



Probing Damage in Fusion Reactor Materials using Laser-Induced Transient Gratings

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Declaration

I declare that this thesis is entirely my own work, and except where otherwise stated,
describes my own research.

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Abstract

Tungsten is the material of choice for plasma facing components in future fusion reactors. During operation, these components receive extreme heat and radiation loads. The radiation and ion infusion from the plasma modify the tungsten lattice, altering its material properties such as the thermal diffusivity. Ion-implantation is a useful proxy for studying neutron irradiation and plasma exposure. However, it gives a thin damaged layer that is difficult to probe using conventional thermal transport measurement techniques.

Transient grating spectroscopy (TGS) is a novel tool for measuring the thermal diffusivity and surface acoustic wave (SAW) speed in thin ion-implanted layers. We present new developments of the TGS technique that enable the measurement of large area 2D maps of thermal diffusivity and SAW speed with targeted measurements and accommodating samples with increased roughness. These capabilities are demonstrated by recording large TGS maps of deuterium implanted tungsten, linear friction welded aerospace alloys and high entropy alloys. The results illustrate the ability to view grain microstructure in elastically anisotropic samples, and to detect anomalies, for example due to irradiation and previous measurements. They also point to the possibility of using TGS to quantify grain size at the surface of polycrystalline materials.

The thermal diffusivity and SAW speed in tungsten exposed to different fluences of deuterium plasma is studied. Scanning electron microscopy (SEM) shows the formation of surface blisters that have similar morphology for all fluences considered. A significant reduction in thermal diffusivity and SAW speed occurs as a result of plasma exposure. A saturation of the thermal diffusivity reduction with fluence is seen. Deuterium ion flux density appears to play a more important role in thermal diffusivity reduction than total fluence.

TGS is used to study the thermal diffusivity of tungsten exposed to different levels of 20 MeV self-ion irradiation. Damage as low as 3.2×10^{-4} displacements per atom (dpa) causes a measurable reduction in thermal diffusivity. Doses of 0.1 dpa and above, up to 10 dpa, give a degradation of ~55% from the pristine value at room temperature. Using a kinetic theory model, the density of irradiation-induced point defects is estimated based on the measured changes in thermal diffusivity as a function of dose. These predictions are compared with point defect and dislocation loop densities observed in transmission electron microscopy (TEM). Molecular dynamics (MD) predictions are combined with the TEM observations to estimate the density of point defects associated with defect clusters too small to be probed by TEM. When these “invisible” defects are accounted for, the total point defect density agrees well with that estimated from TGS for a range of doses spanning 3 orders of magnitude. Kinetic theory modelling is also used to estimate the thermal diffusivity degradation expected due to TEM-visible and invisible defects. Finely distributed invisible defects appear to play a much more important role in the thermal diffusivity reduction than larger TEM-visible dislocation loops. This work demonstrates the capability of TGS, in conjunction with kinetic theory models, to provide rapid, quantitative insight into defect densities and property evolution in irradiated materials.

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Glossary of Abbreviations

APD	Avalanche Photodiode
BCC	Body Centred Cubic
BDTT	Brittle to Ductile Transition Temperature
CFC	Carbon Fibre Composites
DPA	Displacement per Atom
EBS	Electron Backscatter Diffraction
EDX	Energy-dispersive X-ray spectroscopy
FCC	Face Centred Cubic
HCP	Hexagonally Close-packed
HEA	High Entropy Alloy
ITER	International Thermonuclear Experimental Reactor
KMC	Kinetic Monte-Carlo
KT	Kinetic Theory
MD	Molecular Dynamics
ND	Neutral Density
NRA	Nuclear Reaction Analysis
NRT	Norgett-Robinson-Torres
PALS	Positron Annihilation Lifetime Spectroscopy
PBS	Polarising Beam Splitter
PKA	Primary Knock-on Atom
SAW	Surface Acoustic Wave
SEM	Scanning Electron Microscopy
SIA	Self-interstitial Atom
SNR	Signal-to-noise ratio
TDTR	Time-domain Thermorefectance
TEM	Transmission Electron Microscopy
TGS	Transient Grating Spectroscopy
UHP	Ultra High Purity
ZBL	Ziegler-Biersack-Littmark

Contents

1.	Introduction.....	1
2.	Survey of Literature	7
2.1	Fusion irradiation damage.....	8
2.1.1	Displacement Damage	9
2.1.2	Hydrogen and Helium Effects	18
2.1.3	Transmutation	24
2.2	Irradiation and exposure induced material property changes.....	27
2.2.1	Hardening.....	27
2.2.2	Brittle to Ductile Transition	35
2.2.3	Swelling	37
2.2.4	Thermal Conductivity	40
2.3	Crystal defect density measurement and prediction techniques.....	50
2.3.1	Transmission Electron Microscopy	50
2.3.2	Molecular Dynamics Simulations.....	53
2.3.3	Electrical Resistivity Measurements.....	55
2.3.4	Positron Annihilation Lifetime Spectroscopy (PALS)	56
2.3.5	Lattice Swelling	56
2.4	Thermal conductivity measurement techniques	58
2.4.1	The Laser Flash Method	59

2.4.2	Time Domain Thermo-reflectance.....	60
2.4.3	The 3-omega method	62
2.4.4	Transient Grating Spectroscopy.....	63
2.5	Summary of the Literature Review	72
2.6	Research Goals.....	74
3.	Non-contact and non-destructive mapping of thermal diffusivity and surface acoustic wave speed using transient grating spectroscopy	76
3.1	Abstract	76
3.2	Introduction	77
3.3	The Transient Grating Spectroscopy Setup.....	79
3.3.1	Beam Generation	82
3.3.2	Sample Environment.....	84
3.3.3	Targeted Measurements	85
3.3.4	Detection	85
3.3.5	Validation Experiments	86
3.3.6	Modification for samples with uneven surfaces	89
3.4	Results and Discussion.....	91
3.4.1	Deuterium Exposed Tungsten.....	91
3.4.2	Linear friction welded Ti6Al4V	93
3.4.3	Implanted High Entropy Alloy	96
3.4.4	As Cast Equiatomic TiZrHf Alloy	99

4. Transient grating spectroscopy of thermal diffusivity degradation in deuterium implanted tungsten.....	101
4.1 Abstract	101
4.2 Introduction	102
4.3 Materials and Methods	104
4.3.1 Transient Grating Spectroscopy.....	104
4.3.2 Sample Preparation and Plasma Exposure.....	106
4.4 Results and Discussion.....	109
4.4.1 Exposure and Impurity Characterisation	109
4.4.2 Blister Characterisation (SEM).....	111
4.4.3 Transient Grating Spectroscopy.....	113
4.5 Discussion	118
5. Thermal diffusivity degradation and point defect density prediction in self-ion implanted tungsten.....	121
5.1 Abstract	121
5.2 Introduction	122
5.3 Materials and Methods	125
5.3.1 Sample Preparation and Implantation.....	125
5.3.2 Thermal diffusivity measurements	128
5.4 Results and Discussion.....	131
5.4.1 Thermal Diffusivity degradation with dose	131
5.4.2 Inferring defect populations from TGS measurements.....	136

5.4.3	Comparison of defect densities estimated from TGS with transmission electron microscopy and molecular dynamics simulation data	141
6.	Conclusions and Future Work	149
6.1	Conclusions.....	149
6.2	Future Work	153
7.	References.....	154

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1. Introduction

Fusion energy is a promising solution to the world's energy problems [1]. However fusion reactors will create harsh environments that have a significant impact on the materials that they are made of [2–4]. Understanding the performance and evolution of materials under these conditions, especially the degradation of their physical properties, is of utmost importance for the design of future fusion reactors [5]. Shedding light on these irradiation-induced changes in material properties is also of high value to the fission reactor materials arena, since the mechanisms are relatively similar. Most of the current understanding of irradiation-induced degradation in material properties originates from swathes of empirical studies from specimens irradiated at various test and power reactors over the past half-century [5,6]. The co-existence of high temperatures, energetic neutrons, He-ions, and other ion species within the reactor core, and their complex interactions with reactor materials make it challenging to fully understand the resulting evolution of the material's performance. This is the main reason for using empirical methods.

The tungsten first wall and divertor components in a fusion reactor will experience the highest heat fluxes ($\sim 10 \text{ MW/m}^2$ steady state and $\sim 20 \text{ MW/m}^2$ for slow transients) [7]. Fig. 1.1 (a) shows the basic layout of the ITER tokamak and 1.1 (b) depicts the materials chosen for the plasma facing components in the divertor. Pristine tungsten under cooling conditions similar to those anticipated in the reactor melts at 27 MW/m^2 [4]. Fig. 1.2, reproduced from [8] shows the evolution of the tungsten and carbon fibre composite components with increasing heat flux, relevant to normal operation and transients in an ITER tokamak. Fig. 1.3, shows the melting behaviour predicted at higher heat fluxes by [8–10] in mock-up components heated by electron beams in [4]. The ability of the tungsten components to dissipate heat by conducting it to the coolant channels at the rear, is crucial for the smooth and efficient running of the reactor. However, these tungsten divertor components also experience the highest radiation fluxes. In

this study we focus on addressing the degradation in the thermal conductivity of tungsten and other reactor relevant materials.

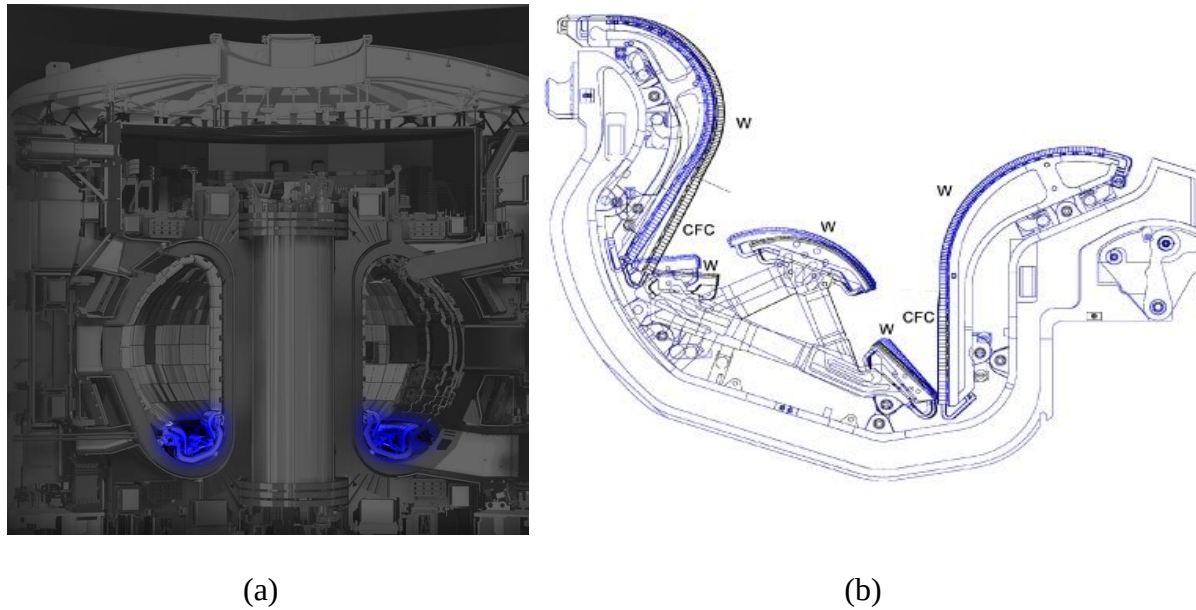


Figure 1.1. Layout of the ITER tokamak with the divertor in blue (a), reproduced from [11] and (b) layout of the divertor with the plasma facing materials tungsten (W) and carbon-fibre composites (CFC), obtained from [8,12].

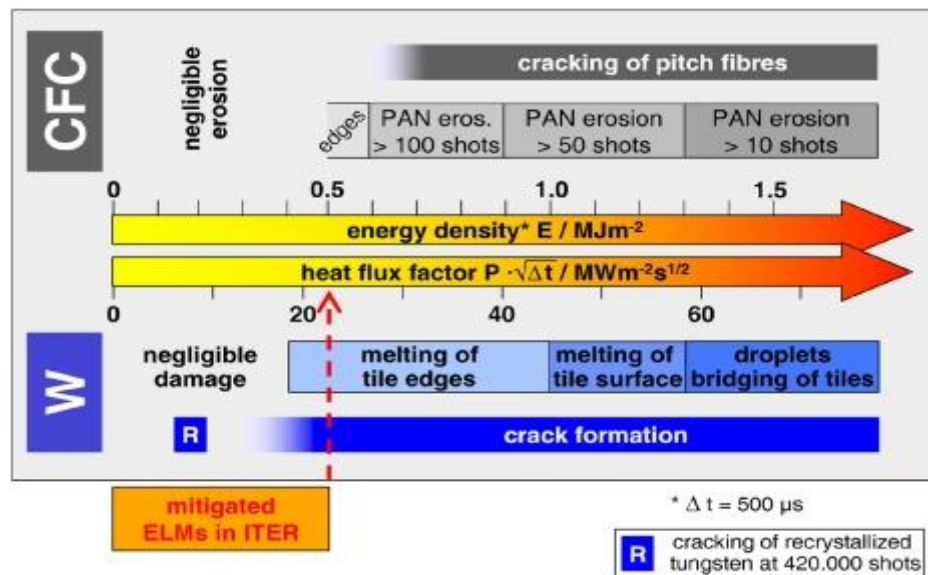


Figure 1.2. Damage evolution as a function of heat flux in the carbon fibre composite and tungsten divertor targets from transients. Figure reproduced from [8].

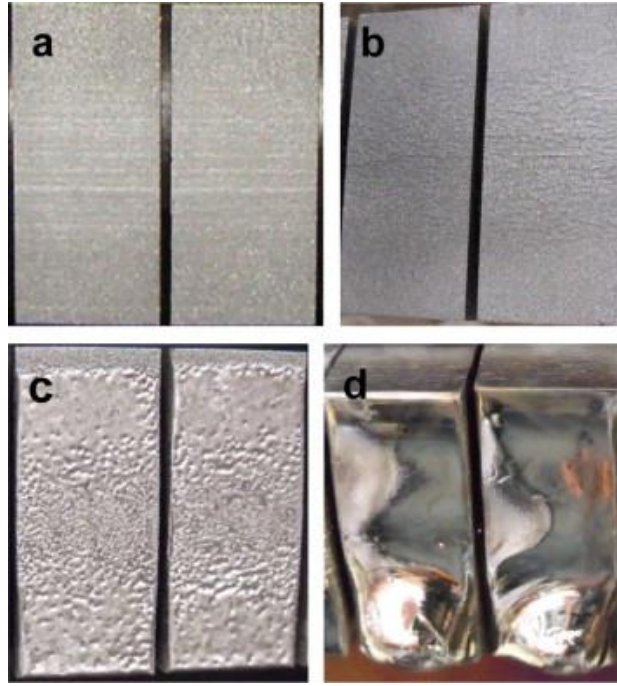


Figure 1.3. Pristine tungsten surface prior to a critical heat flux test (a), after testing to 27 MW/m² (b), 30 MW/m² (c) and >30 MW/m² (d). Figure reproduced from [4]

Tungsten is the front runner material for the fusion reactor divertor, due to its high thermal conductivity and strength at high temperatures [7]. During operation, tungsten armour components will be exposed to the plasma which causes the infusion of a host of ion species, primarily deuterium and helium into the tungsten matrix. Armour components will also be exposed to intense bombardment with high energy (14.1 MeV) fusion neutrons. These neutrons pose a double threat. They can displace atoms within the matrix, called primary knock-on atoms (PKA's), that go on to displace more atoms, creating cascades of displacement damage [13]. In addition, neutron irradiation also causes the transmutation of the tungsten atoms into other elements, such as rhenium, osmium and tantalum, and also produces helium and hydrogen as by-products, that all reduce the purity of the material [14,15]. This effect is called transmutation alloying.

Above room temperature, electron-mediated thermal conduction accounts for ~90% of the thermal conductivity in tungsten, similar to other metals [16]. Gaseous ions like helium and deuterium can self-trap in the tungsten matrix, agglomerating to form bubbles. These bubbles

can act as additional scattering centres for electrons, decreasing the thermal diffusivity [17,18]. The transmutation products effectively convert the pure tungsten matrix into an alloy with varying amounts of rhenium, tantalum and osmium [19], that significantly increase the electron scattering rates and hence decrease thermal diffusivity. The energetic PKA's can displace lattice atoms creating point defects such as interstitials i.e. the displaced atom, vacancies i.e. the vacant lattice site left behind. This damage can interact and evolve, giving a range of crystal lattice defects from point defects to large dislocation loops [13,20–22]. Fig. 1.4, from [5], shows the formation of vacancies and interstitials in a crystal lattice upon the incidence of an energetic projectile, for example a fusion neutron or implantation ions. These defects increase electron scattering rates, thereby further reducing thermal diffusivity [14,23–25].

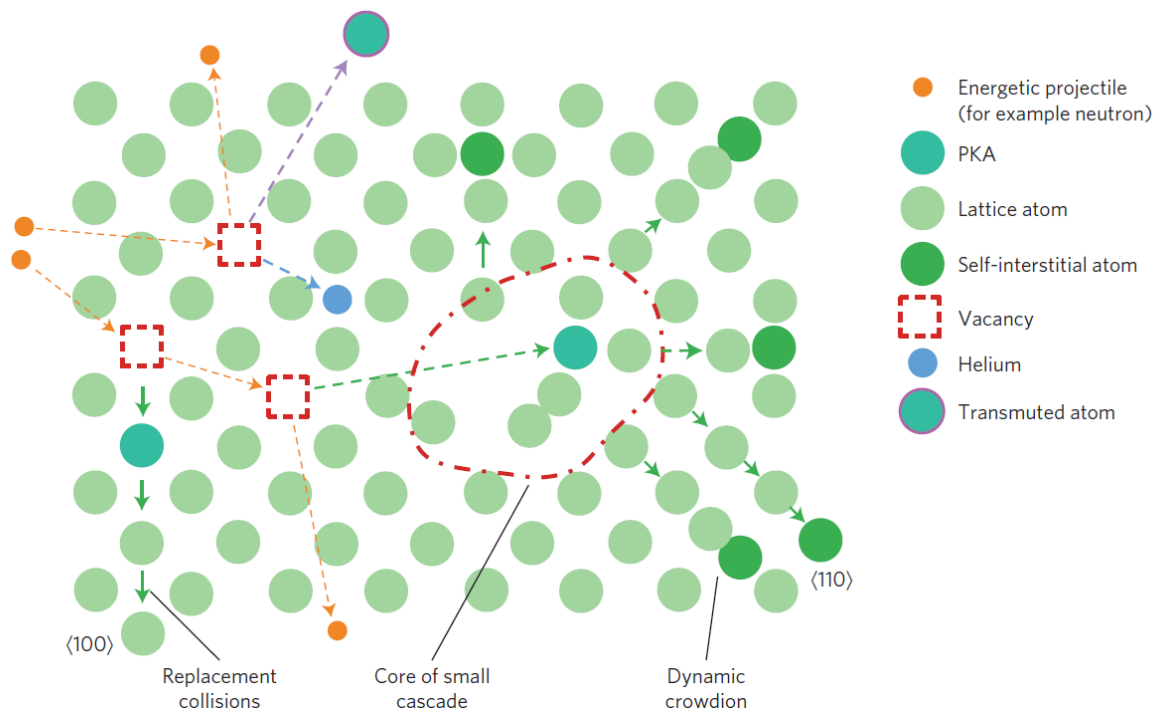


Figure 1.4. The creation of primary displacement damage from an incident energetic projectile [5].

Due to the complexity introduced by the multiple irradiation-induced phenomena, and the hazards associated with neutron-irradiated samples, the use of alternative approaches to explore each effect in isolation is attractive. Self-ion implantation can be used to mimic the

displacement damage created by neutrons [23,26]. Deuterium and helium ion implantation may be used to study the infusion of the respective ions into the matrix [17,24,27]. Finally, alloying provides an effective means of mimicking the effects of transmutation [14,15]. In this study we focus on the thermal diffusivity degradation of tungsten due to self-ion implantation and deuterium ion exposure. There however exists a drawback in using implanted samples. Implantation only produces a few-micron-thick damaged layer [28], in comparison to the bulk irradiation possible by neutrons. This makes it difficult to study ion-irradiation-induced changes using traditional techniques that are optimised for bulk measurements. Transient grating spectroscopy (TGS), is a novel technique that allows the probing of thermal diffusivity and surface acoustic wave (SAW) speed in micron-thick layers with high accuracy [29–32]. As such, in this study, TGS is used to gain an insight into the thermal diffusivity degradation due to exposure to reactor and reactor-like conditions. The TGS method is also developed further as part of this study.

A review of relevant literature and the core TGS theory is presented in chapter 2. Chapters 3-5 present the key studies carried out as part of the PhD. To date three papers have been published in the project [18,33,34]:

Paper 1 focuses on the new developments that were made to optimise the TGS method. I have developed a new TGS instrument that is more robust to misalignment, capable of handling samples with increased surface roughness, and capable of conducting targeted measurements. These capabilities are demonstrated by creating one-of-a-kind large area TGS maps of thermal diffusivity and SAW speed in key engineering materials such as deuterium implanted tungsten, implanted high entropy alloys, linear friction welded aerospace alloys, and as-cast high entropy alloys.

Paper 2 investigates the effect of deuterium ion exposure on the thermal diffusivity of pristine annealed tungsten. The effects of deuterium plasma flux density, exposure time and exposure temperature are investigated using TGS. The surface modifications (blisters) are studied using scanning electron microscopy and the impurities are characterised using energy-dispersive x-ray spectroscopy (EDX).

Paper 3 concentrates on the effect of self-ion implantation on the thermal diffusivity of tungsten. Self-ion implantation is used to mimic the displacement damage created by high energy neutrons in a reactor environment. TGS is used to measure the implantation-induced degradation of thermal diffusivity. This measured degradation, due to the high measurement accuracy, can be used with a simple kinetic theory model for electron scattering to predict the implantation-induced defect density. These predictions are compared to transmission electron microscopy (TEM) and molecular dynamics simulation (MD) predictions of defect densities. The surprising conclusion is that very small defects, below the TEM resolution limit, appear to have a rather large effect on thermal diffusivity degradation.

Each chapter includes a discussion of the relevant observations. The conclusions from this thesis are in chapter 6. They bring together the important takeaways from each chapter and present them in the context of the advances made to thermal diffusivity and defect characterisation methods, and the understanding of radiation induced defects and performance changes.

2. Survey of Literature

This chapter provides an overview of literature on irradiation damage and its effect on the structure and key physical properties of tungsten, focusing on the mechanical and thermal properties. Fig. 2.1 briefly details the irradiation effects and resulting property changes considered in this review. In this chapter we also look at common thermal conductivity measurement techniques (section 2.4), focusing on those used for measuring irradiated samples. Since in our work we also use TGS thermal diffusivity measurements to make defect density predictions, the common methods used for quantifying crystal defects are sampled in section 2.3. These include direct methods and indirect methods such as modelling to predict irradiation damage.

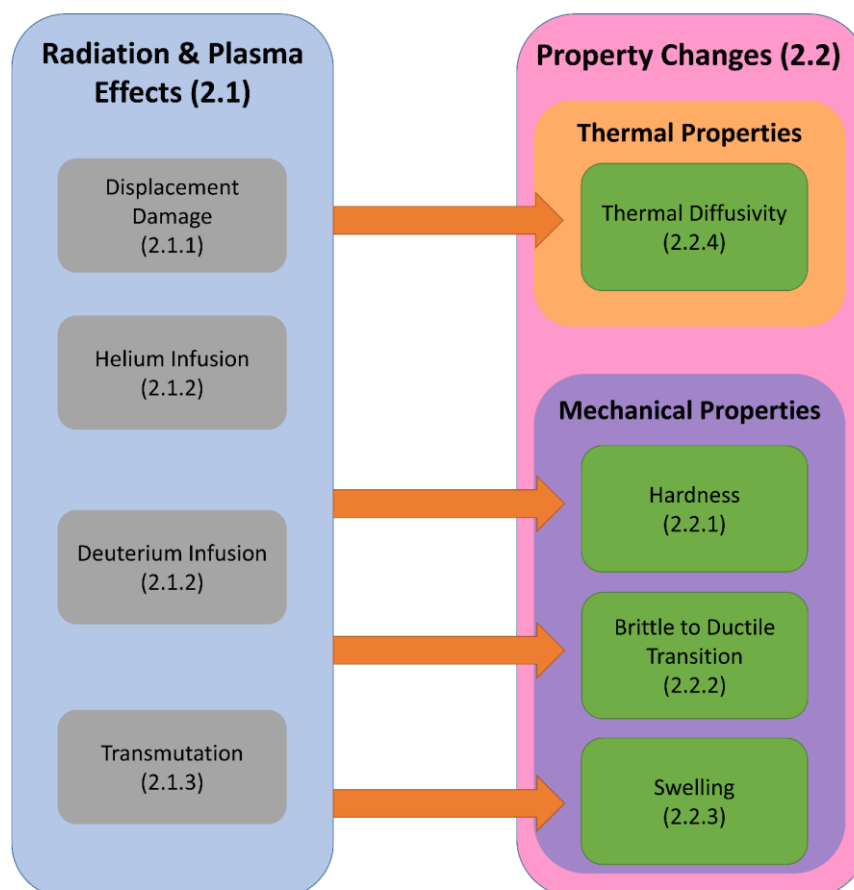


Figure 2.1 Radiation and plasma effects experienced by plasma facing tungsten in a fusion reactor and the resulting key property changes, as considered in this review.

2.1 Fusion irradiation damage

This section briefly covers the basic irradiation damage mechanisms in plasma facing components in fusion reactors, and their effects on the structure of the material.

Only 5% of all matter in the observable universe is recognisable with current technology. The remaining 95 % is ‘dark’. Most of this observable 5% is “empty space”, i.e. the space between and within the atoms that make up the solids, liquids, gases and plasma in our universe [35]. In solids, just the sub-atomic configuration of the atom decides its nuclear properties [36]. The arrangement and behaviour of the electrons orbiting it needs to be considered for its chemical properties. In metals, the nature of the atoms, their arrangement, the level of order/disorder, and changes in the “empty space” between them, dictate the macroscopically-observable material properties. A perfect lowest energy arrangement (lattice) is ideal for properties such as thermal conductivity and ductility, whereas a disordered lattice can contribute favourably towards properties such as hardness [14,37]. Depending on the application, an ordered or disordered lattice is preferred.

The metallic lattice of tungsten, when exposed to fusion neutrons and gaseous ions such as helium and deuterium from the plasma, can undergo a change in its nuclear, electronic and material properties [38]. Tungsten atoms can capture neutrons and transform into transmutation products such as rhenium, osmium and tantalum [19,39–42]. Helium infused from the plasma decreases the homogeneity of the lattice and can also interact with lattice defects [5,27,43,44]. Deuterium infused can behave in a similar manner as well as form larger bubbles within the lattice [45–47]. The highly energetic neutrons can also collide with tungsten lattice atoms, altering their arrangement [13,48,49], to name a few of the effects that a fusion environment can have on the material. The change in the structure originates at the nano length scale and femto timescale and can then evolve to the macro level of meters and years [5]. Fig. 2.2 from

[5] summarises key defect processes that affect the structure and their evolution over time and length scales. These microstructural changes then modify the material properties.

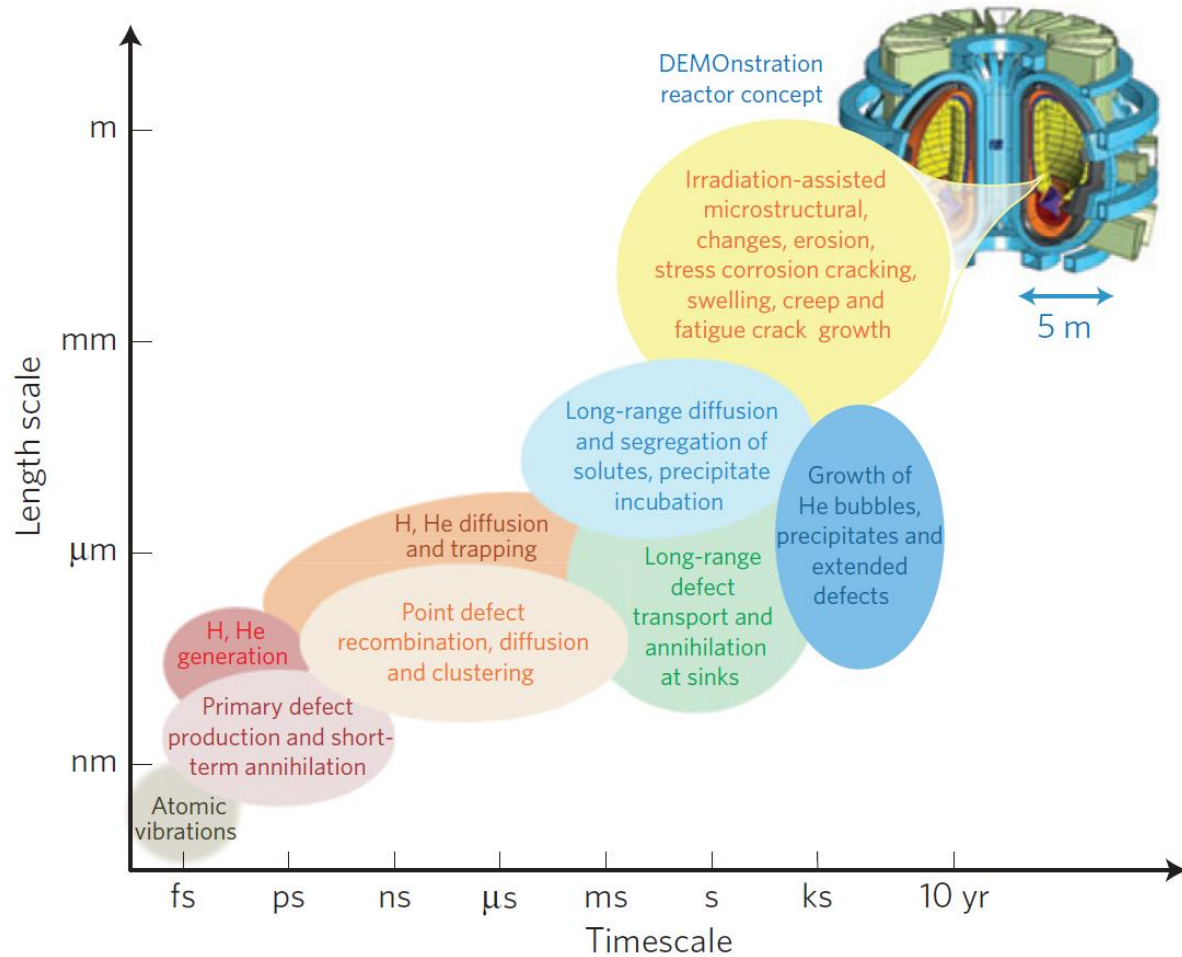


Figure 2.2 Key defect processes and their resulting microstructural changes in plasma facing materials classified by time and length scales. Figure obtained from [5].

In the following subsections, the three key defect mechanisms experienced by the plasma facing tungsten in nuclear fusion reactors are considered in detail.

2.1.1 Displacement Damage

A pristine block of tungsten for use in a fusion reactor would have its atoms arranged in an orderly manner with a small amount of disorder that depends on its temperature and forming methods. The tungsten lattice assumes the body-centred cubic (bcc) crystal structure at room-temperature and up to its melting point of $\sim 3400^\circ\text{C}$. Highly energetic neutrons from fusion

reactions can then impart significant energy to an atom in the lattice, for it to shoot off and collide with neighbouring atoms, displacing them too. An atom displaced from its lattice site is called a self-interstitial atom (SIA) or an ‘interstitial’ and the empty site it leaves behind is called a vacancy (V). The initial atom to be displaced is called the primary knock-on atom (PKA). Fig. 2.3 illustrates this mechanism [5].

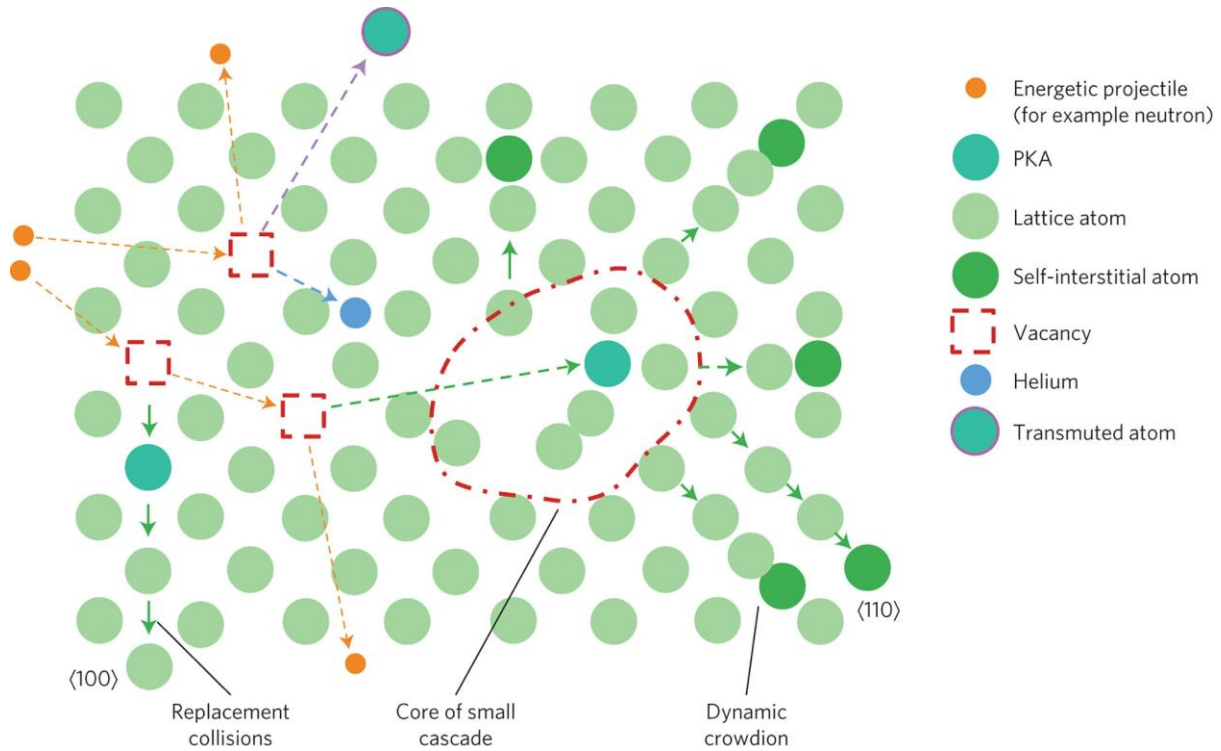


Figure 2.3 Schematic illustration of irradiation damage, obtained from [5].

Typically an incident fusion neutron will leave behind several PKA-initiated cascades, each containing hundreds of Frenkel Pairs [50], which last less than a picosecond as seen in the molecular dynamics (MD) simulations in Fig 2.4 [51]. These hot displaced atoms, eventually cool down and mostly return to perfect lattice sites. Hence this is called a ‘thermal spike’, i.e. the thermal spike phase. This is followed by the quenching phase, which last ~ 10 -50 ps where point defects and clusters may form [13]. This is followed by an annealing phase ($> \text{ns}$), where interaction of defects can take place [21,52], as well as their diffusion away from the cascade [53].

Fig 2.4 shows that eventually the displacement damage left is significantly less than that initially created by the cascade. This is also less than the predicted displacements per atom (dpa) damage, predicted by widely used linear collision cascade models such as the Norgett Torrens Robinson (NRT), or Kinchin-Pease (KP) models [54,55]. Interestingly these formulations specify the damage as ‘displacements’ per atom, which is not incorrect, as in MD simulations, similar levels of displaced atoms are observed, as in Fig 2.4. However most of these SIA’s and vacancies recombine. Hence the number density of interstitials and vacancies contributing to the material property change is much lower, and not predicted by these models.

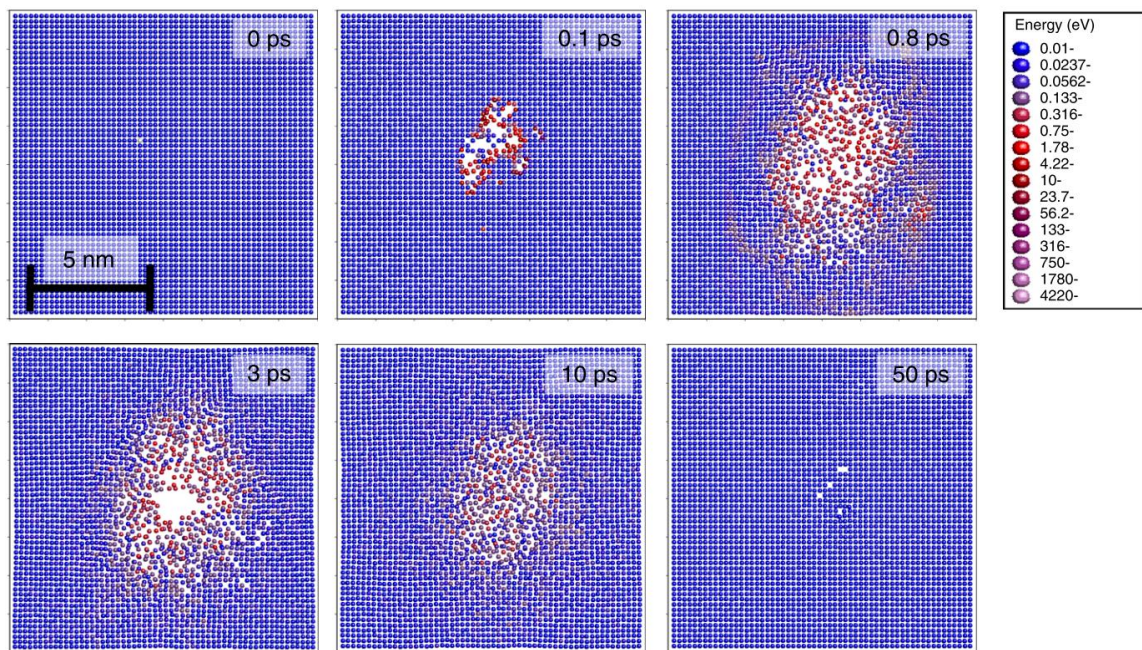


Figure 2.4 Cross-sectional view of a collision cascade in Au from a 10 keV PKA obtained from molecular dynamics simulations [51]. Individual atoms are represented by the dots, with the colour indicating atom temperature/energy.

The proportion of damage retained compared to the NRT-predicted damage is of key interest and called ‘NRT efficiency’[51,56]. MD simulations predict the NRT efficiency in metals such as Ni, Pd, Pt and W to be ~0.2-0.3 actual Frenkel pairs remaining per initially displaced atom. This is discussed further in section 5.4.2, with the TGS predicted NRT efficiency.

Quantifying these ‘true’ defect densities has always been a challenge, with various methods from transmission electron microscopy (TEM) imaging, to positron annihilation lifetime spectroscopy (PALS), lattice-swelling studies, etc... that are briefly covered in section 2.3. Paper 3 of this study introduces TGS as a new method for quantifying these ‘true’ defect densities. Due to the challenges associated with these methods, the traditional displacement per atom (dpa) parameter continues to be used as an estimate for the damage level in the material. MD studies show that the size distribution of the displacement damage created by an energetic PKA follows a power law, as seen in Fig. 2.5. More small defect clusters are formed than large defect clusters. The size of the largest defect clusters formed also increases with increasing PKA energy [57]. However, studies have also shown that for implantation at PKA energies higher than a threshold (~ 160 keV for tungsten), cascade splitting occurs and subcascades form [58]. Hence, a cascade initiated by a 2 MeV PKA will continue to split up, eventually having a defect size distribution similar to that of a 150 keV PKA. This cascade splitting effect sets an upper bound on the size of defects encountered. In tungsten, this upper bound is ~ 10 nm [59].

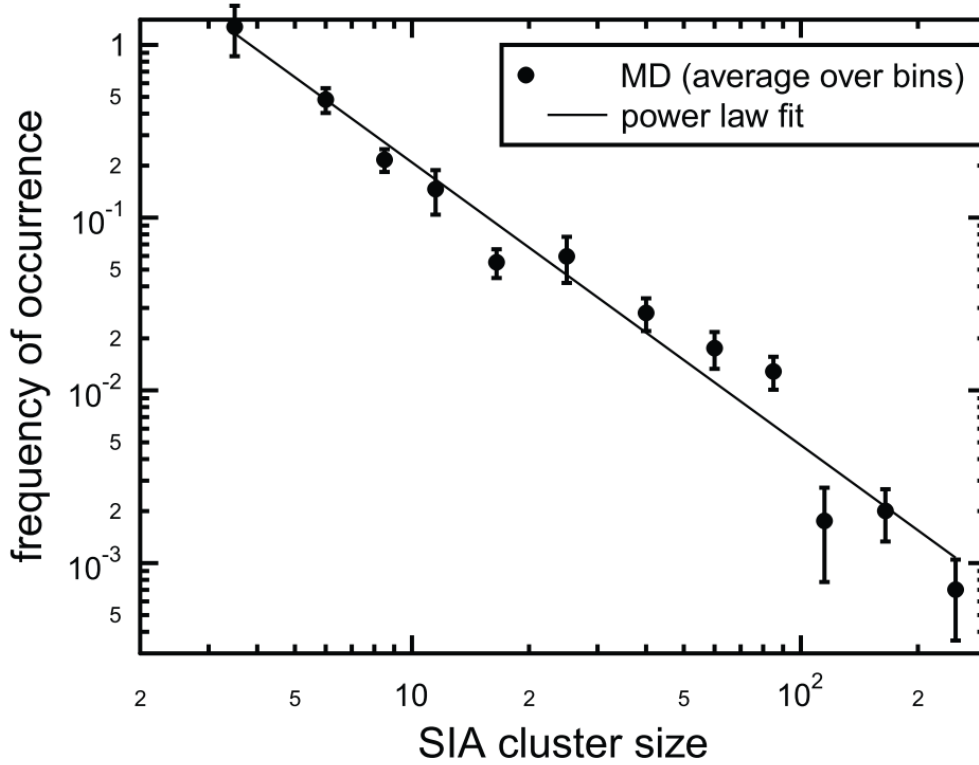


Figure 2.5 Size distribution of SIA clusters from simulations of 150 keV tungsten self-ion cascades. Figure obtained from [60].

MD simulations have also been used to study the effects of overlapping cascade damage [20]. In reactor environments and in the experimental work emulating such environments, the tungsten material receives fairly high doses of irradiation damage [2,38]. Hence simulating PKA's into perfect lattices will not accurately predict the damage created. MD studies on pre-damaged lattices have shown the formation of larger clusters in Fe for such cases whereas in W, this effect is not seen. However, defect morphologies were seen to change, with the formation of complex dislocation networks and structures, rather than the usual population of dislocation loops [20]. Overall, MD simulations have provided a comprehensive understanding of the defect generation processes and resulting primary damage created for low and medium damage doses.

The primary damage can interact with pre-existing dislocations, grain boundaries and free surfaces. Such events can occur during the cascade annealing stage which has a duration on the

order of a few nanoseconds or greater. Kinetic Monte-Carlo (KMC) studies are used to analyse these effects, since it is beyond the timescales that can be simulated using MD [61–63]. The defect emission, interaction, migration, transformation and interaction phenomena that take place are quite extensive and beyond the scope of this review and are available elsewhere [21,52,64,65]. Subsequent to this evolutionary stage of the defects, the remaining defect population consists of a mixture of voids, interstitial and vacancy loops, point defects, and smaller clusters, each to various amounts, depending on the irradiation conditions such as temperature and damage level [66,67].

TEM studies have proven to be quite useful in providing an understanding of the medium and large-scale displacement damage in tungsten. Fig. 2.6 from [67] and references therein shows the different types of damage left for irradiations at different temperatures and doses, observed using TEM. It can be seen that up to ~ 500 °C, the displacement damage imaged by TEM is mainly in the form of dislocation loops. Above temperatures of ~ 500 °C, at low and medium doses (< 1 dpa), void formation occurs in addition to the loops. This is due to the fact that vacancies are mobile at elevated temperatures which then migrate and coalesce to form voids. At higher doses and high temperatures, in neutron irradiated tungsten, the transmutation products can create precipitates [39,68].

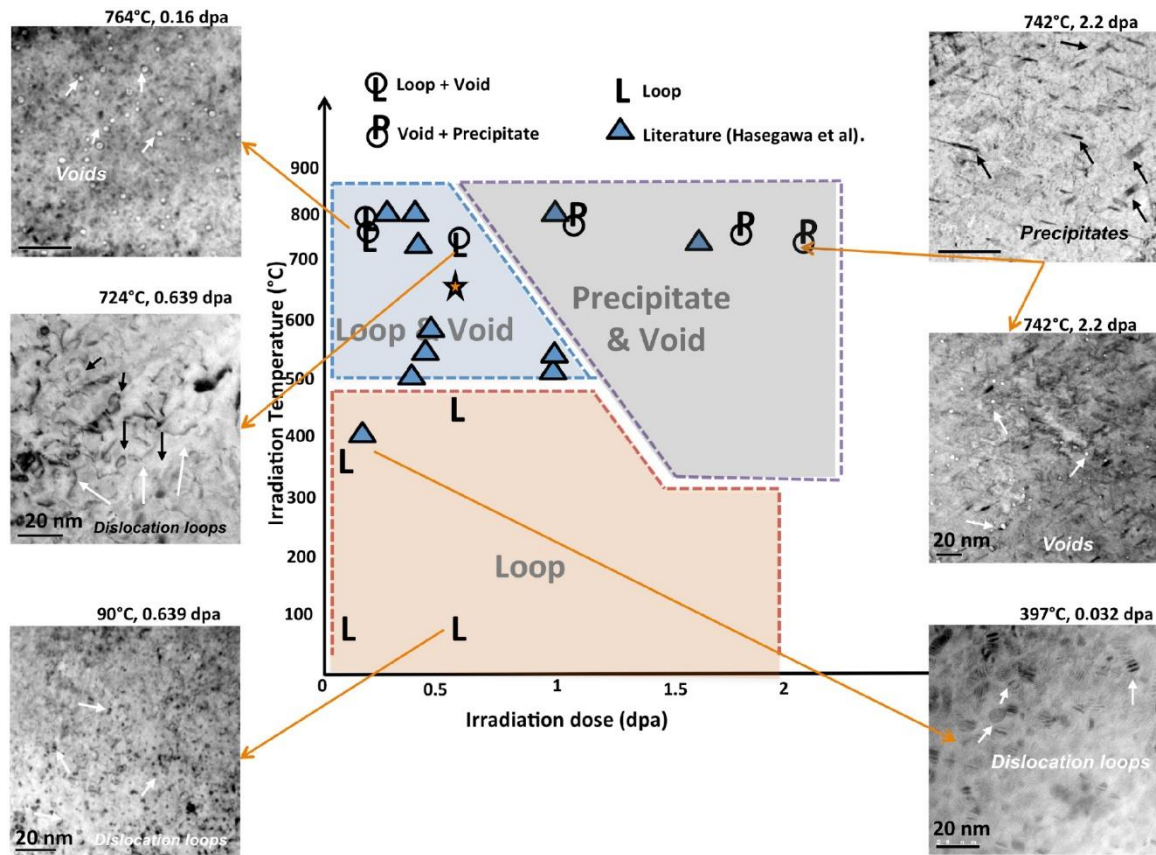


Figure 2.6 Irradiation phase diagram for neutron irradiated tungsten from [67].

Fig. 2.7 shows the defect distributions in tungsten, implanted with 20 MeV self-ions at room temperature [69]. The defect population seems to be dominated by loops, in agreement with the observations in Fig 2.6 from [67]. Since the implantations have been carried out at room temperature, thermal diffusion and growth of defects is not prominent. Hence evenly distributed dislocation loops are the prominent form of displacement damage visible in the TEM images.

