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Motion of W and He atoms during formation of W fuzz

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Abstract
Measurements are conducted to identify the motion of tungsten and helium atoms during the formation of tungsten fuzz. In a first series of experiments the mobility of helium within the growing fuzz was measured by adding ^{3}He to the different stages of plasma exposure under conditions that promoted tungsten fuzz growth. Ion beam analysis was used to quantify the amount of ^{3}He remaining in the samples following the plasma exposure. The results indicate that the retention of helium in bubbles within tungsten is a dynamic process with direct implantation rather than diffusion into the bubbles, best describing the motion of the helium atoms. In the second experiment, an isotopically enriched layer of tungsten (~92.99% ^{182}W) is deposited on the surface of a bulk tungsten sample with the natural abundance of the isotopes. This sample is then exposed to helium plasma at the conditions necessary to support the formation of tungsten 'fuzz'. Depth profiles of the concentration of each of the tungsten isotopes are obtained using secondary ion mass spectrometry (SIMS) before and after the plasma exposure. The depth profiles clearly show mixing of tungsten atoms from the bulk sample toward the surface of the fuzz. This supports a physical picture of the dynamic behavior of helium bubbles which, also, causes an enhanced mixing of tungsten atoms.

I. Introduction

The ability of energetic helium atoms to dramatically alter a variety of metallic surfaces, under certain circumstances, has been well documented [1]. Perhaps the most well studied system is the tungsten-helium system, due to the relevance of tungsten as a plasma-facing material for proposed fusion confinement devices [2]. A recent review documents in detail the changes that can occur during exposure of W to various plasma conditions, including He [3]. Some of the most consequential changes that can occur during He plasma exposure are a change in the surface thermal conductivity making it more difficult to handle the extreme heat flux associated with controlled fusion confinement devices, embrittlement of the surface due to the presence of He atoms making transient heat loads more likely to result in surface cracking and morphology changes to the surface. Any modification to the originally designed surface has the potential to alter the loss rate of material from the plasma-facing component which could adversely affect the confinement properties of the core plasma, therefore, it is essential to have an accurate picture of how the plasma and its surrounding material interact.

Experimental data from high-flux plasma facilities show the following characteristic morphological features of tungsten samples exposed to the flux of helium ions with energies significantly below the sputtering threshold: i) at sample temperatures below about 1000 K a

layer of helium nano-bubbles with the width ~ 30 nm is formed beneath the front surface, and ii) at a temperature between 1000 to 2000 K, a dense series of nano-tendrils (i.e. fuzz) covers the tungsten surface which still contains a bubble-rich layer between the nano-tendrils and the bulk of the tungsten material [4-6]. Although tungsten fuzz structures have been investigated in a variety of ways, there is still no theory explaining the fuzz formation mechanism consistent with all experimental observations. Whereas the formation of nano-bubble layer can be explained by helium trapping with further trap mutation resulting in the formation of helium clusters and, eventually, nano-bubbles. However, many issues regarding both the fuzz and nano-bubble layers, are still conceptually unclear.

In particular: i) once fuzz develops, does it becomes opaque for helium atoms impinging on the sample, or does helium penetrate through the fuzz structure and still reach the base? ii) do helium nano-bubbles in both the fuzz tendrils and the base (in particular those located between the fuzz and the bulk) become "frozen" after they are formed and do not change anymore? iii) does the fuzz growth and nano-bubble layer formation result in the mixing of tungsten atoms and thereby impact the distribution and motion of atoms in the sample?

To shed light on these issues, which can provide very useful information on the physics of both nano-bubble layer formation and fuzz growth, we perform a series of experiments where we study the dynamics of both tungsten and helium atoms in the course of the fuzz growth by employing both helium and tungsten isotopes (^{3}He and ^{182}W) and then tagging their location and concentration with Nuclear Reaction Analysis (NRA) and Secondary Ion Mass Spectrometry (SIMS), respectively.

The PISCES-A linear plasma device [7] is used to expose tungsten samples to helium plasma. The He ion flux for these experiments is in the range of 3-5 x 10^{22} He ions $m^{-2}s^{-1}$ and provides the heat source to the target to get to the desired target temperature. He ions strike the target at an energy of ~ 55 eV, due to the application of a negative potential applied to the tungsten target. This level of energy is chosen to ensure that the incident ions are well below the sputtering threshold energy of tungsten by ^{4}He which is ~120 eV [8]. The duration of the plasma exposures will be described subsequently for the case of each experiment.

II. Dynamics of helium nano-bubbles

In the first experiment, the behavior of helium in the W fuzz is examined by utilizing ^{3}He in the PISCES-A plasma. During the plasma exposure, monitoring the ^{4}He I emission line at 492.193 nm and the ^{3}He I emission line at 492.226 nm with a high-resolution spectrometer provided a measurement of the ^{3}He content throughout the plasma operation. Figure 1 shows an example of the integrated He spectra. The area under the peaks provides a measurement of the relative concentration of each species.

Twenty five mm diameter ITER-grade W disks, supplied by Midwest Tungsten Service, Inc. via powder metallurgy by press-sintering 99.95% pure tungsten powder, were used for this experiment. The samples were exposed to a He plasma fluence of approximately 2 x10^{26} m^{-2} at 1100 K. The surface of the W sample was visibly observed to turn black, the signature of fuzz formation, within the first few minutes of the He plasma exposure. The 90 minute exposures resulted in the formation of roughly 3 μm of fuzz on the surface of the sample, as shown in Figure 2.

