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## Formation of tetragonal gas bubble superlattice in bulk molybdenum under helium ion implantation

C. Sun<sup>a,\*</sup>, D.J. Sprouster<sup>b</sup>, K. Hattar<sup>c</sup>, L.E. Ecker<sup>b</sup>, L. He<sup>a</sup>, Y. Gao<sup>a</sup>, Y. Zhang<sup>a</sup>, J. Gan<sup>a</sup>

<sup>a</sup> Idaho National Laboratory, Idaho Falls, ID 83415, United States

<sup>b</sup> Brookhaven National Laboratory, Untown, NY 11973, United States

<sup>c</sup> Sandia National Laboratories, Albuquerque, NM 87185, United States

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#### ABSTRACT

We report the formation of tetragonal gas bubble superlattice in bulk molybdenum under helium ion implantation at 573 K. The transmission electron microscopy study shows that the helium bubble lattice constant measured from the in-plane d-spacing is ~4.5 nm, while it is ~3.9 nm from the out-of-plane measurement. The results of synchrotron-based small-angle x-ray scattering agree well with the transmission electron microscopy results in terms of the measurement of bubble lattice constant and bubble size. The coupling of transmission electron microscopy and synchrotron high-energy X-ray scattering provides an effective approach to study defect superlattices in irradiated materials.

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Self-organization of nanostructures has significant scientific merit and great technological impact due to the creation of novel physical properties with potential applications in various industries [1-4]. Implantation/irradiation can generate non-equilibrium ordered defect structures, such as gas bubble superlattice (GBS), void superlattice, and stacking fault tetrahedron alignments [5-9]. An intriguing observation is that in most scenarios, these ordered lattice structures are isomorphic with the parent crystal structures. Di et al. [10] reported that helium gas bubbles preferentially nucleate at the nodal points of screw dislocations in gold and result in the formation of bubble superlattice. Dubinko et al. [11] proposed loop punching by over pressurized bubbles as a possible mechanism for GBS formation at low irradiation fluences. Jager et al. [12] pointed out that the isomorphy of the ordered defect structure may be attributed to the low dimensional transport of self-interstitial atoms. The fundamental mechanism of GBS formation, however, is still unclear.

GBS have been reported in various face-centered cubic (fcc), bodycentered cubic (bcc) and hexagonal close-packed (hcp) metals and alloys implanted with gases such as H, He and Ne [13–16]. Johnson et al. [17] reported the spatial ordering of He bubbles in bcc metals, like V, W, Mo, Cr, Fe and Ta, using low energy He ion implantation. The suggested implantation temperature for GBS formation is ~0.2 T<sub>m</sub> (T<sub>m</sub> is the melting point of the metal). Donnelly et al. [15] reported Ne GBS in Fe implanted with 30 keV Ne ions to a fluence of  $2.5 \times 10^{16}$ /cm<sup>2</sup>.

\* Corresponding author.

E-mail address: cheng.sun@inl.gov (C. Sun).

https://doi.org/10.1016/j.scriptamat.2018.01.023 1359-6462/© 2018 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved. Wang et al. [18] went further to investigate the mechanical response of copper with He GBS and pointed out that dislocation motioninduced plasticity can result in the order-disorder transformation of periodic arrangement of He bubbles, while the ordering of bubbles can be maintained if the plasticity occurs due to the deformation twining.

In nuclear fuels, fission GBS was reported in U—7Mo alloys after neutron irradiation at about 373 K to a fission density of  $4.5 \times 10^{21}$  fissions/cm<sup>3</sup> [19,20]. The fission product Xe gas bubbles, with an average bubble size of ~3.5 nm and a bubble lattice constant of ~11.5 nm, exhibit an fcc structure with its major zone axis parallel to that of the bcc U—Mo matrix. Hu et al. [21] believe that the fast 1-D migration of interstitials along (110) directions in the bcc U—Mo matrix causes the gas bubble alignment along (110) directions. The self-organization of gas bubbles into an fcc superlattice on bcc materials has inspired great scientific interest. To date, the formation of highly ordered fission GBS under extremely harsh irradiation environments has yet to be fully understood. Here we report the formation of tetragonal GBS in a bcc model system, He ion implanted bulk Mo with He concentration of 7-10 at.% at 573 K. We examine the He GBS using synchrotron-based small-angle xray scattering, and the results agree well with the transmission electron microscopy (TEM) results in terms of the measurement of GBS lattice constant and gas bubble size.

