Deuterium retention in radiation damaged tungsten exposed to high-flux plasma
\'t Hoen, M.H.J.

Citation for published version (APA):
\'t Hoen, M. H. J. (2014). Deuterium retention in radiation damaged tungsten exposed to high-flux plasma
Nuclear fusion has the potential for large-scale sustainable energy production. Currently, the most promising fusion reactor concept is a tokamak. Scientists and engineers from all over the world are collaborating on building the next-generation fusion reactor: ITER. A critical component of the ITER design is the exhaust, the divertor. The material of choice for the divertor is tungsten in order to be able to withstand the extreme heat and particle fluxes that it experiences during operation. One of the main challenges for ITER operation is the tritium retention in the reactor wall. For safety and efficiency reasons, only a limited in vessel tritium inventory is allowed. High energy neutrons, produced in the fusion process, will create damage in the tungsten crystal lattice and enhance the tritium retention in tungsten. This thesis describes the investigation of deuterium retention in radiation damaged tungsten after high-flux plasma exposure. Our results suggest that tritium retention in the divertor of ITER will not be problematic, even when damage creation by neutrons is included.

Deuterium retention in radiation damaged tungsten exposed to high-flux plasma

Rianne ’t Hoen
Deuterium retention in radiation damaged tungsten exposed to high-flux plasma

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Universiteit van Amsterdam op gezag van de Rector Magnificus prof. dr. D.C. van den Boom ten overstaan van een door het college voor promoties ingestelde commissie, in het openbaar te verdedigen in de Agnietenkapel op dinsdag 6 mei 2014, te 14:00 uur

door

Maria Hendrika Johanna ’t Hoen

geboren te Arnhem
Promotiecommissie

promotor: prof. dr. A.W. Kleijn
co-promotor: dr. P.A. Zeijlmans van Emmichoven
overige leden: dr. M. Mayer
dr. H. Schut
prof. dr. M.S. Golden
prof. dr. G. Rothenberg
prof. dr. T. Gregorkiewicz
prof. dr. ir. M.C.M. van de Sanden

Faculteit der Natuurwetenschappen, Wiskunde en Informatica

’t Hoen, Maria Hendrika Johanna
Deuterium retention in radiation damaged tungsten exposed to high-flux plasma
ISBN: 978-94-6259-130-1

The work described in this dissertation, supported by the European Communities under the Contract of Association between EURATOM/FOM, was carried out within the framework of the European Fusion Programme with financial support of the ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek’ (NWO). The views and opinions expressed herein do not necessarily reflect those of the European Commission. The research was carried out at the FOM Institute DIFFER - Dutch Institute for Fundamental Energy Research, in Nieuwegein, the Netherlands.

© Copyright 2014 Rianne ’t Hoen
Typeset in \LaTeX\ 2ε
# Contents

## Summary

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>v</td>
<td></td>
</tr>
</tbody>
</table>

## Samenvatting

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ix</td>
<td></td>
</tr>
</tbody>
</table>

## 1 Introduction

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Nuclear fusion</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Deuterium retention in tungsten</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>List of publications</td>
<td></td>
</tr>
</tbody>
</table>

## 2 Theoretical background

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Plasma composition</td>
<td></td>
</tr>
<tr>
<td>2.1.1</td>
<td>Ion flux</td>
<td></td>
</tr>
<tr>
<td>2.1.2</td>
<td>Ion impact energy</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>Plasma-surface interactions</td>
<td></td>
</tr>
<tr>
<td>2.2.1</td>
<td>Deuterium back-flux</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>Deuterium retention</td>
<td></td>
</tr>
<tr>
<td>2.3.1</td>
<td>Solubility</td>
<td></td>
</tr>
<tr>
<td>2.3.2</td>
<td>Diffusivity</td>
<td></td>
</tr>
<tr>
<td>2.3.3</td>
<td>Deuterium trapping</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>Defect creation</td>
<td></td>
</tr>
<tr>
<td>2.4.1</td>
<td>Ion versus neutron irradiation</td>
<td></td>
</tr>
<tr>
<td>2.4.2</td>
<td>Plasma damage</td>
<td></td>
</tr>
</tbody>
</table>

## 3 Experiment

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Preparation tungsten material</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Damage creation - W&lt;sup&gt;4+&lt;/sup&gt; pre-irradiation</td>
<td></td>
</tr>
<tr>
<td>3.2.1</td>
<td>SRIM simulation details</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Deuterium exposure - Pilot-PSI</td>
<td></td>
</tr>
<tr>
<td>3.3.1</td>
<td>Diagnostics</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Target analysis</td>
<td></td>
</tr>
<tr>
<td>3.4.1</td>
<td>Nuclear reaction analysis</td>
<td></td>
</tr>
<tr>
<td>3.4.2</td>
<td>Thermal desorption spectroscopy</td>
<td></td>
</tr>
<tr>
<td>3.4.3</td>
<td>Surface imaging</td>
<td></td>
</tr>
<tr>
<td>3.4.3.1</td>
<td>scanning electron microscopy and focused ion beam</td>
<td></td>
</tr>
<tr>
<td>3.4.4</td>
<td>Positron annihilation Doppler broadening</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>TMAPP</td>
<td></td>
</tr>
</tbody>
</table>

## i
## Contents

### 4 Saturation of deuterium retention in self-damaged tungsten 35

4.1 Introduction .................................................. 36
4.2 Experiment ..................................................... 36
4.2.1 Target preparation ........................................... 36
4.2.2 Damage creation - $W^{4+}$ irradiation .................. 37
4.2.3 Deuterium plasma exposure ................................ 38
4.2.4 Nuclear reaction analysis .................................. 39
4.2.5 Thermal desorption spectroscopy ......................... 39
4.3 Results .......................................................... 40
4.3.1 Nuclear reaction analysis .................................. 40
4.3.2 Thermal desorption spectroscopy ......................... 42
4.4 Model ............................................................ 43
4.5 Discussion ...................................................... 44
4.6 Conclusions ..................................................... 45

### 5 Reduced deuterium retention at high tungsten surface temperature 47

5.1 Introduction .................................................... 48
5.2 Experiment ...................................................... 49
5.3 Results .......................................................... 51
5.3.1 X-ray photoelectron spectroscopy ....................... 51
5.3.2 Nuclear reaction analysis .................................. 52
5.3.3 Thermal desorption spectroscopy ......................... 54
5.3.4 Positron annihilation Doppler broadening ............... 55
5.3.5 TMAP7 simulations ......................................... 58
5.4 Discussion ...................................................... 60
5.5 Conclusions ..................................................... 61
5.6 Role of vacancy mobility in deuterium retention in W at high surface temperature ..................................... 63
5.6.1 Experiment .................................................... 63
5.6.2 Results and discussion ..................................... 65
5.6.3 Conclusions .................................................. 67

### 6 Strongly reduced penetration of atomic deuterium in radiation-damaged tungsten 69

6.1 Introduction .................................................... 70
6.2 Experiment ...................................................... 71
6.3 Results .......................................................... 72
6.4 Discussion ...................................................... 73
6.5 Conclusions ..................................................... 75

### 7 Surface morphology and deuterium retention at high-flux deuterium plasmas 77

7.1 Introduction .................................................... 78
7.2 Experiment ...................................................... 78
Deuterium retention in radiation damaged tungsten exposed to high-flux plasma

Summary

Thermonuclear fusion has the potential of large-scale sustainable energy production. A large amount of energy is released during nuclear fusion of the hydrogen isotopes deuterium and tritium into helium and neutrons. In a plasma of deuterium and tritium that is heated to temperatures of 150 million degrees Celsius the Coulomb repulsion can be overcome, so that fusion can occur. The most advanced method for achieving these conditions on earth is via magnetic confinement of hot plasma in a toroidal geometry: ‘tokamak’. ITER is a scientific research machine in such a tokamak configuration and is being built at this moment to demonstrate that fusion is a feasible energy source.

An important component of ITER is the divertor, the ‘exhaust’. Its function is to extract impurities and helium from the plasma. The divertor has to be capable of withstanding heat and particle fluxes of respectively $10\,\text{MW}\,\text{m}^{-2}$ and $10^{24}\,\text{m}^{-2}\,\text{s}^{-1}$. This high-flux ITER divertor regime cannot be accessed by present-day tokamaks. The linear plasma generator Pilot-PSI, is able to create such extreme plasmas. Furthermore, a linear plasma generator has the advantage over tokamaks that it is very well accessible, relatively quick and that its parameters can be tuned independently. This makes them very suitable for investigation of the interaction between plasma and material.

Recently, it has been decided that ITER will operate with a full tungsten divertor from the start. Tungsten is a beneficial material to use in the divertor, because of its good thermal properties and high sputtering threshold for hydrogen. Tritium retention in the reactor wall is one of the key concerns of ITER. Tritium is radioactive and has a half-life of 12.3 year. For safety considerations, the tritium inventory limit that is allowed in ITER is set at 700 g. The tungsten divertor will be subjected to high energy neutrons produced by the fusion reaction. These neutrons create defects in the metal lattice that act as traps for tritium and enhance tritium retention significantly.

The underlying motivation of our work is to predict tritium retention in neutron damaged tungsten under high-flux plasma exposure. Since tritium is radioactive, deuterium, which has similar chemical properties, was employed to investigate hydrogen retention. High-energy tungsten ions were used instead of neutrons for damaging tungsten since the damage is similar and since they do not activate the material. The main topic of this PhD project was to investigate deuterium retention in pre-irradiation damaged tungsten under high-flux plasma bombardment. The three important aspects of the research are: pre-irradiation damage, high-flux plasma exposure and deuterium retention correlated to surface modifications.
Deuterium retention in radiation damaged tungsten was studied by exposing polycrystalline tungsten samples with different levels of pre-irradiation damage to high-flux deuterium plasmas. The experiments were performed at a relatively low temperature of ∼500 K. The retained deuterium was found to saturate at a concentration of 1.4 at.%. This saturation originates in the high energy ion damaging mechanism and was not affected by the high plasma flux. At saturation, the concentration of vacancies and interstitials is at such a high level that every newly created vacancy or interstitial automatically recombines with one already present in the material. This was shown by using a simple geometric model that assumes that the saturation solely originates in the tungsten pre-irradiation and that explains it in terms of overlapping saturated volumes. The average saturated volume per incident MeV ion amounts to $3 \times 10^4 \text{nm}^3$.

The tungsten divertor tiles of ITER are predicted to operate at surface temperatures of around 600 – 1300 K. The above experiment was therefore also carried out in the temperature regime of 800 – 1200 K, which is above the temperature where vacancies in tungsten become mobile (>550 K). The deuterium retention saturated at the same damage level, but the absolute level of deuterium retention was strongly decreased. This reduction originates in the mobility of vacancies that results in their annealing and clustering. The contribution of increased deuterium mobility that causes a lower occupation level of the defects was found to be small.

We studied the effect of fluence (plasma flux multiplied by exposure time) on deuterium retention and found that only very low fractions ($10^{-5} – 10^{-7}$) of deuterium from the incoming plasma beam are retained in tungsten. The radiation-damaged material was used to monitor the diffusion in tungsten. To explain the low penetration, we proposed a mechanism in which the deuterium atoms form a chemisorbed layer at the surface. Incoming deuterium ions (∼5 eV) do not directly enter the material, but interact with the deuterium covering the surface. Energy is redistributed between incoming ions and atoms at the surface, so that they cannot directly penetrate. A thermally activated process is needed to introduce chemisorbed deuterium into the tungsten.

The experiments so far were carried out at self-biased conditions. ITER is anticipated to operate in detached plasma mode, which corresponds indeed to low energy ion energies. However, part of the divertor will experience higher energies as well. We therefore investigated high-flux plasma exposure while the target was biased at a certain negative potential thereby accelerating the ions. It is known that high energy deuterium ions can create surface modifications in tungsten. A comparative study was made to investigate the explicit effects of plasma flux, plasma fluence (time) and pre-irradiation damage on surface modifications and deuterium retention. We distinguished three types of surface modifications: blisters originating in inter-granular cavities, protrusions arising from intra-granular cavities and structures on the nanometer scale. Micrometer-sized blisters form at high-flux plasma exposure and grow in size and quantity with exposure time. We found that pre-damaging with MeV ions decreases the formation of these blisters. On the other hand, protrusions, which are typically hundreds of nanometer in size, were enhanced after exposure to high-flux (∼$10^{24} \text{m}^{-2} \text{s}^{-1}$) plasmas.
In the research described above, all experiments were performed on polycrystalline tungsten. Present-day tokamaks like JET also make use of thin tungsten films. The retention properties are however largely unknown. Also, for fundamental studies of retention behaviour and diffusion in low density tungsten, layers with varying tungsten density and crystallite sizes are of interest. Therefore, we exposed micrometer thick pulsed laser deposited layers to high-flux plasmas. These thin films generally withstand the interaction maintaining overall integrity. However, thin films show considerably more retained deuterium than bulk polycrystalline tungsten, even compared to the pre-damaged tungsten.

In conclusion, the retained fraction of deuterium in polycrystalline tungsten after exposure to high-flux (~$10^{24} \text{ m}^{-2} \text{s}^{-1}$) plasmas is very low. Pre-damaging with MeV ions and increase of the energy of the plasma ions both enhance the retention by approximately an order of magnitude each. The overall retention level though, remains low.
Deuteriumopslag in beschadigd wolfram blootgesteld aan hoge plasma flux

Samenvatting

Kernfusie heeft de potentie om op grote schaal duurzame energie te produceren. Een grote hoeveelheid energie komt vrij tijdens de fusie van de waterstofisotopen deuterium en tritium in helium en neutronen. Wanneer een plasma van deuterium en tritium wordt verwarmd tot een temperatuur van 150 miljoen graden Celsius, kan de Coulomb afstoting worden overwonnen en fusie plaatsvinden. Deze condities kunnen worden bereikt door magnetische opsluiting van plasma in een donut-vormige geometrie: de tokamak. ITER is een wetenschappelijke onderzoeksmachine, die zal werken in zo’n tokamak configuratie, en wordt op dit moment in Zuid Frankrijk gebouwd.

Een belangrijk onderdeel van ITER is de divertor, de uitlaat. Haar functie is om onzuiverheden zoals helium uit het plasma te halen. De divertor moet bestand zijn tegen een extreem hoge stroom, flux, van warmte en deeltjes van respectievelijk 10 MW m\(^{-2}\) en \(10^{24}\) m\(^{-2}\) s\(^{-1}\). Deze hoge-flux divertor condities kunnen niet worden bereikt met heden-daagse tokamaks. De lineaire plasma generator Pilot-PSI is wel in staat om dergelijke extreme plasma’s te creëren. Verder heeft een lineaire plasma generator het voordeel boven een tokamak dat hij goed toegankelijk is, metingen relatief snel kunnen worden uitgevoerd en dat de parameters onafhankelijk kunnen worden veranderd. Dit maakt lineaire plasma generatoren zeer geschikt voor onderzoek naar de interactie tussen plasma en materiaal.

Onlangs is besloten dat ITER vanaf het begin zal werken met een wolfram divertor. Wolfram is een gunstig materiaal voor gebruik in de divertor, vanwege de goede thermische eigenschappen en hoge drempel voor sputtering. Een van de belangrijkste zorgen voor ITER is tritiumopslag in de wand van de reactor. Tritium is radioactief en heeft een halfwaardetijd van 12.3 jaar. Uit veiligheidsverwogenen is de maximale hoeveelheid tritium, die in de machine aanwezig mag zijn, vastgesteld op 700 g. Onbeschadigd wolfram materiaal slaat weinig tritium op. Echter, de wolfram divertor wordt blootgesteld aan hoog energetische neutronen geproduceerd door de fusiereactie, die defecten in het metaalrooster creëren waar het tritium in gevangen kan worden. Hierdoor wordt de tritiumopslag in het materiaal aanzienlijk hoger.

De onderliggende motivatie van ons werk is om tritiumopslag in wolfram, dat door neutronen is beschadigd, te voorspellen na blootstelling aan een hoge plasma flux. Om dat tritium radioactief is, hebben we deuterium, dat nagenoeg dezelfde chemische eigenschappen heeft, gebruikt. De schade werd met hoog energetische wolframionen gecreëerd in plaats van met neutronen. Dergelijke schade is namelijk vergelijkbaar en heeft als voordeel dat het materiaal niet wordt geactiveerd.

We hebben de deuteriumopslag onderzocht, nadat de beschadigde wolfram tref-
plaatjes waren blootgesteld aan plasma. De schade werd vooraf gecreëerd met behulp van hoog energetische wolframionen. Dergelijke hoog energetische deeltjes stoten de wolframatomen van hun roosterpositie, zodat gaten en “interstitials” ontstaan. “Interstitials” zijn wolframatomen die tussen de roosterposities in liggen. Door de mate van schade te variëren ontdekten we dat de deuteriumopslag in het wolfram verzadigde bij een schadeniveau van 0.2 dpa (gemiddeld aantal keer dat een wolframatoon is verplaatst). De deuteriumconcentratie is dan 1.4 at.%. Deze verzadiging wordt veroorzaakt door de manier waarop de schade gemaakt wordt en heeft niets te maken met de hoge plasma flux. Bij verzadiging is de concentratie van gaten en “interstitials” namelijk zo hoog dat ieder nieuw gecreëerd gat en ieder nieuw gecreëerd “interstitial” onmiddellijk recombineren met een reeds aanwezig “interstitial” respectievelijk gat.

Bovenstaande experimenten werden uitgevoerd bij een relatief lage wolframtemperatuur van ~500 K. De voorspelling is echter dat wolfram divertor tegels van ITER zullen werken bij temperaturen van 600 – 1300 K. De experimenten werden dan ook herhaald bij temperaturen van 800 – 1200 K. De deuteriumopslag verzadigde wederom bij hetzelfde schadeniveau van 0.2 dpa, maar het absolute niveau van de deuteriumopslag nam sterk af. Deze vermindering hebben we verklaard door de hogere beweeglijkheid van wolframatomen bij een hogere materiaaltemperatuur. Des te meer de wolframatomen bewegen, des te groter de kans dat “interstitials” een gat vinden, waardoor de schade verdwijnt en er minder deuterium wordt opgeslagen. Daarnaast hebben we gezien dat de gaten groeperen en grotere clusters vormen waarin het nog aanwezige deuterium sterker gebonden is.

Het effect van de totale hoeveelheid deeltjes die per vierkante meter op het materiaal aankomt, de “fluence”, hebben we bestudeerd door de tijd te variëren dat een trefplaatje werd blootgesteld aan plasma. Met behulp van een geavanceerde techniek konden we de diffusie van de deuteriumdeeltjes goed volgen in het beschadigde wolfram. De fractie van deuteriumdeeltjes dat in het wolfram achterblijft, bleek zeer laag (10^{-5} – 10^{-7}). Om deze lage inkomende fractie te verklaren hebben we een mechanisme voorgesteld, waarbij de deuteriumatomen een beschermlaag vormen aan het oppervlak. Daardoor kunnen de deuteriumionen het materiaal niet meteen in, maar botsen ze met de atomen aan het oppervlak waarbij ze energie overdragen. Er is vervolgens een thermisch proces nodig om de deuteriumdeeltjes in het materiaal te introduceren.

Het is te verwachten dat delen van de ITER divertor zullen worden blootgesteld aan een bombardement van ionen uit het plasma met een aanzienlijke kinetische energie. Het is bekend dat hoog energetische deuteriumionen oppervlaktemodificaties kunnen veroorzaken op wolfram. We onderzochten daarom plasma blootstelling van wolfram dat op een negatieve potentiaal werd gebracht, waardoor de positieve ionen naar het oppervlak werden versneld. Hierbij onderzochten we expliciet de effecten van plasma flux, blootstellingstijd en materiaalbeschadiging op oppervlaktemodificaties en deuteriumopslag. We hebben gevonden dat het oppervlak na plasma blootstelling bedekt is met drie soorten oppervlaktemodificaties: blaren, onregelmatige uitstulpingen en nanostructuren. Hoe langer een trefplaatje werd blootgesteld aan het plasma, hoe meer blaren we vonden en hoe groter ze waren. Trefplaatjes met stralingsschade toonden daarentegen minder blaren, terwijl er juist meer uitsteeksels werden gevormd.
De wolfram trefplaatjes, zoals wij die hebben gebruikt, bestaan uit korrels met een grootte van 1 – 5 µm. Hedendaagse tokamaks zoals JET maken echter ook gebruik van dunne wolfram films. De deuteriumopslag-eigenschappen in dit soort films zijn echter nog grotendeels onbekend. In onze experimenten hebben we daarom ook dunne wolframlagen van ongeveer één micrometer dik blootgesteld aan plasma. Deze dunne lagen waren over het algemeen goed bestand tegen de plasma flux en bleken goed gehecht aan de onderliggende wolfram trefplaatjes. De deuteriumopslag was echter wel sterk toegenomen, zelfs in vergelijking met beschadigd wolfram materiaal.

Afsluitend, de deuteriumopslag in wolfram trefplaatjes na blootstelling aan een hoge plasma flux is zeer laag. Beschadiging met hoog energetische wolframionen en plasma blootstelling bij negatieve potentiaal zorgen beide voor een verhoging van de deuteriumopslag met een orde van grootte. Het totale niveau van deuteriumopslag blijft desalniettemin laag en suggereert dat de tritiumopslag in de divertor van ITER niet problematisch zal zijn.
Samenvatting
1 Introduction

The global energy consumption is growing every day \[1\]. Two important trends underly this growth: the world population increases and the energy consumption per capita grows as a result of technical development and increase in living standards. Although development is generally perceived as beneficial, a growing energy need may present the world several severe challenges. The fossil fuel reserves are diminishing, global warming by emission of greenhouse gases asks for rigorous changes \[2\] and a globally available energy resource becomes more and more necessary to prevent political tensions. A secure and affordable energy supply is vital for modern economy.

Enormous improvements are being made in the development of sustainable energy sources (water, wind and sun). However, their shared drawback is the irregularity in both time and place. On the other end of the spectrum, nuclear fission can provide a reliable baseline power. But here, safety risks and long term storage of radioactive waste are problematic. Nuclear fusion provides a solution, that can be used for high baseline power while having no geographical constraints. Energy production by hydrogen fusion is able to provide safe and environmentally benign energy for mankind with nearly unlimited energy reserves \[3, 4\]. Nevertheless, an economically viable reactor has yet not been realized and future research is needed.

1.1 Nuclear fusion

Nuclear fusion is a nuclear reaction in which light nuclei fuse into a heavier nucleus. During this process, part of the mass is released as energy. The best candidate for viable fusion reactors is the fusion of two hydrogen isotopes, deuterium and tritium, into helium and a neutron (figure 1.1). During this process 17.6 MeV of energy is released.

In order to overcome the electric repulsion between the charged nuclei, a high temperature of about 150 million degrees Kelvin is needed. At this temperature the hydrogen is in the state of an ionized gas or plasma. No material is capable of withstanding the enormous temperatures required to surround and contain this hot plasma. However, plasma control of charged particles can be achieved with magnetic fields. Strong interac-

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fusion.png}
\caption{Fusion of deuterium and tritium into helium and a neutron produces energy.}
\end{figure}
tion between charged particles and a magnetic field, causes the particles to gyrate around magnetic field lines. Thus, plasma can be confined in ingenious magnetic field configurations. The most promising design is called the ‘tokamak’ and has been developed in Russia in the 1960’s. The word tokamak, is a Russian abbreviation for toroidal chamber with magnetic coils. A good overview of the fundamentals of the physics behind fusion technology can be found in [5] by F.F. Chen and [6] by W.M. Stacey.

A large international tokamak experiment concerning nuclear fusion is ITER [8] (figure 1.2). This proof-of-principle tokamak is currently being built in Cadarache (France). The first plasma is expected in 2020 and deuterium-tritium operation is planned from 2027 [9]. One of the critical components of the ITER experiment is the divertor (figure 1.3), since it needs to be able to withstand harsh plasma conditions.

Figure 1.2: Design drawing of ITER [7]. The location of the divertor is indicated by the red boxes. To provide scale a person is included in the right bottom corner.
The function of the divertor is to extract heat, helium ash and other impurities from the plasma. This is necessary to prevent extinction of the core plasma. The magnetic field configuration diverts the plasma particles from the core and directs them to the exhaust of the machine. While the first wall experiences only mild loads of $\sim 0.3 \text{ MW m}^{-2}$, most of the plasma flux is concentrated in the divertor region, which results in heat loads of $\sim 10 \text{ MW m}^{-2}$ \cite{3}. The temperature in the core of the plasma is in the order of 10 keV, but plasma strongly cools down on its way to the divertor. As a consequence of this, the temperature decreases and the density increases. Plasma in the divertor region of ITER is expected to have a very high density ($10^{20} - 10^{21} \text{ m}^{-3}$) and at the same time a relatively low temperature (1 – 10 eV). Correspondingly, the divertor has to be able to withstand particle fluxes up to $10^{24} \text{ m}^{-2}\text{s}^{-1}$ \cite{3}.

To carry out research on the interaction between plasma and material and to test materials on their capability of withstanding such extreme conditions, dedicated experiments are necessary. Many experiments are carried out on tokamaks as well as on so-called linear plasma generators. In the latter, a plasma is guided by a linear magnetic field and directed onto the target under study. Linear plasma generators have the advantage over tokamaks that they are easily accessible, relatively quick and dedicated experiments are easier to perform. Moreover, the unique high-flux ITER divertor regime cannot be accessed by present-day tokamaks. Pilot-PSI \cite{10} and Magnum-PSI \cite{11}, both linear plasma generators at the FOM institute DIFFER, are capable of reproducing the conditions that are expected in the divertor of a steady-state fusion reactor \cite{12}.

1.2 Deuterium retention in tungsten

Recently, it has been decided that ITER will start operation with a full tungsten divertor in spite of its potential to affect the core plasma \cite{13}. Tungsten is at first sight an ideal material to use in the divertor. It has good thermal properties, such as a high melting...
temperature and good conductivity, a low solubility for hydrogen isotopes and a high sputtering threshold for hydrogen. However, still many open questions exist concerning the use of tungsten as plasma facing material in the divertor. Several plasma surface processes, such as reflection, recycling, damage creation and hydrogen retention combine into a complex interplay which is only partially understood.

Tritium retention in the reactor wall is one of the key concerns in ITER. Tritium is a radioactive substance and has a half-life of 12.3 year. For safety considerations the total in-vessel tritium inventory that is allowed in ITER is 700 g [14]. Furthermore, a high retention of tritium in the walls would degrade the fuelling efficiency of burning plasmas strongly.

Nuclear fusion of deuterium and tritium produces high energy neutrons (figure 1.1). These highly energetic neutrons are not confined by the magnetic field and create damage in the crystal structure of the surrounding tungsten wall. The defects created in the metal lattice can act as trap for the radioactive tritium. Indeed, pre-irradiation of tungsten with neutrons or MeV particles is known to enhance retention significantly [15–21]. The prediction for the end-of-life damage level in the divertor is ∼0.6 displacements per atom (dpa) [22]. The importance of understanding the behaviour of tungsten is even further emphasized considering that the knowledge of the ITER experiments will be extrapolated to the plasma conditions of ITER’s follow-up DEMO [23]. DEMO, will have to withstand even higher neutron fluxes. Estimations of the neutron radiation damage at the DEMO divertor indicate 1 – 3 dpa per year [24]. The research presented in this thesis contributes to the understanding of tritium retention in neutron damaged tungsten under high-flux plasma irradiation.

Deuterium - The hydrogen isotope tritium is a $\beta^-$ active nucleus, therefore it was not possible for us to work with tritium. Chemically there is virtually no difference between hydrogen isotopes. The binding energies in tungsten are very similar, and differ only hundredths of an eV. Both protium and deuterium are therefore very good alternatives to use. Because the natural background level of deuterium is only 1/8000 compared to protium, deuterium was chosen for our experiments. Their physical differences, mass and nuclear structure, allows deuterium to be differentiated from protium in various analysis techniques. In this thesis, the term hydrogen is used, unless otherwise specified, to refer to any hydrogen isotope; protium, deuterium or tritium.

High energy W$^{4+}$ ions - Experiments with neutron irradiation of tungsten are very time-consuming and require significant safety precautions because tungsten becomes activated. In this thesis, high energy tungsten ions were used to simulate the 14.1 MeV neutron irradiation. High energy ions are a good proxy for fusion neutrons and have the huge advantage that the time period needed to reach a similar damage level is orders of magnitude lower. Any unwanted chemical side-effects are avoided by using tungsten as high energy ion. An extensive comparison between the irradiation techniques can be found in section 2.4.1. Using high energy tungsten ions as neutron proxy allows us to investigate the physical processes of interaction between hydrogen and pre-irradiation damaged material.
1.3 This work

The main topic of this PhD project was the investigation of deuterium retention in pre-irradiation damaged tungsten under high-flux plasma bombardment. The work is aimed to improve our understanding about the interaction between hydrogen and radiation damage under high-flux plasma exposure. This knowledge can be used for simulations and predictions on the level of tritium retention in the divertor of ITER. The research question is formulated as follows:

What is the effect of pre-irradiation damage on the deuterium retention in tungsten under high-flux plasma exposure?

This research question contains three important aspects:

Pre-irradiation damage - First, we investigated how much deuterium can be trapped in damage created by MeV tungsten ions. Nuclear reaction analysis (NRA) and thermal desorption spectroscopy (TDS) provide us with information on location and trapping energy of the deuterium. TDS in combination with TMAP7 simulations help to correlate this to the defect type. In chapter 4, different samples with various levels of pre-irradiation damage are studied after high-flux deuterium plasma exposure in order to investigate deuterium trapping after increasing radiation damage.

Chapter 5 reports on experiments in which the radiation damaged tungsten is exposed to deuterium plasma at high surface temperatures. These surface temperatures were chosen to be above the temperature at which vacancies become mobile (>550 K). Using positron annihilation and thermal desorption, the type of defects that trap the deuterium could be investigated. In Appendix 5.A, experiments are presented that show that the decrease in deuterium retention at high surface temperatures is dominated by vacancy clustering and annealing. In experiments with alternating damaging and heating before plasma exposure, the heating and deuterium implantation is decoupled.

Plasma surface interactions at high-flux - In chapter 6, pre-irradiation damaged tungsten was exposed to high-flux plasmas for a range of exposure times. We observed that only a very low fraction ($10^{-5} - 10^{-7}$) of deuterium was found to be retained in the material. In chapter 6, the pre-irradiation damaged material is used to monitor the diffusion into the tungsten material and in this way determine the effective penetration during plasma bombardment.

Deuterium retention and surface modifications - High-flux plasma exposure with target biasing (increase of the ion energy) creates surface modifications in tungsten. Chapter 7 investigates the defects that are created by plasma bombardment. Here, the effect of the plasma flux and the exposure time is effectively decoupled. Also, the surface modifications as result of high-flux plasma exposure on pre-irradiation damaged tungsten targets are investigated. In this experiment, a distinction is made between the deuterium trapped in pre-irradiation damage and plasma damage.
In the research described above, measurements are carried out on polycrystalline tungsten. In chapter 8 tungsten layers with various density and crystallite sizes were deposited on bulk tungsten material using pulsed laser deposition and subsequently exposed to high-flux deuterium plasmas. The dependency of deuterium retention on the tungsten material structure and the induced surface modifications will be described.