Typically NRA is used to profile the D depth distribution in a material using an energetic ^{3}He ion beam as described in [9]. Nuclear reactions between the ^{3}He and D atoms produce energetic protons and ^{4}He particles and the energy distribution of these reaction products

emerging from the sample provides information on the amount and depth of the retained D in the sample. In our experiments, using ^{3}He allows quantification of the amount of helium residing in the tungsten after the plasma exposure by NRA utilizing a D ion beam and the ^{3}He(D,p)^{4}He reaction. The analysis depth of the deuterium beam is approximately 2 μm for the applied energy in fully dense tungsten. Since the porosity of tungsten fuzz is approximately 95% for the conditions in this work [10], the probe beam will easily penetrate and sample the extent of the fuzz and another 1.8 – 1.9 μm into the bulk W substrate. The analysis should, therefore, detect all the ^{3}He in both the fuzz and the interface region between the fuzz and the bulk material. The depth profile analysis is complicated by the fact that the W density of the fuzzy layer is less than that of pure W. We can, therefore, only provide some amount of depth analysis of the ^{3}He by wiping away part of the fuzzy layer and measuring the ^{3}He remaining in the W substrate, the difference being the total amount of ^{3}He contained in the fuzz.. Any ^{3}He migrating deeper than a couple of micometers will not be detected in the W sample.

Different tungsten samples were exposed to similar plasma conditions, while the timing of ^{3}He addition to the plasma was altered for each sample. Two helium supply cylinders were used in the experiments; one containing pure ^{4}He gas and a second cylinder containing a mixture of 25% ^{3}He and 75% ^{4}He gas. The flow from each cylinder was independently controlled so that the composition of the plasma could be varied while the plasma was still operating. After removal from PISCES-A, the resulting tungsten fuzz layer was wiped off of one half of the sample surface and then the samples were subsequently analyzed at IPP-Garching using NRA as described above. In Figures 3-5 we present the NRA data from four different samples corresponding to different timing of ^{3}He irradiation.

In the first sample, which was exposed to the time-independent mixed-He plasma containing 25% ^{3}He for one hour, the majority (~80%) of the ^{3}He contained in the sample resides below the fuzz layer. The ^{3}He distribution is measured at several locations across the face of this sample (Figure 3) is reproduced here from a previous experimental campaign [11] to facilitate comparison to the experiments with time-varying ^{3}He flux. However, one particular open question, that [11] could not provide any information on, is: whether the He residing in the bulk was incident during the initial period of the plasma exposure (before fuzz tendrils were starting to form), with subsequent incident He ions populating primarily the growing tendrils, or whether He ions continue to arrive at the base of the fuzz even once it has formed?

To answer this question, we irradiate the second sample for 60 minutes of pure ^{4}He plasma followed by 30 minutes of a mixed plasma containing 10% ^{3}He (so that the timing of ^{3}He flux is incident on a well-developed fuzzy structure) The NRA data from this sample (see Figure 4), show the presence of ^{3}He in both fuzz and the base, undoubtedly demonstrating that fuzz is not completely opaque for helium ions, which continually penetrate into the base of the sample.

To address the issue of the "frozenness" of nano-bubbles, the third sample was initially irradiated for 30 minutes using plasma containing a mixture of helium isotopes, specifically 5% ^{3}He. After that, the ^{3}He containing cylinder was valved off and a pure ^{4}He plasma continued uninterrupted for an additional 60 minutes. The NRA found no measurable ^{3}He ($< 5 \times 10^{17}$ m^{-2}) remaining in this sample after the whole cycle of helium irradiation, neither in the half with the fuzz intact, nor in the half with the fuzz removed. This clearly demonstrates the dynamic behavior of the helium nano-bubbles within tungsten, as the ^{3}He that is initially contained within the fuzz growing for 30 minutes and in the base (assuming a similar distribution to that shown in Figure 3) is eventually removed from the tungsten during the subsequent 60 minutes of ^{4}He plasma exposure. Moreover, the dynamic behavior is exhibited not only in the nano-bubbles

located within the tendrils, but also in the nano-bubbles situated at the interface between the fuzz and bulk.

This is an important observation, because a potential energy barrier of approximately 6-9 eV exists for helium to overcome in order to enter into the tungsten bulk from vacuum [12, 13]. It is, therefore, reasonable to assume that helium residing within voids, or bubbles in tungsten, faces a similar energy barrier (or effective binding energy in a nano-bubble) to be released from the bubble. This implies that helium contained within bubbles in tungsten will not escape from the bubbles at temperature ~1000 K. Molecular dynamics simulations of helium in tungsten [14] support this idea as over-pressurized helium-filled bubbles tend to grow in size by trap mutation (i.e. the creation of dislocation loops that are generated near the bubble surface) rather than releasing the over pressure of He from inside the bubble into the tungsten matrix. Although, the bubbles situated close to the base surface can burst through the surface and release helium [14]. Such bursting and, possibly, re-forming processes can explain removal of ^{3}He from both the nano-tendrils and the bubbles which are located at the base of the fuzz structures.