Bulk Mo with purity of 99.95 wt% was purchased from Goodfellow. He ion implantation at an energy of 150 keV was performed in bulk Mo samples at a flux of  $6.5 \times 10^{13}$  ions/cm<sup>2</sup>/s to a fluence of  $1.2 \times 10^{17}$  ions/cm<sup>2</sup> at 573 K in the Ion Beam Lab at Sandia National Laboratories. The stopping and range of ions in matter (SRIM) code



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[22], using the Kinchin-Pease method, predicts that the total penetration depth of He ions is ~550 nm, and the peak He concentration of 10 at.% occurs at the depth between 350 and 400 nm, as seen in Fig. 1a. The displacement energy of 60 eV [23,24] was used in the calculation for Mo. Cross-sectional and plane-view TEM lamellas were prepared by Focused Ion Beam (FIB) equipped in a FEI Quanta Scanning Electron Microscope (SEM), and the thickness of the lamellas were measured using Convergent Beam Electron Diffraction (CBED) method (see Fig. S1 in the supplementary document). Artifacts induced by FIB were minimized by low-energy (2 keV) Ga ion polishing for 10–15 min on each side of the lamellas. The TEM characterization was performed on both JEOL-2010 (200 keV) and Tecnai-F30 (300 keV) transmission electron microscopes equipped with Gatan CCD cameras.

Glancing Incidence Small Angle X-ray Scattering (GISAXS) measurements were performed at the G1 beamline at the Cornell High Energy Synchrotron Source using 9.95 keV (1.25 Å) X-rays. The scattering intensity I(Q), where Q is the scattering vector defined by  $Q = (4\pi/\lambda)^{*}\sin\theta, \lambda$  is the wavelength of the incident x rays and  $\theta$  is half the scattering angle, was collected for 10 s at a camera length of 1179 mm at glancing angles of 0.1–1.4° (in 0.1° steps). The scattering pattern from an unimplanted Mo sample was subtracted from all He implanted patterns. Bubble diameter distributions were determined using nonlinear least square fitting procedures and a log normal particle distribution in the IGOR-Pro-based software package [25]. The detailed GISAXS data analysis was described in the supplementary document.

In Fig. 1a, the profile of He ions distribution was predicted by SRIM, the superimposed cross-sectional TEM micrograph shows a high



**Fig. 1.** Bulk Mo after He implantation at energy of 150 keV to a fluence of  $1.2 \times 10^{17}$ /cm<sup>2</sup> at 573 K. (a) SRIM simulated He concentration profile as a function of ion penetration depth. The superimposed cross-sectional TEM micrograph under under-focusing imaging condition shows the helium bubbles in the peak damage region. (b) Helium bubble density distribution vs. ion penetration depth. The peak helium bubble density occurs at depth of 330–450 nm.