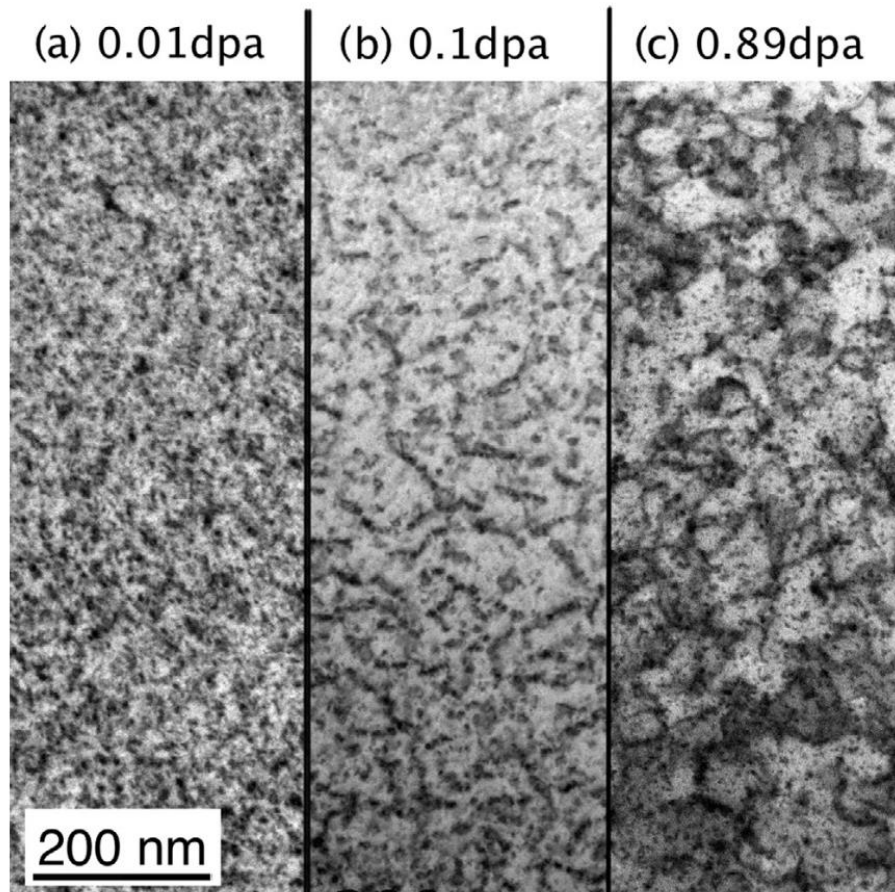


Figure 2.7 TEM images of defect distributions in damaged zones of 20 MeV self-ion implanted tungsten. Implantation temperature was at RT. Figure obtained from [69].

At the low damage level of 0.01 dpa, it can be seen that damage consists predominantly of finely distributed small loops. At the moderate dose level of 0.1 dpa, coarsening and entangling of the defects occur as predicted by MD simulations [20]. At the higher dose level of 0.89 dpa, significant overlap of defects occur, along with entangling of the loops, in agreement with MD predictions.

With increasing dose, the displacement damage is expected to increase. However it is expected that there will exist an equilibrium concentration of displacement damage after which there would be a saturation in the defect density with increasing dose. Fig. 2.8 from the TEM study in [21] shows that around a dose of 1 dpa, this saturation seems to occur.

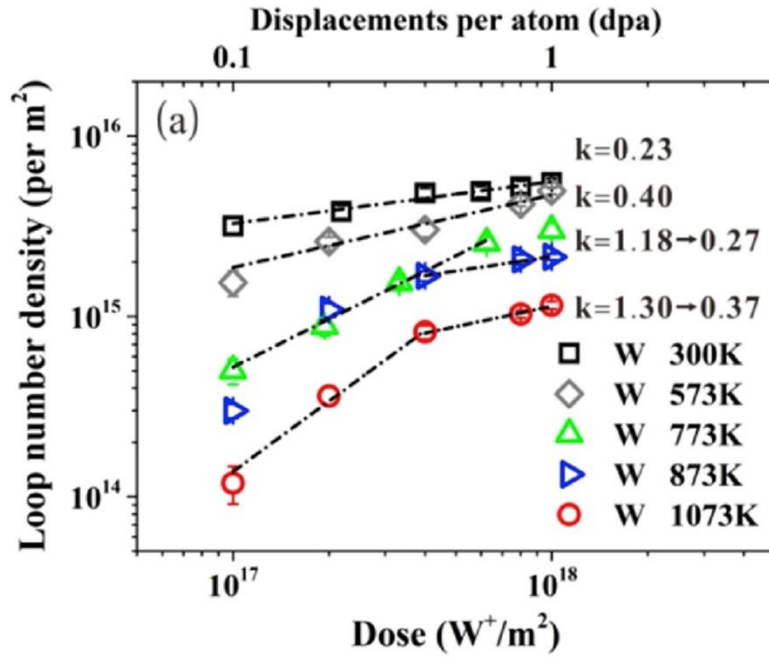


Figure 2.8 The evolution of defect population as a function of dose and temperature for self-ion implanted tungsten. The data in this figure is from in-situ TEM. Figure obtained from [21].

It should be noted that obtaining such quantitative data from TEM is quite labour intensive and this is one of the few, if not the only TEM study to cover self-ion implanted tungsten over a wide range of doses and temperatures. Also seen in Fig. 2.8 is the reduction in the defect densities at higher temperatures. This is believed to be from the enhanced annihilation of defects due to thermal migration.

2.1.2 Hydrogen and Helium Effects

Effect of Helium

For tungsten in plasma facing components, the primary source of helium impurities is from the plasma directly. Helium formed as a result of transmutation, ~36 appm after 5 years of operation, is insignificant in comparison and it will take 300 years of service for the transmutation produced helium to have an effect on the embrittlement of the tungsten components [40,70]. The helium infused can form nano-sized bubbles in the matrix that evolve and migrate depending on factors such as the temperature and stress gradients [71].

Helium filled bubbles near the surface can pop, initiating fuzz growth [44,72]. The fuzz can grow up to several micron, depending on the helium exposure levels [73], as seen in scanning electron microscopy (SEM) micrographs in Fig. 2.9, from [74]. Although the fuzz grows to a few microns, it can be observed to be nano-structured.

It is expected that the fuzz will increase the quantity of tungsten sputtered into the plasma and polluting it. However, fuzzy tungsten is observed to have lower sputtering rates, which decreases with increasing fuzz thickness, and is believed to stem from the increased porosity [75]. The fuzz formation may have effects on cross-plane thermal transport into the bulk but is yet to be explored.

The more problematic effect of helium infusion into the matrix, is from the nano-bubbles formed. The bubbles can diffuse further into the bulk at higher temperatures, affecting the tungsten component as a whole [74,76]. The infused helium ions and helium bubbles can strongly interact with vacancies, dislocations and other imperfections in the material such as grain boundaries to significantly alter material properties such as hardness [27,77,78]. Section 2.2 considers key studies on these effects.

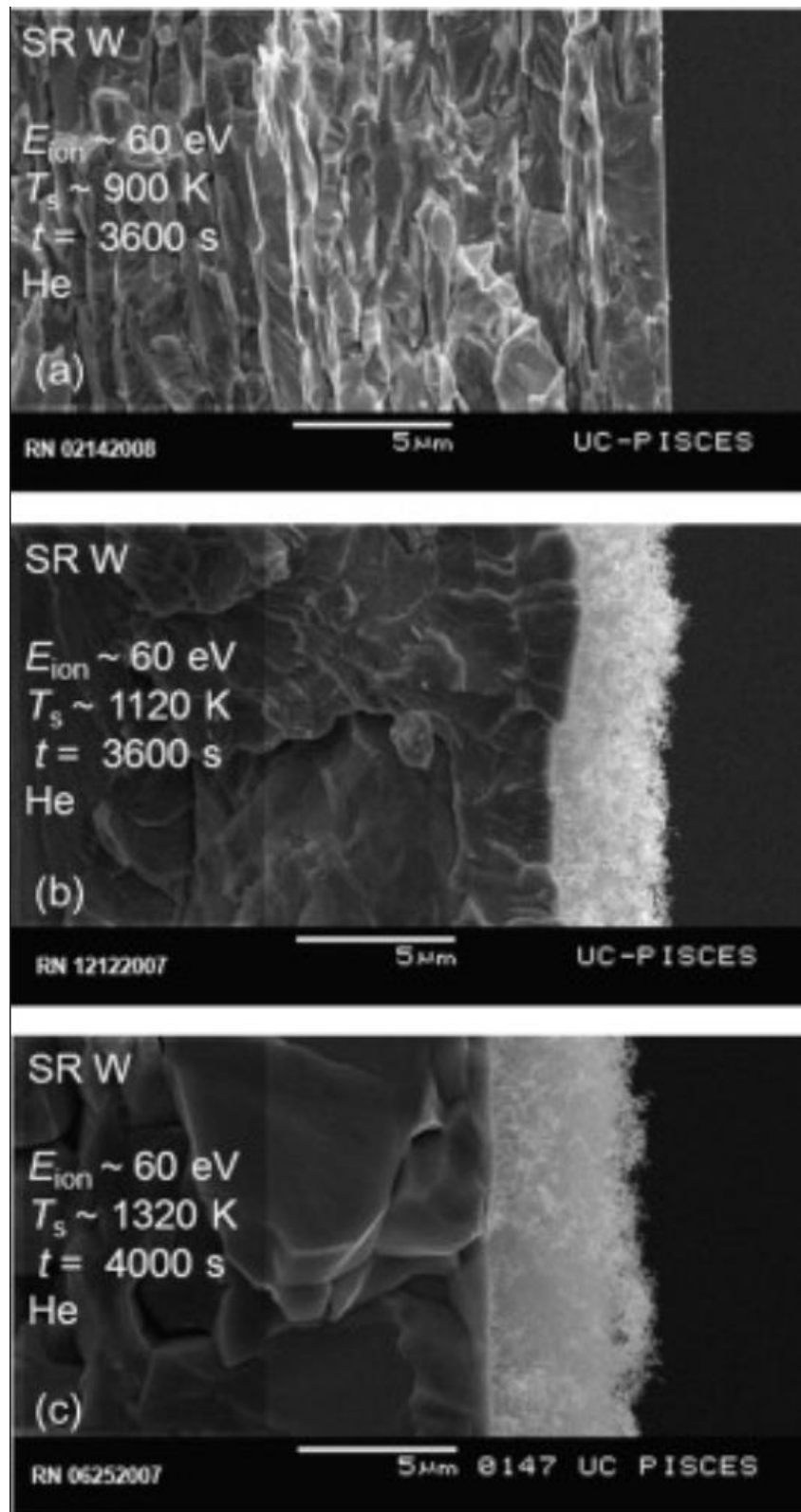


Figure 2.9 Cross-sectional micrographs of tungsten exposed to 60 eV He plasma at 900, 1120 and 1320 K, at the PISCES facility. Figure obtained from [74].

Effect of Deuterium

The plasma facing components also experience an infusion of hydrogen isotopes such as deuterium into the matrix. The uptake of hydrogen isotopes into tungsten due to plasma exposure has been studied extensively [79–85]. A brief description of the mechanisms and its effects on the material structure is given here.

For fusion relevant temperatures, hydrogen isotopes are mobile within the tungsten matrix [84]. Hence, deuterium atoms implanted into the thin surface layer ($\sim$ nm) [86], thin due to the low energy of the plasma ($\sim$ 50 keV), can diffuse further into the material [80]. For low deuterium fluences ($< 10^{22}$ ions/m²), the retention of hydrogen isotopes is quite low and most are desorbed between 400 and 600 K [87]. The diffusing deuterium ions can get ‘trapped’ at imperfect locations in the matrix such as grain boundaries, dislocations, vacancies, voids, and also self-trap [46,88,89]. The ions then agglomerate to form bubbles with high pressure within them. These bubbles can be up to a few microns in size and are visible in an SEM.

The nature of the blisters and bubbles created depends on the exposure levels, temperature, sample and sample surface preparation and microstructure [90]. Fig. 2.10 from [91] shows the variation of the blistering patterns observed as a function of exposure temperature, deuterium flux density and grain size. The cross-sectional SEM micrograph in Fig. 2.11 shows such bubbles and blisters in pristine tungsten that has received a deuterium ion fluence of $\sim 10^{25}$ ions/m² [86]. The surface blistering as seen in an SEM for a similar sample is shown in Fig. 2.12.

At temperatures below the brittle to ductile transition temperature (BDTT) cracking has been observed across grains, due to the increased stresses from the deuterium and bubbles formed [92]. An alternative explanation for the cracking observed is that the precipitate forming tungsten hydrides are a source for increased stresses in the material [92]. At temperatures

higher than the BDTT, there is less cracking due to the lower resistance to bubble growth. This is due to the fact that the bubble growth relaxes the pressure within the bubble and hence the stresses that normally lead to cracking are less too. However it is believed that these larger bubbles and blisters may be decorated with micro cracks that are below the resolution of SEM's and allow the deuterium to escape the bubbles [92].

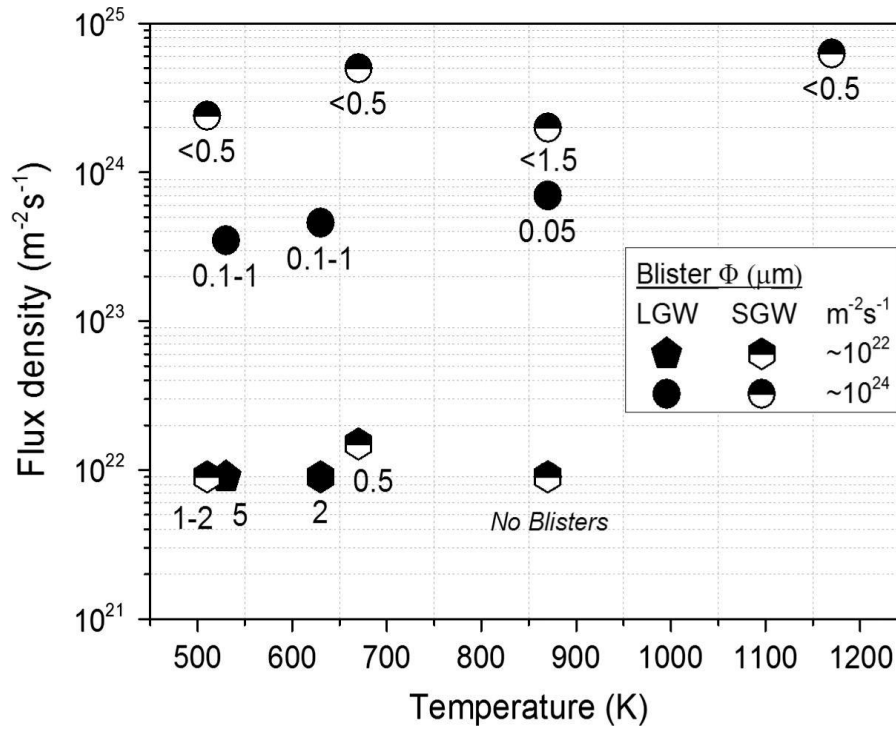


Figure 2.10 Blister diameters observed in tungsten exposed to deuterium plasma as a function of temperature and flux density. Data is provided for large (LGW) and fine grain (SGW) tungsten. Figure reproduced from [91].

These changes in the structure of the tungsten components due to the bubbling and blistering effects, affect the thermal and mechanical properties, for which examples are given in section 2.2. Chapter 4, based on paper 2, studies the thermal diffusivity degradation due to this phenomena. Synergistic effects between deuterium infusion and displacement damage as well as helium implantation have been observed to affect the microstructure even more. The deuterium retention in tungsten pre-irradiated with He ions is known to be greater than without helium pre-irradiation [45,87]. The high density of small helium bubbles are believed to

significantly increase the trapping of the infused deuterium, due to the availability of more trapping sites.

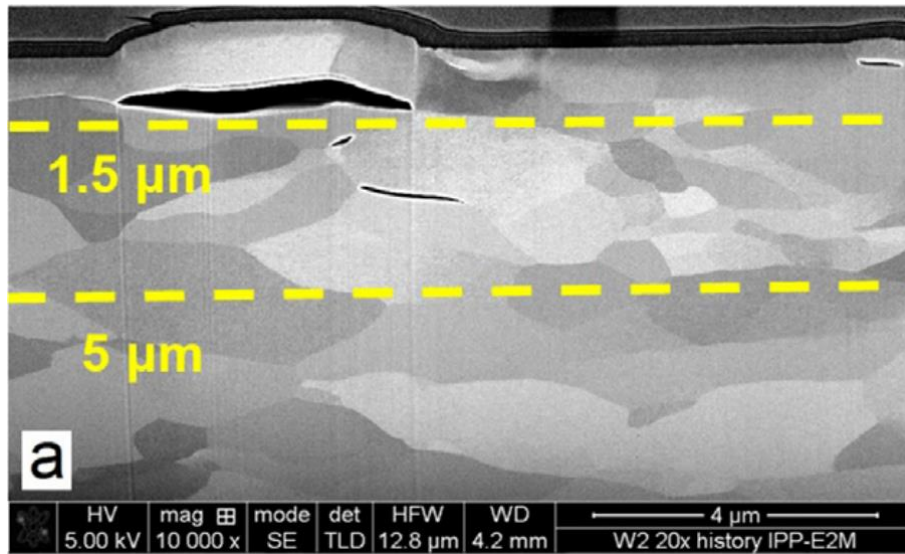


Figure 2.11 Cross-sectional micrograph of pure tungsten exposed to high-flux low-energy deuterium plasma. FIB milling is used to prepare the cross section. Figure obtained from [86].

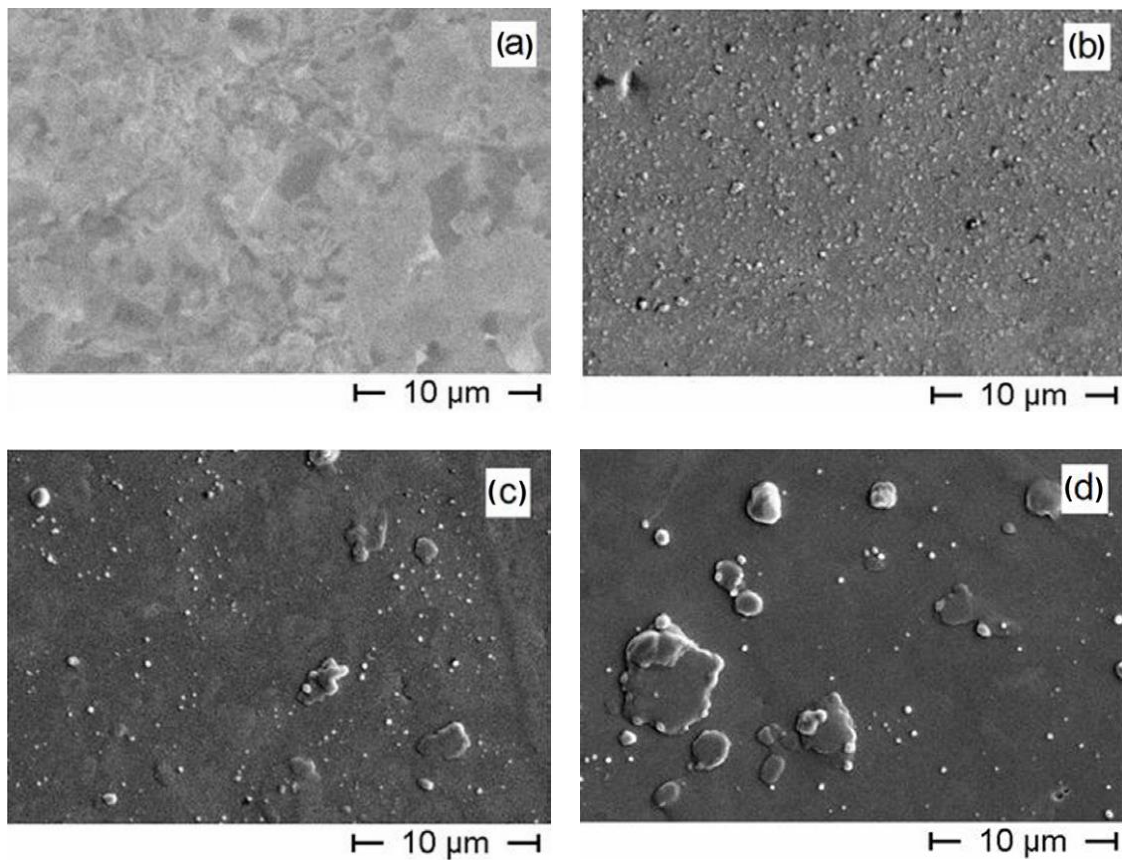


Figure 2.12 SEM micrographs showing the surface blistering in tungsten exposed to increasing levels of deuterium plasma at ~ 500 K. (a) - pristine, (b) 5×10^{25} ions/m², (c) 3.5×10^{26} ions/m² and (d) 10^{27} ions/m² from [17].

Displacement damage studies with sequential high-energy (20 MeV) self-ion irradiation and low energy deuterium plasma exposure (15 eV), have indicated a stabilising of the cascade damage by the infused deuterium [46,93]. A comparison of sequential and simultaneous self-ion irradiation with deuterium plasma exposure has shown that the retained maximum deuterium concentration in the simultaneous irradiation case is almost two times higher than when sequentially implanted [93].

2.1.3 Transmutation

Tungsten nuclei in the matrix can absorb fusion neutrons and transmute into rhenium, osmium as well as tantalum [42]. Modelling work predicts ~ 4 at% rhenium and ~ 1 at% osmium formed after 5 years of operation [40,42,67]. Figure 2.13 shows the evolution of pristine tungsten in a typical plasma facing component over 2 years of operation, due to transmutation effects [67]. Studies also show that the quantity of each transmutation product produced will vary depending on the location of the component in the reactor as well as depending on the location within the component, as seen in Fig 2.14 [40]. The presence of these transmutation products effectively converts the tungsten material into a dilute alloy, and can significantly modify its material properties including the thermal conductivity [14,24], discussed in further detail in section 2.2.

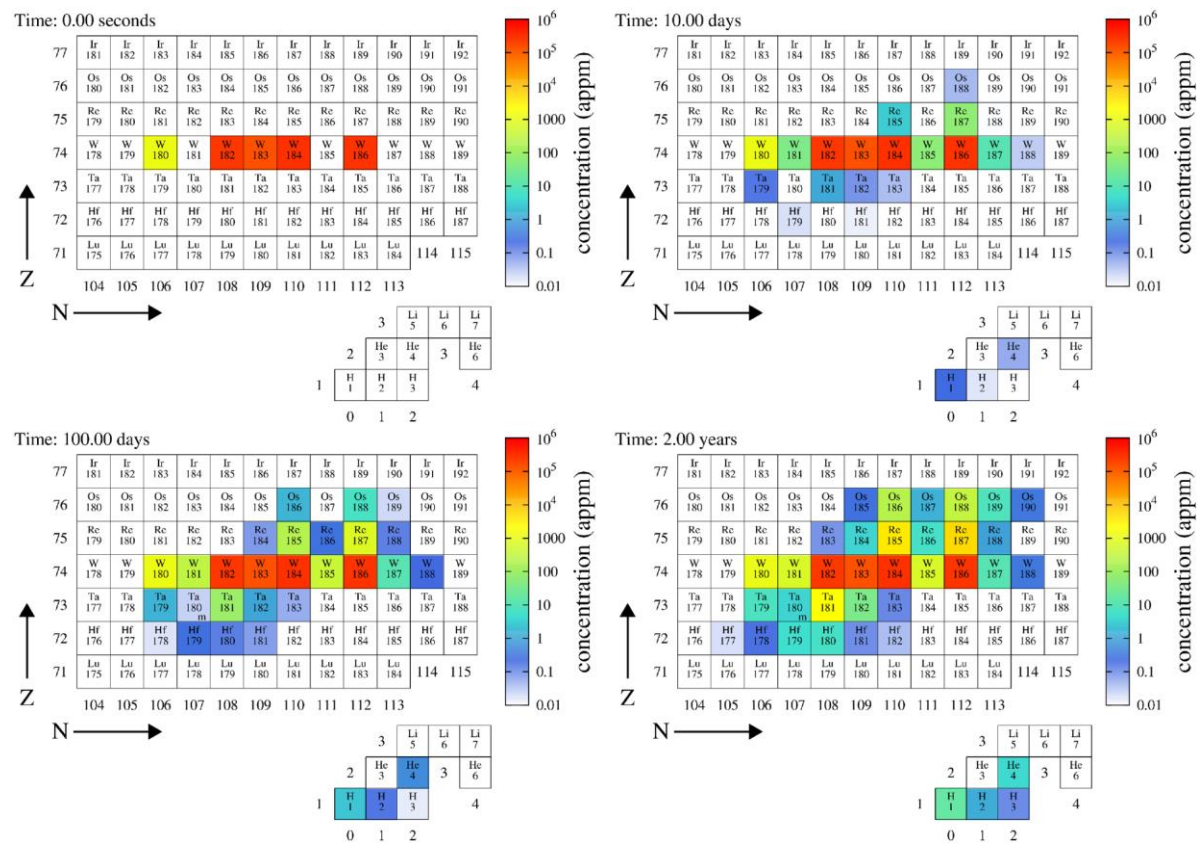


Figure 2.13 Nuclide maps showing the evolution of pure tungsten due to transmutation over 2 years in a DEMO type reactor. Figure obtained from [67].

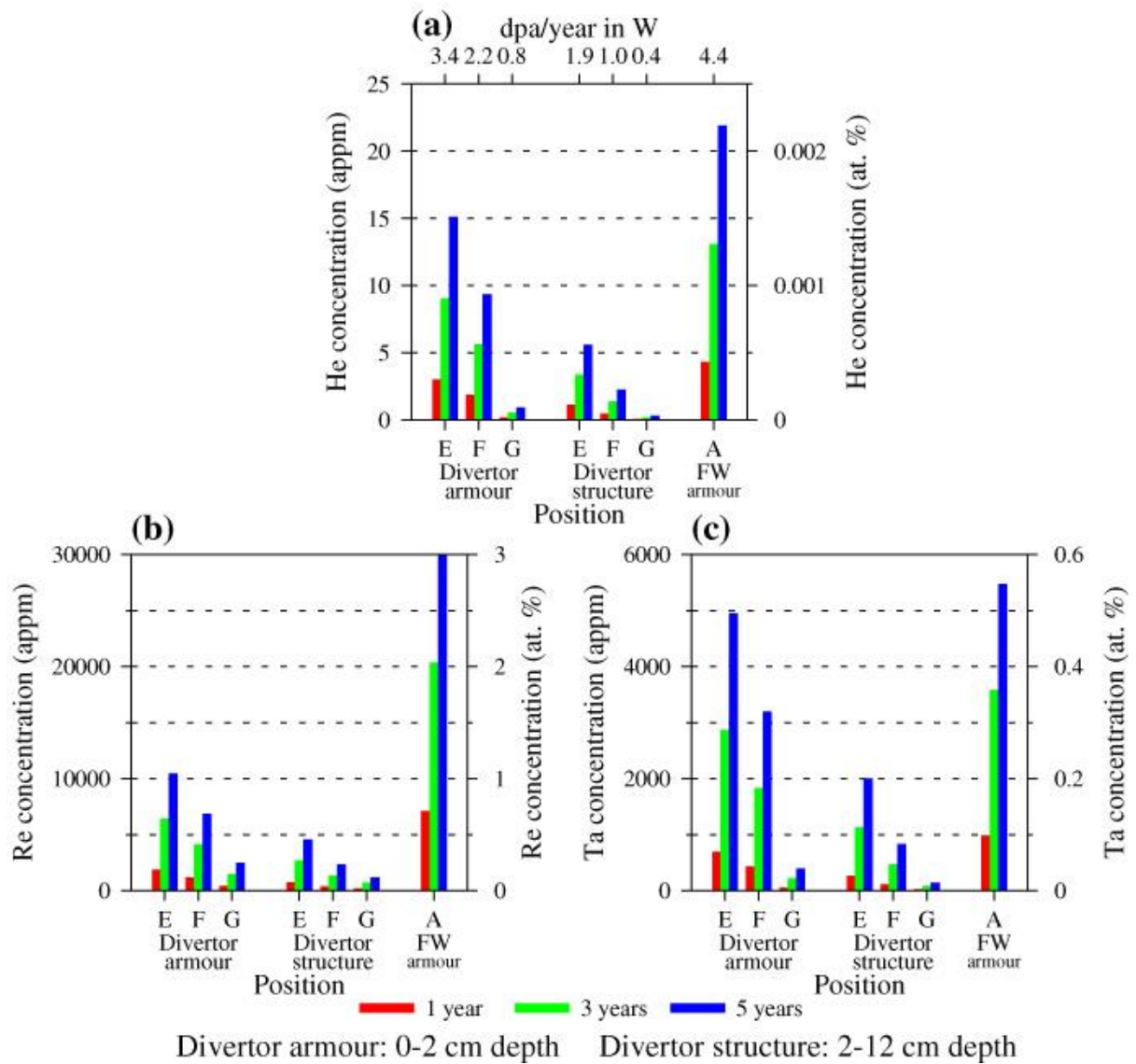


Figure 2.14 Concentrations of (a) He, (b) Re and (c) Ta produced in the divertor and first wall (FW) armour in a DEMO type reactor. Figure sourced from [40].

The introduction of rhenium from transmutation into the tungsten solution has potential benefits, including improved ductility [14,94]. However, significant clustering in tungsten with even 2 at% Re and precipitation of W-5Re under ion-irradiation, has been observed which can further change material properties including hardening [37,95]. This phenomenon is discussed in further detail in section 2.2.1. Fig 2.15 shows the clustering of Re in W-2Re under W self-ion irradiation, from [95]. The formation of these clusters and precipitates can suppress the formation of dislocation loops and voids [39].

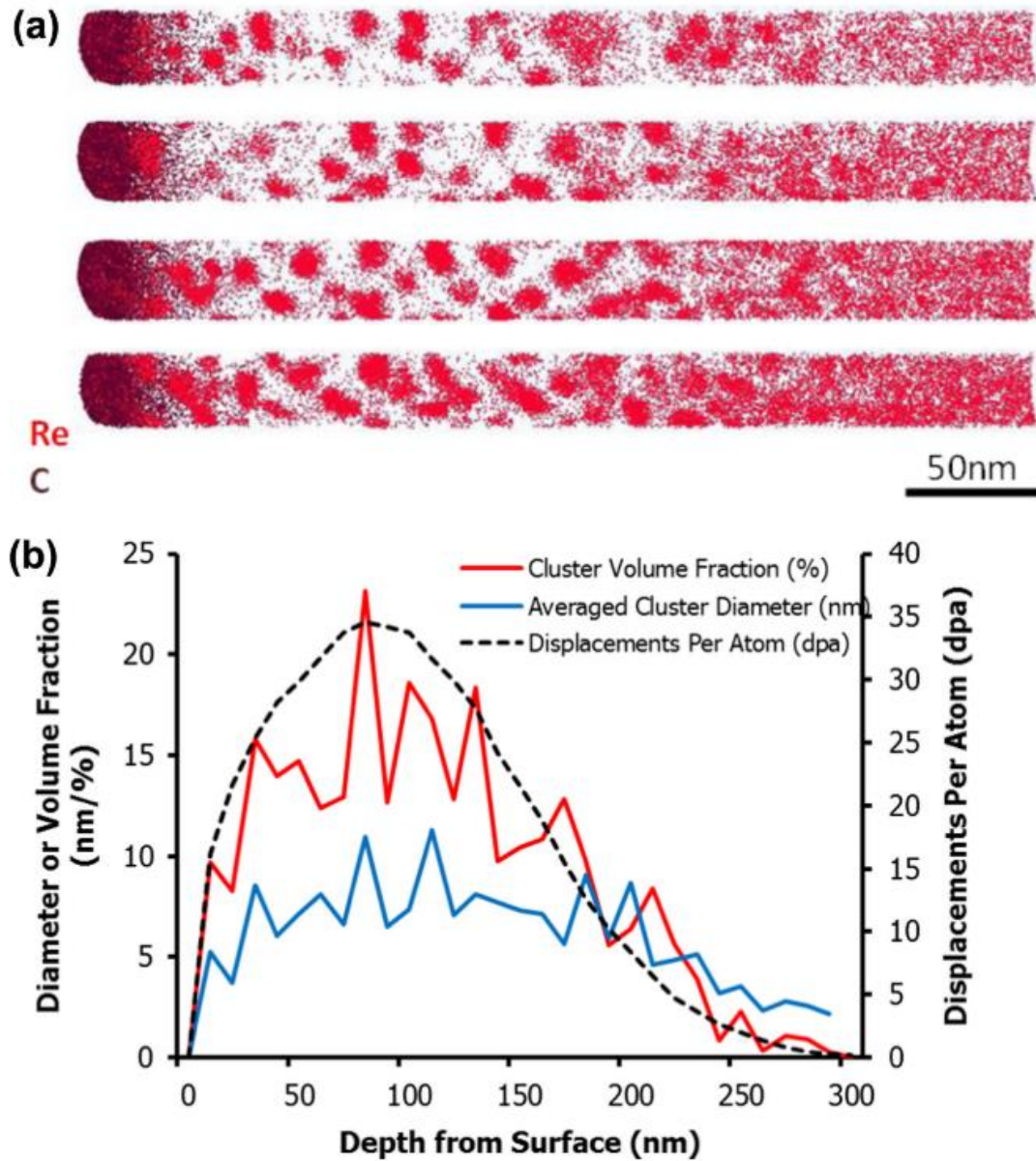


Figure 2.15 Atom probe tomography map of tungsten with 2 at% Re following 33 dpa implantation at 773 K (a) showing extensive clustering. (b) Cluster diameter and volume fraction considering 10 nm slices. Also superimposed on (b) is the implantation dose in dpa from SRIM [28]. Figure reproduced from [95].

2.2 Irradiation and exposure induced material property changes

Reviewed in this section are key thermal and mechanical properties of tungsten that are altered due to irradiation and exposure to plasma in a fusion environment, as detailed in the previous section.

2.2.1 Hardening

Neutron irradiation [68], self-ion irradiation [78,96], helium [97] and deuterium [98] ion exposure as well as irradiation induced transmutation [68] are known to affect the hardness of tungsten. There is extensive literature about these effects, as well as synergistic effects of the different radiation damage phenomena on the hardness in tungsten. Divertor and first wall tungsten components undergo high thermomechanical stresses during normal operation and transients [4,99,100]. Deterioration of the mechanical properties due to irradiation effects, such as an increase in hardness and loss of ductility, would significantly limit the safe envelope of operating conditions. Hence great importance is placed on the irradiation-induced increase of the hardness in tungsten, in both neutron-irradiated [68] and ion-implanted material [27,96,101].

Tanno et al. [68] showed that upon neutron irradiation, beyond damage levels of 1.54 dpa at 750 °C, the formation of precipitates causes a hardness increase. This increased linearly with rhenium content. Tungsten with 3 and 5 mass % osmium also showed a marked increase in hardness, when compared to pure tungsten. However these neutron irradiation studies show hardness increases > 50% (except [102] which shows a 19 % increase for pure tungsten), which are significantly higher than those reported by ion-irradiation studies (23% increase at 13 dpa) [78].

Fig. 2.16 from [37] shows an increase in hardness for ultra-high purity (UHP) tungsten and W-5Re due to self-ion irradiation at 300 °C. It should be noted that the authors recommend the

exclusion of data up to a depth of 75 nm in Fig. 2.16, due to tip shape effects and the initial pop-in from the nano-indentation. Excluding this, there is a hardness increase up to 0.4 dpa, after which it saturates, with only a slight increase even as it reaches 33 dpa. Unlike the implanted UHP tungsten, in the implanted W-5Re, the hardness increase doesn't saturate, even at 33 dpa. The hardness, at 1000 nm in the 33 dpa sample, doesn't return to the unimplanted value. This is interesting since the implanted layer thickness in this study is ~300 nm [37]. It is believed that the very high hardness at the surface contributes to the hardness at this depth.

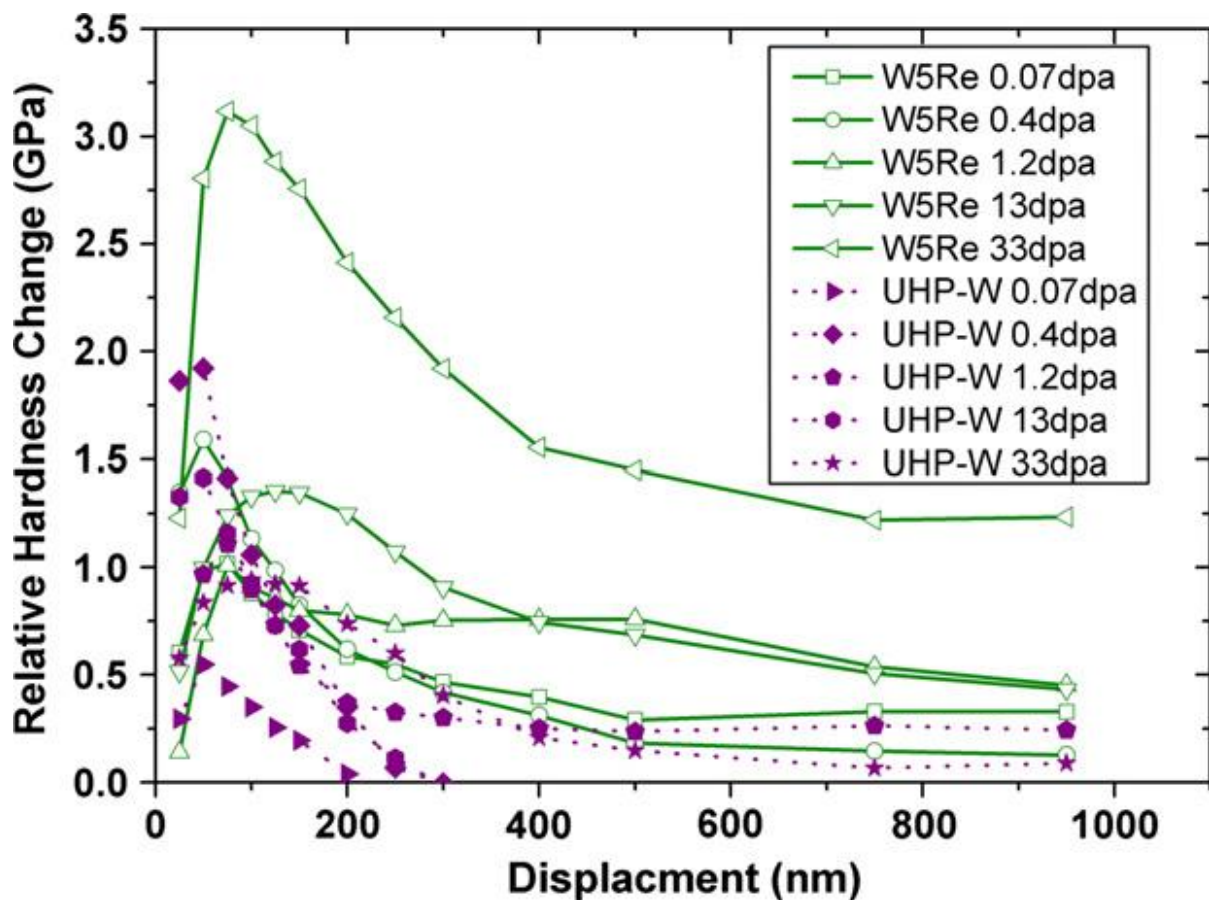


Figure 2.16 Relative hardness increase measured by nano-indentation, due to self-ion implantation up to 32 dpa, in UHP-W and W-5Re. Figure sourced from [37].

Fig. 2.17 shows the change in hardness of W and W-3Re implanted with self-ions at 500 and 800 °C, up to 5 dpa [96]. The hardness increase is seen to saturate around the second damage level of 1.2 dpa. The values reported for the change in hardness however seems to be significantly higher than those from the self-ion work in [37].

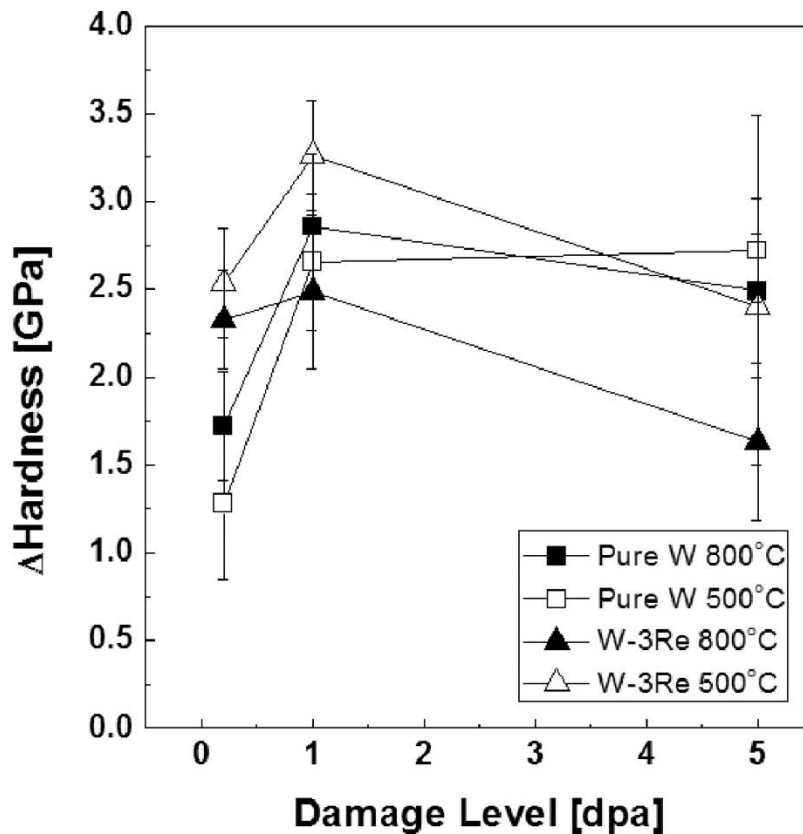


Figure 2.17 Hardness change in pure W and W-3Re alloy, irradiated by self-ions at 500 and 800 °C [96]. Hardness at a given damage level was obtained at a depth of 500 nm for each sample. Figure obtained from [96].

A comparison of the self-ion implanted tungsten hardness studies to measurements on neutron irradiated tungsten is important. However, the range of temperatures and limited damage ranges considered in the neutron irradiated tungsten work make it tricky to make comparisons. Fig. 2.18 from [37] shows several literature studies on the changes in hardness in neutron irradiated tungsten and tungsten-rhenium alloy. The data is from [37] and references therein. Significant differences can be observed between the data reported. In most of the neutron irradiated studies, the hardness increases are significantly higher than those from self-ion implanted studies [37,96]. The author in [37] indicates that disparities between hardness changes reported from neutron irradiated studies and ion-implanted ones can originate from several sources. This could be the starting purity of the material as well as irradiation temperatures and dose-rates [37].

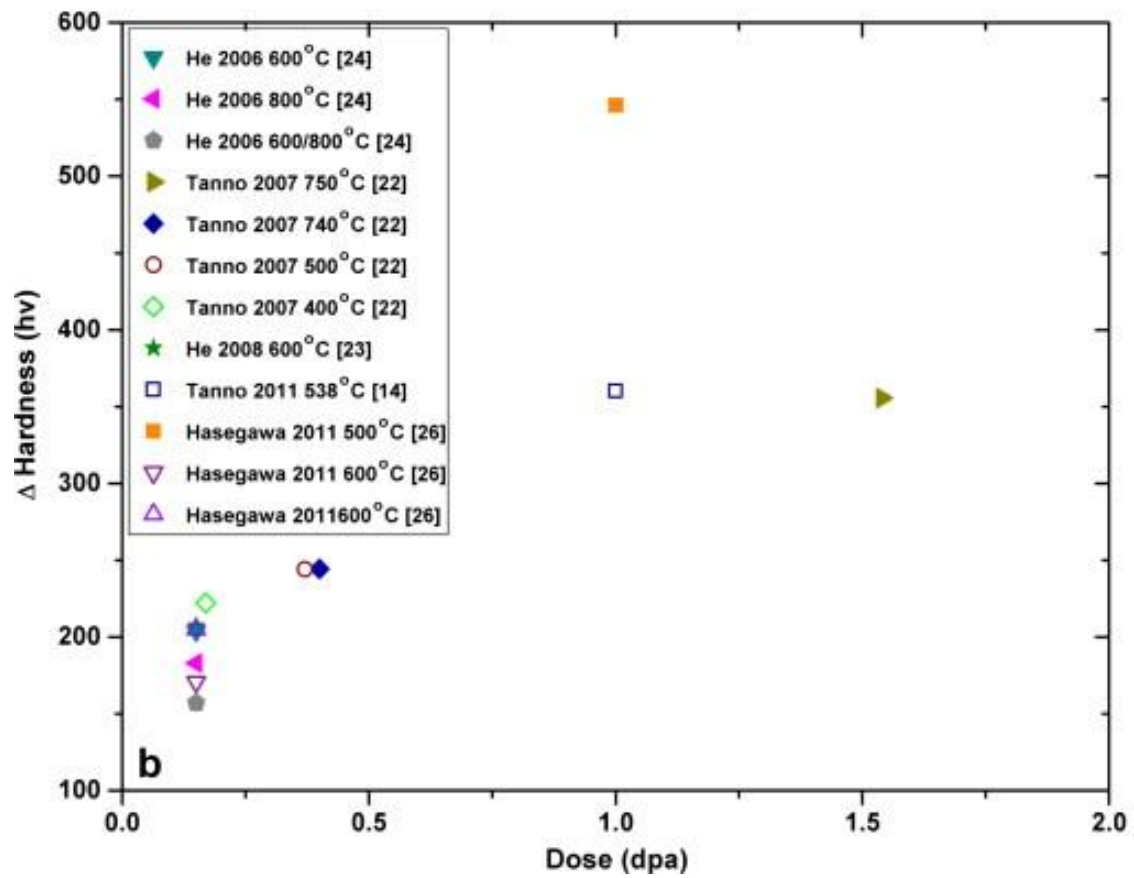
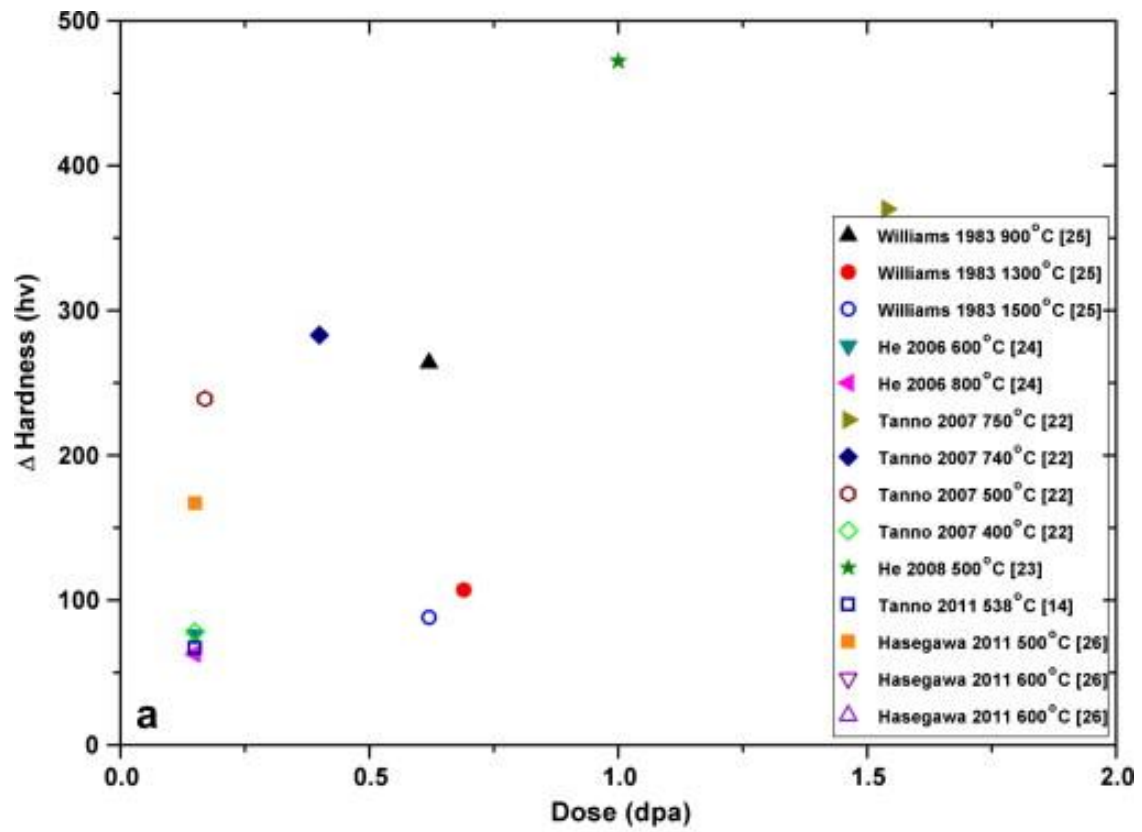


Figure 2.18 Hardness change in (a) W-5Re and (b) pure tungsten subjected to neutron irradiation at various temperatures. Figure sourced from [37].

Studies on rhenium ion implanted and helium plasma exposed tungsten [97] showed an increase in hardness for both low energy (~ 20 eV) high fluence ($\sim 10^{25}$ ions/m²) helium plasma as well as for 2 MeV Re²⁺ implantations as shown in Fig. 2.17. The implantations with rhenium ions were up to ~ 5.2 dpa, to emulate displacement damage as well as neutron induced transmutations. These changes in room-temperature hardness, observed through nano-indentation, were present at both irradiation temperatures of 473 and 1273 K. It should be noted that for the depth region considered in the study in Fig 2.19 the damage level is 1 dpa.