To address this issue of the transport properties of helium through the tungsten, a fourth sample was irradiated for 85 minutes with pure ^{4}He plasma, followed by 5 minutes of the mixed plasma containing 5% of ^{3}He. The NRA data from this sample are shown in Figure 5. We note that the total helium ion fluence to second and fourth samples were nearly identical, although total fluence of ^{3}He to the second and fourth samples were $\Phi_2 = 6.8 \times 10^{24}$ m^{-2} and $\Phi_4 = 3.5 \times 10^{23}$ m^{-2}, respectively. Comparing the ratio of the amount of ^{3}He stored in these samples after plasma exposure (see Figs. 4 and 5) we find that it is close to the ratio of corresponding fluences (~ factor 20), which supports a "direct implantation" or convective-like transport of ^{3}He in the sample rather than a diffusive-like transport (where the ^{3}He content would be proportional to the square root of the incident fluence).

A recent model describes the possibility of ballistic He penetration through a fuzzy structure [15]. This model provides calculations of He penetration through a relatively thin fuzzy structure, but in this case, the fuzz layer is measured to be 3 μm thick (Figure 2) which would likely be difficult for the presented model to replicate. However, the basic concept of the ballistic transport of He to all regions of the fuzz and base is supported by these measurements. The measurements actually go further in this regard, as they also show the loss of previously implanted He at the base of the tendrils as subsequent He continues to be incident on the existing structures.

The concept of a dynamic bubble layer, with bubbles continually forming, growing and bursting, is further supported by additional data published in [11]. The data shows that for exposure temperatures below that needed for fuzz formation, the concentration of helium residing in the thin sub-surface nano-bubble layer remains constant with increasing fluence. This also implies a continual release of implanted helium ions, as would be the case with a dynamic bubble system.

III. Dynamics of tungsten atoms

The dynamic behavior of helium nano-bubbles in the course of helium plasma irradiation implies the displacement of tungsten atoms surrounding nano-bubbles. Moreover, it is plausible that these displacements are irregular and, result in enhanced mixing (diffusion) of tungsten atoms at least within both tendrils and nano-bubble layer. To address this issue a sample was created at ORNL which contained a deposited surface layer of enriched ^{182}W isotope. The thickness of the deposited layer was measured to be approximately 15 ± 3 nm on an adjacent Si witness sample

using a KLA Tencor Alphastep 500 Surface Profilometer. The isotopically enriched surface consisted of ~92.99% ^{182}W, as can be seen in the inset of Figure 6. For this experiment, the sample was exposed to helium plasma for one hour to a fluence of 1 x 10^{26} m^{-2} at a temperature of 1150 K. The plasma exposure resulted in the formation of a fuzzy tungsten surface on the sample. Depth profiles of the various tungsten isotopes were obtained by Secondary Ion Mass Spectrometry (SIMS) performed by Evans Analytical using a 2 keV oxygen beam, both before and after the plasma exposure. The depth of the sputtered crater in the W sample was measured by confocal microscopy following the SIMS analysis. The composition of each isotope is monitored each second during the 10 minute long sputtering measurement. The fact that the sputtering yield from the fuzzy surface is less than that of a fully-dense surface is compensated by the porosity of the fuzz [10]. Therefore, each measurement time is assumed to be an equal sputtered depth into the profile. The thickness of the fuzzy layer is measured by cross-sectional SEM imaging (Figure 6) and is superimposed on the SIMS depth profile.

The resultant depth profiles are shown in Figure 6 for the three primary tungsten isotopes (^{182}W: 26.50% natural abundance, ^{184}W: 30.64% natural abundance and ^{186}W: 28.43% natural abundance). As can be seen from the figure, the original isotopic enrichment of the surface (92.99% ^{182}W, 2.84% ^{183}W (not shown for clarity), 2.79% ^{184}W and 1.38% ^{186}W) is lost when the tungsten fuzz grows.

A simple integration of the depth profiles obtained from before and after the plasma exposure can also be made to ensure that the plasma did not erode through the initial ^{182}W layer. Assuming the ^{182}W layer, enriched to 92.99%, had 100% theoretical density, a 15 nm thick layer would amount to 8.78 x 10^{20} ^{182}W atoms/m^2 initially deposited on the sample surface. Following the exposure the ^{182}W depth profile can be integrated to reveal how much of the deposited ^{182}W remains in the sample. Assuming the natural abundance of ^{182}W follows a similar profile shape to that of ^{184}W and ^{186}W as a function of depth into the fuzz as seen in Figure 7, we can integrate the ^{182}W curve over the thickness of the fuzz layer. Once the average porosity of the 500 nm thick fuzz layer ($\rho \sim 0.3$) [11] is taken into account, we obtain 8 x 10^{20} ^{182}W atoms/m^2 atoms still remaining in the fuzz and hence no erosion occurred under these conditions as anticipated for this ion energy. This result clearly indicates the tendency for mixing of the tungsten atoms from beneath the growing tendrils with the material further up toward their tips.