In the final chapter of this thesis, Conclusions and outlook, an overview of the main results will be given. It will be shown that for the high-flux plasma exposure of the tungsten targets under all conditions as used in this thesis, the retained fraction of deuterium is low as compared to the plasma fluence. We will conclude with an outlook for future experiments.

1.4 List of publications

The results presented in this thesis have been published in or have been submitted to refereed journals. A list of journal and conference contributions related to this thesis is given below.

Publications (first author)

- M.H.J. ’t Hoen, M. Mayer, A.W. Kleyn, H. Schut and P.A. Zeijlmans van Emmichoven, Reduced deuterium retention in self-damaged tungsten exposed to high-flux plasmas at high surface temperatures, Nuclear Fusion 53 043003 (2013)
- M.H.J. ’t Hoen, D. Dellasega, M. Passoni, A.W. Kleyn and P.A. Zeijlmans van Emmichoven, Deuterium retention and surface modifications of thin tungsten films exposed to high-flux plasma, in preparation for publication

Publications (co-author)


1 Introduction
2 Theoretical background

Deuterium retention in pre-damaged tungsten is the result of a complicated interplay between many processes, including implantation, diffusion and deuterium trapping. Figure 2.1 illustrates these plasma-surface interaction (PSI) processes. When the deuterium ions from the plasma strike the tungsten target, they are neutralized and a large part will be reflected directly. The remaining part will penetrate into the tungsten and reach depths of typically a few nm. After thermalization, deuterium atoms diffuse through the material. At the surface they can recombine and leave the material. In the tungsten they can be trapped in pre-existing defects or in deuterium traps created by implantation of high-energy tungsten ions prior to the plasma exposure.

This chapter describes the above processes and the implementation at Pilot-PSI in more detail. The composition of the plasma produced in the Pilot-PSI setup is outlined in section 2.1, the interaction of this plasma with the tungsten surface is discussed in section 2.2, the deuterium retention processes are explained in section 2.3 and defect creation is described in section 2.4. A comparison between high-energy ion and neutrons irradiation is made in section 2.4.1 and the plasma damage processes and the blister formation mechanisms are described in section 2.4.2.

2.1 Plasma composition

The plasma composition, the ion flux and ion impact energy at the tungsten target determine the reflection, penetration and damage creation in tungsten. Deuterium plasmas...
produced in the experiments described in this thesis typically have an electron density \(n_e\) of \(\sim 10^{20} \text{ m}^{-3}\) and an electron temperature \((T_e)\) of \(\sim 1\) eV (section 3.3.1). The plasma is quasi-neutral \((n_i = n_e)\) and the electron-ion collision frequency is high, so that electrons and ions are in thermal equilibrium \((T_i = T_e)\).

Hydrogen plasmas are dominated by \(\text{H}^+\) ions and contain only small fractions of neutral species in the beam centre (see also section 3.3, [25–29]). Note that these experiments are performed using protium instead of deuterium, but the behaviour of deuterium plasmas is assumed to be identical.

### 2.1.1 Ion flux

The ion flux \((\Gamma_i)\) is estimated according to general plasma sheath theory [30]. Here, it is assumed that the ions are accelerated to the sound velocity at the sheath entrance (Bohm criterion [31]) and that the plasma density at the sheath entrance drops by a factor of two compared to the pre-sheath value. The ion flux is given by

\[
\Gamma_i = \frac{n_e^2}{2} \sqrt{\frac{k_B(T_e + \gamma T_i)}{m_i}} = \frac{n_e^2}{2} \sqrt{\frac{4k_BT_e}{3m_p}} \left[\text{m}^{-2}\text{s}^{-1}\right],
\]

with \(m_i\) as the deuterium ion mass and \(m_p\) as the proton mass. The adiabatic index \((\gamma)\) was taken to be 5/3 (adiabatic flow with isotrope pressure). The total amount of deuterium ions that arrive at the target can be calculated by integration of the ion flux over the target. This value can also be found using the ion saturation current. The ion saturation current \((I_{\text{sat}})\) is reached at sufficient negative target bias, when all electrons are repelled and only ions arrive at the target. The amount of ions can then easily be calculated as follows: \(I_{\text{sat}}/q\), where \(q\) is the elementary charge. Both methods for calculating the total amount of deuterium ions always agreed within factor two.

### 2.1.2 Ion impact energy

Calculation of the ion impact energy \((E_{\text{ion}})\) is unfortunately not straightforward, because the plasma potential varies over the radius of the plasma beam. Indeed, Shumack et al [32] and Wieggers et al [33] showed that a radial electric field formed in the plasma beam and a radial development of the current distribution. This means that the target effectively short-circuits the plasma beam leading to local differences from the floating potential. To estimate the ion energy, we ignore the radial dependence, assume 1D linear geometry, no ionisation and a non-collisional sheath. This allows us to use the formulation derived by Stangeby [30].

The ion impact energy is the sum of the ion energy at the entrance of the plasma sheath \((E_{\text{se}})\), and the energy gained during acceleration in the sheath \((eV_{\text{drop}})\). The minimal requirement for ions to enter the sheath is the sound speed [31] with an energy \((E_{\text{se}})\) of \(\sim 2k_BT_i\) (see chap. 2.5 in [30]). The voltage drop \((V_{\text{drop}})\) across the sheath is approximately \(3k_BT_e/e\) [30]. Consequently, the ion energy of a floating target is \(\sim 5k_BT_e\).
2.2 Plasma-surface interactions

Given the normal Pilot-PSI operating conditions, \( E_{\text{ion}} \) is about 5 eV for a floating tungsten target.

In the case of externally biasing the target, the potential drop in the sheath is equal to the difference between the plasma potential \( (V_p) \) and the biasing voltage \( (V_{\text{bias}}) \). The ion impact energy is then given by \( E_{\text{ion}} \approx 2k_B T_e + e(V_p - V_{\text{bias}}) \). The plasma potential is estimated by adding the voltage drop over the sheath to the floating potential \( (V_{\text{float}}) \): \( V_p = V_{\text{float}} + 3k_B T_e / e \). Here, it is assumed that the plasma potential does not change when a bias is applied. Under the plasma conditions used in experiments in this thesis, the floating potential was only a few V \( (\sim -2 \text{ V}) \). The contribution of \( V_{\text{float}} \) and thereby the variation in \( V_{\text{float}} \) is only small with respect to a bias of typically 40 V, so that the ion impact energy is \( \sim 40 \text{ eV} \).

2.2 Plasma-surface interactions

A comprehensive and extensive overview of plasma-surface interactions (PSI) and related technological issues is presented in The plasma boundary of magnetic fusion devices by P. Stangeby [30] and in review article Plasma-material interactions in current tokamaks and their implications for next step fusion reactors by G. Federici et al [34]. Hydrogen recycling on plasma facing materials (PFM) is discussed by Wu [35]. In this section the PSI processes are specified for low temperature, high density deuterium Pilot-PSI plasmas impinging on tungsten.

**Reflection** - The fraction of incoming ions that are directly scattered depends mainly on the incident energy, angle, material and surface structure. During the collision, the incoming deuterium ions pick-up an electron from the surface, thereby recoiling as atomic deuterium. The binary collision approximation [36] used normally is not valid in the low energy range \((< 10 \text{ eV})\) under which our experiments have been carried out. Molecular dynamic simulations indicated very low sticking coefficients [37]. These agree with experiments of deuterium atoms on tungsten where reflections of 0.96 ± 0.02 were found [38]. In this thesis, we assume a reflection of 95%.

**Erosion** - Physical sputtering occurs due to momentum and energy transfer in collisions between incoming particles and target atoms. When the target atom receives an energy in excess of the surface binding energy (in case of tungsten, this is 8.9 eV [39]) the atom will be ejected, i.e. the surface is eroded. The threshold for physical sputtering of deuterium on tungsten is about 200 eV [40]. Since the incoming ion energies of Pilot-PSI plasmas stay below 50 eV (section [2.1.2]), we do not have to consider physical sputtering.

Besides physical sputtering, chemical sputtering can occur. The chemical reaction between an incoming particle and the material lowers the surface binding energy, so that the newly formed compound easily can be eroded. This is an important sputtering mechanism for carbon PFMs. Hydrocarbons that are formed are eroded from the surface and contaminate the plasma. Tungsten is a refractory metal, no chemical erosion of deuterium takes place.
Implantation - Particles that are not reflected will instantaneously neutralize when they arrive at the target. Depending on their ion impact energy, they either interact with the deuterium covering the surface and form a chemisorbed layer \[41\] or they penetrate into the material. The typical implantation depth of deuterium atoms with an energy of 10 – 40 eV is in the nanometer range as calculated with SRIM \[42\]. The kinetic energy of the incoming atoms (5 – 40 eV) is much higher than the thermal energy of deuterium (0.01 – 0.1 eV). The difference in energy is lost in interatomic collisions with the atoms in the tungsten lattice. Once the deuterium is thermalized it will occupy an interstitial position. The retention processes within the material are further described in section 2.3.

Surface processes - Surface reactions are interactions that involve adsorption of one of the reactants. The rate equations of these mechanisms are of importance for an accurate estimation of the D₂ molecules that leave the surface and enter the plasma.

Two atoms, that are adsorbed on the tungsten, freely diffuse over the material surface and have a probability to recombine once they meet each other. The binding energy of D₂ to the tungsten surface is low. The molecular deuterium desorbs from the surface due to exothermic recombination. This reaction is referred to as the Langmuir-Hinshelwood mechanism (figure 2.2a). The molecule release rate is given by

\[ J_r = K_{\text{rec}} C_s^2 \quad \text{[m}^{-2}\text{s}^{-1}] , \]

where \( K_{\text{rec}} \) is the recombination rate coefficient \( (K_{\text{rec}} = K_0 \exp[-E_{\text{rec}}/k_B T]) \) and \( C_s \) the deuterium concentration in the surface monolayer. The recombination rate coefficients reported in literature are very scattered \[43-47\]. The values measured by Anderl et al \( (K_0 = 3.2 \times 10^{-15} \text{ m}^4 \text{s}^{-1}, E_{\text{rec}} = 1.16 \text{ eV}) \) \[43\] are most accepted and will be used in this thesis.

A secondary mechanism is the Eley-Rideal recombination \[48\]. Figure 2.2b shows Eley-Rideal recombination, where only one of the two atoms is adsorbed, the other one directly reacts from the gas phase. Eley-Rideal recombination is a non-thermal surface reaction. This process could also include reaction with deuterium ions directly from the incoming plasma.

### 2.2.1 Deuterium back-flux

The released deuterium molecules and the reflected deuterium atoms combined cause a back-flux of particles that interfere with the plasma beam. In this section, we estimate the
interaction of the back-flux with the plasma beam to assess the relative importance.

The rate coefficient \((k_r)\) for charge exchange between \(D_2\) and \(D^+\) in the energy range
\(< 10\, \text{eV}\) is at maximum \(10^{-15}\, \text{m}^3\, \text{s}^{-1}\) \([49]\). The relative velocity \((v)\) of about \(10\, \text{km}\, \text{s}^{-1}\)
\([28]\) and \(D^+\) density \((n_i)\) of \(\sim 10^{20}\, \text{m}^{-3}\) can be used to estimate the mean free path,
\[
\lambda_{\text{mfp}, D_2} = \frac{v}{k_r n_i} > 0.1\, \text{m}.
\] 
(2.3)
The full width at half maximum of the plasma beam is typically 1 cm. Thus, the \(D_2\)
molecules fly right through.

The interaction of the deuterium atoms with the plasma flux also takes place via
charge exchange. The reaction rate coefficient between \(D\) and \(D^+\) is an order of magni-
tude higher: \(k_r \approx 10^{-14}\, \text{m}^3\, \text{s}^{-1}\) \([50]\), so that
\[
\lambda_{\text{mfp}, D} = \frac{v}{k_r n_i} \approx 0.01\, \text{m}.
\] 
(2.4)
Significant part of the reflected neutrals experience charge exchange with the ions from
the plasma beam. The ions created via charge exchange can be accelerated towards the
target. The particle flux might therefore be somewhat higher than calculated solely with
equation [2.1]

## 2.3 Deuterium retention

Deuterium retention refers to a whole range of processes in which deuterium is lost
from the plasma and incorporated in the wall material. The energy diagram of deute-
rium dissolved in tungsten is schematically depicted in figure [2.3]. In the solute state, the
deuterium atom is highly mobile; by hopping between interstitial positions it can easily
diffuse through the material. In this diffusion process, the atom can either reach a
crystallographic defect and get trapped or reach the surface and desorb.

### 2.3.1 Solubility

Sieverts’ law relates the equilibrium concentration of solute atoms in a metal to the partial
pressure above the surface of the metal \([57]\). The concentration of solute deuterium at the
surface \((C_s)\) of a material exposed to a deuterium gas at pressure \(p\) is given by
\[
C_s = K_{\text{sol}} p^{1/2} \quad \text{[m}^{-3}], \quad \text{where}
\] 
(2.5)
\[
K_{\text{sol}} = S_0 \exp \left[ \frac{-E_S}{k_B T} \right] \quad \text{[m}^{-3}\text{Pa}^{-1/2}],
\] 
(2.6)
with the Boltzmann constant \(k_B\) and the sample temperature \(T\). The solubility, \(K_{\text{sol}}\), is
determined by the enthalpy of solution \((E_S)\) and the solubility coefficient \((S_0)\). Capture
of deuterium in tungsten is an endotherm process, i.e. energy must be added to intro-
duce deuterium into solution. The mostly used values of the solubility are measured by
Frauenfelder: \(S_0 = 17.7 \times 10^{23}\, \text{m}^{-3}\text{Pa}^{-1/2}, E_S = 1.04\, \text{eV}\) \([53]\) and were used for the work
presented in this thesis.
2 Theoretical background

Figure 2.3: Energy diagram of hydrogen in tungsten. The dissociation energy of deuterium from the D₂ molecule is \( \frac{1}{2}E^D_{D_2} \). The chemisorption energy \( E_C \) at the surface, the enthalpy of solution \( E_S \), the migration barrier \( E_M \) and the trapping energies \( E_t \) of deuterium in crystallographic defects are indicated. Their values are given in table 2.1.

<table>
<thead>
<tr>
<th>Activation energy</th>
<th>eV</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>dissociation energy ( \frac{1}{2}E^D_{D_2} )</td>
<td>2.3</td>
<td>[S1]</td>
</tr>
<tr>
<td>chemisorption energy ( E_C )</td>
<td>0.4–0.9</td>
<td>[S2] 0.48–0.92 [S1]</td>
</tr>
<tr>
<td>migration barrier ( E_M )</td>
<td>0.39</td>
<td>[S3]</td>
</tr>
<tr>
<td>enthalpy of solution ( E_S )</td>
<td>1.04</td>
<td>[S3]</td>
</tr>
</tbody>
</table>

trapping energy of deuterium in atomic form \( (D) \) in a
- dislocation \( E^\text{dis}_{t,D} = E_m + E^\text{dis}_b \) 0.85 [S4]
- grain boundary \( E^\text{gb}_{t,D} = E_m + E^\text{gb}_b \) 0.85 [S4]
- vacancy \( E^\text{vac}_{t,D} = E_m + E^\text{vac}_b \) 1.45 [S4], 1.43–1.55 [S1], 1.07–1.34 [S5], 1.17–1.6 [S6]
- vacancy cluster \( E^\text{vc}_{t,D} = E_c + E_s + E_m \) 1.9–2.3 [S1], 1.84–2.34 [S2], 2.1 [S5]

trapping energy of molecular deuterium \( (D_2) \) in a vacancy cluster \( E^\text{vc}_{t,\frac{1}{2}D_2} = E_s + E_m \) 1.45 [S2], 1.4 [S1]

Table 2.1: The diffusion parameters and trapping energies \( (E_{\text{type of defect}}^{\text{species}}) \) of deuterium in tungsten.

2.3.2 Diffusivity

Deuterium movement through tungsten is determined by atomic diffusion. Diffusion is a jump process of interstitial deuterium via thermal excitation and is defined by

\[
D_{\text{dif}} = D_0 \exp \left[ \frac{-E_M}{k_B T} \right] \quad [m^2 \text{ s}^{-1}] .
\]  

(2.7)
2.3 Deuterium retention

The pre-exponential factor ($D_0$) and the migration barrier ($E_M$) vary over a broad range in literature between $3.5 \times 10^{-11} – 6 \times 10^{-4}$ and $0.25 – 1.80$ eV, respectively \[44, 46, 53, 58-61\]. The recommended \[61\] and widely accepted values determined by Frauenfelder were used in the work presented in this thesis: $D_0 = 4.1 \times 10^{-7} \text{m}^2 \text{s}^{-1}$, $E_M = 0.39$ eV \[53\].

Diffusion of deuterium in tungsten is described by the transport equation,

$$\frac{\partial C_D(x, t)}{\partial t} = D_{\text{dif}} \frac{\partial^2 C_D(x, t)}{\partial x^2} + S(x, t). \quad (2.8)$$

$C_D(x, t)$ is the deuterium concentration in m$^{-3}$ as function of depth ($x$) and time ($t$). The diffusion rate ($D_{\text{dif}}$) is assumed constant throughout the sample. $S(x, t)$ is the particle source/sink term, it is negative in case of trapping and positive for de-trapping. The one-dimensional case can be solved analytically, when neglecting trapping and de-trapping ($S = 0$) and assuming a constant surface concentration over time ($C_D(0, t) = C_s$). The solution is then given by

$$C_D(x, t) = C_s \text{erfc} \left[ \frac{x}{2 \sqrt{D_{\text{dif}} t}} \right] = C_s \text{erfc} \left[ \frac{x}{\lambda_D(t)} \right], \quad (2.9)$$

where $\text{erfc}$ is the complementary error function and $\lambda_D(t)$ the typical diffusion length (see also figure 2.4). In figure 2.4 the situation is shown for a case where deuterium is lost by trapping in defects. In this example, we assume a situation with a high trap energy, i.e. the probability for release is negligible. As result of particle trapping, the diffusion slows down. The typical depth up to where the traps are filled ($\lambda_{\text{eff}}(t)$), is proportional to the effective diffusion length ($\propto \sqrt{D_{\text{eff}} t}$).

\[ \text{Figure 2.4: a) The solid lines represent the solute concentration of deuterium versus the depth (complementary error function, equation 2.9), the associated diffusion length ($\lambda_D$) is indicated by the dotted lines. After an exposure time that is four times as long (blue), the deuterium diffuses twice as deep into the material (red). b) The trapped deuterium concentration ($\rho_t$) in the case of trapping in high energy traps, where the probability for release is negligible, is approximately a moving front. The typical depth ($\lambda_{\text{eff}}$) of the deuterium is related to the effective diffusion coefficient.} \]
2.3.3 Deuterium trapping

In general, ‘trapping’ refers to extra low energy sites for atoms dissolved in the tungsten lattice. Crystallographic defects that trap deuterium are for example vacancies, dislocations, grain boundaries and voids (figure 2.5). These can exist naturally in the material, i.e. pre-existing, or be produced by damage creation. One can distinguish between saturable and unsaturable traps. Saturable traps fit a maximum number of deuterium atoms, while unsaturable traps can accommodate a variable number of deuterium atoms, for example a void with variable deuterium pressure.

![Figure 2.5: Schematic representation of material defects.](image)

Each of the defect types can be characterized by a trap energy $E_{t, \text{species}}$ (figure 2.3) and a defect density $\rho_{\text{trap}}(x,t)$. Table 2.1 gives an overview of trap energies mentioned in the literature. Pre-existing defects are typically homogeneously distributed over the full depth range, their concentration depends on the material and fabrication. Defects created by high energy tungsten ions (section 3.2) extend only over the first 1.5 µm. Damage created during plasma exposure develops over time $t$.

The deuterium sink as result of trapping ($S_{\text{trap}}$) depends on the diffusion coefficient, the concentration of solute deuterium ($C_D$) and the concentration of empty traps ($\rho_{\text{trap}}^e$):

$$S_{\text{trap}} = -\frac{\alpha_{\text{t}} \rho_{\text{trap}}^e}{N} C_D = -\frac{D_{\text{dif}}^e \rho_{\text{trap}}^e}{N} C_D \quad [\text{m}^{-3}\text{s}^{-1}],$$  

(2.10)

where $N$ is the lattice atom density ($N_W = 6.3 \cdot 10^{28} \text{ m}^{-3}$), $\lambda$ the lattice parameter ($\lambda_W = 3.15 \text{ Å}$) and $\alpha_t$ the trapping rate coefficient, which is determined by $D_{\text{dif}}/\lambda^2$. Once trapped, the de-trapping depends on the trap energy and occupation of the trap. The de-trapping particle source is given by

$$S_{\text{de-trap}} = \alpha_{\text{r}} \rho_{\text{trap}}^D = \nu_0 \exp \left[ -\frac{E_{t, \text{species}}}{k_B T} \right] \rho_{\text{trap}}^D \quad [\text{m}^{-3}\text{s}^{-1}],$$  

(2.11)

in which $\rho_{\text{trap}}^D$ is the concentration of traps occupied by deuterium. The release rate ($\alpha_r$) is calculated by multiplying the attempt frequency by the success rate. The nominal attempt frequency is typically the Debye frequency ($\nu_0$), which under our conditions is in the order of $10^{13} \text{ s}^{-1}$. The success rate is given by $\exp \left[ -\frac{E_{t, \text{species}}}{k_B T} \right]$. 

16
2.4 Defect creation

2.4.1 Ion versus neutron irradiation

The 14.1 MeV neutrons, created by DT fusion, are not confined by the magnetic field. When escaping through the wall of the fusion reactor they produce damage. Due to the low interaction cross-section of these neutrons with the wall material, the introduced defects will be distributed homogeneously throughout the entire thickness of the tungsten components. This is expected to have a significant effect on the material properties and hydrogen retention. Unfortunately, neutron irradiation experiments at relevant conditions are time consuming and require costly infrastructure. Alternatively, for the work presented in this theses high energy tungsten ions were used to simulate neutron damage. In this section we will give a short summary of the damage creation process and focus on the differences and similarities between ion and neutron damage in tungsten. An extensive description of radiation damage mechanisms can be found in \[62\] by Was.

Radiation damage mechanism

The use of energetic particle irradiation, such as protons, electrons and ions, as surrogate for neutron irradiation benefits from a shorter experiment time, production of little or no radioactivity and lower costs. Deuterium retention in damage created by electrons \[64\], protons \[20\] \[65\] \[67\] and heavy ions \[16\] \[17\] have been investigated. Each type of irradiation creates a different damage morphology. Figure 2.6 illustrates the different damage morphologies after 1 MeV particle irradiation of pure nickel \[63\].

Electrons produce isolated Frenkel pairs, which are vacancy and interstitial pairs, in the depth range of a few micrometers, while protons produce small and widely spaced damage cascades over the whole depth range. Because of the small mass in both cases, the typical damage rate (defined in displacements per atom (dpa) per second) is small.

![Figure 2.6: Schematic representation of the damage morphology after various type of particle irradiation (same energy) on pure nickel. The average PKA energy (\(T\)) and the displacement efficiency (\(\varepsilon\)) is specified for each case \[63\]. The line schematically shows the path of the incident particle. A vacancy is represented by a square, an interstitial by a dot and the size of the formed defect clusters are illustrated by the ovals.](image-url)
2 Theoretical background

In comparison, heavy ions and neutrons produce damage in large clusters. Heavy ions are very efficient in creating a large damage cascade, reaching a damage level equivalent to a year of neutron irradiation within hours. Although it is well-known that the effects of neutron irradiation cannot fully be simulated, high energy ion irradiation is the most promising approach to neutron irradiation.

Both neutron and high energy ion impact transfer a large amount of kinetic energy to the tungsten material. The energy transfer from an incident particle to a lattice atom, the so-called primary knock-on atom (PKA), takes place on a typical timescale of attoseconds. Afterwards, the PKA can penetrate further within the sample. If its energy is sufficient it can cause further collisions and in such a way form collision cascades. Two elementary types of defects are formed: vacancies and interstitials. Interstitials are highly mobile, and they can disperse away from the main cascade. The result is a depleted zone in the centre of the collision cascade, surrounded by an interstitial mantle. These collision cascades are created within 0.1 ps. During the following tens of picoseconds, the absorbed energy dissipates. Spontaneous recombination and clustering take place, so that stable Frenkel pairs and defect clusters are formed. On longer timescales (>10^{-8} s) thermal migration causes defect reactions.

Neutron irradiation

Neutrons do not have an electrical charge and therefore easily penetrate into a material, where they produce atomic displacements, embrittlement and nuclear reactions. Nuclear reactions in tungsten can cause transmutation into Rh, Ta and He. Due to the short range interaction of the nuclear potential, collisions with large energy transfer to the lattice atom dominate. The average energy transfer, \( \overline{T} \), of a neutron to the PKA is given by

\[
\overline{T} = \frac{\gamma E_i}{2}, \quad \text{where} \quad \gamma = \frac{4mM}{(M+m)^2}.
\]  

(2.12)

For neutron irradiation \((m = 1 \text{ u})\) at \(E_i = 14.1 \text{ MeV}\) on tungsten \((M = 184 \text{ u})\), the average energy of the PKA is \(\overline{T} \approx 152 \text{ keV}\).

High energy ion irradiation

The average PKA energy of the 12.3 MeV \(\text{W}^{4+}\) ions was estimated using SRIM to be \(~17 \text{ keV}\). Although heavy ions come closest to reproduce the energy distribution of the recoils as obtained under neutron irradiation, the projected range of the heavy ions is short. The high electronic energy loss results in a non-uniform defect depth distribution (see also figure 3.3). The differences in depth distribution between neutron and ion are not necessarily a problem. The time- and length-scale of deuterium diffusion are much smaller than the typical ion damage depth range (\(\mu\text{m}\)), thus not affected by the damage distribution. In conclusion, ion irradiation will be able to provide us with useful information for understanding of the physical processes.
2.4 Defect creation

2.4.2 Plasma damage

Depending on the specific plasma conditions, extra damage can be created in the material during deuterium loading. An incoming deuterium particle requires an energy of at least 2 keV to knock a heavy tungsten atom from its lattice position \( E_{\text{displ}} = 90 \text{ eV} \) [68], such energies are by far not reached in Pilot-PSI. A more relevant process in which damage can be created is when more deuterium is forced into the material than can be contained in a solute state (section 2.3.1). At such high flux, cavity growth might take place and subsequently blister-like features can be formed. Surface blistering is unfavourable for ITER operation and needs to be avoided as it may alter mechanical properties (decrease the heat conduction, create areas with high strain fields or cause embrittlement), store tritium or enhance tungsten erosion when blisters burst. Tungsten erosion will efficiently cool the plasma via Brehmstralung, and possibly kill the fusion process.

Blister formation process

Due to its relevance, blistering induced by hydrogen loading has been extensively studied \([69, 70]\) in relation to plasma-surface interactions in nuclear fusion devices \([14]\) as well as for semi-conductor technology \([71, 72]\). Blistering occurs in metals with a low solubility, at low temperatures and for very high fluences \([70]\). Depending on the bombardment conditions, such as the ion-energy \([73, 74]\), particle fluence and surface temperature, and material grade, such as grain structure, impurity content and pre-treatment, various types of blister-like features are formed. The reported surface features vary from smooth spherical blisters \([69, 75]\) to plateau-like \([76]\) and stepped high dome structures \([77–79]\).

In the blister formation process, two stages can be distinguished. First, deuterium accumulates at a nucleation point, which is then followed by growth of the cavity. Currently, there is no consensus about how the initial nucleation takes place. Of course, any pre-existing defects in the material, such as dislocations, grain boundaries or vacancies can serve as a nucleation site \([80]\). In addition, Fukai \([81]\) argues that the hydrogen in the tungsten lattice can lower the vacancy formation energy and Poon \([82]\) suggests that plasma impurities, such as nitrogen and oxygen, are able to create crystallographic defects that serve as nucleation point. Hydrogen precipitates at these nucleation sites \([70, 83]\). Since the solubility of hydrogen in tungsten is very low, atomic hydrogen in solution can recombine into \( \text{H}_2 \) gas \([84]\). The next step is cavity growth. Three mechanisms for cavity growth are proposed by Condon \([70]\): plastic deformation, dislocation loop punching and vacancy clustering.

Cavity formation by plastic deformation requires hydrogen supersaturation. First, pressure builds up in a void or between grain boundaries as result of a high solute deuterium concentration (Sieverts’ law). When the pressure exceeds a critical value it creates mechanical deformation in the surrounding material. If this occurs close to the surface, this leads to material bulging outwards.
Figure 2.7: Schematic representation of cavity growth by loop punching. (a) Initial nucleation of hydrogen at a nucleation site, (b) excess pressure deforms surrounding atom planes and shunting process allows expansion of the bubble and creation of an interstitial loop, (c) bubble grows by ejection of edge dislocation loops (from [69, 70]).

Figure 2.7 shows dislocation loop punching. Dislocation loop punching also requires hydrogen supersaturation. Initially, hydrogen is accumulated at a nucleation site (figure 2.7a), the gas pressure increases by absorbing the dissolved hydrogen. When the pressure exceeds \(\sim 0.2\mu\) (\(\mu\) is the shear modulus, the shear modulus of tungsten is \(\sim 160\) GPa) patches of material are forced into the surrounding bulk material to form an interstitial loop (figure 2.7b). The dislocation loop is pushed away from the cavity, moving along the direction of its Burgers vector (figure 2.7c). During this process, the volume of the bubble increases. This leads to a decrease in pressure and the process repeats itself.

Vacancy clustering is independent of the dissolved hydrogen but requires vacancy supersaturation and a temperature above the vacancy mobility temperature (\(\sim 550\) K) [85]. When vacancies are mobile, they can encounter each other and form small clusters.

The values mentioned for the gas pressure of \(\text{H}_2\) in cavities vary over a wide range: a rough estimate from measurements performed by Shu et al [78] is a few GPa to a few tens of GPa. Shu et al compare this to similar pressures of hydrogen in voids of tungsten mentioned by van Veen et al [64]. Van Veen et al refer to the rough estimate given by Mills et al [86] based on the equation of state for \(\text{H}_2\) gas that yields a corresponding pressure of the order of 10 GPa, which is lower than, but close to, the pressures required for loop punching. Evans et al expect volume increase by loop punching for bubbles in tungsten with diameters in the order of 1 nm beyond 10 GPa. Balden et al [87] report of estimated values of \(\sim 1\) GPa and You [88] predicts with finite element studies that a few hundred MPa should be enough to start blister formation.
3 Experiment

The general experimental procedure used in the work presented in this thesis is described in this chapter. The order of presentation follows the sequence in which the experiments were performed (figure 3.1). First, the preparation procedure of the tungsten targets is described (section 3.1). Section 3.2 explains the damage creation using high energy tungsten ion implantation. Exposure of the targets to a deuterium plasma was carried out using the linear plasma generator Pilot-PSI. The experimental Pilot-PSI set-up and the relevant diagnostics are described briefly in section 3.3. The diagnostics used to analyse the targets after deuterium exposure are described in section 3.4. At last, the details about the TMAP7 simulations and the input parameters that were used are given (section 3.5).