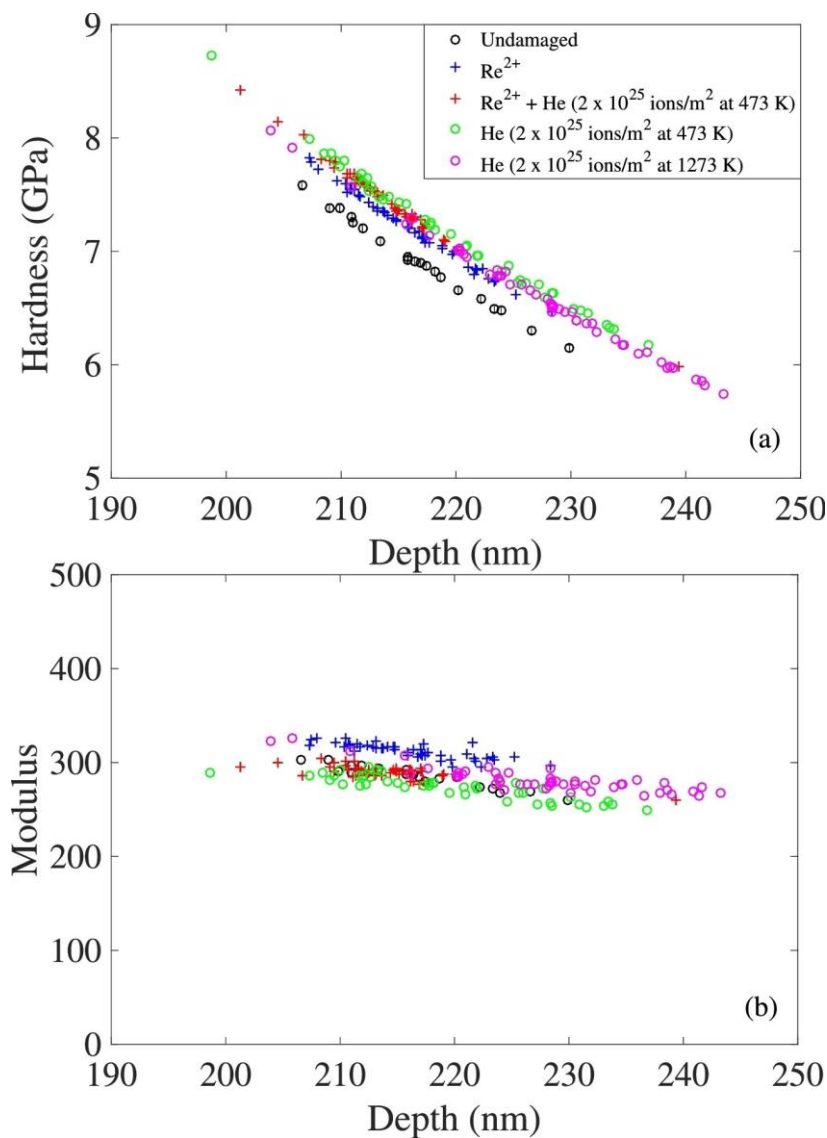


Figure 2.19 Depth profiles of hardness and Young's modulus for W irradiated with Re²⁺ and exposed to He plasma in [97]. Figure obtained from [97].

The authors in [97] attribute the hardness changes for the helium exposed samples, to helium trapped in vacancies and the presence of helium nano-bubbles in the matrix. For the samples irradiated only with rhenium, the hardness change, of ~2% is attributed to the dislocation loops formed. This argument does seem to agree with observations on hardness changes in other self-ion irradiated tungsten studies [78]. Interestingly, the Young's modulus remains more or less unchanged due to the exposure and irradiation.

In tungsten implanted with self-ions (0.4 and 13 dpa) and helium ions (300 and 3000 appm) it has been observed that the effect of helium alone on the hardness increase was greater than the effect of helium implanted on to already self-ion implanted tungsten [78], as shown in Fig 2.20. This is due to the fact that helium trapped in vacancies distributed finely across the matrix has a more prominent effect than when trapped in vacancies that are in dislocation loops created by the self-ion implantation.

Similarly, in tungsten exposed to deuterium (~50 eV), a significant increase in hardness is observed as well as a saturation with increasing deuterium fluence [98] as shown in Fig. 2.21. Tungsten exposed to both, 1 and 20 shots of deuterium plasma, where 1 shot of deuterium represents an incident fluence of $\sim 5 \times 10^{25}$ ions/m², showed an increase in hardness. A saturation in the increase is also observed, evident in Fig. 2.21 (a) and (b). The exposures are at 450 K and 650 K. There is a slight effect of thermal diffusion of the deuterium further into the bulk evident in the hardness values further in, for the higher temperature exposures. Interestingly, the author compares tungsten exposed to identical conditions but which underwent different sample preparation methods. Fig. 2.21 (a) provides the hardness curves for tungsten where the grains aren't recrystallized and contain internal strains, whereas the samples in Fig. 2.21 (b) have fully recrystallized grains.

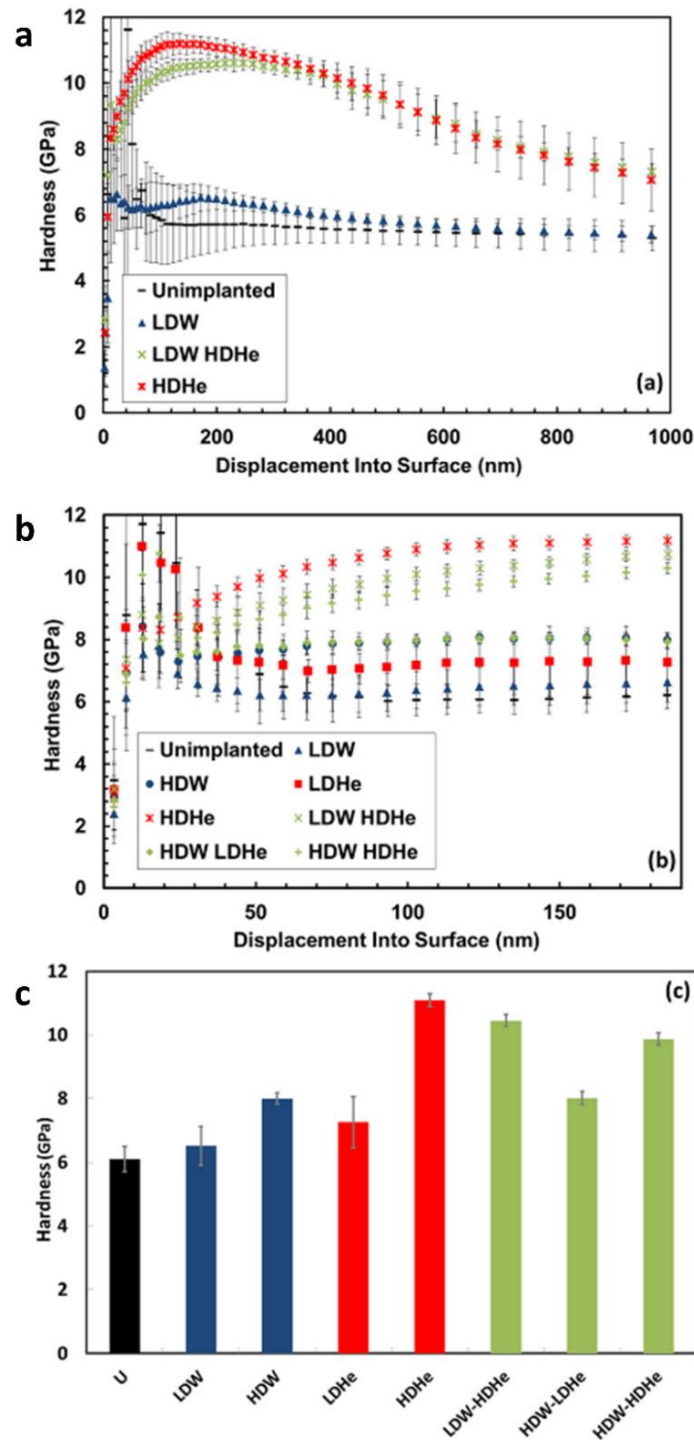


Figure 2.20 Hardness vs. depth curves for unimplanted tungsten and tungsten implanted with self-ions and helium ions (300 and 3000 appm) individually and sequentially [78]. U – unimplanted, LD – low dose, HD-high dose. Low dose is 0.4 dpa and 300 appm for W and He respectively. High dose is 13 dpa and 3000 appm respectively for W and He. (a) – Complete curves for U, LDW, LDW HDHe and HDHe, (b) up to 200 nm for all samples, (s) average hardness values for all samples for depth between 100 and 200 nm.

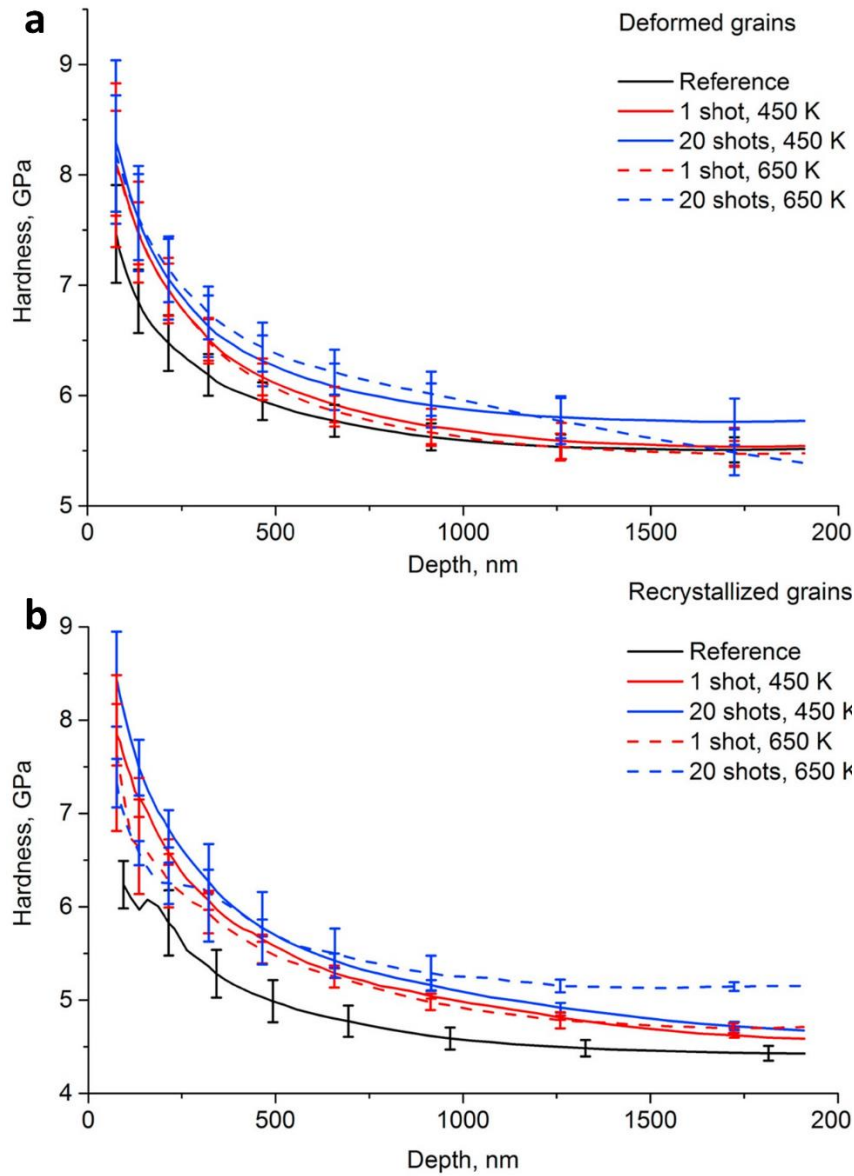


Figure 2.21 Hardness vs. depth curves for tungsten with (a) – deformed grains and (b) – recrystallized grains, exposed to 1 and 20 shots of deuterium plasma at 450 K and 650 K, from [98]. 1 shot of deuterium represents an incident fluence of $\sim 5 \times 10^{25}$ ions/m².

The deuterium penetration and effectively the hardness increase appears to persist deeper in the sample for the recrystallized case. This is attributed to the increased ion diffusivity in such grains [98]. This shows that sample preparation, especially the heat treatments carried out prior to the implantations, can affect the hardness values obtained. This further strengthens the explanation of the author in [37] about the disparities between hardness values measured from the various neutron irradiated campaigns in Fig. 2.18.

2.2.2 Brittle to Ductile Transition

Below a specified temperature, known as the brittle to ductile transition temperature (BDTT), most metals undergo brittle fracture. Brittle fracture needs to be avoided in almost all engineering applications, primarily because of the significantly lower energy absorbed in the failure process and the occurrence of the fracturing process without any prior warning. Generally in metals, the BDTT is a fraction of the melting point, and around 0.1-0.15 in pristine well-annealed bcc metals as seen in Fig. 2.22 from [103]. Due to the high melting point of tungsten, this gives a BDTT of ~400-500 K, depending on the strain rate [103–105]. The lower temperature limits in the envelope of operating conditions for the tungsten divertor depends heavily on this BDTT and radiation hardening [38]. An increase in the BDTT due to irradiation and exposure effects would raise the minimum operating temperature, further constraining operation. It has been observed that hardening, void formation and the presence of gas bubbles in the matrix can all contribute to an increase in the BDTT [106–108].

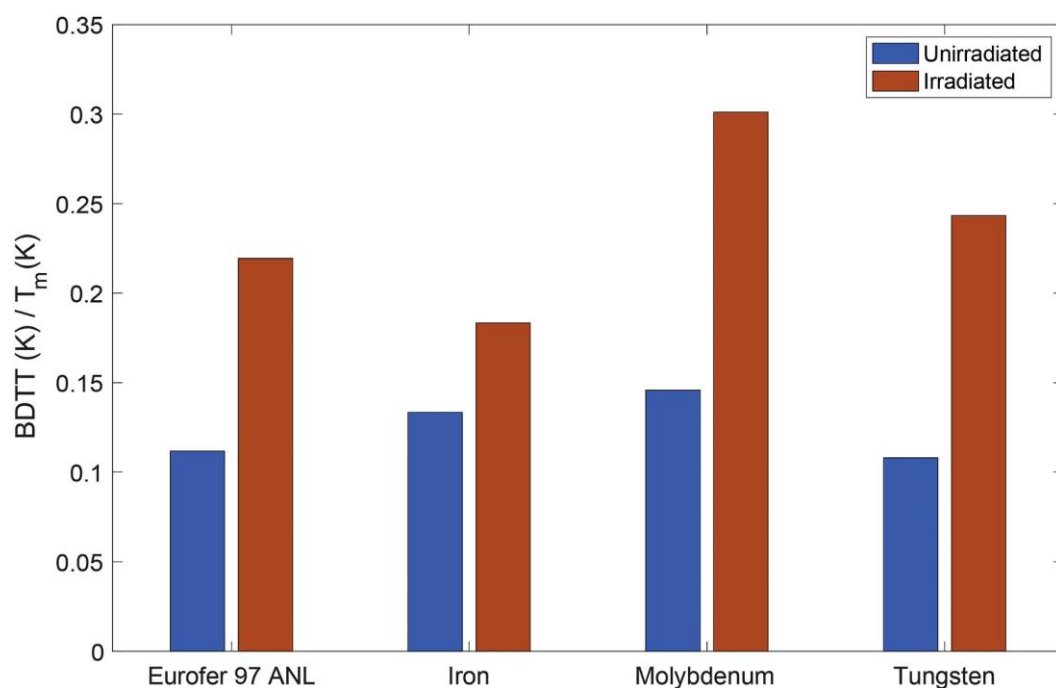


Figure 2.22 Increase in BDTT of various bcc metals after neutron irradiation. Eurofer 97 ANL data from [109] is for irradiation up to 16.3 dpa at 573 K, for iron it is 0.4 dpa at 678 K from [110], for molybdenum it is up to 2.2 dpa at 782 K, and for tungsten it is up to 1.67 dpa at 1173 K from [103]. Figure obtained from [103].

Fig. 2.22 from [103] shows the BDTT as a fraction of the melting point, before and after neutron irradiation for EUROFER 97 [109], iron [110], molybdenum [111] and tungsten [103]. Abernethy et al. in [103] argues that it is not sufficient to only provide a BDTT before and after irradiation, but indeed the strain rate needs to be specified. This is proven by their results on the change in the BDTT as a function of strain, in tungsten, shown in Fig. 2.23.

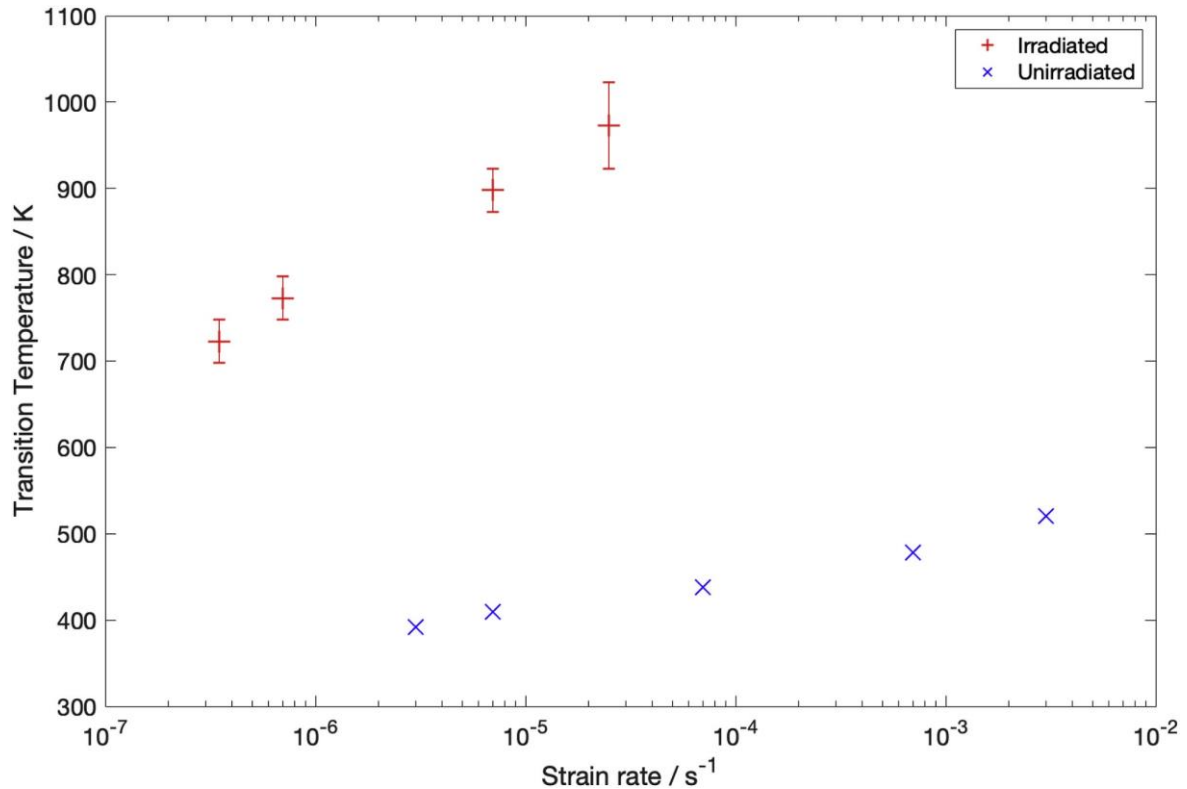


Figure 2.23 Brittle to ductile transition temperature in single-crystalline tungsten, irradiated to 1.67 dpa at 1173 K, as a function of strain rate. Figure sourced from [103].

The authors in [103] also make an interesting observation regarding the effect of rhenium on the BDTT in tungsten. A previous study [112] indicated that the introduction of rhenium to the tungsten matrix lowers the BDTT for rhenium content as low as 1.9 %. However in [103] the eventual rhenium content as a result of transmutation is 1.4 wt% but this effect is not observed. It maybe observable at higher levels, but this is not covered in that study or elsewhere. Also, an approximate doubling of the BDTT from ~400-500 K to ~800-1000 K after irradiation in agreement with modelling predictions is reported [113].

Overall, a deterioration of the BDTT is reported for tungsten upon irradiation, in a similar fashion to other mechanical properties. Further studies are warranted for higher damage levels, higher rhenium content, and for polycrystalline tungsten.

2.2.3 Swelling

All three modes of irradiation and plasma exposure related damage covered in section 2.1, i.e. displacement damage, ion infusion, and transmutation can induce swelling in plasma facing materials such as tungsten [61,114–116]. It is known that factors such as crystallographic orientation, composition, micro-chemical evolution and temperature history affect the swelling rates in metals [117]. It is fairly well understood that the swelling rates of fcc iron alloys at reactor relevant damage rates and temperatures are $\sim 1\%$ per dpa [117–120]. The crystallographic influence, plays a major role in swelling behaviour, with bcc metals believed to have swelling rates two to four times lower than their fcc counterparts [117].

Tungsten in general has lower swelling rates due to its bcc crystal structure [121–123]. However, changes in composition due to transmutation effects do need to be considered. Since tungsten is historically known to be quite well-behaved in terms of swelling, there exist only a handful of studies related to its macroscopic swelling behaviour [124–126]. The studies [124,125] show that the addition of rhenium to tungsten, significantly reduces swelling effects from irradiation. This is believed to originate from the suppression of void formation in tungsten due to rhenium. Similar effects are expected from other transmutation elements such as osmium [41,68]. Fig. 2.24 from [125], of tungsten irradiated with fast neutrons up to 9.5 dpa, shows this effect. Hence the effects of transmutation on the swelling behaviour of tungsten is not of great concern.

Helium and deuterium infusion are known to cause blistering or fuzz formation at the surface of the tungsten components in reactor relevant conditions as discussed in section 2.1.2. Since

these are surface effects and have been covered above, it is not revisited in detail here. However it should be noted that the influence of helium and deuterium on void nucleation, that plays a key role in swelling behaviour has not been explored, with respect to swelling at the macroscopic level [121].

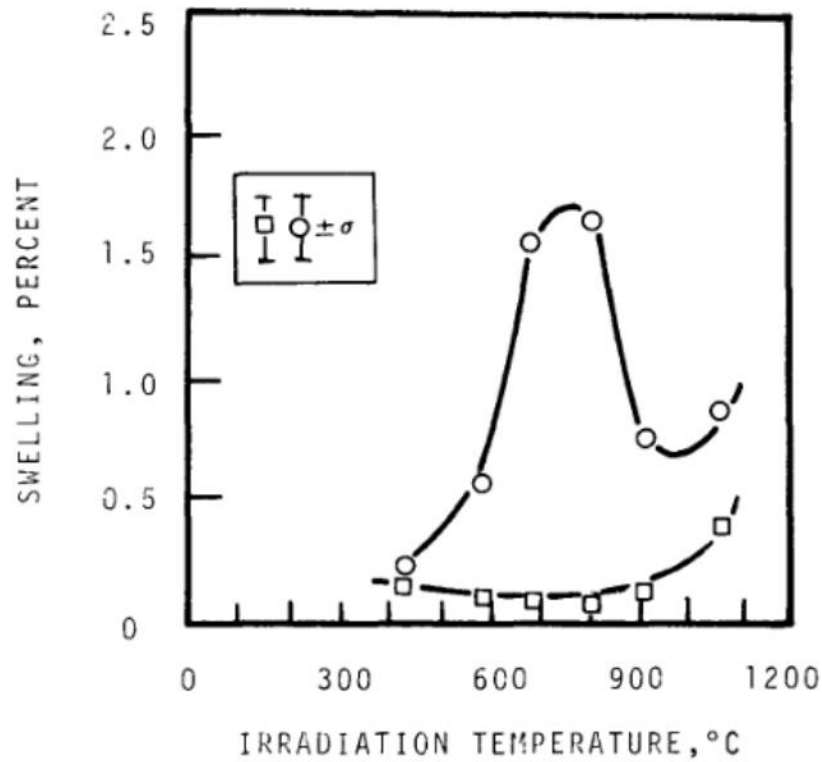


Figure 2.24 Observed swelling in irradiated tungsten and tungsten-25 rhenium. Figure obtained from [125]. Circular markers are for irradiated pure tungsten and square ones are for the tungsten-25 rhenium ones.

Swelling at the nano and micro scales of the tungsten lattice has been studied with regards to helium implantation and studies are ongoing with respect to self-ion irradiated tungsten [127,128]. X-ray diffraction experiments, coupled with density functional theory (DFT) modelling are used to study the effects and kinetics of displacement damage induced swelling [116], by probing the lattice strain. Lattice strain is an interesting topic due to the fact that its behaviour can deviate from that of the volumetric strain [128]. Studies on self-ion implanted tungsten have shown that in the low-dose regime (< 0.05 dpa) the lattice and volumetric strain

increase with dose, due to the formation of SIA's and vacancies. Above 0.05 dpa, the volumetric strain continues to rise, but the lattice strain can plateau and then decrease. This is due to the fact that the interstitials start to cluster and form dislocation loops that grow in size and coalesce, forming new crystal planes [128].

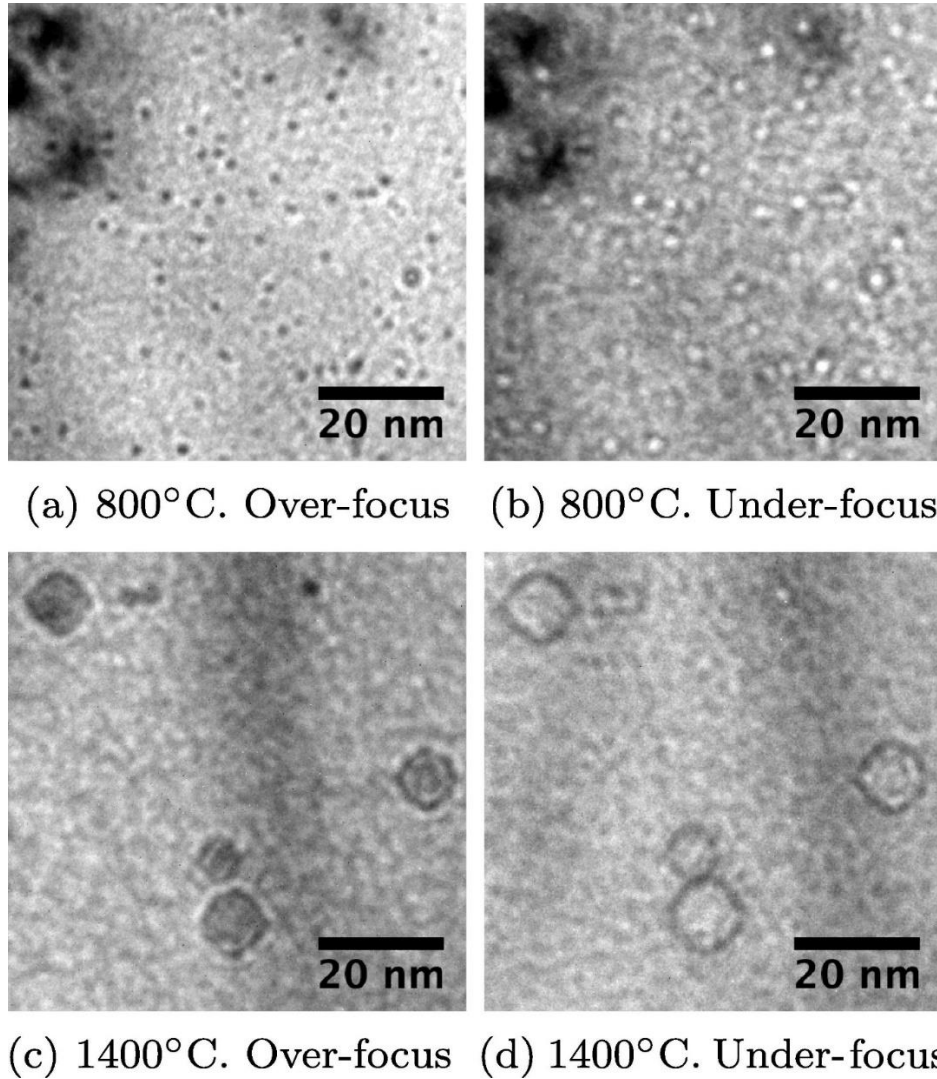


Figure 2.25 Voids in tungsten implanted with self-ions up to 1.5 dpa at 500 °C. Figure obtained from [126].

The measured lattice strain can also appear to decrease, depending on the orientation of these newly formed crystal planes [128]. This evolution of the SIA's is what gives rise to the interesting behaviour of the lattice strain. The vacancies on the other hand can agglomerate,

when mobile at higher temperatures, to form voids. Fig. 2.25 from [126] shows extensive void formation in self-ion implanted tungsten up to 1.5 dpa, at elevated temperatures.

2.2.4 Thermal Conductivity

At room temperature, tungsten has around 90% of its thermal conductivity from electrons, and the phonon contribution is about 10% [15]. The Wiedemann-Franz law, states that the thermal conductivity of a diffusive metal is proportional to its electrical conductivity. Hence, data on electrical resistivity changes, can be used to assess changes in the thermal conductivity of such metals with significant accuracy. Historically, due to electrical resistivity measurements being more accurate than thermal conductivity measurement techniques, most studies on thermal conductivity were carried out using electrical resistivity measurements and utilising the Wiedemann-Franz law.

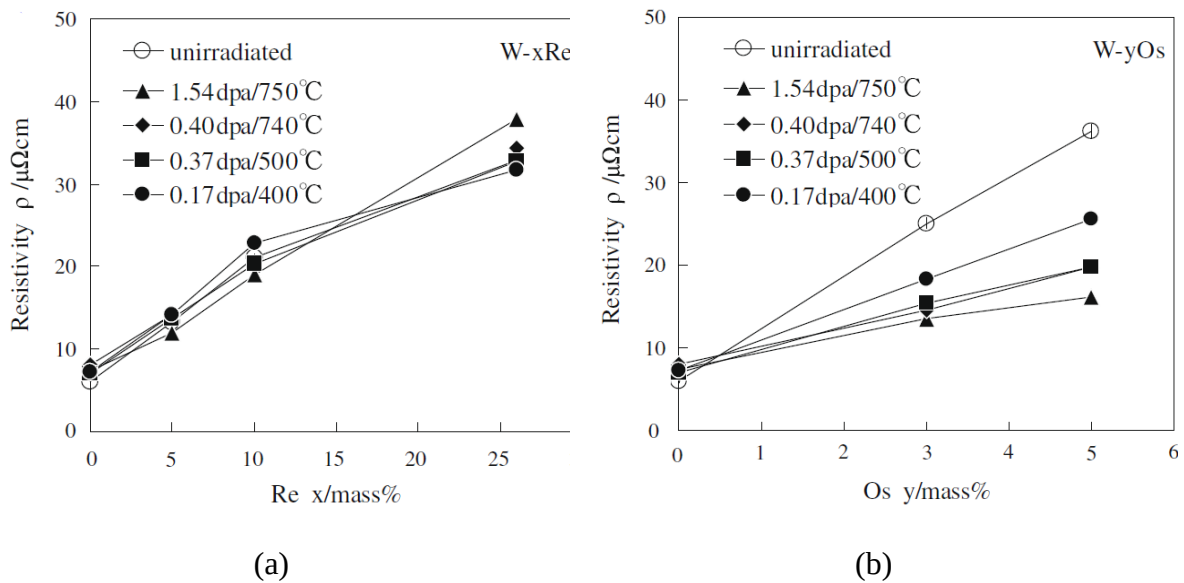


Figure 2.26 Electrical resistivity changes of W-Re (a) and W-Os (b) alloys after irradiation. Figure sourced from [41].

A study on tungsten-based model alloys, alloyed with rhenium and osmium, to simulate the transmutation effects of neutron irradiation, demonstrated a clear increase in the electrical resistivity of the metals, with the increase in alloying content, as seen in Fig. 2.26 from [41]. This indicates a decrease in the thermal conductivity with the increase in rhenium and osmium

content in the tungsten lattice. It is observed here that the addition of rhenium contributes to the degradation of the thermal conductivity rather than countering it, as was seen in swelling and the BDTT. It is also noticeable that for the higher dose irradiation (1.54 dpa) on rhenium alloyed tungsten, given by the triangle markers in Fig. 2.26 (a), that the increase in resistivity with alloying content hasn't saturated by 25 % rhenium content by mass, unlike the lower dose cases. However more data points at larger rhenium levels would be required to make a definitive conclusion of this. The fact that studies predict rhenium concentrations of only ~4% after even 5 years of operation hasn't motivated studies into such effects at higher rhenium concentrations [40].

The effect of helium ion implantation on the thermal conductivity of tungsten is evident from Fig. 2.27 [24]. Helium implantation levels even as low as 280 appm, cause significant reductions in the thermal diffusivity. Fig. 2.28, sourced from [129] shows a similar trend where the helium ion exposure has caused a significant deterioration of the thermal conductivity of bulk and thin film tungsten. The samples were exposed to 2×10^{24} ions/m² with energies of ~60 eV at ~438 K.

The mechanism for this degradation is believed to be due to the fact that helium ions can bind to vacancies and SIA's within the tungsten matrix, which act as scattering centres for the electrons that mediate thermal transport. At the surface, the fuzz and blister formation can also significantly affect thermal conductivity at the macro-scale. We expect a similar effect in deuterium implanted tungsten, given the structure modification observed due to deuterium infusion as sampled in section 2.1.2 and their effects on material properties such as hardening.

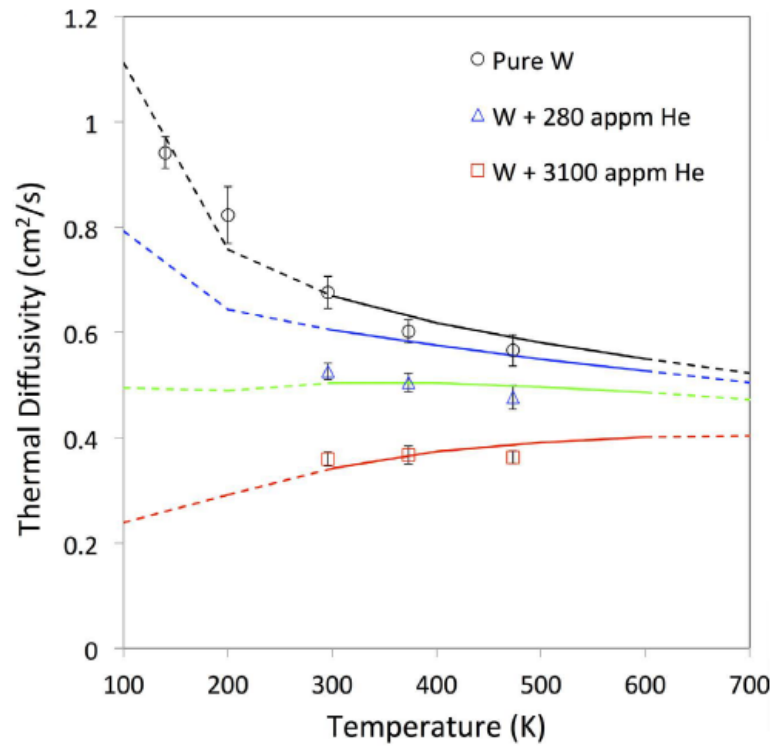


Figure 2.27 Measured thermal diffusivity in pure and helium implanted tungsten (markers). Solid lines indicated modelled data and dotted lines mark extrapolated data. Figure sourced from [24].

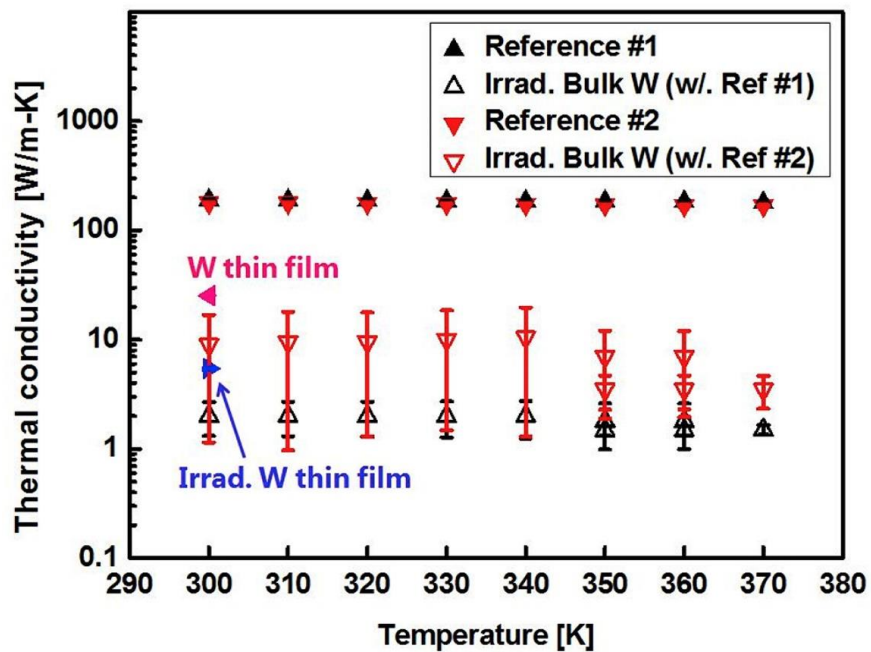


Figure 2.28 Thermal conductivity of tungsten bulk and thin films exposed to low energy helium plasma (~60 eV). Figure obtained from [129].

From reviewing literature for studies on displacement damage effects on the thermal conductivity of reactor materials, it is observed that extensive studies have been performed to investigate the effects of irradiation on the thermal conductivity of fission reactor uranium dioxide [130–133]. However since uranium dioxide is a ceramic, it has predominantly phonon mediated thermal transport and thus may not aid the understanding of the thermal transport degradation in tungsten. The phonon contribution to thermal transport in tungsten is small when compared to the electronic contribution.

Studies of irradiation effects on the thermal conductivity of steels and zircaloy could be useful in this regard. Irradiation effects in steels were studied extensively due to their usage in reactor pressure vessels and as fuel cladding in many fission reactor designs, and likewise zircaloy is used in fuel cladding. Experimental studies [134,135] have revealed significant decreases in the thermal conductivity, of both steels and zircaloy, upon irradiation, as evident in Fig. 2.29.

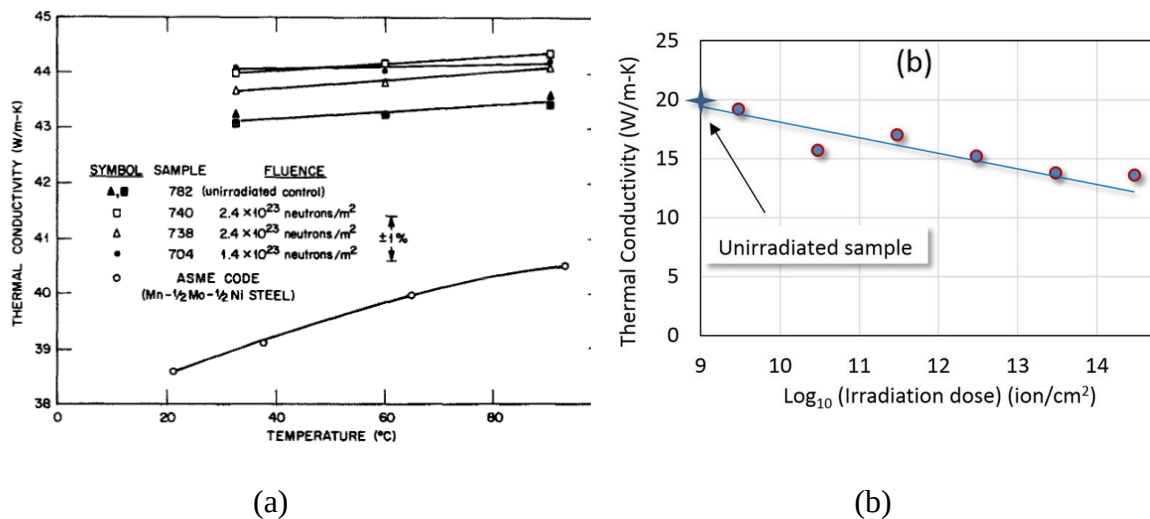


Figure 2.29 Effect of irradiation on the thermal conductivity of RPV steels (a) and zircaloy (b), with temperature. Figure (a) sourced from [135] and (b) from [134].

Only a few studies have attempted to investigate the effect of irradiation on the thermal conductivity of tungsten. Fig. 2.30 sourced from [14], shows the effect of neutron irradiation at low doses on the thermal conductivity of tungsten. Sufficient data is not available to calculate the damage level in dpa, and only the neutron fluences are available. The thermal and fast

neutrons fluences experienced by the samples were $\sim 1 \times 10^{20}$ and $\sim 3 \times 10^{19}$ n/cm² respectively, at ~ 330 K. Thermal conductivity is observed to decrease with irradiation as expected.

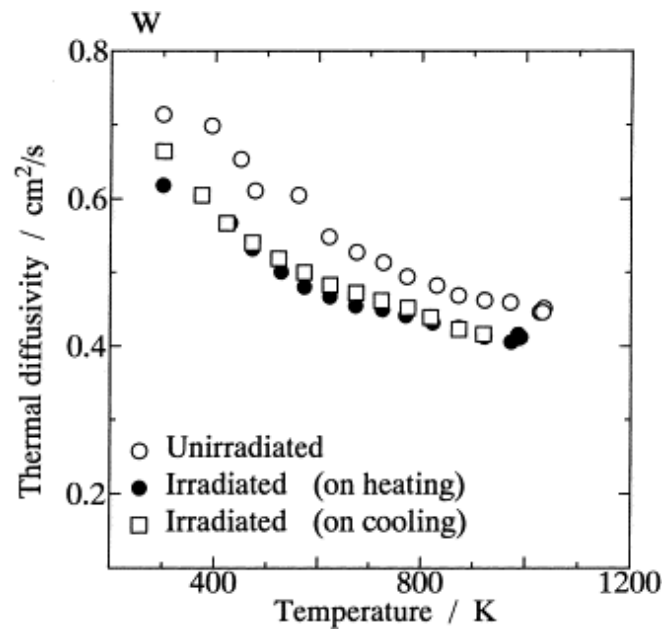


Figure 2.30 The variation of the thermal conductivity of neutron irradiated tungsten with temperature for tungsten. Figure sourced from [14].

Other more recent studies on the thermal conductivity degradation in neutron irradiated tungsten have also indicated at reductions due to irradiation. Fig. 2.31 from [3] shows the thermal conductivity degradation in tungsten exposed to neutrons under ITER conditions up to 0.1 and 0.6 dpa at 200 °C. It is quite noticeable that the room temperature thermal conductivity significantly decreases with irradiation.

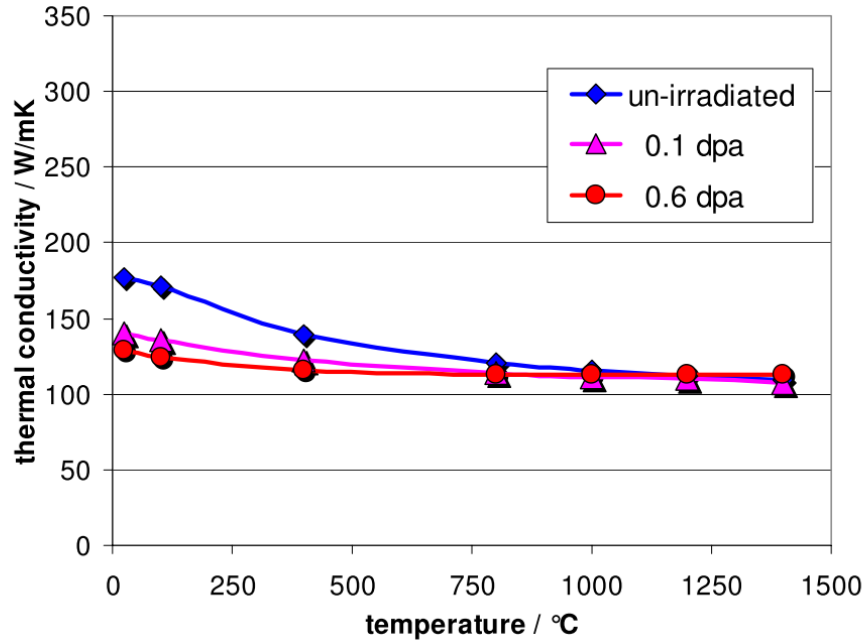


Figure 2.31 Thermal conductivity of pristine and neutron irradiated tungsten up to 0.1 and 0.6 dpa at 200°C. Figure obtained from [3].

Similarly, for tungsten irradiated with spallation neutrons and protons up to 5.8 dpa, at an irradiation temperature of ~100-150 °C, a significant decrease in the thermal diffusivity can be observed as seen in Fig. 2.32 from [136]. It should be noted that the authors in [136] report helium concentrations of up to 245 appm in the irradiated samples. This helium concentration can also contribute towards the thermal diffusivity degradation as observed in [24]. Also in the study, samples that were irradiated to higher doses were left out, since the activity of the samples was too high for manual handling and measurement.

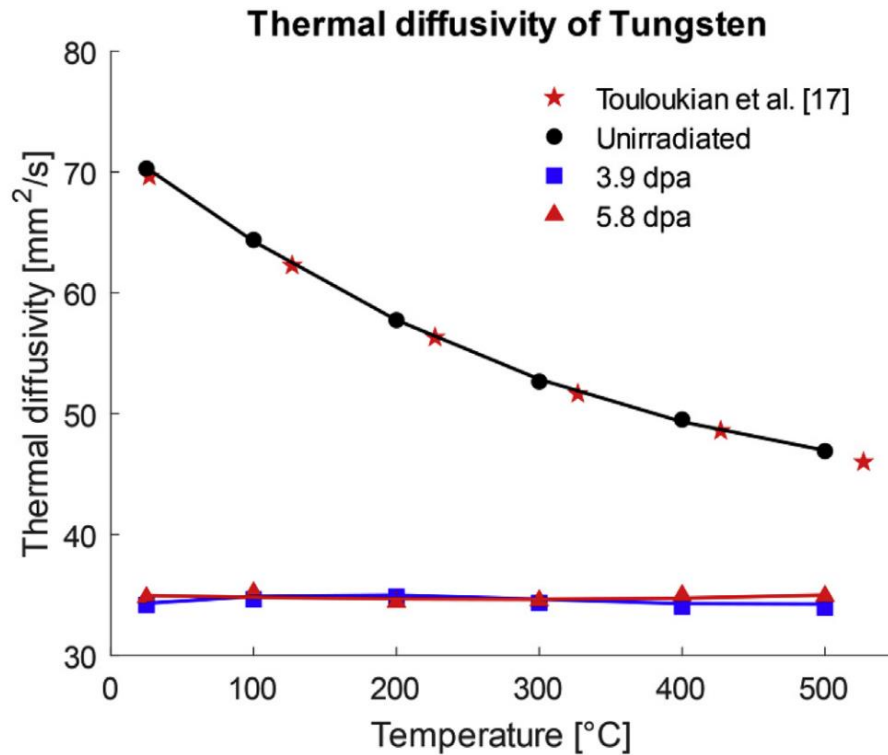


Figure 2.32 Thermal diffusivity of pristine tungsten and tungsten irradiated with spallation neutrons and protons up to 5.8 dpa at $\sim 150^{\circ}\text{C}$. Figure obtained from [136]. Also in the figure is data for unirradiated tungsten from the NIST standard [137].

Due to the issue of activated samples and the presence of transmutation products in neutron irradiated tungsten, ion-implantation is used as a proxy to mimic the displacement damage caused by neutrons. Fig. 2.33 from [138] shows the thermal conductivity of tungsten implanted with copper ions up to 0.2 dpa at room temperature. Cu ions at 500 keV, 2 MeV and 5 MeV had been utilised in order to obtain a reasonably flat damage profile. A significant decrease can be observed in this case too. However questions can be raised if the presence of the Cu ions as interstitials will introduce additional effects that need to be considered. Hence, where possible, self-ions should be preferred for such ion-implantation studies.