In the absence of the mixing of tungsten atoms caused by the dynamics of helium nano-bubbles, one would expect that the surface would continue to be enriched with ^{182}W and regions deeper in the fuzz structures would contain the isotopic mix of the bulk material. Clearly this is not observed in our experiment; instead we see a mixture of tungsten isotopes at the surface and a gradual depth profile approaching the concentrations of the bulk tungsten. On the other hand, the inter-diffusion of tungsten isotopes is too slow at this temperature [16] and cannot explain the experimentally observed depth distributions. Therefore, the experimental data presented in both Sections II, and III, support a physical picture of the dynamic behavior of helium nano-bubbles which, also, causes an enhanced mixing of tungsten atoms.

A similar result has recently been reported by Fiflis [17], where a thin tungsten coating was applied to a molybdenum wire and the entire structure was subjected to conditions where a fuzzy W surface should form. Even though the experiment utilized two different elements, the result also showed the motion of the substrate material up through the surface layer toward the tips of the tendrils. It is interesting to note that even in the experiments by Fiflis, using much thicker W coatings (100 and 200 nm thick) evidence of the Mo substrate could be found at the surface following fuzz formation.

IV. Conclusion

Two different types of experiments on tungsten samples exposure by helium plasma have been performed. The experiments employed helium and tungsten isotopes, to address the following conceptual issues: i) does the fuzz become opaque for helium ions impinging on the sample? ii) are helium nano-bubbles in both the fuzz tendrils, and at their base, "frozen" after they are formed and no longer undergo changes? iii) does the fuzz growth, and nano-bubble layer formation, result in the mixing of tungsten atoms and thereby impact the distribution of atoms in the sample?

In the experiments presented in the Sections II, ^{3}He was included in the initial phase of the plasma discharge in one sample and toward the end of the plasma discharge in other samples. No evidence of ^{3}He was observed retained in the tungsten when the ^{3}He was only present in the plasma initially. On the other hand, ^{3}He was detected in the samples exposed to ^{3}He containing plasma at the end of the discharge. The amount of ^{3}He in the tungsten sample appears to scale directly with the fluence to the samples, rather than with a square root of time, which would be expected for diffusive-like process. An increase proportional to the incident fluence suggests a direct implantation pathway for He to enter the tungsten substrate. In the Section III, the results from an experiment are described where an isotopically enriched ^{182}W surface layer was deposited on a tungsten substrate having the normal tungsten isotopic distribution. Depth profiles of the surface before and after fuzz growth revealed the mixing of the tungsten isotopes in the substrate with the material closer toward the tips of the growing tendrils.

These results demonstrate that: i) fuzz is not completely opaque for helium ions impinging on the sample and, at least, some incident ions penetrate through to the fuzz base; ii) helium nano-bubbles exhibit a dynamic behavior which is manifested in nano-bubble bursting and reformation; iii) as a result of this dynamic process the motion of tungsten atoms in the region of helium filled bubbles demonstrate enhanced mobility which results in their strong mixing.

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References

[1] S. Kajita, T. Ishida, N. Ohno et al., Sci. Rep. **6**, 30380; doi: 10.1038/srep30380 (2016).
[2] R. A. Pitts, S. Carpentier, F. Escourbiac et al., J. Nucl. Mater. 438 (2013) S48.
[3] G. De Temmerman, T. Hirai and R. A. Pitts, Plasma Phys. Control. Fusion 60(2018)044018.
[4] S. Kajita, W. Sakaguchi, N. Ohno, N. Yoshida and T. Saeki, Nucl. Fusion 49(2009)095005.
[5] M. J. Baldwin and R. P. Doerner, Nucl. Fusion 48 (2008) 035001.
[6] S. Kajita, N. Yoshida, R. Yoshihara, N. Ohno and M. Yamagiwa, J. Nucl. Mat. 418(2011)152.
[7] D. M. Goebel, Y. Hirooka, R. W. Conn et al., J. Nucl. Mater 145-147 (1987)61.

[8] W. Eckstein, Sputtering Yields, in: R. Behrisch, W. Eckstein (Eds.): Sputtering by Particle Bombardment IV, Top. Appl. Phys. 110 (Springer, Berlin, Heidelberg 2007).
[9] M. Mayer, Nucl. Instrum. Methods B 266(2008)1852.
[10] D. Nishijima, M. J. Baldwin, R. P. Doerner and J. H. Yu, J. Nucl. Mater. 415 (2011) S96.
[11] R. P. Doerner, M. J. Baldwin, M. Simmonds et al., Nucl. Mater. and Energy 12 (2017)372.
[12] H. Ullmaier, Nucl. Fusion 24 (1984) 1039.
[13] M. Thompson, A. Deslandes, T. W. Morgan et al, Nucl. Fusion 56 (2016) 104002.
[14] B. D. Wirth, K. D. Hammond, S. I. Krasheninnikov and D. Maroudas, J. Nucl. Mater. 463 (2015) 30.
[15] T. P. C. Klaven, K. Nordlund, T. W. Morgan et al., Nucl. Fusion 56(2016)126015.
[16] J. N. Mundy, S. J. Rothman, N. Q. Lam, H. A. Hoff and L.J. Nowicki, Phys. Rev. B 18(1978)6566.
[17] P. Fiflis, N. Connolly and D. N. Ruzic, J. Nucl. Mater. 482 (2016) 201.