3.1 Preparation tungsten material

Tungsten is beneficial as divertor wall material because of its very good thermal properties, such as high melting temperature (3685 K) and high thermal conductivity (178 W m$^{-1}$K$^{-1}$). The crystal structure of tungsten is bcc, and the number density of tungsten atoms is $6.3 \times 10^{28}$ m$^{-3}$. Polycrystalline tungsten discs were purchased from PLANSEE [89] with a purity of 99.97% (0.01% is molybdenum). During the production process a tungsten rod (Ø 20 mm) is formed by forging. Subsequently, disks with a thickness of 1 mm are cut from this rod. In this method, the typical grain size obtained was between 0.5 – 5 µm. A typical cross-section of this material is shown in figure 3.2a. An alternative material was made using a different manufacturing procedure. These targets were cut from a rolled sheet of 0.9 mm thick. A cross-section of the rolled tungsten is shown in figure 3.2b. This rolled material is well-characterized by Manhard et al [74] and was used for the experiments described in chapter 7 in order to directly compare our findings with the material research performed at IPP-Garching.

![Figure 3.1: Schematic sequence of the performed experiments.](image)

Figure 3.1: Schematic sequence of the performed experiments. After target preparation, the targets are pre-irradiated to create material defects. During deuterium plasma exposure, deuterium is introduced into the material. Several analysis techniques were used to characterize the retention level and material properties after the exposure.
The tungsten samples (chapter 5.A – 7) were mechanically polished to a mirror finish by grounding with silicon carbide paper (grits: 200 – 2400) and diamond polishing suspensions (supreme diamond suspension, 3 µm and 1 µm MetaDi) on Buehler TexMet cloth for polishing. The samples were finished using Buehler MicroCloth and MasterMet colloidal silica (~0.05 µm). All samples were stress-relieved in vacuum (<10⁻⁴ Pa) at 1273 K for 1 h and sonic cleaned in acetone and ethanol for 10 min.

### 3.2 Damage creation - W⁴⁺ pre-irradiation

To avoid potential chemical composition changes, tungsten ions were chosen for irradiation. Damage in the tungsten samples was created by W⁴⁺ irradiation in the 3 MV tandem accelerator at IPP Garching [90]. In the accelerator, negative ions are created by sputtering a tungsten carbide cathode with cesium ions. The beam of negative ions (WC⁻) is accelerated to a high voltage terminal, where the electrons are stripped by a N₂ gas stripper and a positively charged tungsten ion beam is produced. Subsequently, the ions are accelerated in the high energy acceleration tube. By using magnets, the ions with the desired charge are deflected to the target. An accelerator voltage of 2.5 MV was used to create a beam of 12.3 MeV W⁴⁺. The background pressure in the implantation chamber was below 10⁻⁵ Pa and the targets were kept at room temperature during irradiation. In order to obtain homogeneous irradiation, the beam of 3 mm diameter was raster-scanned across the surface. The beam position and ion flux were controlled by an arrangement of four small-diameter Faraday cups located at four corners of the sample mask. The implanted fluence Φₖ is determined by

\[
Φₖ = \frac{q_{\text{total}}}{eAQ} \left[ \text{ions m}^{-2} \right]. \tag{3.1}
\]
Here, $q_{total}$ is the total collected charge by the Faraday cups, $e$ is the elementary charge $(1.6 \times 10^{-19} \text{C})$, $A$ is the total area of all four Faraday cups and $Q$ the charge of the ions that were implanted. The diameter of the area damaged by the tungsten bombardment was 12 mm for the non-polished tungsten samples and 18 mm for the polished samples used in the experiments for this thesis. The damage rate was $1 - 4 \times 10^{-4} \text{dpa s}^{-1}$.

### 3.2.1 SRIM simulation details

Details on the damage level are simulated using SRIM given the pre-irradiation data from the accelerator in order to improve the understanding of the deuterium retention. SRIM, Stopping Range in Matter, is a Monte-Carlo simulation tool that uses the binary collision approximation \[48\] to calculate the interactions of energetic ions with amorphous targets \[42, 91\]. The interaction between an ion and an atom is characterized by a screened Coulomb collision. The settings chosen in the SRIM simulations were as follows:

- type of calculation: ‘Detailed calculation with full damage cascades’
- ion data: 12.3 MeV tungsten, angle of incidence $= 0$
- target data: tungsten with damage energies:
  - displacement energy: 90 eV \[68\]
  - lattice binding energy: 3 eV
  - surface binding energy: 8.9 eV \[39\]

In figure 3.3 the damage trajectories of an example calculation are graphically shown. The simulation output on i.a. vacancy creation, ionization and phonon production was used to derive the defect depth profile.

### 3.3 Deuterium exposure - Pilot-PSI

The targets were loaded with deuterium using Pilot-PSI at FOM-DIFFER \[10\]. This linear plasma generator is capable of producing plasma conditions, similar to the expected fluxes in the divertor of ITER: high density ($\sim 10^{24} \text{m}^{-3}$) and low temperature ($\sim 1 \text{eV}$) hydrogen plasmas.

Figure 3.4 shows the experimental setup of Pilot-PSI with the location of the diagnostics to measure the surface temperature (infra-red imaging) and the local plasma conditions (Thomson scattering). The deuterium plasma is produced with a cascaded arc source \[92\], originally developed at the Eindhoven University of Technology \[93, 94\] and optimized in-house. The cascaded arc source was operated in ‘trumpet configuration’
3 Experiment

Figure 3.4: Schematic drawing of Pilot-PSI plasma generator as seen from above. The location of the infra-red camera and Thomson scattering diagnostics are indicated.

as described by Shumack [28]. The operation regime of the deuterium gas flow into the source was between 1 – 3 slm (standard litre per minute, which corresponds to 4.5·10^{20} particles per second). The plasma is formed in the discharge channel by an ionizing current of 150 – 250 A. The plasma then expands out of the high pressure source into a cylindrical vacuum vessel (Ø 0.4 m and ~1 m long). During plasma operation the pressure in the vacuum chamber typically was 1 – 3 Pa. The vacuum chamber is surrounded by oil cooled coils that produce an axial magnetic field of 0.4 – 1.6 T axi-symmetric to the source. The magnetic field radially confines the expanding of the plasma and generates an intense magnetized cylindrical beam to the target. Due to the cooling requirement of the coils, Pilot-PSI runs in pulsed mode.

The target is installed perpendicular in the plasma beam. It is clamped onto a copper heat sink, that is cooled with water (1 – 6 L/min). To maximize the thermal contact, a grafoil layer is added between the sample and the heat sink. The targets can be floating, grounded or attached to an external, independent power supply. In this way the target can be negatively biased with respect to the plasma potential. Negative biasing up to -40 V was used (chapter 7) in order to increase the ion energy.

Composition plasma beam

Characteristics of the hydrogen beam are briefly summarized in this section and interested readers are encouraged to read the extensive research described in the theses of A.E. Shumack [28] and R.C. Wieggers [29].
Shumack observed hollow emission beam profiles with optical emission spectroscopy (Balmer-β) as result of the low molecular deuterium density in the centre of the plasma beam [25]. This low density was found to be caused by a high H$_2$ dissociation degree and short penetration depth resulting from an effective charge exchange process. Similar low molecule concentrations were also obtained in Pilot-PSI simulations as reported by Wieggers [29]. In addition, Shumack measured an ionization degree of $>85\%$ in the centre of the beam [26]. Wieggers investigated the neutral inventory of the Pilot-PSI beam in front of the target with Eunomia simulations [27, 29]. The simulations confirm low concentrations of neutral species (less than 10\%). In this thesis, we can therefore safely assume that deuterium plasmas are dominated by D$^+$ ions and we neglect the neutral species in front of the target.

### 3.3.1 Diagnostics

**Plasma parameters ($n_e, T_e$) - Thomson scattering**

Thomson scattering (TS) is defined as the elastic scattering of electromagnetic radiation by free electrons. The electron density ($n_e$) can be easily deduced from the total amount of light scattered, while the electron temperature ($T_e$) is related to the Doppler broadening of the spectrum. The electron density and temperature are measured at about 20 mm from the target (see figure 3.4). The scattered light of the laser beam (Nd:YAG, 532 nm, 10 Hz) is focussed on 50 fibres at a scattering angle of 90° and led to the spectrometer. The signal is integrated over 30 consecutive pulses. Absolute calibration of the electron density was performed by Rayleigh scattering on a known argon background pressure in a separate experiment. Finally, data was corrected for stray-light and each fibre spectrum was fitted with a Gaussian to obtain spatial $n_e$ and $T_e$ profiles. Typical spatial distributions are shown in figure 3.5a. The particle flux was calculated using $n_e$ and $T_e$ using equation 2.1, the result is shown in figure 3.5b. Details on the DIFFER specific TS system, including a discussion on the observational errors can be found in [95, 96].

![Figure 3.5: a) Typical electron density (solid triangles) and temperature (open diamonds) profiles](image)

<table>
<thead>
<tr>
<th>a)</th>
<th>b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron density ($10^{20}$ m$^{-3}$)</td>
<td>electron temperature (eV)</td>
</tr>
<tr>
<td>flux ($10^{21}$ m$^{-2}$s$^{-1}$)</td>
<td>temperature (K)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>position (mm)</th>
<th>position (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

25
Surface temperature - infra-red imaging

A fast infra-red (IR) camera (FLIR SC7500-MB) was used to monitor the spatial (2D) and temporal surface temperature evolutions of the samples during plasma exposure. The system is sensitive for radiation in the wavelength range from 3.5 – 5.0 µm. Although the InSb detector has a spectral response in the wavelength range 1.5 – 5.1 µm, the lens used only has a spectral band of 3.5 – 5 µm. The viewing window at Pilot-PSI is made of CaF and has a transmission of 0.95 in the above spectral range.

The surface temperature is derived from the intensity of the emitted IR radiation. The light collected by the infra-red camera consists of the following contributions (see figure 3.6a):

1. Any infra-red light from the surroundings that is reflected by the target \( W_{\text{refl}} \).
2. The radiation emitted by the object. Planck’s law of radiation predicts the emission of a black body at a certain temperature \( W_{\text{obj}} \). However, in practice, bodies are rarely fully black and their emissivity \( \varepsilon \) characterizes the radiation, \( \varepsilon W_{\text{obj}} \).
3. Infra-red light from the mirror and the window \( W_{\text{other}} \). Additionally, their transmission \( \tau \) reduces the infra-red light arriving at the camera.

The total IR radiation \( Q_{\text{meas}} \) measured by the camera becomes then:

\[
Q_{\text{meas}}(T) = \tau [\varepsilon W_{\text{obj}} + (1 - \varepsilon) W_{\text{refl}}] + W_{\text{other}}
\]  

(3.2)

Actually, only the first term depends on the sample temperature. The second and third term can be omitted when subtracting the signal by a reference background measurement at a known temperature \( T_0 \), e.g. room temperature:

\[
Q_{\text{meas}}(T) - Q_{\text{meas}}(T_0) = \tau \varepsilon (W_{\text{obj}}(T) - W_{\text{obj}}(T_0))
\]  

(3.3)

Note that we implicitly assume that \( \varepsilon, \tau, W_{\text{refl}} \) and \( W_{\text{other}} \) stay constant in both measurements. The radiated power of the target \( W_{\text{obj}}(T_0) \) is known from Planck’s law and the target emissivity. Thus, the target temperature can be extracted using:

\[
W_{\text{obj}}(T) = \frac{Q_{\text{meas}}(T) - Q_{\text{meas}}(T_0)}{\tau \varepsilon} + W_{\text{obj}}(T_0)) = f_{\text{Planck}}(T_{\text{obj}})
\]  

(3.4)

Figure 3.6: Contributions to the infra-red signal.
The emissivity of tungsten $\varepsilon$ was verified ex-situ with the help of a thermocouple measurement. The obtained values were close to the temperature dependent emissivity curve found by Sergienko [97]. An emissivity of 0.06 was used for the analysis of the measurements in the low temperature regime (<550 K). The largest uncertainties in the temperature calculation are systematic errors in the system settings, such as a dirty window or mirror or heating of the vessel. A variation of 10% in the transmission coefficient, affects the calculated temperature with $\pm20$ K in the temperature range of 400 – 600 K. The effect of heating of the vessel could be checked by comparison of the analysis with a background measurement just before the plasma shot starts and a background measurement just after plasma exposure. The calculated temperature varied with 5 – 10 K.

The radial distribution of the surface temperature and a typical infra-red image are shown in figure 3.5b. The surface temperature is determined by the balance between the heat flux on the target and the water-cooling. Therefore, the temperature profile follows the ion flux profile closely. Using the surface temperature profiles from IR measurement and the cooling-water temperature, the temperature distribution within the sample was calculated by ANSYS [98]. The result of this calculation is shown in figure 3.7. Figure 3.7b shows the temperature variation as function of depth in the centre of the sample. The maximum temperature gradient is 0.035 K/µm. Radially, the maximum temperature gradient is 0.025 K/µm. The length-scales of the deuterium retention processes are much smaller than the temperature variation. Therefore, we do not consider temperature gradients in our the simulations. Figure 3.7c shows the temperature evolution at the centre of the target. Note the effective cooling: After switching off the plasma, the temperature of the targets was back to room temperature within typically 1 – 2 s.
3.4 Target analysis

Various diagnostics for target analysis were used for the research described in this thesis. Local deuterium depth profiles were measured with nuclear reaction analysis (NRA). The total deuterium retention and estimates of the trapping energies were obtained using thermal desorption spectroscopy (TDS), the surface morphology was studied by scanning electron microscope (SEM) and information about the region below the surface modifications was obtained by combining SEM imaging with focussed ion beam (FIB) cutting. Finally, positron annihilation Doppler broadening (PADB) was used for defect characterization.

3.4.1 Nuclear reaction analysis

Nuclear reaction analysis (NRA) offers a non-destructive method to determine light elements in a heavy material. The local deuterium depth profiles were measured using the nuclear reaction D($^3$He,p)$^4$He \[99\]. By injecting $^3$He, a nuclear reaction is initiated with the deuterium present in the material. The intensity of the resulting emitted radiation is directly related to the deuterium concentration. Depth information can be acquired by tuning the incoming beam energy (the differential cross-section is maximal at 620 keV). In our measurements, the beam energy was scanned from 690 keV to 4.0 MeV, so that deuterium up to a depth of 6 µm could be detected. The D($^3$He,p)$^4$He reaction has inverse kinematics, i.e. the lower the energy of the incident $^3$He particle, the higher the energy of the emerging protons. The proton detector is installed at a back-scattering angle of 135°.

The depth profiles of retained deuterium were derived from the measured proton energy distributions using the NRA-DC program \[100\]. The analyzed area is about 1 mm\(^2\) in size, this is determined by the $^3$He beam spot. A scan along the radius of the sample was performed to investigate the radial dependence of the deuterium depth profiles. The total amount of deuterium in the top layer, 6 µm, is obtained by volume integration over the depth profile.

3.4.2 Thermal desorption spectroscopy

Thermal desorption spectroscopy (TDS), also known as temperature programmed desorption, measures the desorption of molecules from a material during a heating cycle. The basics of this method are described by Redhead \[101\] and are extensively covered in the thesis of van Gorkum \[102\].

In short, a sample that is placed in a vacuum vessel is heated with a linear temperature ramp. When the internal thermal energy increases, the deuterium atoms can overcome their trap energies and diffuse to the surface, where they recombine and finally desorb as molecule into the vacuum vessel. The release rate of the molecules is measured by a mass spectrometer to yield a thermal desorption spectrum. An example of such a spectrum can be found in figure 3.9.
3.4 Target analysis

TDS setup

A schematic representation of the TDS setup is shown in figure 3.8. The sample is placed into a vacuum vessel, which is kept at high-vacuum conditions (<5×10⁻⁷ mbar). A Balzers QMA125 quadrupole mass spectrometer monitors the mass 4 (D₂) and mass 3 (HD) partial pressure in the vacuum chamber. The absolute sensitivity of the desorption rate is determined by connecting a D₂ and H₂ calibrated deuterium leak to the vessel. For the sensitivity of the HD signal, the average of the sensitivities of the mass 2 and mass 4 signal was taken. The sample is clamped to a ceramic heater and heated under a linear ramp of 1 K/s to 1273 K. The temperature of the sample was continuously monitored using a thermocouple. The linear heating rate was controlled by a proportional-integral-derivative (PID) control loop.

Once the system has reached equilibrium at pressure \( p_{eq} \), the rate of particles leaking into the vessel (\( L \)) equals the pump speed (\( S \)) by,

\[
L = N_0 S p_{eq} \quad [s^{-1}] \tag{3.5}
\]

where \( N_0 \) is \( 2.4 \times 10^{20} \) m⁻³ at 1 Pa and 300 K. During the desorption cycle the particles entering the system, i.e. the desorbed particles plus the leak rate (\( L \)), equals the particles

![Figure 3.8: Schematic drawing of the thermal desorption system.](image)
that are pumped away plus the rate of pressure change:

\[
\frac{dN(t)}{dt} + L = N_0 V \left( \frac{p}{\tau} + \frac{dp}{dt} \right)
\]  

(3.6)

\(N(t)\) is the number of particles that are not yet desorbed, \(V\) the desorption volume, \(p\) the partial pressure and \(\tau\) is the typical time scale of the pump. \(\tau\) can be calculated by dividing the desorption volume \((V)\) by the pumping speed \((S)\). For our TDS system this characteristic pump time is \(\sim 0.065\) s.

During static operation there is no external pumping \((\tau \to \infty)\), so that the derivative of the pressure is proportional to the desorption rate. During dynamic operation deliberate pumping is present. In our situation, where \(\frac{dp}{dt} \ll \frac{p}{\tau}\), the desorption rate can be approximated by

\[
\frac{dN(t)}{dt} = N_0 V \frac{p}{\tau} - L.
\]  

(3.7)

Therefore, the measured pressure is directly proportional to the desorption rate. A typical desorption spectrum is shown in figure 3.9. Although the measurement is relatively straightforward, interpretation is non-ambiguous and complex for several reasons. The probability of de-trapping increases with increasing temperature, but at the same time the amount of particles available for desorption decreases. In this way a desorption peak is formed at a specific temperature, which is characteristic for a certain trap energy. However, this peak position is also dependent on the local deuterium distribution, i.e. deuterium concentration and fill fraction as a function of depth. Also the heating ramp rate affects position of the desorption peak, since it determines the time lag between release from the trap and measurement by the mass spectrometer. A diffusion-trapping model (section 3.5) was used for interpretation of the desorption spectrum. Time-integration of the thermal desorption spectrum yields the total amount of deuterium retained in the sample.

Before every TDS measurement, calibration with the calibrated deuterium leak was performed. The standard deviation of this calibration is 5%. Variations of the Pilot-PSI deuterium plasma at the same settings, can cause deviations in the deuterium retention of samples exposed to similar plasma conditions. To test the reproducibility, three undamaged samples were exposed to similar deuterium plasmas conditions within the same measurement series (figure 3.9). While, for undamaged samples the results from session to session can differ significantly, the sample-to-sample variation within a session is small \((\sim 10\%)\). Additionally, two pre-irradiated samples were exposed to similar plasma conditions in two different measurement sessions (figure 3.9). Because the deuterium retention is determined mainly by pre-irradiation damage and the contribution from the plasma damage small, these results are comparable. The above experiments confirm the robustness of the setup.

All samples were desorbed at least a week after exposure. We found that the desorption profile in the first week can change significantly as result of the mobile deuterium and deuterium trapped at very low energies leaving the sample. After this period, the deuterium retention does not change significantly.
3.4 Target analysis

3.4.3 Surface imaging
scanning electron microscopy and focused ion beam

The topography of the surface was investigated with a scanning electron microscopy (SEM) in combination with a focussed ion beam (FIB). The surface images were acquired with a Helios NanoLab600 (FEI). This system consists of an electron gun for SEM, a gallium-ion beam for FIB cutting, gas injection for surface coating and multiple detectors.

SEM images were typically taken with a 5 keV electron beam. A Ga-ion beam with an impact energy of 30 keV was used to create cross-sections, the current of the ion beam was varied between 2 – 20 nA. Prior to the cross-sectional cutting, the area of interest (typically µm-sized) was coated with a Pt-C film to reduce artefacts during the cutting process. The surface normal was aligned with the Ga-ion beam and the angle between the Ga-ion and electron beam was 52°. The sample was cut slice-by-slice and SEM images were taken after each cut.

3.4.4 Positron annihilation Doppler broadening

Positron annihilation Doppler broadening (PADB) was used to monitor the formation and clustering of defects [103][104]. The annihilation reaction of an electron with a positron produces two gammas, each with an average energy of 511 keV. As a consequence of momentum conservation, the momentum of the electron-positron pair results in a Doppler broadening of the 511 keV annihilation energy.

The PADB experiments were performed with the Variable Energy Positron beam at the TU Delft. Positrons emitted from a $^{22}\text{Na}$ source were, after moderation to thermal energies and subsequent acceleration, directed to the samples with a kinetic energy in the range of 0.1 to 25 keV. The beam intensity was about $10^4$ positrons s$^{-1}$ and the beam
diameter at the target about 8 mm. The mean implantation depth of the positrons, \( \langle z \rangle \), scales with the implantation energy, according to \( \langle z \rangle \propto A/\rho \times E^{1.62} \) \[105\]. In tungsten, a positron energy of 25 keV corresponds to an implantation depth of about 400 nm.

A typical measurement of a gamma spectrum is shown in figure 3.10. The shape can be defined by two parameters, namely \( S \) and \( W \). The \( S \) (sharpness) parameter is defined as the ratio of counts registered in a fixed central electron momentum window \((|p_\parallel| < 3.5 \times 10^{-3} m_0c)\) to the total number of counts in the photon peak. This choice of momentum window makes the \( S \) parameter sensitive to annihilations with low momentum valence electrons and the \( S \) parameter will therefore be relatively high for a defect rich material: for a positron trapped in an open volume defect (such as a dislocation, mono-vacancy or vacancy cluster) the probability for annihilation with a valence electron is enhanced at the expense of annihilation with a core electron. Similarly, the \( W \) (wing) parameter is obtained from the high momentum regions, \( W_{\text{left}} \) and \( W_{\text{right}} \), for which \( 1 \times 10^{-2} < |p_\parallel| < 26 \times 10^{-3} m_0c \). This area accounts for annihilations with high momentum core electrons. Therefore, the \( W \) parameter will be relatively high in a defect-free material. Note that as function of the defect concentration the behaviour of \( S \) and \( W \) parameter is opposite.

Plotting the \( S \) parameter versus the \( W \) parameter gives insight about the vacancy behaviour. Without any lattice defects, each material has a characteristic \( S \) and \( W \) value (\( S_{\text{bulk}} \) and \( W_{\text{bulk}} \)). The same holds for each defect type: \( S_d \) and \( W_d \). The measured \( S \) parameter is a summation of all of these:

\[
S = f_{\text{bulk}}S_{\text{bulk}} + \sum_n f_{d,n}S_{d,n}, \tag{3.8}
\]

with \( f_{\text{bulk}} \) the fraction of positrons annihilated at the free, i.e. non-trapped state, and \( f_{d,n} \) the fraction annihilated in the \( n \)th defect type. In a sample with only one type of defect present, the \((S,W)\) point lie on along a straight line from the defect-dominated to the defect-free \((S,W)\) point, given by

\[
S = (W - W_{\text{bulk}}) \frac{S_{d1} - S_{\text{bulk}}}{W_{d1} - W_{\text{bulk}}} + S_{\text{bulk}}. \tag{3.9}
\]

If there is more than one defect types present or chemical composition of the material changes, the \( SW \)-plot will be non-linear \[106\].
3.5 TMAP7

Tritium Migration Analysis Program 7 (TMAP7), developed by G.R. Longhurst at the Idaho National Lab [107], was used for the simulation of the deuterium implantation and to interpret the thermal desorption spectra (section 3.4.2). TMAP7 is a one-dimensional solver that evaluates the diffusion equation for hydrogen in materials [107]. The program calculates the diffusion of hydrogen through the material and trapping and de-trapping rates of hydrogen in defects. Also, dissociation of and recombination to molecules at the surface are calculated. TMAP7 has the possibility of including deuterium sources and three types of defects, i.e. trap energies.

The TMAP7 code uses a model in which the material is divided in so-called nodes with different thicknesses. Each node contains a concentration of mobile deuterium (section 2.3.1). In addition, a pre-defined concentration of saturable traps can be assigned to each node. These saturable traps are defined by their concentration and trap energy. For each node, the occupation of the traps is calculated. The deuterium flow from one layer to another is determined by the difference in mobile concentration between two nodes. For the surface boundary, a special node without thickness is defined. To these special nodes, not a mobile and trapped deuterium inventory are assigned, but the specific surface concentrations.

Modelling input

TMAP7 was used for the simulation of both the deuterium diffusion during plasma exposure as well as the deuterium desorption as result of the heat rate during TDS. The first was realized by defining a deuterium source in the first tungsten layer. The latter by defining the temperature of the target and increasing it linearly with a heat rate of 1 K/s.

Material input - For the simulations presented in this thesis a tungsten material was simulated by defining the number density of \(6.3 \times 10^{28} \text{ m}^{-3}\). The tungsten material of 1 mm thickness was separated into 64 depth layers, with a thickness varying from 2.5 nm at the surface to 1 \(\mu\text{m}\) at the backside. The trapped concentration and depth distributions of deuterium traps need to be specified according to the experimental settings. For example, for a pre-irradiated target the trap concentrations (in atomic fraction, at.fr.) were defined as follows:

<table>
<thead>
<tr>
<th>(E_{\text{trap}})</th>
<th>trap concentration</th>
<th>depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85 eV</td>
<td>(1.0 \times 10^{-4}) at.fr.</td>
<td>homogeneous</td>
</tr>
<tr>
<td>1.4 eV</td>
<td>(5.0 \times 10^{-3}) at.fr.</td>
<td>(&lt;1.5 \mu\text{m})</td>
</tr>
<tr>
<td>1.85 eV</td>
<td>(7.0 \times 10^{-3}) at.fr.</td>
<td>(&lt;1.5 \mu\text{m})</td>
</tr>
</tbody>
</table>

Deuterium input - The mobile concentration at the start of both implantation and desorption simulations was chosen to be zero. As mentioned earlier, all TDS measurements were carried out more than a week after plasma exposure, so that the solute deuterium present in the tungsten was negligible.
Equation input - The diffusion behaviour is defined by the equations of diffusion (section 2.3.2), the trapping rate coefficient (equation 2.10), the trap release rate coefficient (equation 2.11) and recombination at the surface (equation 2.2).

The exact details from the simulation are specified in the chapters where relevant.
4 Saturation of deuterium retention in self-damaged tungsten exposed to high-flux plasmas

M.H.J. ’t Hoen¹, B. Tyburska-Püschel²,³, K. Ertl³, M. Mayer³, J. Rapp¹, A.W. Kleyn¹,⁴ and P.A. Zeijlmans van Emmichoven¹

¹ FOM institute for Plasma Physics Rijnhuizen, NL-3439 MN Nieuwegein, the Netherlands
² Department of Engineering Physics, University of Wisconsin-Madison, Madison, WI, U.S.A
³ Max-Planck-Institut für Plasmaphysik, Boltzmannstraße 2, D-85748 Garching, Germany
⁴ University of Amsterdam, Science Park 904, NL-1098 XH Amsterdam, the Netherlands

Abstract

Polycrystalline, annealed tungsten targets were bombarded to various damage levels with 12.3 MeV W⁴⁺ ions. Deuterium was implanted by high-flux plasmas in Pilot-PSI (>10²⁴ m⁻² s⁻¹) at a surface temperature below 525 K. Deuterium retention has been studied by nuclear reaction analysis and by thermal desorption spectroscopy. We found that deuterium retention is strongly enhanced by the tungsten bombardment and that saturation occurs at a W⁴⁺ fluence of about 3 × 10¹⁷ m⁻². The maximum deuterium concentration in the damaged region was measured to be 1.4 at.% This is in accordance with other experiments that were carried out at much lower fluxes. We therefore conclude that the saturation behaviour and the maximum retention are not affected by the high fluxes used in our experiments.

A simple geometric model is presented that assumes that the saturation solely originates in the tungsten irradiation and that explains it in terms of overlapping saturated volumes. The saturated volume per incident MeV ion amounts to 3 × 10⁴ nm³. From our results, we are able to obtain an approximate value for the average occupation number of the vacancies.

published in: Nuclear Fusion 52 023008 (2012)
4 Saturation of deuterium retention in self-damaged tungsten

4.1 Introduction

In future magnetic fusion devices as ITER, tungsten is foreseen as divertor material. The divertor has to withstand high density, low temperature plasma fluxes. Good thermal properties as its high melting point, high thermal conductivity and low erosion rate make tungsten favourable over other materials. However, there is concern that hydrogen isotopes are retained in tungsten. Firstly, for safety reasons, it has been decided for ITER that the tritium inventory should be kept below 700 g [14]. Secondly, for efficiency reasons, it is important that the fuel is not retained in the wall. Understanding the retention properties of tungsten is important for ITER and for fusion reactors beyond ITER. Continuous bombardment with 14.1 MeV neutrons degrades material properties and introduces damage into the material. In this paper we focus on the influence of damage in tungsten on deuterium retention.

Several studies have shown that irradiation damage strongly enhances deuterium retention [16][17][19]. Tyburska et al [16] noticed that a linear increase of damage did not lead to a linear increase of deuterium stored in the sample and that the defects can be removed by annealing. Saturation of the deuterium retention was observed at 0.3 displacements per atom (dpa), independent of implantation fluence. Wright et al [19], who did similar experiments at a much higher flux, showed that the deuterium retained in damaged tungsten saturates below 0.22 dpa.

The main aim of this investigation is to determine the irradiation damage level where deuterium retention in tungsten saturates for high-flux plasmas, and to understand the saturation behaviour. A systematic study of deuterium retention in tungsten as a function of target temperature and irradiation damage level was performed. Analysis was done by nuclear reaction analysis (NRA) and thermal desorption spectroscopy (TDS). The results are explained by a simple geometric model based on overlapping volumes.

