summary of traps in PCW under single species and dual species ion irradiations.*
Chapter 6 Conclusion

D Trapping for D\(^{+}\)-Only Irradiations:

PCW foil specimens (for both the old- and new-batch PCW from Rembar) were irradiated with 500 eV-D\(^{+}\) ions at 300, 500, and 700 K. Deuterium was found to desorb at ~ 500 K and ~ 650 K for the case of 300 K irradiations, and ~ 700 K for the 500 K irradiation cases. No D was retained for 700 K implantations. Reviewing the literature and drawing logical deductions from the TDS data, we propose that the higher temperature peaks (at ~ 650 K and ~ 700 K) are associated with D trapped at vacancy sites in the near surface, and beyond the near-surface region, along grain boundaries and dislocations. The lower temperature peak (only observed for the 300 K irradiation cases) is associated with surface adsorbed D and a second D atom at a DV complex. When the irradiation temperature is increased to 500 K, we observe decreased retention for all fluences, in agreement with some but not all published results. Comparing D retention for \(10^{24} \text{D}^{+}/\text{m}^{2}\) at 500 K for both new and old-batch PCW we observe a clear discrepancy in D trapping behavior. We postulate that the new-batch PCW contains some form of impurity, with preliminary evidence indicating the presence of tungsten-carbide (WC) in the surface layer of pre-annealed and post-annealed virgin specimens [74]. The WC layer in the specimens is thought to impede the diffusion of D into the bulk, with additional C impurities in the bulk potentially impeding the trapping of D by occupying trapping sites. With this proposed mechanism we could draw conclusions about the trapping behavior of D at 500 K. It is evident that bulk trapping of D is less dominant at lower fluences, with reasonably good agreement between new and old-batch PCW for this case. At higher fluences there is an order of magnitude discrepancy between our results with the new-batch PCW and those published in the literature, suggesting that the majority of D is trapped beyond the near surface for higher fluence implants at 500 K in uncontaminated PCW.

He Trapping for He\(^{+}\)-Only Irradiations:

Helium was also implanted into PCW specimens at energies of 500 eV/He\(^{+}\) ion and at temperatures of 300 K, 500 K and 700 K. The total retention values for He appeared to be temperature and fluence dependent, though to a significantly smaller degree than were observed for D. In general, it was found that He inventories decreased as the temperature was increased,
and as intuition would suggest, He inventories increased with greater incident He\(^+\) fluence. In general, He was found to desorb over a larger range of temperatures in TDS analyses, with many peaks and shoulders. Based on the current results as well as published studies we propose trapping mechanisms for peaks at specific temperatures and/or temperature ranges. Lower temperature peaks in the range \(~ 500 – 800 \text{ K}\) have been associated with He trapping at impurity sites in the lattice, with lower temperature \(500 – 600 \text{ K}\) desorption also being associated to He clusters along grain boundaries, within the lattice, and at dislocations surrounding \(\text{He}_n\text{V}_m\) complexes. Peaks in the range of \(~ 900 – 1500 \text{ K}\) are associated with \(\text{He}_n\text{V}\) complexes in the specimens, with greater occupancy for lower temperature desorption. Based on results from [11] and [35] we have assigned peaks in the ranges of \(900 – 950 \text{ K}, 1200 – 1250\text{K}, 1300 – 1350 \text{ K}\) and \(~ 1450 \text{ K}\) to be associated with the simultaneous desorption of a \(\text{He}_n\text{V}\) complex, and as the first, second and third He atoms from a \(\text{He}_3\text{V}\) complex, respectively. Increasing He\(^+\) fluence for all irradiation temperatures had the general effect of increasing He inventories, and increased desorption at lower temperatures. We attribute this to preferential high occupancy \(\text{He}_n\text{V}_m\) formation (by punching out of self-interstitial atom), and increased He cluster formation (as the intermediate temperatures do not appear to be substantially increased). As the temperature is increased, we observe a general tendency of reduced desorption at lower temperatures (likely because these lower energy traps desorb during irradiation, but may be re-populated by He desorbing from higher energy traps once the specimen cools). Since the He inventories decrease with increasing temperature, we cannot conclude that \(\text{He}_n\text{V}_m\) formation is enhanced by increased irradiation temperature.

