Microstructure changes and thermal conductivity reduction in UO₂ following 3.9 MeV He²⁺ ion irradiation

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Abstract

The microstructural changes and associated effects on thermal conductivity were examined in UO_2 after irradiation using 3.9 MeV He^{2+} ions. Lattice expansion of UO_2 was observed in x-ray diffraction after ion irradiation up to $5 \times 10^{16} \text{ He}^{2+}/\text{cm}^2$ at low-temperature ($< 200 \text{ }^\circ\text{C}$). Transmission electron microscopy (TEM) showed homogenous irradiation damage across an 8 μm thick plateau region, which consisted of small dislocation loops accompanied by dislocation segments. Dome-shaped blisters were observed at the peak damage region (depth around 8.5 μm) in the sample subjected to $5 \times 10^{16} \text{ He}^{2+}/\text{cm}^2$, the highest fluence reached, while similar features were not detected at $9 \times 10^{15} \text{ He}^{2+}/\text{cm}^2$. Laser-based thermo-reflectance measurements showed that the thermal conductivity for the irradiated layer decreased about 55 % for the high fluence sample and 35% for the low fluence sample as compared to an un-irradiated reference sample. Detailed analysis for the thermal conductivity indicated that the conductivity reduction was caused by the irradiation induced point defects.

Keywords: depleted UO_2 , He^{2+} irradiation, irradiation damage, thermal conductivity, TEM, XRD

1. Introduction

Thermal conductivity is a critical property of ceramic nuclear fuels such as uranium dioxide. A number of studies have been performed to obtain conductivity of a fresh fuel with various levels of off-stoichiometry and doping [1-3] and to obtain a correlation between conductivity and fuel burn-up. [4-6] Recently, a few reports have been made that consider the intrinsic properties of UO_2 . [7- 9] While the impact of off-stoichiometry and fission products on thermal conductivity is widely studied and somewhat understood, [3, 10, 11], the contribution from irradiation damage is not as well examined and the (single) irradiation damage term in most thermal conductivity models include contribution from various microstructural changes, such as voids, point defects and point defect clusters, and dislocations altogether. [12] Furthermore, some of the irradiation-induced defects anneal out by the time the actual post-reactor measurements are performed, which may hinder factors contributing to the thermal conductivity in nuclear fuel under operation.

The objective of the current work is to determine the impact of specific irradiation induced lattice defects, Frenkel pairs and dislocation loops, on the thermal conductivity in ion irradiated depleted UO_2 . These defect microstructures develop during nuclear plant operation due to lattice damage created by energetic fission products, alpha and beta decay, and neutrons. [13] Ion irradiations of depleted UO_2 with soluble and insoluble fission products (such as La and Kr, respectively) have been demonstrated to provide insight into the microstructure evolution process in UO_2 . [14] However, the resulting ion irradiation damage tends to show gradients in displacement dose and concentration of implanted ions. With light ions, such as He or H, nearly

homogenous plateau damage regions extending over several tens of microns can be obtained, but the implanted gas concentration peaks at the main ion stopping region raising a risk for blistering. [15, 16] The displacement damage and implantation gas gradients may also be used as an advantage; spatially resolved Raman measurements for a cross section of 25 MeV He ion implanted UO_2 have produced detailed information about the defect types as a function of displacement damage along the depth into the sample. [17] Interestingly, the activation of three types of defect-related Raman modes has been found. One of the irradiation-activated Raman modes was related to forbidden LO-mode due symmetry breakdown of the UO_2 unit cell, while the two others were related to local hyper- and hypo-stoichiometric configurations within the UO_2 lattice. [17] In addition to Raman, methods such as positron annihilation spectroscopy (PAS), [18] neutron scattering, [19] and X-ray absorption spectroscopy (XAS) [20] and diffraction (XRD) [21, 22] have been used to characterize point defects and point defect clusters in UO_2 and UO_{2+x} . In general, the experimental results indicate that point defects in both U and O sub-lattice are prominent upon irradiation above energies of 1 MeV. In addition to the substantial experimental work, defect formation and stability in UO_2 has been extensively studied theoretically. [23]