4.2 Experiment

4.2.1 Target preparation

Polycrystalline tungsten targets (PLANSEE, 99.96% purity) were annealed for 1 h at 1273 K at a background pressure of 5 × 10^{-4} Pa. The dimensions of the targets are 20 mm in diameter and 1 mm in thickness. In the present experiments, unpolished targets were used. The cleanliness of the targets was checked by XPS before and after plasma exposure. In both cases, the XPS signal was dominated by carbon (40 – 70%) and oxygen (20 – 40%). This can be ascribed to native carbon and oxide layers of a few nanometres thick, present on the targets due to their exposure to air. Under ambient conditions hydrocarbons are deposited onto the tungsten target. During plasma exposure, the chemical erosion of carbon [108] is an efficient process and formation of water removes the oxide layer. It is therefore likely that during plasma exposures no carbon nor oxide was present. The tungsten signal was only about 10%. This low signal is partly caused by the rough surface of the target; polished samples showed an increase of the signal by a factor 3.
With XPS, trace amounts of copper and calcium were measured after Pilot-PSI [10] exposure. They were deposited on the targets during plasma exposure. Their contribution to the XPS signal was very limited and well below 1%.

4.2.2 Damage creation - W\(^{4+}\) irradiation

Damage caused by neutron irradiation was simulated by heavy ion bombardment. Radiation damage by neutrons and by heavy ions is to some extent comparable [62]. For both neutrons and heavy ions, the ratio of low-energy to high-energy primary knock-on atoms is low, and they both create dense collision cascades [109]. However, one should realize that there are also differences between heavy ion and neutron irradiation. Damage created by heavy ions is concentrated in a narrow region below the surface, while neutron damage exhibits a homogeneous defect concentration very deep in the material. Furthermore, the detailed nature of the defects is unclear and may be different and neutron collisions will lead to transmutations whereas heavy ions will not.

The samples were bombarded at normal incidence with 12.3 MeV W\(^{4+}\) ions. The W\(^{4+}\) ions, accelerated through a potential difference of 2.5 MV, were implanted with the 3 MV tandem ion accelerator at IPP-Garching. In order to obtain homogeneous irradiation, the beam (Ø ~ 3 mm) was raster scanned across the surface. The area damaged by the tungsten bombardment was 12 mm in diameter. The damage rate at which the targets were damaged was \((3 \pm 1) \times 10^{-4} \text{ dpa s}^{-1}\). During the tungsten irradiation, the targets were kept at room temperature. To predict the irradiation damage, calculations were done

Figure 4.1: SRIM results of damage distribution for tungsten irradiated by 12.3 MeV W\(^{4+}\) ions. For comparison with the results of Tyburska et al [16], the 0.3 dpa damage profile created by 5.5 MeV W\(^{2+}\) ions is depicted as well (reconstructed from [16] and scaled to \(E_{\text{displ}} = 90 \text{ eV}\)).
with the binary collision transport code SRIM [42]. SRIM profiles were calculated for 0 K. The absolute level of displacement damage decreases approximately linearly with an increase of the displacement threshold energy ($E_{\text{displ}}$). In the literature, a wide range of values has been used: Sakamoto et al [110] and Tokunaga et al [111] used 40 eV determined by Lucasson et al [112]. Maury et al [113] measured by electron irradiation a value of 42 ± 1 eV in the ⟨100⟩ direction and 44 ± 1 eV for ⟨111⟩ orientation. Xu et al [114] showed with molecular dynamics simulations that the displacement threshold energy is indeed strongly dependent on the crystal orientation and ranges from 68 up to 250 eV. Others, like Ogorodnikova et al [115], use an average displacement energy of 90 eV as reported by [68]. In this paper the average value of 90 eV is used, unless stated otherwise.

The SRIM results are shown in figure 4.1. Damage profiles extend to 1.5 µm below the surface and have a maximum damage level at about 0.8 µm depth. The targets were subjected to W$^{4+}$ ion fluences up to $6.5 \times 10^{17}$ m$^{-2}$, which corresponds to peak damage levels of up to 0.45 dpa. These peak damage levels are used as reference for our experiments. For comparison with the results of Tyburska et al, the 0.4 dpa damage profile created by 5.5 MeV W$^{2+}$ ions is also depicted. It is clear that 12.3 MeV ions penetrate deeper in the material and that the maximum damage level occurs at larger depth.

### 4.2.3 Deuterium plasma exposure

Pilot-PSI is a linear plasma generator for plasma surface interaction (PSI) studies in support of the international fusion experiment ITER [10, 12]. Deuterium plasma is produced by a cascaded arc, which facilitates the production of unique plasma conditions. Particle fluxes of up to $10^{24}$ m$^{-2}$s$^{-1}$ are obtained with energy fluxes up to 10 MW m$^{-2}$ and electron temperatures of 0.5 – 5 eV. The damaged targets have been exposed for 100 s in Pilot-PSI in an axial magnetic field of 0.4 T.

Electron density and temperature of the plasma beam were determined by the Thomson scattering technique [96]. The plasma beam has a Gaussian profile with an electron density of about $3.0 \times 10^{20}$ m$^{-3}$ in the centre and a full width half maximum of ~1 cm. The maximum electron temperature was measured to be 0.7 eV.

During plasma exposure, the targets were electrically floating. Assuming that the ion temperature equals the electron temperature and using the Bohm criterion [31], the peak deuterium ion plasma flux can be determined to be $1.2 \times 10^{24}$ m$^{-2}$s$^{-1}$. The flux on and the surface temperature of the target are shown in figure 4.2. The deuterium implantation area (Ø 16 mm) covered the pre-irradiated area. The surface temperature is determined by the heat flux of the plasma and by cooling of the target. In all experiments, temperature profiles of the surface of the target have been measured with a fast infrared camera (FLIR SC7500-MB). The maximum surface temperature was 525 K ± 10 K. The emissivity of tungsten at these temperatures is very low and dependent on the surface structure. It is therefore possible that a systematic error of maximum 30 K was introduced by an error in the emissivity coefficient. The cooling of the target was very effective; after switching off the plasma, the temperature of the targets was back to room temperature within typically 1 – 2 s.
4.2.4 Nuclear reaction analysis

NRA of the targets was performed at IPP-Garching four weeks after plasma exposure. The nuclear reaction $D(\text{^3He}, p)^4\text{He}$ was used to obtain a local measurement of the deuterium concentration as a function of depth \cite{99, 116}. The $\text{^3He}$ beam spot of 1 mm in diameter was positioned at four spots on the target to extract a radial scan. At each position, the energy was scanned from 690 keV to 4.0 MeV to determine the deuterium concentration with a resolution of $\sim$0.5 µm down to 6 µm depth. The depth profiles of the retained deuterium were calculated from the measured proton energy distributions by use of the SimNRA program \cite{117}. The surface roughness of the targets did not allow us to extract information from the alpha spectrum to obtain a near-surface deuterium concentration with a better resolution. The total amount of deuterium present in the top 6 µm of the target was obtained by integrating the depth profiles.

4.2.5 Thermal desorption spectroscopy

The targets were analysed with TDS at FOM-Rijnhuizen seven weeks after plasma exposure. The tungsten target was clamped to a ceramic heater and heated with a linear temperature ramp of 1 K/s to 1273 K. A Balzers QMA125 quadrupole mass spectrometer (QMS) monitored the mass 4 (D$_2$) and mass 3 (HD) signals in the residual gas in the chamber, to determine the total amount of deuterium released from the target during the temperature ramp. The absolute sensitivity was determined using calibrated leaks of H$_2$ and D$_2$. For the sensitivity of the mass 3 signal, the average of the sensitivities of mass 2 and mass 4 was taken.
4.3 Results

4.3.1 Nuclear reaction analysis

NRA was carried out at several positions on the target to obtain deuterium depth distributions as function of temperature and flux. The results are shown in figure 4.3. Also the retention for an undamaged target is shown. From figure 4.3, it is clear that W\textsuperscript{4+} pre-irradiation strongly enhances deuterium retention. The deuterium retention decreases as function of depth. The deuterium retention beyond 3 µm was below the detection limit of 10 ppm.

At the measurement points in the centre of the target and 1 mm off-centre, which were exposed to the highest particle flux and which had the highest surface temperature, the deuterium was found deepest in the material. This agrees with the observations of Wright et al. \cite{19}, who found that in this temperature regime, deuterium retention is primarily determined by diffusion: at the highest surface temperature, deuterium diffuses deepest into the tungsten material (figure 4.3).

![Figure 4.3](image)

Figure 4.3: Depth distributions of retained deuterium in damaged tungsten targets, pre-irradiated to (a) 0.045, (b) 0.09, (c) 0.22 and (d) 0.45 dpa. The shown deuterium depth profiles were measured at 4 spots on the target: in the centre (\textasciitilde 525 K); 1 mm off-centre (\textasciitilde 520 K); 3 mm off-centre (\textasciitilde 510 K); 5 mm off-centre (\textasciitilde 480 K). The grey data points and dotted line indicate the deuterium retention (multiplied by 10) of an undamaged tungsten target.
For the measurements nearest to the surface (0.25 µm), deuterium retention is independent of position and thus of surface temperature and particle flux. Deuterium retention does clearly increase with damage level, which indicates that the retention at the surface is mostly determined by the defect concentration. The maximum in deuterium retention is about 1.4 at.%, which agrees well with the maximum deuterium concentration of 1.5 at.% found by others [16, 19, 20]. Both Tyburska et al. [16] and Fukumoto et al. [20] found an additional surface effect, where the retained deuterium is much higher in a very thin layer at the surface. By investigation of the surface morphology, it became clear that these high values originated from cracks and blister formation. This surface effect can also be observed in our experiments, as is clear from the experiments on the undamaged target, but only gives a minor contribution to the retention of the damaged targets (related to the limited depth resolution of 0.5 µm).

The measured deuterium retention profiles do not match the calculated damage profiles as shown in figure 4.1, with the measured retention deeper in the material being significantly lower than expected from the damage profiles. This also holds when the effect of saturation on the damage profiles is considered, leading to flatter profiles. The mismatch is probably caused by the limited diffusion. This is supported by the fact that for a specific target, the retention at the surface is the same for all positions whereas deeper in the material retention is larger in the centre (where flux and temperature are higher).

![Figure 4.4](image)

**Figure 4.4:** Amount of deuterium retained in the first 6 µm as a function of pre-irradiation W^4+ ion fluence. Saturation of deuterium retention is reached around 0.2 dpa. A comparison with the TDS data is made by dividing the total amount of deuterium desorbed during TDS by the surface area.
The integrated NRA data, i.e. the deuterium retained in the first 6 µm of the target, is shown in figure 4.4. Clearly, the retention is close to its saturation value at a W\(^{4+}\) pre-irradiation fluence of 3 \times 10^{17} \text{ m}^{-2}. Using a value of 90 eV for the displacement energy, this corresponds to 0.2 dpa.

### 4.3.2 Thermal desorption spectroscopy

We investigated our targets with TDS to get information on the defect types in which the deuterium is trapped. The TDS results for the D\(_2\) signal are shown in figure 4.5. The undamaged target shows a small low temperature peak at around 550 K, caused by deuterium trapped in intrinsic defects usually associated with dislocations and grain boundaries [19]. It is likely that these naturally exist in the material, as the annealing temperature of 1273 K is still below the recrystallization temperature of tungsten. Since the deuterium ion energy is much lower than the displacement threshold of tungsten, it does not seem likely that these defects are created by plasma exposure. This can however not be excluded, several mechanisms have been suggested for defect creation by deuterium ion implantation below this threshold: e.g., plastic deformation by deuterium

![Thermal desorption spectra (D\(_2\) signal) of the targets, temperature ramp was 1 K/s. The background signal was measured at a target that was not irradiated by tungsten ions, nor exposed to deuterium plasma, and is virtually 0 at all temperatures. Unfortunately, the measurement at 0.45 dpa was not successful due to technical problems in the heating rate. However, the integrated TDS profile could be used to calculate the total deuterium retention.](image)
super-saturation \cite{118} and creation of vacancies by recoil implantation of carbon and oxygen impurities arriving at the tungsten surface \cite{82}.

Pre-irradiation of the targets enhances the intensity of the low temperature peak and introduces a high temperature peak at about 850 K. The enhancement and broadening of the low temperature peak towards higher temperatures can be explained by defect creation. In literature, various defect types have been identified in the temperature range 400 – 650 K, i.e. dislocations and grain boundaries \cite{52,119}, and single vacancies (with one \cite{78,119} or two \cite{55} deuterium atoms trapped). The high temperature peak is usually associated with deuterium trapped in vacancy clusters \cite{20,52,67}. The high temperature peak measured by Wright et al \cite{19} is significantly less pronounced than the one in our experiments. This might be caused by the lower surface temperature during plasma exposure as used in their experiments (480 K), which limits the clustering of vacancies.

The total deuterium retained by TDS divided by the damaged surface area (Ø 12 mm) is shown in figure 4.4. The average value obtained by TDS is somewhat lower than the local deuterium retention (NRA) at 5 mm off-centre. This may be caused by a misalignment between the centre of the plasma beam and the centre of the self-implantation area of 1 mm.

4.4 Model

The deuterium retention in the first 6 \textmu m underneath the surface as function of pre-irradiation fluence is shown in figure 4.4. The retention clearly saturates at a W^{4+} fluence of about $3 \times 10^{17}$ m$^{-2}$. We developed a simple geometric model that assumes that the saturation solely originates in the tungsten pre-irradiation and that explains this saturation in terms of overlapping volumes.

The model is an extension of a 2D model, where a surface with area $A$ is randomly covered with objects with surface area $a$. The expectation value of the fraction $f(n)$ of surface $A$ covered with $n$ such objects is given by the following differential equation:

$$\frac{df}{dn} = \frac{a}{A} (1 - f(n)).$$

(4.1)

The solution of this equation is given by:

$$f(n) = 1 - \exp \left[ -\frac{na}{A} \right].$$

(4.2)

MeV ions bombarding a material create Frenkel pairs. At sufficiently high pre-irradiation fluence, the material becomes saturated with Frenkel pairs: a newly created vacancy will immediately recombine with an interstitial present in the material. This spontaneous recombination leads to a maximum concentration of vacancies. Each single vacancy occupies an average spontaneous recombination volume, $V_{\text{vac}}$.

Each individual MeV ion creates a unique, very complex, 3D distribution of vacancies. SRIM simulates these individual distributions and calculates, among others, the number of vacancies as function of depth averaged over many MeV ions. The shape of
this average vacancy distribution as function of depth \(d\), \(\text{vac}_{\text{SRIM}}(d)\), resembles the graphs shown in figure 4.1. In our model we assume that, instead of a unique distribution, each individual MeV ion creates this average vacancy distribution. The average effective damage volume of an ion, \(V_{\text{ion}}^{\text{eff}}\), can be expressed in terms of \(V_{\text{vac}}^{\text{SRIM}}\) in the following way:

\[
V_{\text{ion}}^{\text{eff}} = V_{\text{vac}}^{\text{SRIM}} \sum_{\text{layers}} \text{vac}_{\text{SRIM}}(d). \tag{4.3}
\]

\(V_{\text{ion}}^{\text{eff}}\) represents the damage volume created by a single MeV ion saturated with vacancies. With the MeV ions incident at random positions on the target, the damage volumes will start to overlap as soon as the fluence is sufficiently high, and saturation occurs.

We extended the 2D case (equation 4.2) to a 3D model by splitting up the target in \(N\) layers, parallel to the surface and of equal thickness. The surface area \(a\) in equation 4.2 has to be taken differently for each layer. The relative values are determined by the shape of \(\text{vac}_{\text{SRIM}}(d)\). We furthermore replace the fraction \(f(n)\) by the deuterium retention. The model leads to the following function, where the summation is taken over the \(N\) contributing layers:

\[
D_{\text{ret}}(F) = \frac{D_{\text{sat}}}{N} \sum_{\text{layers}} \left\{ 1 - \exp \left[ -F \cdot \text{vac}_{\text{SRIM}}(d) \cdot \frac{V_{\text{vac}}^{\text{SRIM}}}{\Delta d} \right] \right\} \tag{4.4}
\]

Here, \(D_{\text{ret}}(F)\) is the deuterium retention as function of the pre-irradiation fluence \(F\) and \(D_{\text{sat}}\) the maximum deuterium retention when the sample is saturated with vacancies. The thickness of the layers is given by \(\Delta d\). The function (equation 4.4) was fitted to the four sets of data points shown in figure 4.4, with \(D_{\text{sat}}\) and \(V_{\text{vac}}^{\text{SRIM}}\) as fit parameters. Note that, although \(\text{vac}_{\text{SRIM}}(d)\) and \(V_{\text{vac}}^{\text{SRIM}}\) are both directly affected by the choice of \(E_{\text{displ}}\), \(V_{\text{ion}}^{\text{eff}}\) is not.

In figure 4.4, the data with the fits are shown. It is clear that the fit function describes the measurements quite well. The deuterium retention from a single MeV ion, incident on a non-irradiated target, amounts to \((1.3 – 1.7) \times 10^4\) D/ion, which can be directly obtained from the slope at zero fluence. The average effective damage volume of an MeV ion, \(V_{\text{ion}}^{\text{eff}}\), was found to be \((3 \pm 1) \times 10^4\) nm$^3$.

### 4.5 Discussion

We have studied deuterium retention for targets pre-irradiated with \(12.3\) MeV W$^{4+}$ ions and subsequently exposed in Pilot-PSI to high-flux plasmas. From integrated NRA data, it is clear that saturation of deuterium retention takes place at a W$^{4+}$ fluence of about \(3 \times 10^{17}\) m$^{-2}$, which corresponds to \(\sim 0.2\) dpa. Since the absolute value of the created damage is inversely proportional to the displacement threshold energy, we can rescale the saturation point found by Tyburska et al [16] to \(\sim 0.3\) dpa \((E_{\text{displ}} = 90\) eV\), measured at fluxes of about \(10^{22}\) m$^{-2}$s$^{-1}$. Since these values are very close and, in addition, since the maximum retention levels are quite similar, we conclude that the high flux of about \(10^{24}\) m$^{-2}$s$^{-1}$ as used in the present experiments does not significantly affect deuterium...
4.6 Conclusions

Polycrystalline, annealed and pre-damaged tungsten targets were exposed to high-flux plasmas in Pilot-PSI at a surface temperature below 525 K. The deuterium retention has been investigated by NRA and TDS. We found that the deuterium retention is enhanced by pre-irradiation with 12.3 MeV W^{4+} ions and that it saturates at a W^{4+} ion fluence of $3 \times 10^{17}$ m$^{-2}$, which corresponds to $0.2$ dpa ($E_{\text{displ}} = 90$ eV). We found that the retention. This agrees with our model that assumes that the saturation behaviour solely originates in the damage created before the deuterium implantation.

From the analysis of our measurements, we were able to obtain the average effective damage volume of the MeV ions used in our experiments and the number of deuterium atoms retained per MeV ion. With this information an estimate of the occupation number of the vacancies can be made.

We have estimated the number of vacancies created by an MeV ion in two different ways. The first method uses the number of Frenkel pairs derived from the Norgett-Robinson-Torrens (NRT) formula \[120\]. The integrated damage energy output files of SRIM were used to calculate the number of Frenkel pairs created by each MeV ion: on average $2.0 \times 10^4$ vacancies. Note that the calculated number of vacancies depends on the choice made for $E_{\text{displ}}$. However, the actual number of vacancies per incident ion is lower, since the NRT formula does not take into account the recombination of defects produced in the collision cascade itself. Molecular dynamics simulations (MD) have shown that the recombination drastically decreases the amount of vacancies \[121, 122\]. Troev et al \[122\] used MD simulations of tungsten to determine the cascade efficiency, defined as the ratio between Frenkel pairs calculated by MD and the theoretical number of Frenkel pairs derived by the NRT formula. They found that 20 – 25% of the Frenkel pairs survive, the rest annihilates. The damaged volume of the MeV ion after recombination within the collision cascade is then $(4 – 5) \times 10^3$ vacancies. The second method uses the spontaneous recombination volume of Frenkel pairs. From our experiments we found an average effective damage volume of an MeV ion of about $3 \times 10^4$ nm$^3$. In literature, the spontaneous recombination volume of Frenkel pairs in tungsten is reported to be in the range of 100 – 200 atomic volumes \[123, 124\] or 1.6 – 3.2 nm$^3$. Hence, the effective damage volume corresponds to $(0.9 – 1.9) \times 10^4$ vacancies. The results from the two methods are somewhat different, and further investigation is needed.

From our experiments, we deduced a number for the amount of retained deuterium: $(1.3 – 1.7) \times 10^4$ deuterium atoms per incident MeV ion. Dividing this experimental number by the number of vacancies as discussed above, yields a value for the average occupation number of a vacancy of 2.6 – 4.2 for method 1 and 0.7 – 1.8 for method 2. It seems that even though the fluence as used in our experiments was not sufficiently high to fully saturate all created vacancies (diffusion limited, see discussion figure 4.3), the average occupation number is at least close to 1. At longer exposure times, therefore, deuterium retention will be enhanced and the average occupation number is anticipated to increase further.

4.6 Conclusions
deuterium saturation retention in the damaged tungsten is not significantly affected by
the high fluxes of $\sim 10^{24} \text{ m}^{-2}\text{s}^{-1}$ used in our experiments, and that it is dominated by the
pre-irradiation damage. This is in accordance with the fact that our data fit quite well to
the simple geometric model, which assumes that the saturation of deuterium retention in
the tungsten material solely originates in the $\text{W}^{4+}$ self-implantation. We further found
that the average occupation number of the vacancies is at least close to 1 and that it will
increase for higher fluences.

We used heavy ions ($\text{W}^{4+}$) to simulate the effect of neutron irradiation with heavy
ion bombardment on tungsten as present in the divertor of fusion reactors like ITER.
Assuming neutron damage to be comparable to damage from heavy ions, the hydrogen
retention would amount to a maximum value of 1.4 at.\% for surface temperatures below
525 K. At higher surface temperatures the retention is expected to be less, because of
annealing of the vacancies.

In the present study, we focussed on deuterium retention in the first few micrometers.
Here, the deuterium retention is dominated by the pre-irradiation damage. Further inves-
tigations are needed on the effect of high-flux plasmas on surface morphology, blistering
etc. These studies will be carried out in the future.

Acknowledgements

This work, supported by the European Communities under the contract of Association
between EURATOM/FOM, was carried out within the framework of the European Fusion
Programme with financial support from NWO. The views and opinions expressed herein
do not necessarily reflect those of the European Commission.

The authors would like to thank R.S. Al for the technical assistance at the Pilot-PSI
measurements, J. Dorner and M. Fußeder (IPP-Garching) for their technical assistance
with the $^3\text{He}$ beam analysis and E. Zoethout for the XPS analysis of the samples.
Reduced deuterium retention in self-damaged tungsten exposed to high-flux plasmas at high surface temperatures

M.H.J. ’t Hoen, M. Mayer, A.W. Kleyn, H. Schut and P.A. Zeijlmans van Emmichoven

1 FOM institute DIFFER, Association EURATOM-FOM, Partner in the Trilateral Euregio Cluster, NL-3439 MN Nieuwegein, the Netherlands
2 Max-Planck-Institut für Plasmaphysik, Boltzmannstraße 2, D-85748 Garching, Germany
3 University of Amsterdam, Science Park 904, NL-1098 XH Amsterdam, the Netherlands
4 Delft University of Technology, Mekelweg 15, NL-2629 JB Delft, the Netherlands

Abstract

We investigated the effect of surface temperature on deuterium retention in self-damaged tungsten exposed to high-flux deuterium plasmas. The retention saturates at a W^{4+} fluence of about $3 \times 10^{17} \text{ m}^{-2}$ and is strongly reduced for the present high surface temperatures of 800 – 1200 K as compared to previous experiments at 470 – 525 K. Combination of nuclear reaction analysis (NRA), thermal desorption spectroscopy and positron annihilation Doppler broadening (PADB) was used to investigate the reduction in deuterium retention. The NRA showed a strong reduction of retention at the surface at high surface temperatures. The PADB measurements suggest that during plasma exposure defects are mobile and cluster into larger clusters containing up to a few tens of vacancies. Tritium Migration Analysis Program 7 simulations show that trapping and de-trapping rates are very high for defects with trapping energies below $\sim 1.5 \text{ eV}$. The strong reduction in retention seems to be caused by the reduced amount of mono-vacancies and small vacancy clusters in combination with their strong depopulation due to thermal trapping and de-trapping.\(^1\)

\(^{1}\)Re-implantation of a target that was exposed to plasma at a high surface temperature with deuterium plasma at a low surface temperature showed that the dominating effect lies in the vacancy mobility. These experiments are described in Appendix [5.A](#).
5 Reduced deuterium retention at high tungsten surface temperature

5.1 Introduction

Tungsten is foreseen as divertor material in future magnetic fusion devices such as ITER. Its good thermal properties such as high thermal conductivity, its high melting point and low erosion rate make tungsten favourable over other materials. For safety and efficiency reasons, it has been decided that the tritium inventory should be kept below 700 g [14]. It is therefore important to understand the effect of high-flux hydrogen plasmas on the material in detail. The solubility of hydrogen isotopes in tungsten is low. However, continuous bombardment with 14.1 MeV neutrons degrades the material properties and introduces damage, which may act as trap sites for hydrogen.

Hydrogen isotope retention in neutron-irradiated tungsten was studied in Refs. [15, 125, 126]. Since neutron irradiation is very time-consuming, MeV range heavy ions have frequently been used to simulate neutron damage. Previously, high-energy ion bombardment was found to increase the deuterium retention [16, 17, 19] and the deuterium concentration in the damage zone reaches 1.4 at.% [127]. This concentration was measured at surface temperatures below 550 K, where vacancies are not mobile. However, the divertor is predicted to operate at temperatures of around 600 – 1300 K [128]. In this study, the focus is on the influence of elevated surface temperatures on deuterium retention in self-damaged tungsten. Damage in tungsten was created by pre-irradiation with 12.3 MeV W\(^{4+}\) ions.

The damage cascade of a high-energy ion has a complicated structure. The process of damage creation has been discussed in many papers, also the book by Was [62] gives a good overview. A high-energy ion entering the lattice transfers part of its energy to atoms, the so-called primary knock-on atoms (PKA’s). These PKA’s cause further collisions cascades. Molecular dynamics simulations of these cascades have been carried out by several research groups to determine the amount and size of the vacancies and vacancy clusters that are created. Guinan and Kinney [129] showed that due to intra-cascade recombination in the cool-down phase of the damage cascade, the amount of initially produced defects is reduced. Caturla \textit{et al} [130] used the recoil spectra of 1.9 GeV protons and simulated the damage evolution with kinetic Monte Carlo to investigate the cascade efficiency for the production of defects and their size distribution. They found large recovery of the damage during the cool-down phase. The remaining defect type was dominated by mono-vacancies and interstitials, only few clusters consisting of 2 – 3 vacancies and 2 – 4 interstitials were found. Troev \textit{et al} [122] performed numerical calculations of damage in tungsten irradiated by fusion neutrons. They also show formation of mono-vacancies, di-vacancies, a few vacancy clusters, interstitials and small number of interstitial clusters containing more than three atoms. Fikar \textit{et al} [131] studied the influence of different tungsten inter-atomic potentials on the amount and type of radiation damage. No important difference in the defect production was found. In all cases, mostly mono-vacancies were produced. The rest of the defects (35%) formed mainly small clusters, the maximum cluster size was about 35 vacancies. The probability for clustering and the size of the largest clusters tend to increase with increasing PKA energy [132]. Note that TEM studies show that in addition to vacancies also large numbers of dislocation loops are formed during irradiation [133].
Eleved and van Veen [85] used positron annihilation techniques to study the effect of stepwise heating on the damage in tungsten induced by 15 keV deuterium ions. They found that vacancy clustering takes place at $\sim 650$ K and argue that the clusters have sizes of four to ten vacancies. Further cluster growth proceeded in two stages. At $\sim 1050$ K the initially formed clusters broke up and formed clusters with 11 – 16 vacancies. These vacancy clusters disappeared at around 1450 K in favour of clusters containing 40 – 60 vacancies. Finally, these clusters were removed by annealing above 1700 K.

In this paper, we have studied the effect of temperature on deuterium retention in self-damaged tungsten at temperatures up to 1200 K. The results will be discussed in terms of the diffusion of deuterium in tungsten, trapping and de-trapping from vacancies and vacancy clusters, and the mobility of vacancies.

### 5.2 Experiment

The work presented was performed with the same experimental techniques as described in [127], but with a three times higher power input. Briefly, the polycrystalline tungsten materials (99.96% purity) were provided by PLANSEE and annealed for 1 h at 1273 K prior to implantation. The cleanliness of the targets was checked by X-ray photoelectron spectroscopy (XPS) before and after plasma exposure. Material damage was created by W$^{4+}$ ions with a kinetic energy of 12.3 MeV. The 3 MV tandem ion accelerator at IPP-Garching irradiated an implantation area of 12 mm in diameter, homogeneously, at normal incidence and at room temperature. Damage levels were calculated by SRIM [42] using the average value of 90 eV for the displacement threshold energy as reported by Ref. [68]. Varying the ion irradiation time resulted in peak damage levels of up to 0.45 displacements per atom (dpa). These peak damage levels are used as reference for our experiments. Damage profiles extend up to 1.5 µm depth. The damage rate at which the targets were damaged was $(3 \pm 1) \times 10^{-4}$ dpa s$^{-1}$.

All targets were implanted with deuterium at similar plasma conditions in the linear plasma generator Pilot-PSI [10]. The damaged targets have been exposed to four 20 s plasma pulses in an axial magnetic field of 0.8 T. Thomson scattering measurements were used to determine the electron density and electron temperature of the plasma beam [96]. The shape of the plasma beam is approximately Gaussian with an electron density of $9.0 \times 10^{20}$ m$^{-3}$ in the centre and a full width half maximum of about 14 mm. The maximum electron temperature of 1.6 eV was measured in the centre of the beam. The targets were electrically floating during plasma exposure. Assuming that the ion temperature equals the electron temperature and using the Bohm criterion [31], the peak deuterium ion plasma flux is calculated to be $5.6 \times 10^{24}$ m$^{-2}$s$^{-1}$. Temperature profiles of the surface of the target were measured with a fast infrared camera (FLIR SC7500-MB). The maximum surface temperature was 1250 K at the beginning of the plasma pulse; during the 20 s plasma pulse this decreased to 1150 K. The profiles of the surface temperature of the target averaged over the plasma pulse and of the flux are shown in figure 5.1. The target was effectively cooled via a water-cooled copper block; after switching off the plasma, the temperature of the targets was back to room temperature within typically 1 s.
Reduced deuterium retention at high tungsten surface temperature

Figure 5.1: Radial dependence of the plasma flux (solid triangles) and average surface temperature (open diamonds). The insert shows a typical infrared image of the tungsten sample during plasma exposure.

Deuterium depth profiles were measured by nuclear reaction analysis (NRA) at IPP-Garching four weeks after plasma exposure by using the nuclear reaction \( D(\text{^{3}He}, p)^{4}\text{He} \) [99, 116]. Radial scans were made by positioning the \(^{3}\text{He} \) beam spot of 1 mm in diameter at seven locations on the targets. The energy was scanned from 690 keV to 4.0 MeV at each position, so that the deuterium concentration could be measured down to 6 \( \mu \)m depth. The measured proton energy distributions were used to determine the depth profiles of the retained deuterium by use of the SimNRA program [117].