**Sequential He\(^+\)-D\(^+\) Irradiations:**

We then studied the interaction of D and He under dual He\(^+\)-D\(^+\) irradiation by comparing TDS profiles to the single species irradiation cases. Though not expected to occur in an actual tokamak environment, we performed experiments where specimens were irradiated sequentially with He\(^+\) first and D\(^+\) second, as well as in reverse order. These additional experiments were performed to gain additional insight into the actual mechanisms that govern the interactions of D and He under simultaneous irradiations. For the sequential He\(^+\)-D\(^+\) case it was generally found that He was desorbed by D\(^+\) post-irradiation, with little discrimination of He traps. However, as irradiation temperature is increased we find a larger fraction of He to desorb at higher
temperatures. This effect arises from the desorption during irradiation and D\textsuperscript{+} post-irradiation de-trapping of the lower energy traps. As fluence was increased this de-trapping effect was amplified. From the alternative perspective, He\textsuperscript{+} pre-irradiation decreases D retention due to occupancy of surface vacancy sites and blocking the diffusion of D into the bulk for the case of 300 K irradiation (since greatest reduction in D retention was observed in \(\sim 600 \text{–} 700\) K range, which is associated to D trapping at vacancy sites or beyond the near-surface region). The remaining \(\sim 500\) K desorption peak was likely related to the second D atom of a D\textsubscript{2}V complex to a small degree, with some non-vacancy related trapping at surface sites to account for the decrease in desorption of DV complexes. Interestingly, for the 500 K irradiation case, D retention was found to increase due to He\textsuperscript{+} pre-irradiation. Considering the proposed diffusion blocking effects of WC in the new-batch PCW we postulate that this increased retention arose from the interaction of He\textsuperscript{+} with WC impurities, thereby reducing their diffusion blocking effect on D. As per expectations, no D retention was observed at 700 K, though D\textsuperscript{+} post-irradiation still led to de-trapping of He.

**Sequential D\textsuperscript{+}-He\textsuperscript{+} Irradiations:**

For the case of sequential D\textsuperscript{+}-He\textsuperscript{+} irradiations some interesting behavior was observed. In all cases D retention was reduced following He\textsuperscript{+} post-irradiation, suggesting that He de-traps D. There appears to be little discrimination in the decreased retention at particular temperatures, though it is postulated that He\textsuperscript{+} post-irradiation de-traps D at vacancy-related traps (second and first D atoms of a D\textsubscript{2}V complex), as well as other surface sites. ERD results from [39] confirm that He does not reach D atoms trapped beyond the near-surface region. At 500 K we observe the greatest reduction in D retention for the high-fluence case (which is the result that differs the most from those in the literature). We postulate that the diffusion blocking effects of WC on D\textsuperscript{+} results in D trapping predominantly at surface vacancy sites, and since He\textsuperscript{+} post-irradiation preferentially de-traps surface bound D then we observe a large reduction in total D retention. This gives us an accurate measure of the effect He\textsuperscript{+} post-irradiation has on de-trapping of D from surface traps, leading to at least 90% reduction in D bound at vacancy sites, and also confirms our suspicions that D diffusion into the bulk is greatly reduced in the new-batch PCW (since this contribution would generally remain unaffected by He\textsuperscript{+} post-irradiation). D\textsuperscript{+} pre-irradiation in fact leads to enhanced He\textsubscript{n}V\textsubscript{m} complex formation under all irradiation conditions, with
preferential increase of high occupancy \((n = 6, m = 1)\) \(\text{He}_n\text{V}_m\) complexes in the temperature ranges of \(\sim 900 – 1200\) K. We propose that \(\text{D}^+\) pre-irradiation creates an increased amount of vacancy sites for \(\text{He}_n\text{V}_m\) formation.

**Simultaneous \(\text{D}^+\)-\(\text{He}^+\) Irradiations:**

In experiments in which specimens were simultaneously irradiated with \(\text{D}^+\) and \(\text{He}^+\) ions we observed many competing mechanisms that were independently observed in the sequential irradiation experiments. For the 300 K case, there was increased lower occupancy \(\text{He}_n\text{V}_m\) complex formation/vacancy cluster trapping, associated with either \(\text{He}_3\text{V}\) or \(\text{He}_2\text{V}\) complexes or He bound at vacancy clusters. Again, as was discussed in section 5.5.1, this was postulated to arise from an increase in vacancy creation from \(\text{D}^+\) co-bombardment. Furthermore, competing processes of de-trapping of He and increased \(\text{He}_n\text{V}_m\) complex formation was thought to arise during \(\text{D}^+\) co-irradiation. Similarly, \(\text{He}^+\) co-bombardment led to decreased DV complex formation, likely due to increased occupancy of vacancy sites by He and de-trapping of bound D. At 500 K and 700 K we observe a preferential increase of \(\text{He}_n\text{V}_m\) complex formation (predominantly for \(\text{He}_6\text{V}\) complexes), leading us to postulate that \(\text{D}^+\) co-bombardment creates additional vacancy sites for \(\text{He}_n\text{V}_m\) complex formation. For the 500 K case, the D retention was found to decrease again, with more dramatic impact at higher fluences. For this case we observed a preferential decrease in higher temperature desorption, which for new-batch PCW is believed to be associated with DV complexes. Therefore, we conclude that \(\text{D}^+\)-\(\text{He}^+\) co-bombardment leads to decreased D bound at vacancy sites due to de-trapping of existing DV complexes by \(\text{He}^+\), and pre-occupancy of vacancy sites by He that would otherwise trap D atoms.
REFERENCES


[46] The Rembar Company, LLC., Statement of Quality, .001”x6”xRL Tungsten Foil, Serial # P506, Purchase Order # 10104, Acknowledgement # R70844.