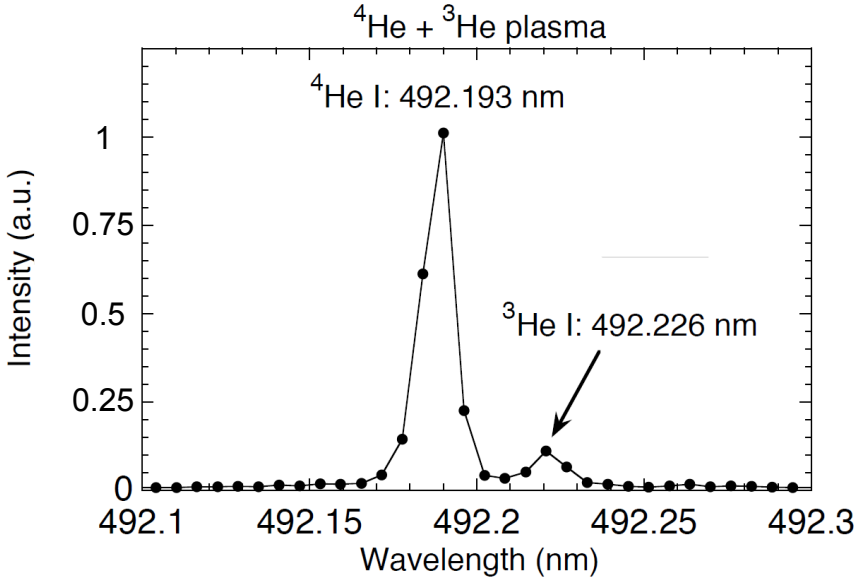

Figure 1 – Spectroscopic composition measurement of helium isotope content in the PISCES-A plasma.

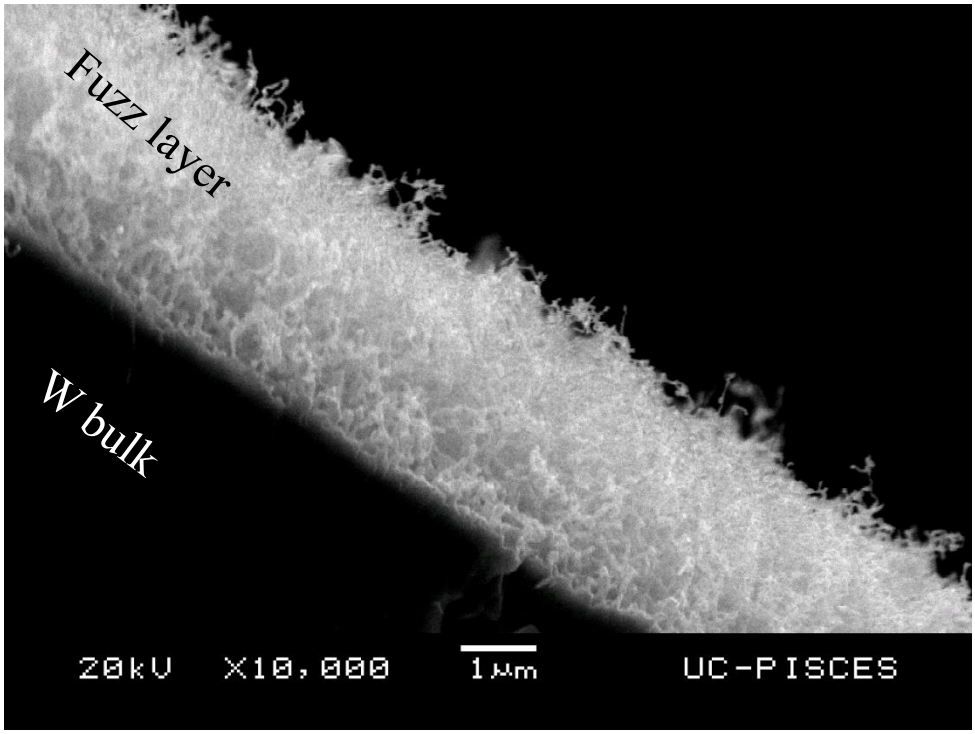

Figure 2 – Cross section of tungsten fuzz layer following 90 minute He plasma exposure.