After NRA, about eight weeks after plasma exposure, the total deuterium retention and the desorption temperature peaks of the deuterium were determined by thermal desorption spectroscopy (TDS). With a ceramic heater, the tungsten samples were heated with a linear temperature ramp of 1 K/s to 1273 K. A Balzers QMA125 quadrupole mass spectrometer monitored the mass 4 (\( D_{2} \)) and mass 3 (HD) signals in the residual gas in the chamber, to determine the total amount of deuterium released from the target during the temperature ramp. The absolute sensitivity was determined using calibrated leaks of \( H_{2} \) and \( D_{2} \). For the sensitivity of the mass 3 signal, the average of the sensitivities of mass 2 and mass 4 was taken. Mass 19 and 20, respectively HDO and \( D_{2}O \), were also detected. Qualitative analysis showed that these signals did not significantly exceed the background values.

Positron annihilation Doppler broadening (PADB) was used to monitor formation and clustering of defects [103, 104]. The annihilation reaction of an electron with a positron produces two gammas, each with an average energy of 511 keV. As a consequence of momentum conservation, the momentum of the electron-positron pair results in a Doppler broadening of the 511 keV annihilation energy. A typical measurement of the gamma spectrum can be found in the insert of figure 5.7. The \( S \) (sharpness) parameter is calculated as the ratio of counts registered in a fixed central electron momentum window.
5.3 Results

(|p|| < 3.5 × 10^{-3} m_0c) to the total number of counts in the photon peak. This choice of momentum window makes the S parameter sensitive to annihilations with low momentum valence electrons and implies that the S parameter is relatively high for a defect rich material: for a positron trapped in an open volume defect (such as a dislocation, a monovacancy or a vacancy cluster) the probability for annihilation with a valence electron is enhanced at the cost of annihilation with a core electron. Similarly, the W (wing) parameter is obtained from the high momentum regions $W_{\text{left}}$ and $W_{\text{right}}$ (10 × 10^{-3} m_0c < |p|| < 26 × 10^{-3} m_0c) and accounts for annihilations with high momentum core electrons. Therefore, the W parameter is relatively high for a defect-free material. In conclusion, as a function of defect concentration the behaviour of S and W parameter is opposite.

In this study, the PADB experiments were performed with the Delft Variable Energy Positron beam (VEP). Positrons emitted from a 22Na source were, after moderation to thermal energies and subsequent acceleration, injected in the samples with a kinetic energy from 0.1 to 25 keV. The beam intensity is about 10^4 positrons per second, the beam diameter at the target 8 mm. The mean implantation depth of the positrons, ⟨z⟩, scales with the implantation energy according to $⟨z⟩ = A/ρ × E^{1.62}$ [105]. Here, A is the material independent parameter (4 × 10^{-5} kg m^{-2} keV^{-1.62}), ρ is the sample density (19.3 × 10^3 kg m^{-3}) and E is the positron implantation energy (keV). For tungsten, the positron energy of 25 keV corresponds to an implantation depth of about 400 nm.

To investigate the effect of temperature on the radiation damage in tungsten, the temperature evolution of the S and W parameters of four samples were monitored with PADB during several annealing stages. These samples were prepared in the following way. First, all samples were annealed for 1 h at 1273 K. Then, two of these tungsten samples were pre-irradiated with W^{2+} ions with a kinetic energy of 5.5 MeV. One of these pre-irradiated samples was subsequently exposed to deuterium plasma in Pilot-PSI to implant deuterium. Also, one of the two non-damaged samples was exposed to deuterium plasma. The kinetic ion energy of 5.5 MeV was used for pre-irradiation, so that in the tungsten material only a shallow region of 600 nm with a maximum at 250 nm was damaged. This range is close to the range covered by the PADB measurements. Deuterium plasma exposure was performed at a peak electron density of 2 × 10^{20} m^{-3} and a maximum electron temperature of about 0.6 eV. The surface temperature was chosen at about 520 K, in order to stay below the temperature where vacancies become mobile. Next, all four samples were annealed in vacuum to the indicated temperatures in figure [5.6] followed by PADB measurements after each heating step. All S and W parameters reported here, are normalized with respect to almost defect-free tungsten (heated for 24 h at 1800 K).

5.3 Results

5.3.1 X-ray photoelectron spectroscopy

Before plasma exposure, tungsten (10%), carbon (40 – 60%) and oxygen (20 – 40%) were observed with XPS. XPS typically probes the top ∼10 nm of a tungsten sample. As
Reduced deuterium retention at high tungsten surface temperature discussed in Ref. [127], oxygen and carbon form a native layer of a few nanometer on top of tungsten when stored under ambient conditions. This layer will be removed during the initial stages of plasma exposure. Similar amounts of tungsten, carbon and oxygen were observed after plasma exposure. In addition, the surfaces contained calcium and fluorine concentrations up to 6% and boron with a maximum concentration of 10.5%.

The boron concentration decreased with the time that the source was in operation, i.e. targets exposed at a later moment contained less impurities. A decrease in boron content of a factor of 2 was found between the first and the last sample. The self-damaged samples were exposed to plasma in random order with respect to the level of damage. No effect on the deuterium retention of the order of exposure was observed. E.g. the shape of the saturation curves is smooth and similar as in previous experiments while the amount of boron is reduced with a factor two. From this, we conclude that boron and other impurities did not have a significant effect on the amount of retained deuterium. It is predominantly determined by the damage level and not by the sequence in which the samples were exposed.

5.3.2 Nuclear reaction analysis

We investigated our targets with NRA to get information on the local depth distribution of the retained deuterium. Measurements were carried out at different positions on the target: 0, 1, 3 and 6 mm from the centre, which were exposed at temperatures of respectively 1195, 1185, 1050 and 800 K and plasma fluxes of $5.6, 5.4, 4.5$ and $3.2 \times 10^{24} \text{m}^{-2}\text{s}^{-1}$.

![Figure 5.2: Radial dependence of the total retained deuterium as function of measurement position at the target.](image-url)
5.3 Results

Figure 5.3: Deuterium retention saturates as function of $W^{4+}$ pre-irradiation fluence. The solid points show the deuterium retention at different positions of the targets. The open triangles are data \[127\] from a tungsten target exposed at 525 K. The dotted line marked with stars show the total integrated TDS signal divided by the area damaged by pre-irradiation.

The integrated amount of deuterium retained in the top 6 µm of the sample as function of radial position is shown in figure 5.2. The amount strongly depends on the radial position as well as on the pre-irradiation damage. In the centre, where temperature and flux are maximal, the retention is minimal.

The integrated amount of retained deuterium as function of pre-irradiation fluence is shown in figure 5.3. For comparison, the results of our previous experiments at a surface temperature of 525 K, the low temperature regime, are also plotted \[127\]. It is clear that the present results, like the previous ones, show saturation at the damage level of about 0.25 dpa. The deuterium retained in the tungsten targets from the present high surface temperature exposures is drastically lower than in the low temperature regime.

The measured NRA depth profiles are shown in figure 5.4. The measured amount of deuterium increases with pre-irradiation damage. For all samples, the deuterium depth profiles show a strong reduction in the centre of the target, where particle fluxes and surface temperatures are highest. In the near-surface layer (<0.5 µm) the reduction is in particular strong.

The reduction in the deuterium retention in the centre of the target is most likely related to the local high surface temperature. An increase of particle flux of the deuterium implantation would not lead to a decrease of particles stored in the tungsten. The reduction in retention may be the result of the high trapping and de-trapping rates at these
5 Reduced deuterium retention at high tungsten surface temperature

Figure 5.4: Depth distributions of the deuterium, retained in damaged tungsten targets, pre-irradiated to (a) 0.045, (b) 0.09, (c) 0.22 and (d) 0.45 dpa. The shown deuterium depth profiles were measured at four spots on the target: in the centre (1195 K, \(5.6 \times 10^{24} \text{ m}^{-2} \text{s}^{-1}\)), 1 mm off-centre (1185 K, \(5.4 \times 10^{24} \text{ m}^{-2} \text{s}^{-1}\)), 3 mm off-centre (1050 K, \(4.5 \times 10^{24} \text{ m}^{-2} \text{s}^{-1}\)) and 6 mm off-centre (800 K, \(3.2 \times 10^{24} \text{ m}^{-2} \text{s}^{-1}\)). The dotted line with asterisk symbols show the deuterium depth profile in the undamaged tungsten target.

high surface temperatures, which would reduce the fraction of defects that are filled with deuterium. We studied this possibility with TMAP7, a one-dimensional transport code. Another possible explanation could be that the mobility of defects at these elevated temperatures results in removing and clustering of defects. This may lead to a reduction in retention as well. PADB was used to collect information on the defect behaviour as a function of the surface temperature.

5.3.3 Thermal desorption spectroscopy

In figure 5.5 the TDS results are shown for the damaged targets. For comparison, the result for a damaged target exposed to plasma at lower surface temperature \(^{127}\) is displayed. Virtually no difference is observed between the 0.22 dpa and 0.45 dpa samples. This shows that the tungsten material is saturated with defects at 0.22 dpa. The undamaged sample (0 dpa) shows the contribution of the deuterium trapped in intrinsic traps and damage created during the plasma exposure itself. As compared to our previous results obtained at the low surface temperature exposure, the desorption peak at low temperature (\(\sim 550 \text{ K}\)) is strongly reduced and has shifted to higher temperatures. The high-temperature peak has shifted from 880 K to 975 K and has become narrower.

For the samples that were exposed at high surface temperature, the TDS signal is dominated by the deuterium released from the periphery region of the sample. Not only did we find that the local deuterium retention at 6 mm distance from the centre is a factor 3 – 4 higher than in the centre (figure 5.2), also the area of the periphery is large compared to the central region.
5.3 Results

Figure 5.5: TDS mass 4 ($D_2$) signal. The temperature was ramped at a speed of 1 K/s. For comparison, the results from the low temperature exposure \[127\] are plotted in grey.

5.3.4 Positron annihilation Doppler broadening

With PADB, we investigated the behaviour of the defects as function of temperature in a qualitative way. Figure 5.6 shows the measured $S$ parameter as a function of positron energy of the sample that was pre-irradiated with 5.5 MeV W$^{2+}$ ions (without any plasma exposure). The measured $S$ parameter distributions are also shown after heating the sample to the temperatures as indicated in figure 5.6.

To determine the material specific $S$ parameter of almost defect-free tungsten, a sample was recrystallized by heating for 24 h at 1800 K (shown in figure 5.6 by the red stars). Detailed VEPFIT (Variable Energy Positron fit) \[134\] analysis of the change in $S$ parameter as function of implantation energy, yields a positron diffusion length of about 100 nm and an $S$ parameter bulk value of 0.468. This value was used for normalization. The observed gradual change of $S$ parameter from the surface value ($S_{\text{surface}}$) at low positron energy towards the bulk value (figure 5.6) at high-energy is due to the energy dependent broadening of the positron implantation profile (straggling) and diffusion of positrons after stopping and thermalization.

The normalized $S_{\text{bulk}}$ parameter of the annealed sample is 1.04 (figure 5.6 $\bigcirc$). The 4% higher $S$ value readily shows that the annealed sample still contains defects that effectively trap positrons. This is confirmed by the small positron diffusion length of 15 nm, found by VEPFIT analysis, which is well below the above-discussed value of 100 nm for defect-free tungsten. The elevated $S$ value is typical for positrons trapped at defects.
After pre-irradiation with MeV ions, the normalized $S$ parameter in the damaged regime increases to a value of up to 1.14 (figure 5.6). As discussed in Ref. [85], such an $S$ parameter indicates the presence of additional small vacancy clusters generated in the material due to the ion irradiation. By heating the target for 5 min at 550 and 625 K, the $S$ parameter increases to a value of up to 1.19. Further increase of $S$ to 1.25 is observed after heating of the target at 650 K for 30 min. This increase of $S$ is an indication for the growth of vacancy clusters. Subsequent heating steps of 4 h at 625 K, 1 h at 750 K and 1 h at 950 K, did not cause any further change in the $S$ parameter. This indicates that the vacancy clusters were stable and did not significantly change in size [64]. As a final step, the target was heated for a short time to 1725 K after which the measured $S$ parameters dropped to values close to those of the annealed target. This means that vacancy clusters became mobile and were removed from the material. Note that the measured $S$ parameters agree very well to the results from Eleveld et al [85]. Obviously, although the damage was created in a different way, i.e., high-energy tungsten ion damage (our work) versus high-energy deuterium ion implantation [85], the defects and their temperature behaviour are rather similar.

Without any lattice defects, a material exhibits characteristic $S$ and $W$ values. As discussed in the experimental section, introduction of defects increases $S$ and decreases $W$. It is instructive to plot the normalized $S$ parameters of our samples against the normalized $W$ values (the $W$ values were also normalized to the values found for defect-free tungsten). The $SW$ plot with data points of all samples is given in figure 5.7. Each data point shown consists of the average $S$ and $W$ parameters in the positron implantation energy range of 5 – 10 keV. We chose this range because at smaller implantation energies, the surface affects the $S$ and $W$ values. At higher implantation energies, positrons annihilated beyond the damaged range contribute to the signal. The $SW$ defect-free point is also indicated in figure 5.7.

Annealed tungsten, without pre-irradiation, has a normalized $S$ parameter of about 1.05 and a normalized $W$ parameter of about 0.78. Increasing the temperature in steps, as indicated in figure 5.6 and determining the $S$ and $W$ parameters shows a linear change in the $S$ and $W$ parameters towards the values for defect-free tungsten. This linear behaviour indicates the presence of defects and their removal by the heating steps [106]. Due to the heating less defects are available, so that the positrons will annihilate predominantly with tungsten core electrons. The $SW$ point (1.14, 0.6) for tungsten after pre-irradiation with MeV ions is also indicated in figure 5.7. Upon heating with similar heating steps to 950 K, the behaviour is opposite from that of the non-irradiated targets. The $S$ parameter increases up to a value of about 1.25 (at 950 K) and the $W$ parameter decreases to about 0.46. After briefly heating to 1725 K, the $SW$ measurements points of the pre-irradiated samples end up close to the defect-free $SW$ point (not shown in figure 5.7). Additionally, note that the differences between plasma-exposed and unexposed targets are small. The deuterium implanted in the tungsten did not influence the PADB results.

The observed increase in $S$ parameter for the pre-irradiated target can be explained by either the increase of defect concentration or the growth of formation of vacancy clusters. As the irradiation produced defect concentration is above the thermal equilibrium concentration, the more likely explanation for the increase in $S$ parameter is the growth.
5.3 Results

**Figure 5.6:** The $S$ parameter versus positron energy after different annealing stages of the target that was irradiated with 5.5 MeV W$^{2+}$ ions. Before irradiation the target was annealed for 1 h at 1273 K. For comparison, the $S$ parameter distributions for a recrystallized target (24 h at 1800 K) with very low defect density are also shown. On the second $x$-axis the average implantation depth is given according to the Makhov distribution.

**Figure 5.7:** Plot of the $SW$ values of the four samples after the different heating steps mentioned in figure 5.6. The samples irradiated with MeV W$^{4+}$ ions and non-irradiated samples react in an opposite way to heating up to 950 K. The insert shows a typical gamma energy distribution resulting from positron-electron annihilations, the definition of $S$ and $W$ parameters is marked by the hatched areas.
5 Reduced deuterium retention at high tungsten surface temperature

of vacancy clusters. The opposite behaviour of pre-damaged and non-damaged targets in the SW plot would then be explained by the difference in initial defect density. At low initial defect density, the defects have a high probability of reaching the surface or grain boundaries and anneal. In the pre-irradiated targets, in other words at high defect density, the defects are more likely to form larger clusters. These clusters are stable at higher temperatures. The change in slope of the irradiated and non-irradiated targets also strengthens the difference in type of defects involved.

5.3.5 TMAP7 simulations

TMAP7 is a program to simulate diffusion and trapping of hydrogen in materials. An elaborate description of the code is given in Ref. [107]. TMAP7 was used to simulate the diffusion during the implantation process of deuterium by plasma exposure at a flux of $4 \times 10^{24} \text{m}^{-2}\text{s}^{-1}$ and the desorption of deuterium by ramping the temperature. Diffusion and solubility values of hydrogen in tungsten from Frauenfelder [53] were used. The tungsten material was separated into 64 depth layers, with a thickness varying from 2.5 nm at the surface to 1 µm at the backside.

Trapping and de-trapping rates are strongly dependent on the temperature. To investigate its effect on the deuterium retention, we used the following approach. First, the TDS results presented in Ref. [127], were fitted with TMAP7. These results were obtained at lower surface temperature exposures (below 525 K), where defects were not mobile. In the fits, flat damage profiles up to 1.25 µm depth were assumed and the trapping energies and absolute vacancy densities were varied until reasonable agreement with the experiments was obtained. The results were then used as an input parameter for simulation of the diffusion during implantation at higher temperatures, thereby initially assuming that the defect distribution was not affected.

In figure 5.8, the TMAP7 simulation of the TDS profile together with the experimental results from the 0.22 dpa low temperature exposure is shown (dashed red line). In the fit three types of traps were used, the first with a trapping energy of 1.2 eV and a density of 0.5 at.%, the second with a trapping energy of 1.4 eV and a density of 0.2 at.% and the third with a trapping energy of 1.85 eV and a density of 0.7 at.%. The densities were chosen such that the total defect density adds up to the experimentally observed 1.4 at.% [127]. Here, we assume one deuterium atom per defect. Implantation of deuterium at higher temperatures reduces the fraction of deuterium-filled defects of all three defects, because de-trapping takes place. This is illustrated in table 5.1.

<table>
<thead>
<tr>
<th>surface temperature (K)</th>
<th>1.2 eV</th>
<th>1.4 eV</th>
<th>1.85 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>800</td>
<td>63%</td>
<td>97%</td>
<td>100%</td>
</tr>
<tr>
<td>1000</td>
<td>5.0%</td>
<td>35%</td>
<td>99%</td>
</tr>
<tr>
<td>1200</td>
<td>0.5%</td>
<td>3.4%</td>
<td>73%</td>
</tr>
</tbody>
</table>

Table 5.1: Fraction of retained particles at four different temperatures for three trapping energies.
The TDS profile of the TMAP7 run for an implantation temperature of 1000 K is shown figure 5.8 (dashed blue line). This temperature is approximately the average temperature of the targets during implantation at high temperatures. Indeed, the low temperature peak significantly decreases as result of the strong depopulation of the traps at 1.2 and 1.4 eV. The intensity of the high temperature peak does not decrease. However, in the experiment the high temperature peak is located at significantly higher temperatures than in the simulations. Running TMAP7 again and increasing the 1.85 eV trapping energy to 2.05 eV, led to the result shown by the dotted blue curve. In this simulation, the peak at about 975 K agrees quite well with the experiments. In the temperature range of 700 – 850 K some intensity seems to be ‘missing’. The reason may be that the actual trapping energies are most likely not strictly defined, but rather characterized by a broader distribution. TMAP7 cannot correctly represent such a distribution. It may also be that mono-vacancies and/or small vacancy clusters are still present in the target during the experiments, but not taken into account in the simulations.

**Figure 5.8:** The solid lines show the experimental TDS results. The low surface temperature (0.22 dpa) is plotted in red and the high temperature TDS profile (0.22 dpa) in blue. The dashed and dotted lines are the results from the TMAP7 simulations of the TDS profile. For the low temperature regime three traps were assumed up to a depth of 1.25 µm: 1.2 eV, 1.4 eV and 1.85 eV with a trap density of respectively $5 \times 10^{-3}$, $2 \times 10^{-3}$ and $7 \times 10^{-3}$ atomic fraction. Implantation of the same damage profile at 1000 K results in the dashed blue desorption profile. The shift of the high temperature peak could only be fitted by choosing a trapping energy of 2.05 eV (blue dotted line).
5 Reduced deuterium retention at high tungsten surface temperature

It should finally be noted that we have also simulated the desorption of deuterium during the 1 s cool down phase as possible cause for the reduction in retention. This did not lead to any significant desorption of deuterium. During the exposure most of the deuterium is released (99.95%), only a factor $1 \times 10^{-6}$ of the deuterium is retained in the material.

5.4 Discussion

As discussed in Ref. [127], the saturation of deuterium retention as a function of pre-irradiation W$^{4+}$ ion fluence for targets exposed to plasmas at surface temperatures up to 525 K is caused by saturation of damage creation in the pre-irradiation phase. The same holds for targets exposed to plasmas at higher surface temperatures (800 – 1200 K). However, the maximum amount of retained deuterium is significantly reduced (figure 5.3). The NRA results in figure 5.2 clearly show that the surface temperature plays an important role. We have used NRA, TDS, positron annihilation techniques, and TMAP7 simulations to understand this reduced deuterium retention in more detail.

The PADB experiments presented in figure 5.6 yield information on the defects in tungsten. Directly after pre-irradiation, the $S$ parameter has increased up to 14% above the defect-free reference value. It was discussed in Ref. [85] that this $S$ parameter indicates creation of additional vacancies and vacancy clusters. This is in line with MD simulations on irradiation damage in materials: Caturla et al [130] and Fikar et al [131] have shown that for an average PKA energy of $\sim 17$ keV, the value we estimated using SRIM for 12.3 MeV W$^{4+}$ ions, significant amounts of defects are produced.

In the TDS spectrum for the targets exposed to plasma at low surface temperatures up to 525 K (figure 5.8), two distinct peaks were observed. Heinola et al [56] have shown with density-functional theory calculations that a mono-vacancy can hold up to six hydrogen atoms. The corresponding trapping energies range from 1.6 eV for the first atom down to 1.2 eV for the fifth atom and 0.64 eV for the sixth. These values are in the range of what we found for the TDS peak at low temperature ($\sim 550$ K), which suggests that deuterium trapped in mono-vacancies contributes to this peak. It should be noted that deuterium trapped in dislocations, which is not taken into account in our simulations, may also contribute to this low temperature peak. As discussed in the introduction, irradiation of materials with the MeV range ions also creates small vacancy clusters. The desorption peak at higher temperatures ($\sim 880$ K) may be related to deuterium trapped in such small clusters, either in atomic or molecular form.

The behaviour of defects with temperature was studied with PADB. In the PADB experiments, the targets were subsequently heated in steps, initially leading to an increase in the $S$ parameter. After heating for 30 min at 650 K, the normalized $S$ parameter has increased to about 1.25. As discussed in the previous section, this increase in $S$ is probably caused by the growth of vacancy clusters. According to Ref. [85], the clusters are thought to contain up to about ten vacancies. In further heating steps, the $S$ parameter remained constant even after heating the target for 1 h at 950 K. Only after a brief heating step at 1725 K, the $S$ parameter was significantly reduced.
During the plasma experiments at high surface temperatures the targets reached temperatures in the range of 800 – 1200 K. In this temperature regime, according to the PADB experiments, growth of vacancy clusters will take place during plasma exposure. The periphery region of the surface, i.e. with the lowest exposure temperatures, will contain clusters containing up to about ten vacancies (corresponding to a normalized S parameter of about 1.25 in the PADB experiments). These larger clusters have also formed in the centre area, exposed at higher temperatures up to 1200 K. Additionally, defects close to the surface were able to reach the surface and annihilate. This is supported by our NRA results. In figure 5.4, the strong reduction of deuterium retention in the surface region was measured.

This clustering of mono-vacancies and small vacancy clusters into larger clusters was confirmed by TDS. Apart from the significant decrease of the low temperature peak, a shift of the high temperature peak to \( \sim 975 \) K was observed. According to the TMAP7 simulations, this high temperature peak corresponds to a trapping energy of 2.05 eV. This energy is close to the value of 2.1 eV that was interpreted by several others [19, 20, 55] as trapping of deuterium in voids. Ogorodnikova et al [52] reported a trap energy of 1.84 – 2.34 eV from chemisorption of atomic deuterium on the internal surface of a void. Interesting was, that TMAP7 did not reproduce the fact that the measured high temperature peak was much narrower. To explain this, we need the NRA depth profiles from figure 5.4. Here, we found that the deuterium retention in the surface region was strongly reduced. Retention of deuterium in a narrower damage profile will lead to a narrow peak in the TDS.

Our results suggest that during plasma exposure at high temperatures, mono-vacancies and small vacancy clusters are mobile and form larger clusters containing tens of vacancies. Some smaller clusters however also remain present, although their contribution to the retention is significantly less because of the strong depopulation of these lower energy traps at the used high temperatures. The amount of deuterium trapped in the larger clusters present in the high temperature exposures is similar to the amount in the smaller clusters as produced in the irradiation process and still present during low temperature plasma exposures. The strong reduction in retention observed at high temperature exposures, therefore, seems to be caused by the reduced amount of mono-vacancies and small clusters in combination with their strong depopulation due to thermal trapping and detrapping. In addition, the number of dislocations are also expected to be strongly reduced after high temperature exposures.

## 5.5 Conclusions

We investigated the effect of surface temperature on deuterium retention above the temperature where vacancies become mobile. The saturation behaviour of the retention that we observed for low temperature exposures and that originates in the pre-irradiation damage, is still present. The absolute retention at these high surface temperatures is however strongly reduced. The reduction is strongest close to the surface. Our results suggest that the reduction in deuterium retention is the result of both the reduced amount of mono-
vacancies and small vacancy clusters and their reduced population due to thermal trapping and de-trapping. The PADB data on defect evolution in tungsten upon heat treatment indicated formation of vacancy clusters, which are stable at higher temperatures. The shift of the high temperature peak in the TDS spectrum can be explained by the clustering of mono-vacancies and small vacancy clusters into larger clusters. From TMAP7 simulations we found that depopulation due to thermal trapping and de-trapping is strong for traps with a low binding energy. The strong reduction of the deuterium retention in the region close to the surface can be explained by the annealing of vacancies.

**Acknowledgements**

This work, supported by the European Communities under the contract of Association between EURATOM/FOM, was carried out within the framework of the European Fusion Programme with financial support from NWO. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

The authors would like to thank R.S. Al for the technical support at Pilot-PSI, J. Dorner and M. Fußeder for the technical assistance with the $^3$He beam analysis and E. Zoethout for the XPS analysis.
5.A Role of vacancy mobility in deuterium retention in W at high surface temperature

High temperature plasma exposure (>550 K) decreases the deuterium retention significantly in undamaged tungsten [76, 135, 136] and in pre-irradiated tungsten (chapter 5). The increased mobility at higher temperatures underlies this reduction. Higher mobility of the deuterium atoms result in a higher trapping and de-trapping rate, so that the occupation degree of the deuterium in defects is lowered. Annealing and clustering of vacancies take place as result of the vacancy mobility, so that less traps for the deuterium exist in the tungsten material. In this appendix, we show that the dominating effect for the reduced retention lies in the vacancy mobility.

The reduction of deuterium retention at high temperature raises another important question: How does defect mobility during high temperature exposure affect the saturation of deuterium retention? In previous experiments (chapter 4) we measured saturation of pre-irradiation damage in tungsten and attributed this to the spontaneous recombination [127]. In the experiments of chapter 5, a lower saturation level was found after plasma exposure at a high surface temperature [137]. Also, we described the clustering of vacancies, which was measured using positron annihilation Doppler broadening. However, in a fusion reactor damaging, heating and plasma exposures take place simultaneously. In the present experiment we decouple damaging, heating and plasma exposure. We performed a measurement series in which pre-irradiation damage and heating are alternated, and found that the deuterium retention decreased after an extra heating and pre-irradiation step.

5.A.1 Experiment

All polycrystalline tungsten targets (PLANSEE, 99.96% purity) were polished until mirror finish and annealed for 1 h at 1273 K at a background pressure of $5 \times 10^{-4}$ Pa. The dimensions of the targets are 20 mm in diameter and 1 mm in thickness.

Re-implantation of a sample exposed at high surface temperature

Three polycrystalline tungsten targets were pre-damaged for the re-implantation experiment at IPP Garching with 12.3 MeV W$^{4+}$ ions to a damage level of 0.45 dpa (assuming $E_{\text{displ}} = 90$ eV [68]). The targets were exposed at self-biased conditions to high-flux deuterium plasmas in the linear plasma generator Pilot-PSI at FOM-DIFFER [10]. Electron density and temperature were measured using the Thomson scattering technique [96]. These were used to calculate the particle flux in figure 5.9 according to the method described in section 2.1.1.

The low temperature target, target 1, was exposed to a surface temperature of 540 K in the centre and 460 K at the edge. The high surface temperature target, target 2, was carried out at a temperature range of 850 – 950 K. The re-implanted target, target 3, was first exposed at the high surface temperature followed by a low surface temperature exposure. For the low temperature exposure a magnetic field of 0.4 T was used, and the
5 Reduced deuterium retention at high tungsten surface temperature

Figure 5.9: Particle flux of the targets used in the re-implantation experiment. Both low temperature and high temperature exposures were reproducible.

duration of the plasma exposure was 3 times 75 s. A magnetic field of 0.8 T was used to obtain the high surface temperatures. For these sample, 8 shots of 25 s were used to implant the deuterium.

Subsequent damaging and heating

The experiments concerning subsequent heating and damaging, involved four targets that were damaged with high energy MeV tungsten ions with heating steps in between. During the ‘damaging step’ targets were bombarded with 12.3 MeV W$^{4+}$ ions to a damage level of 0.45 dpa. For the heating step, the samples were heated for 1 h at 950 K, so that the clustering of vacancies into larger clusters could take place (chapter[5]). The samples were heated in a high-vacuum oven at a pressure of 10$^{-3}$ Pa. The experimental sequence of the different targets was as follows:

1) pre-damage
2) pre-damage → 1 h at 950 K
3) pre-damage → 1 h at 950 K → pre-damage
4) pre-damage → 1 h at 950 K → pre-damage → 1 h at 950 K → pre-damage

After the target preparation, all targets were exposed simultaneously to deuterium plasmas in PlaQ at IPP Garching [138]. The samples were exposed at a flux of $\sim 10^{20} \text{ m}^{-2}\text{s}^{-1}$ for 72 h, so that a particle fluence of $3 \times 10^{25} \text{ m}^{-2}$ was reached. During plasma exposure the sample temperature was 400 K. Targets were analysed with thermal desorption spectroscopy (TDS), nuclear reaction analysis (NRA) and positron annihilation Doppler broadening (PADB). Details of these analysis techniques can be found in chapter[5].
5.A Role of vacancy mobility in deuterium retention in W at high surface temperature

5.A.2 Results and discussion

Re-implantation of a sample exposed at high surface temperature

The deuterium depth profiles can be derived from the NRA results. In figure 5.10 the proton counts are shown as function of the $^3$He ion energy. The ion energy is related to the depth of the measurement, the proton counts are a measure for the amount of deuterium retained. The results are shown for two positions on the target: the centre and 6 mm from the centre. On both positions similar proton counts were detected for targets 2 and 3. Thus, there is virtually no difference in deuterium depth distribution between the high temperature and the re-implanted sample.

