Measuring temperature effects on nano-bubble growth in tungsten with grazing incidence small angle X-ray scattering

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\section*{Abstract}

W samples were exposed to He plasma in the MAGPIE, NAGDIS-II and PISCES-A across a range of sample temperatures between 473–1123 K. GISAXS was used to quantify the effect of plasma fluence and W surface temperature on He nano-bubble size distributions. In NAGDIS-II at 873 K nano-bubbles are exponentially distributed with mean diameters $\mu = 0.64 \pm 0.01$ nm, similar to the value of $\mu = 0.62 \pm 0.01$ nm found for the MAGPIE plasma device at the much lower temperature of 473 K. Above $\sim 900$ K nano-bubbles followed an approximately exponential distribution with $\mu > 0.72$ nm demonstrating a significant increase in nano-bubble sizes at higher temperatures.

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\section*{1. Introduction}

Temperature has a significant effect on He nano-bubble formation in W, where higher temperatures are usually associated with the formation of larger bubbles [1]. Molecular dynamics simulations show a complex dynamic relation between nano-bubble growth characteristics and temperature [2]. Small clusters of up to 7 He atoms are relatively mobile but become immobile on molecular dynamics timescales once they become large enough to relieve their internal pressure via loop punching. At lower temperatures, this process of cluster immobilisation would reduce nano-bubble diffusion to the point where it is negligible, preventing growth via coalescence of larger clusters. On the other hand, at higher temperatures nano-bubbles are free to diffuse throughout the material, allowing growth via coalescence.

Presently, it is not clear precisely where the dividing line between diffusion-driven and coalescence-driven bubble growth occurs. Miyamoto et al. [3] suggest that the crossover temperature may depend to some extent on the nature of the sample itself, with a lower merger threshold temperature observed under \textit{in situ} TEM than that for a bulk sample exposed to He plasma. On the other hand, El-Atwani et al. [4] observed no bubble coalescence during \textit{in-situ} TEM even for temperatures up to 1223 K. Instead, they found that bubble growth was more sensitive to vacancy availability, with larger bubbles forming where vacancies were abundant. This was achieved by using He implantation energies above the threshold required for Frenkel pair formation in W. Taken together, these studies indicate a complex relationship between incident He ion energy (vacancy availability) and temperature (vacancy and nano-bubble mobility) on nano-bubble formation.

To date, detailed studies into the behaviour of He nano-bubbles have been hamstrung by the difficulty of measuring these bubbles. To overcome the sampling limitations of TEM, we performed grazing incidence small angle X-ray scattering (GISAXS) on W samples exposed to He plasma across temperatures ranging from 473 K to 1123 K. As GISAXS is a volumetric technique, one can simultaneously obtain information from millions of structures throughout an extended volume of material, allowing full nano-bubble size distributions to be determined [5,6].

\section*{2. Experimental procedure}

Polycrystalline W samples were exposed to pure He plasma in the MAGPIE [7], PISCES-A [8], and NAGDIS-II [9] linear plasma de-
The GISAXS patterns of (a) an undamaged reference sample and (b) a sample exposed to helium plasma in Pisces-A at 773 K are shown. Fitting was performed by taking slices of data, as shown in (b). Examples of how the x-ray intensity varies along (c) vertical and (d) horizontal slices are also shown.

<table>
<thead>
<tr>
<th>Device</th>
<th>Temperature (K)</th>
<th>Fluence (He/m²)</th>
<th>Mean nano-bubble diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAGPIE</td>
<td>473</td>
<td>$2.2 \times 10^{25}$</td>
<td>$0.62 \pm 0.01$</td>
</tr>
<tr>
<td>PISCES-A</td>
<td>643–673</td>
<td>$6.8 \times 10^{25}$</td>
<td>$0.69 \pm 0.01$</td>
</tr>
<tr>
<td>PISCES-A</td>
<td>773</td>
<td>$1 \times 10^{26}$</td>
<td>$0.75 \pm 0.01$</td>
</tr>
<tr>
<td>PISCES-A</td>
<td>973</td>
<td>$1 \times 10^{26}$</td>
<td>$0.72 \pm 0.01$</td>
</tr>
<tr>
<td>NAGDIS-II</td>
<td>843–903</td>
<td>$5.3 \times 10^{25}$</td>
<td>$0.64 \pm 0.01$</td>
</tr>
<tr>
<td>NAGDIS-II</td>
<td>943</td>
<td>$4.4 \times 10^{25}$</td>
<td>$0.79 \pm 0.01$</td>
</tr>
<tr>
<td>NAGDIS-II</td>
<td>1123</td>
<td>$4.2 \times 10^{25}$</td>
<td>$0.74 \pm 0.01$</td>
</tr>
</tbody>
</table>

Table 1

Sample exposure conditions.

Fig. 1. The GISAXS patterns of (a) an undamaged reference sample and (b) a sample exposed to helium plasma in Pisces-A at 773 K are shown. Fitting was performed by taking slices of data, as shown in (b). Examples of how the x-ray intensity varies along (c) vertical and (d) horizontal slices are also shown.