density of He gas bubbles formed at a depth of 350–400 nm with a He ion concentration ( $C_{He}$ ) of 7–10 at.%. In Fig. 1b, the He gas bubble density measured from cross-sectional TEM micrograph was plotted as a function of He ion implantation depth, and the peak He gas bubble density, ~1.3  $\times$  10<sup>24</sup>/m<sup>3</sup>, occurred at a depth between 350 and 400 nm. The distribution of He bubbles across the implantation region indicates the stages of GBS lattice development. Fig. 2 shows the cross-sectional TEM micrographs at different implantation depth (Please see Fig. S2 for the cross-sectional TEM micrographs at lower magnification). In Fig. 2a, the zone axis is close to [001], no clear He bubbles were observed with 0-2 at.% He. In Fig. 2b, with 2-7 at.% He, randomly distributed He gas bubbles formed. When utilizing an over-focusing imaging condition, the gas bubbles exhibit dark contrast, as seen in Fig. 2a-c. As the He concentration increases up to ~10 at.%, the gas bubble density increases monotonically to ~1.3  $\times$  10<sup>24</sup>/m<sup>3</sup>. The GBS was formed when the local He concentration was within 7-10 at.%. Compared to those taken from the area with lower He concentration, the fast Fourier transformation (FFT) of the micrograph with 7-10 at.% He exhibits clear satellite spots, originating from the formation of GBS. The schematics in Fig. 2d shows the helium bubbles and their ordering in bulk Mo after ion implantation. The orientations of out-of-plane (Z), in-plane (X) and inplane (Y) were defined. The inverse FFT technique was used to measure the lattice constant of the gas bubbles in Figs. 2e-f. The bubble lattice constant (a) was estimated through the d-spacing (d) of gas bubbles on (110) plane by  $a = \sqrt{2}d$  (see Fig. S3 in the supplementary document). The statistical study in Fig. 2g shows that the average bubble lattice constant measured from in-plane d-spacing was 4.5  $\pm$  0.2 nm, while it is  $3.9 \pm 0.2$  nm from out-of-plane measurement.

Fig. 3 shows the plane-view TEM micrographs at an implantation depth of 370 nm with ~10 at.% He. The over-focusing imaging conditions in Fig. 3a confirmed the formation and self-organization of gas bubbles, and the inset FFT implied the formation of GBS. The statistical study of gas bubble size shows that the average bubble diameter is ~1.1 nm (see Fig. S4 in the supplementary document). In Fig. 3b, the average bubble lattice constants of the two in-plane orientations of [110] and [1 $\overline{10}$ ] are identical (4.5 ± 0.2 nm), which is consistent with the bubble lattice constant measured from the in-plane d-spacing through cross-sectional TEM, as seen in Fig. 2d and f.

GISAXS patterns were measured for the pristine unimplanted Mo and He implanted bulk Mo. Compared to the pristine Mo in Fig. 4a, the 2D GISAXS pattern of He implanted Mo shows extra scattering signal, as seen in Fig. 4b, suggesting the existence of the superlattice. The scattering intensity as a function of d-spacing was plotted for He implanted Mo (red), pristine Mo (blue) and the subtraction of He implanted Mo by pristine Mo (green). A clear scattering peak of (110) at d-spacing of 3.5  $\pm$  0.7 nm in the He implanted Mo originates from the gas bubble superlattice, consistent with the TEM results discussed above, the extra intensity at larger d-spacing (50-60 nm range) in Fig. 4c is attributed to a slight increase in specular scattering. The gas bubble lattice constant was estimated to be 4.9  $\pm$  0.9 nm. Fig. 4d shows the plot of the scattering intensity as a function of scattering vector (Q) for He implanted (red) and pristine Mo (blue). The additional intensity in the ion implanted sample is directly attributed to the He bubbles and the implantation-induced defects (2D defects such as dislocation loops). The inset shows that the refined average bubble diameter is ~1.3 nm, which is in good agreement with the value of ~1.1 nm measured via TEM. The slightly larger size and asymmetric size distribution to larger sizes is attributed to a contribution of the larger 2D defects.

After He implantation at 573 K, the development of He gas bubbles in bulk Mo sample in this study exhibits two striking stages at different He concentration levels: (1) the formation of random small-bubbles at 2–7 at.% He and, (2) ordered gas bubble arrays at 7–10 at.% He. A similar He concentration at which He GBS are formed has been reported in different metals [26–28]. He gas bubbles are randomly distributed in He implanted Ni with  $C_{He} = 3$  at.%, while gas bubble alignment along traces Download English Version:

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