The NRA measurements at the centre position (figure 5.10) show that the reduction of retention originates in the vacancy mobility. Target 2, exposed at high surface temperature, retains less deuterium than target 1 that was exposed at low surface temperature. In the case that the defects would still have been present in the material, but not occupied by deuterium because of the high trapping and de-trapping rates, the re-implanted sample should have retained similar amounts of deuterium as target 1 (low temperature). The present experiment shows however that the deuterium retention did not increase after re-implantation. This indicates that all defects were already occupied by deuterium after the high temperature exposure and that the reduction is a result of the removal of traps.

The NRA measurements at 6 mm from the centre shows opposite behaviour. The target contains less deuterium at this position after low temperature exposure as compared to the high temperature and the re-implanted samples. Presumably, the temperature at the edge of the target was not high enough to cause annealing and clustering. The increased diffusion as result of the increased temperature dominates the retention behaviour.

![Figure 5.10](image-url)

**Figure 5.10:** Nuclear reaction analysis shows that there is no difference between the high temperature and the re-implanted target. The measurement at the centre position shows the re-implanted sample contains less deuterium than the low temperature target.
Subsequent damaging and heating

The targets concerning the subsequent damaging experiment were analysed with positron annihilation Doppler broadening (PADB) after the sequences of alternating damaging and heating and after plasma exposure. PADB was used to obtain information about the vacancy (cluster) size. The results are shown in figure 5.11. The S parameter increased after one damaging and one heating step. This indicates growth of small vacancy clusters [137]. After additional damaging, heating and damaging, the S parameter returned to its original value. Note that the penetration depth of positrons is very low. Energies up to 25 keV typically probe up to 400 nm depth. The results are thus only valid for the 400 nm just below the surface. Another remark must be made according to these results: The critical eye immediately notices that these S parameters are typically lower than what we found in chapter 5. This is most likely due to the fact that in the present experiment the vacancies were filled with deuterium. It is known that deuterium atoms occupying the vacancy (clusters), can passivate the trap for a positron, so that the positrons are only partly sensitive for these vacancy (clusters).

The TDS results are shown in figure 5.12. The deuterium retention after the heating step is reduced by almost 50% with respect to target 1 that was only damaged. Damaging again (target 3) increases the deuterium retention although not to the level of target 1. The same holds for target 4.

The TDS results clearly show that heating after damaging reduces deuterium retention. Repetition of the damaging increases the deuterium retention although not to the level of target 1. On the contrary, the results with PADB did not show any difference between target 1 and target 4. It seems that in the first 400 nm of the samples the damage is fully recovered after re-damaging.

Figure 5.11: Positron annihilation Doppler broadening. Heating of the sample increases the S parameter, which indicates clustering. As result of subsequent damaging the S parameter returns to its original level in the first 400 nm below the surface.
5.A Role of vacancy mobility in deuterium retention in W at high surface temperature

As possible mechanism for the fact that the pre-irradiation damage does not return to its original level, we propose the following mechanism. The vacancy clusters formed after heating act as sink for the interstitials created in the new damage cascade during pre-irradiation. A large part of the created vacancies and interstitials therefore disappear quickly, the retention cannot build up as quickly as in the non-irradiated sample. Therefore the W\textsuperscript{4+} fluence to reach saturation might be higher.

5.A.3 Conclusions

The strong reduction in deuterium retention of pre-damaged samples exposed to high-flux deuterium plasmas at high surface temperatures (above the vacancy mobility) was investigated. Exposure at high surface temperature followed by low surface temperature exposure showed that the reduction predominantly originates in the vacancy mobility. The role of trapping/de-trapping in the reduction seems to be minor.

Alternating damaging (0.45 dpa) and heating (950 K) of tungsten before plasma exposure was investigated as well. Our measurements confirmed that heating after damaging reduces deuterium retention. Repetition of the damage step increases the deuterium retention although not to the original level. We propose that the small vacancy clusters formed during heating act as sinks for newly created interstitials in the damage cascade. The pre-irradiation fluence to reach saturation may therefore be higher.
5 Reduced deuterium retention at high tungsten surface temperature
Strongly reduced penetration of atomic deuterium in radiation-damaged tungsten

M.H.J. ’t Hoen¹, M. Mayer², A.W. Kleyn¹,³ and P.A. Zeijlmans van Emmichoven¹

¹ FOM institute DIFFER, Association EURATOM-FOM, Partner in the Trilateral Euregio Cluster, NL-3439 MN Nieuwegein, the Netherlands
² Max-Planck-Institut für Plasmaphysik, Boltzmannstraße 2, D-85748 Garching, Germany
³ Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, NL-1098 XH Amsterdam, the Netherlands

Abstract

Radiation-damaged tungsten is exposed to high-flux, low-energy deuterium plasmas at self-biased conditions. We observed that the fraction of deuterium that penetrates, is only $10^{-5} – 10^{-7}$ of the plasma flux and strongly dependent on the local surface temperature. We propose that deuterium does not directly penetrate bulk tungsten but that it thermalizes at the surface where it forms a protective chemisorbed layer. We found an energy barrier of 1 – 2 eV between surface and bulk, causing the influx of deuterium to be low as compared to the number of defects and leading to slow filling of the damaged layer.

Published in: Physical Review Letters 111 225001 (2013)
6 Strongly reduced penetration of atomic deuterium in radiation-damaged tungsten

6.1 Introduction

Tungsten is foreseen as the main candidate material for use in the divertor of the experimental fusion reactor ITER. The divertor serves as the exhaust of the tokamak where the helium ash is removed. It is particular in this region where strong interaction of plasma with plasma facing components (PFC’s) takes place. The plasma in the divertor region has a high electron density \(10^{20} - 10^{21} \text{ m}^{-3}\) and a temperature of \(1 - 10 \text{ eV}\). This leads to extremely intense particle and energy flux densities of \(\sim 10^{24} \text{ m}^{-2} \text{s}^{-1}\) and \(\sim 10 \text{ MW m}^{-2}\) respectively \[34\]. Its high thermal conductivity and melting point as well as its low erosion rate make tungsten favourable over many other materials. Another essential property of PFC’s is that the uptake of tritium should be limited. For safety and efficiency reasons, the total tritium inventory in ITER should be kept below 700 g \[14\]. For tungsten it is known that the retention of hydrogen particles is low \(<10^{-4} \text{ atomic fraction}\). However, radiation damage in a fusion reactor can lead to enhancement of the retention by orders of magnitude \[15, 127\].

In this Letter we present deuterium retention studies for radiation damaged tungsten targets, exposed to atomic deuterium plasmas under ITER-like conditions. For ion temperatures of a few eV it is known that 90 – 95\% of the deuterium is directly reflected \[37, 38\]. However, the plasma flux is so high that there are large amounts of remaining deuterium atoms that interact with the tungsten surface. This results in a very complex plasma-surface interaction leading to adsorption of deuterium at the surface, recombination of atomic deuterium to molecules and release into the vacuum and/or back into the plasma \[139, 140\], penetration of deuterium in tungsten, etc. The situation is very schematically depicted in figure 6.1 with the plasma flux (\(\Phi_{\text{plasma}}\)) and the back flux (\(\Phi_{\text{back}}\)) containing directly reflected deuterium as well as thermalized deuterium leaving the surface as atoms and/or molecules. The effective ingoing flux, \(\Phi_{\text{in}}\), is the fraction \(f\) of the plasma flux that enters the tungsten material. In the present work we have monitored the diffusion of deuterium inwards from which we were able to directly determine \(\Phi_{\text{in}}\) and thereby the fraction \(f\). We obtain a value for \(f\) that is very small, \(10^{-5} - 10^{-7}\). This fraction is strongly dependent on the local surface temperature and orders of magnitude lower than expected on the basis of the direct reflection mentioned above. We propose that this small value for \(f\) originates in the deuterium not directly entering bulk tungsten but thermalising and neutralising at the surface forming a protective chemisorbed layer. Before diffusing into the bulk, the deuterium atoms need to cross an energy barrier that strongly limits the influx. We will show that an activation energy for crossing the barrier of \(1 - 2 \text{ eV}\) is consistent with the temperature dependence of the influx.

![Figure 6.1: The influx, \(\Phi_{\text{in}}\), is only a small fraction \(f\) of the incoming plasma flux, \(\Phi_{\text{plasma}}\).](image-url)
6.2 Experiment

Polycrystalline tungsten targets (PLANSEE, 99.96% purity, Ø 20 mm, 1 mm thick) were mechanically polished until mirror finish and subsequently heated for 1 h at 1273 K at a background pressure of $5 \times 10^{-4}$ Pa. The targets were pre-irradiated at room temperature with 12.3 MeV W$^{4+}$ ions at the 3 MV ion accelerator at IPP Garching to homogeneous lateral damage. The fluence of the pre-irradiations was taken such that a damage level of 0.45 displacements per atom was reached (average displacement energy 90 eV). We have previously shown that this fluence is sufficient to saturate the damage level and that the damage extends to a depth of about 1.5 µm below the surface [127]. The surface cleanliness was checked by X-ray photoelectron spectroscopy. Since the targets were stored under ambient conditions, they were covered with nanometer-thick native layers of oxygen and carbon [127, 137]. During plasma exposure, most of these layers are removed within the first few seconds although the presence of in particular some oxygen cannot be excluded [141]. After plasma exposure, small amounts of Mo, Ca and F were found to be present on the surface. In most cases the concentrations were well below 10%. These impurities may slightly affect the protective layer and the energy barrier that we found in our measurements.

The pre-damaged tungsten targets were exposed to intense deuterium plasma beams at the linear plasma generator Pilot-PSI [10]. The plasma was created by a cascaded arc source and transported to the target by an axial magnetic field of 0.4 T. During the exposures, the targets were water-cooled and electrically floating. Electron density and temperature profiles of the plasma beam were determined by Thomson scattering [96]. The plasma beam has approximately a Gaussian profile with maximum electron density and temperature of about $4 \times 10^{20}$ m$^{-3}$ and 1 eV respectively. The ion flux on the targets can be estimated by applying the Bohm criterion [31] and ranges from $2 \times 10^{24}$ ions m$^{-2}$ s$^{-1}$ in the centre of the target to $5 \times 10^{23}$ ions m$^{-2}$ s$^{-1}$ at the edges. For our experimental conditions, the deuterium in the plasma predominantly consists of atomic ions [25] [27].

The kinetic energy of the ions arriving at the surface can be estimated by considering a drifting Maxwellian velocity distribution for the ions in the plasma and an acceleration over the plasma sheath towards the surface. Assuming equal electron and ion temperatures in the plasma [25], this leads to an ion kinetic energy of roughly 5 eV. The temperature profile of the tungsten surface during exposure was measured with a fast infrared camera (FLIR SC7500-MB) and varies between 560 K in the centre of the target to 470 K at the edges (the emissivity of the tungsten targets used was 0.06, a value verified ex situ with the help of a thermocouple measurement). The absolute uncertainty in the temperatures is of order 25 K and is mainly caused by the uncertainty in the emissivity and the transmission of the infrared radiation through the vacuum window. The relative uncertainty in the temperatures is a few K.

Deuterium depth profiles were measured one month after plasma exposure by nuclear reaction analysis (NRA) making use of the nuclear reaction $^3$He($^3$He,p)$^4$He [99]. The $^3$He beam spot of about 1 mm in diameter was positioned at six spots on the target: two close to the centre, two at 3 mm and two at 6 mm from the centre at opposite sides. In this way, we obtained deuterium depth profiles for three different exposure temperatures,
6 Strongly reduced penetration of atomic deuterium in radiation-damaged tungsten

i.e. 560 K, 530 K and 500 K. Differences between the measurements taken at the same temperature were small and only averages will be shown. At each position, the beam energy was scanned from 690 keV to 4.0 MeV to determine the deuterium concentration with a resolution of about 0.5 µm down to a depth of 6 µm. The depth profiles of retained deuterium were calculated from the measured proton energy distributions with the NRA-DC program [100]. The total amount of deuterium in the top 6 µm was obtained by integrating the depth profiles.

Five identical tungsten targets were exposed to deuterium plasma. The plasma fluxes and the corresponding surface temperatures were very similar in all experiments. The difference between the targets was the exposure time that was varied over almost two orders of magnitude, from 30 s to 2250 s. This means a variation in deuterium ion fluence in the centre of the targets from about $6 \times 10^{25} \text{m}^{-2}$ to $4.5 \times 10^{27} \text{m}^{-2}$ (fluence equals time integrated flux).

### 6.3 Results

The NRA results for three of the targets are shown in figures 6.2a – c. For the one but shortest exposure time (figure 6.2a), the deuterium is retained mostly within 0.5 µm from the surface for all three temperatures. At longer exposure times (figure 6.2b) it is clear that, in particular for the highest temperature, deuterium penetrates deeper in the material. This penetration continues for the longest exposure time as shown in figure 6.2c. The observations qualitatively agree with a process that is determined by diffusion: deeper penetration of deuterium for longer exposures and higher temperatures. For comparison, we also show the NRA results for a target that was exposed for 675 s to deuterium plasma at similar plasma conditions but biased at a potential of $-40$ V (figure 6.2d). In contrast to the self-biased experiments, for all three temperatures the damaged slab has been filled with deuterium as result of direct penetration of tungsten. This clearly different result will be discussed in more detail later.

![Figure 6.2: Deuterium depth distributions in damaged (0.45 dpa) tungsten targets exposed to high-flux deuterium plasmas at self-biased conditions (a-c) and biased at $-40$ V (d). The exposure times are as indicated. The deuterium depth profiles were measured at three positions on the target (6 mm off-centre at 500 K, triangles; 3 mm off-centre at 530 K, circles; centre at 560 K, squares).](image-url)
6.4 Discussion

In figure 6.3 we show the integrated, total amounts of deuterium in the top 6 µm for the self-biased experiments. It is clear that for the highest temperature of 560 K, deuterium retention saturates after approximately 1000 s. The deuterium inventory at saturation corresponds to the damaged layer (thickness about 1.5 µm) being completely filled with deuterium (1.2 at.%). For 530 K, it seems that saturation is reached for the longest exposure time of 2250 s. For the lowest temperature of 500 K, full saturation is never obtained.

6.4 Discussion

The experimentally observed durations for complete saturation of the damaged layer with deuterium are long as compared to what would be expected on the basis of the large plasma flux and the diffusion of deuterium in tungsten. Using the Frauenfelder diffusion coefficient of deuterium in tungsten of \( D_F = D_0 \exp(-0.39/(k_B T)) \) with \( D_0 = 2.9 \times 10^{-7} \) m\(^2\) s\(^{-1}\) [53], shows that for temperatures of 500 – 560 K deuterium diffuses in less than a second through the damaged layer. The damaged layer has an areal density of trapped deuterium of \(~10^{21} \) m\(^{-2}\). The plasma flux, after correction for the direct reflection of deuterium from tungsten, amounts to \(~10^{23} \) m\(^{-2}\) s\(^{-1}\). This means that in one second plasma exposure there is ample deuterium available to fill the traps. Thus, this simple estimation yields a timescale that is more than three orders of magnitude faster than the experimentally observed saturation times. Uncertainties in the Frauenfelder diffusion coefficient [61] cannot explain this.
Why then is the experimentally observed filling of traps with deuterium three orders of magnitude slower than expected on the basis of plasma flux and diffusion? The assumption in the above considerations is that the high-flux plasma, after correction for reflection, directly penetrates into the outermost layers of the target. This seems to be a realistic assumption since the introduction of atomic deuterium in tungsten is known to be exothermic \cite{64} and since the incoming ions in addition have a kinetic energy of 5 eV. However, our results strongly suggest that the assumption is not valid. We propose that instead of directly penetrating tungsten, the deuterium ions thermalize and neutralize at the surface where they form a chemisorbed layer. Presence of this layer in fact plays an important role in the thermalization process: deuterium-deuterium collisions cause energy pooling, thereby decreasing the energy of the incoming ions preventing direct penetration. This interpretation is supported by other experiments where it was shown that a chemisorbed deuterium layer on a barium surface actively decreases the interaction between incoming deuterium and barium atoms \cite{142}. The contribution of the chemisorbed layer to the thermalization of deuterium means that it ‘protects’ tungsten from direct penetration by deuterium. To diffuse from this protective chemisorbed layer at the surface into bulk tungsten, deuterium needs to be activated over an energy barrier of a few eV \cite{64,143}. This energy barrier reduces the effective influx of deuterium by many orders of magnitude to values so low that the filling of the damaged layer with deuterium is limited by the amount of traps and not by the diffusion coefficient. We will show that this interpretation leads to a consistent picture explaining the filling of the damaged layer being orders of magnitude slower than initially expected.

To determine values for $\Phi_{in}$ that are consistent with our experimental observations, we carried out TMAP7 simulations. TMAP7 is a program that solves the one-dimensional diffusion equation for deuterium in materials \cite{107}. The program includes trapping of deuterium and recombination to molecules at the surface. Following our previous results \cite{137}, we assume three different trap sites for deuterium in tungsten with trap densities of $2 \times 10^{-1}$ at.%, $4.5 \times 10^{-1}$ at.%, and $6.5 \times 10^{-1}$ at.% for trapping energies of 1.2 eV, 1.4 eV, and 1.85 eV respectively. For the diffusion coefficients of deuterium in tungsten, the above mentioned Frauenfelder values were used. For recombination of two atoms at the surface to a molecule, a coefficient of $3.2 \times 10^{-15} \text{ m}^4 \text{s}^{-1} \exp[-1.16/(k_B T)]$ was taken \cite{43}. The simulations were run with the flux varied until good agreement with the experiments was obtained. The results of the simulations are shown in figure 6.3. The deuterium influxes, $\Phi_{in}$, used were $2 \times 10^{19} \text{ m}^{-2} \text{s}^{-1}$ (560 K), $1.8 \times 10^{18} \text{ m}^{-2} \text{s}^{-1}$ (530 K), and $2.5 \times 10^{17} \text{ m}^{-2} \text{s}^{-1}$ (500 K), which means that $f$ is in the range of $10^{-5}$ to $10^{-7}$. Note that $\Phi_{in}$ is the deuterium influx in the first nanometer of the material. Part of this influx leaves the surface again via recombination. To fit the experimental data, the simulated curves have slightly been shifted upwards by $1 \times 10^{20} \text{ m}^{-2}$. The kinks in the simulated curves for the two highest temperatures at 750 s and 2200 s correspond to the times where the damaged layer is filled with deuterium. The simulations reproduce the experiments well. The effective influx turns out to be strongly dependent on temperature: almost two orders of magnitude variation is obtained in the temperature range of only 60 K. This dependence is much stronger than the variation in plasma flux, which varies only by about 30%. 

74
6.5 Conclusions

In figure 6.4, the simulated influx is plotted as function of the inverse temperature. The data-points follow quite well a straight line showing that the process has Arrhenius-type behaviour ($\Phi_{in} = \Phi_{in}(T_\infty) \exp[-E_a/k_B T]$) with $\Phi_{in}$ the influx of deuterium, $k_B$ Boltzmann constant and $T$ the local temperature of the surface during plasma exposure. The activation energy $E_a$ directly follows from the slope and amounts to 1.6 eV. The pre-exponential factor, $\Phi_{in}(T_\infty)$, represents the surface coverage of chemisorbed deuterium, $(1 - 2 \times 10^{19} \text{ m}^{-2})$ [144] multiplied by the attempt frequency, typically in the order of $10^{13} \text{ s}^{-1}$. We fixed this value at $10^{32} \text{ m}^{-2} \text{ s}^{-1}$. Taking into account the uncertainties in the experimental values for the temperature, the results become $E_a = (1 - 2) \text{ eV}$. $E_a$ is close to the reported energy barriers of around 2 eV for diffusion of chemisorbed deuterium from the surface to the bulk [64, 143].

6.5 Conclusions

In conclusion, we have shown that the experimentally observed, slow diffusion of deuterium in pre-irradiated tungsten is consistent with the deuterium atomic ions not directly penetrating in bulk tungsten but forming a chemisorbed layer at the surface. This leads to a reduction in the effective influx of deuterium by many orders of magnitude as compared to the plasma flux. Obviously, at self-biased conditions, the kinetic energy of the atomic ions arriving at the surface of roughly 5 eV is not sufficient for penetration of the surface with its protective layer. For a target biased at a potential of $-40 \text{ V}$, on the other hand, we observed that the damaged layer is filled on a much shorter timescale. This suggests that, upon their acceleration towards the surface by the bias potential, the ions directly penetrate the bulk, leading to high concentrations of deuterium and fast filling of the damaged layer. Our results are to some extent reminiscent of what has been observed by others on the diffusion of deuterium in tungsten containing considerable amounts of defects [75]. Also in these experiments the trapping of deuterium per unit time was the limiting factor for diffusion. However, the kinetic energy of the deuterium ions was so high that di-
Strongly reduced penetration of atomic deuterium in radiation-damaged tungsten occurred. Our observations are furthermore qualitatively consistent with the molecular dynamics simulations of Henriksson et al. where it was shown that individual hydrogen atoms incident on perfect tungsten at kinetic energies up to 3 eV either reflect from or stick at the surface whereas at 10 eV a small fraction directly penetrates. In a comparison with these simulations, one should realize that our high-flux plasma leads to the presence of large amounts of deuterium in the neighbourhood of the surface including a chemisorbed layer. As discussed, this chemisorbed layer can act as a protective layer preventing direct penetration. Finally, our results shed light on previously reported strong surface modifications of tungsten during exposure to deuterium plasmas at biased conditions as opposed to the absence of such modifications for self-biased conditions. The surface modifications can be related to an oversaturation of tungsten with deuterium originating in the direct penetration. The absence of surface modifications at self-biased conditions can readily be understood in terms of the absence of direct penetration, as was shown in the present Letter.

**Acknowledgements**

This work, supported by the European Communities under the contract of Association between EURATOM/FOM, was carried out within the framework of the European Fusion Programme with financial support from NWO. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

The authors would like to thank R.S. Al for the technical assistance at the Pilot-PSI measurements, J. Dorner and M. Fußeder for their technical assistance with the $^3$He beam analysis and E. Zoethout for the XPS analysis of the samples.
Surface morphology and deuterium retention of tungsten after low- and high-flux deuterium plasma exposure

M.H.J. ’t Hoen\(^1\), M. Balden\(^2\), A. Manhard\(^2\), M. Mayer\(^2\), S. Elgeti\(^2\), A.W. Kleyn\(^{1,3,4}\) and P.A. Zeijlmans van Emmichoven\(^1\)

\(^1\) FOM institute DIFFER, Association EURATOM-FOM, Partner in the Trilateral Euregio Cluster, NL-3439 MN Nieuwegein, the Netherlands
\(^2\) Max-Planck-Institut für Plasmaphysik, Boltzmannstraße 2, D-85748 Garching, Germany
\(^3\) University of Amsterdam, Science Park 904, NL-1098 XH Amsterdam, the Netherlands
\(^4\) Chengdu Development centre for Science and Technology, Shuangliu, Chengdu, Sichuan 610207, People’s Republic of China

Abstract

The surface morphology and deuterium retention were investigated of polycrystalline tungsten targets that were exposed to deuterium plasmas at widely varying conditions. By changing only one parameter at a time, the isolated effects of flux, time and pre-damaging on surface modifications and deuterium retention were studied. The sample exposed to low-flux plasma \((10^{20} \text{ m}^{-2}\text{s}^{-1})\) is mostly smooth with only a few areas containing very large blisters \((50–500 \text{ µm})\). The samples exposed to high-flux \((10^{24} \text{ m}^{-2}\text{s}^{-1})\) plasmas show large numbers of smaller blisters \((1–10 \text{ µm})\) and in addition even smaller protrusions \((<750 \text{ nm})\). The size of the blisters and their density strongly increase with fluence. Pre-damaging tungsten with MeV ions leads to less blisters but to more protrusions. In addition to these (sub-)micrometer-sized structures, all samples show formation of nanostructures. It is shown that the blisters and protrusions originate in inter- and intra-granular cavities, respectively. The depth of the cavities underneath the surface correlates well with the depth distributions of the retained deuterium. Trapping of significant amounts of deuterium therefore seems to take place in and/or close to these cavities and gives rise to an additional peak in the thermal desorption spectrum at 700 K.
7 Surface morphology and deuterium retention at high-flux deuterium plasmas

7.1 Introduction

It has recently been decided that tungsten will be used in the divertor of the experimental fusion reactor ITER from the beginning of operation [13]. The divertor serves as the exhaust of the tokamak where the helium ash is removed. It is particular in this region where strong interaction of plasma with plasma facing components takes place. The partially detached plasma in the divertor region will experience a high electron density ($\sim 10^{20}\, \text{m}^{-3}$) and electron temperatures of $1 - 10\, \text{eV}$ [34, 147]. This leads to extremely intense particle and heat flux densities on the divertor of $\sim 10^{24}\, \text{ions}\, \text{m}^{-2}\, \text{s}^{-1}$ and $\sim 10\, \text{MW}\, \text{m}^{-2}$, respectively. Its high thermal conductivity and melting point as well as its low erosion rate make tungsten favourable over many other materials. It is in addition well known that the uptake of hydrogen by tungsten is low, which is important since, for safety and efficiency reasons, the total tritium inventory in ITER should be kept below 700 g [14].

Even though the physical properties of tungsten seem to be quite good, it has been shown in several experiments that the extreme conditions as expected in part of the ITER divertor may lead to severe modifications of tungsten [17, 79, 80, 84, 148]. This also occurs when the incident energy is far below the threshold for displacement damage and is strongly dependent on the specific tungsten material structure. Blister formation originating from growth of inter-granular voids is one example that has been studied extensively [87, 88]. Although this type of material (rolled tungsten) will not be be used for the ITER divertor, investigation of such materials are necessary to improve understanding of the blister formation mechanism. Surface morphology changes may lead to degradation of material properties as well as to enhanced erosion and formation of dust. It has also been shown that surface modifications can lead to enhanced hydrogen retention [61, 149]. In several experiments it has furthermore been shown that the retention will be significantly enhanced by radiation damage due to the bombardment with neutrons or with MeV particles [15, 16, 19, 127].

In this paper we study the effect of flux, fluence and pre-irradiation damage on surface modifications and deuterium retention. We will show that the sizes of the surface modifications range from the nm to the µm scale and that the depth distributions of trapped deuterium correlate with damage in the material. It will also be shown that experiments carried out at similar fluence but at different flux show large differences in surface modifications as well as in deuterium retention.

7.2 Experiment

Four polycrystalline tungsten targets were cut from a rolled sheet (PLANSEE, 0.9 mm thick, 99.96% purity) [150]. They were mechanically polished until the surface was mirror-like, so that changes in surface morphology could easily be studied. Subsequently, the samples were ultrasonically cleaned in isopropanol and heated for 1 h at 1200 K in vacuum ($<10^{-6}\, \text{Pa}$) to relieve material stresses, for hydrogen degassing and oxide layer removal. One of the samples was pre-irradiated with 12.3 MeV $\text{W}^{4+}$ ions to a damage level of 0.45 dpa (displacements per atom, $E_{\text{displacement}} = 90\, \text{eV}$ [68]) to simulate the neu-
tron damage that is expected in ITER. The 3 MV tandem ion accelerator at IPP-Garching irradiated an area of 18 mm in diameter.

7.2.1 Deuterium plasma exposure

The tungsten targets were exposed in two devices, PlaQ [138] and Pilot-PSI [10]. PlaQ, located at IPP-Garching, produces plasma fluxes of about $10^{20}\text{ m}^{-2}\text{s}^{-1}$. The plasma ions mainly consist of $\text{D}_3^+$ with an ion energy of 38 eV per atom. The exposure is homogeneous across the rectangular specimen ($12 \times 15\text{ mm}$). The target was heated with a boralectric heater to a surface temperature of 500 K. After plasma exposure and simultaneously switching off the heater, cooling is relatively slow: the first 50 K typically takes about 5 minutes, 30 minutes are needed to reach 320 K.

Pilot-PSI, which is located at FOM-DIFFER, produces $\text{D}^+$ particle fluxes of typically $10^{24}\text{ m}^{-2}\text{s}^{-1}$ in a magnetic field of 0.4 T. A bias voltage of –40 V was applied to the targets ($\varnothing 20\text{ mm}$). The plasma potential is not precisely known [32, 33] but is only a few eV. The ion energy is therefore dominated by the target bias and close to 40 eV. The electron density and temperature of the Pilot-plasma were measured with Thomson scattering [96]. This measurement was used to estimate the ion flux on the target by applying the Bohm criterion [31]. In figure 7.1 the radial distribution of the flux is shown. The Gaussian flux profile is the result from the measured Gaussian electron density profile and the plasma temperature profile. The plasma beam heats the target, therefore the temperature profile resembles the flux distribution (figure 7.1). At the start of each plasma shot, it typically takes 1 – 2 seconds before the sample reaches its steady-state temperature. The temperature profile of the tungsten surface during exposure was measured with a fast infrared camera (FLIR SC7500-MB) and ranges between 545 K in the centre of the

![Figure 7.1: Radial dependence of the plasma flux (solid triangles) and surface temperature (open diamonds) at the target during plasma exposure of sample D.](image)
7 Surface morphology and deuterium retention at high-flux deuterium plasmas

<table>
<thead>
<tr>
<th></th>
<th>sample A low-flux</th>
<th>sample B low-fluence</th>
<th>sample C high-fluence</th>
<th>sample D pre-damaged</th>
</tr>
</thead>
<tbody>
<tr>
<td>pre-irradiation</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>0.45 dpa</td>
</tr>
<tr>
<td>flux (Γ)</td>
<td>10^{20} m^{-2}s^{-1}</td>
<td>1.1×10^{24} m^{-2}s^{-1}</td>
<td>1.0×10^{24} m^{-2}s^{-1}</td>
<td>1.1×10^{24} m^{-2}s^{-1}</td>
</tr>
<tr>
<td>fluence (F)</td>
<td>10^{26} m^{-2}</td>
<td>0.8×10^{26} m^{-2}</td>
<td>0.8×10^{27} m^{-2}</td>
<td>0.8×10^{27} m^{-2}</td>
</tr>
<tr>
<td>temperature</td>
<td>500 K</td>
<td>515 K</td>
<td>530 K</td>
<td>530 K</td>
</tr>
<tr>
<td>ion energy</td>
<td>38 eV/D</td>
<td>~40 eV/D</td>
<td>~40 eV/D</td>
<td>~40 eV/D</td>
</tr>
</tbody>
</table>

**Table 7.1:** Overview of the exposure conditions of the four investigated samples. The plasma conditions and surface temperature of sample A are constant over the whole sample. Plasma exposure at Pilot-PSI (samples B – D) results in an inhomogeneous surface temperature profile (figure 7.1). The temperature mentioned for samples B – D is given at 2 mm from the centre, where the SEM investigations and NRA measurements were performed.

The four samples were exposed to plasma under very different conditions. From one sample to the next, however, only one parameter was varied whereas all the others were kept as close as possible. In this way we are able to study the isolated effects of plasma flux, plasma fluence (time) and pre-irradiation damage on surface modifications and deuterium retention.