Samples were heated directly from the plasma, with sample temperature being controlled by varying the plasma flux. As a higher plasma flux was necessary to achieve higher temperatures, samples exposed to higher temperature plasma required shorter exposure times to maintain comparable helium fluxes. Sample surface temperatures and fluxes are listed in Table 1.

GISAXS was performed on the SAXS/WAXS beamline of the Australian Synchrotron with 10 keV X-rays. Measurements were taken at an incident angle of 1° and a camera length of 964 mm. Data was recorded on a 2D Dectris Pilatus 1 M CCD detector. GISAXS data was interpreted by fitting a diffraction model to the raw data along a selection of 1D “slices”, as indicated in Fig. 1. These slices were selected to avoid the bright central streak that appears as a consequence of surface reflections, as well as the region below 0.5° from the horizontal plane as these regions are more sensitive to surface roughness and are likely to include features other than the nano-bubbles that are the focus of this study. More details of this procedure and the diffraction model used for fitting are described in [6]. The nano-bubble diameter distributions were approximated with an exponential probability density function, given by:

$$P(x) = \frac{1}{\mu} e^{-\frac{x}{\mu}}$$

(1)

Here, $x$ is the nano-bubble diameter and $\mu$ is the mean nano-bubble diameter. A spheroidal form factor was used to approximate the shape of the nano-bubbles, where the axis of rotational symmetry was fixed to be normal to the sample surface. The mean diameter, the height-width aspect ratio of the spheroids, a constant background factor (to account for stray scattering from the collimating slits), and a scaling factor were optimised to minimising the $x^2$ score during fitting.

3. Results

He is also known to produce surface pitting in W [1], as shown in the SEM micrographs in Fig. 2. Here, surface pits several 10 s of nm across are readily apparent at 943 K and 1123 K, but are
not visible on the surface of the ~843–903 K sample. The minimum temperature for surface pitting appears to be the same as that for nano-bubble agglomeration, suggesting that the two phenomena are closely related. Other work into the effect of nano-bubble growth in copper exposed to He ion irradiation suggests that a small population of very large nano-bubbles form during post-irradiation annealing [10], which are likely to migrate to the surface as a consequence of the temperature gradient (and consequent vacancy concentration gradient) between the bulk and the surface [11].

The difference in scale between the nano-bubbles measured by GISAXS and the surface pits supports the coalescence-driven growth mechanism modelled in [10], where large nano-bubbles constitute only a small minority of all bubbles. Quantitative comparisons between this work and precedent models (such as [11]) is difficult as models of He nano-bubble coalescence typically only model the behaviour of randomly distributed nano-bubbles during annealing. This is in stark contrast to the experimental case where nano-bubbles are in a continuous dynamic process of nucleation, migration and coalescence, which one would expect should feature a larger population of smaller nano-bubbles which have recently nucleated.

Fig. 3 shows the effect of temperature on nano-bubble diameters for samples exposed to He plasma in MAGPIE, NAGDIS-II and PISCES-A, along with example nano-bubble diameter distributions from the NAGDIS-II sample set. Samples exposed to NAGDIS-II show a significant increase in nano-bubble sizes as temperatures increase from ~873 K to 943 K, but a slight reduction in bubble sizes beyond this. This is consistent with the dynamic model of nano-bubble growth described above.

GISAXS measurements probe a finite range of spatial frequencies, determined by the x-ray wavelength and camera length used for the measurement. In this work, the wavelength and camera length combination were optimised for nano-bubbles with sizes in the range 0.5–5 nm. Bubble migration and mergers would reduce the density of bubbles within the material, leaving more room for the precipitation of new bubbles. This would lower the average bubble size being measured by GISAXS, with the effect being greater the faster bubble coalescence occurs.

The PISCES-A exposed samples show a similar qualitative behaviour with nano-bubbles first increasing, then decreasing in size as one moves towards higher temperatures. The transition temperature for the formation of larger nano-bubbles in PISCES-A plasma exposure was significantly lower than that observed in NAGDIS-II. The plasma environment is very different in different devices (which could affect helium retention fractions and implantation depths), and different suppliers and polishing methods were used for samples used in the two sets of experiments (which would lead to different concentrations and distributions of vacancies and other defects). Consequently, one should be careful about trying to draw quantitative comparisons between experiments conducted in these different devices.

4. Summary

The effect of temperature on He nano-bubble formation in W was studied on samples exposed to He plasma in the MAGPIE, NAGDIS-II, and PISCES-A linear plasma devices. These results indicate that nano-bubble formation can be broadly characterised in terms of “low” and “high” temperature growth regimes, with “high” temperature nano-bubbles being significantly larger than their “low” temperature counterparts. This change in behaviour occurs for a relatively small change in temperature (< 150 K), providing strong support for the hypothesis that a fundamental shift in nano-bubble growth behaviour occurs at higher temperatures. In the “low” temperature regime nano-bubble growth is likely dominated by the migration of individual He atoms or small clusters towards immobile bubbles, while at higher temperatures bubbles become mobile and grow via coalescence.
At the highest temperatures measured a small reduction in average nano-bubble size was observed via GISAXS. This is likely a consequence of bubble coalescence leading to the formation of a relatively small number bubbles too large to be measured with the GISAXS set-up of this experiment, reducing the bubble density and making room for new bubbles to nucleate and grow.

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References


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