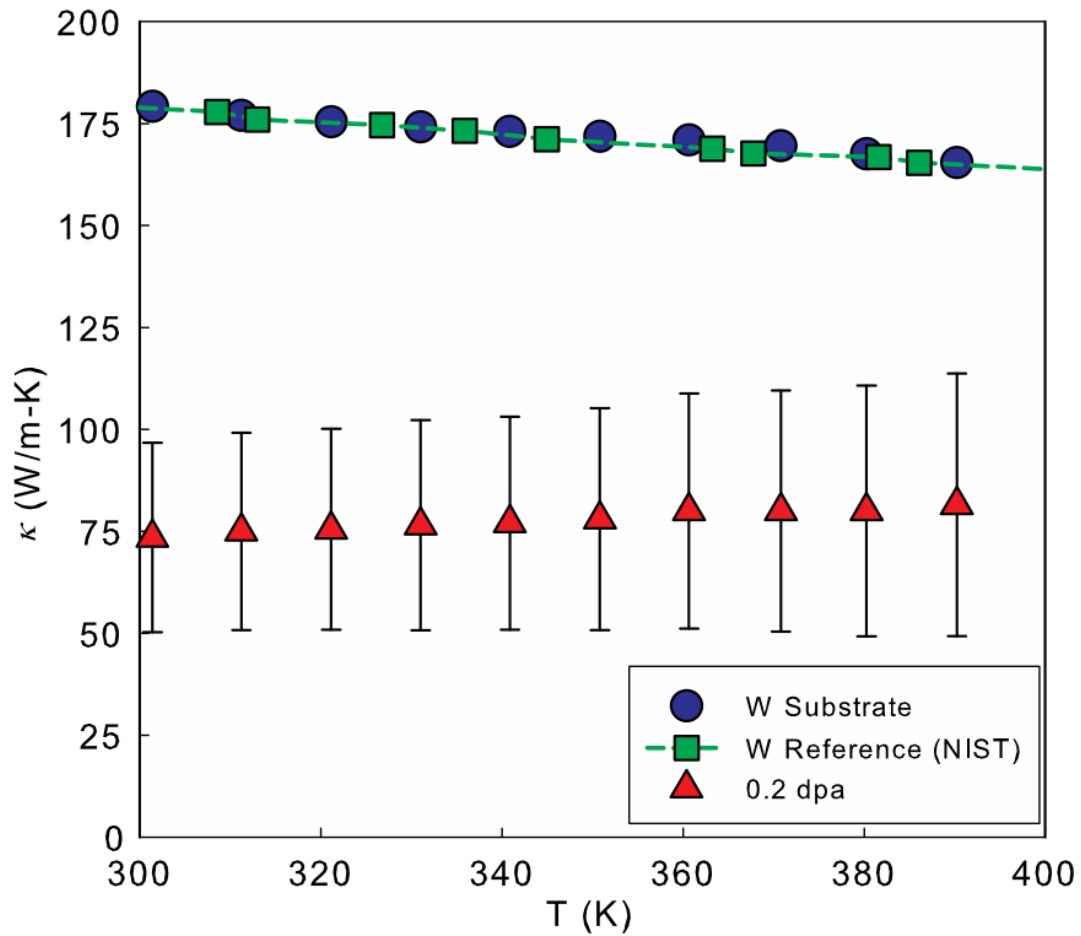


Figure 2.33 Thermal conductivity of pristine and Cu-ion implanted tungsten at 0.2 dpa. Ion implantations were at room temperature. Figure obtained from [138] with NIST reference data from [137].

The only study available in the literature on the thermal conductivity degradation studied via tungsten self-ion implantation is summarised in Fig. 2.34 from [23]. Tungsten exposed to Cu-ions, as well as samples exposed to W ions at 300 K and 1000 K with 0.2 dpa have been studied. At 0.2 dpa, the sample implanted at 300 K shows a significant degradation in its thermal conductivity. There doesn't seem to be a noticeable difference between samples implanted by Cu or W ions as long as the implantation temperature and damage level is the same.

However, the dose resolution, large error bars, and the number of data points seem to be inadequate in order to extract firm conclusions from this study. This leads to one of the motivations of our study, where the TGS method allows for lesser uncertainty than the 3-omega

method used [23]. This is due to the fact that TGS can probe within the few micron thick implanted region [24] unlike the 3-omega method [138]. The 3-omega method and the sources of its uncertainties is discussed in further detail in section 2.4.3. In our study we consider 13 damage levels which gives greater resolution in dose, and also investigate if the presence of these implanted interstitials have an effect on the thermal diffusivity degradation.

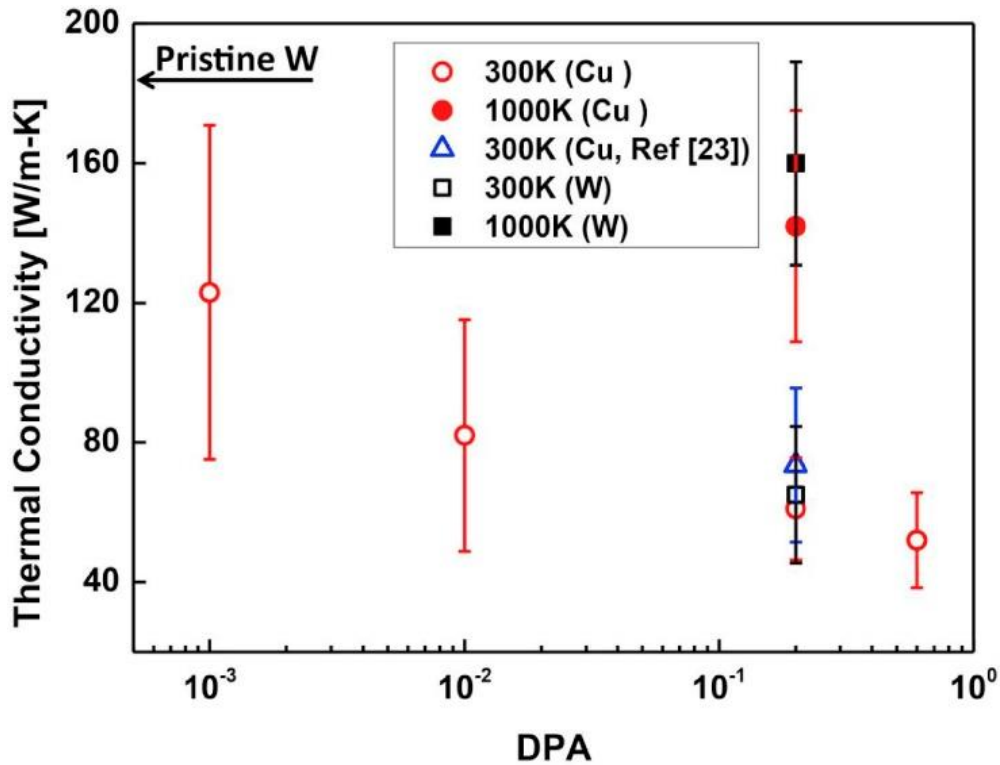


Figure 2.34 Thermal conductivity of tungsten implanted with Cu ions as well as those implanted with W self-ions at 300 and 1000 K. Figure obtained from [23]. The reference data given by the blue markers is from the study [138] also given in Fig. 2.31.

A thorough scrutiny of literature, did not reveal any further comprehensive experimental studies on the effect of irradiation on the thermal conductivity of tungsten. A phase-field modelling study of tungsten [139], was able to predict a decrease in the thermal conductivity of polycrystalline tungsten, with increasing porosity, as seen in Fig. 2.35. The study also reveals a decrease in thermal conductivity with the decrease in grain size.

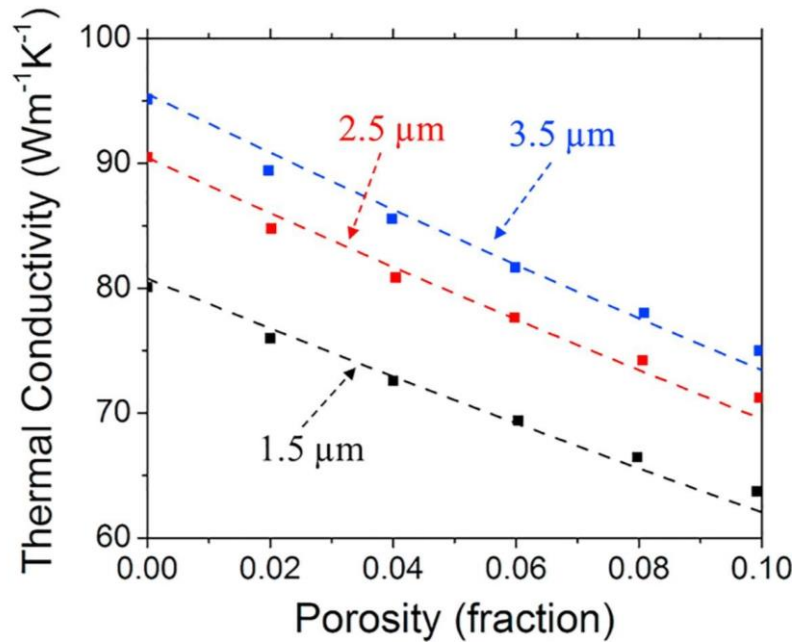


Figure 2.35 The simulated change in the thermal conductivity of tungsten, with the level of porosity. Symbols denote the simulation results and dashed lines represent theoretical predictions. Figure sourced from [139].

The studies obtained from literature, are either only for a narrow range of temperatures or damage doses. They have indicated a general decrease in the thermal conductivity upon irradiation, but haven't investigated the individual contributions of the various types of material damage. A key reason for this is the difficulty in obtaining neutron irradiated tungsten samples. This study will utilise self-ion implanted tungsten to investigate the effect of the damage cascades created by irradiation. Deuterium implanted tungsten will be used to study the effects that the deuterium infusion into the tungsten components has on its thermal properties. This effectively will cover a major part of the effect of neutron irradiation on thermal transport, through proxies.

However the challenge that lies when using ion-implanted samples is that most of the damage is in a thin layer near the surface $< 2 \mu\text{m}$. Hence the thermal transport has to be measured accurately within a very thin surface layer. This is quite difficult and only has recently become possible using either the 3-omega technique, time domain thermo-reflectance, or transient grating techniques.

2.3 Crystal defect density measurement and prediction techniques

There exist quite a few methods for quantifying irradiation damage in metals. They can be experimental techniques such as transmission electron microscopy (TEM), positron annihilation lifetime spectroscopy (PALS), electrical resistivity measurements and lattice swelling measurements using X-rays, or modelling techniques such as molecular dynamics (MD) simulations. Each technique has been built and tailored to different requirements, and has drawbacks as well as advantages. In this section the most common methods used to study radiation damage in tungsten are reviewed.

2.3.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) has the capability of imaging down up to clusters of atoms. It is useful in imaging medium and large defect clusters that may be in the form of dislocations loops or voids. Hence it has been used extensively for characterising irradiation damage including numerous studies on such damage in tungsten [21,72,78,126,140].

The method relies on the preparation of thin foil samples, usually < 100 nm thick, which are then irradiated/implanted and imaged using the TEM. Visual identification of defects are then required which tend to be quite time consuming if quantitative data on defect populations are required. Recently, machine learning techniques have been developed in order to automate this process, but are still work in progress [141,142]. Nevertheless, TEM has continued to be the most common method used for the characterisation of irradiation induced defects in nuclear materials.

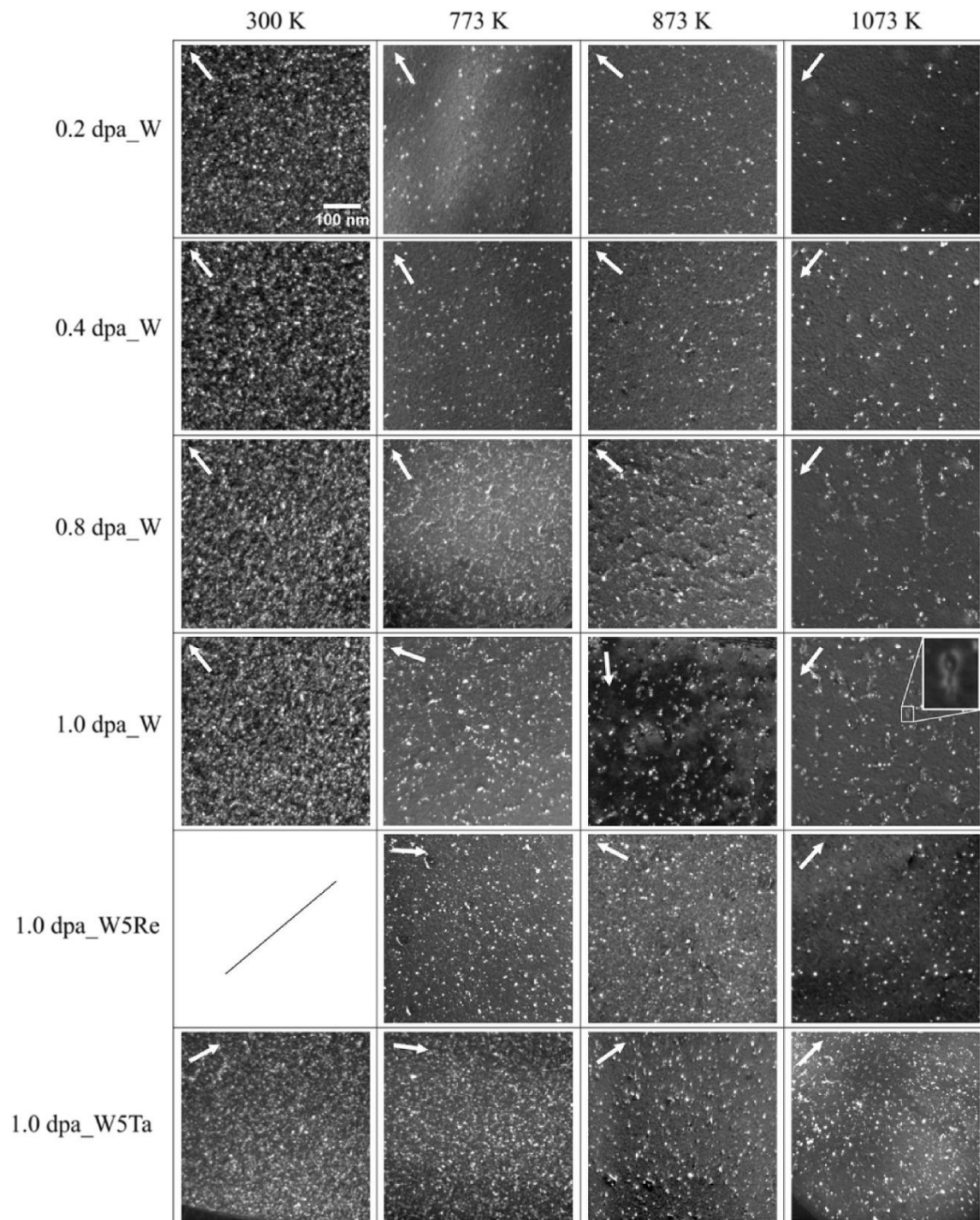


Figure 2.36 In-situ TEM images depicting dislocation loops in tungsten, tungsten-5 rhenium, and tungsten –5 tantalum for various damage doses and irradiation temperatures. Figure obtained from [21].

Incorporation of TEM's into implantation beamlines provide the additional capability of in-situ characterisation of crystal defects, as seen in Fig. 2.36 from [21] for self-ion irradiated tungsten and tungsten alloys. The annealing kinetics of crystal defects can also be studied using

TEM with the inclusion of in-situ heating capabilities. Fig. 2.37 from [126] shows the evolution of defect loops in self-ion irradiated tungsten at high temperatures.

The drawbacks of TEM have been the time consuming nature of the sample preparation required, and analysis of TEM images. Also there exists a limit in the sensitivity where defect structures smaller than ~ 1.5 nm do not provide enough contrast to be imaged accurately [143]. This makes TEM unsuitable for imaging point defects and small clusters.

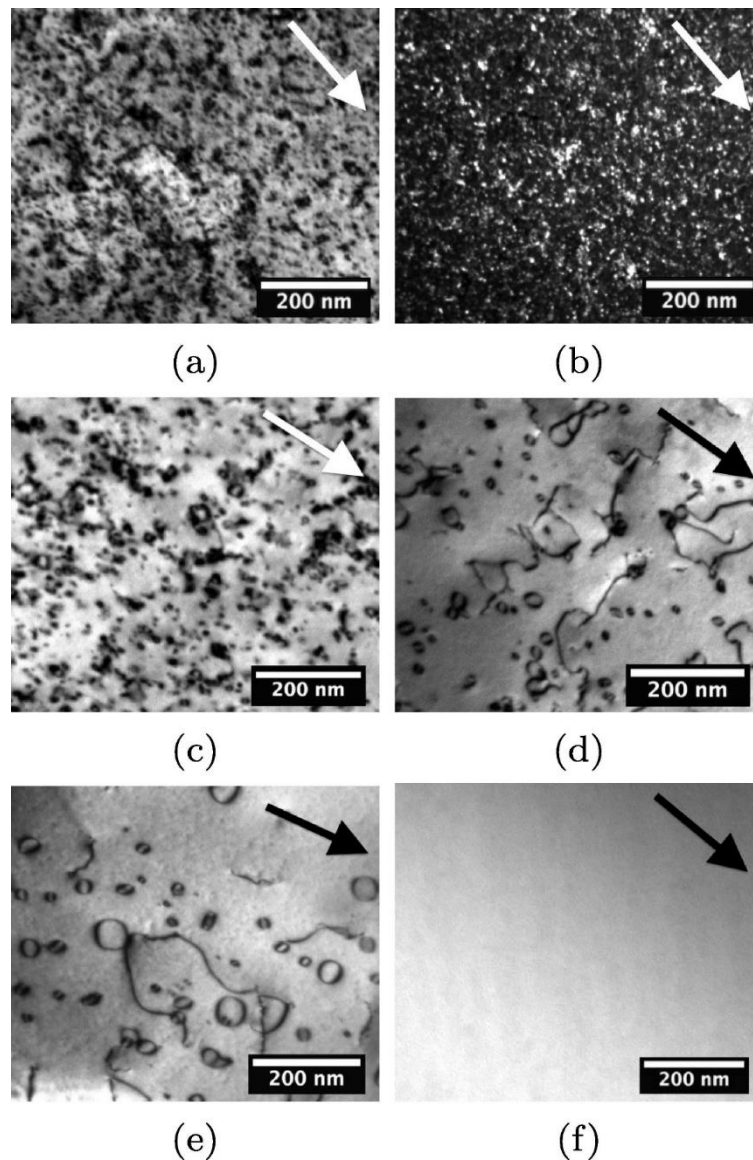


Figure 2.37 TEM micrographs depicting damage microstructures in self-ion implanted tungsten irradiated to 1.5 dpa at 500 °C. (a) – as irradiated bright-field image, (b) – as-irradiated dark-field image, (c) - annealed at 800 °C for 1 h, (d) – 950 °C for 1 h, (e) – 1100 °C for 1 h, and (f) – 1400 °C for 1 h. Image obtained from [126].

2.3.2 Molecular Dynamics Simulations

Molecular dynamics simulations have proven useful for predicting defect populations at the atomic scale [13,60,144]. Interactions between the atoms are modelled using interatomic potentials, such as the ZBL potential [145] and other modified potentials for tungsten [146,147]. Such potentials are derived from density-functional theory and electronic structure calculations. The reliability of the results obtained heavily depends on the potentials used since these represent the real-world physical interactions taking place in the material. Energetic PKA's can be introduced into the simulation box and the evolution of the system is studied. Fig. 2.38 from [59] shows typical final-state configurations of the damage created by energetic collision cascades in tungsten foil, simulated using MD.

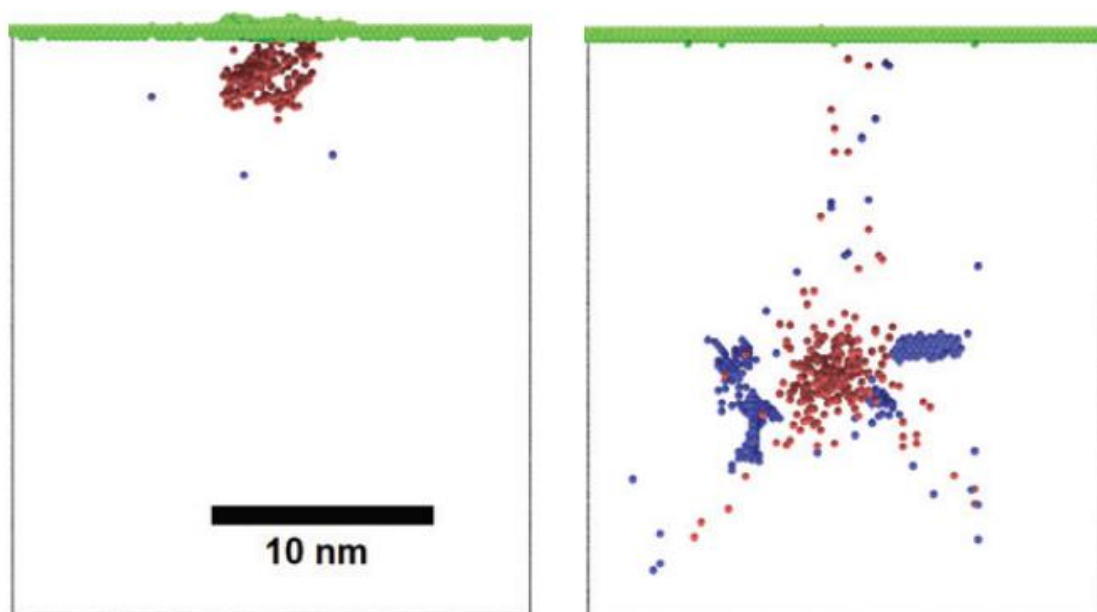


Figure 2.38 MD simulation results for tungsten foil subjected to 30 keV (left) and 150 keV (right) collision cascades. Red spheres denote vacancies, blue are interstitials and green are surface atoms. Figure obtained from [59].

MD simulations however do possess a few drawbacks when used for studying irradiation-induced defects. Significant computing power is required for simulations, and this places a limitation on the time length that can be simulated ($\sim$ ns). This doesn't allow for the annealing,

annihilation or diffusion processes, i.e. the third stage of defect evolution to be simulated. It is in this third stage that larger defect clusters form. Hence, MD cannot be used to study the formation and behaviour of larger defect clusters or the long-range migration of defects. Kinetic Monte-Carlo (KMC) techniques are used to model this evolution stage of cascade damage [63,148].

Fig. 2.39 from [59] shows the defect sizes simulated by MD for self-ion collision cascades in tungsten, superimposed with the defect sizes for similar self-ion cascades imaged using TEM from [21]. The MD simulations cover the smaller defect sizes that TEM is unable to image. TEM on the other hand captures the medium and large defects.

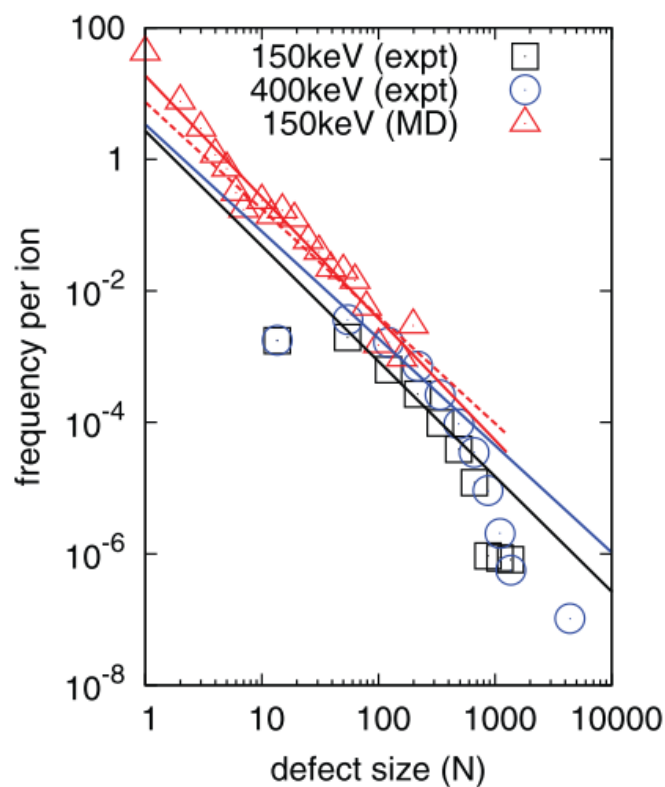


Figure 2.39 Histogram of defect size obtained from MD simulations (red) and imaged using TEM from experiments (black / blue). The histograms are normalised to account for the total number of defects counted. Figure obtained from [59].

2.3.3 Electrical Resistivity Measurements

Crystal defects that scatter electrons and hinder their motion within the metal, affect the thermal transport and also the electrical resistivity [149]. Hence the increase in electrical resistivity due to the presence of crystal defects can be used to gauge the quantity of crystal defects in the material [150–152]. This method however is well established for electron and neutron irradiated samples, which have a more uniform and macroscopic damaged region than ion-implanted materials [151]. Electrical resistivity measurements are also sensitive to both interstitials and vacancies, since both types of defects can scatter electrons, similar to thermal diffusivity measurements. For a material decorated with interstitials and vacancies, the change in resistivity is given by

$$\Delta\rho = \rho(T) - \rho_o \quad (2.1)$$

where $\Delta\rho$ will have the contribution from interstitials $\Delta\rho_i$ and from vacancies $\Delta\rho_v$, given by equation 2.2.

$$\Delta\rho = \Delta\rho_i + \Delta\rho_v \quad (2.2)$$

Both components of the resistivity degradation will depend on the change in resistivity per unit defect r_x , which depends on the defect type x , and the concentration of that defect type N_x , as shown in eqns. 2.3 and 2.4.

$$\Delta\rho_i = N_i \times r_i \quad (2.3)$$

$$\Delta\rho_v = N_v \times r_v \quad (2.4)$$

By combining equations 2.1-2.4, and making reasonable assumptions, the defect densities can be extracted from the electrical resistivity measurements.

Electrical resistivity measurements were used extensively to indirectly quantify radiation induced defects in tungsten prior to the availability of TEM's [153–155]. The uncertainty in the probing depth is an issue when measuring thin ion-implanted layers using this technique.

2.3.4 Positron Annihilation Lifetime Spectroscopy (PALS)

Low energy positrons injected into a metal, annihilate through interactions with electrons, emitting gamma rays that can be detected. When vacancy, or vacancy clusters exist in the matrix, essentially there is a region missing a positively charged ion and it can accommodate a positron for a small time period more than usual, ($\sim$ ns), before it annihilates by interacting with an electron. This is long enough for the delay to be detectable, i.e. allowing us to study the vacancy population in a metallic sample [140,151,156,157]. Recent studies combine TEM with PALS to investigate the defect populations in irradiated tungsten [158,159]. In these studies, PALS was able to detect the presence of vacancy clusters, small and large, and TEM was able to then image the larger voids. PALS is proven to be useful in detecting TEM invisible voids and works for ion-implanted as well as neutron irradiated samples. PALS has also been included in ion-irradiated beamlines, allowing for in-situ studies of vacancy type defects [160,161]. The drawback of this technique is that it is insensitive to interstitial type defects and only gives an indication of the presence of vacancies.

2.3.5 Lattice Swelling

As discussed in section 2.2.3, crystal defects such as interstitials and vacancies can cause the swelling of the lattice at the nano and micro scales. Interstitials possess positive relaxation volumes, and vacancies negative, giving lattice swelling and contraction respectively [116]. Changes in these lattice spacing due to such effects can be detected by X-ray diffraction measurements [27,116,162]. However, X-ray diffraction detects the integral effect of both, microscopic lattice swelling due to interstitials and contraction due to vacancies. This then

provides a lower bound estimate of the defects present in the material. Lattice swelling measurements work well for neutron irradiated materials as well as ion-implanted materials with thin surface damage layers. This is due to the fact that the probing depth can be adjusted by varying the angle of incidence of the X-rays on the sample. Techniques also exist for deconvolution of the signal as a function of depth at the detector [116].

2.4 Thermal conductivity measurement techniques

There are many techniques for measuring the thermal transport properties of materials. These methods can be classified based on the time dependence of the thermal response and the heating method. Considering the time dependence of the response, the methods can be classified as steady state methods or transient methods [163].

The heating method can be contact-heating or non-contact heating. Contact heating is utilised in methods such as scanning thermal microscopy [164,165] and the 3-omega method [166]. Non-contact heating usually utilises the heat absorbed from incident radiation. Methods such as the laser flash method [167,168], time-domain thermo-reflectance [169,170] and the transient grating method [29–31], utilise this approach.

The key advantages of non-contact measurements are that the risk of damaging intricate samples is reduced and the issue of contact resistance is avoided. This also simplifies sample preparation, since in most cases, a relatively flat sample surface is adequate. However the drawback is that it is difficult to quantify the amount of heat absorbed by the sample. Hence thermal diffusivity, rather than thermal conductivity is generally measured. The density and specific heat of the material are then required to calculate thermal conductivity. These material properties can be determined by well-established methods such as differential scanning calorimetry for the specific heat capacity and pycnometry for the density.

In the following, methods most commonly used for studying thermal transport properties of irradiation-damaged samples are reviewed in more detail.

2.4.1 The Laser Flash Method

The laser flash method is currently the main technique used for measuring the thermal conductivity of bulk materials, especially above room temperature [14,163,167,168]. The sample is heated on one side by a laser pulse, and the temperature response at the other side is measured by an infrared camera or a thermocouple. This makes it a straightforward process for measuring bulk samples. However it is not the ideal method for measuring layered samples such as thin films or irradiated samples. It has however been used for measuring thin films on substrates [171,172], but it requires a heat conduction model [173] to de-convolve the substrate and thin film conductivities. For very thin surface layers, such as those associated with ion-implantation, it lacks sensitivity. Also the laser flash method only measures out-of-plane thermal diffusivity. Fig. 2.40 adapted from [163,167] shows a basic schematic of the procedure and the temperature response recorded by the thermometer at the rear, from which the thermal diffusivity is extracted.

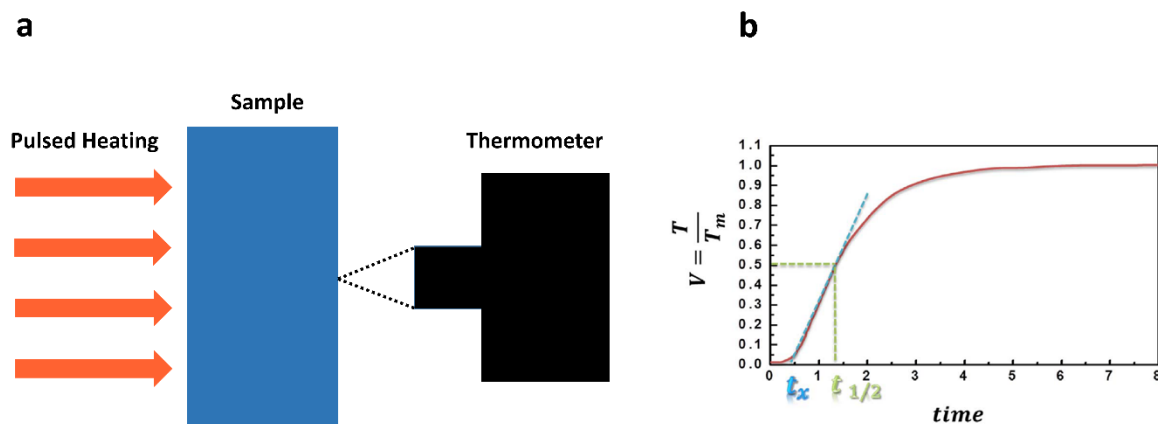


Figure 2.40 The laser flash method for the determination of thermal diffusivity. (a) schematic of the method, and (b) is the normalised temperature response recorded at the rear, from which the samples's thermal diffusivity is extracted. Figure adapted from [163,167].

Eqn. 2.5 shows the half-rise time method [167] to extract the thermal diffusivity of the sample from the temperature reading at the back. The thermal diffusivity ' α ' is given by

$$\alpha = \frac{L^2}{\pi^2 t_{1/2}} \quad (2.5)$$

where ‘L’ is the thickness of the material, and $t_{1/2}$ is the time taken for the rear of the specimen to reach half the maximum temperature.

2.4.2 Time Domain Thermo-reflectance

The time domain thermo-reflectance (TDTR) method is one of the preferred methods for measuring the thermal conductivity of thin films on substrates [169,170]. It is inherently a pump-probe technique, since it relies on the heating of the sample surface by a pulsed laser. This creates a local temperature increase, which causes an increase in the surface reflectivity. The change in intensity of a reflected probe laser, off the same spot is then used to obtain the change in the surface reflectivity due to this heating. By assuming the change in reflectivity to be proportional to the temperature change, analysing the reflectivity response of the material, the thermal response and hence the thermal diffusivity can be obtained.

This method is efficient for the measurement of thin films, since the heating and probing are from the same side of the sample and is also non-contact. However it requires that the thermo-reflectance coefficient, which is the proportionality coefficient between the surface reflectivity and temperature, be sufficiently high at the probing wavelength.

Also certain materials such as tungsten do not exhibit large changes in surface reflectivity with temperature, whereas aluminium does. In practise, almost always an aluminium layer is deposited on the sample surface to act as a transducer for the measurement, since it has a large thermo-reflectance coefficient. However, the introduction of this layer, brings back the problem of contact/boundary resistance. So the efficiency of the thermo-reflectance method varies, depending on the material and intended usage [163]. Fig. 2.41 from [174] shows the

typical setup for TDTR measurements in thin films and bulk materials, and the schematic of a typical TDTR setup.

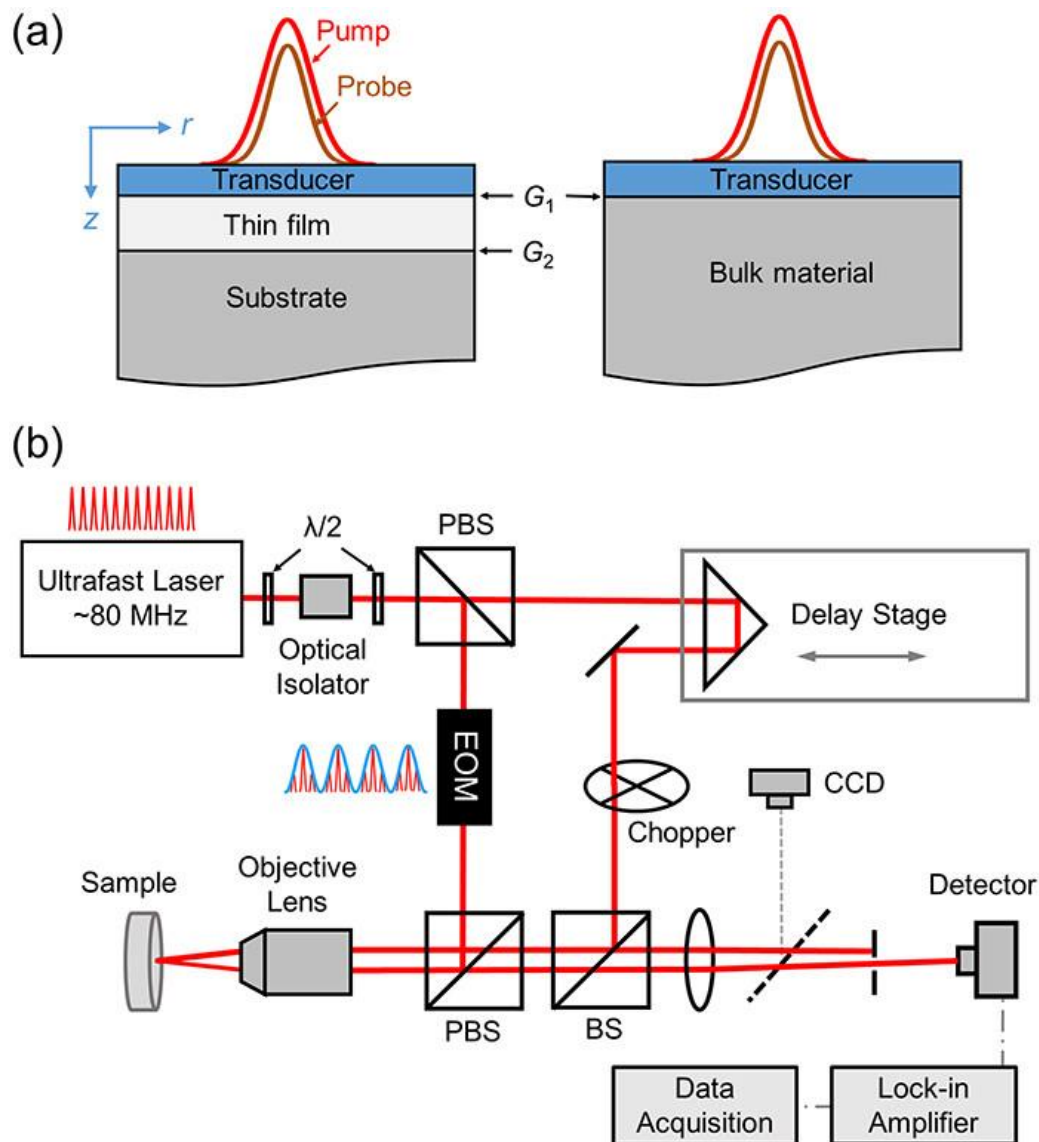


Figure 2.41 Typical sample configurations for thin films and bulk material measurements using TDTR (a) and schematic of a TDTR setup (b). Figure obtained from [174].

The equations used for analysis and extraction of the thermal diffusivity for the thermoreflectance method can be done in the time domain as well as the frequency domain. This is available in detail in [175].

2.4.3 The 3-omega method

The 3-omega method is a frequency domain method for measuring the thermal conductivity, developed by Cahill [176]. It requires the attachment of metallic strips that act as heaters and thermometers on the sample surface. The metallic strips attached to the sample are used to heat the sample in a periodic manner. As the temperature of the sample increases, this increases the temperature of the metallic strips too, and increases their electrical resistivity and vice versa. Adjusting the frequency of the periodic heating signal allows for control of the probing depth. This has turned out to be useful in terms of measuring thin films [177,178] and samples with thin ion-irradiated layers [138]. Fig. 2.42 from [138] shows an illustration of the setup for the thermal conductivity measurement of ion-irradiated tungsten, and an image of it from an SEM.

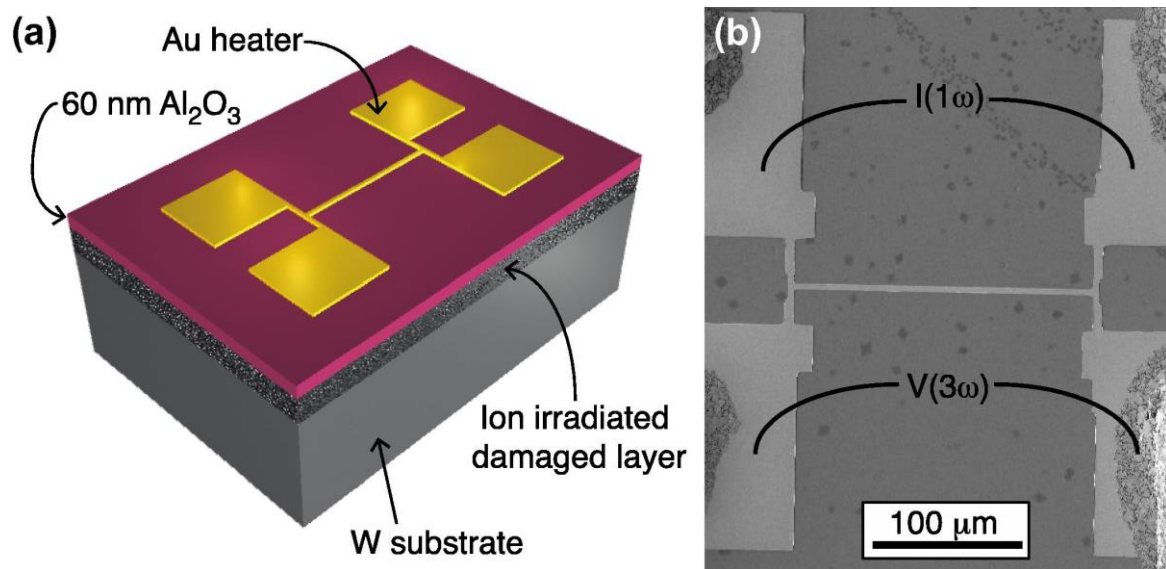


Figure 2.42 Diagram of a 3-omega device used for measuring the thermal conductivity of a thin ion-irradiated layer on tungsten - (a). An electrically insulating alumina layer is used to shield the sample from the electrodes. (b) - SEM image of the setup on the W sample. Figure obtained from [138].

Advancements in micro machining and layer deposition techniques such as focussed ion beam (FIB) machining and deposition, allow for the preparation and deposition of smaller metallic contacts, further increasing the spatial resolution of the method ($\sim 10\text{-}100\text{ }\mu\text{m}$) [23,176]. A drawback of the method is the uncertainty introduced due to the extremely small temperature

drop across the thickness of the implanted layer when compared to the temperature drop across the bulk. In ion-implanted tungsten samples in [138], the temperature drop across the damaged layer (~ 0.36 K) was only 10% of the total temperature rise of the irradiated sample (3.6 K). Another drawback is the instability of the electrodes at higher temperatures (> 500 °C) [176].

2.4.4 Transient Grating Spectroscopy

Transient grating spectroscopy is a non-contact method for measuring the thermal diffusivity and surface acoustic velocity in thin near-surface layers of interest [29,31,32,179]. Since its initial development in the 1980s [180] it has been modified for several applications such as the study of thin-film semiconductors [31], microsphere lattices [181], superconductors [182] and many others [32]. Recently it has been used to study the thermal diffusivity in ion-implanted tungsten, since the probing depth can be matched quite well with the micron thick ion-implanted layers in tungsten [24].

In TGS, two coherent pulsed laser beams are crossed at the sample surface to give an intensity grating of a specified wavelength, as seen in Fig. 2.43 (a) from [24]. The sample surface absorbs this grating, and the resulting spatially periodic heating and thermal expansion gives a temperature and displacement grating at the sample surface. These gratings decay as heat flows from peaks to troughs and into the bulk, at a rate that depends on the thermal diffusivity of the material. A third continuous laser beam is diffracted off this “transient grating”, as shown in Fig. 2.43 (b) [24]. The decay of this diffracted beam’s intensity, can be fitted to obtain the thermal diffusivity. The elastic response of the sample to the spatially periodic excitation kicks off two counter propagating surface acoustic waves that superimpose an oscillation on to the TGS signal as seen in Fig. 2.43 (c). A detailed description of the basic TGS theory in a reflective geometry, used for opaque materials, is given below, largely obtained from [31].

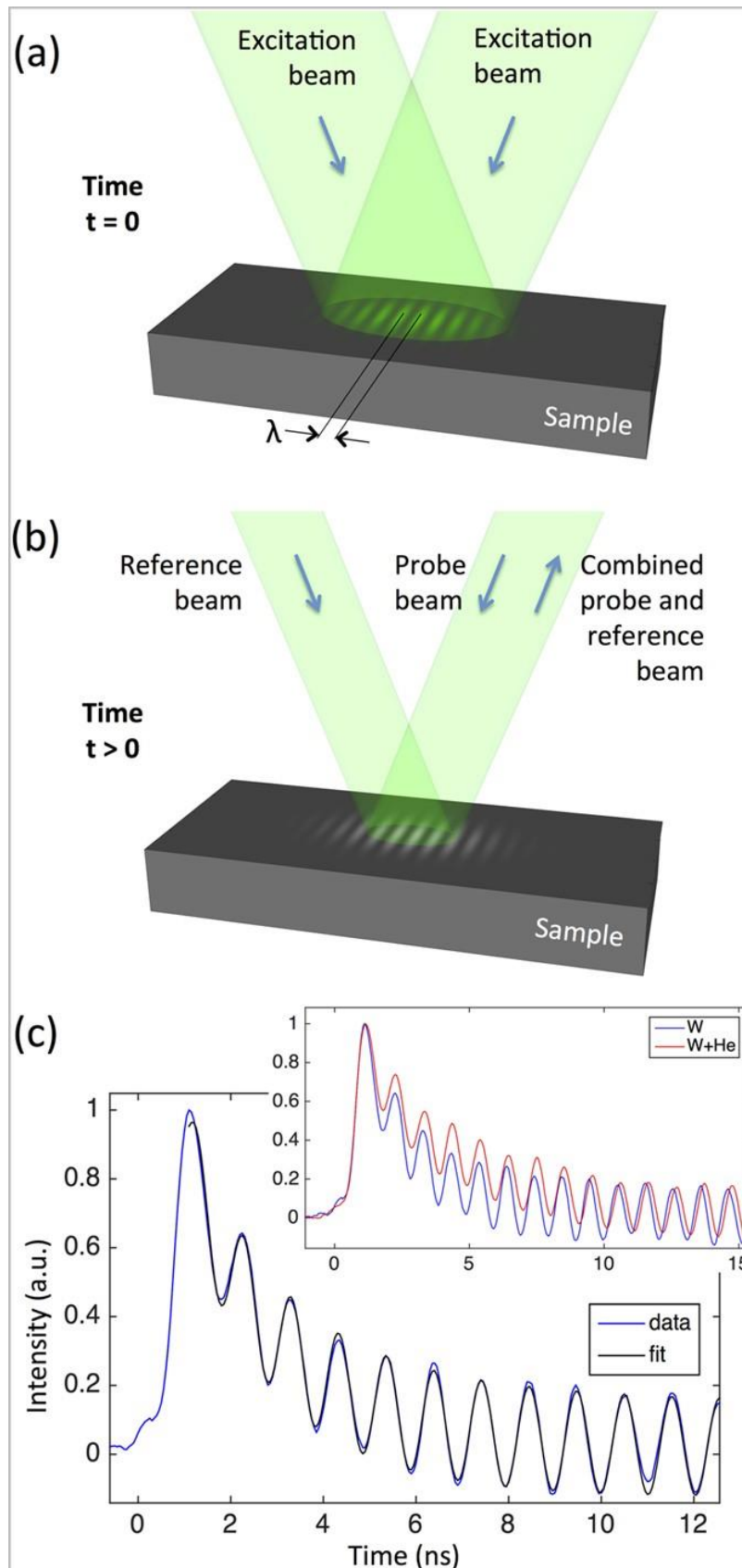


Figure 2.43 Typical excitation (a) and (b) detection mechanisms and sample trace with fit (c), in a TGS setup [24]. The inset in (c) shows traces from pristine and He ion implanted tungsten samples. Figure obtained from [24].

The crossing of the two pump beams of wavelength λ_e , gives the periodic intensity profile near the sample surface with fringe spacing given by

$$L = \frac{2\pi}{q} = \frac{\lambda_e}{2 \sin(\theta/2)} \quad (2.6)$$

where θ is the crossing angle of the beams at the surface and q is the transient grating wave vector, as seen in Fig. 2.43(a).

To generate the two crossed beams, a 4f imaging system is used to re-image a phase mask onto the sample. For a phase mask spacing of λ_0 , the grating spacing at the sample surface is given by

$$\lambda = \frac{M\lambda_0}{2} \quad (2.7)$$

M is the magnification ratio of the lens system, $M = f_2/f_1$ where f_2 and f_1 are the focal lengths of the lenses in the imaging system.

The surface displacement profile, i.e. the displacement grating, is responsible for the phase component in the signal. In a sample with isotropic thermal diffusivity, the decay of the surface displacement profile due to the temperature grating decay is given by [29]:

$$\frac{\partial u_z}{\partial x} \propto \text{erfc}(q\sqrt{\alpha t}) \quad (2.8)$$

where u_z is the sample surface displacement in the vertical direction, q is the transient grating wave vector, α is the thermal diffusivity and t is the time. The temperature grating is responsible for the amplitude modulation of the signal. The decay of the surface temperature profile, i.e. the temperature grating is given by [29]:

$$\frac{\partial T}{\partial x} \propto \frac{1}{\sqrt{t}} \exp(-q^2 \alpha t) \quad (2.9)$$

To investigate the TG signal components, the incident beams are considered as plane waves [31]. The optical fields of the probe and reference beams can be given as the following respectively.

$$E_P = E_{0P} \exp(i(k_P^2 - q^2/4)^{1/2}z - i(q/2)x - i\omega_P t + i\phi_P) \quad (2.10)$$

$$E_R = t_R E_{0P} \exp(i(k_P^2 - q^2/4)^{1/2}z + i(q/2)x - i\omega_P t + i\phi_R) \quad (2.11)$$

where E_{0P} is the initial probe beam amplitude, k_P is the optical wavevector, ω_P is the optical frequency of the probe beams, ϕ_P is the probe beam phase, ϕ_R is the reference beam phase and t_r is the attenuation factor of the reference beam from a neutral density filter.

Considering the grating as a small perturbation, the complex transfer function, which is the combination of the complex reflection coefficient and the phase change due to the surface displacement, is given from [31] by

$$t * (t) = r_0(1 + \cos(qx)[r'(t) + i(r''(t) - 2k_P u(t)\cos\beta_P)]) \quad (2.12)$$

where the dynamic complex reflection coefficient is given by $r^*(t) = r_0[1 + r'(t) + ir''(t)]$. r_0 is the constant reflectivity term, $r'(t)$ is the time varying coefficient of the real reflectivity component that gives rise to the amplitude modulation, and $r''(t)$ is the time varying coefficient for the imaginary reflectivity component that gives rise to the phase modulation. $u(t)$ is the surface displacement outwards, and β_P is the incidence angle of the probe beam on the surface.