An overview of the main parameters as used in the experiments is given in table 7.1. Sample A, which we call the **low-flux sample**, was exposed in PlaQ [151]. The other samples (B – D) were exposed to high-flux deuterium plasmas in Pilot-PSI. The surface temperatures mentioned for samples B – D are the values at 2 mm from the centre of the spot on the round sample, where the surface morphology and the deuterium retention were studied. The main difference between the exposure conditions of samples A and B was the flux that varied by four orders of magnitude. Also the deuterium plasma fluence was kept close, i.e. the samples were exposed to similar amounts of particles. In order to reach the particle fluence of $10^{26} \text{ m}^{-2}$ in PlaQ, the sample was exposed for about 12 days. Sample B, which we will call the **low-fluence sample**, reached a similar particle fluence already after seven shots of 10 s in Pilot-PSI. Sample C, which we will call the **high-fluence sample**, was exposed to ten plasma shots of 75 s, so that a fluence of $0.8 \times 10^{27} \text{ m}^{-2}$ was reached. The major difference between the exposures of the low-fluence and high-fluence samples is the exposure time. In this way, the effect of exposure time during high-flux plasma exposure was studied. Sample D is the sample that was pre-irradiated to a damage level of 0.45 dpa prior to plasma exposure and is called the **pre-damaged sample**. All plasma exposure conditions of sample D were very close to those of sample C.
7.2 Experiment

7.2.2 Target analysis

After deuterium implantation, all four samples were investigated in detail to study surface morphology and deuterium retention. Surface modifications were studied with optical and scanning electron microscopy (SEM). As will be discussed, blisters of different sizes were observed. Several blisters were cut with a focussed ion beam (FIB) to determine the bulk structure beneath them. Subsequently, the samples were investigated by nuclear reaction analysis (NRA) to study the deuterium depth distributions. Thermal desorption spectroscopy (TDS) was used to get information about the binding energies of the deuterium retained in tungsten.

Scanning electron microscopy images were acquired with a Helios NanoLab600 (FEI) at IPP-Garching. Images were typically taken using a 5 keV electron beam. The magnification was varied in order to study the sub-µm range, the µm range and the 100-µm range. For the largest magnification an emersion lens was switched on in addition to the tube-lens-detector that was used to detect secondary electrons. The µm and 100-µm range were studied by using a segmented annular solid state detector to measure the back-scattered electrons. Subtracting the signals of the segments from each other, allows to eliminate the contrast dependence on the material mass and to accentuate the topography (custom mode). This accentuation of the height differences makes blisters easier to observe. The surface of the low-flux target (A) was also analysed with a confocal laser scanning microscope (CLSM).

Information about the region underneath the blisters was obtained by combining SEM imaging with focused ion beam cutting. The Ga-ion beam of the Helios NanoLab600 with an energy of 30 keV and current between 2 and 20 nA was used to create cross-sections. To reduce artefacts due to the cutting process, the area of interest was coated with a Pt-C film prior to the cutting. The surface normal was aligned with the ion beam. The angle between Ga-ion and electron beam was 52°. Therefore, the cross-sections are imaged under 38°, causing a difference between the horizontal and vertical scale. The length of the vertical scale bars in the images are therefore 0.79 of the horizontal scale bars.

Nuclear reaction analysis of the targets exposed in Pilot-PSI was performed two weeks after plasma exposure at IPP-Garching. The nuclear reaction $^3\text{He}, p)^4\text{He}$ was used to obtain a local measurement of the deuterium concentration as function of depth. The $^3\text{He}$ beam spot of 1 mm² size was positioned for the samples B – D 2 mm off-centre of the Pilot-PSI exposure spot. The energy was varied in 6 steps from 690 keV to 4.0 MeV to determine the deuterium concentration down to a depth of 6 µm. The low-flux sample (A) was analysed using slightly different energies. The depth profiles of retained deuterium were calculated from the measured proton energy distributions by use of the NRA-DC program.

The targets were analysed with thermal desorption spectroscopy at FOM-DIFFER 5 months after Pilot-PSI plasma exposure. The tungsten targets were clamped to a ceramic heater and heated with a linear temperature ramp of 1 K/s to 1273 K and held for 10 min at 1273 K. A Balzers QMA125 quadrupole mass spectrometer monitored the mass 4 ($D_2$) signals in the residual gas in the chamber. To determine the total amount of deuterium released from the target during the temperature ramp, the absolute sensitivity
7 Surface morphology and deuterium retention at high-flux deuterium plasmas

was determined using a calibrated D$_2$ leak. The mass 3 (HD) signal was in all cases less than 20% of the mass 4 signal.

7.3 Results

7.3.1 Surface morphology

CLSM and SEM images of the four investigated samples are shown in figure 7.2. The four images taken at the lowest magnification show the 100-µm range with large blisters covering several grains. At higher magnification, individual grains become visible that

Figure 7.2: CLSM and SEM images of the four samples. From left to right the (A) low-flux, (B) low-fluence, (C) high-fluence and (D) pre-damaged sample. The SEM images were taken at three magnifications to show the 100-µm range, the µm range and the sub-µm range. The lowest magnification of the low-flux sample (A) is the only one taken with a confocal laser scanning microscope, its scale differs from the other images.
contain smaller blisters for three of the targets. At the largest magnification, it is clear that all four targets contain structures on the nanometer scale.

On the low-flux sample (A), only few (about 60) but very large blisters (50 – 500 µm) and some smaller micrometer-sized blisters were observed. The blisters are irregularly distributed over the sample surface and seem to appear in groups. One such region with three of these blisters is shown in figure 7.2A. Note that this image is taken with a confocal laser scanning microscope and that the scale differs from the other images. The surface of the area shown is smooth except for the blisters. In addition, a few micrometer-sized blisters (1 – 10 µm) are observed. These smaller blisters are predominantly found in the neighbourhood and on top of the large blisters. The high-resolution SEM images mostly show a smooth surface on the micrometer scale and a nanostructured surface on the sub-micrometer scale. The type of nanostructure changes at the grain boundaries, indicating that the structure depends on the grain orientation. Stripe-like surface structures are observed as well as more randomly shaped structures.

The (high-flux) low-fluence sample is shown in figure 7.2B. It is covered by large amounts of blisters of only a few micrometer in diameter. These micrometer-sized blisters often extend over more than one grain. Zooming in at larger magnification reveals, in addition to the blisters, irregularly shaped features in the sub-µm range. We will call these 100 – 750 nm large features protrusions. Most of the protrusions appear within grains whereas their density strongly varies from one grain to the other. Zooming in even further reveals a nanostructured surface. Densely packed, randomly shaped structures with a size of 10 – 20 nm cover the surface. It should be noted that at locations not shown in figure 7.2B also weak stripe-like structures appear. The appearance varies again from grain to grain.

The surface morphology of the high-fluence sample is shown in figure 7.2C. Both the amount of blisters as their size has increased as compared to the low-fluence sample. Zooming in reveals similar protrusions as observed on the low-fluence sample. It is not possible to determine whether their amount has increased or decreased, because of their irregular distribution and because they are only visible at a large magnification. Pronounced nanostructures are observed for the largest magnification, their detailed appearance being clearly correlated to the specific grains and therefore probably to grain orientation.

![Figure 7.3](image)

**Figure 7.3:** a) Large blister on the low-flux sample is cut by FIB. b) The associated cavity is found about 5 µm below the surface (the cavity is partly filled during the FIB cutting by redeposited material). c) FIB cross-section of another cavity, where the cracks follow the grain boundaries.
In figure 7.2D the SEM images for the pre-damaged sample are shown. Comparing to figure 7.2C shows that the amount of micrometer-sized blisters has decreased. This is the case also for other areas on the surface. Zooming in reveals a lot of small protrusions (<250 nm) formed within specific grains. The highest magnification shows again the appearance of nanostructures.

Figure 7.4: SEM images of the FIB cuts of the a) low-fluence (B) and b) high-fluence (C) sample. The cavities that appear within a grain are indicated with a white box.
7.3 Results

7.3.2 Sub-surface morphology

A focused ion beam in combination with a SEM was used to create cross-sectional images of the blisters. A typical cross-section of one of the large blisters on the low-flux sample (A) is shown in figure 7.3. A large cavity is visible below the blister. As discussed in [69, 70, 87, 88], the solubility of hydrogen in tungsten is very low. This promotes the accumulation of deuterium gas in cavities. The pressure that builds up is a driving force for cavity growth. Material can be pushed upwards and deform the surface: a blister is formed. The cavity associated with the blister in figure 7.3a appears at a depth of about 5 µm. Cutting other blisters revealed cavities at even larger depths up to 30 µm. The cracks follow the grain boundaries (figure 7.3b). Furthermore, the blisters did not collapse during the FIB cutting, which means that they are stable and were formed in a plastic deformation process [87].

The smaller micrometer-sized blisters that predominantly show up in the high-flux samples were also studied with the FIB in combination with SEM (figure 7.4). These blisters originate in cavities at grain boundaries as well and can extend over several grains. The cavities of the low-fluence sample (B) are typically observed up to about 1 µm below the surface (figure 7.4a). Cavities for the high-fluence sample (C) typically extend deeper in the material and are observed up to 2 µm depth. It is also clear that the cavities are significantly larger in volume than the ones in the low-fluence sample. In figure 7.4 also a few cavities are shown that appear within a grain. These cavities are a few hundred nanometer in size and occur close to the sample surface. As result of this cavity formation, the before mentioned protrusions appear at the surface.

In figure 7.5 a cross-sectional view of the pre-damaged sample (D) is shown. The image clearly shows the difference between a micrometer-sized blister and the smaller protrusions. The blister is associated with a cavity that arises along grain boundaries about parallel to the surface (indicated by the dotted box). It is difficult to recognize

[Image of SEM images of cross-sections of the pre-damaged sample showing both an inter-granular cavity (black dotted rectangle) as well as intra-granular cracks (white rectangles)].

Figure 7.5: SEM images of cross-sections of the pre-damaged sample showing both an inter-granular cavity (black dotted rectangle) as well as intra-granular cracks (white rectangles).
7 Surface morphology and deuterium retention at high-flux deuterium plasmas

this blister at the surface since its width is large compared to its height. The protrusions (indicated by the solid boxes) are associated with cracks within a grain. These cracks are located much closer to the surface at less than 100 nm depth. Deeper in the grain no cracks have been observed. In conclusion, the blisters originate in inter-granular cavities, protrusions arise from intra-granular cavities.

7.3.3 Deuterium depth profiling

In figure 7.6 the NRA depth profiles of the retained deuterium are shown. Whereas the deuterium concentration for all four targets is similar and relatively high at the surface, in the bulk significant differences are observed. For the low-flux sample (A) a constant deuterium concentration of about $10^{-4}$ atomic fraction (at.fr.) was measured over at least the first 10 µm. This result follows from fitting the measured proton energy distributions

![Deuterium depth profiles](image)

**Figure 7.6:** Deuterium depth profiles of the four samples (results from NRA-DC). The squares indicate the samples exposed to low-fluence ($10^{26}$ m$^{-2}$) plasmas, the triangles the ones to a higher fluence of $10^{27}$ m$^{-2}$. The low-flux sample (A, $10^{20}$ m$^{-2}$s$^{-1}$, PlaQ) is plotted with the thick red solid line, the low-fluence sample (B, $10^{24}$ m$^{-2}$s$^{-1}$, Pilot-PSI) with the orange dashed line. The dotted blue line with open triangles represents the high-fluence sample (C), the green dash-dotted line with solid triangles the pre-damaged sample (D).
7.3 Results

with the NRA-DC program [100]. This constant concentration is in the same range as reported values for deuterium trapped in pre-existing defects [55], which depends on the tungsten grade. Note that this concentration is below the other three curves up to depths of 2 – 3 µm. Beyond this depth, the concentrations of the other samples are still decreasing and probably decrease below the fraction of the low-flux sample. Obviously, the exposure time of 12 days for the low-flux sample allowed the deuterium to diffuse deeper into the material as compared to the high-flux samples.

For the low-fluence sample (B), the deuterium concentration is highest at the surface, followed by a dip at ~200 nm. A local maximum in the deuterium concentration is observed at 0.5 µm, after which the concentration slowly decreases. Investigation of the high-fluence sample (C) shows similar behaviour as the low-fluence sample. A small dip in the concentration just below the surface is followed by a local maximum at 0.7 µm and then the concentration decreases slowly. The difference to the low-fluence sample is that the deuterium has penetrated deeper in the material. This corresponds well with the FIB results, where the cavities were found deeper in the material (figure 7.4).

The pre-damaged sample (D), finally, contains the largest concentration of retained deuterium, i.e. $1.2 - 1.4 \times 10^{-2}$ at.fr. in the first micrometer. This is consistent with our previous findings where it was shown that the deuterium is trapped predominantly in single vacancies, small vacancy clusters and dislocations [127].

Integration of the deuterium concentration over the depth yields the total deuterium retained in the first 6 µm (for the low-flux sample this is the first 12 µm for as result of the difference in chosen NRA energies). For the low-flux, low-fluence, high-fluence and pre-damaged samples, the total deuterium retention at the investigated positions is 0.7, 2.5, 4.5 and $12.8 \times 10^{20}$ m$^{-2}$, respectively.

7.3.4 Deuterium desorption

The TDS results for the three experiments carried out at high-flux are shown in figure [7.7]. For comparison, also the TDS spectrum of a pre-damaged unpolished target is shown that was exposed for 100 s to high-flux plasma at self-biased conditions [127], at a surface temperature of 550 K in the centre of the exposure spot. The latter target did not show any surface blistering, although it should be mentioned that blisters are difficult to observe on a rough surface. Similar observations were made by Nishijima et al [152]. The desorption spectrum was rescaled by matching the peak at 900 K to the corresponding peak of the present pre-damaged target, so that the ratio of the desorption peaks can easily be compared.

In figure [7.7], three clear desorption peaks can be distinguished located at about 550 K, 700 K and 900 K. The low-fluence sample (B), with the least plasma damage of the high-flux samples, shows a desorption peak at 550 K and a small shoulder at higher energies. In the desorption spectrum of the high-fluence sample (C), with significantly more plasma damage, two peaks are present: at 550 K and at 700 K. The pre-damaged sample (D), finally, shows strongly increased retention and three desorption peaks: at 550, at 700 and at 900 K. The rescaled pre-damaged sample from [127] shows two pronounced desorption peaks at 550 K and at 900 K, and a small shoulder at 700 K.
Figure 7.7: Thermal desorption spectra of the experiments carried out at high-flux (Pilot-PSI). The heating rate was 1 K/s. The low-fluence sample (B) is shown by the orange-dashed line, the high-fluence sample (C) by the blue dotted line, and the pre-damaged sample (D) by the green dash-dotted line. The TDS spectrum of a previous pre-damaged sample (from [127]) is shown by the solid grey line. The latter spectrum was rescaled by matching the peak at 900 K to the corresponding peak of the present pre-damaged sample. At the top of the image, the ranges of trapping energies that correspond to the position of the peaks are shown, in the case that the deuterium is retained as block profile in the first 1 – 2 µm.

TMAP7 simulations [107] were used to estimate the peak positions in the TDS spectra as function of deuterium trap energy. In the simulations, block profiles of deuterium traps up to a depth of 1, 1.5 and 2 µm were used to take into account the range of depths at which deuterium is trapped. The ranges of the deuterium trap energies are indicated above the curves.

The desorption peak at 550 K is observed in all spectra. Based on the trapping energy of 0.8 – 1.2 eV, its presence can be ascribed to trapping of deuterium at dislocations, grain boundaries and/or mono-vacancies [127]. The peak is larger for the high-fluence sample as compared to the low-fluence sample. For the pre-damaged sample the peak seems to have increased even further.

The desorption peak at 700 K appears as a small shoulder in the low-fluence sample. In the high-fluence as well as in the pre-damaged sample this desorption peak is clearly distinguishable. These are the two targets where plasma induced blisters and small protrusions are most pronounced. The rescaled pre-damaged sample from [127], where no blistering is observed, does not show a pronounced desorption peak at 700 K. This cor-
relation suggests that the desorption peak at 700 K is related to the plasma-induced modifications and that these modifications trap deuterium at energies of 1.4 – 1.6 eV.

The 900 K desorption peak appears only for the pre-damaged targets and corresponds to trapping of deuterium at 1.8 – 2.0 eV. This peak was attributed to trapping of deuterium in small vacancy clusters that are caused by the irradiation with MeV heavy ions [127, 137].

7.4 Discussion

In the present experimental results, three different types of surface modifications have been distinguished (table 7.2): blisters, protrusions and nanostructures. Blisters are hemispherical structures in the 1 – 500 µm range that appear on the surface and that are caused by cavities below the surface. These cavities are formed at grain boundaries and are thus inter-granular. The second feature, the protrusions, have sizes of tens to hundreds of nanometers. Protrusions have an irregular shape and much sharper edges than the blisters. Cross-sections with the FIB show that the associated cavities are intra-granular (figure 7.5). Protrusions appear with a large number density on certain grains whereas on others they are completely absent. This is probably related to the grain orientation [146]. The nanostructures, finally, typically have sizes of 10 – 40 nm. These structures have been well characterized by Xu et al for high-flux plasma conditions: they correlated the spongy, lamellae and triangular structures to $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$ grain orientations, respectively [146].

Formation of blisters has been studied extensively in the past [69, 70, 87]. Tungsten has a very low solubility for hydrogen. In case the interstitial deuterium concentration exceeds the solubility, i.e. in case of supersaturation, deuterium starts to precipitate. Accumulation of deuterium is expected to happen at nucleation points, which can be defects like dislocations, grain boundaries and vacancies. Subsequently, cavity growth can take place. Condon [70] distinguished three mechanisms for cavity growth: plastic deformation, dislocation loop punching and growth by vacancy clustering. For the last mechanism, temperatures above the temperature where vacancies get mobile are needed ($\sim 550$ K). The surface temperatures during plasma exposure were below this temperature. Although there is a possibility that the presence of deuterium enhances the vacancy

<table>
<thead>
<tr>
<th>type of surface morphology</th>
<th>size</th>
<th>depth</th>
<th>shape</th>
<th>location</th>
</tr>
</thead>
<tbody>
<tr>
<td>blisters</td>
<td>huge</td>
<td>50 – 500 µm</td>
<td>5 – 30 µm</td>
<td>inter-</td>
</tr>
<tr>
<td>micrometer-sized</td>
<td>1 – 10 µm</td>
<td>&lt;2 µm</td>
<td>smooth</td>
<td>granular</td>
</tr>
<tr>
<td>protrusions</td>
<td>normal</td>
<td>&lt;750 nm</td>
<td>100 nm</td>
<td>intra-</td>
</tr>
<tr>
<td>small</td>
<td>&lt;250 nm</td>
<td></td>
<td>irregular</td>
<td>granular</td>
</tr>
<tr>
<td>nanostructures</td>
<td>10 – 40 nm</td>
<td>various</td>
<td>(sub)surface</td>
<td></td>
</tr>
</tbody>
</table>

*Table 7.2:* Classification of the surface modifications.
mobility \[153, 154\], it is not likely that cavity growth by vacancy clustering played a role. Plastic deformation as well as dislocation loop punching start with pressure build up inside a cavity. To cause plastic deformation of grains, pressures in the range of a few hundred MPa have been reported \[151\], for plastic deformation caused by dislocation loop punching a few GPa is needed \[64, 84\]. From our results we are not able to distinguish between these two mechanisms.

The low-flux sample (A) does only show blisters on a few locations on the surface. Most striking are the very large ones with the underlying cavities being present at large depths of 5 – 30 µm. The fact that most of the surface is free of blisters and that where the blisters appear they do so in groups, indicates that the material contains weak grain boundaries in specific areas at large depths. These very large blisters only appear on the low-flux sample, because the long exposure time (four orders of magnitude higher than the high-flux exposures) allows the deuterium to accumulate at these large depths (see figure 7.6).

The high-flux samples are covered with micrometer-sized blisters. They originate in cavities at grain boundaries. The blisters do not collapse during cutting with the FIB, which means that they are plastically deformed. The increase of the size of the micrometer-sized blisters with exposure time (high-fluence (C) versus low-fluence (B) target) is probably related to the pressure build up over time. The increased amount of blisters and corresponding cavities can be explained by deuterium diffusing to larger depths and thereby reaching more nucleation points. Less micrometer-sized blisters are formed on the pre-damaged sample (D). This was observed before in other experiments carried out at lower flux and fluence \[155\]. The reason may be the presence of large amounts of nucleation points inside the grains that are decorated with deuterium. Possibly, these decorated traps can adapt better to stresses accumulated at the grain boundaries because of hydrogen enhanced local plasticity \[153, 154\].

On the high-flux samples, we also observed the formation of protrusions with sizes up to 750 nm. We have shown that they originate in cavities within grains. On the low-flux sample such protrusions were not observed. Obviously, the hydrogen interstitial concentration needs to be high enough to promote cavity formation within a grain. The formation probably starts at a nucleation point that is already present in the material before plasma exposure. This is consistent with the fact that in the pre-damaged target, with many vacancies and small vacancy clusters present, the number of protrusions is significantly larger than in the undamaged targets. The protrusions do not collapse during the cutting process with the FIB, which means that they are plastically deformed.

The NRA results for the low- and high-fluence samples show significant retention at 0.5 – 2 µm depth. This depth range correlates well with the locations at which the cavities associated with the blisters were observed. It therefore seems that a significant part of the deuterium is trapped in and/or close to the cavities. In our TDS studies we have related the peak at 700 K to the plasma induced modifications (figure 7.7). Using TMAP7 and applying single traps, this peak was assigned to trapping energies of 1.4 – 1.6 eV. This energy is too high for the release of deuterium from dislocations (\[\sim 0.85 \text{ eV} \ [51, 54]\)) and too low for deuterium chemisorbed at the inner surfaces of the cavities to penetrate the grains (\[\sim 2.1 \text{ eV} \ [20, 55, 156]\]). After excluding the before mentioned possibilities,
7.5 Conclusions

we can only speculate about the origin of the 700 K desorption peak. Obviously, this desorption does not take place via dissociation and chemisorption at the cavity surface (trapping energy of $\sim 2.1$ eV). One possibility would be that gaseous molecular deuterium desorbs via migration along the grain boundaries, i.e. deuterium is released from the cavities via grain boundaries connecting the cavities with the surface area. After all, the growth of the cavities results from pressure build up by accumulation of molecular deuterium. Molecular dynamics simulations by Von Toussaint et al. [157] have indeed shown that grain boundaries in polycrystalline tungsten can provide important transport channels. Another option is that during TDS blister bursting occurs [158].

The pre-damaged sample shows in addition a desorption peak at 900 K. This peak has been related to deuterium escaping from vacancy clusters created by the pre-irradiation with the MeV ions [64, 137, 159]. These small vacancy clusters are located inside the grains.

The deuterium depth profiles of all samples show a large surface concentration of deuterium (0 – 100 nm depth). This is much than can be explained by a monolayer of chemisorbed deuterium at the surface ($2 \times 10^{19}$ m$^{-2}$). In addition, it is likely that molecular deuterium will form. Deuterium molecules have a very low binding to the surface and are likely to desorb. Therefore, we think that the surface peak is a result of the deuterium trapped slightly deeper in the material. Nanostructures and protrusions are both likely candidates, although the NRA resolution is not good enough to distinguish between the two. In addition, we cannot exclude the contribution of plasma impurities, even though the target bias is only –40 V.

7.5 Conclusions

In the present experiments, three types of surface modifications were distinguished: inter-granular blisters, intra-granular protrusions and nanostructured surface morphologies. The surface modifications are present well beyond the implantation region. Since the implantation energy is far below the displacement damage threshold, the driving mechanism is most probably super-saturation of the tungsten lattice and subsequent pressure build up at nucleation points. Blisters have been assigned to inter-granular cavities that plastically deform full grains and protrusions to intra-granular cavities that lead to plastic deformation of parts of grains. The detailed mechanisms for the formation of the nanostructures are not clear.

Based on the correlation between depth distributions of cavities and retained deuterium, it seems that a significant part of the deuterium is trapped in and/or close to the cavities. The release of deuterium related to this is observed in the TDS spectrum by means of a desorption peak at 700 K. This may be related to transport of deuterium via grain boundaries or to the bursting of blisters during TDS. Further research is needed to study these results in more detail.

Between the experiments carried out at different plasma flux, large differences were observed. In the low-flux case, i.e. large exposure time, the deuterium penetrated much deeper in the material. This resulted in very large blisters in specific areas on the surface,
probably related to weak grain boundaries in the material. High-flux exposure leads to many more but significantly smaller blisters as well as to protrusion formation.

The present results clearly show that experiments carried out at different flux but with the same fluence yield very different results. This is important to consider in cases where extrapolations are made from low-flux experiments to conditions as present in the ITER divertor.

**Acknowledgements**

Part of this work, supported by the European Communities under the contract of Association between EURATOM/FOM, was carried out within the framework of the European Fusion Programme with financial support from NWO. The views and opinions expressed herein do not necessarily reflect those of the European Commission. Part of this project has received funding from the Euratom research and training programme 2014 – 2018.

The authors would like to thank R.S. Al for the technical assistance at the Pilot-PSI measurements and J. Dorner and M. Fußeder (IPP-Garching) for their technical assistance with the $^3$He beam analysis.
Deuterium retention and surface modifications of thin tungsten films exposed to high-flux plasmas

M.H.J. ’t Hoen¹, D. Dellasega², M. Passoni², A.W. Kleyn¹,³,⁴ and P.A. Zeijlmans van Emmichoven¹

¹ FOM institute DIFFER, Association EURATOM-FOM, Partner in the Trilateral Euregio Cluster, NL-3439 MN Nieuwegein, the Netherlands
² Dipartimento di Energia, Politecnico di Milano, Istituto di Fisica del Plasma, Consiglio Nazionale delle Ricerche, EURATOM-ENEA-CNR Association, Milano, Italy
³ University of Amsterdam, Science Park 904, NL-1098 XH Amsterdam, the Netherlands
⁴ Chengdu Development centre for Science and Technology, Shuangliu, Chengdu, Sichuan 610207, People’s Republic of China

Abstract

Deuterium retention studies will be presented for nanostructured tungsten films exposed to high-flux deuterium plasmas. The thin tungsten films of ~1 µm thickness were deposited with pulsed laser deposition on bulk tungsten. Surface modifications were studied with scanning electron microscopy and deuterium retention with thermal desorption spectroscopy.

Three different types of pulsed laser deposition films were studied, columnar (density ~18 × 10³ kg m⁻³, crystallite size ~15 nm), nanocrystalline (density ~15 × 10³ kg m⁻³, crystallite size ~12 nm) and amorphous-like (density ~12 × 10³ kg m⁻³, crystallite size ~2 nm). The targets were exposed to deuterium plasmas while being biased at −40 V. Exposures are carried out either at low temperature, where the surface temperature ranged from about 460 K at the periphery to about 520 K at the centre of the targets or at high surface temperature (Tmax = 1000 K). Generally, the films withstand the intense plasma exposure maintaining overall integrity. An increase of deuterium retention was observed with decreasing tungsten density. At the same time, the deuterium desorbed at lower temperatures. We found formation of micrometer-sized blisters as well as structures on the nanometer scale depending on the layer type. The relation between the density of the film and the plasma-induced modifications and amount of retained deuterium will be discussed.

in preparation for publication
8 D retention and surface modifications of thin W films exposed to high-flux plasmas

8.1 Introduction

Tungsten is foreseen as divertor material in future magnetic fusion devices such as ITER [13]. The divertor tiles of ITER are predicted to handle high particle fluxes (10^{24} \text{m}^{-2}\text{s}^{-1}) and heat fluxes (10 \text{MW m}^{-2}) [8]. Apart from the extreme conditions that these tiles need to survive, the tritium inventory and surface modifications are important criteria for the specific material choice. The tritium inventory in ITER should be kept low (<700 g [14]) for safety and efficiency reasons. Surface modifications might be problematic, because they can lead to degradation of heat conductivity. These modifications may enhance erosion, which could be problematic because tungsten cannot be tolerated in the core plasma.

Pulsed laser deposition (PLD) makes it possible to grow films of any composition and with very different morphology and structure [160]. The micrometer thick PLD layers were exposed to high-flux deuterium plasmas to investigate surface modifications and deuterium retention. Besides the fundamental interest in these phenomena, there is also a practical motivation for this work. Present-day tokamaks like JET make use of thin tungsten films, while the retention properties are largely unknown. Furthermore, redeposition of thin films of tungsten may occur during operation of ITER.

In this chapter, experiments are described in which thin PLD tungsten layers with different compositions are tested in high-flux plasmas. Materials are tested both at low surface temperature (<520 K) and at high surface temperature (<1000 K) conditions. For the film with the highest density (columnar tungsten), the layer thickness was varied as well. Targets with thin films show a considerably larger fraction of deuterium retained in the material than bulk polycrystalline tungsten, even after pre-damaging the latter with MeV tungsten ions.

8.2 Experiment

Polycrystalline tungsten targets (PLANSEE, 99.96% purity, Ø 20 mm, 1 mm thick) consisting of micrometer-sized grains were mechanically polished until mirror finish and coated with thin films by PLD. Different background pressures were chosen during deposition in order to create three different PLD structures [160]. The most dense is the ‘columnar’ structure with a density that is 7% less than bulk tungsten: \approx 18 \times 10^3 \text{kg m}^{-3} and consists of typical crystallite sizes of \approx 15 \text{nm}. The tungsten coating with a density of \approx 15 \times 10^3 \text{kg m}^{-3} and a crystallite size of around 12 \text{nm} is referred to as ‘nanocrystalline’ structure. The most open layer type is the ‘amorphous-like’ structure, with crystalline domains of only \approx 2 \text{nm}. Its density is only 60% of the polycrystalline bulk tungsten: \approx 12 \times 10^3 \text{kg m}^{-3}. Before the amorphous-like layer was deposited on tungsten, first a 150 nm thick layer of the columnar structure was coated, in order to improve adhesion.

The targets were exposed to high-flux deuterium plasmas in the linear plasma generator Pilot-PSI at FOM-DIFFER [10]. Two types of deuterium plasma exposures were used resulting in a low surface temperature (T_{\text{max}} = 520 \text{K}) and a high surface temperature (T_{\text{max}} = 1000 \text{K}). The electron density and temperature of the plasma were measured with Thomson scattering [96]. They were used to calculate the particle flux shown in fig-
8.3 Results

8.3.1 Blister formation

The surfaces of the thin films showed blister formation on micrometer scale upon plasma bombardment at low surface temperature. Optical microscope images of the centre of the targets, where the flux is typically $\sim 1.4 \times 10^{24} \text{ m}^{-2}\text{s}^{-1}$, are shown in figure 8.2. Polycrystalline bulk tungsten shows only a few small blisters (figure 8.2a). These blisters are similar to the ones described in chapter 7 and probably caused by plastic deformation. On columnar coatings many more and larger blisters than on polycrystalline tungsten are found (figure 8.2b). These blisters are uniformly distributed over the sample and have a typical size of 20 – 30 µm. The nanocrystalline coating shows similar blisters (figure 8.2c). However, the blister formation on nanocrystalline tungsten is less frequent than on columnar and concentrated at the periphery of the sample. Amorphous-like tungsten exhibits a large number of blisters (average size 20 – 60 µm), which are concentrated at
Figure 8.2: Blister formation on the samples. a) Polycrystalline bulk tungsten, b) 1 µm columnar tungsten, c) 1 µm nanocrystalline tungsten and d) 1 µm amorphous-like tungsten.