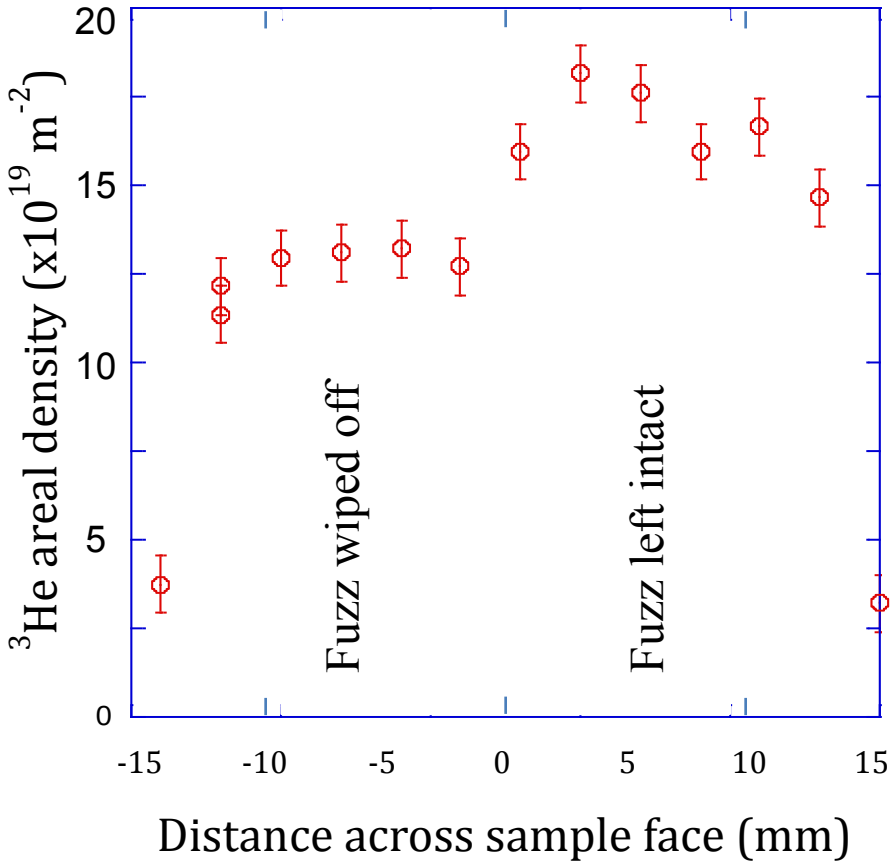

Figure 3 – ^{3}He isotope areal density measured in a fuzzy tungsten sample after 60 minutes of plasma containing 25% ^{3}He content. Measurements were made across the sample where half the fuzz has been wiped off the surface, compared to the other half showing the helium content in the region with fuzz.

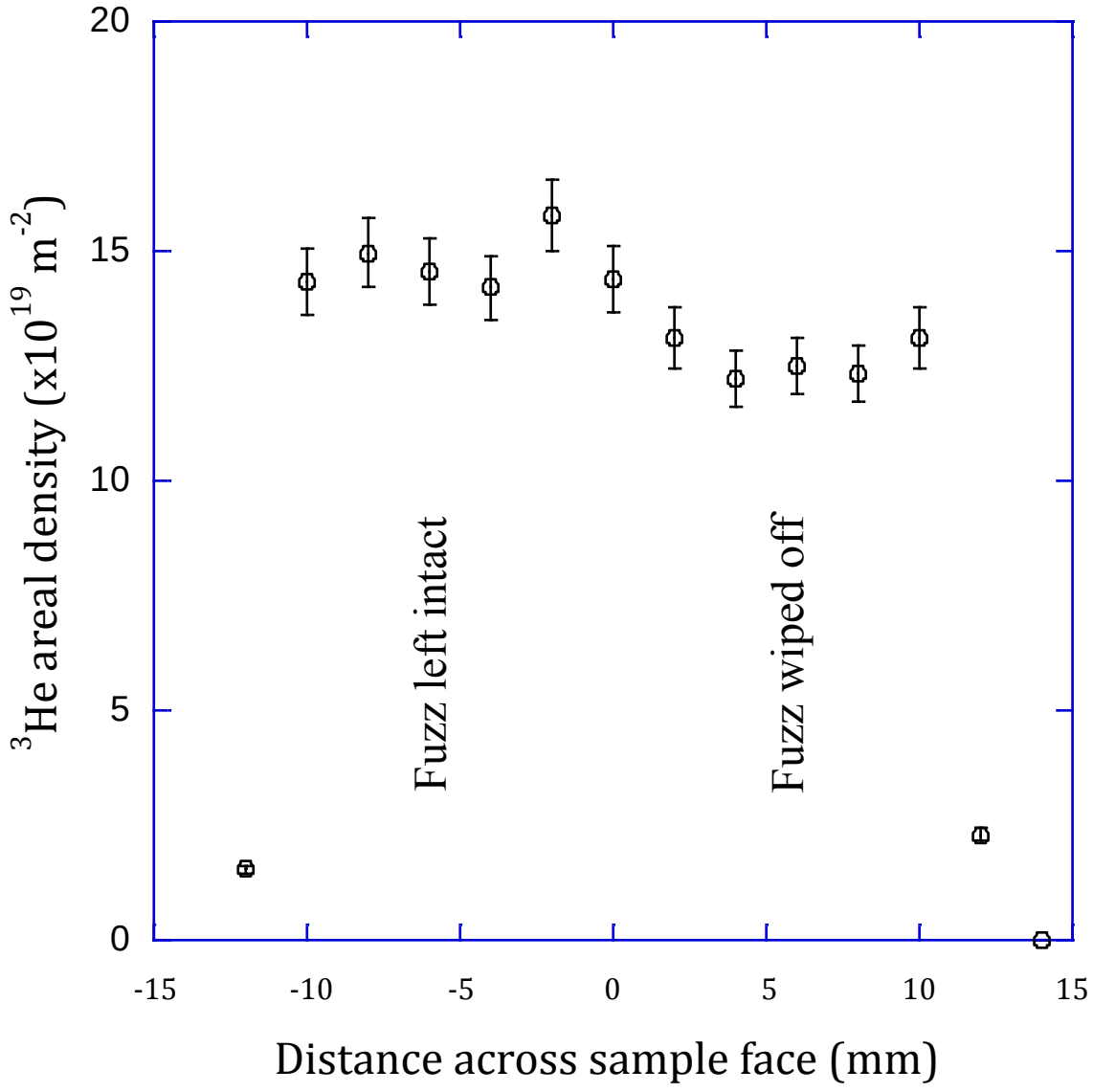

Figure 4 - ^{3}He isotope areal density in a fuzzy tungsten sample where the fuzz is removed from one half of the sample. This sample was first exposed to 60 minutes of pure ^{4}He helium plasma followed by 30 minutes of plasma containing 10% ^{3}He.