For the +1 diffracted order of the probe beam, the optical field can be obtained by the product of the input field with the transfer function, which results in the following expression for the diffracted probe beam.

$$\begin{aligned}
E_{P(+1)} = & \frac{1}{2}r_0E_{0P}[r'(t) + i(r''(t) \\
& - 2k_P u(t)\cos\beta_P)]\exp(-i(k_P^2 - q^2/4)^{1/2}z - i(q/2)x \\
& - i\omega_P t + i\phi_P)
\end{aligned} \tag{2.13}$$

The diffracted probe on its own, called the homodyne signal, has the following expression for its intensity,

$$\begin{aligned}
I_{Hom} = & \frac{1}{2}R_0I_{0P}[r'^2(t) + r''^2(t) - 4r''(t)k_P u(t)\cos\beta_P \\
& + 4k_P^2 u^2(t)\cos^2(\beta_P)]
\end{aligned} \tag{2.14}$$

The zero order reference beam, has the same expression as a simply reflected one,

$$E_{R(0)} = r_0 t_r E_{0P} \exp(-i(k_P^2 - q^2/4)^{1/2}z - i(q/2)x - i\omega_P t + i\phi_R) \tag{2.15}$$

The reference and probe beams are collinear and hence their interference gives an intensity of the form

$$\begin{aligned}
I_S = & \frac{1}{2}R_0I_{0P}[t_r^2 + r'^2(t) + (r''(t) + 2k_P^2 u^2(t)\cos\beta_P)^2 + 2t_r(r'(t)\cos(\phi) \\
& - ((r''(t) - 2k_P u(t)\cos\beta_P)\sin(\phi))]
\end{aligned} \tag{2.16}$$

where I_{0P} is the intensity of the incident probe beam, $R_0 = |r_0|^2$ is the DC surface reflectivity, and $\phi = \phi_P - \phi_R$, the relative phase of the two beams, is the heterodyne phase.

When the reference signal intensity is much higher than the diffracted probe intensity, ($t_r \gg r', r'', k_P u$), the heterodyne signal intensity reduces to

$$I_{Het} = t_r R_0 I_{0P} [r'(t)\cos(\phi) - (r''(t) - 2k_P u(t)\cos\beta_P)\sin(\phi)] \tag{2.17}$$

By changing the heterodyne phase ϕ , to $0, \pm \pi$, the response will be only composed of the reflectivity/amplitude grating signal, and at $\phi = 0, \pm \pi/2$, it will have a mixture of the amplitude and phase grating. The phase grating is created by the surface displacements and the amplitude grating is created by the spatial and temporal variation of the surface reflectivity.

If we consider the signal in terms of incident beam intensities [30], we have the following expression for the time varying heterodyned signal $I_S(t)$

$$I_S(t) = I_R + I_P(t) + \sqrt{2I_R I_P(t)} \cos(\phi) \quad (2.18)$$

Obtaining signals at phases of 0 and 180°, and taking their difference, would effectively cancel out the first two terms in eqn. 2.18. This results in a signal of larger amplitude as follows

$$I_S^{Tot}(t) = I_S^0(t) - I_S^{180}(t) = 2I_R I_P(t) \quad (2.19)$$

Not only does this method amplify the signal, it also removes a significant amount of the systematic noise, giving a better signal to noise ratio (SNR). This technique is known as the dual heterodyne method [31,183].

The intensity of this dual heterodyne signal depends on the surface displacement and temperature profiles [29]. The proportion of this signal that arises from the surface displacement (phase grating) and temperature profile (amplitude grating) depends on the temperature coefficient of expansion and temperature coefficient of reflectivity of the material. Tungsten has a low temperature coefficient of reflectivity ~2-9% [184], and hence the TGS signal is predominantly the phase grating component, arising from the displacement grating. Hence the time-decay of the signal follows the expression in eqn. 2.8. Taking into account the SAW components and any background signal, the final expression used for the fit is given in eqn. 2.20, from [24]:

$$I = A \operatorname{erfc}(q\sqrt{\alpha t}) + C \sin(2\pi f t + E) \exp(-t/F) + G \quad (2.20)$$

where q is the transient grating wave vector and f is the SAW frequency. A and C are the proportionality constants for the thermal decay and SAW oscillations respectively, E is the initial phase offset of the SAW oscillations, F is the time constant for the decay in the SAW oscillations and G is the background in the signal.

The probing depth for the thermal diffusivity and SAW frequency is reported to be λ/π and $\lambda/2$ respectively, where λ is the grating period on the sample [29].

Overall, the advantages of the TGS method is the fact that it is non-contact, works for a wide range of temperatures and has a tuneable probing depth. Drawbacks include the complexity of the setup compared to laser-flash or 3-omega, and its sensitiveness to misalignments.

In an ion-implanted sample with reduced thermal diffusivity, the rate of decay of the signal would be less than for a pristine one. The inset in Fig. 2.43 (c) shows this effect, where for the He-ion implanted sample, the TGS signal persists for longer, than for the pristine tungsten sample. Fig. 2.44 shows the thermal diffusivity degradation of tungsten rhenium alloys and helium ion implanted tungsten, studied using TGS from [24]. The thickness of the helium implanted layer in Fig. 2.44 (b) was 2.6 μm , to which the TGS probing depth was matched.

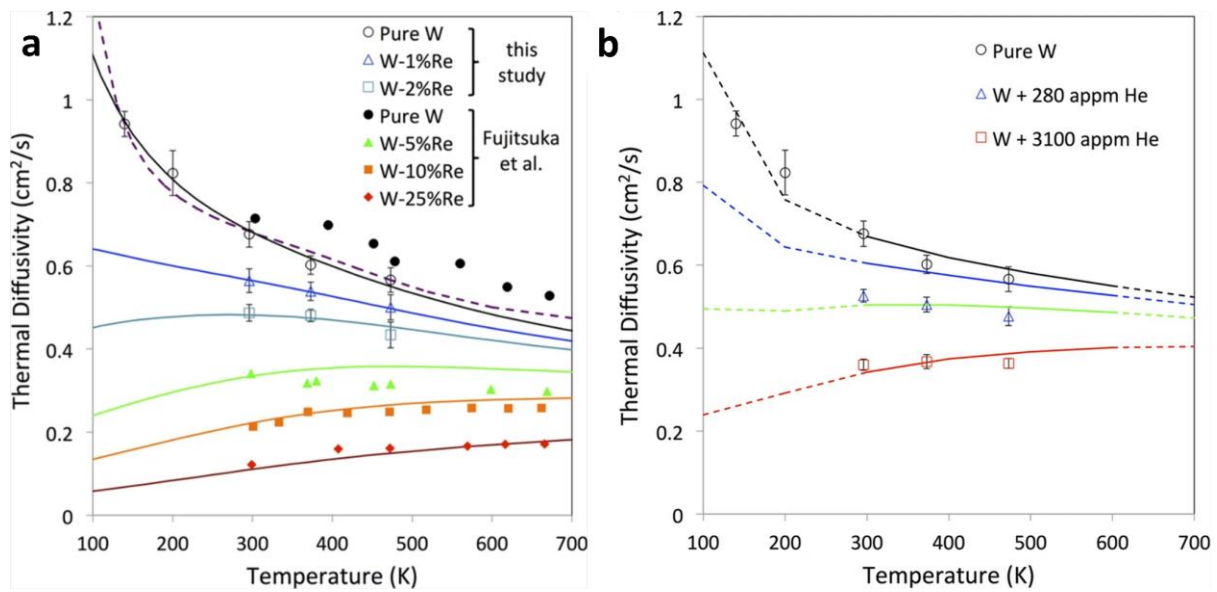


Figure 2.44 TGS plots of thermal diffusivity for tungsten-rhenium alloys (a) and helium implanted tungsten (b). Figure obtained from [24].

After the study in [24] demonstrated the usefulness of TGS in measuring the thermal diffusivity of ion-implanted samples, studies have been carried out to utilise this method for studying the

irradiation-induced degradation of the thermal diffusivity in various samples. Extensions were also carried out, to improve the time resolution [183] and add in-situ ion-implantation capabilities [185]. Fig. 2.45 from [185], shows the in-situ thermal diffusivity evolution in very low dose helium ion implanted tungsten (3 appm) at room temperature, and self-ion implanted nickel at 550 °C using TGS. The study in Fig. 2.46 used TGS to measure the thermal diffusivity degradation in single-crystal niobium [25]. It should be noted that the studies in Fig. 2.46 and 2.44 are quite recent, and have been published in just 2019.

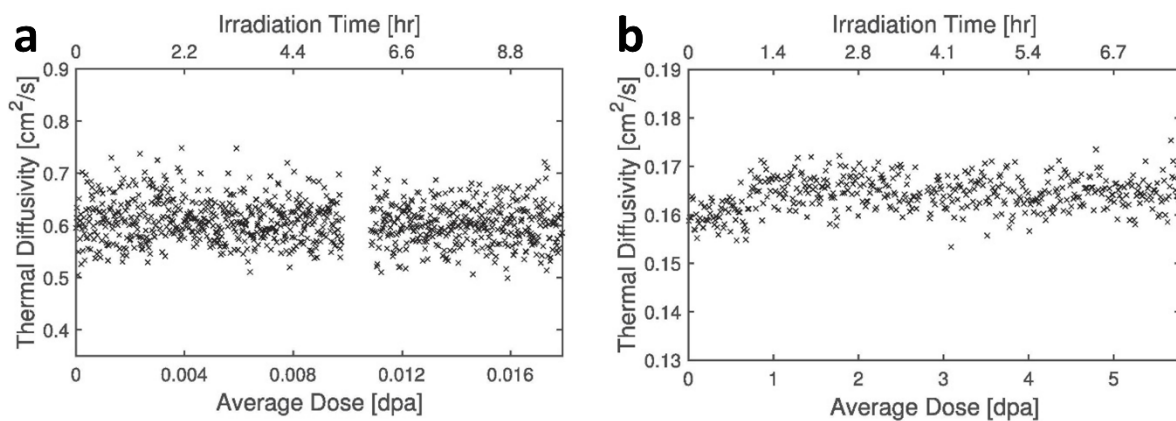


Figure 2.45 Thermal diffusivity of He implanted tungsten at room temperature (a) and self-ion implanted Ni at 550 °C (b), using in-situ TGS with implantation. Figure obtained from [185].

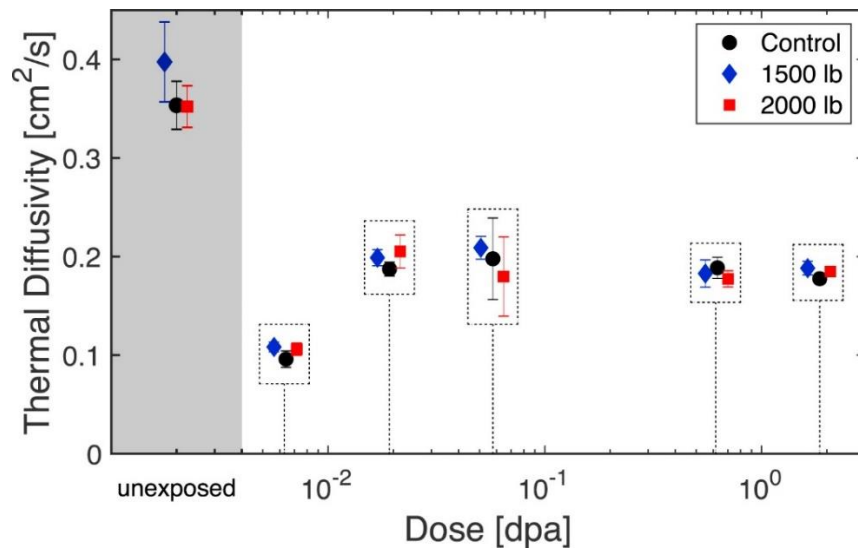


Figure 2.46 Thermal diffusivity degradation in Si ion irradiated niobium. Data for cold worked samples to 1500 and 2500 lb loads are also included. Figure obtained from [25].

2.5 Summary of the Literature Review

This literature review has shown the importance of considering the effects of neutron irradiation and plasma exposure on plasma facing materials, due to the property changes induced. Damage to the matrix at the nanoscale such as displacement damage can evolve to the micro and macro scale, changing material structure and eventually key physical properties.

Infusion of gaseous impurities from the plasma, such as hydrogen isotopes and helium can cause modifications in the form of nano-bubbles, which are invisible to TEM, to micron sized blisters that can be seen using SEM's. All these nano and micro scale defects can be seen to affect macroscopic material properties such as hardness and thermal diffusivity. An increase in hardness generally correlates with an increase in the brittleness of the material which is known to increase the likelihood of brittle failure. A decrease in the thermal conductivity can impair the heat removal capabilities which decreases the efficiency of the plant, and can also cause local overheating. Studies show that there exists a maximum heat flux that pristine tungsten can take under reactor cooling conditions before cracking [4]. With impaired heat removal capabilities due to a decreased thermal diffusivity of the tungsten components, the maximum heat flux that can be accommodated could decrease such that it would lie within the usual operational heat flux levels which would cause extensive cracking, pollution of the plasma and eventual failure.

The deuterium and helium effects however are seen to be confined to a surface layer, due to the limited penetration into the tungsten surface. However they still decrease the thermal conductivity and increase hardness significantly and need to be understood well for the safe operation of reactors.

The transmutation of the tungsten ions into rhenium osmium and tantalum are also seen to cause property and behavioural changes in the tungsten matrix. These transmutation products

are seen to decrease the thermal conductivity significantly, decrease irradiation induced swelling and affect the clustering behaviour of the radiation damage.

The review also covered the common crystal defect density measurement techniques, assessing their strengths and limitations. Likewise we also sampled through the few techniques available for measuring the thermal diffusivity in thin ion-implanted layers.

2.6 Research Goals

The literature review also exposed several gaps in the understanding of the effects of radiation and plasma exposure on tungsten.

Radiation damage in tungsten has been characterised quite well using TEM, where dislocation loops, voids, and their annealing kinetics are quantified. However, such studies do not cover defects that are invisible to the TEM. MD studies have indicated that this sub-population of defects is actually quite high in number. Hence we develop transient grating spectroscopy (TGS) with kinetic theory (KT) models to provide quantitative information about these TEM invisible defects in this thesis (Chapter 5).

From the thermal diffusivity/conductivity methods covered, apart from TGS, there didn't exist a non-contact method that could reliably measure the thermal diffusivity in thin ion-implanted layers in tungsten over a wide range of temperatures. The TDTR method, while able to measure thin surface layers and over a wider range of temperatures, requires a transducer layer to be deposited on the samples since tungsten has a low temperature coefficient of reflectivity. Photothermal displacement techniques are non-contact and do not require a transducer layer unlike TDTR. However knowledge of the Poisson's ratio and surface reflectivity is needed [163,186]. This data is not readily available for ion-implanted tungsten. In addition to this, the photothermal displacement technique has higher uncertainty than TGS [163]. This is due to a combination of factors, including the fact that TGS has heterodyne detection capabilities and requires less surface smoothness. TGS also possesses the unique capability of being able to set the spatial wavelength of the excitation, which then sets the length scale of the problem. This presents an advantage over point-source techniques such as TDTR and photothermal deflection.

The laser-flash method is non-contact and can perform such measurements over a wide range of temperatures, but is not established as a method to measure thin surface layers of interest. The 3-omega method, requires the deposition of electrodes on to the sample surface, has quite large error bars when measuring thin surface layers, and only works for a limited range of temperatures. Hence we expand the TGS technique for the measurement of thin ion-implanted samples with lower uncertainty due to increased statistics, automation, and spatial mapping; and increased robustness to non-planarity of sample surfaces (Chapter 3). The higher accuracy allows for the usage of thermal diffusivity measurements to be used to predict underlying crystal defect densities (Chapter 5).

The effect of radiation damage on the thermal diffusivity of tungsten has been studied in literature but not comprehensively. Early studies exist on neutron irradiated samples, which have quite a few limitations. Due to the activation of samples at higher doses, only a limited range of doses have been studied. Also, due to the difficulty in obtaining neutron irradiated samples, these studies have poor resolution in dose. Due to the combined effects of displacement damage, transmutation and helium and deuterium effects, it is difficult to separate the different contributions that the different mechanisms make to the thermal diffusivity degradation. Studies have been conducted on the thermal diffusivity degradation in helium ion exposed tungsten and tungsten alloyed with transmutation products. Only one study was found for the thermal diffusivity degradation in self-ion irradiated tungsten, which contained just one data point for self-ion implanted tungsten, and a few for other heavy-ion irradiated tungsten. Therefore in this work, we look at the thermal diffusivity degradation due to deuterium ion exposure and self-ion implantation. The self-ion implantation study is carried out over a wide range of doses with high dose resolution (Chapters 4 and 5).

3. Non-contact and non-destructive mapping of thermal diffusivity and surface acoustic wave speed using transient grating spectroscopy

This chapter reports the work on expanding the TGS method to increase the robustness of measurements, targeted measurements, perform spatial mapping and create grain maps of elastically anisotropic materials with large grains. The content of this chapter is in publication format based on the article “A. Reza, C.A. Dennett, M.P. Short, J. Waite, Y. Zayachuk, C.M. Magazzeni, S. Hills, F. Hofmann, Non-contact, non-destructive mapping of thermal diffusivity and surface acoustic wave speed using transient grating spectroscopy, *Rev. Sci. Instrum.* 91 (2020) 054902. doi:10.1063/5.0003742” [33].

C.A.Dennett and M.P. Short provided valuable insight during the build of the setup. J.Waite, Y.Zayachuk and C.M. Magazzeni provided the samples used in sections 3.4.1 to 3.4.4. S.Hills contributed towards the design and manufacturing of the vacuum chamber for the setup. Rest of the work was carried out by the author under the supervision of F. Hofmann.

3.1 Abstract

We present new developments of the laser-induced transient grating spectroscopy (TGS) technique that enable the measurement of large area 2D maps of thermal diffusivity and surface acoustic wave speed. Additional capabilities include targeted measurements and the ability to accommodate samples with increased surface roughness. These new capabilities are demonstrated by recording large TGS maps of deuterium implanted tungsten, linear friction welded aerospace alloys and high entropy alloys with a range of grain sizes. The results illustrate the ability to view grain microstructure in elastically anisotropic samples, and to

detect anomalies in samples, for example due to irradiation and previous measurements. They also point to the possibility of using TGS to quantify grain size at the surface of polycrystalline materials.

3.2 Introduction

Advances in the characterisation of engineering material properties are essential to keep up the pace of material innovation. For applications in heat engines, gas turbines, and extreme environments, such as nuclear fusion reactors, mechanical and physical properties, as well as their evolution in service, are very important [2,187]. Transient grating spectroscopy (TGS) presents a multi-modal non-destructive characterisation method that enables rapid insight into both the elastic and thermal transport properties of materials [29–32,183].

TGS measures the surface acoustic wave (SAW) speed, from which the elastic constants can be obtained [127]. Not only does the SAW speed provide quantitative insight into the elastic properties, it can also be used to pin-point microstructural changes, such as void swelling in irradiated materials [26] and for the evaluation of the properties of micron-thick surface layers [188–190]. Thermal diffusivity measurements from TGS have been used to detect the presence of crystal defects and impurities in metals [24], as well as to monitor irradiation-induced microstructural evolution for example in single-crystal niobium [25] and tungsten [18,24,34].

TGS presents several key advantages over other more conventional thermal diffusivity and acoustic property measurement methods: It is non-contact, non-destructive, and quite rapid (< 2 s for a spot measurement). The only requirement for the measurement is a flat sample surface polished to a mirror finish. Heterodyne detection [179] and the newer dual-heterodyne detection [183] allow high sensitivity measurements, thereby reducing the laser power required and thus the risk of surface modification due to the laser exposure. TGS also allows the depth-sensitive probing of properties, making it possible to specifically probe micron thick surface

layers of interest, for example in semiconductors [31], or in ion-irradiated nuclear materials [24]. The nature of the measurement also does not impose an intrinsic limit to the sample temperatures at which TGS can be performed, making TGS attractive for in-situ measurements, e.g. during sample heating.

A substantial drawback of TGS measurements has been the need for frequent manual intervention when carrying out multiple measurements, as the geometry is rather sensitive to even small sample misalignments. This has prevented the automated measurement of large spatial maps, rather only point measurements have been possible. Setting these up, especially when capturing spatial variation is required, was tedious and time consuming. Spatial mapping of SAW velocity tends to be less challenging than the mapping of thermal diffusivity, since it only requires the frequency component in the signal rather than the entire thermal decay. Rapid spatial mapping of SAW velocity using TGS excitation with a point probe has been successfully implemented, however with significantly larger probing depths ($>10\text{ }\mu\text{m}$) [191,192]. Thermal diffusivity mapping using time-domain thermo-reflectance (TDTR), with finer spatial resolution ($\sim 2\text{ }\mu\text{m}$), has also been implemented [193]. The advantage of TGS over these approaches is that it provides both the SAW velocity and thermal diffusivity in one measurement and with high temporal resolution ($< 2\text{ s}$ for a spot measurement).

There is anecdotal evidence that others have used a similar technique to that used in this work for combatting sample misalignment issues, and have also carried out TGS spatial mapping of very flat semiconductor samples. The key novelty of this work is the combination of these, with simultaneous dual-heterodyning [183], that has enabled us to create large area thermal diffusivity and SAW velocity maps on samples that aren't as flat, with high time resolution.

3.3 The Transient Grating Spectroscopy Setup

In the following we provide a brief summary of the TGS method. A detailed description of TGS theory and methodology, can be found in section 2.4.4.

In TGS, two coherent laser pulses are crossed with a well-defined angle at the sample surface. The crossing of the beams creates a spatially periodic interference pattern on the sample surface with a tunable wavelength λ . Absorption of the light from this intensity grating results in a spatially periodic heating of the sample, i.e. the formation of a temperature grating. Thermal expansion leads to a displacement of the sample surface, creating a displacement grating. Together the temperature and displacement gratings are referred to as the “transient grating”. A third “probe beam” (continuous wave) incident on the excited sample surface is diffracted by the transient grating, and reflected by the sample surface. As heat in the temperature grating diffuses from peaks to troughs and into the bulk, the grating decays. The rate of decay is linked to the thermal diffusivity of the sample [29], and manifests itself in the intensity decay of the diffracted probe signal as seen in Fig. 3.1.

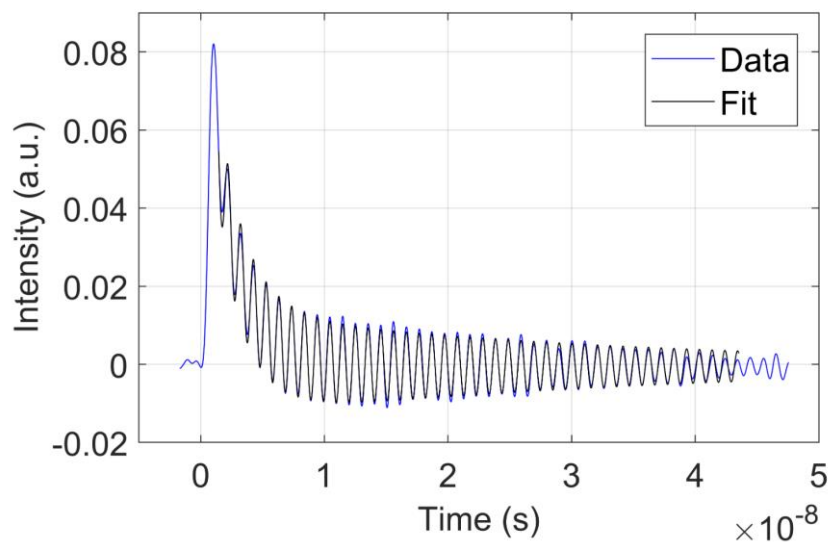


Figure 3.1 Sample TGS trace from an annealed, polycrystalline, 99.99% purity tungsten sample. Also shown is a fit to the experimental data using the expression outlined in [24].

Rapid thermal expansion of the sample also launches two counter-propagating surface acoustic waves (SAWs), with the same well-defined wavelength, λ , as the transient grating. The SAW's superimpose an oscillation on the transient grating in the sample that results in a superimposed oscillation in the TGS signal, as seen in Fig. 3.1. The SAW frequency depends on the elastic properties of the material [194]. To extract SAW frequency and thermal diffusivity, the TGS traces are fitted with the expressions given in [29]. There are a number of examples for this [18,24,34,195] with custom routines in MATLAB frequently being used to do the fitting.

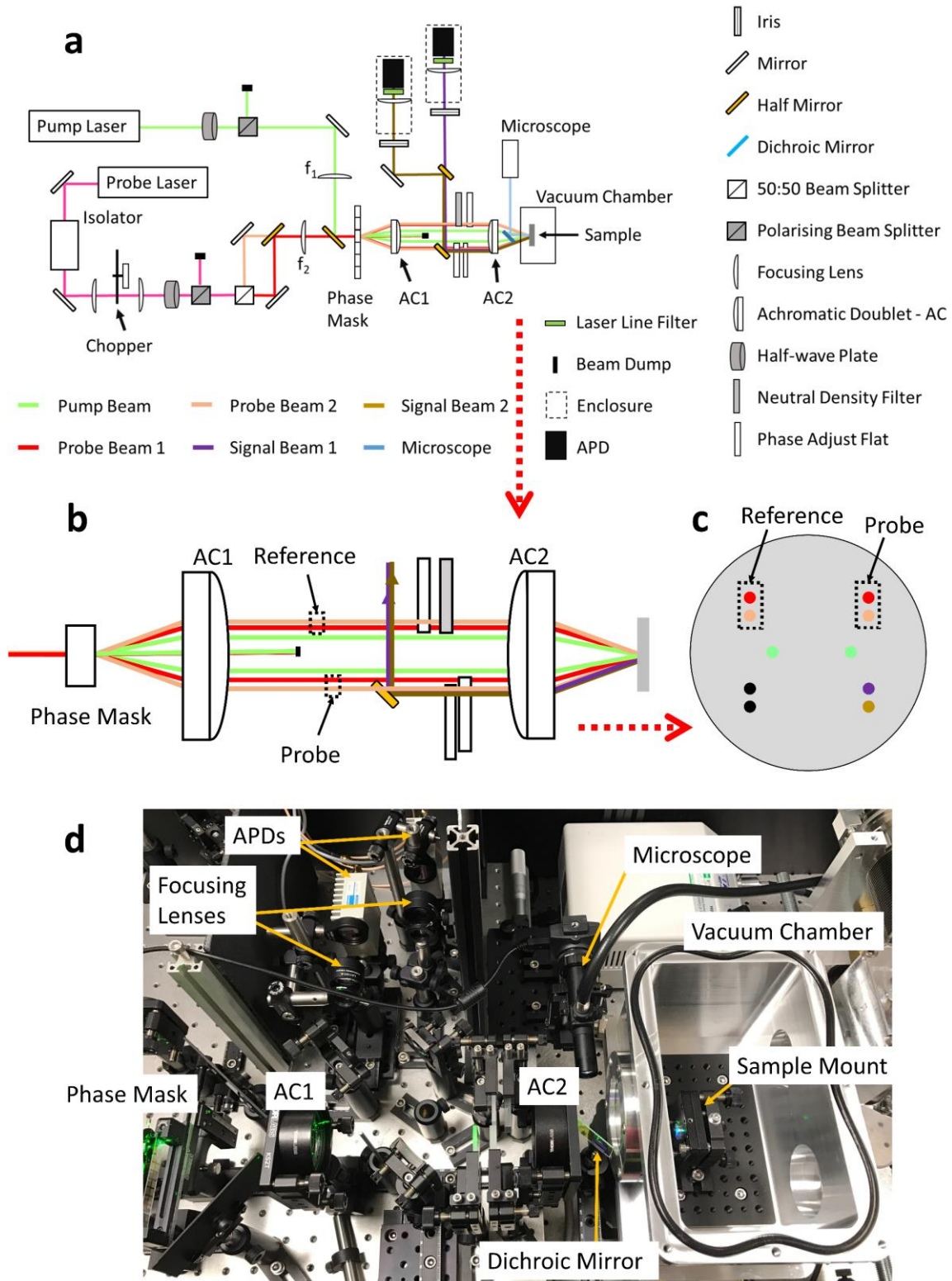


Figure 3.2 Layout of the TGS setup. (a) System overview indicating key components. (b) Layout of the 4f imaging system with the two achromats labelled AC1 and AC2. For clarity the dichroic mirror is not shown in (b). (c) Cross-sectional layout of the optical beams at achromat AC2, looking in the direction of the incident pump beams. Shown are the pump (green), probe (red and cream), signal (purple and brown) and the reflected “waste” probe beams (black). (d) Image of the setup from the phase mask onwards with key components labelled.

The following subsections detail the various parts of the setup and improvements implemented here.

3.3.1 Beam Generation

The pump beams are obtained from a 532 nm Q-switched microchip laser (Teem Photonics, PNG-M02010-120), with a pulse length of ~ 0.5 ns, maximum energy per pulse of 20 μJ and 1 kHz repetition rate. A combination of a half wave plate and a polarising beam splitter (PBS) are used to control the beam power, giving ~ 2 μJ per pulse at the sample. An advantage of this system is that the laser power can be regulated without having to interfere with the laser or beam path. An additional advantage is that the optics downstream do not have to accommodate excess laser beam energy, which is re-directed to a beam dump by the PBS.

The TGS setup developed in this study is based on previous iterations and includes heterodyne detection [30], the box-car geometry [196], and the more recently developed dual-heterodyne TGS configuration [183]. Heterodyne detection increases the signal amplitude, hence reducing the required laser beam power. The box-car geometry uses common optics for all pump and probe beams, as shown in Fig. 3.2(b), and permits very high relative phase stability between beams [196]. Dual-heterodyne detection allows the simultaneous detection of two heterodyne phases without the need for manual intervention. This improves the time resolution and repeatability.

The pump beam (green in Fig. 3.2 (a)) is focussed (using a plano-convex spherical lens with a focal length of 150 mm, lens f_1 in Fig. 3.2(a)) onto a phase mask with a spot size of 140 μm ($1/e^2$). The phase mask is optimised such that $\sim 50\%$ of the incident light is directed in the +1 and -1 diffraction orders. All other diffracted orders, as well as the 0th order beam are blocked. The transmitted first order diffracted beams are re-imaged onto the sample using two achromatic doublets (AC1 and AC2) in a 4f imaging system (the box-car) with the pump beams

maintained in the horizontal plane. Use of achromatic doublets minimises chromatic aberrations due to differences in the probe and pump beam wavelengths. It should be noted that it is essential to have different probe and pump wavelengths in order to be able to spectrally separate the TGS signal from pump beam scatter at the detectors.

The probe beams are generated using a 561 nm Coherent Genesis MX 561 laser with large coherence length (500 mW max. power, single-longitudinal mode). The continuous wave beam is chopped at 1 kHz using a mechanical chopper with a 25% duty cycle, and synchronised to the output of the pump laser. In a similar fashion to the pump beams, the probe beam power is regulated using a half wave plate and PBS combination. Back-reflected beams are prevented from re-entering the laser using a Thorlabs polarisation-dependent isolator (IO-5-560-HP, 560 nm).

Since the dual heterodyne technique requires two sets of probe beams, a 50:50 beam splitter is used to split the probe beams evenly (red and light brown beams in Fig. 3.2(a)). Separate mirrors are used to align these probe beams parallel to the optical axis of an aspheric focusing lens ($f = 100$ mm, lens f_2 in Fig. 3.2(a)), but at different heights. This improvement from previous TGS iterations allows independent adjustment of the probe beams, greatly simplifying alignment. The lens f_2 is then used to focus the probes onto the phase mask with a $90\text{ }\mu\text{m}$ spot ($1/e^2$). Similar to the pump beams, only the first order diffracted beams from the phase mask are transmitted, whilst all other diffraction orders and the direct beam are blocked. For each probe the +1 diffracted beam acts as the “probing arm” and the -1 diffracted beam as the “reference arm”, as shown in Fig. 3.2(b) and (c). The reference beams are attenuated by a factor of 100 using an ND2 filter. Phase adjust flats are used on the probing arm to allow accurate shifting of the probe beams’ phase with respect to their respective reference beams, with relative phases φ_1 and φ_2 for the two probes.

An additional optical flat is introduced to the upper reference beam, to match the total path length of the reference and probe beams and achieve a higher phase stability. A cross-sectional view of the pump, probe, and signal beams at achromatic lens AC2, prior to focusing on the sample, is shown in Fig. 3.2(c). The 4f imaging system, reproduces the same pump and probe spots sizes at the phase mask (140 μm and 90 μm) on to the sample.

3.3.2 Sample Environment

In the reflection TGS geometry, SAW measurements can be conducted at atmospheric pressure. However, thermal diffusivity measurements require a vacuum environment to remove the effects of excitations in air near the sample surface commonly observed in ambient conditions [30]. For this purpose, a vacuum chamber was built (see Fig. 3.2(d)). An Edwards Vacuum T-Station 85 setup that utilises a turbo-molecular pump and dry scroll pump is used to evacuate the chamber. A vacuum level of 10^{-3} mbar is sufficient for thermal diffusivity measurements at room temperature. Calibration tungsten samples returned a thermal diffusivity of $\sim(6.6 \pm 0.2) \times 10^{-5} \text{ m}^2\text{s}^{-1}$ at this vacuum level, which agrees very well with previous measurements, as well as the values given in the literature [14,197,198].

To create the TGS maps, automated sample stages are used in the directions perpendicular to the axis of the beams (Thorlabs motorised lab jack MLJ150 and Physik Instrumente L-511 linear stage for the vertical and horizontal translation, respectively). Translation along the beam is carried out using a manual stage. The range of motion currently available is 100 mm and 50 mm in the horizontal and vertical directions respectively. At present the size of the largest thermal diffusivity scan is limited by the size of the viewport on the vacuum chamber, which is ~ 50 mm in diameter.

3.3.3 Targeted Measurements

Targeting TGS measurement to a particular location on the sample surface is important for the investigation of specific microstructural or sample features. Here we incorporate an Edmund Optics in-line microscope with 3X magnification into the setup (TECHSPEC® In-Line CompactTL Telecentric Lens). At a fixed working distance of 110 mm this microscope has a field of view of $1.6 \times 1.1 \text{ mm}^2$ when used with a Thorlabs DCC1645C 1.3 megapixel camera. The pixel size in this case is $1.3 \text{ }\mu\text{m}$, with a spatial resolution of $10 \text{ }\mu\text{m}$. The beam geometry and sample environment only permits viewing of the sample through the same viewport also used by the laser beams. A dichroic mirror was used to allow the passage of the microscope illumination without affecting the TGS beams. The dichroic (Thorlabs long-pass dichroic with a 505 nm cut-off), was chosen such that it transmits the 532 nm pump and 561 nm probe beams and but reflects the blue microscope illuminator light. This enables viewing of the sample in-situ, during TGS measurements using the microscope. The microscope and dichroic mirror setup are shown in Fig. 3.2(a) and (d). The presence of the dichroic mirror in the path of the pump beams does not affect the wavelength of the TGS grating on the sample since it acts on both arms of the pump and probe beams. This was confirmed by comparing the SAW frequency in a calibration tungsten sample, with $(468.7 \pm 0.5 \text{ MHz})$ and without $(468.8 \pm 0.4 \text{ MHz})$ the dichroic mirror in place.

3.3.4 Detection

The duration of the TGS signal that follows the 0.5 ns pump pulse may range from 50 ns (for small grating periods and samples with high thermal diffusivity e.g. tungsten) up to several microseconds (for large grating periods and samples with low thermal diffusivity e.g. ceramics). In this TGS implementation, silicon avalanche photo diodes (APDs) were used (Hamamatsu C5658). The lower and upper cut-off frequencies of these APDs are 50 kHz and 1 GHz respectively. The upper cut-off is evident in Fig. 3.3(b) where the SAW frequencies

measured are accurate up to ~ 1.4 GHz. A Teledyne LeCroy WavePro 760 Zi, 6 GHz digital oscilloscope is used to readout the APD signals. Scripts in MATLAB [199] are used to control the oscilloscope data acquisition.

In the TGS setup, depending on the roughness of the sample surface, a significant amount of scattered pump light can accompany the signal beams up to the detectors. Laser line filters, as well as an iris positioned in front of each APD are used to remove this scatter (see Fig. 3.2). Scatter from other components in the setup is blocked by enclosing the detection optics, including the APDs. In addition, plano-convex lenses are used to focus the signal beams on to the 0.5 mm diameter active region of the APDs. This is discussed in further detail in the section ‘Modification for samples with uneven surfaces’.

3.3.5 Validation Experiments

Validation experiments were carried out to benchmark performance of the setup. This included thermal diffusivity and SAW frequency measurements on tungsten samples while the sample was taken to vacuum from ambient conditions, measurements over long periods of time, as well as varying pump and probe powers.

To explore the upper cut-off frequency of the setup, a silicon wafer (0.32 mm thick, with a $\langle 111 \rangle$ out-of-plane orientation), was measured using various nominal grating periods from 2.8 to 8.8 μm on the sample. Fig. 3.3 shows that up to a frequency of 1.4 GHz there is the expected linear relationship between SAW frequency and $1/\lambda$, where the slope of the line gives the SAW velocity. This suggests an upper frequency limit of the setup of ~ 1.4 GHz, consistent with the excitation laser pulse length, as well as the APD cut-off frequency. The SAW frequency for a tungsten single crystal (1.0 mm thick, with a $\langle 111 \rangle$ out-of-plane orientation) was also measured for the same grating periods and is plotted in Fig. 3.3.

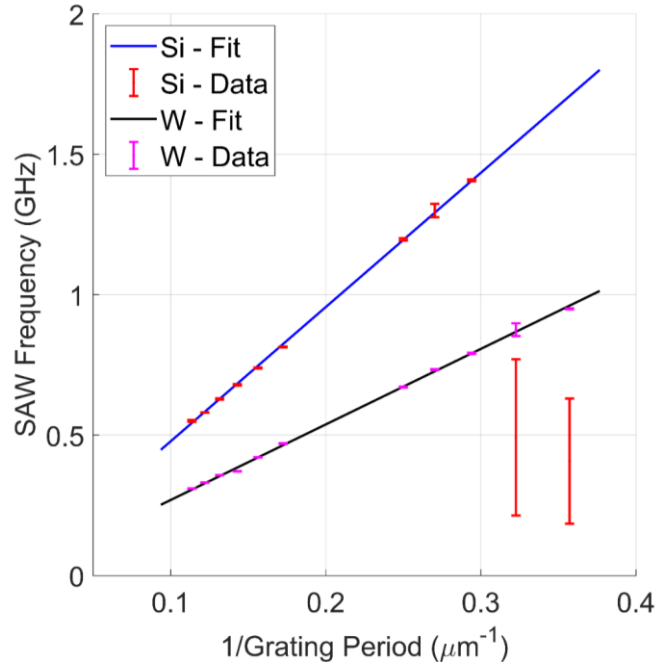


Figure 3.3 Surface acoustic wave frequency vs. 1 / nominal grating period for a <111> silicon single crystal and a <111> tungsten single crystal.

To assess the repeatability of the measurements, and to determine whether the pulsed laser heating affects the TGS measurements, continuous scans were carried out over a period of 5+ hours on a single spot in pristine and self-ion implanted tungsten (0.32 dpa, 20 MeV, RT). The tungsten samples were polycrystalline with random crystalline orientation (tungsten has the lowest elastic anisotropy among metals [200]). Further details of the samples, the implantation and its effects can be found in [34].

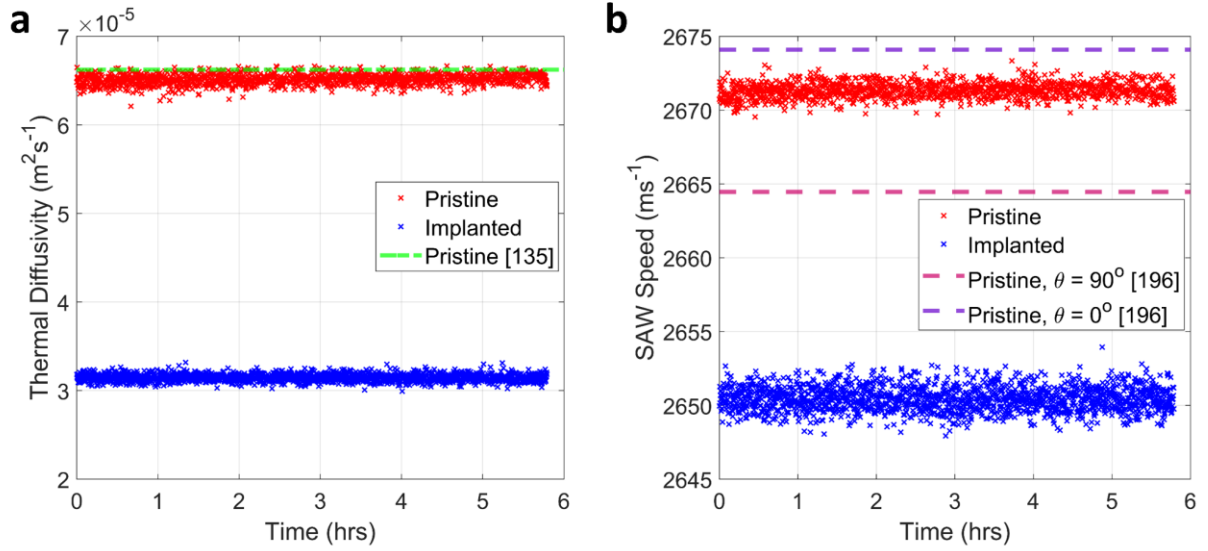


Figure 3.4 Long duration TGS scans on pristine and self-ion implanted tungsten. (a) Thermal diffusivity and (b) SAW speed. Also superimposed on the plots are the book values for pristine tungsten. The angles in (b) denote the SAW propagation direction in a $\langle 110 \rangle$ crystal.

Fig. 3.4(a) and (b) show that there is no change in the measured value of the thermal diffusivity or the SAW speed over the entire duration of the test for either of the samples. Superimposed on the plots are data from literature for pristine tungsten [137,200]. The SAW speed literature data [200] is for single crystal tungsten, and represents upper and lower bounds of SAW speed due to the small elastic anisotropy of tungsten. As expected our values lie within this range, since our measurements are averaged over multiple grains with varying orientation. This is due to the measurement spot ($\sim 90 \mu\text{m}$) being larger than the average grain size ($\sim 20 \mu\text{m}$) [34]. If laser heating were significant, the measured thermal diffusivity in pristine tungsten would be lower than the room temperature book value. Fig 3.4(a) does not show this effect. Similarly the lack of long-term evolution of thermal diffusivity and SAW speed suggests that the heating does not modify the underlying defect microstructure in the self-ion-implanted tungsten sample.

The standard deviation of the thermal diffusivity and SAW speed measurements is $\sim 1\%$ and 0.03% respectively. This is an indication of the repeatability of the measurements and depends

on the number of averages taken [183,192] . In this study 2000 – 5000 averages were deemed sufficient. The absolute error in the thermal diffusivity, considering the deviation from the book value for the pristine tungsten sample [137] is ~4%. This is an improvement over other thermal diffusivity measurement techniques that report values between 5 and 10 % [163]. The TDTR thermal diffusivity mapping study [193] reported an uncertainty of 8% in the thermal diffusivity. The SAW speed uncertainty (0.03%) is comparable to previous measurements (0.5 - 0.05%) [192].

3.3.6 Modification for samples with uneven surfaces

Dual heterodyne TGS requires six beams to cross at the same position on the sample surface with a precision greater than 50 μm (see Fig. 3.2(a, b and c)). The signal beams leaving the sample surface consist of the two diffracted probe beams, each combined with a heterodyne reference beam. Slight changes in sample surface orientation lead to a pointing error and hence misalignment of the signal beams at the detector. Any unevenness of the sample surface with the length scale of the beam spot sizes or larger, will change the exit angle of the signal beams, that then shift laterally downstream of AC2 as illustrated by red arrows in Fig. 3.5. When the setup is configured for single point measurements, this is not a problem as the sample orientation can be aligned. However, for the automated mapping of larger samples that are not perfectly flat, the exit angle of the signal beams may vary depending on the location on the sample. The consequent lateral shift of the signal beams can be sufficient to lead to a loss of signal on the APDs, which have a 500 μm diameter sensitive area.

To compensate for sample slope errors, plano-convex focusing lenses were placed in the path of the signal beams with the detector active area at the focal plane. With this modification, even with a lateral or slight directional shift of the signal beams, the signal still reaches the detector, enabling the creation of larger TGS maps. To quantify this capability, a flat, well-polished tungsten sample was aligned normal to the beams. The maximum sample tilt angle in the

vertical and horizontal plane that still gave a signal with $(1/e)$ of the maximum signal amplitude was then measured. Without the focussing lenses in place the maximum tilt, α , was 0.2° and 0.1° in the horizontal and vertical planes respectively. With the lenses in place, the sample could be tilted by up to 2.0° and 1.5° in the horizontal and vertical planes, respectively. This means that our setup can tolerate an order of magnitude larger sample non-planarity than in previous works without this modification. It should be noted that a 2° inclination in the sample surface changes the transient grating period by $\sim 0.06\%$. This is comparable to the repeatability of the SAW speed measurement and substantially less than the uncertainty in the thermal diffusivity measurement.

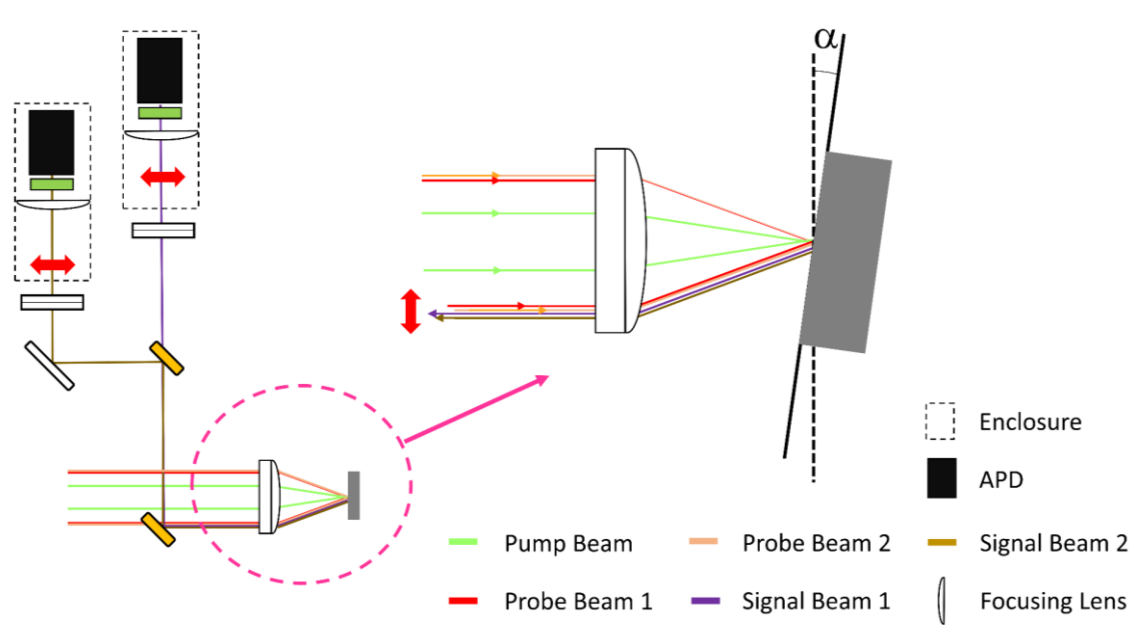


Figure 3.5 Schematic of the sample arrangement for the experiment to determine the maximum permissible sample surface angle. The red double-arrows indicate the lateral shift of the beams due to the sample tilt. The optics key is the same as in Fig. 3.2 (a).

3.4 Results and Discussion

3.4.1 Deuterium Exposed Tungsten

The TGS setup was used to study the effects of deuterium ion exposure on tungsten, a promising contender for fusion reactor armour components. Detailed results of this study are provided in [18]. Here the same sample is used to illustrate the 2D mapping capability of the TGS setup.