Figure 8.3: Nanostructure formation in the centre of the thin tungsten layers, where the plasma flux was typically $\sim 1.4 \times 10^{24} \text{ m}^{-2}\text{s}^{-1}$. a) Polycrystalline bulk tungsten, b) 1 µm columnar tungsten, c) 1 µm nanocrystalline tungsten and d) 1 µm amorphous-like tungsten.
8.3 Results

the periphery of the film (figure 8.2d). The black circles indicate blisters that were burst and delaminated. Delaminated blisters lost their blister caps. These blisters are larger than the normal blisters as if the latter is still developing until a critical size is reached. The critical size of the delaminated blisters is strongly dependent on the radial position. On the other PLD structures, generally, no delaminated blisters were found.

8.3.2 Nanostructure formation

SEM analysis revealed the formation of structures on the nanometer scale after high-flux plasma exposure (figure 8.3). On the polycrystalline tungsten substrate, grains are clearly distinguishable. These grains show different nanostructures (figure 8.3a). The grain in the top of the image shows a lamellae structure, the grain in the lower part, a triangular-like morphology. These nanostructures resemble the formations of chapter 7 Xu et al characterized such structures and found that their appearance is dependent on the grain orientation [146]. The nanostructures formed on the columnar tungsten (figure 8.3b) seems to reflect the grain orientations of the substrate. It seems therefore likely that the columnar structures grow according to the orientation of the substrate. This results in a sharp interface between the triangular-like and the lamellae structures. On the nanocrystalline tungsten (figure 8.3c) the different nanoscale structures are still distinguishable: on the top left lamellae are observed and the bottom left shows a triangular-like nanostructure. There is no sharp interface between the nanostructures. The amorphous-like layer exhibits a mixture of randomly orientated lamellae (figure 8.3d). Thus, for decreasing density and crystallite size, the coupling with the substrate becomes less evident.

8.3.3 Deuterium retention

The deuterium retention of the samples was measured by thermal desorption spectroscopy (figure 8.4). The polycrystalline tungsten, the bulk material on which the layers are deposited, retains only a very small amount of deuterium ($\sim 0.9 \times 10^{20} \text{m}^{-2}$). The target with a columnar PLD structure, the layer with the highest density of the thin films, retained much more deuterium and revealed two desorption peaks, one at 500 K and one at 700 K. A decrease of the layer density, increased the total retention (nanocrystalline sample). The amorphous-like tungsten, finally, shows a large increase of the retention. The 500 K peak strongly increases, while the 700 K desorption peak disappears. In conclusion, the total retention increases with decreasing density. The fraction of deuterium retained in the polycrystalline sample is very low compared to the retention in the layers. Thus, the polycrystalline bulk tungsten underneath the coated PLD hardly contributes to the total retention.

As a comparison, a polycrystalline sample that was pre-irradiated with $W^{4+}$ ions to a damage level of 0.45 dpa was exposed in the same measurement series to similar plasma conditions. In chapter 5 is described that the created damage consists of mono-vacancies and small vacancy clusters and extends to a depth of 1.5 µm, which is comparable to the thickness of the PLD layers. The blister formation was found to be somewhat less than
8.3.4 Film thickness

Three different layer thicknesses of the columnar structure were deposited on polycrystalline samples. These thicknesses were 0.15, 0.5 and 1.0 µm. Subsequently, the samples were exposed to high-flux deuterium plasma at low surface temperature \( T_{\text{max}} = 520 \text{ K} \). The thermal desorption spectra are shown in figure 8.5. The shape of the spectra hardly change with thickness, only the absolute level. The small shift of the low temperature peak may be a result of differences in depth where the deuterium is retained. In figure 8.5b the integrated retention is plotted as function of thickness. A fit through the data shows a linear dependence of the deuterium retention, \( D_{\text{tot}} \), as function of thickness \( d \):

\[
D_{\text{tot}} = 2 \times 10^{20} + 7.4 \times 10^{26} \cdot d.
\]

When we assume that the columnar layer is homogeneously filled with deuterium, the interpretation of this fit is as follows: The constant value \( 2 \times 10^{20} \text{ m}^{-2} \) is the surface coverage, similar for all thicknesses. The linear term \( 7.4 \times 10^{26} \text{ m}^{-3} \) indicates the volumetric retention of the columnar structure and corresponds to 1.2 at.%. SEM analysis of the columnar 0.15 and 0.5 µm layers revealed similar nanostructure formation as on the 1 µm thick layer (figure 8.5b). The blister formation, on the contrary, is dependent on the layer thickness. The typical size of the blisters found on the 0.5 µm columnar layer was typically smaller than for the 1.0 µm columnar layer. The 0.15 nm columnar layer did not show any blisters at all.

Figure 8.4: Thermal desorption spectra of the samples with PLD layers. The low temperature plasma exposures \( T_{\text{max}} = 520 \text{ K} \) are shown in the left graph, at the right the TDS spectra after high temperature plasma exposure are plotted. The heating rate was 1 K/s. For the polycrystalline tungsten, which agrees with our findings of chapter 7. The nanostructures did not differ. The deuterium retention measured by TDS was \( 5.4 \times 10^{20} \text{ m}^{-2} \), which is almost a factor two lower than the retention in the columnar layer. Thus, the retained fraction in the nanostructured layers is larger than in the pre-damaged sample. The low temperature desorption peak is found at the same temperature of 500 K. The high temperature desorption peak is however different and was found to appear at 900 K.

8 D retention and surface modifications of thin W films exposed to high-flux plasmas
8.3 Results

Figure 8.5: Deuterium retention in columnar PLD layers. a) Desorption of three different layer thicknesses: 0.15, 0.5 and 1 µm (1K/s). b) Total deuterium retained in these layers averaged over the plasma exposed area. The fit through the measurement data is shown.

8.3.5 High temperature

The PLD structures were also exposed to plasma at high surface temperature ($T_{\text{max}} = 1000 \text{ K}$). The thickness of the nanocrystalline and columnar tungsten was 0.5 µm. The amorphous-like sample was deposited with a coating of 1 µm. High temperature exposure enhances the formation of blisters on the amorphous-like sample. Typically, large blisters (up to 70 µm) were observed, of which a large fraction was burst. On columnar and nanocrystalline tungsten films blisters of 5 – 20 µm arose, uniformly distributed over the sample surface. Close inspection by SEM (figure 8.6) revealed micrometer-sized cracks in the columnar films and cracked blisters on the nanocrystalline films.

SEM analysis revealed nano-droplet formation (30 – 50 nm) on all inspected samples, both on polycrystalline tungsten as on the PLD layers. In figure 8.7, the SEM images of these droplets are shown in the centre and halfway between the centre and edge for the amorphous-like tungsten. A radial dependence of the droplet size and density is observed.

Figure 8.6: a) High temperature plasma exposure induced micrometer-sized cracks on the columnar film. b) Cracked blisters appeared on the nanocrystalline sample.
Towards the edge of the sample the plasma flux is lower, just as the surface temperature. These differences resulted in the formation of smaller droplets. EDS analysis of the amorphous-like sample did not show any impurities apart from the standard oxygen and carbon concentrations. However, EDS is averaged over hundreds of nm depth. Therefore, the possibility remains that very small surface quantities are below the detection limit.

In figure 8.4b the desorption spectra after high surface temperature exposure are shown. Note that the scale on the vertical axis differs from the low temperature desorption spectra. Furthermore, the nanocrystalline and columnar sample correspond to a layer of only 0.5 µm thick. These samples exposed at high temperature retained respectively 62% and 51% of the deuterium found in the equivalent layer of 1 µm thick films exposed at low surface temperature. In the TDS spectra of the columnar tungsten in figure 8.5a it is indeed clear that the total retention of the 0.5 µm layer exposed to low and high temperature is very similar. There ratio between the low temperature and high temperature desorption changes are result of the differences in surface temperature. The deuterium retention of the amorphous-like sample, did change considerably: for the same thickness films, the total retention increased with a factor of two and a desorption peak at a temperature of 800 K appeared.

8.4 Discussion

An overview of the layer structure (material density and crystallite size), the blister formation, nanostructure formation and deuterium retention is shown in table 8.1. Generally, the PLD layers withstand the plasma interaction maintaining the overall integrity. Nevertheless, abundant blister formation was found on the PLD layers. The amount, distribution and shape depend on the PLD structure and layer thickness. The nanostructures increase in disorder with decreasing layer density. The deuterium retention strongly increased for PLD layers with respect to the polycrystalline tungsten. Decrease of the layer density resulted in an increase of the deuterium retention.
The volumetric deuterium retention was found to be $7.4 \times 10^{26} \text{ m}^{-3}$ in columnar tungsten (section 8.3.4). The deuterium retention of the 0.5 µm columnar layers exposed at low surface temperature and high surface temperature is comparable (figure 8.5). This suggests that in both cases the PLD layer is completely filled with deuterium. Thus, the nano-droplets found on the tungsten surfaces are not likely to have affected the deuterium retention. The volumetric deuterium retention ($7.4 \times 10^{26} \text{ m}^{-3}$) of the columnar layer is comparable to the saturation of deuterium retention in pre-damaged polycrystalline tungsten at 0.45 dpa ($1.4 \text{ at.\%} \approx 8.8 \times 10^{26} \text{ m}^{-3}$, chapter 4). However, the retained fraction in $\text{D/m}_2$ of the pre-damaged tungsten is a factor two lower. It seems that the penetration of deuterium into columnar tungsten is quicker than penetration into pre-damaged tungsten. It provides insight to compare the volumetric retention in columnar tungsten to its density. Although 7% of the tungsten lattice is empty, the concentration of deuterium is only 1.25 at.%.

The TDS spectrum of the amorphous-like tungsten film shows a large retention peak at around 500 K. The total retention is much higher than in the other films. This low temperature desorption peak is usually assigned to grain boundaries and dislocations [52]. The crystallite size is typically $\sim 2 \text{ nm}$ and the density is only 60% of polycrystalline tungsten. Thus, the amorphous-like sample indeed contains many grain boundaries that presumably trap the deuterium. Comparison of the volumetric retention of the amorphous-like layer with its density amounts to 5.4 at.%.

## 8.5 Conclusions

An experimental study is presented in which the properties of tungsten films, deposited by PLD, are analysed after high-flux deuterium plasma exposure ($T_{\text{max}} = 520 \text{ K}$). Generally speaking, all the coatings withstand the high-flux plasma interaction. Nevertheless, the thin films showed abundant formation of micrometer-sized blisters. The nanostructures that were formed on the tungsten films, were more disordered with decreasing film density.

<table>
<thead>
<tr>
<th></th>
<th>polycrystalline</th>
<th>columnar</th>
<th>nanocrystalline</th>
<th>amorphous-like</th>
</tr>
</thead>
<tbody>
<tr>
<td>density (kg m$^{-3}$)</td>
<td>$19.3 \times 10^3$</td>
<td>$\sim 18 \times 10^3$</td>
<td>$\sim 15 \times 10^3$</td>
<td>$\sim 12 \times 10^3$</td>
</tr>
<tr>
<td>crystallite size</td>
<td>$\sim \mu\text{m}$</td>
<td>15 nm</td>
<td>12 nm</td>
<td>2 nm</td>
</tr>
<tr>
<td>blisters</td>
<td>few</td>
<td>uniform</td>
<td>periphery</td>
<td>periphery</td>
</tr>
<tr>
<td></td>
<td>none burst</td>
<td>none burst</td>
<td>none burst</td>
<td>often burst</td>
</tr>
<tr>
<td>nanostructure</td>
<td>grain dependent</td>
<td>grain dependent</td>
<td>partly mixed</td>
<td>mixture</td>
</tr>
<tr>
<td>D retention</td>
<td>$8.6 \times 10^{19} \text{ m}^{-2}$</td>
<td>$9.6 \times 10^{20} \text{ m}^{-2}$</td>
<td>$1.3 \times 10^{21} \text{ m}^{-2}$</td>
<td>$2.1 \times 10^{21} \text{ m}^{-2}$</td>
</tr>
</tbody>
</table>

**Table 8.1:** Overview of the blister formation, nanostructure and deuterium retention on the different type of layers after low temperature exposure.
The retained fraction of deuterium in all thin films was found to be higher than in polycrystalline tungsten, even after pre-damaging with W$^{4+}$ ions to 0.45 dpa. Thermal desorption measurements showed that the retention properties are highly affected by the film density. A low film density led to very high deuterium retention with a low trapping energy. Variation in layer thickness of the columnar film allowed us to estimate the deuterium retention in the layer to be $7.4 \times 10^{26} \text{ m}^{-3}$.

During high temperature plasma exposure ($T_{\text{max}} = 1000 \text{ K}$) very small droplets (30 – 50 nm) were formed on all films. The amorphous-like film showed delaminated blisters at the periphery, the blisters on the nanocrystalline layers are cracked and also on the columnar films micrometer-sized cracks are observed.

Acknowledgements

This work, supported by the European Communities under the contract of Association between EURATOM/FOM, was carried out within the framework of the European Fusion Program with financial support from NWO. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

The authors would like to thank R.S. Al for the technical assistance at the Pilot-PSI measurements. M. Mayer, J. Dorner and M. Fußeder (IPP-Garching) are greatly thanked for providing the pre-irradiation damaged sample.
9 Conclusions and outlook

This thesis presents the results of deuterium retention experiments on pre-irradiation damaged tungsten exposed to high-flux (∼10^{24} \text{m}^{-2}\text{s}^{-1}) deuterium plasmas. Chapters 4 and 5 describe the effect that pre-irradiation with high energy W^{4+} ions has on the trapping of deuterium. The penetration of deuterium into the pre-irradiation damaged material under high-flux plasma exposure is described in chapter 6. Chapter 7 discusses surface modifications created during high-flux plasma exposure, and its effect on deuterium retention. In addition, the effect of pre-irradiation damage on surface modifications was studied. Finally, the deuterium retention in μm thick tungsten films with varying density and nanostructure was investigated in chapter 8.

In this chapter we gather all the results from previous chapters to discuss the progress made addressing the main research question:

*What is the effect of pre-irradiation damage on the deuterium retention in tungsten under high-flux plasma exposure?*

As the underlying motivation for this research is the applicability of tungsten in the divertor of ITER, the implications of our findings towards understanding tritium retention under neutron irradiation in the ITER divertor and suggestions for continuation in this area are described in the outlook (section 9.2).

9.1 Conclusions

9.1.1 Main results

In chapter 4 it was shown that the deuterium retention in pre-irradiated targets after high-flux plasma exposure at surface temperatures below 525 K saturates at a concentration of 1.4 at.%. This saturation occurs at a pre-irradiation damage level of 0.2 dpa. The saturation originates in the ion damaging mechanism and was not affected by the high plasma flux. At 0.2 dpa, the concentration of vacancies and interstitials is at such a high level that every newly created vacancy or interstitial automatically recombines with one already present in the material. The average saturated volume per incident MeV ion is 3 \times 10^4 \text{nm}^3. Saturation still occurs at a damage level of 0.2 dpa after plasma exposure at higher surface temperatures (above 800 K), although the absolute level of deuterium retention strongly decreased (chapter 5). This reduction is caused by the mobility of vacancies which results in their annealing and clustering (appendix 5.A). A low occupation level of the defects caused by increased deuterium mobility was found not to be relevant.

The penetration of deuterium into pre-irradiated tungsten was measured to be very low at self-biasing conditions and only a fraction of 10^{-5} – 10^{-7} of deuterium from the incoming plasma beam is retained within the material (chapter 6). To explain this low penetration, we propose a mechanism in which the deuterium atoms form a chemisorbed layer at the surface. Incoming deuterium ions (∼5 eV) therefore can not directly enter the
material, but interact instead with this deuterium surface layer. The energy is effectively transferred from incoming ions to atoms at the surface, preventing the ions to directly penetrate. Actually, an additional thermal process is needed to allow chemisorbed deuterium to enter the tungsten.

Experiments with target biasing during plasma exposure showed various type of surface modifications as discussed in chapter 7. We distinguished three types of surface modifications: blisters originating from inter-granular cavities, protrusions arising from intra-granular cavities and nanometer structure formation. The micrometer-sized blisters grow in size and quantity with exposure time. We found less formation of these blisters on pre-irradiation damaged targets. Protrusions, typically hundreds of nanometer in size, were only observed after exposure to high-flux plasmas. The driving mechanism of blisters and protrusions is therefore most probably super-saturation within the tungsten lattice that leads to cavity growth and plastic deformation of tungsten.

Finally, micrometer thick tungsten layers with different structures (density and crystallite size) were exposed to deuterium plasmas. The thin tungsten films show a considerably higher retained fraction than the bulk polycrystalline tungsten, even when compared to pre-damaged tungsten samples. In fact, the lower the density of the thin tungsten film, the higher the deuterium retention and the lower the temperatures at which desorption takes place.

9.1.2 Undamaged tungsten

In order to isolate the effect of radiation damage, we first need to understand deuterium retention in tungsten under plasma exposure only. Figure 9.1 shows the retained deuterium fraction as function of incoming plasma fluence. Here, all data discussed in this thesis without pre-damage have been grouped. The fluence represents the average incoming deuterium ions per surface area and is calculated by integration of the flux profile (equation 2.1) over the surface multiplied by the plasma exposure time and divided by the surface area. The retained fraction is defined as the deuterium stored in the sample, measured by TDS, divided by the total incoming deuterium ion fluence. Note that these samples differ in exposure conditions, such as bias, surface temperature and surface condition (as-received or mirror polished). Also, the time between plasma exposure and TDS measurement varied between two weeks and a few months. The bulk of the experiments was performed at low surface temperature, which means that the surface temperature in the centre is at maximum 560 K. The two experiments that were carried out at high surface temperature are indicated by a grey filling of the data points.

Targets exposed at low temperature and at self-biased conditions are shown by orange data points. Targets that had a rough surface (as-received) are indicated with a square and mirror polished samples with circles. The orange line is drawn to guide the eye. The slope of this line is chosen to be proportional to $\sqrt{t}$, indicating diffusion behaviour. Note that the retained fraction of all self-biased targets is very low and only $\lesssim 10^{-7}$ of the deuterium ions in the plasma beam. As self-biased samples showed no surface modifications, the deuterium appears to be retained in intrinsic defects, which are homogeneously distributed throughout the material ($10^{-4} - 10^{-6}$ atomic fraction).
9.1 Conclusions

Figure 9.1: Deuterium retained fraction of undamaged samples plotted versus the plasma fluence. Self-biased exposures are shown in orange: Ch.3 represent the samples from section 3.4.2. Ch.4 the undamaged sample from chapter 4. Ch.6 II is exposed during the measurement series of chapter 6 and Ch.5 the undamaged sample exposed to high surface temperature (chapter 5). The biased (–40 V) samples are shown in blue: Ch.3 are the samples from section 3.4.2. Ch.7 represents the undamaged samples from chapter 7. Additionally, a sample that was exposed to high temperature is shown (carried out during the measurement series of Ch.7).

The targets that were exposed at a bias of –40 V are plotted in blue. Again, a line to guide the eye is drawn to indicate diffusion scaling. Although the retained deuterium has increased with an order of magnitude with respect to the self-biased targets, it is still only a small fraction with respect to the incoming plasma beam. As discussed in chapter 7, deuterium is predominantly retained in defects created by plasma exposure induced damage, such as blisters and protrusions that originate from inter-granular and intra-granular cavities, respectively. The modifications and the trapped deuterium are present well beyond the implantation region and extend micrometers into the tungsten material.

The self-biased sample exposed at high surface temperature contains a higher retained fraction than the sample exposed at low surface temperature, mainly because more deuterium could diffuse into the tungsten. On the contrary, the biased high temperature sample retained less than the low temperature counterpart. No blister formation was found on this sample, which is in agreement with fewer traps being available for the deuterium.
9 Conclusions and outlook

9.1.3 Radiation damaged tungsten

In chapter 4 it was shown that the saturation of pre-irradiation damage is reached at 0.2 dpa. Figure 9.2 shows all targets that were pre-irradiated to a damage level of 0.2 dpa or higher. The as-received samples with rough surfaces are indicated by diamonds, while triangles represent all mirror polished samples. It must be noted, that the rough samples were pre-damaged over a smaller radius ($r_{\text{dam}} = 6 \text{ mm}$) than the plasma exposure ($r_{\text{plasma}} = 8 \text{ mm}$). For the mirror polished samples $r_{\text{dam}}$ was 9 mm.

The self-biased samples are shown in red (mirror polished) and purple (as-received). It seems that the as-received targets have somewhat higher deuterium retention. The red data points follow a $\sqrt{t}$ behaviour as described in chapter 6. Note that the TDS results are an average over the whole sample surface and therefore yield lower values than the locally retained fraction in the centre (NRA results in figure 6.3).

Pre-damaged targets were also exposed to a high-flux plasma under biased conditions. The biased targets (–40 V) are plotted in green in figure 9.2. Compared to the polished targets at unbiased conditions, a higher deuterium fraction is implanted. In this way the total retained fraction increases with about an order of magnitude. The overall retention level however, remains again low and is around $10^{-5} - 10^{-6}$.

In conclusion, the retained fraction is very low under high-flux plasma exposure.

![radiation damaged tungsten](image)

**Figure 9.2:** Deuterium retention of samples pre-irradiated to a damage level of >0.2 dpa. Ch.4 represents the samples from chapter 4. Ch.4 II are samples from a follow-up measurement series, Ch.5A is the sample from appendix 5.A. Ch.6 corresponds to the measurement series of chapter 6 and Ch.6 II to a follow-up experiment under similar conditions. The green data points represent the pre-irradiated targets exposed at –40 V.
9.2 Outlook

Direct extrapolation of figure 9.2 gives a rough estimation for the tritium retention in the ITER divertor at the end of its lifetime (i.e. after $2 \times 10^7$ s), which corresponds to a fluence of $2 \times 10^{31} \text{m}^{-2}$. Predictions for the divertor end-of-life damage level is 0.6 dpa, this is above the saturation of the pre-irradiation damage of 0.2 dpa. The worst case scenario is represented by the green line that corresponds to the retention in both pre-irradiation damaged and plasma damaged targets. The retained fraction at the fluence of $2 \times 10^{31} \text{m}^{-2}$ is only $1.1 \times 10^{-8}$, or in absolute terms $2.2 \times 10^{23} \text{m}^{-2}$. In the case that we assume that deuterium and tritium are equally distributed in the $\sim 50$ m$^2$ divertor, this corresponds to $\sim 30$ g tritium. A divertor operating at $< 560 \text{K}$ retains only 4% of the allowed tritium in-vessel inventory.

Although the results show low levels of retention, care should be taken to extrapolate these results over four orders of magnitude to the relevant regime for ITER. It is possible that other effects will occur at long exposure times. Therefore, it is important that future experiments focus on accessing the high-fluence regime. The superconducting magnet upgrade that is planned for Magnum-PSI will give the opportunity to explore this fluence region. The second note is that this work solely focusses on the deuterium retention properties of tungsten pre-damaged with high energy tungsten ions. Neither the change of mechanical properties nor secondary effects of neutron irradiation damage, such as embrittlement, swelling and transmutations are considered. These are of course relevant aspects for a working divertor. Another difference between the extrapolation and the ITER divertor is the material temperature. Most of this thesis was carried out at low temperature, i.e. $< 550 \text{K}$, while only a few experiments were performed at temperatures above the vacancy mobility of tungsten. Nevertheless, we have observed a reduced deuterium inventory as a result of the annealing of vacancies at high temperature. However, at the same time the diffusion speed increases with temperature. Therefore, it is of interest to study the effect of temperature on deuterium penetration in more detail. One could think of monitoring diffusion during plasma exposure at elevated surface temperatures, MeV ion pre-irradiations at elevated temperatures and/or interchanging the order of MeV irradiation, heating and plasma exposure.

Another interesting research line would build further on the experiments reported in chapter 8 and concerns the fundamental process of diffusion. In this thesis, we assumed for the diffusion coefficient in the TMAP7 simulations a perfect tungsten lattice. However, in the experiments we used polycrystalline materials that contain grain boundaries. Grain boundaries might act as a diffusion barrier, thereby slowing down diffusion, or act as ‘high ways’ and increase the diffusion. Nanostructured layers with varying density would provide an interesting tool to investigate the diffusion process in tungsten.

The last concern is that blister formation was found to occur beyond the implantation region. Although we believe that blister formation happens by plastic deformation, the exact mechanism is not yet known. Future studies will need to focus on the process of blister formation. One of the key mechanisms that remains unknown is the interstitial or...
mobile concentration during plasma exposure. The determination of the in-situ mobile concentration would greatly help to understand how much pressure is built up in the tungsten lattice and cavities as well as to understand how cavity growth takes place.

Our results suggest that the tritium retention in the divertor of ITER will not be problematic. Nevertheless, still many challenges exist for the use of tungsten in the divertor of ITER.
Acknowledgements

During four years of working on my PhD, I have learned so much more than just the intricacies of deuterium retention. Not just from my own work, but also from all the wonderful people whom I was lucky enough to collaborate with. To all of you: ‘Thank you!’; I have learned a lot from all the advices, the comments, our numerous discussions on both theory and experiments and your help with setting up and interpreting the diagnostics. Equally important was the welcome distraction from friends and family. I would like to thank you all!

Nevertheless, there are some I would like to mention in particular. First and foremost, I would like to thank my daily supervisor, Pedro Zeijlmans van Emmichoven. Pedro, thank you very much for your guidance over the years. I have learned so much from our inspiring discussions and greatly appreciated your apt feedback on my surely sometimes unreadable texts. During countless hours of assistance, you always helped me look through the web of details to the underlying relevant questions and to put everything in the right context. Thank you for your encouragement.

Many thanks also go to my promotor Aart Kleijn, for exploring the work from different perspectives and for all our interesting discussions. I also would like to thank Gregory De Temmerman, for sharing his vast knowledge and advice over the years and I am thankful to all the members of the committee for carefully reading the manuscript and giving me useful feedback.

I could not have carried out the experiments without the help from my colleagues in the PSI group: Richard, the Pilot-hero, who could (almost) always figure out what was wrong with Pilot and solve it. Without you, all the results shown here would simply not exist. Hennie, who always found the time in the chaos to help me with TS, whenever necessary. I acknowledge Erwin Zoethout for performing countless XPS measurements and Ronald Wolbeer for the assistance with the target preparation. A big thanks goes also to the technical staff from the workshop for being able to interpret my amazing design drawings and to make, and remake, the components I needed. When I was working on Magnum-PSI, a whole team was always available to support my experiments: John, Marc, Andries, Serge, Miranda, Hans, Alex, Paul and many more.

A special thanks goes to all my fellow PhD students and post-docs for their helpful insights and who were always willing to volunteer to be second, third, n-th safety person; Amy, Wouter, Jeroen, Graham, Oliver, Rob, Kirill, Kuba, Gijs, Irem, Niek, Tom and Sébastien. I also thank all master, bachelor and interns that joined our team over the years. And then there are Hugo, Gerard and Wim whose doors were always open for questions on the plasma processes in newly created plasmas. Also, I would like to thank our international guests, among them in particular Haiyan, Long, Tyler and of course the ‘tritium team’ Yevhen and Mirosław, for sharing their knowledge, culture and stories.

It has been a privilege to have worked with many people outside DIFFER and I am grateful that you shared your knowledge and expertise with me. Thank you, Matej Mayer, for making it possible for me to perform all the experiments at IPP Garching and Beata Tyburska-Püschel for introducing me to the accelerator and teaching me all its secrets.
Martin Balden, Armin Manhard, Stefan Elgeti, Klaus Schmid, Udo von Toussaint, Thomas Schwartz-Selinger, Vladimir Alimov, Wolfgang Jacob, Elena Markina and the rest of the team, for all the interesting discussions that sparked new ideas which kept me awake on the long train trip back from München. A special thanks goes to Joachim Doerner and Michael Fußeder for their extensive technical assistance on the accelerator, which sometimes even included a Bayern breakfast. Across the Alps, also a warm thanks to Matteo Passoni and David Dellasega for our collaboration on pulsed lased deposited tungsten and the constructive work that we performed together.

There was never a dull moment at DIFFER thanks to many. First of all, I want to thank my roomy Wolf, for four years we have shared the office and enjoyed all the good (papers accepted), the bad (papers rejected) and the ugly (last-minute \LaTeX hacking). Your early presence in the office with a waiting coffee helped me more than you can imagine. You were always there to listen, discuss and laugh, so that I enjoyed every day at work, and it is because of you that I kept on joining the football team.

My time at DIFFER has been most enjoyable due to all the wonderful personalities at the laboratory and department. The many interesting conversations at the coffee machine and lunch table with all those mentioned above, but also Jonathan, Gieljan, Vivi and many others, created the great atmosphere which makes DIFFER such a special place.

I would like to thank my cabaret team (Britta, José, Joost, Oli, Noud and Frits) for our memorable performance and all the fun we had during the preparation evenings; the OVR (Miranda, Bob, Frits, Bram, Sander and Marc) for the many lively activities that we organised; the soccer team (Anton, Toon, Dick, Frank, Hans, Kirill, Wolf, Erik, Sébastien, Teo, Wei, Sebastiaan, Gijs and many other old-players: Joeri, Jonathan, Rolf, Robin, Oscar and more) to help me to keep my mind ánd body fit; and finally of course, the ORD (Arian, Gerben, Frank, Ben, Han and Hennie) from whom I have learned an incredible amount of meeting skills and insights that will definitely be useful in the future.

Participating in the ‘Dance your PhD’ contest gave me the unique opportunity to combine my greatest passion with my research. I would like to thank the beautiful dancers (Mariska, Margot, Marloes, Fineke and also Esther) for daring to dance around and on top of Magnum-PSI. The credits also go to Bram Lamers and Gijs ’t Hoen for arranging the filming and lighting on a level that could compete against any professional video. Many thanks also to Gieljan and Irene for sharing ideas and for their overall assistance during the film weekend.

Many things have changed in these four years, but one thing has always stayed the same; the Tuesday-dinners with my physics friends from university, or ‘supermerden’ in short. Merel, Erik, Nici, Sanne, Roel and Minne, thank you for always being there and for all the fun and culinary dinner parties we have had together and for those which are surely still to come.

Last, but most importantly, I would like to thank Thijs, without whom I wouldn’t have been able to finish. I just started this PhD, when I met you in the ‘world capital’ city of Lunteren. Who could have know that you would be proofreading my thesis four years later, after travelling thousands of kilometers between Utrecht and Oxford. I am sure we will travel a lot more kilometers together. Thank you for your endless support, home-made bread and everything else!
Bibliography