The most distinct observation upon He^{2+} irradiation of UO_2 at low temperature is lattice expansion upon increasing the ion fluence. [22] XRD studies have shown that the maximum amount of implanted He is around few at% at the peak damage region, and that the lattice expands upon irradiation and the expansion saturates around 1 % upon increasing the fluence, but the exact values vary depending on irradiation depth (ion energy), irradiation source (natural alpha emitter vs. ion beam), and applied post-irradiation thermal treatments. [22, 21, 24, 25]

UO₂ lattice expansion of upon irradiation has been attributed to Frenkel pairs in both U and O sub-lattices [22] and small vacancy-He defects. [21]

In this work, thermal conductivity and irradiation damage were studied in 3.9 MeV He²⁺ irradiated depleted UO₂. Irradiation microstructures were explored by transmission electron microscopy (TEM) and XRD and the thermal conductivity of the irradiated layer was determined using a time resolved thermal wave microscopy (TRTWM) technique [26].

2. Experimental Details

The polycrystalline depleted UO₂ sample pellets used in the present work were sintered at Los Alamos National Laboratory following the procedure given in [15]. The sintered UO₂ pellets were roughly 5.2 mm in diameter and 4.3 mm in height, and found to be between 95 and 96 % of the theoretical density. The O/U ratio was fixed at 2 by cooling the pellets at Ar-6%H mixture after sintering. The pellets were sliced to 0.6 mm disks with a low speed diamond saw in a radiological hood and polished to mirror finish prior He²⁺ irradiations.

A toroidal volume ion source (Torvis) produced He²⁺ ions for the irradiation. The He²⁺ ions were accelerated to 3.9 MeV with a Pelletron® tandem accelerator (University of Wisconsin-Madison [27]). The sample temperature was monitored through the irradiations with thermocouples, which were attached to the sample stage right next to the UO₂ disks. The beam was rastered across the specimens and the beam current and specimen temperature were recorded throughout the irradiations. The temperature, as indicated by the thermocouples, was kept at 150 - 200 °C during the irradiations. Ion beam current of approximately 1 µA was applied and no external heating or cooling source was applied during the irradiations (beam heating only). The irradiation chamber vacuum was in the range 10⁻⁶ – 10⁻⁷ bar.

Two samples were irradiated with 3.9 MeV He^{2+} ions. One sample was irradiated to a fluence of 5×10^{16} ions / cm^2 . Target fluence for the second sample was the same, but due to ion beam instrumentation problems, the ion fluence remained lower and was estimated to be about 9×10^{15} ions / cm^2 . The Stopping and Range of Ions in Matter (SRIM) computer code was used to simulate the profiles of atomic displacements in UO_2 as a function of depth. [28] The procedure outlined in [29] was utilized in calculating the displacement damage by using the “quick” Kinchin-Pease (KP) calculation mode and the phonon results, Fig. 1 (a) and (b). A weighted average of the threshold displacement energies for oxygen and uranium, 20 and 40 eV, [13] was applied. The SRIM calculation was also performed in the full cascade (FC) mode to determine the displacements for U and O separately. While the FC mode gave slightly higher values for the peak damage as compared to the KP mode (1.25 dpa for FC vs 1.16 dpa for KP), the low dose plateau values were practically same regardless of the applied method, Fig.1. (c). Peak and plateau values for the displacement damage and He at% as a function of fluence are collected to Table 1.