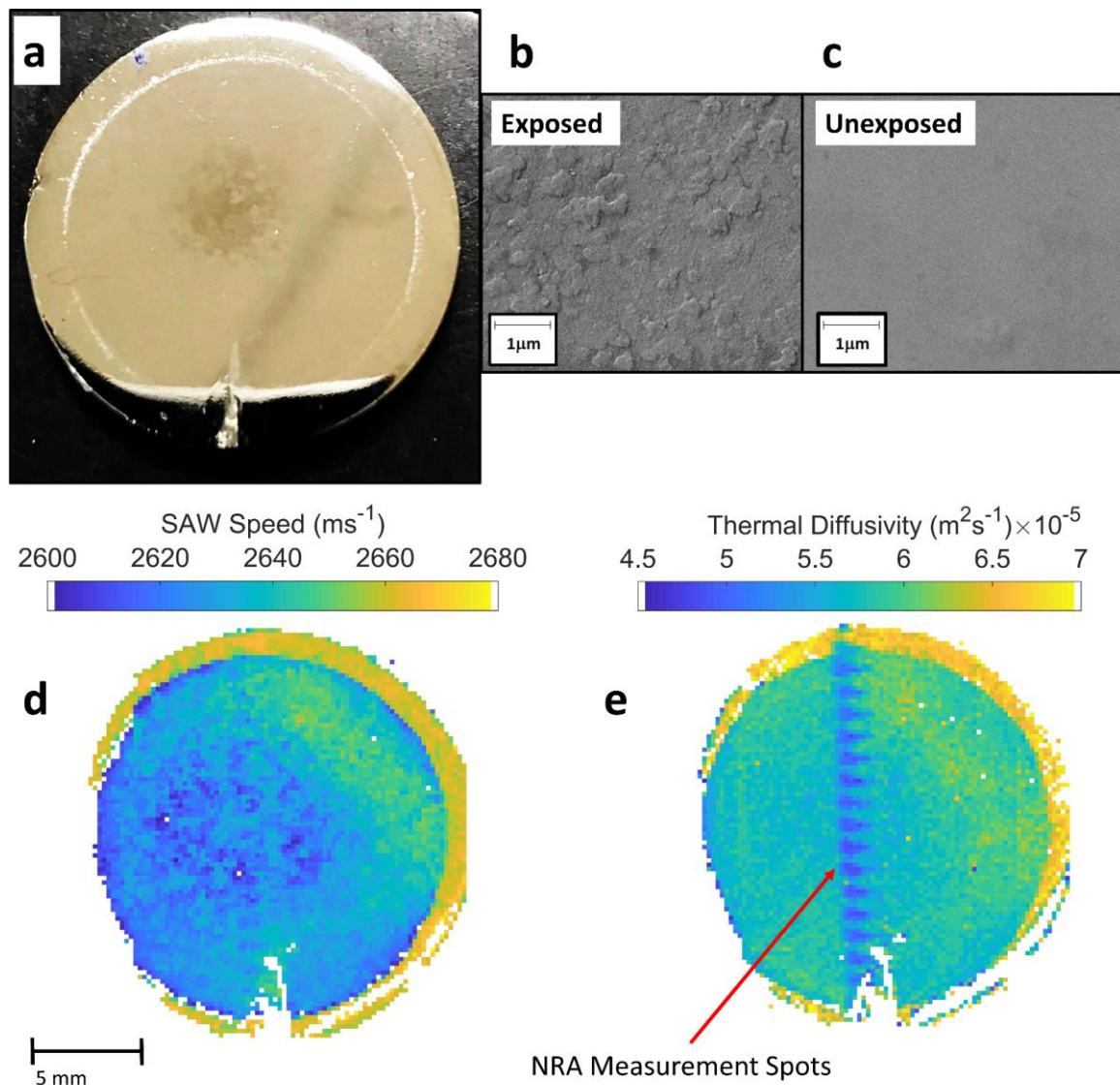


Figure 3.6 Deuterium-exposed tungsten sample. The central region was exposed to deuterium, whilst the edge of the sample was shielded during the exposure. (a) Optical image of the sample. SEM micrographs of the central exposed region (b) and unexposed edge (c). (d) SAW map of the whole sample measured by TGS. (e) Thermal diffusivity map. The same scale bar applies to (a), (d) and (e).

The tungsten sample was exposed to deuterium ion fluences of $\sim 10^{27}$ ions m^{-2} with Gaussian flux and temperature profiles ($T_{\text{max}} \sim 450\text{K}$ in the centre of the sample). The edges were shielded during exposure. A circular scratch, visible in Fig. 3.6(a), marks the boundary between exposed and unexposed regions. Deuterium exposure leads to the formation of surface and sub-surface blisters, as seen in Fig. 3.6(b). A detailed discussion of the responsible mechanisms is provided elsewhere [45,86,90]. Our previous work showed a significant degradation of thermal diffusivity and reduction in SAW speed in the exposed area [18]. Using the mapping capability of the TGS setup we have measured a map of thermal diffusivity and SAW speed that spans the entire sample (Fig. 3.6(d) and (e)). It consists of over 9000 spatial locations with a step size of $200 \mu\text{m}$ between measurement points. A grating period of $2.758 \pm 0.002 \mu\text{m}$ on the sample surface was used, such that the measurements will be dominated by the $\sim 1 \mu\text{m}$ thick deuterium affected surface layer [29].

The SAW speed and thermal diffusivity maps in Fig. 3.6, clearly show higher values for thermal diffusivity and SAW speed in the pristine unexposed regions. The measured values are in very good agreement with literature values for well-annealed tungsten [15,197,198,200]. Reduced SAW speed and lower thermal diffusivity due to the ion exposure are evident in the central region of the maps.

An interesting feature is a line of points with significantly further reduced thermal diffusivity that crosses the central region of the sample (see Fig. 3.6(e)). These positions correspond to the locations of previous nuclear reaction analysis (NRA) measurements used to obtain depth profiles of the deuterium concentration in the samples [86]. NRA measurements bombard the sample with particular reactive nuclei and detect the emission of ionising radiation from the resulting nuclear reaction [201]. In this case the NRA technique used helium ions of different energies from 500 keV to 4.5 MeV [86,202]. These energies are sufficiently high to cause irradiation damage [13]. Given that the bombardment energies are up to a few MeV, the

damaged layer is expected to be several microns thick, hence affecting the TGS measurements [28]. Indeed, our previous measurements showed that even small doses of helium injected at these energies can lead to a dramatic reduction in room temperature thermal diffusivity of tungsten [24]. The mapping capability has effectively spotted this additional irradiation damage due to the NRA measurements. By conducting spot measurements or line scans only, these spurious effects of NRA measurements could have easily been missed, highlighting the benefit of the 2D mapping capability of the TGS setup.

3.4.2 Linear friction welded Ti6Al4V

We also carried out 2D scans of a linear friction welded Ti6Al4V aerospace alloy. Friction welding is increasingly popular due to its advantages over fusion welding, such as avoiding of melting, lower porosity and fewer impurities due to the absence of a filler material [203,204]. However, there still is a significant change in the microstructure in the weld region that can lead to changes in material properties.

Here we considered a 5x10 mm, 2mm thick section through a Ti6Al4V friction weld. An optical micrograph of the central region of this sample is shown in Fig. 3.7(a). Phase maps of the parent material from EBSD revealed it to be 99% Ti-alpha and less than 1% Ti-beta. An electron back-scatter diffraction (EBSD) scan of central sample region shows that the weld line has a width of ~500 μm (Fig. 7(b)), with much smaller grains in the weld (~1 μm) than the surrounding parent material (~10-15 μm). EBSD also shows that the material in the weld is strongly textured, whereas grains in the parent material are more randomly oriented.

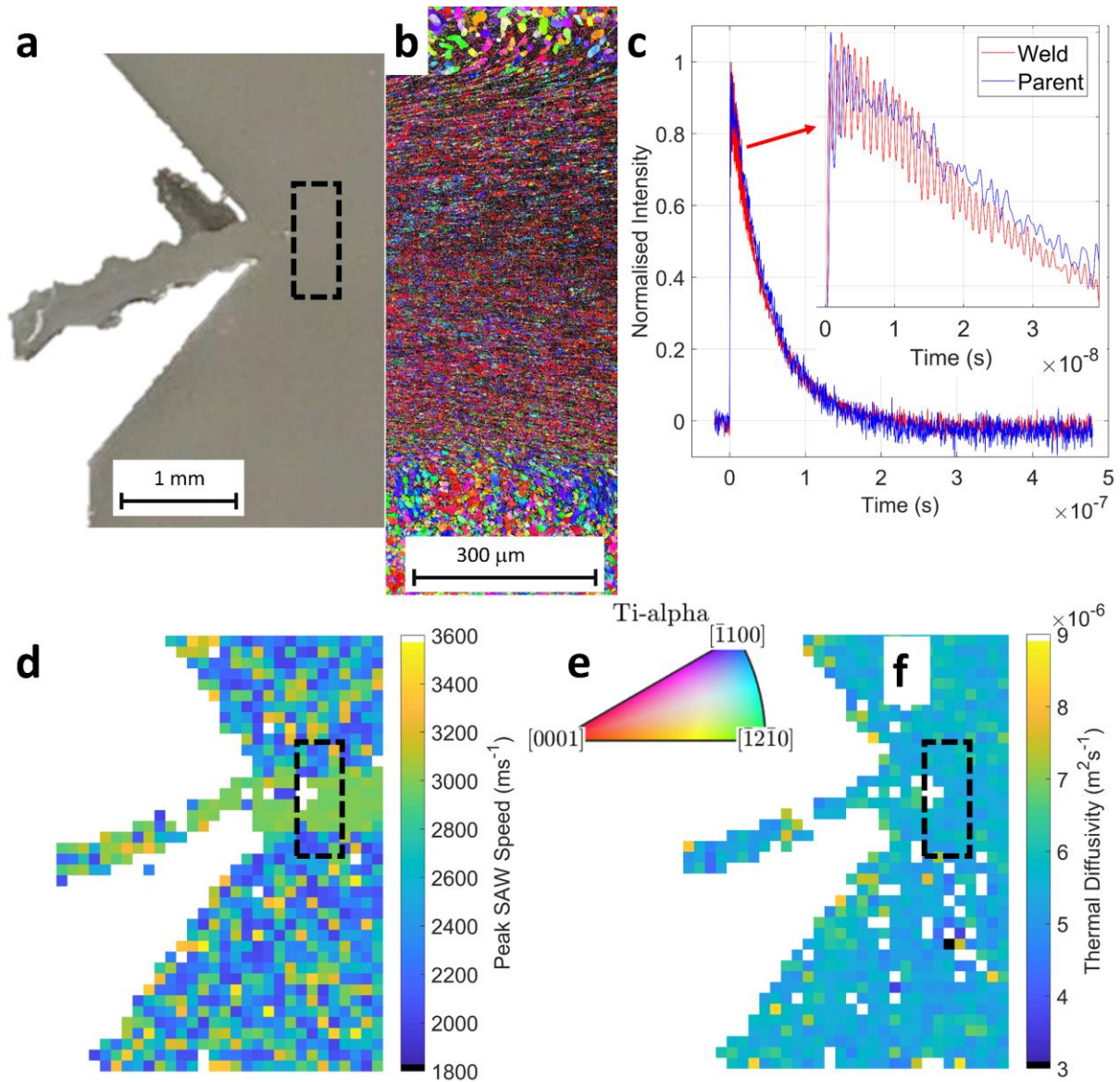


Figure 3.7 Linear friction welded Ti6Al4V sample. (a) Optical micrograph showing the weld and flash extruded from the weld line. (b) EBSD scan showing grain sizes and orientations, (c) sample TGS traces from the weld and parent regions, (d) TGS SAW speed map, (e) EBSD colormap and (f) TGS thermal diffusivity map. The location of the EBSD scan is demarcated by the dashed region. The same scale bar applies to the TGS maps and the optical image.

Interestingly even in the parent material there are domains with grains of similar orientation, seen as red and blue regions in Fig. 3.7(b) reminiscent of macrozones observed in this alloy [205–207], which corresponds to crystallographic orientations of $[0001]$ and $[\bar{1}100]$. These macrozones are also identifiable in the SAW map in Fig. 3.7(d), where there are regions of blue and yellow/green, which correspond to SAW speeds of $2200\text{--}2400\text{ ms}^{-1}$ and $2800\text{--}3200\text{ ms}^{-1}$. SAW speed in anisotropic materials depends on the crystal orientation and TGS wavevector

direction [200]. Hence we expect such variations in the SAW speed given the elastically anisotropic hexagonally close packed (HCP) structure of Ti-alpha.

Also noticeable in the map is the uniform SAW speed in the weld. This uniformity in the SAW speed is due to the uniformity of texture in the weld. This demonstrates the ability of the setup to identify regions of uniform orientation and random orientation in elastically anisotropic materials. The SAW speed depends on the elastic modulus alone for elastically isotropic materials and on the stiffness tensor, wave vector direction and crystal orientation for elastically anisotropic materials [127,200]. Hence this method can be used to quantify the effect of welds on the elastic properties of macroscopic components.

The thermal diffusivity map in Fig. 3.7(e) shows little variation of thermal diffusivity, indicating that thermal transport in the weld is very similar to that in the parent material. This is a desirable result, which indicates that the weld does not affect the overall thermal conductivity of the component. As is the case with the larger SAW maps, the larger thermal diffusivity map allows us to identify inhomogeneous regions that may lead to anomalies in the dissipation of heat. The fact that we are able to create such maps encompassing the weld, the parent material, as well as the weld flash (material extruded at the joint line during the friction welding process), demonstrates the capabilities of TGS for rapid characterisation of macroscopic engineering components.

Fig. 3.7(c) shows another interesting feature. The SAW oscillations in the TGS signal persist for longer in the weld than in the parent material. This is believed to be a result of the grain size and orientation. In the weld, the grains are smaller than the TGS wavelength and have similar orientation (strong texture). Hence when the SAW move from one grain to the next, the SAW velocity and wavelength are very similar due to the similar crystal orientation. The probe still meets the diffraction condition for the SAW displacements in the new grain. In the parent,

the grains are more comparable in size to the excited spot of 140 μm , and have random orientation. Initially SAWs with the same wavelength, but at different frequencies depending on SAW velocity, are generated in different grains within the excitation spot. When a SAW generated in a particular grain propagates into a neighbouring grain with different SAW velocity for that propagation direction, the frequency must stay the same. Hence, in order to match the new SAW velocity, the SAW wavelength must change. The resulting grating with a new wavelength no longer fulfils the diffraction condition for the probe beam, and effectively becomes invisible. Hence the SAWs seem to disappear quickly, but the temperature profile persists.

It should be noted that the lifetime of the SAW component in the TGS signal until the SAW leaves the grain is still long enough for it to be picked up in a Fourier transform of the trace. From the traces in Fig. 3.7(c), we observe six SAW oscillations in the TGS trace from the parent material. With the TGS wavelength of 2.758 μm , this predicts a grain size of 16.5 μm , which is close to the 10-15 μm grain size seen in EBSD (See Fig. 3.7(b)).

3.4.3 Implanted High Entropy Alloy

TGS was also used to map a high entropy alloy (HEA) partly implanted with vanadium ions. An optical micrograph of the sample (recorded using an ALICONA Infinitfocus G5 microscope) is shown in Fig. 3.8 (a). The alloy consisted of 32.5% Ti, 15% V, 15% Zr, 16.5% Hf and 20% Ta. The sample was produced by arc melting under an Argon atmosphere and then annealed at 1400 $^{\circ}\text{C}$ for 24 hrs under a vacuum of ~ 0.03 mbar. The sample was ground to 4000 grit and polished with colloidal silica. Diamond paste polishing caused surface pitting too rough for EBSD measurements, and therefore was omitted. The implantations were carried out using 2 MeV V^+ ions at 500 $^{\circ}\text{C}$ up to a dose of 3 displacements per atom (dpa) on part of the sample demarcated by a circular scratch. The microstructure was determined to be bcc with

rocksalt structured precipitates due to small amounts of carbon and nitrogen infusion from the furnace during fabrication.

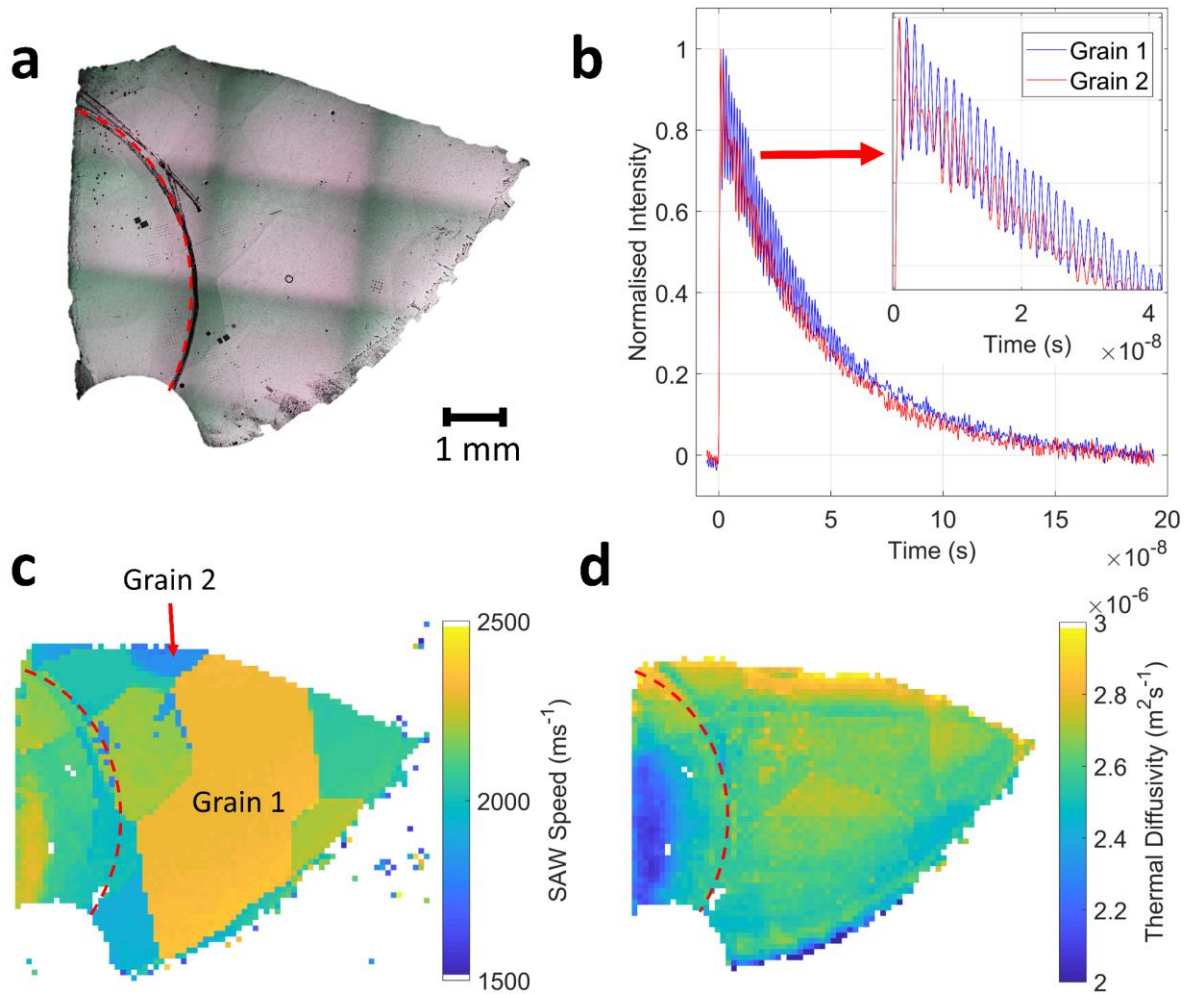


Figure 3.8 Implanted high entropy alloy. Optical micrograph (a), sample TGS traces (b), TGS SAW speed map (c) and TGS thermal diffusivity map (d). The implanted region is indicated by the red dashed line. The same scale bar applies to the micrograph and the TGS maps.

Although the sample surface was too rough for EBSD, the SAW and thermal diffusivity maps, Fig. 3.8(c) and (d), could be measured with relative ease. Fig. 3.8(b) shows sample TGS traces for two different grains. A closer look at the traces reveals the variation in SAW frequency.

The scans were carried out using a step size of 200 μm . It is evident from the TGS maps and from the optical micrograph in Fig. 3.8(a), that the setup could readily map the entire sample, despite the relatively poor surface finish. The SAW speed map clearly shows differences

between specific grains, indicating that this HEA must be elastically anisotropic. The boundaries between the regions of different SAW speed closely match the grain boundaries visible in the optical micrograph. The SAW map effectively provides a grain map for elastically anisotropic samples. It also points at the possibility of combining such maps with modelling predictions of SAW speeds as a function of orientation to produce large scale TGS crystal orientation maps [192,208].

The thermal diffusivity varies little between different grains (Fig. 3.8(d)). This is expected since cubic crystals have isotropic thermal conductivity [209]. Interestingly the implanted region shows a clear reduction in thermal diffusivity. Metals and metallic alloys are known to be quite susceptible to thermal diffusivity degradation as a result of implantation [34,135,210]. This is due to the fact that the predominant thermal energy carriers in metals/alloys are electrons, which can be readily scattered by irradiation induced defects. In the SAW map (Fig. 3.8(c)) an increase in the SAW speed in the irradiated region of the HEA is noticeable. This behaviour is opposite to the reduction in SAW velocity observed for the irradiated regions in the deuterium implanted tungsten sample (See Fig. 3.5(d)). Unlike the thermal diffusivity, the SAW velocity can increase due to various factors such as stiffening, or decrease due to softening/swelling of the material. The dominant effect depends on the type of material, alloying content, crystal structure, exposure conditions and temperature [26,117,211,212]. Further analysis would be required to determine the dominant effect in this case, which is out of the scope of this work.

3.4.4 As Cast Equiatomic TiZrHf Alloy

As a final example we considered another equiatomic alloy composed of TiZrHf, on which EBSD was not possible, which was mapped using the TGS setup. The HEA was produced by arc melting of elemental powders as a 10 g ingot under a vacuum of ~ 0.03 mbar. The sample was ground to 4000 grit and polished with colloidal silica. Further polishing of the sample was not carried out since diamond paste polishing resulted in surface pitting. EBSD measurements were not possible due to the surface roughness. However, the entire surface area of the sample was mapped using the TGS setup, with a spatial resolution of $200\text{ }\mu\text{m}$ and probing depth of $\sim 1\text{ }\mu\text{m}$. An optical micrograph of the sample, captured using an ALICONA Infinitfocus G5, is shown in Fig. 3.9 (a).

Fairly large grains are clearly visible in the optical micrograph (Fig. 3.9(a)). These grains can also be identified in the SAW speed map in Fig. 3.9(b). This is also due to the elastic anisotropy present, as is the case with most HEA's [213]. The possible elastic anisotropy evident here is less than that of the HEA in Fig. 8. The darker grains in the optical micrograph can be seen to correspond to regions of higher SAW speed and vice versa. The fact that the grains aren't at the nano-scale, which rules out grain boundary effects, leads us to believe that this is an effect of the elastic anisotropy. Ascertaining this would require direct correlations with EBSD measurements which were not possible on these samples due to their surface roughness. Slight variations in thermal diffusivity are evident across the sample, as expected, due to the HCP crystalline structure. Also evident are lateral bands of higher and lower thermal diffusivity, which may be a cooling rate effect, though this requires further investigation in future.

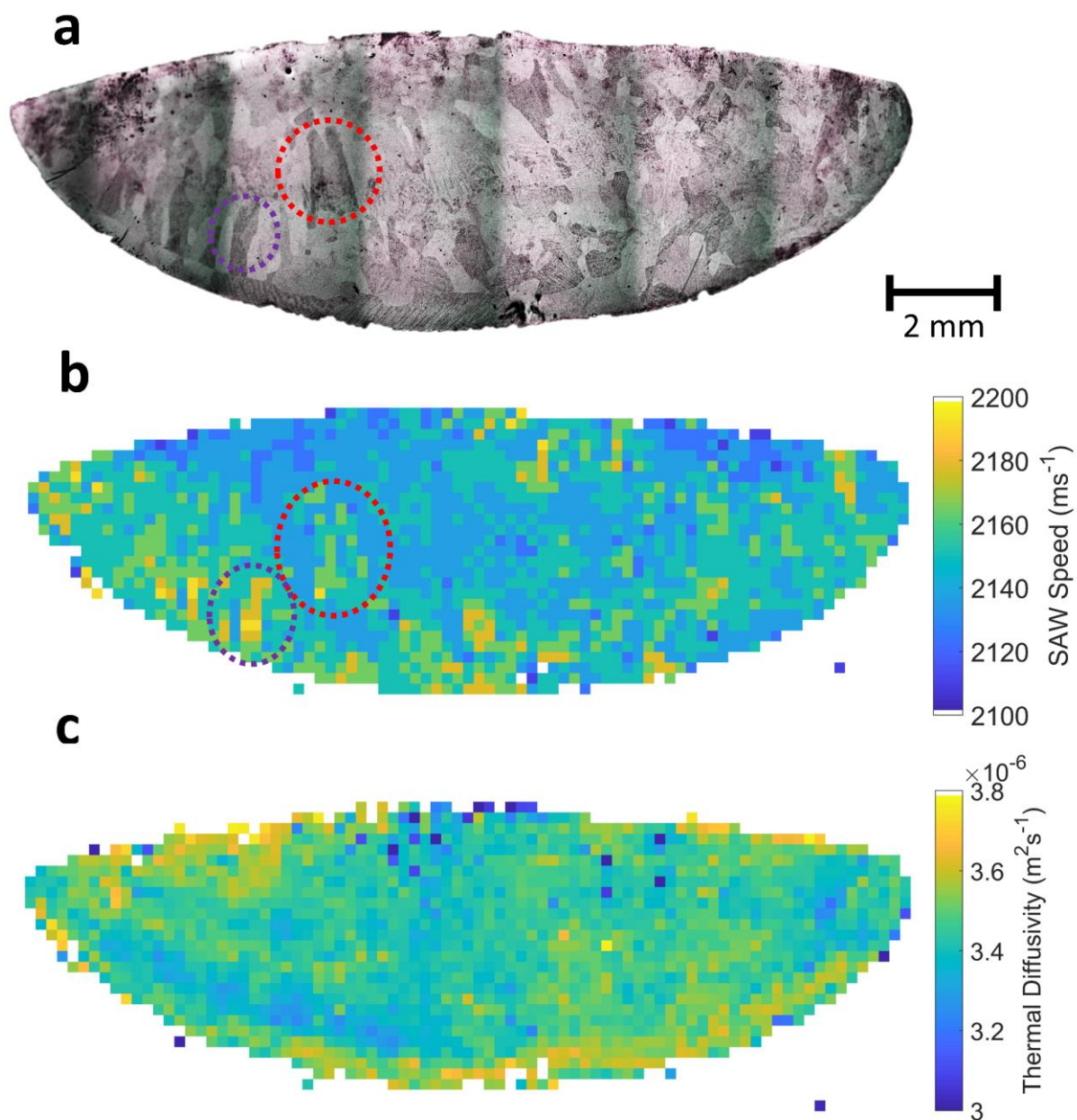


Figure 3.9 TiZrHf equiatomic alloy. Optical micrograph showing different grains (a), SAW speed TGS map (b) and thermal diffusivity TGS map (c). Dashed regions indicate examples of identified grains. The same scale bar applies to the micrographs and the TGS maps.

4. Transient grating spectroscopy of thermal diffusivity degradation in deuterium implanted tungsten

This chapter is based on the study that has been published in Scripta Materialia as “A. Reza, Y. Zayachuk, H. Yu, F. Hofmann, Transient grating spectroscopy of thermal diffusivity degradation in deuterium implanted tungsten, Scr. Mater. 174 (2020) 6–10. doi:10.1016/J.SCRIPTAMAT.2019.08.014” [18].

Y. Zayachuk supplied the samples, exposure profile data, cross-sectional micrographs and EBSD maps. H. Yu assisted with the SEM imaging of blisters. Rest of the work was carried out by the author under the supervision of F. Hofmann.

4.1 Abstract

Using transient grating spectroscopy, we measure thermal diffusivity and surface acoustic wave speed in tungsten exposed to different fluences of deuterium plasma. Scanning electron microscopy (SEM) shows the formation of surface blisters that have similar morphology for all fluences considered. A significant reduction in thermal diffusivity and surface acoustic wave speed occurs as a result of plasma exposure. A saturation of the thermal diffusivity reduction with fluence is seen. Deuterium ion flux density appears to play a more important role in thermal diffusivity reduction than exposure time. These observations have important implications for plasma facing components in future fusion reactors.

4.2 Introduction

Mitigating climate change will require new long-term solutions for sustainable power generation. Nuclear fusion could provide a carbon-neutral and sustainable long-term solution. However, there are major engineering challenges to be addressed on the path to its commercialisation. One such challenge is the performance of plasma-facing materials, especially those used in the divertor, which will face the harshest conditions. Tungsten is the front runner for divertor armour due to its high melting point, low sputtering yield, strength at high temperature and high thermal conductivity [38]. As such, a detailed exploration of its performance under fusion reactor relevant conditions is of high importance [2,7,38].

Understanding material property evolution due to harsh environments is key for the success of ITER and DEMO fusion programs [2]. It is anticipated that tungsten divertor armour in a tokamak reactor will be exposed to high heat fluxes ($\sim 10 \text{ MW/m}^2$ during steady state operation and $\sim 20 \text{ MW/m}^2$ during slow transients [4,214]), intense radiation with 14.1 MeV fusion neutrons and bombardment with ions, predominantly hydrogen and helium isotopes. A particular challenge is that hydrogen isotopes readily diffuse into the metal matrix, where they can substantially modify material properties and structure [90,98,215,216]. Trapping of deuterium at defects and self-trapping have been observed to lead to the formation of voids in the material and the emergence of surface blisters [90,98,216]. Since tungsten armour components will be exposed to high heat loads, this raises concerns, as blisters are expected to degrade the heat removal capability of plasma facing components by reducing near-surface thermal diffusivity. This in turn would lead to higher than predicted surface temperatures, potentially causing localised melting. In this study we quantify the effect of deuterium plasma on the thermal diffusivity of tungsten over a range of operation-relevant temperatures, flux densities and exposure times.

Deuterium injected into the material from the plasma affects the near surface region up to depths of a few microns [86]. Bulk thermal transport measurement techniques are not suitable for measuring the properties of this thin layer. Instead a different approach, called transient grating spectroscopy (TGS) [29,31,179,183] is used in this study. It allows selective probing of the properties of few-micron-thick surface layers. A detailed description of the technique is provided in section 2.4.4 of this thesis and elsewhere [31,32,183].

4.3 Materials and Methods

4.3.1 Transient Grating Spectroscopy

Briefly, in TGS two short, coherent laser pulses (0.5 ns, 532 nm) are overlapped on the sample surface with a well-defined angle. Interferences of the beams creates an intensity grating with wavelength λ on the sample surface. For tungsten, ~50% of the light is absorbed, with an expected penetration depth of ~9 nm [217], leading to the formation of a temperature grating in the sample. This grating decays as thermal energy diffuses from maxima to minima and into the bulk. In addition, rapid thermal expansion launches two counter-propagating surface acoustic waves (SAWs).

Both the SAWs and the temperature grating lead to a modification of the sample surface height. This “transient” grating acts as a reflective diffraction grating and can be probed by the diffraction of a second beam (continuous wave, 559.5 nm). The thermal diffusivity of a surface layer with thickness λ/π determines the rate at which the transient grating decays. Hence, by analysing the amplitude decay of the diffracted probe beam, the thermal diffusivity can be determined [29]. A detailed description of TGS theory is given in section 2.4.4. Details of the TGS setup used is given in section 3.3.

The TGS setup used in this study incorporates the simultaneous dual heterodyne method [183]. The transient grating wavelength on the sample was $\lambda = 2.758 \pm 0.001 \mu\text{m}$, quantified using the SAW frequency of a tungsten calibration sample. This was chosen to get a probing depth of ~1 μm [29]. The average power at the sample was 1.5 mW for the pump (1 kHz repetition rate with 1.5 μJ per excitation) and 22 mW for the probe (88 mW optically chopped at 1 kHz with a 25% duty cycle). Given a reflectivity of ~50%, the pump and probe power absorbed were ~0.75 mW and ~11 mW respectively. The probe and excitation spots on the sample were

90 μm and 140 μm respectively ($1/e^2$ level). Measurements were performed in a vacuum of $\sim 1 \times 10^{-3}$ mbar at room temperature.

TGS measurements were performed for three parallel lines across each sample with a step of 200 μm giving 80 points per line, and a spacing of 200 μm between the lines. At each position ten measurements were recorded, each averaged over 2000 consecutive pump pulses at 1 kHz. The traces were fitted to extract thermal diffusivity and SAW speed [24]. Details of the fit and fitting equations are given in section 2.4.4. Measurement uncertainty for the thermal diffusivity was less than 5%, and less than 0.07% for the SAW speed. Fig. 4.1 shows a TGS trace and the fit used.

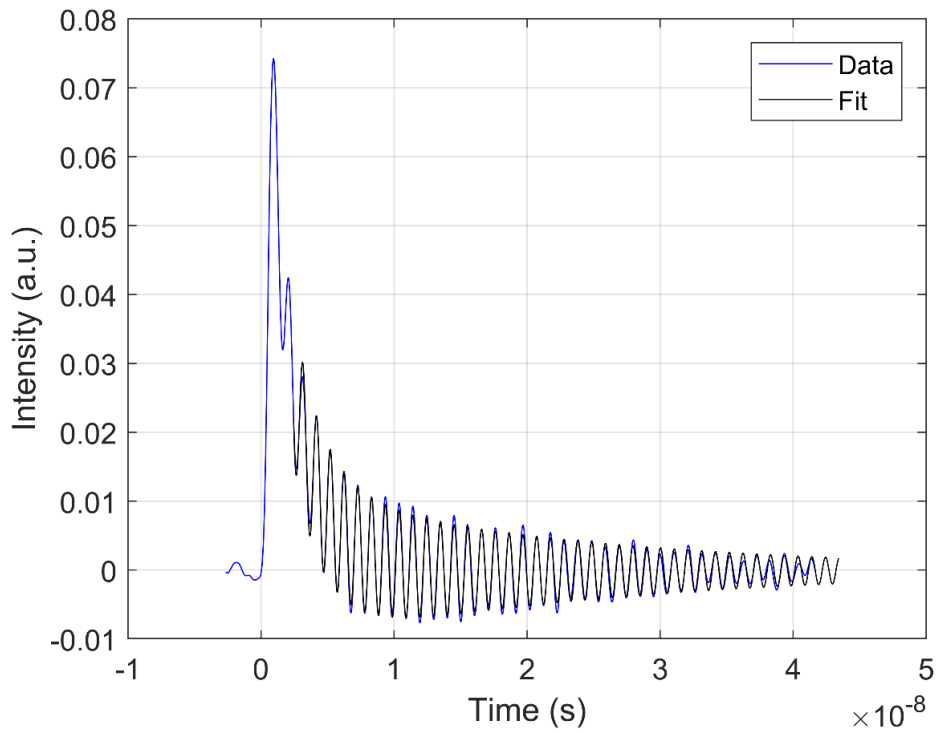


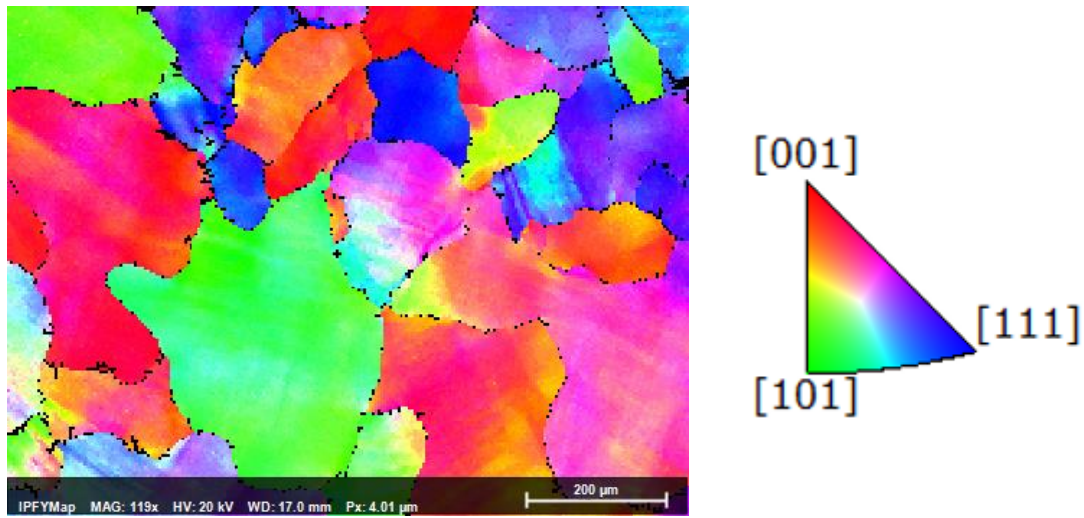
Figure 4.1 Transient grating signal and fitted trace for the unimplanted region in the low temperature high dose (LT HD) sample.

4.3.2 Sample Preparation and Plasma Exposure

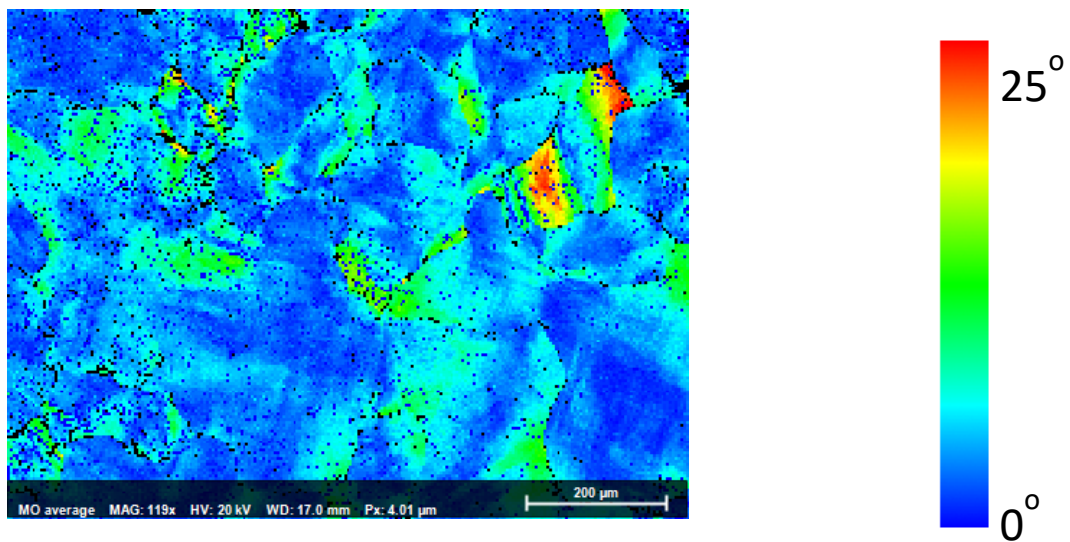
Polycrystalline tungsten discs with 20 mm diameter, 1 mm thickness and 99.95% purity were used. The sample surface was ground with SiC abrasive paper down to 2500 grit, followed by mechanical polishing with 3 and 1 μm diamond suspension on NLH polishing cloths. The samples were electrochemically polished in 0.5 wt % NaOH water solution at 12 V and heat treated at 1300 K in vacuum ($\sim 10^{-5}$ mbar) for 1 hour. Fig. 4.2 shows electron back scatter diffraction (EBSD) maps of the microstructure. Deuterium plasma exposures were performed at the linear plasma generator Pilot-PSI [218] (ion energy ~ 50 eV, Gaussian beam profile with ~ 10 mm FWHM). Ion flux profiles were obtained from Thomson scattering and the surface temperature was measured using an IR camera (FLIR SC7500-MB, 0.4 mm pixel size on sample). Details of the exposures can be found in [86]. Scanning electron microscopy (SEM) was performed on an Auriga Zeiss dual-beam FIB-SEM.

To investigate how thermal diffusivity varies with deuterium flux, fluence and exposure temperature, an experimental matrix with four exposure conditions was used: high temperature high dose (HT HD), high temperature low dose (HT LD), low temperature low dose (LT LD) and low temperature high dose (LT HD). “LT” refers to ~ 450 K, “HT” to ~ 650 K, “LD” to $\sim 5 \times 10^{25} \text{ m}^{-2}$ (70 seconds exposure), and “HD” to $\sim 10^{27} \text{ m}^{-2}$ (1400 seconds exposure). The Gaussian nature of the ion beam allowed a spatial variation of flux and fluence across the sample. A 2 mm wide region around the sample edge was shielded from the plasma by a molybdenum clamping ring. Fig. 4.3 shows the deuterium ion fluence profiles and temperature profiles for all samples.

(a)



(b)



(c)

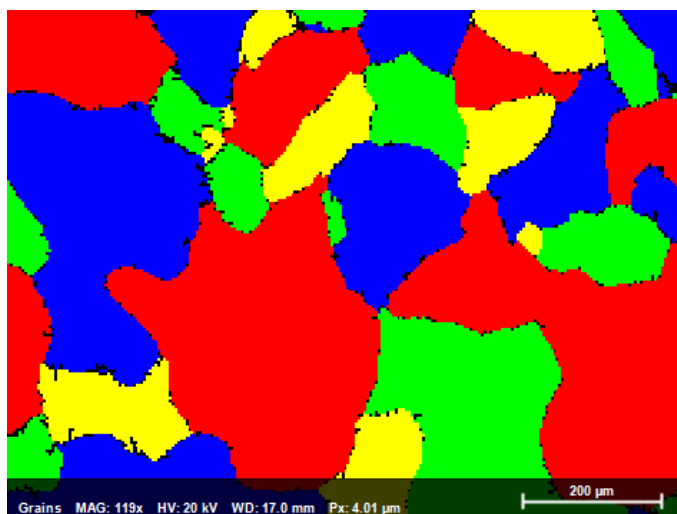


Figure 4.2 Microstructure of the investigated tungsten following heat treatment, determined by EBSD: (a) Orientation map (IPFY); (b) misorientation map; (c) identified grains.

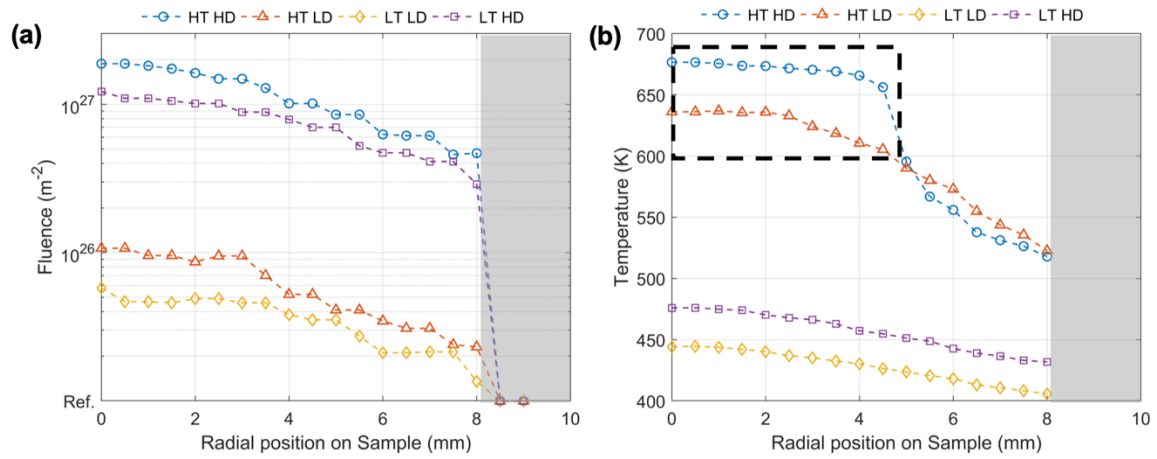


Figure 4.3 (a) Profile of incident deuterium ion fluence for the four samples. The reference fluence at the shielded sample edges is zero. (b) Surface temperature profiles for the four different samples. The temperature of the shielded edges is assumed to be consistent with the near-Gaussian nature of the temperature profile. Boxed region in the centre depicts the molybdenum-contaminated regions. The shielded region is depicted by grey shading.

4.4 Results and Discussion

4.4.1 Exposure and Impurity Characterisation

During the exposure, the central region of the two samples exposed at high temperature was contaminated with molybdenum originating from the plasma source. This contamination was characterised using energy-dispersive x-ray spectroscopy (EDX).

Table 4.1 Tungsten and molybdenum concentrations obtained by energy-dispersive x-ray spectroscopy with varied probing depth. Probing depths were estimated using simulations in CASINO [219]. The probing depths given for the 15 and 20 keV scenarios are the average of the probing depths for the 2 characteristic x-rays, MV and LIII.

		Centre		5 mm off-centre		Unimplanted	
Electron	Probing	W	Mo	W	Mo	W	Mo
energy	Depth	(at%)	(at%)	(at%)	(at%)	(at%)	(at%)
(keV)	(1/e ² nm)						
HT HD							
5	39	11.1	88.9	99.8	0.2	100.0	0.0
10	112	17.7	82.3	100.0	0.0		
15	169	31.4	68.6				
20	280	39.8	60.2				
HT LD							
5	39	60.7	39.3	99.8	0.2	100.0	0.0
10	112	86.0	14.0				
15	169	91.6	8.4				
20	280	94.2	5.8				
LT HD							
5	39	97.9	2.1				
10	112	99.5	0.5				
15	169						
20	280						

CASINO [219] was used to estimate the electron probing depths for different energies. The centre of the HT HD sample, showed ~60% molybdenum for a 280 nm probing depth. The HT LD sample showed ~6% molybdenum for the same depth. Away from the centre and in the unimplanted regions, both samples showed no molybdenum even for a 39 nm probing depth. The LT HD sample had 2% molybdenum at the centre with the same probing depth and insignificant amounts at further in. Hence, given the TGS probing depth of ~1 μm , the molybdenum surface contamination is expected to have little effect except in the central regions of the HT samples, which have been excluded from this study (boxed region in Fig. 4.3).

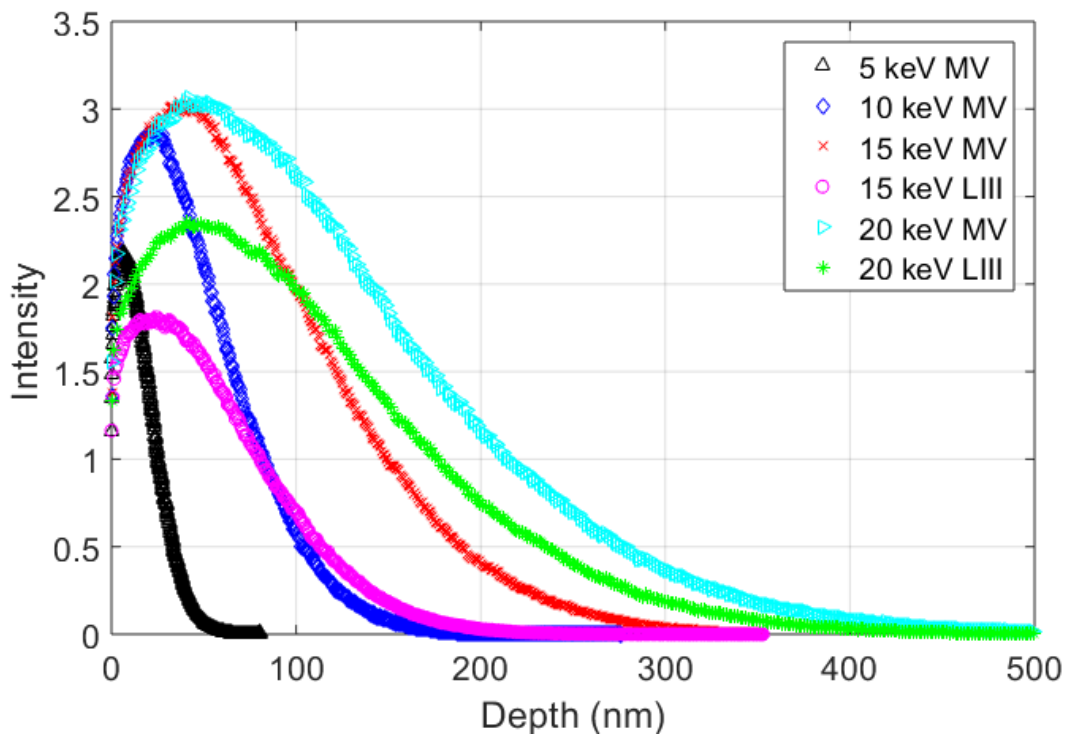


Figure 4.4 EDX X-ray generation depths for the different electron energies considered. MV and LIII denote the two characteristic x-rays generated for tungsten.

4.4.2 Blister Characterisation (SEM)

SEM micrographs of the exposed regions show prominent blistering in all samples (Fig. 4.5), while unexposed regions are blister free (Fig. 4.6). For the LT samples there is no obvious spatial variation of blister morphology. Blister diameters are $\sim 0.5\text{-}1\text{ }\mu\text{m}$, consistent with previous studies [91]. Micrographs from the LT-LD sample (Fig. 4.5 (a) and (b)) and the LT-HD sample (Fig. 4.5 (c) and (d)) shows similar blistering, despite the fact that the LT-HD sample received a dose 20 times higher than the LT-LD sample. This suggests that, at least for the conditions considered here, the blistering effects is largely independent of deuterium flux and fluence. The micrographs of samples exposed to deuterium at the higher temperature (HT) (Fig. 4.5 (e) and (f)) show blisters that seem slightly ($\sim 5\text{-}10\%$) smaller than the low temperature ones. However, the morphology seems to vary little with deuterium dose. The contrast in the HT HD sample, Fig. 4.5 (f) is believed to originate from the molybdenum contamination.