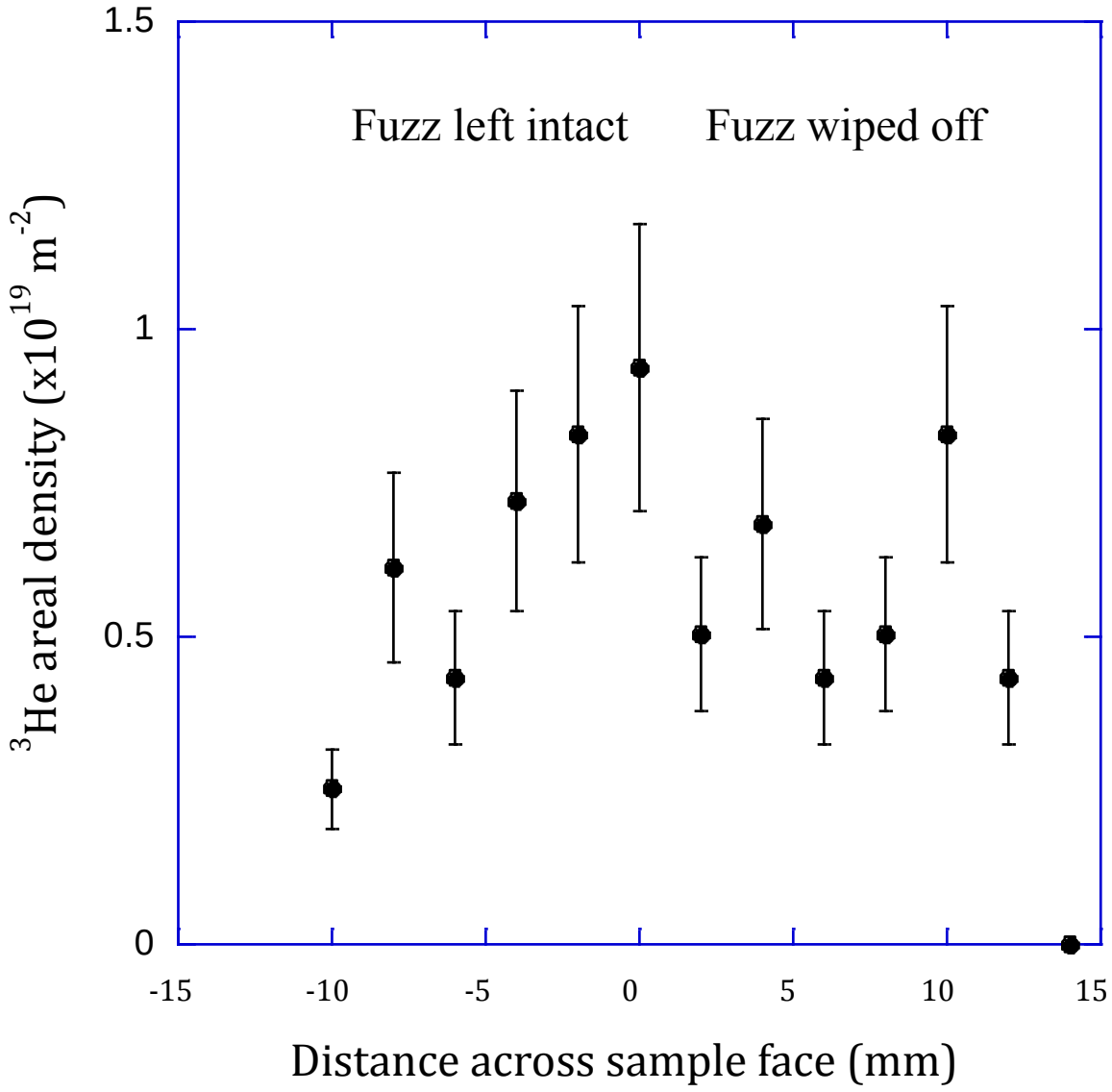

Figure 5 – ^{3}He isotope areal density in a fuzzy tungsten sample where the fuzz is removed from one half of the sample. This sample was first exposed to 85 minutes of pure ^{4}He helium plasma followed by 5 minutes of plasma containing 5% ^{3}He. (Note y-axis scale difference with figures 3 and 4.)