The samples were examined before and after the He^{2+} irradiations by XRD. Transmission electron microscopy (TEM) was performed for the irradiated specimens and non-irradiated reference samples from the same heat of material. A Siemens Stoe X-ray diffractometer using Cu $K\alpha$ radiation (40 kV, 2.5 mA) was used in omega-2theta geometry. A Technai TF-30 field-emission gun TEM was used for microstructural analysis. Cross-sections perpendicular to the disks surfaces were prepared in a Quanta 3D FEG focused ion beam (FIB) system by a following procedure. A protective platinum layer was first deposited onto the surface. A lamella was then created by coarse trenching $15 \mu\text{m} \times 10 \mu\text{m} \times 1 \mu\text{m}$ sample using the FIB. The lamella was then welded to a copper TEM grid and thinned to a final thickness of roughly 100 nm using 30 keV

Ga ions. Final cleaning of the sample was conducted first using 5 and subsequently 2 keV. Both the TEM and FIB were performed at the Center for Advanced Energy Studies (CAES) in Idaho Falls, ID.

Thermal conductivity of the plateau region was measured using time resolved thermal wave microscopy (TRTWM) technique [26] for the same samples that were examined with TEM and XRD. It is noted that the thermal conductivity evolution at the 8.5 μm irradiated layer would not be possible by conventional bulk sensitive thermal conductivity methods, such as laser flash analysis. Prior to the TRTWM measurement a 60 nm thick aluminum (Al) layer was thermally evaporated on top of two irradiated and unirradiated reference UO_2 samples and fused quartz microscope slide. The latter is used as a reference for measurement of thermal conductivity of Al layer. The details of experimental approach to measure thermal waves have been previously described in [26]. Here we only present analysis steps used to determine thermal conductivity of the plateau region. The analysis involves comparison of measured thermal wave profiles over frequency range spanning 1-100 kHz to the thermal diffusion model corresponding to each sample. For frequencies over 10 kHz the observed thermal wave profiles are barely affected by the peak damage region. However, over the same frequency range the profiles are sensitive to film's properties. Therefore to minimize error associated with additional parameters needed to account for film we chose to analyze lower frequency profiles. Overall there is a tradeoff between high frequency response sensitive to film properties and low frequency response sensitive to peak damage region. In our analysis we assume that specific heat and densities of UO_2 and Al are known and obtained from literature. We also assume that specific heat and density of UO_2 are not affected by irradiation and the damage across the plateau region is uniform. Determination of thermal conductivities of Al (κ_{Al}) and UO_2 (κ_{UO_2}) is performed

using a two-layer model corresponding to a thin film on a substrate geometry. Conductivity of Al is determined from the analysis of a thermal wave profile obtained from the reference fused quartz sample [26]. Subsequently, κ of unirradiated UO_2 was determined by fitting the measured thermal wave profile obtained from the unirradiated UO_2 reference to the two-layer model. To determine κ of plateau region in irradiated sample we consider a 3-layer model: thin metal film, plateau region and unirradiated substrate. Only κ of plateau region was used as fitting parameter. As a last step we performed analysis using a 4-layer where we consider the effect of peak damage region and blistering. This latter step allowed us to determine that our approach is not sensitive to the peak damage region: (1) we cannot determine peak damage layer's conductivity with sufficient degree of confidence and (2) when we assign a lowest possible $\kappa_{\min} = 2 \text{ W/mK}$ to the peak damage region our extracted value for the plateau region increases only by about few percent. Such insensitivity is due to the fact that the peak damage region revealed by SRIM simulations is so much thinner than the plateau region. As a result it was decided that the 3-layer model is the most appropriate for our analysis.

Because the field of view of TRTWM is only a few tens of microns, the technique provides a specially localized measurement of thermal conductivity, which is insensitive to the sample porosity.