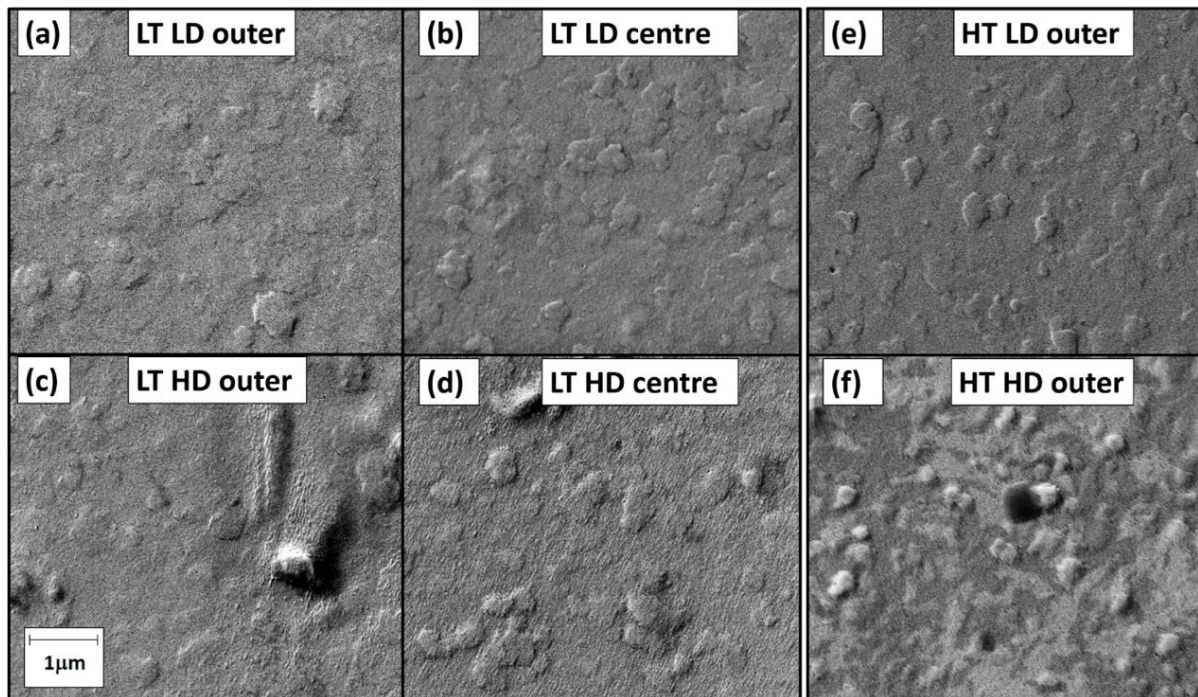


Figure 4.5 SEM micrographs of the exposed samples at different radial locations 'r'. (a) LT LD $r = 5\text{ mm}$, (b) LT LD $r = 0\text{ mm}$, (c) LT HD $r = 5\text{ mm}$, (d) LT HD $r = 0\text{ mm}$, (e) HT LD $r = 5\text{ mm}$, (f) HT HD $r = 5\text{ mm}$. The same scale bar applies to all micrographs.

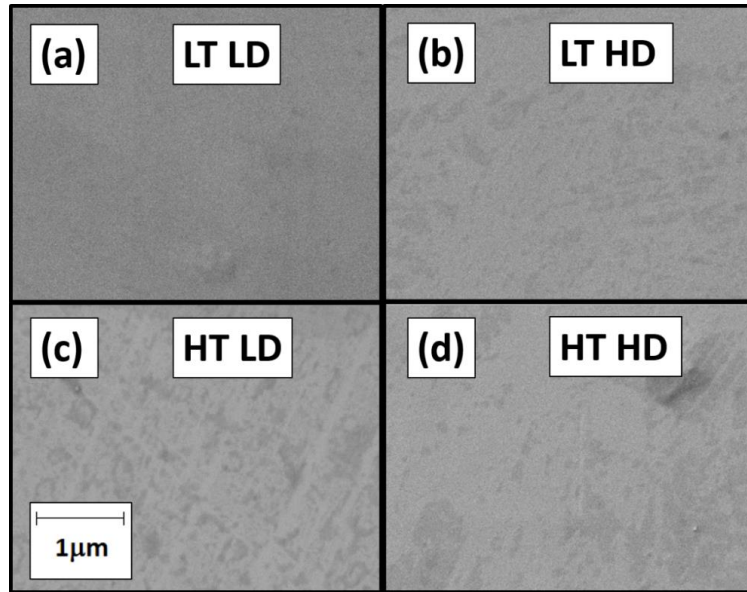


Figure 4.6 SEM micrographs for the unimplanted regions in the LT LD (a), LT HD (b), HT LD (c) and HT HD (d) samples.

Cross-sectional micrographs of the LT LD sample showed that blisters extend up depths of 0.8 – 1 μm (Fig. 4.7 and 4.8).

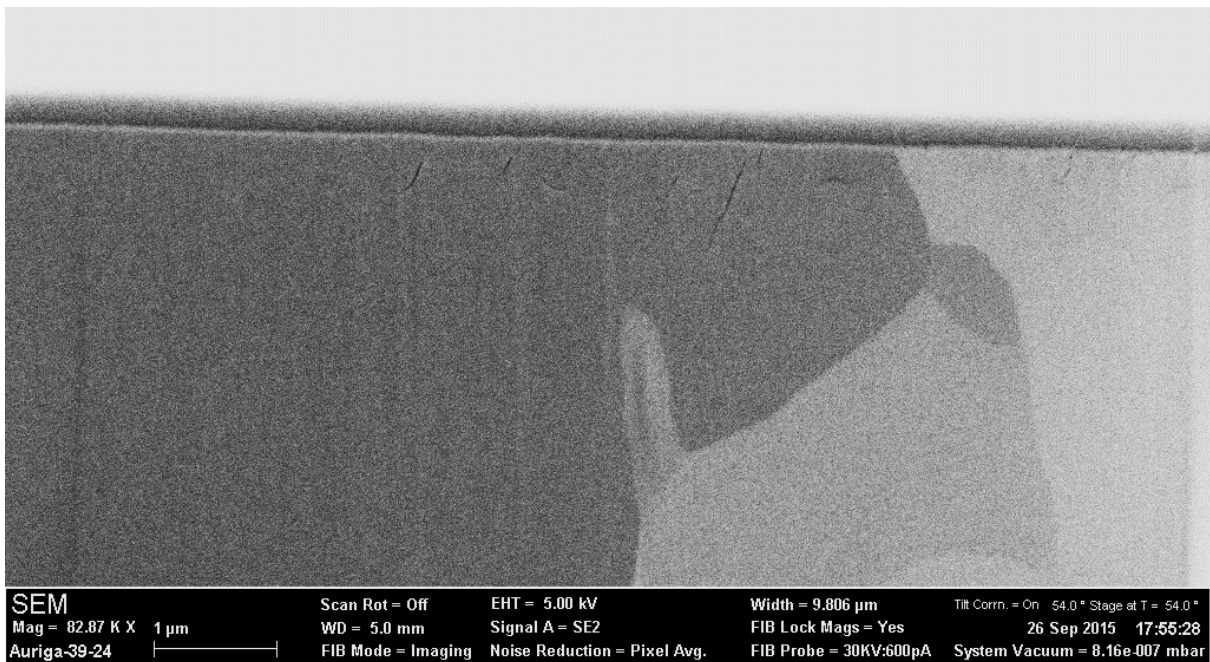


Figure 4.7 Cross-sectional micrograph of the low temperature low dose (LT LD) sample at 82.87K zoom. The presence of sub –surface cavities is evident up to depths of $\sim 1 \mu\text{m}$. The scale bar corresponds to 1 μm .

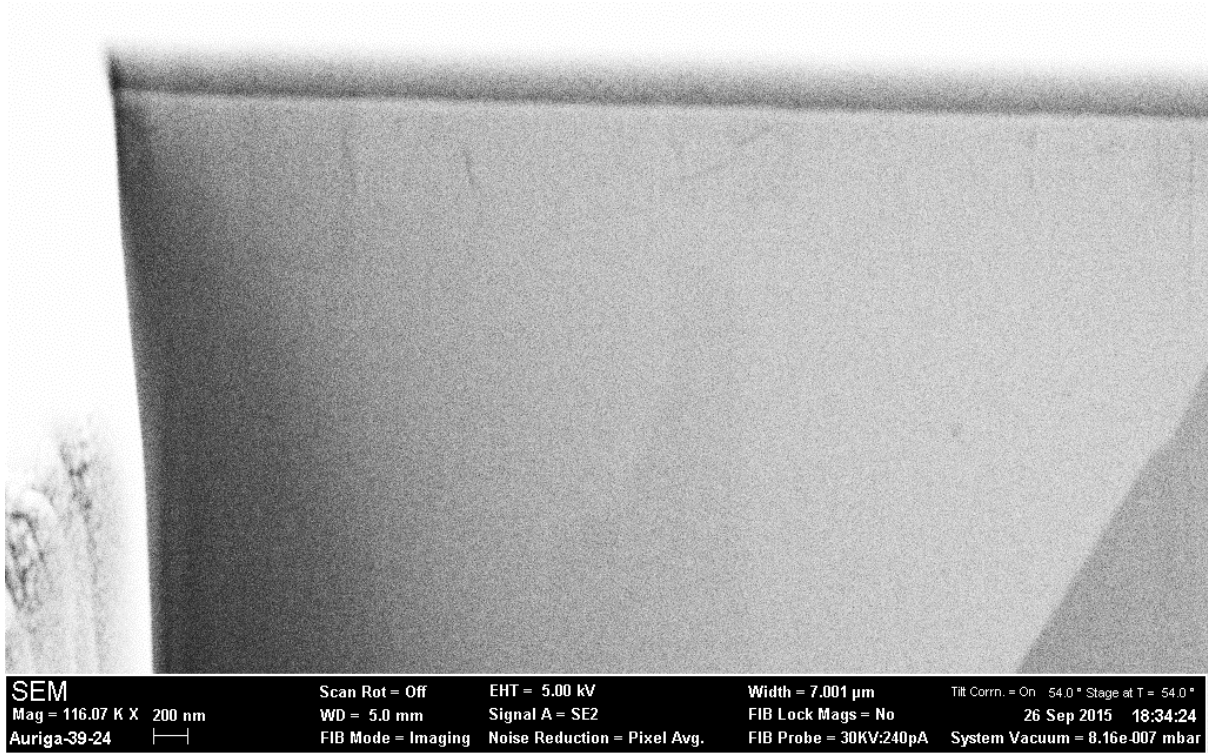


Figure 4.8 Cross-sectional micrograph of the low temperature low dose (LT LD) sample at 116K zoom. The presence of sub-surface cavities is evident up to depths of $\sim 1 \mu\text{m}$. The scale bar corresponds to 200 nm.

4.4.3 Transient Grating Spectroscopy

The TGS scans included the unexposed sample edges as a built-in reference. Fig. 4.9 shows thermal diffusivity and SAW speed as a function of position in the LT-HD sample. Profiles for the LT-LD, HT-LD and HT-HD samples are given in Figs. 4.10, 4.11 and 4.12 respectively. The unexposed edges are identified by their higher thermal diffusivity and SAW speed. The changes between unexposed and exposed regions are also evident from TGS traces representative of both areas. The unexposed regions for all samples have a thermal diffusivity of $(6.6 \pm 0.2) \times 10^{-5} \text{ m}^2\text{s}^{-1}$, which agrees well with literature values for pristine tungsten [14,15,197,198]. Thermal diffusivity in the exposed region reduces to between 5.5 and $6.1 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ for all samples.

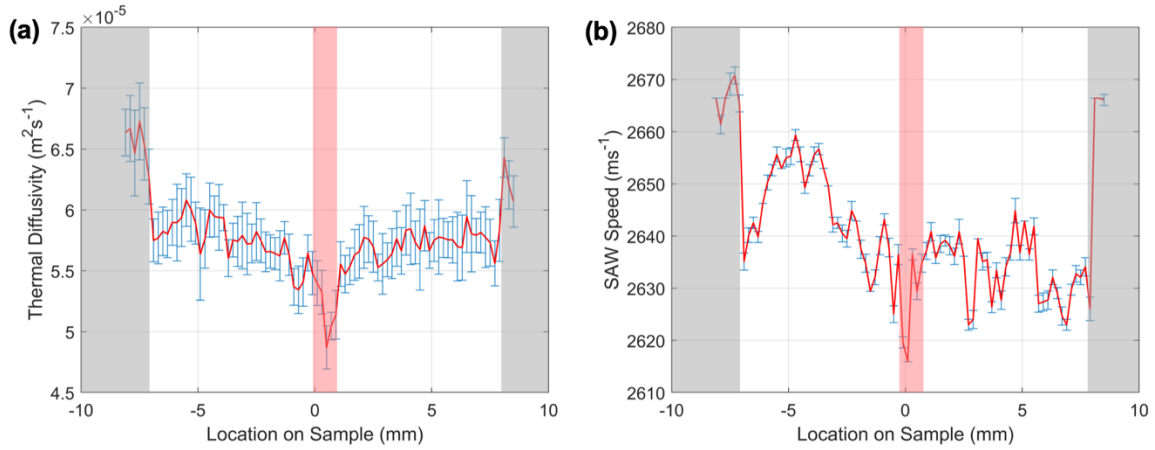


Figure 4.9 Thermal diffusivity (a) and SAW frequency (b) profiles for the low temperature low dose (LT HD) sample. Error bars are the standard deviation for each point, obtained over 10 measurements. The x-axis is corrected for the centre of the incident ion beam. The red shaded region depicts data excluded from the analysis due to surface contamination. The grey shaded region was not exposed to deuterium.

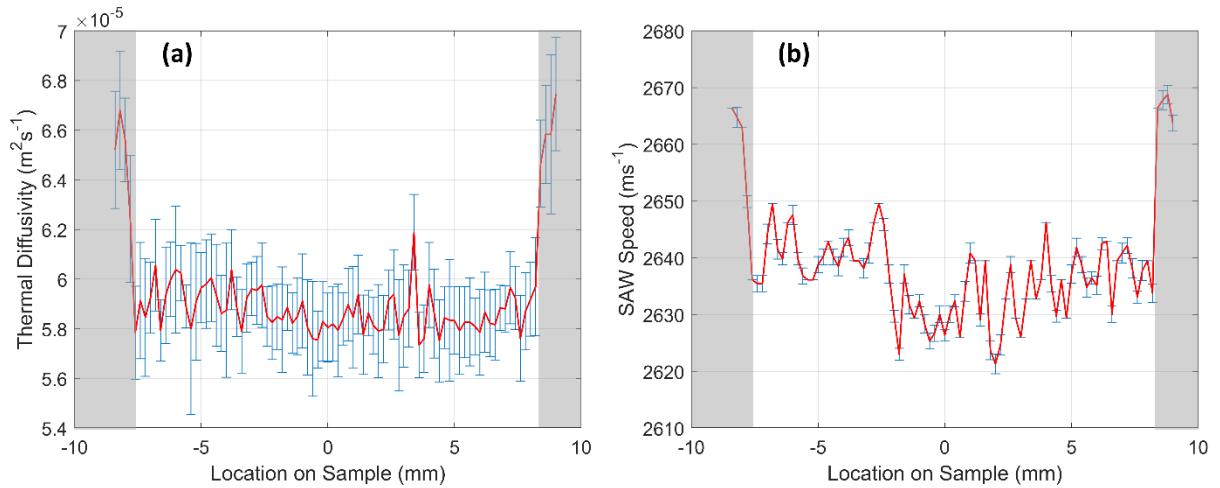


Figure 4.10 Thermal diffusivity (a) and SAW profile (b) for the low temperature low dose (LT LD) sample. Error bars are the standard deviation for each point, obtained over 10 measurements. The grey shaded region was not exposed to deuterium.

At the centre of the LT-HD sample there is a sharp drop in thermal diffusivity to $\sim 5.0 \times 10^{-5} \text{ m}^2\text{s}^{-1}$. Since the samples were exposed to temperature variations and deuterium beams with near-Gaussian shape, this feature is surprising. This drop is the consequence of nuclear reaction analysis (NRA) previously performed on these samples [86]. The NRA study involved irradiation with helium ions to a damage level of 3.2 dpa and is seen to have a substantial effect on the thermal diffusivity. These points were hence excluded from the present analysis of deuterium-exposure effects.

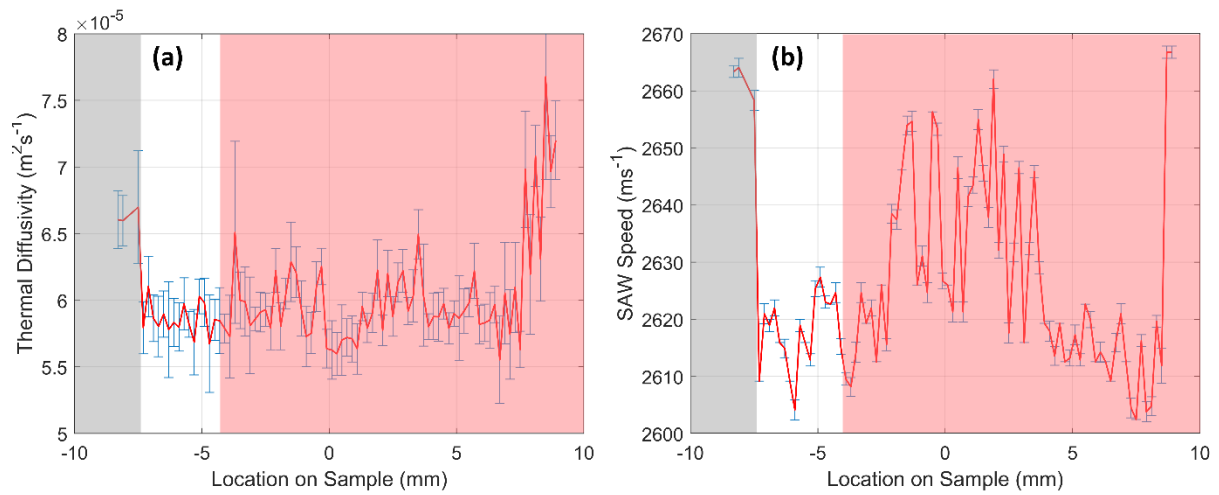


Figure 4.11 Thermal diffusivity (a) and SAW profile (b) for the high temperature low dose (HT LD) sample. Error bars are the standard deviation for each point, obtained over 10 measurements. The red shaded region depicts data excluded from the analysis due to surface and molybdenum contamination. The grey shaded region was not exposed to deuterium plasma.

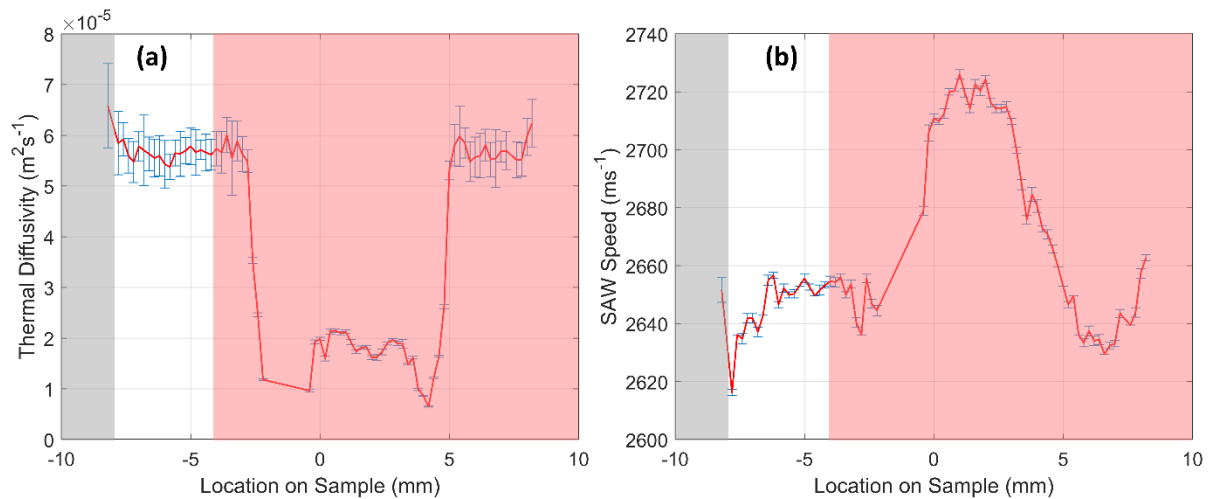


Figure 4.12 Thermal diffusivity (a) and SAW profile (b) for the high temperature high dose (HT HD) sample. Error bars are the standard deviation for each point, obtained over 10 measurements. The red shaded region depicts data excluded from the analysis due to molybdenum contamination. The grey shaded region was not exposed to deuterium.

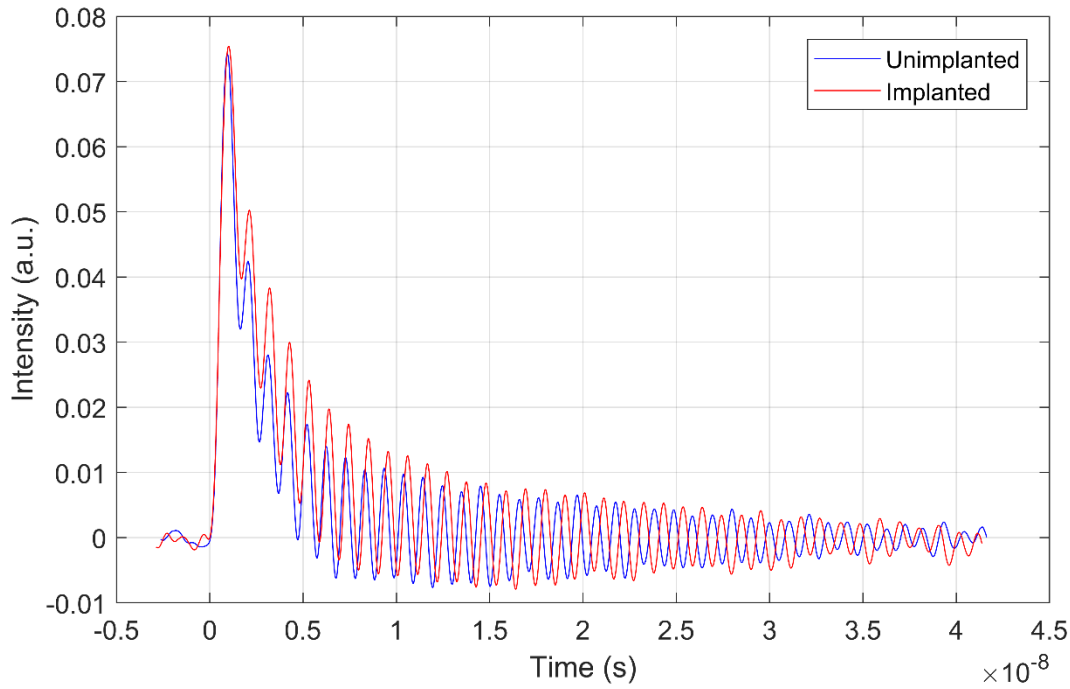


Figure 4.13 Transient grating signal for a single measurement at the unimplanted edge (blue) and implanted centre (red) of the LT HD sample

The SAW speed of the unexposed edges in all samples except the HTHD is $2668 \pm 2 \text{ ms}^{-1}$, in good agreement with previous measurements [200]. In the HTHD sample it is $\sim 2655 \text{ ms}^{-1}$. The SAW speed drops steeply from the unexposed to exposed region and then continues to gradually decrease towards the centre of the sample. The fluctuations of SAW speed with a period of $\sim 0.8 \text{ mm}$ in the exposed region are reliably found in repeated measurements (Figs. 4.9-4.11 (b)). Such fluctuations are not evident in either the flux or temperature profiles (Fig. 4.3). Therefore, it cannot be the result of a fluctuation in flux or temperature. It is also not present in the thermal diffusivity results, hence it is not a measurement error. Thus, it is likely that this is an effect of the grain dependent elastic anisotropy. This variation has a magnitude of $\sim 10 \text{ ms}^{-1}$, which agrees with previous work on the elastic anisotropy of tungsten [200]. EBSD scans in Fig. 4.2 show grain sizes of $200 - 400 \text{ }\mu\text{m}$ which is comparable to the length scale of these fluctuations, reaffirming this.

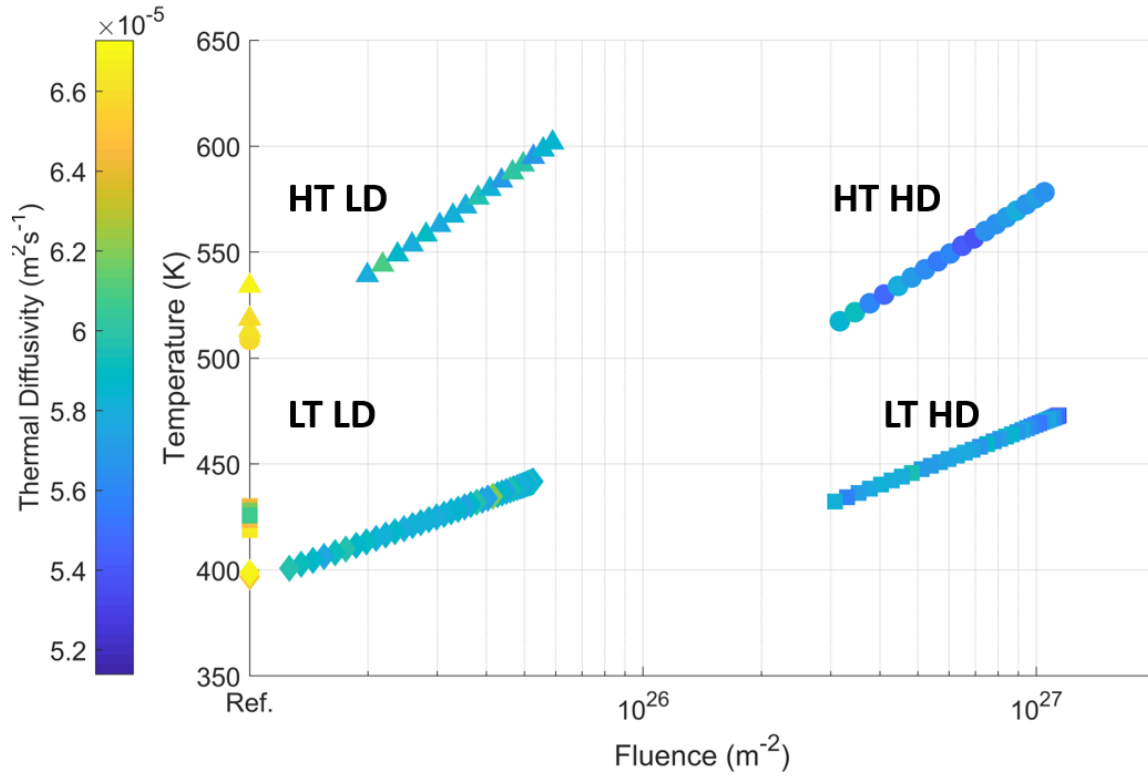


Figure 4.14 Measured thermal diffusivity with fluence and temperature for the four samples considered. Data from the high temperature high dose sample (HT HD) is depicted by circles, high temperature low dose (HT LD) by triangles, low temperature low dose (LT LD) by diamonds and low temperature high dose (LT HD) by squares. Reference fluence is zero, which is the value for the unexposed region.

Fig. 4.14 summarises the thermal diffusivity measurements, plotted as a function of exposure temperature and fluence. The unimplanted regions in all four samples have thermal diffusivity greater than $6.5 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ in agreement with previous studies [14,15,197,198]. There is a significant drop in thermal diffusivity between virgin and deuterium-exposed areas, irrespective of fluence and exposure temperature. The high dose (HD) samples show a larger reduction in thermal diffusivity compared to their low dose counterparts. The drop in diffusivity between the LD and HD samples (from $6.0 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ to $5.5 \times 10^{-5} \text{ m}^2\text{s}^{-1}$), is similar in magnitude to the drop between the LD samples and unexposed regions (from $6.6 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ to $6.0 \times 10^{-5} \text{ m}^2\text{s}^{-1}$). However, HD samples received a 20 times higher dose than LD samples, meaning that the drop in thermal diffusivity is not proportional to fluence.

4.5 Discussion

A similar trend has been observed by NRA, where the sub-surface deuterium concentration in deuterium plasma-exposed tungsten samples was measured for different fluences [86]. NRA profiles showed a large difference in deuterium concentration between unimplanted regions and regions exposed to a fluence of $\sim 5 \times 10^{25} \text{ m}^{-2}$, similar to the exposures considered here. The deuterium concentration in the samples exposed to $\sim 10^{27} \text{ m}^{-2}$ was only slightly higher. This suggests that with increasing fluence the deuterium concentration, blistering and thermal diffusivity reduction saturate. The fluence at which this saturation occurs may vary and depends on a number of factors such as the crystallography, heat treatment and surface polishing [90,98]. Since we observe little change in thermal diffusivity when fluence is increased by more than one order of magnitude, it is likely that our fluences are within this saturation regime.

The thermal diffusivity seems to correlate quite well with blister morphology, which remains largely unchanged between low and high dose exposed samples. Previous studies [45] reported an increase in blistering with fluence for fluences of $\sim 10^{23} - 10^{25} \text{ m}^{-2}$. This suggests that the initial increase in blistering with fluence is followed by the saturation observed in this study. In the HT HD sample, with increasing temperature and fluence there is an initial decrease in thermal diffusivity followed by a recovery, depicted by the transition from light blue markers to dark blue and then back to light blue at higher temperatures. This effect is not evident in the LT HD sample. Previous studies [220] showed decreased near-surface ($<1 \text{ }\mu\text{m}$) deuterium concentrations at temperatures above 490 K. Hence this feature is believed to be an effect of the elevated temperature, which has initiated a recovery of thermal diffusivity, despite the higher D fluence.

Previous studies suggest different mechanisms for thermal diffusivity reduction due to plasma exposure/ion implantation [14,15,23,24,129]. Defects created by high energy ions or neutrons can function as effective electron scattering sites, thereby reducing thermal diffusivity, which for tungsten at room temperature is dominated by electron-mediated transport. Significant reductions in thermal diffusivity have been reported for self-ion implanted tungsten [23,129]. However, the deuterium ion energy used in this study (~ 50 eV) was much lower than usual self-ion implantation energies (150 keV - 30 MeV)[23,185], and below the threshold required to produce displacement damage [221]. Hence displacement damage does not play a prominent role.

However studies have shown that foreign gaseous ions such as deuterium and helium infused into the tungsten matrix can self-trap, i.e. an interstitial deuterium ion is attracted to another [24,27,46,85,89]. These ions then cluster, forming bubbles with increasing pressure, resulting in blisters. From the SEM micrographs in Fig. 4.5, it is clear that there is extensive surface blistering in all samples. These blisters are surface manifestations of such sub-surface gas-filled cavities [88]. These act as additional scattering centres and also suppress thermal diffusivity by reducing thermal contact between the surface and the bulk.

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5. Thermal diffusivity degradation and point defect density prediction in self-ion implanted tungsten

This chapter is based on the study that has been published in Acta Materialia as “A. Reza, H. Yu, K. Mizohata, F. Hofmann, Thermal diffusivity degradation and point defect density in self-ion implanted tungsten, Acta Mater. 193 (2020) 270–279. doi:10.1016/j.actamat.2020.03.034.” [34]. The samples were prepared by H. Yu and implanted by K. Mizohata. H. Yu obtained the EBSD map. Rest of the work in this chapter was carried out by the author under the supervision of F. Hofmann.

5.1 Abstract

Using transient grating spectroscopy (TGS) we measure the thermal diffusivity of tungsten exposed to different levels of 20 MeV self-ion irradiation. Damage as low as 3.2×10^{-4} displacements per atom (dpa) causes a measurable reduction in thermal diffusivity. Doses of 0.1 dpa and above, up to 10 dpa, give a degradation of ~55% from the pristine value at room temperature. Using a kinetic theory model, the density of irradiation-induced point defects is estimated based on the measured changes in thermal diffusivity as a function of dose. These predictions are compared with point defect and dislocation loop densities observed in transmission electron microscopy (TEM). Molecular dynamics (MD) predictions are combined with the TEM observations to estimate the density of point defects associated with defect clusters too small to be probed by TEM. When these “invisible” defects are accounted for, the total point defect density agrees well with that estimated from TGS for a range of doses spanning 3 orders of magnitude. Kinetic theory modelling is also used to estimate the thermal diffusivity degradation expected due to TEM-visible and invisible defects. Finely distributed

invisible defects appear to play a much more important role in the thermal diffusivity reduction than larger TEM-visible dislocation loops. This work demonstrates the capability of TGS, in conjunction with kinetic theory models, to provide rapid, quantitative insight into defect densities and property evolution in irradiated materials.

5.2 Introduction

A comprehensive understanding of the effect of irradiation on the properties of nuclear-relevant materials remains a substantial challenge [6,38,222–224]. Current understanding of the degradation of fission reactor material properties with irradiation has largely stemmed from empirical models derived from swathes of neutron irradiation experiments undertaken at various irradiation facilities [5,225]. Fusion reactor environments present additional challenges in the materials domain, since the radiation and heat loads will be significantly larger than in their fission counterparts [2,226]. The diverter, which removes the exhaust gases from the reactor core, experiences the largest heat and radiation fluxes [4,214]. Tungsten, due to its high melting point, high thermal diffusivity, low sputtering yield and low vapour pressure is a prime contender for the diverter armour [7]. Hence understanding the evolution of thermal diffusivity in tungsten with irradiation is of key value and is undertaken in this study.

The fusion reactor core presents a hostile environment. Apart from high heat loads, the tungsten armour will be bombarded by high energy neutrons (14.1 MeV), alpha particles, deuterium ions, as well as other species [7]. The neutrons can impart sufficient energy to displace tungsten atoms from their lattice sites. These primary knock on atoms (PKAs) will dislodge further atoms from their lattice sites, creating cascades of displacement damage [13,20]. The resulting lattice defects lead to a locally increased electron scattering rate, degrading thermal diffusivity. Neutrons also cause transmutation of tungsten into rhenium, tantalum and osmium that act as effective electron scattering sites and reduce thermal diffusivity [14]. Transmutation also

causes the formation of helium, which agglomerates to form bubbles within the tungsten matrix and also decreases the thermal diffusivity [24]. Similarly the diffusion of hydrogen and its isotopes from the plasma into the tungsten matrix leads to the formation of blisters that can also cause a degradation of the thermal diffusivity [18]. A significant reduction in thermal diffusivity is of concern, as it would lead to steeper temperature gradients within components for the same heat flux. This would cause (a) higher surface temperatures and an associated increased risk of melting and (b) increase thermal stresses that are largely responsible for fatigue of armour components [4].

The complexity of the different processes associated with neutron irradiation makes it attractive to consider alternative approaches that allow a specific aspect to be singled out and analysed separately. For example alloying with transmutation products such as rhenium, tantalum and osmium has been used to study the effects of transmutation [15,24]. Self-ion irradiation is attractive for singling out displacement damage for detailed analysis [21,23].

Self-ion implantation provides a shallow damaged layer, only a few microns thick, even for implantation energies of tens of MeV. Hence bulk measurement techniques for thermal characterisation are unsuitable. Transient grating spectroscopy (TGS) [29–32,183] enables thermal diffusivity measurements in micron thick surface layers with high temporal (few seconds) and spatial ($\sim 100\text{ }\mu\text{m}$) resolution. The effect of irradiation damage on thermal transport has been successfully investigated using ion implantation and TGS on helium implanted tungsten [24] and more recently on self-ion implanted copper [26] and silicon implanted niobium [25]. Inferring radiation damage through thermal transport measurements is novel, compared to electrical resistivity measurement techniques. Recently, thermal transport measurements using time-domain thermo-reflectance [227–229] and TGS [25] have been used to qualitatively understand the underlying irradiation damage.

In this study, we perform thermal diffusivity measurements of self-ion implanted tungsten, spanning damage levels from 10^{-4} displacements per atom (dpa) to 10 dpa. A kinetic theory (KT) model is used to interpret the measured thermal diffusivity in terms of the underlying point defect densities resulting from the self-ion irradiation. This data is compared to transmission electron microscopy (TEM) observations [21] and predictions from molecular dynamics (MD) simulations [59] of irradiation-induced defects in tungsten. The kinetic theory model is also used to infer the thermal diffusivity reductions expected for the defect densities reported by the TEM and MD studies. The results highlight the capability of TGS to provide quantitative information about the production of irradiation damage, as well as to enable new insights into the relative importance of different types of defects in controlling thermal diffusivity degradation. Fig. 5.1 shows a flowchart of the core analysis work carried out in this study.

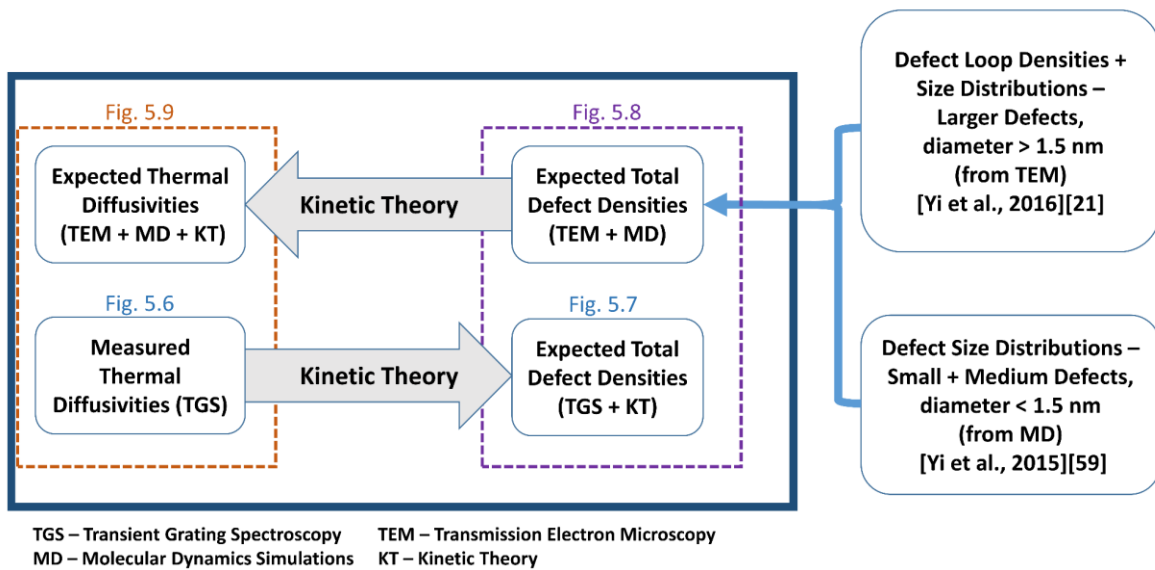


Figure 5.1 Flowchart of the core work carried out in this study, including the comparisons between the measured and expected thermal diffusivities, and TGS predicted and TEM + MD expected defect densities.

5.3 Materials and Methods

5.3.1 Sample Preparation and Implantation

Polycrystalline tungsten samples (99.97 wt% purity, procured from Plansee) 10 x 10 mm square, 1 mm thick, were annealed at 1500 °C for 24 hours in vacuum (10^{-5} mbar) to allow full recrystallisation. The samples were then mechanically ground using 600 to 1200 grade abrasive papers followed by diamond slurry polishing. They were finally electrochemically polished at room temperature in a bath of 0.1 % NaOH in deionised water for 1-2 minutes at 8V to remove any polishing-induced defects and produce a high quality mirror finish. Electron back scatter diffraction (EBSD) measurements were carried out to examine the microstructure using a Merlin FEG SEM. Fig. 5.2(a) shows a representative EBSD map.

Ion implantations at room temperature were carried out at the Helsinki Accelerator Laboratory with 20 MeV $^{184}\text{W}^{5+}$ ions with a 5 MV tandem accelerator [230]. Raster scanning was used to obtain a spatially uniform implantation profile across a sample area of 15 x 15 mm², with a beam spot size of ~5 mm. A beam profilometer was used to monitor the beam current and dose. The beam current measurement was calibrated using a Faraday cup in the target chamber. The lowest dose samples (10^{-4} and 3.2×10^{-4} dpa) were implanted using beam currents of ~0.5 nA/cm², and high dose samples (3.2 and 10 dpa) were exposed at beam currents of ~90 nA/cm². These correspond to flux densities of 6.2×10^8 and 1.1×10^{11} ions/cm²/s respectively. The remaining samples were irradiated using a flux density of $\sim 3.1 - 5.0 \times 10^{10}$ ions/cm²/s.

The Stopping and Range of Ions in Matter (SRIM) code [28] was used to estimate the fluences required for specific damage levels. The model used for dpa estimation was the Quick Kinchin-Pease calculation model, and the threshold displacement energy for the tungsten target was taken as 68 eV [231]. Injection of 20 MeV tungsten ions was modelled at normal incidence, averaging over 70022 ion calculations. While SRIM estimates the displacement damage

created by ions, it does not account for any recombination of defects. Fig. 5.2(b) shows the predicted depth variation of displacement damage, as well as the implanted ion concentration for the 1 dpa sample. Superimposed on the plot in Fig. 5.2 (b) is the depth probed by TGS – approximately 1 μm , which is well within the damaged layer.

For the implantations, 13 damage levels were considered from 10^{-4} to 10 dpa, where the damage level refers to the peak of the damage profile. An unimplanted sample, which had undergone the same polishing and annealing steps was used as a reference. An additional as-received sample (not annealed) was also considered. Table 5.1 details the damage levels considered and the corresponding implantation flux and fluences.

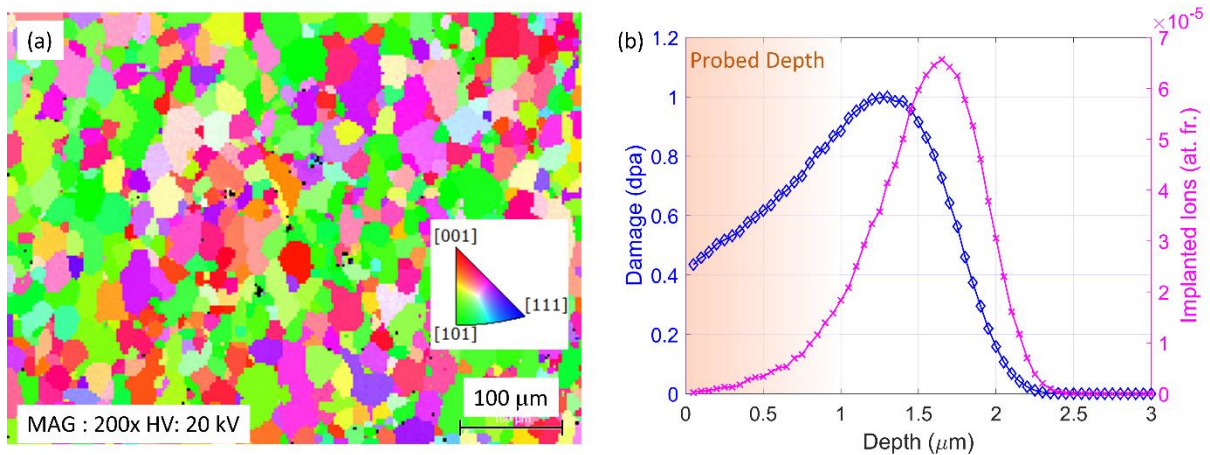


Figure 5.2 (a) Representative EBSD map of the annealed tungsten material. (b) Damage and implantation profiles predicted using SRIM for the 1 dpa sample. The TGS probing depth is shown as a shaded region.

Table 5.1 The 13 dose levels considered with their SRIM calculated fluences, incident ion fluences, beam current densities, ion flux densities and damage rates.

Dose (dpa)	Calculated Fluence (ions/cm²)	Incident Fluence (ions/cm²)	Beam Current (nA/cm²)	Flux Density (ions/cm²/s)	Damage Rate (dpa/s)
0.0001	2.53×10^{10}	2.7×10^{10}	0.5	6.24×10^8	2.3×10^{-6}
0.00032	8.10×10^{10}	8.13×10^{10}			
0.001	2.53×10^{11}	2.42×10^{11}	25-40	$3.1-5.0 \times 10^{10}$	$1.2 - 2.0 \times 10^{-4}$
0.0032	8.10×10^{11}	8.03×10^{11}			
0.01	2.53×10^{12}	2.55×10^{12}			
0.018	4.55×10^{12}	4.61×10^{12}			
0.032	8.10×10^{12}	8.20×10^{12}			
0.056	1.42×10^{13}	1.42×10^{13}			
0.1	2.53×10^{13}	2.54×10^{13}			
0.32	8.10×10^{13}	8.11×10^{13}			
1.0	2.53×10^{14}	2.53×10^{14}	90	1.12×10^{11}	4.4×10^{-4}
3.2	8.10×10^{14}	8.10×10^{14}			
10.0	2.53×10^{15}	2.53×10^{15}			

5.3.2 Thermal diffusivity measurements

Thermal diffusivity was measured using the laser-induced transient grating spectroscopy (TGS) method [24,29–32,183]. TGS involves excitation of the sample with two pulsed laser beams (1 kHz repetition rate, 0.5 ns pulse duration, 532 nm wavelength) that are crossed at the sample surface with a well-defined angle. Interference of the beams creates a periodic intensity pattern with selectable wavelength. Some of the light is absorbed by the sample surface, which heats up and undergoes rapid thermal expansion, creating a spatially periodic temperature and displacement grating i.e. the ‘transient grating’. As heat diffuses from peaks to troughs and into the bulk, the temperature grating decays. The sudden thermal expansion of the sample also launches two counter-propagating surface acoustic waves (SAW) with the same wavelength as the excitation grating. The SAW wave speed provides information about the elastic properties of the sample [127,200]. By comparing the SAW wave speed measured from a tungsten reference sample with literature data [127,200,232,233] the TGS wavelength was calibrated and found to be $\lambda = 2.758 \pm 0.001 \mu\text{m}$. Tungsten is particularly suitable for use as a calibration standard since it is almost perfectly elastically isotropic [200]. Detailed descriptions of the TGS theory and the TGS setup used are given in sections 2.4.4 and 3.3 respectively.

The response of the sample to the excitation is probed by diffraction of a continuous wave probe beam (561 nm wavelength) from the transient temperature and surface height profiles in the sample. The diffracted probe beam is combined with a reflected reference beam (561 nm wavelength) to allow heterodyne detection. The resulting signal is recorded using a fast avalanche photo diode and oscilloscope, and analysed to obtain the thermal diffusivity and SAW wave speed data. Two probe and heterodyne beams are used in the dual-heterodyne configuration [183], which greatly increases the time resolution and signal to noise ratios. The experimental setup used here is based on the “boxcar” geometry which allows very high relative phase stability between the pump and probe beams [196]. The average probe beam

power was ~ 22 mW (total for 2 probe beams and 2 heterodyne reference beams, chopped with a 0.25 duty cycle). The average pump (excitation) power at the sample was 1.5 mW (1.5 μ J per pulse/excitation at a 1 kHz repetition rate). The measured reflectivity was $\sim 50\%$, giving the absorbed pump and probe energies by the sample as ~ 0.75 mW and 11 mW respectively. The excitation and probing spot sizes were ~ 140 μ m and ~ 90 μ m ($1/e^2$) respectively. The measurements were carried out at room temperature, and under a vacuum of $\sim 10^{-3}$ mbar. Sample TGS traces for implanted and unimplanted specimens are provided in Fig. 5.3. It can be seen that the signal decays faster in the unimplanted sample, as the higher thermal diffusivity results in a more rapid decay of the transient temperature grating. A change in SAW frequency with implantation is also noticeable. The oscillations of the unimplanted trace are to the left of those in the 0.01 dpa and 10 dpa traces due to the higher frequency.

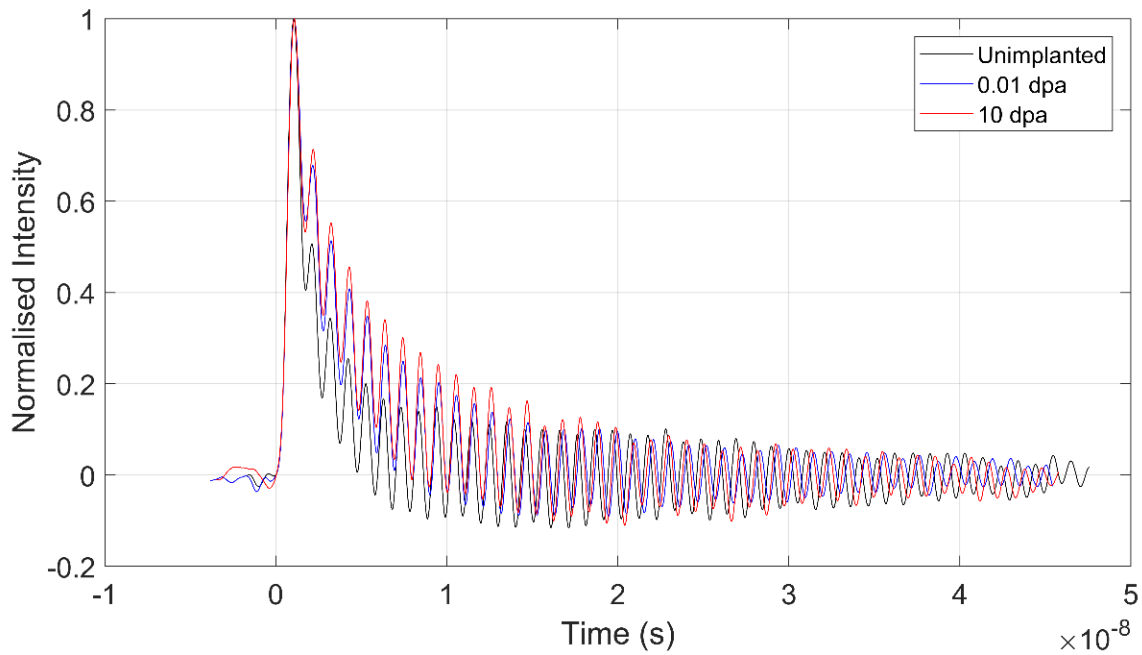


Figure 5.3 Sample TGS traces for the unimplanted, 0.01 dpa and 10 dpa samples. The signal intensity is normalised to account for the variation due to slight changes in sample surface reflectivity.