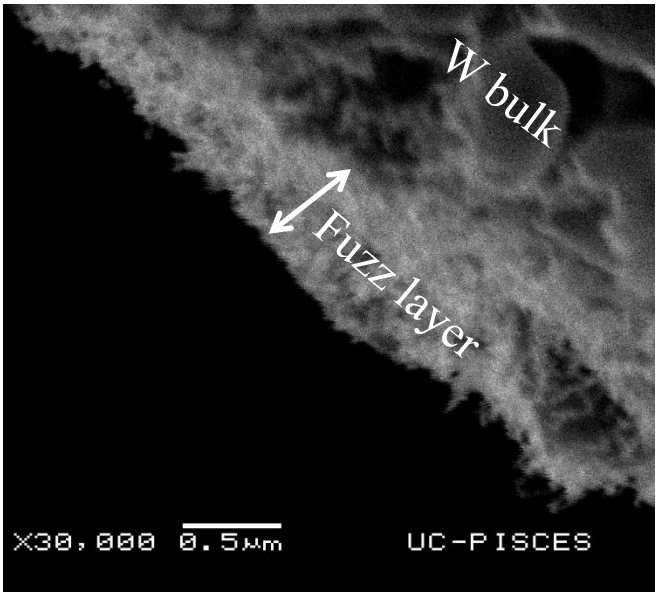

Figure 6 - Cross section of tungsten fuzz layer formed on the sample containing the isotopically enriched surface layer following 60 minute He plasma exposure.

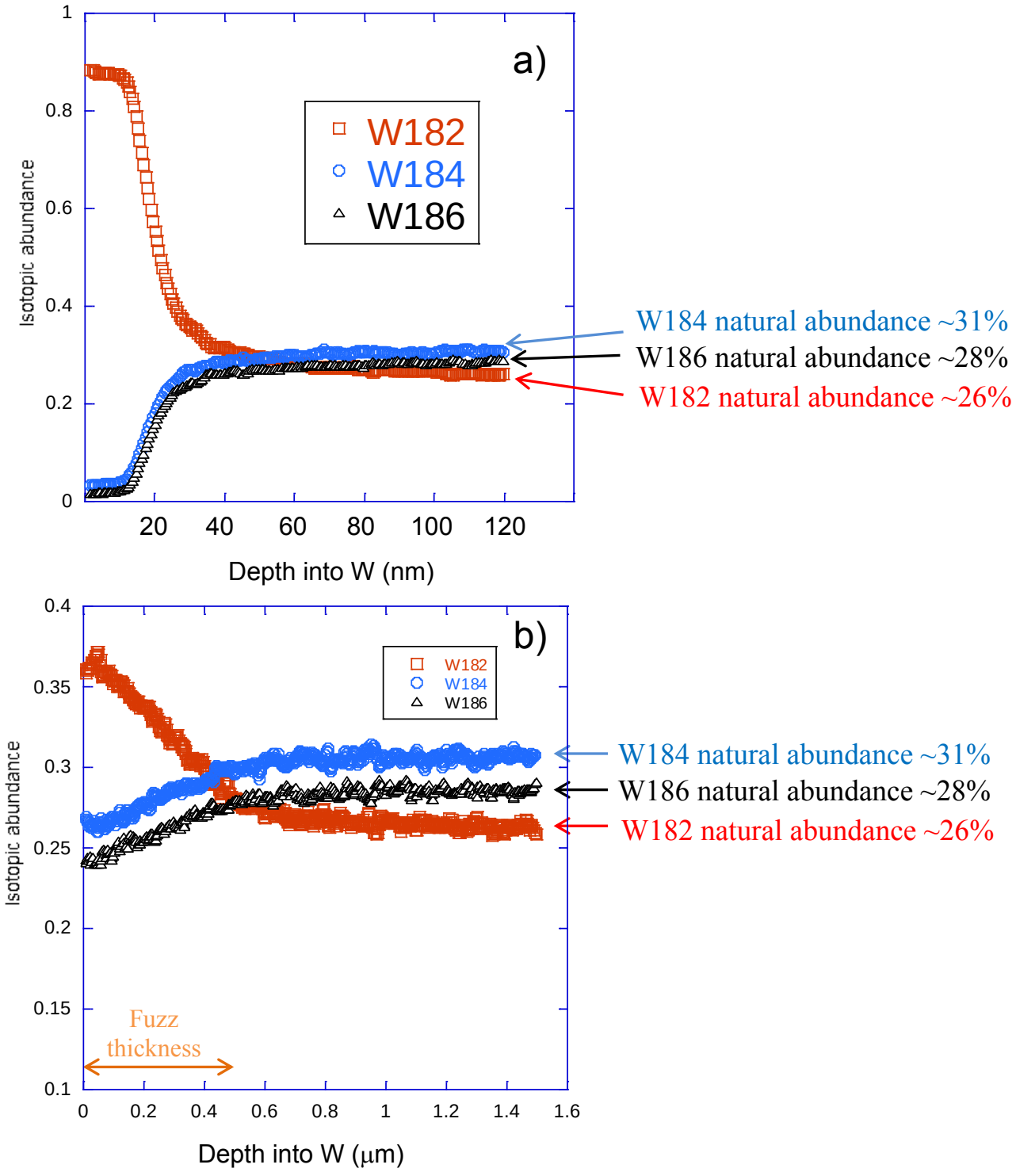

Figure 7 - Depth profiles of tungsten isotopes from a sample coated with a 15 nm thick layer of ^{182}W isotopes, a) before and b) after one hour of helium plasma exposure under conditions suitable for fuzz growth.