3. Results and Discussion

3.1 XRD and TEM

XRD peak position for the (224) reflection, Fig.2 (a), was used to determine the lattice constant before and after the ion irradiations. The high order reflection was chosen to obtain a probing depth of approximately $1.6 \text{ }\mu\text{m}$ and to reduce the uncertainty originating from the

slightly varying displacement dose as a function of depth (Fig.1.). The sample with the high fluence ($5 \times 10^{16} \text{ He}^{2+} \text{ ion/cm}^2$) showed the largest peak shift, as expected, indicating a substantial lattice expansion of 0.55 %. The low fluence sample ($9 \times 10^{15} \text{ He}^{2+} \text{ ion/cm}^2$) also showed a clear shift for the (224) diffraction peak position but the shift was smaller (corresponding to a lattice expansion of 0.11 %) as compared to the sample with higher fluence. In Fig.2 (b) the determined lattice constants, a , are shown as open red squares and superimposed to the results from literature (green solid squares connected by line). Despite that the cited reference work [22] was performed with a semi-infinite alpha particle source for a single crystal UO_2 with slightly higher ion energy (about 5 MeV), the lattice constant versus dpa values show a good agreement.

Irradiation damage microstructure was studied by TEM. The examined cross sections were prepared by FIB milling as described previously. The small-scale irradiation induced features at the plateau region (depth $< 8 \text{ } \mu\text{m}$) did not differ significantly between the samples. As shown in Fig.3 (a) and (b), the damage imaged close to the (011) pole with $\mathbf{g} = [-1-11]$ consisted of small dislocation loops ($< 10 \text{ nm}$ in diameter) seen as dark spots, and possibly some segments of dislocations. It was noted, however, that the microstructure was complex and did not show any well-defined features, such as precipitates or edge-on loops, which would create distinct strain contrast in conventional TEM. The complex microstructures are likely due to the low irradiation temperature accompanied by minimal displacement damage in general (only 0.035 dpa for the high fluence sample). A rough estimate for the dislocation loop density was made based on bright-field TEM images to give an idea as to how much they affect the thermal conductivity (next section). The sample thickness was deducted based on thickness fringes at the FIB foil edge and the loop density was calculated in ten locations for all samples. A careful comparison with the non-irradiated reference sample was performed to remove the contribution

of FIB damage. The determined loop densities were 6 ± 3 and $13 \pm 3 \times 10^{21}$ loop/m³ for the 9×10^{15} He²⁺/cm² and 5×10^{16} He²⁺/cm² sample, respectively, and the average loop diameter increased from 7.3 nm to 8.5 nm upon increasing the fluence. According to the previous work, most of the irradiation damage is believed to freeze in the lattice at low temperatures (< 200 °C) [30]. Also, He-induced precipitates or bubbles have not been observed unless post-irradiation annealing has been performed for low temperature He irradiated UO₂. [31] Point defects and most of the smallest point defect clusters are well below the TEM resolution. The observation that the irradiation damage is mainly in point defect scale agrees with the XRD results, because point defects and small defect clusters cause more distinct effect on the XRD as compared to extended irradiation damage. [32, 33] Large lattice expansion in XRD indicates that no lattice recovery took place due to beam heating, e.g., there was no significant difference between the temperature at the sample surface and the temperature measured with the thermocouples right next to the samples.

While the appearance of irradiation damage in the low displacement damage region did not differ remarkably between the low and high fluence samples (9×10^{15} He²⁺/cm² and 5×10^{16} He²⁺/cm², respectively), the TEM observations for the peak damage regions showed a clear difference, Fig.4. Distinct features were observed at the peak damage region of the high-fluence sample but not to the same extent in the low-fluence sample, Fig.4 (a) and (b). The peculiar outlook of the features, with a zero-contrast line in the middle of them, originates from an isotropic strain likely due to He blister formation and the TEM imaging conditions. One of these features with well-defined imaging conditions is shown in Fig.5. The diffraction vector $\mathbf{g} = [220]$ (selective area diffraction pattern shown at the inset) is perpendicular to the zero contrast line seen in the middle of the feature at the bright field image, Fig.5 (a), and more prominently in

the dark field imaging conditions, Fig.5 (b), with the same g . Similar features have also been observed in in-situ He ion irradiated UO_2 but not without post-irradiation annealing. [31] Apparently, the He at% at the peak damage region and the displacement damage allowed atomic diffusion to such an extent that the blister formation was possible to begin in the current work without post irradiation annealing. The TEM observations from the peak damage region are consistent with the XRD results, as they clearly show more pronounced damage for the high-fluence sample as compared to the low-fluence sample.