To ascertain if the TGS laser pulses affected the samples or the damage in the implanted material, the 0.32 dpa sample was measured continuously for over 5 hours. The measured thermal diffusivity remained constant over this period as seen in Fig. 5.4 indicating that the TGS measurement does not cause any modification of the sample. Fluctuations in the wavelength of the excitation and probe beams, heating up of the optical elements, electronic noise, and other environmental effects could be possible sources for the scatter observed in the thermal diffusivity. The scatter observed was seen to follow a normal distribution, with the mean thermal diffusivity being $3.15 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ with a standard deviation of $0.04 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$.

Previous calculations indicate that the thermal diffusivity probed by TGS is dominated by a sample surface layer of thickness $\sim \lambda/\pi$ [29]. Thus, for the present TGS wavelength, the probed depth is slightly less than 1 μm , which is well within the thickness of the implanted layer (see Fig. 5.2(b)). As such the thermal diffusivity measured by TGS will be dominated by the ion-irradiated material.

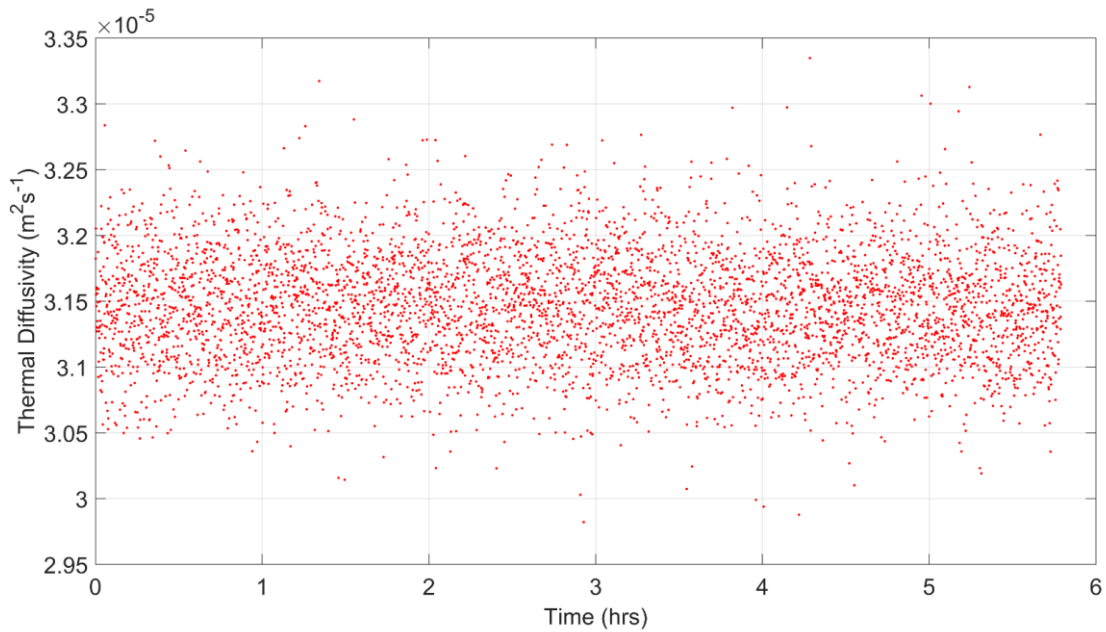


Figure 5.4 Thermal diffusivity recorded for 5000 consecutive TGS measurements on the 0.32 dpa implanted tungsten sample. Each measurement consisted of 2000 laser pulses.

5.4 Results and Discussion

5.4.1 Thermal Diffusivity degradation with dose

TGS was used to create thermal diffusivity maps of $\sim 1\text{-}2\text{ mm}^2$ in each sample with a step size of $150\text{ }\mu\text{m}$, resulting in 40-50 measurement points per map. 20,000 excitations (10 measurements/point with 2,000 excitations/measurement) were sampled for each point, resulting in an uncertainty of $<6\%$ in the measured thermal diffusivity. Fitting of the experimental data was carried out in MATLAB [199]. Fig. 5.5 shows a sample trace with fit.

The TGS traces were fit to the following equation from [24] using MATLAB [199] .

$$I = A \operatorname{erfc}(q\sqrt{\alpha t}) + C \sin(2\pi f t + E) \exp(-t/F) + G \quad (5.1)$$

α is the thermal diffusivity, f is the SAW frequency, and t is time. A and C are the proportionality constants for the thermal decay and SAW oscillations respectively, E is the initial phase offset of the SAW oscillations, F is the time constant for the decay in the SAW oscillations and G is the background in the signal.

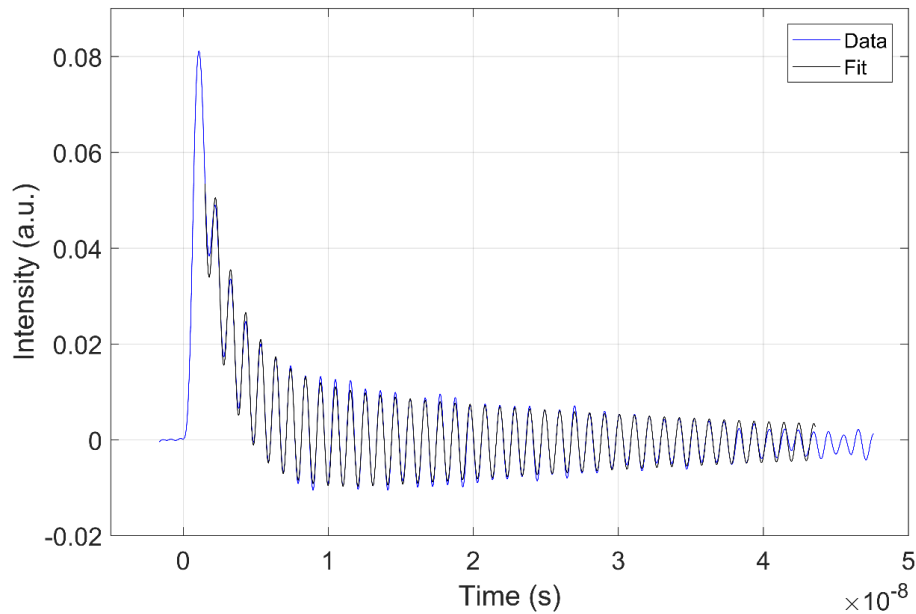


Figure 5.5 Sample TGS trace and fit for the unimplanted tungsten sample.

The average thermal diffusivity value from each map was then taken as the value at the corresponding damage level. Fig. 5.6 shows the measured thermal diffusivity values for the self-ion implanted samples for damage doses from 0.0001 dpa to 10 dpa.

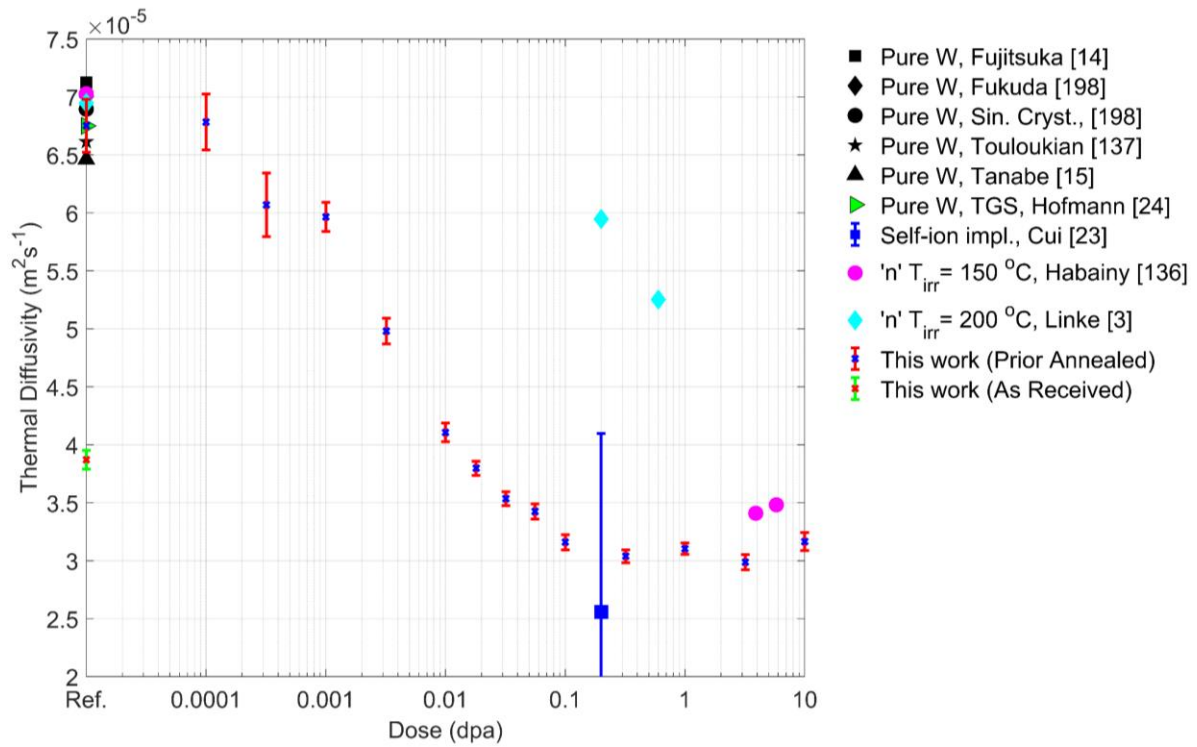


Figure 5.6 Measured thermal diffusivity values for unimplanted, as-received and self-ion implanted tungsten samples exposed to different damage doses. Literature data from previous studies on pure and irradiated tungsten is also shown.

Measurements of an unimplanted reference sample and of a sample that had been polished but not annealed (as rolled) are also shown in Fig. 5.6. The thermal diffusivity obtained for pristine, annealed tungsten is $\sim 6.8 \times 10^{-5} \text{ m}^2\text{s}^{-1}$. This agrees very well with room temperature measurements of thermal diffusivity in unimplanted tungsten from previous studies using conventional methods [14,15,137,198] and TGS [24](also shown in Fig. 5.6). The error bars of our measurement also fall within the range of values obtained in these studies. It is worth noting that previous thermal diffusivity measurements [198] on pure single and polycrystalline

samples yielded very similar results (the samples in the present study are polycrystalline). This is expected since tungsten has a cubic lattice structure, and hence isotropic thermal diffusivity.

For comparison of the measured thermal diffusivity in ion-irradiated tungsten samples, literature data from previous tungsten irradiation experiments has also been plotted in Fig. 5.6: Self-ion implanted tungsten (at ambient conditions) [23]; tungsten irradiated with protons and spallation neutrons (at 115-140 °C) [136]; neutron irradiated tungsten (at 200 °C) [3]. From these studies just one is on self-ion implanted tungsten [23], and at just one dose level. The error bars observed in that study are significantly larger due to the measurement uncertainty in the 3-omega method used [23]. Fig. 5.6 demonstrates that TGS allows measurements with significantly lower uncertainty.

The error bars are larger for the unimplanted, 0.0001 dpa and 0.00032 dpa samples and become progressively smaller with increasing damage level. We ascribe this to impurities in the tungsten samples. Depending on the spatial location the impurity levels will vary, giving slightly different values of thermal diffusivity. For the samples with higher damage, on the other hand, thermal diffusivity reduction due to defects is the dominant effect.

The thermal diffusivity of the implanted samples begins to drop at ~ 0.00032 dpa, and then reduces steadily to a value of $\sim 4 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at 0.01 dpa, a 40 % drop, after which it begins to saturate. Full saturation is achieved by 0.1 dpa, at a value of $\sim 3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, corresponding to a 55% decrease in room temperature thermal diffusivity. The thermal diffusivity then stays constant with further implantation up to 10 dpa. The dose values seen in Fig. 5.6 for the onset and completion of saturation agree closely with those identified for saturation of irradiation-induced defects in TEM studies [21]. This link is further explored in sections 5.4.2 and 5.4.3.

Previous data from neutron irradiated tungsten show a higher thermal diffusivity than measured here for damage levels of 0.2 and 0.6 dpa [3]. This was initially thought to stem from the higher irradiation temperature (200 °C), which favours migration, resulting in the annihilation of defects. However studies [21,126] have shown that such effects are dominant above ~400 °C, so the temperature alone cannot account for the increased thermal diffusivity observed in this case. However, there is insufficient data on the experimental methods and procedures used for the work in [3] to confidently ascertain the source of this higher than expected thermal diffusivity value. Data from tungsten irradiated with spallation neutrons and protons [136] at a temperature of 110 – 140 °C, also shown in Fig. 5.6, does not exhibit this increase. It should be noted that these samples have significant helium and rhenium content. The 3.9 dpa sample is reported to have 158 ppm and the 5.8 dpa sample 245 ppm of helium. The rhenium fraction is estimated to be around 2% in both samples. Previous thermal diffusivity studies on tungsten-rhenium alloys indicate a thermal diffusivity drop of more than 30% for a 2% rhenium content [14,24]. A 10% reduction in the thermal diffusivity of tungsten has been observed for 280 ppm helium [24]. Hence it is likely that for the work in [136] the effect of the higher irradiation temperature in ‘healing’ some of the irradiation induced defects is countered by the helium and rhenium content accumulated in the samples. It should be noted that the rhenium content is the result of transmutation due to the neutron irradiation and the helium content is also due to the exposure. Hence, in neutron irradiated samples, there exist competing interactions that affect the thermal diffusivity. De-convolving these effects to build an effective understanding is challenging. Self-ion irradiation is attractive as it makes it possible to study the effect of displacement damage in isolation.

Fig. 5.6 also shows an interesting result for the as-rolled, un-annealed tungsten sample, which has a thermal diffusivity of $\sim 3.9 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, 40% less than the annealed sample. Given that impurity content will be the same in both, this difference must be due to dislocations introduced

by the rolling process, highlighting that crystal defects have a substantial influence on thermal transport in tungsten. The thermal diffusivity of the as-rolled tungsten is similar to that of an annealed sample exposed to a damage dose of 0.01 dpa. If un-annealed tungsten were to be used for fusion reactor armour, a reduced value of thermal diffusivity should be used for design, rather than the book value, to account for the reduced diffusivity from fabrication-induced defects.

An interesting question concerns the effect of dose rate on the irradiation induced thermal diffusivity degradation. Studies on loop and void damage in ion-implanted tungsten have shown a relatively small effect of dose rate [114]. In self-ion implanted Fe-Cr alloys, on the other hand, dose rate is seen to have a significant effect on irradiation hardening [212]. In our work, other than for the 1×10^{-4} and 3.2×10^{-4} dpa samples which had a damage rate of $\sim 2.3 \times 10^{-6}$ dpa/s, all the samples were exposed to damage rates of $\sim 10^{-4}$ dpa/s. If the damage rate within this range of doses were to affect the thermal diffusivity, it would be expected that the lower damage rate would cause a larger change in the material property, i.e. the thermal diffusivity, as seen in the irradiation-induced hardening study [212]. However, we do not see such an effect in the thermal diffusivity of the samples irradiated at lower dose rates. Similarly, the samples with the highest dose rates, the 3.2 and 10 dpa samples (dose rate of 4.4×10^{-4} dpa/s from table 5.1), would then be expected to have a higher thermal diffusivity than the 1 dpa sample. However, Fig. 5.6 does not show this effect. This suggests that, for the dose rates used in this study, the effect of dose rate on the thermal diffusivity is small. More generally, the question of dose rate dependence is a very important one, especially at high damage rates where a substantial fraction of cascades overlap. Detailed investigation of this question is reserved for a future study.

5.4.2 Inferring defect populations from TGS measurements

At room temperature, electrons are the main carriers of heat in pure metals [234]. Disorder introduced into the tungsten lattice by irradiation-induced defects increases electron scattering rates, thereby reducing thermal diffusivity. In this section, the reduction in thermal diffusivity, due to ion implantation-induced damage, is used to estimate the underlying defect population.

A single tungsten atom, dislodged by a PKA, leaves behind a vacancy. The presence of a vacancy increases the scattering rate of the surrounding atoms. The dislodged atom, now called a self-interstitial atom (SIA), also has an increased scattering rate compared to when it was in the matrix. This increased electron scattering rate is responsible for the decrease in electron-mediated thermal diffusivity. A PKA streaming through the matrix creates cascades of such damage that can then interact and evolve, giving clusters and loops of interstitials and vacancies [13,60].

To infer defect populations from TGS thermal diffusivity measurements, a simple kinetic theory model for electron-mediated thermal transport is used. Here the electronic thermal conductivity is given by

$$\kappa_e = \frac{1}{3} C_e v_F^2 \tau_e \quad (5.2)$$

where C_e is the electronic heat capacity, v_F is the Fermi velocity and τ_e is the electron scattering time [209]. Considering the damaged tungsten as a dilute alloy of the pure tungsten matrix with vacancies and interstitials as ‘alloying entities’, the electron scattering time at a point defect (alloying atom) of type ‘m’ in the matrix is given by

$$\tau_{e,m} = (\sigma_{0,m} + \sigma_1 T + \sigma_2 T^2)^{-1} \quad (5.3)$$

where $\sigma_{0,m}$ is the impurity scattering term, $\sigma_1 T$ captures electron-phonon scattering, $\sigma_2 T^2$ is the electron-electron scattering term, and T is the absolute temperature [234–236]. σ_1 and σ_2 are experimentally determined constants for the pure material [24], and $\sigma_{0,m}$ is the scattering rate contribution from the disorder created by the defect.

The thermal conductivity for a matrix containing various defect types, with atomic fractions c_m and scattering time $\tau_{e,m}$ is then given by

$$\kappa_e = \frac{1}{3} C_e v_F^2 \left(\sum_m \frac{c_m}{\tau_{e,m}} + \left(1 - \sum_m c_m \right) \frac{1}{\tau_e} \right)^{-1} \quad (5.4)$$

where τ_e is the electron scattering time for the pure material [24].

Irradiation forms complex populations of defects with different sizes [13,59,66]. The exact nature of this distribution depends on irradiation conditions, temperature and impurities in the sample to mention but a few factors. This distribution is very complex and not known a-priori. Because of the large number of unknowns, including this explicitly in a scattering model is impractical.

Hence, we proceed using the simplest possible model linking defects to thermal diffusivity, concentrating on the number of point defects required to give the observed thermal diffusivity degradation. In this regard the following assumptions are made:

1. All the defects are point defects, of which there are just two types, vacancies and self-interstitials.
2. No loss of interstitials at the free surface, i.e. the vacancy and interstitial densities are equal.
3. No clustering of defects i.e. the environment of the defect is not considered. This is already an implicit assumption in the impurity scattering kinetic theory model – each atom is considered in isolation.

Rearranging eqn. 5.2 gives the following expression for the Frenkel pair density c_{FP} in terms of the thermal diffusivity α

$$c_{FP} = c_v = c_i = \left[\frac{\frac{\tau_e C_e v_F^2}{3\rho C_P \alpha} - 1}{\tau_e (\sigma'_i + \sigma'_v) - 2} \right] \quad (5.5)$$

where $\sigma'_i = 1/\tau_{e,i}$ and $\sigma'_v = 1/\tau_{e,v}$ are the adjusted scattering rates at interstitial and vacancy sites respectively. ρ is the mass density and C_P is the specific heat capacity. Values for σ'_i and σ'_v were obtained using literature data on the rate of change of electrical resistivity per interstitial and vacancy in tungsten [237]. Using the Wiedemann-Franz law, eqn. 5.4 can be re-written in terms of electrical resistivity ρ_e , Lorentz number L and the defect densities as

$$\rho_e = \frac{3LT}{C_e v_F^2} \left[\frac{c_v}{\tau_{e,v}} + \frac{c_i}{\tau_{e,i}} + \frac{(1 - c_i - c_v)}{\tau_e} \right] \quad (5.6)$$

By differentiating eqn. 5.6 with respect to the relevant defect densities c_i and c_v , we get values for $\tau_{e,i}$ and $\tau_{e,v}$. These are then inverted to give the scattering rates for eqn. 5.5. Since the measurements were carried out at constant temperature, the value of τ_e remains the same throughout. Hence, it was obtained by substituting the value of the thermal diffusivity measured for the pure tungsten sample into eqn. 5.2. The remaining constants C_e , v_F , C_P are obtained from literature [137,236]. Table 5.2 contains the numerical values and sources of the parameters used.

Table 5.2 Numerical values of parameters used and their source.

Parameter	Value	Source
τ_e	21.93 fs	Calculated
σ'_i	17.3 fs ⁻¹	
σ'_v	6.1 fs ⁻¹	
C_e	26208 J m ⁻³ K ⁻¹	[236]
C_P	132 J kg ⁻¹ K ⁻¹	[137]
v_F	9.50 Å fs ⁻¹	[236]

The Frenkel pair densities that are obtained by feeding the measured thermal diffusivities into eqn. 5.5 are shown in Fig. 5.7. The error bars show the uncertainty in the number of Frenkel defects, estimated based on the uncertainty in the thermal diffusivity measurements. The uncertainty was obtained from the following expression

$$\delta(c_{FP}) = \left| \frac{\frac{\tau_e C_e v_F^2}{3\rho C_p}}{[\tau_e(\sigma'_i + \sigma'_v) - 2](\alpha^2)} \right| \delta(\alpha) \quad (5.7)$$

where $\delta(\alpha)$ is the uncertainty in the thermal diffusivity, and $\sigma'_i = 1/\tau_{e,i}$ and $\sigma'_v = 1/\tau_{e,v}$ are the adjusted scattering rates for interstitials and vacancies respectively. ρ is the mass density [137], C_p is the specific heat capacity [137], C_e is the electronic heat capacity [236], v_F is the Fermi velocity [236] and τ_e is the electron scattering time.

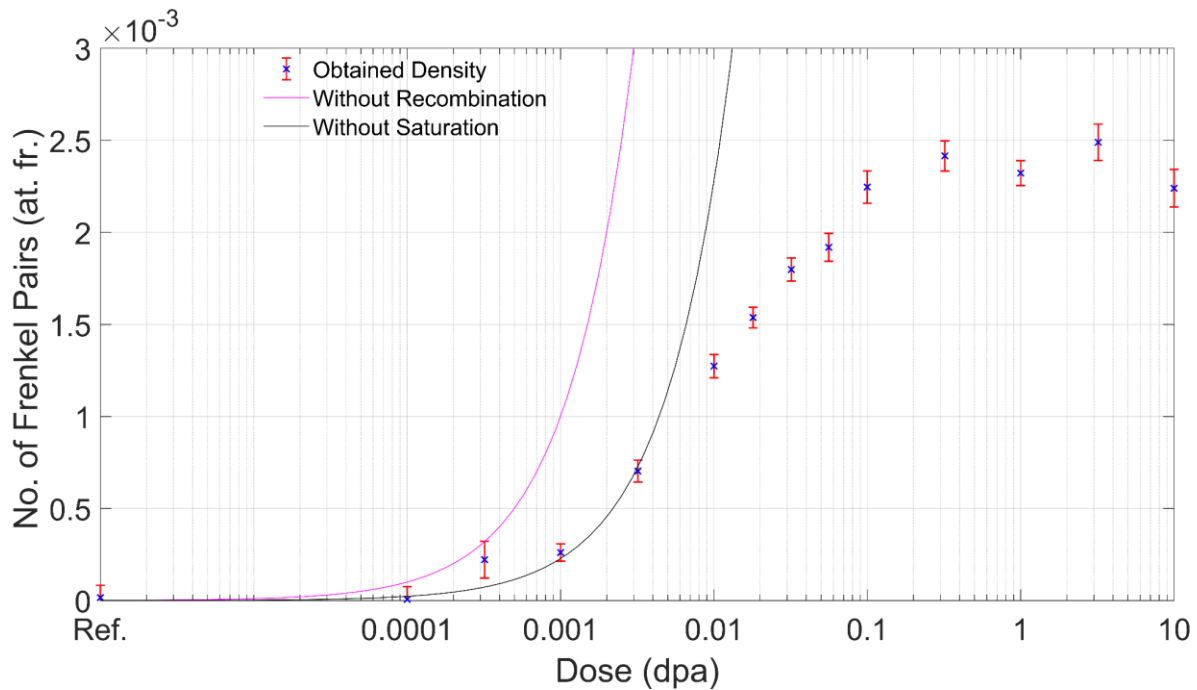


Figure 5.7 Point defect densities estimated from the measured thermal diffusivity for the unimplanted and ion-implanted tungsten samples. The magenta line denotes the defect densities expected based on SRIM calculations if there were no recombination of defects. The black curve denotes the expected densities if there were no saturation of defects. Error bars included are from the TGS measurement uncertainty only.

For doses greater than 0.00032 dpa Fig. 5.7 shows a noticeable increase in Frenkel defect density, which rises steadily up to an atomic fraction of defects of $\sim 0.13\%$ at 0.01 dpa. Above 0.1 dpa the defect density saturates at $\sim 0.24\%$. This density of $\sim 0.24\%$ at. fr. is associated with a room temperature thermal diffusivity of $\sim 3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (see Fig. 5.6).

Defect Retention Estimation

Most of the vacancies and interstitials created by the implantation recombine. Only a small fraction of the damage created is retained. Without this recombination, the atomic fraction of Frenkel pairs in the matrix would be equal to the damage dose in displacements per atom (dpa), shown by the magenta curve in Fig. 5.7, i.e. all the damage created would be retained.

At lower doses a linear accumulation of damage with dose has been observed. This is the regime where there is no significant overlap of displacement damage cascades [21]. The black line in Fig. 5.7 shows a linear scaling of defect density with dose, fitted to damage levels up to 0.0032 dpa. It is seen to fit quite well for the doses up to 0.0032 dpa, with a gradient of 0.23 ± 0.08 Frenkel Pairs per dpa, which is an estimation of the proportion of damage retained, also known as the NRT efficiency [56]. MD simulations of primary radiation damage in metals such as Ni, Pd, and Pt, for implantation energies of 30-200 keV are reported to give NRT efficiencies of 0.2 - 0.3 Frenkel Pairs per dpa [56]. Similar behaviour has been observed for tungsten in [51]. This NRT efficiency should translate well to higher ion energies such as the 20 MeV used in this study, due to the cascade splitting which is reported to take place above ~ 150 keV in tungsten [58,144]. Hence this TGS predicted defect retention estimate lies well within the bounds predicted by MD simulations. As such TGS provides a direct way of mapping out the retention of damage as a function of dose.

5.4.3 Comparison of defect densities estimated from TGS with transmission electron microscopy and molecular dynamics simulation data

It is interesting to compare the point defect densities estimated from thermal diffusivity measurements to those observed in TEM and MD simulations. TEM and MD provide information on defect cluster densities as well as damage formation and evolution. A recent detailed in-situ TEM study considered the implantation of ~150 keV tungsten ions into the tungsten matrix to mimic the effect of PKA damage [21].

A brief description of PKA damage evolution is as follows; the PKA displaces other tungsten atoms, which go on to dislodge further atoms, creating a cascade of displacement damage. Initially, this damage takes the form of a high vacancy concentration core, surrounded by interstitial atoms [13,20]. Within a few nano-seconds much of the cascade damage recombines, leaving behind a population of defects ranging from single atom (point) defects to defect clusters and dislocation loops up to several nanometres in size. These further evolve on longer time-scales through elastic interactions, as well as thermally-activated migration [59].

Previous TEM and MD studies have shown that the size distribution of this defect population obeys a power law [59,60,238]. The power law exponent is known to be between -1.6 for 400 keV ions and -1.8 for 150 keV ions [59]. However, TEM studies are not able to cover the entire range of defect sizes due to the following problem: TEM of implantation damage only permits the imaging of loops that have a diameter greater than ~1.5 nm [21,66]. Although this is larger than the ultimate spatial resolution of modern TEMs, TEM measurements are not sufficiently sensitive to probe the small contrast associated with loops smaller than 1.5 nm [143]. Since defect number density and defect size are related by a power law with a negative exponent, it is clear that whilst these “invisible” defects are small, we expect a large number density of such

defects. These small defects, although invisible, can affect material properties such as thermal diffusivity at the macroscopic level.

MD simulations of self-ion damage have been successfully used to capture the creation of cascade damage and its short term evolution [59]. Specifically, for cryogenic experiments the visible defect populations predicted by MD simulations and observed by TEM are in remarkably good agreement [59]. Importantly MD simulations provide information about the whole defect microstructure, from single atom defects to large dislocation loops several nanometres in size [59,60]. Unfortunately, computational limits on the simulation time, for the time being, mean that MD simulations cannot capture the long time-scale evolution of defects, or the effect of damage accumulation during high damage dose exposures. In this section, we combine in-situ TEM results [21] with MD simulations [59] of self-ion implanted tungsten to estimate the total Frenkel pair densities for various damage levels from 10^{-3} dpa to 1 dpa. This data is then compared to the defect densities inferred from TGS.

TEM analysis in [21] provides the areal number density of irradiation defects (loops greater than 1.5 nm in diameter) for the dose range of 0.001 to 0.01 and 0.1 to 1 dpa and the defect loop size distribution at 0.01 dpa. The MD study in [59] contains the loop size distribution, including defects less than 1.5 nm in diameter. Combining these two gives a more complete distribution at 0.01 dpa. Considering the full defect size distribution (combined TEM & MD) the number density of Frenkel pairs (FP) at 0.01 dpa can be estimated as:

$$N_{FP\ 0.01} = \left(\phi_{0.01} \sum_{i=all\ bins} n_{0.01\ i} b_i s_i \right) / (d\ n_W) , \quad (5.8)$$

where $\phi_{0.01}$ is the ion fluence in ions/m², $n_{0.01\ i}$ is the loop number density per incident ion at 0.01 dpa in a specific bin i , b_i is the bin width and s_i is the size of defects (i.e. the number of

FPs in the loop) in a particular bin i . d is the thickness of the implanted layer and n_W is number of tungsten atoms per m^3 .

For thermal diffusivity changes, the total number of point defects within loops may not be the most relevant quantity to consider, since thermal diffusivity reduction depends on the lattice distortion associated with defects [24]. This distortion to the lattice at and near the vacancies or interstitials that make up the loop increases the electron scattering rates resulting in a thermal diffusivity reduction. For a dislocation loop, the strain energy scales with the dislocation line length, i.e. loop circumference. As such a second scenario, where only defects on the circumference of dislocation loops are counted, might be more appropriate for comparison with TGS results. Here $N_{FPC\ 0.01}$, i.e. the number of Frenkel pairs associated with the circumference of dislocation loops in the 0.01 dpa sample, is:

$$N_{FPC\ 0.01} = \left(\phi_{0.01} \sum_{i=\text{all bins}} n_{0.01\ i} b_i c_i \right) / (d n_W) , \quad (5.9)$$

where c_i is the number of defects around the circumference of a given loop with size corresponding to the i^{th} bin. An interesting point to note is that while for large dislocations loops only a comparatively small number of point defects lie around the loop circumference, for small defect clusters the majority of constituent point defects lie on the circumference.

Unfortunately, there is no information in the literature about the variation of the defect size distribution with damage dose. Thus we assume that the defect size distribution is similar over the damage range from 0.001 to 1 dpa. The number of Frenkel pairs for a given damage level ‘D’ can then be obtained as follows:

$$N_{FP\ D} = \frac{m_D}{m_{0.01}} N_{FP\ 0.01} \quad (5.10)$$

where m_D and $m_{0.01}$ are the loop areal number densities in [21] for the given damage level ‘D’ and 0.01 dpa respectively.

$$m_{0.01} = \phi_{0.01} \sum_{i=\text{all bins}} n_{0.01 i} b_i \quad (5.11)$$

Fig. 5.8 shows the comparison between the point defect densities estimated based on the TGS measurements and the densities obtained from TEM and MD data from [21,59].

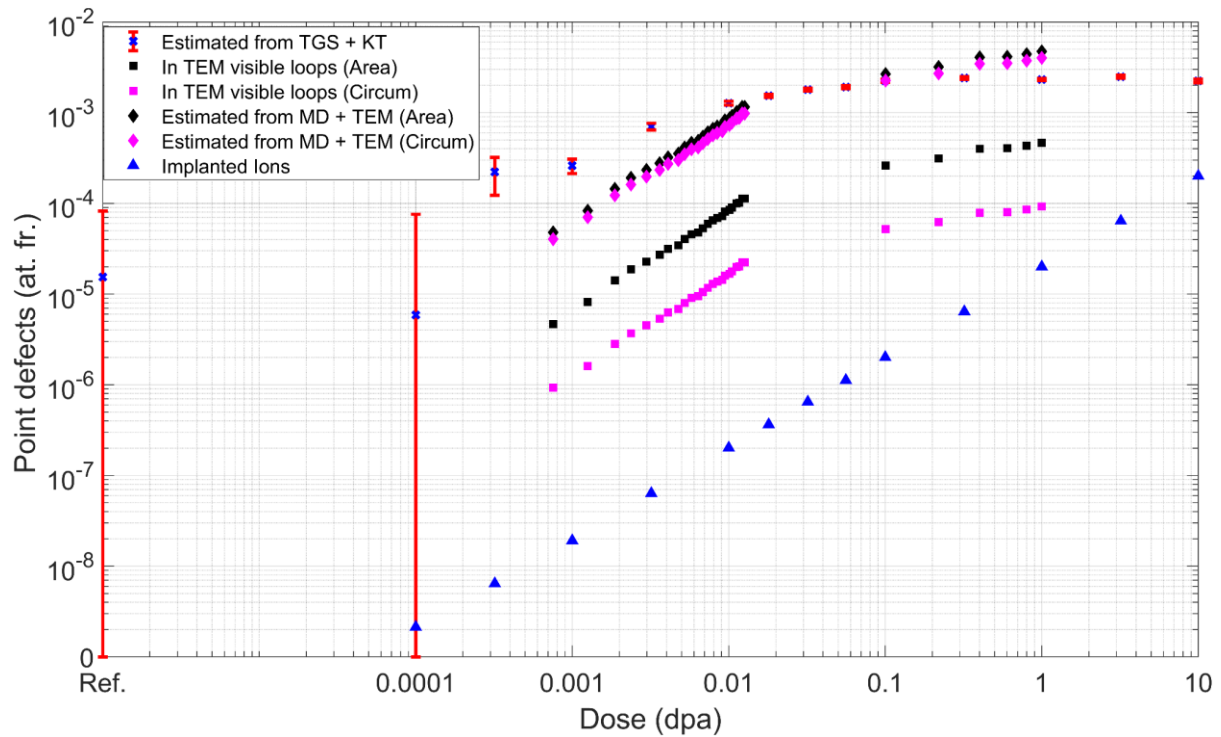


Figure 5.8 Point defect number densities estimated from TGS data with kinetic theory (KT), from TEM visible loops with the area and circumference scenarios and from combined TEM and MD data for the same scenarios. Also included in the plot are the implanted ion number densities. A loop with 10 defects is accounted for as 10 point defects in this computation. Error bars included are from the TGS measurement uncertainty only.

The densities of TEM visible defects (square markers in Fig. 5.8) are significantly lower than the defect densities estimated from TGS. This suggests that a significant proportion of defects is unaccounted for by TEM. Fig. 5.8 also shows that, for TEM visible defects, there is a substantial difference between the defect densities when all point defects within loops are considered and when only defects on the circumference of loops are counted.

Next, we consider the combined number density of defects visible in TEM, as well as point defects and small defect clusters (smaller than 1.5 nm) anticipated from MD predictions. In the low dose range (0.00032 dpa to 0.01 dpa) TEM visible defect densities vary from atomic fractions of 1×10^{-6} at 0.001 dpa to 2×10^{-5} at 0.01 dpa, whereas the combined TEM + MD estimate gives defect number densities of 4×10^{-5} to 1×10^{-3} at the same damage levels. The TGS predicted densities and combined TEM + MD predicted densities agree to within better than an order of magnitude and both rise steadily with dose. After a dose of around 0.1 dpa, the TGS predicted defect densities and the TEM + MD defect densities saturate, and match to within a factor of 2. The transition to saturation is in the same range of doses (0.01 – 0.1 dpa). The saturation Frenkel pair densities for the TGS + KT as well as TEM+MD is $\sim 2-5 \times 10^{-3}$ at. fr., which also agrees with literature values obtained from electrical-resistivity measurements in neutron irradiated tungsten [152], and MD studies [239]. Interestingly, when the smaller defects are included (TEM +MD), the circumference and area treatments differ little. The reason is that for small defects the majority of the atoms involved sit on the circumference of the defect.

The level of agreement is quite remarkable, especially considering that we are using a very simple kinetic theory model to estimate defect densities from thermal diffusivity changes. We are comparing to defect densities from TEM experiments carried out at a much lower ion implantation energy (150 keV vs 20 MeV) and using thin foil samples. The MD calculations also used a 150 keV ion energy, but only cover a comparatively short time period. The results suggest that the defects generated by ion-irradiation are in fact consistent for a given dpa level, even if quite different ion-implantation energies are used, at least for the defects that affect the thermal diffusivity. MD studies also predict that above ~ 150 keV in tungsten, the self-ion initiated cascades undergo cascade fragmentation and sub-cascade splitting, resulting in a deviation from the power law for cascade size [58,144]. Hence, the 20 MeV cascades won't be

as different to 150 keV cascades, as might be expected if the power law were simply extrapolated to higher energies. Our results also highlight that there is a large number of small point defects that are not picked up by TEM, but significantly change material properties.

An important question concerns whether the implanted tungsten ions make a significant contribution to thermal diffusivity degradation. The implanted ion number densities, used to achieve the various damage levels as listed in Tab. 5.1, are superimposed on Fig. 5.8. Even at the highest dose, 10 dpa, the number density of injected ions is an order of magnitude lower than the defect density estimated from TGS. In the range from 0.001 to 1 dpa, where the comparison between defect densities from TGS and TEM + MD was made, the injected ion concentration is at least two orders of magnitude smaller than required to explain the measured reduction in thermal diffusivity. This suggests that the injected ions do not significantly contribute to the observed thermal diffusivity degradation. This is also affirmed by the fact that the thermal diffusivity degradation saturates at higher dose levels. The implanted ion number densities, on the other hand, increase linearly with dose. If the implanted ions did have a significant effect on thermal diffusivity such a saturation with dose would not be observed.

In addition to comparing defect densities estimated by TGS to those observed in TEM and MD simulations, eqn. 5.4 can also be used to estimate the anticipated thermal diffusivity based on observed or estimated point defect densities. Fig. 5.9 shows the predicted evolution in thermal diffusivity considering the full defect population based on TEM and MD, as well considering the TEM-visible defects only.

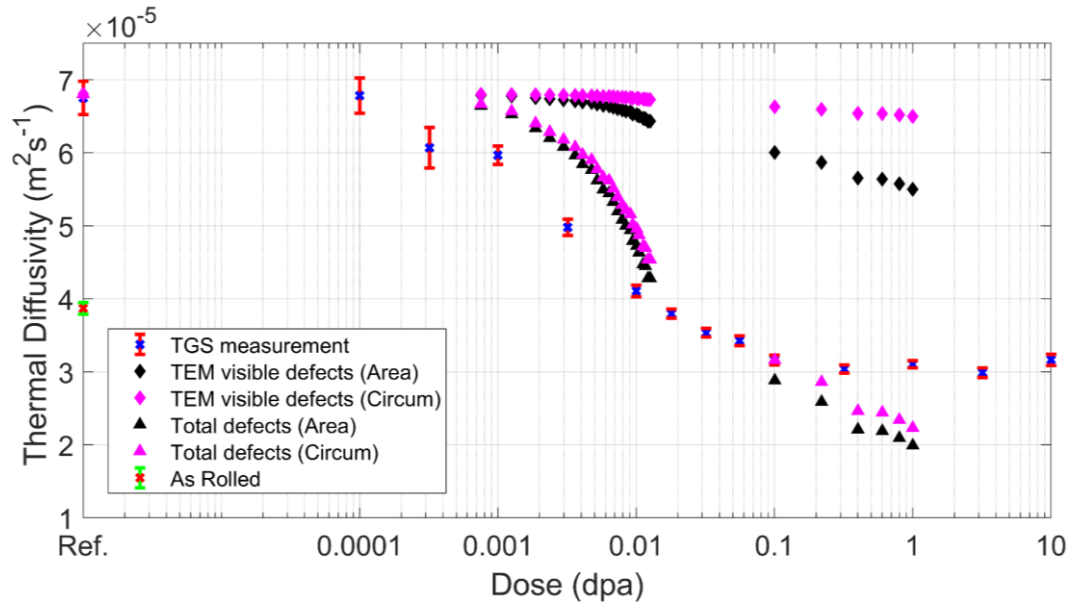


Figure 5.9 Comparison of measured thermal diffusivity using TGS, and expected thermal diffusivity values for the defect densities predicted based on TEM visible defects only and total defect densities (TEM + MD), for self-ion implanted tungsten.

Fig. 5.9 shows that, when only TEM visible defects are considered, the thermal diffusivity is expected to reduce to $\sim 5.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at 1 dpa. This is significantly higher than the actual thermal diffusivity measured by TGS of $\sim 3.0 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at 1 dpa. When the smaller defects are also accounted for, i.e. the TEM + MD scenario, the anticipated thermal diffusivity at 1 dpa is $\sim 2.3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, significantly closer to the TGS-measured value. This agreement is also seen at lower doses. As such it appears that TEM-invisible defects play a more prominent role in controlling thermal diffusivity degradation than the larger defects that are visible in TEM. This is consistent with previous studies on He-ion implanted tungsten where a substantial reduction in thermal diffusivity was observed although all defects are well below the TEM visibility limit [24].

A complication for the study of point defects and defect clusters smaller than $\sim 1.5 \text{ nm}$ is that they cannot be easily probed with TEM [143]. As such, most studies of irradiation damage have concentrated on the creation and evolution of defects that are visible in TEM. For example, the inability to probe small defects is the reason for the apparent incubation dose

required in iron and iron alloys for the appearance of TEM-visible defects [22]. Finding techniques that easily allow the characterisation of TEM-invisible defects is challenging. Lattice swelling and electrical resistivity are sensitive to all defects but have shortcomings: Electrical resistivity methods provide only an average value over the whole specimen and are not suitable for the characterisation of few micron-thick surface layers produced by ion-irradiation [151,240]. Lattice swelling gives an integral measure of defect content [241]. However, while self-interstitials cause a lattice expansion, vacancies cause a lattice contraction. This means that the effects of interstitials and vacancies can cancel out, meaning that lattice swelling measurements will always provide a lower bound estimate of defect number density [27,162]. Ongoing studies using positron annihilation spectroscopy also attempt at gauging TEM invisible defect densities by estimating the vacancy population [140,157]. TGS measurements are attractive because they are sensitive to the total number of defects, since both interstitials and vacancies lead to a reduction in thermal diffusivity. In addition, TGS is sensitive even to very small defect number densities, as seen for doses as low as 0.00032 dpa in this study, and can probe few-micron-thick ion-damaged surface layers.

6. Conclusions and Future Work

6.1 Conclusions

This thesis presents significant and substantial advances in the characterisation and understanding of irradiation damage and its effect on material properties in tungsten, the primary candidate for armour components in future fusion reactors. Several capabilities have been added to the TGS method and demonstrated for key engineering materials. The novel capability of providing quantitative insight into irradiation induced defect population via TGS was developed, demonstrated and validated.

The extensions of the TGS method allows the automated measurement of large SAW speed and thermal diffusivity maps. This implementation of TGS as a microscopy tool offers a number of benefits that are successfully demonstrated.

- Automated large area maps are made across welds. Large scans of implanted areas provide a more comprehensive evaluation of the sample condition. These scans are able to decipher the actual lateral implantation profile, grain orientations, macrozones and pick up anomalies that spot measurements and line scans would fail to show. They also picked up the effects of other measurements, such as NRA, on the sample.
- In elastically anisotropic samples, quite accurate large scale grain maps are can be measured.
- The high signal-to-noise ratio and automation of scanning and data capture provides many more points spatially, which results in significantly better statistics than previous TGS, thermal diffusivity or SAW studies.
- The modified setup is more robust to misalignment as seen with the relatively rough HEA's measured. These were samples that were too rough for EBSD measurements.

This is also important for samples with surface slope errors, as well as samples that evolve, e.g. during in-situ heating or deformation.

- Using the online microscope, targeted measurements of specific regions of interest can be made. This allows us to pick out implanted/unimplanted or weld/parent regions in samples for spot measurements as well as to set the boundaries for 2D map measurements. For samples where scans up to an edge are not possible, the microscope makes it possible to identify specific features of interest that have been located by another technique, EBSD perhaps, and allows us to directly correlate measurements.

Deuterium Exposed Tungsten: Key points

The results on deuterium exposed tungsten have important implications for the design of armour components in future fusion reactors.

- Significant blistering was observed for all exposure temperatures and doses.
- A decrease in the thermal diffusivity of the exposed regions was also measured for the entire range of temperature and ion fluence.
- The thermal diffusivity degradation saturated with increasing ion fluence.
- The thermal diffusivity degradation in deuterium exposed tungsten matches the blistering behaviour.

In test components pristine tungsten was observed to undergo extensive melting at heat fluxes of 27-30 MW/m² [4], while future fusion reactors are expected to have peak heat fluxes of 10-20 MW/m² in the divertor [214]. A reduction of thermal diffusivity will decrease the maximum heat flux that can be accommodated without melting. As such it is key that degradation of thermal transport properties is accounted for in the design of armour components. A positive conclusion from our results is that the deuterium-exposure-induced reduction in thermal

diffusivity appears to saturate quickly, rather than continuing to progress with extended exposure.

Self-ion implanted tungsten; thermal diffusivity and defect estimation: Key points

We have measured the thermal diffusivity degradation of tungsten as a result of self-ion irradiation spanning five orders of magnitude in dose from 10^{-4} to 10 dpa at room temperature. Accuracy of the measurements is higher than any previous study, and the range and resolution in dose are higher than in any previous ex-situ work. Using a kinetic theory model, the measured thermal diffusivity is used to estimate the underlying point defect number density. This is directly compared to TEM observations and MD predictions of ion-implantation-induced defects in tungsten as a function of damage dose. A number of conclusions can be drawn from this work:

- Even very small irradiation doses (as low as 0.00032 dpa) decrease the thermal diffusivity of tungsten. Thermal diffusivity decreases with increasing dose, reaching a 55% reduction at 0.1 dpa. It then remains constant up to 10 dpa, the largest investigated dose.
- Defect number densities estimated from TGS are consistent with those anticipated from TEM and MD with better than order-of-magnitude agreement over three orders of magnitude in dose. This agreement is quite remarkable given the very simple kinetic theory model used and the use of different ion energy and sample geometry in ion-implantation experiments and MD simulations.
- Point defects and defect clusters smaller than ~ 1.5 nm play a dominant role in controlling thermal diffusivity degradation. These defects are challenging to probe since TEM is not sufficiently sensitive to detect them. Thermal diffusivity degradation

is dramatically underestimated when only large defects that are visible in TEM are accounted for.

- The ability of TGS to provide quantitative defect microstructure information, in the form of point defect number densities, is demonstrated. As such TGS provides a convenient tool for probing the entire defect distribution, with excellent sensitivity even to very low defect concentrations.

It is encouraging that for tungsten, as a prototypical bcc material system, we can find consistency between material structure and physical property change. Our results highlight that it will be very important to account for irradiation-induced changes not only in mechanical properties, but also physical properties if tungsten is used as a plasma-facing armour material in future fusion reactors.

6.2 Future Work

Next, an extension is currently underway to enable TGS measurements with in-situ heating. The new in-situ heater is nearing completion of the testing stage and we have demonstrated measurements up to 800°C. It will then be used to measure the effects of annealing on the thermal diffusivity of ion-implanted tungsten. Higher temperatures facilitate the diffusion of interstitials and vacancies, enhancing recombination, which is expected to remove a significant proportion of the implantation-induced defects. The kinetic theory model will be used to compute the defect densities for a direct calculation of the proportion of defects removed by annealing, for comparison with results from TEM.

A research proposal recently submitted to undertake TGS measurements on tungsten during implantation with self-ions in-situ at Sandia National Laboratories has been accepted. These measurements will aid in pinpointing the onset of different interesting phenomena observed in other ex-situ studies, such as the defect saturation reported in chapter 5. The main goal of this study will be to compare in-situ and ex-situ measurements of thermal diffusivity and SAW speed, now that the study in chapter 5 has provided a useful ex-situ dataset.

Alongside this, the work in this thesis is being expanded to other irradiation-damaged materials that are important, such as iron-chrome alloys and tungsten-carbide etc... The goal is to develop a systematic understanding of irradiation-induced property changes across a whole range of reactor-relevant materials.

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