The unirradiated matrix beyond the irradiated region showed features typical for a large scale FIB damage. It is likely that the strain gradient between the un-irradiated matrix and the peak damage region bends the lamella slightly during the FIB milling and the region is subsequently overcut by FIB (e.g., the features are artifacts from sample preparation using FIB). Furthermore, to support the given scenario, the features travel in the ion milling direction in both samples regardless of the crystal orientations (stress-induced cracking would most likely propagate via preferential crystal directions).

It is interesting to compare the peak damage microstructures, namely the appearance of large He blisters, to the microstructures found in the other ceramic-materials irradiated with light ions. H ions (i.e. protons) have been shown to create sharp needle like cavities at the peak implanted region in fusion-related ceramics. [16] Also, pile-up of H at the peak damage region has also been proposed to induce flaking upon modest fluences in UO_2 . [15] In contrary, the He ions have been shown to interact with the lattice in a different fashion; in particular the blisters are less restricted on the plane of peak implantation but show wider three dimensional structures. [16] The large blisters seen at the peak damage region are thus in agreement with the earlier

observations, and indicate that He ions tend to form less sharp cavities at the peak damage region than H ions.

The types of defects produced in UO_2 by He ion irradiation were briefly mentioned in the introduction, and can be discussed based on the presented results. Spatially resolved Raman measurements clearly show the presence of different defects as a function of depth, and in turn the displacement dose, in He-irradiated UO_2 . [17] The additional Raman mode observed at the low dose plateau region was proposed to originate from a deviation from a perfect fluorite crystal due to irradiation. In this work, TEM for the plateau damage showed the presence of small-scale irradiation damage, and most prominently, the XRD observations provided evidence of lattice expansion. Both the TEM and XRD observations are in line with the proposed explanation of crystal deformation induced appearance for the forbidden LO Raman mode. Also, the Raman measurements showed an activation of new types of defect modes, especially at the peak damage region. These defect modes were proposed to originate from small hypo- and hyperstoichiometric clusters in the stoichiometric UO_2 lattice. [17] The U_4O_9 (hyperstoichiometric) clusters form in UO_2 upon oxidation [19] but their presence under irradiation of stoichiometric UO_2 has not been confirmed. Because the irradiations of this work were performed for stoichiometric UO_2 under high vacuum, no excess O was available for forming these clusters but they would need to form from interstitial O and would thus lead to O depletion of other regions in the host lattice. While such small hyper/hypo -stoichiometric defect clusters could not be identified in this work, it was clear that the microstructures at the peak damage region clearly differs from the plateau damage region, therefore partially agreeing with the spatially resolved Raman results. Raman results thus give an evidence of local stoichiometric

changes at the mesoscale in UO_2 lattices under irradiation, even if the initial composition is perfectly stoichiometric.

3.2 Thermal conductivity

The measured thermal conductivity of the plateau region is $4.9 \pm 0.3 \text{ W/m}^2\text{K}$ and $7.2 \pm 0.3 \text{ W/m}^2\text{K}$ for high and low dose samples, respectively. Conductivity of the unirradiated reference was measured using same technique and found to be $11.0 \pm 0.3 \text{ W/m}^2\text{K}$. The value is somewhat larger than suggested for the polycrystalline UO_2 fuel [34] but in the range of some other reports [35, 36] and we attribute it to our measurement being a local measurement not influenced by the porosity. To avoid systematic errors associated with the approach we consider the relative reduction in conductivity of the damage layer. Most notably, the conductivity was reduced by 55% for the high dose sample and 35% for the low dose sample as compared to the un-irradiated reference UO_2 sample.

First, it is interesting to compare our results to hyper stoichiometric UO_{2+x} for which thermal conductivity values have been well documented. [1-4] Conductivity reduction in UO_{2+x} is generally attributed to the presence of oxygen defects. Based on SRIM calculation the concentration of oxygen Frenkel pairs in the plateau region of the high-fluence sample is $n(\text{OFP}) = 0.026$ per U. For comparison we consider conductivities of our sample and hyperstoichiometric UO_{2+x} that have same amount of oxygen interstitials. For that we look at $\text{UO}_{2+0.026}$ and see that conductivity reduction is only 20%. Therefore our results are consistent with the fact that point defects other than O_i are also responsible for the degradation of thermal transport in irradiated sample.

Further analysis of thermal conductivity was performed based on a thermal transport model, the results of which are summarized in Fig. 6. In UO_2 the thermal transport is governed by lattice vibration referred to as phonons. The thermal conductivity depends on phonon velocity and phonon scattering. In unirradiated UO_2 , intrinsic 3-phonon scattering processes limit thermal transport at high temperatures. In irradiated UO_2 , impurities and irradiation induced defects limit thermal transport by acting as phonon scattering centers. We implement a model based on Klemens Callaway approach to analyze our results. This model allows consideration of intrinsic 3-phonon scattering, point defects and extended defects. [37]

Phonon mediated thermal conductivity assuming single-band Debye phonon dispersion and relaxation time approximation for scattering is given by: [38]

$$\kappa = \frac{k_B}{2\pi^2 v} \int_0^{\omega_D} \tau(T, \omega) \frac{x^2 e^x}{(1 - e^x)^2} \omega^2 d\omega, \quad (1)$$

where, ω is the phonon frequency, T the temperature, $x = \hbar \omega / k_B T$, $\hbar$ Plank's constant, k_B Boltzmann constant, v the sound velocity, and ω_D is Debye phonon frequency. Phonon Scattering rate $\tau^{-1}(\omega)$ combines the following phonon scattering processes: intrinsic 3-phonon processes, impurities in the as-received sample and irradiation induced point defects, and dislocation loops, all added using the Matthiessen rule. [39] For the Umklapp, or the 3-phonon, scattering and impurity scattering we use the relation $\tau_{3ph}^{-1}(T, \omega) = B T \omega^2 \exp(-T_D/3T)$ and $\tau_{imp}^{-1}(\omega) = A_0 \omega^4$, respectively, where $B = 1.6 \times 10^{-18} \text{s/K}$, and $A_0 = 1.0 \times 10^{-42} \text{s}^3$ are obtained from the fitting of the bulk data assuming literature values of $\omega_D = 43 \text{ THz}$, $T_D = 328 \text{ K}$, and $v = 2644 \text{ m/s}$. [3] Irradiation induced point defects are accounted using $\tau_{pd}^{-1}(\omega) = A_i \omega^4$, where

$A_i = \Gamma V_0 / 4\pi N v^3$ and Γ point defect scattering parameter proportional to defect concentration.

Parameter Γ is given by:

$$\Gamma = \sum f_i \left[\left(\frac{\Delta M_i}{M} \right)^2 + \varepsilon \left(\frac{\Delta r_i}{r_a} \right)^2 \right], \quad (2)$$

where f_i is the concentration of defect i . First term represent mass difference contributed by the defect and second term captures the strain associated with the ionic radius mismatch, similar effect that causes lattice expansion.

The impact of point defects and dislocation loops on the thermal conductivity was considered separately. Willis type defect structures and cub-octahedral clusters are often discussed in the context of UO_{2+x} . Since there is no direct evidence for their appearance as a result of irradiation we don't consider them here to keep the analysis simple. As a result, we confine our discussion to 4 types of point defects consisting of oxygen interstitial, oxygen vacancy, uranium interstitial and uranium vacancy. The concentration of vacancies was obtained from SRIM calculation, which roughly provides an estimate for ratio of oxygen to uranium defects equals 2. We make an assumption that for every vacancy there is an interstitial and all defects are frozen upon creation, i.e. we neglected the fact some of defect might have annihilated or formed larger clusters. For the point defect contribution, a number of reports are available that provide a recipe for estimation of Γ in UO_2 based systems. They follow a method that requires precise knowledge of defect structures, which includes the charge state of uranium atoms. [2, 40, 41] To estimate the strain component of Γ , we follow a different approach that relies on the estimates of lattice expansion provided by previous DFT calculations [23] listed in Table II, where we assumed that $\Delta r_i / r_a = \Delta a_i / a$. The mass mismatch for the oxygen and uranium defects

is estimated using $\Delta M_i/M = M_o/M_{UO_2} = 0.059$ and $\Delta M_i/M = M_U/M_{UO_2} = 0.88$, where the mass mismatch is same for both interstitials and vacancies.[3, 42] The above described model based on $\epsilon = 100$ provides an estimate which agrees well with the experiment (dotted line in Fig. 6). This analysis suggests that uranium defects have the largest influence and strain field has heavier contribution. This further justifies our approach neglecting oxygen defect clustering for the purpose of thermal conductivity analysis.

To our knowledge there is no analytical expression specifically derived for the contribution of dislocation loops on thermal conductivity. Two approximations were then applied. In the first, the circumferences of the loops are considered as dislocation lines, and in the second the internal feature of the loop itself is considered as a stacking fault. Both of these features, dislocation lines and stacking faults, have been considered by Klemens for which he derived analytical expressions. [39] The dislocation line model, which includes contribution from strain field by neglecting scattering from the core suggests:

$$\tau_{line}^{-1} = 0.06\gamma^2 b^2 N_d \omega, \quad (3)$$

where γ is the Gruneisen parameter, b the Burgers vector, and $N_d (=N_d=2\pi R n_d)$ the dislocation line density defined as a number of lines per unit area. While the phonon scattering contribution from stacking faults is:

$$\tau_{fault}^{-1} = \frac{0.7a^2\gamma^2 N_s}{v} \omega^2, \quad (4)$$

where a is the lattice constant and N_s is a number of stacking faults per unit length, $N_s=\pi R^2 n_d$.

The contribution of dislocation loops alone is shown in Fig. 6 as either dash-dotted or dashed line based on dislocation line and stacking fault models, respectively. It appears that dislocation lines induce a negligible reduction in conductivity while the stacking faults result in a noticeable reduction. However, when the effect of loops using a stacking fault approach is considered in combination with the point defects it provides only a minimal correction to the overall conductivity reduction. Therefore we conclude that observed conductivity reduction is primarily due to isolated point defects, or that the loops models considered above are not adequate to describe the loop scattering mechanisms.

It should be noted that even though the result of previous DFT calculation combined with our simple microstructure description provided a good estimate for conductivity reduction, they failed to provide a good estimate for the observed lattice expansion. This suggests that further modeling work is needed to understand the role of point defects on lattice expansion and thermal conductivity in UO_2 . Also, systematic experimental studies that include low temperature thermal conductivity measurements and larger set of doses than presented here are in process and are expected to provide more accurate definitions for the scattering mechanism.

4. Conclusions

Irradiation microstructures were examined upon 3.9 MeV He^{2+} ion irradiations. The plateau damage consisted of small dislocation loops and dislocation segments. While the plateau microstructures in the $9 \times 10^{15} \text{ He}^{2+}/\text{cm}^2$ and $5 \times 10^{16} \text{ He}^{2+}/\text{cm}^2$ samples did not show major differences aside from the loop density and size, the damage at the peak damage region clearly differed between the samples. Large dome-shaped features originating from isotropic strain at the expected blister initiation sites were detected most prominently at the high fluence sample, while not to the same extent at the low fluence sample. Thermal conductivity was measured by

using laser-based thermo-reflectance method. A major reduction up to 55% was detected in thermal conductivity and further analysis showed that it was most likely due to phonon scattering from irradiation-induced point defects.

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Figure captions

Fig.1. SRIM simulation results for the displacement damage and He at% for (a) the 9×10^{15} ion/cm² sample and (b) the 5×10^{16} ion/cm² sample. (c) The plateau damage values did not show a major difference if the SRIM calculation was done with the quick KP option or using full cascade simulation.

Fig.2.(a) Evidence of lattice expansion during irradiation revealed by a shift of the (224) XRD diffraction peak. (b) The lattice constants calculated from the (224) diffraction peak position (red, open squares) were in good agreement with earlier work (green, solid squares connected by line) [22].

Fig.3. Irradiation microstructures at the plateau region at (a) the 9×10^{15} He²⁺/cm² sample and (b) the 5×10^{16} He²⁺/cm² sample. No major differences were observed at the defect types between the samples.

Fig.4. Small magnification view revealed clear differences at the peak damage regions of the 9×10^{15} ion/cm² and (b) the 5×10^{16} ion/cm² samples. Distinct microstructures were detected at peak damage / He at% region for the high fluence sample, while not to same extent at the low fluence sample. Based on earlier work, [31] these features indicate isotropic lattice strain at an initial stage of a blister formation.

Fig.5. Isotropic strain at the peak damage region produced large dome-like features in TEM. A zero contrast line perpendicular to the diffraction vector $\mathbf{g} = [220]$ indicates spherical shape for the clusters/early stage blisters and was prominent in (a) bright and (b) dark field TEM.

Fig. 6. The experimental thermal conductivities (red circles) were modeled by considering the impact of dislocation lines (black circles), stacking faults (green circles), vacancies (cyan triangles), and combined effect of vacancies and stacking faults (blue squares).

Table I. dpa and H at % from SRIM simulations. The plateau values were taken at the depth of 4 μm and are based on KP SRIM calculation.

Sample ID	Fluence ($\times 10^{16} \text{ He}^{2+}/\text{cm}^2$)	Dpa (plateau)	He at% (plateau)	Dpa (peak)	He at% (peak)	T (°C)
Ref	0	0.0	0	0	0	-
1	0.9	0.007	< 0.001	0.21	0.21	< 200
2	5.0	0.038	< 0.001	1.16	1.18	< 200

Table II. Point defect parameters used in analysis of experimental data based on first principles calculations. [23]

Defect type	Lattice expansion, $\Delta a/a$	Ionic radius mismatch, $(\Delta r/r)^2$	Mass mismatch, $(\Delta M/M)^2$
Oxygen interstitial	-1.9×10^{-2}	3.7×10^{-4}	3.5×10^{-3}
Oxygen vacancy	1.3×10^{-2}	1.8×10^{-4}	3.5×10^{-3}
Uranium interstitial	1.9×10^{-1}	3.6×10^{-2}	7.7×10^{-1}
Uranium vacancy	-0.7×10^{-1}	5.1×10^{-3}	7.7×10^{-1}
Oxygen dimer	5.0×10^{-2}		

Table III. Point defect concentration based on SRIM FC calculations.

	as-received	0.007 dpa	0.038 dpa
Oxygen interstitial, $f(\text{O}_i)$ (per U atom)	-	0.005	0.026
Oxygen vacancy, $f(\text{O}_v)$ (per U atom)	-	0.005	0.026
Uranium interstitial, $f(\text{U}_i)$ (per U atom)	-	0.002	0.013
Uranium vacancy, $f(\text{U}_v)$ (per U atom)	-	0.002	0.013
Measured lattice expansion, $\Delta a/a$	-	1.1×10^{-3}	5.5×10^{-3}
Predicted lattice expansion, $\Delta a/a$	-	0.2×10^{-3}	1.4×10^{-3}

Fig.1.

Fig.2.

Fig.3

Fig.4.

Fig.5.

Fig. 6.