Effect of high fluence Au ion irradiation on nanocrystalline tungsten film

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1. Introduction

Material failure is one of the key problems urgently to be solved in the design and development of the advanced nuclear energy systems where materials will be in-service under extreme conditions with high fluence radiation, high temperature (~1000 °C) and corrosion [1,2]. High fluence radiation of neutrons and energetic particles generated by nuclear reactions can induce a large number of defects in the materials. The damage level can reach up to hundreds of dpa in the generation IV fission reactors and future fusion reactors [3]. The subsequent behavior of the irradiation-induced point defects (interstitials and vacancies) is usually detrimental to the macroscopic structure and the properties of the materials. One practicable way to enhance radiation-tolerance of material is to suppress accumulation and enhance annihilation of point defects in radiated materials [4,5].

Previous studies have revealed that free surfaces [6] and interfaces [5,7] such as grain boundaries and inter-phase interfaces can act as sinks to annihilate freely-migrating point defects. Consisting of a large volume fraction of interfaces and a mass of small crystallites (<100 nm), nanocrystalline materials usually have novel physical and chemical properties, differing from those of the conventional bulk materials with large grain size (>1 μm) [8]. The small grains and large amount of grain boundaries in nanocrystalline materials play a dominant role in the annihilation of radiation-induced defects. They are deduced to be effective sinks for radiation-induced defects in both computer simulations [9] and experiments [10] and expected to significantly hinder the accumulation of point defects. Hence, nanostructured materials have been widely studied to achieve more tolerance against radiation by atomic-scale design [11].

The radiation tolerance of a single-phase nanostructure depends on the grain size and the structure [4]. The performance of nanocrystalline material such as electrical transport, optical, catalytic and mechanical properties depends on the grain size and the microstructure as well [12]. Thus, the stability of phase and microstructure of nanocrystalline materials is the basis for the concept of enhancing radiation-tolerance or otherwise it will be detrimental to the performance. However, the phase of nanocrystalline material, especially metastable form may not be stable under radiation [13–17], and the radiation-induced grain growth sometimes concomitantly occurs [18,19]. Therefore, controlling the stability of phase and structure of nanocrystalline material by preparation or other modification means is required. Radiation effect and ion beam modification on nanocrystalline materials such as zirconia, tungsten, nickel and ceria have been studied experimentally or theoretically in recent years [12,18,20,21].

Due to the high melting point, very low sputtering yield and low evaporative coefficients and good tolerance against neutron radiation, polymeric nanocrystalline tungsten has been chosen as a candidate material for first wall material in future fusion reactors [22,23]. For nanocrystalline tungsten, the microstructure with nano-size grains not only increases the strength, hardness and wear properties, but also partly reinstates its ductility [24,25]. Since boundary effects in nanocrystalline tungsten is prominent, it is expected that nanocrystalline tungsten will behave better radiation tolerance. However, possible phase transformation and microstructure damage under high fluence irradiation need to be considered since they will impact the structural integrity. This requires more systematic

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study to better understand the effects of energetic ion bombardment on nanocrystalline tungsten. In this study, we are aimed to study the radiation effect on the structure of sputtered tungsten film when it is subjected to high energy Au ions.

2. Experimental

The nanocrystalline tungsten films with a thickness of 600 nm were deposited on oxidized silicon samples by the ATCOrion sputtering system. The vacuum chamber was evacuated to a base pressure of less than 2 × 10⁻⁷ Torr before deposition. During the deposition, the pressure was maintained at 3 × 10⁻³ Torr under argon partial pressure and the deposition rate was kept about 2.5 nm/min at a direct current power of 50 W. After deposition, the tungsten film was annealed at 550 °C under the mixture of argon and hydrogen gas for 2 h to eliminate the residual stress in the film.

The samples were then irradiated by 4 MeV Au ions at room temperature with fluences ranging from 6 × 10¹⁴ ions/cm² to 1 × 10¹⁶ ions/cm². The beam current was kept at 300 nA during ion irradiation. In order to correlate microstructure evolution to the damage induced by 4 MeV Au ion irradiation, the damage profile in the units of dpa for W films was calculated by the SRIM code [26] with the threshold displacement energy of 90 eV [27] for W.

Phase transformation and grain size of the samples were determined by grazing incidence X-ray diffraction (GIXRD) measurements at Beijing Synchrotron Radiation Facility (BSRF). The incidence angle was chosen as 1.5° in order to ensure that the X-ray was reflected primarily from the damaged region by 4 MeV Au ions. The diffraction patterns were recorded with synchrotron radiation (λ = 1.54 Å) in a 0–2θ scattering geometry ranging from 30° to 77°. Cross-sectional transmission electron microscopy (XTEM) observations were performed in a Tecnai F30 TEM operated at 300 kV to compare the microstructure before and after Au ion irradiation. The samples for cross-sectional view were prepared with the mechanical lapping technique followed by ion thinning with low energy Ar ions.

3. Results

3.1. The structure of as-deposited tungsten film

A bright-field XTEM image of the as-deposited tungsten thin film is shown in Fig. 1a. The film is approximately 600 nm thick and consists of columnar grains. The corresponding selected area electron diffraction (SAED) pattern shown in Fig. 1b reveals the film has the polycrystalline structure nature. The features of the SAED patterns were recorded in the 2θ range from 30° to 77° at a grazing incidence of 1.5°. For the as-deposited sample, as shown in Fig. 2(a), all the five reflection peaks match the simple cubic diffraction patterns of (200), (210), (211), (3 20) and (3 2 1), respectively. It indicates the existence of the pure β phase in as-deposited tungsten film, which is consistent with the result obtained by the indices on SAED pattern in Fig. 1b. No reflection peaks from other phases are observed.

3.2. Phase transformation and grain growth under irradiation

The GIXRD patterns of irradiated films with the Au ion fluences of 6 × 10¹⁴ ions/cm², 3 × 10¹⁵ ions/cm², and 1 × 10¹⁶ ions/cm² are shown by spectra (b–d) in Fig. 2, respectively. The peak intensities are normalized based on the background counts. Apparently, the simple cubic tungsten (β phase) began to transform into bcc tungsten (α phase) when the samples were irradiated with the increase of ion fluence. At the lowest fluence, 6 × 10¹⁴ ions/cm² (6 dpa according to SRIM code at damage peak, similarly hereinafter), as indicated by the spectrum (b), no new peak is observed but a reduction in peak intensities of all the five peaks corresponding to β-W, suggesting that the grain texture of β-W becomes weaker. At 3 × 10¹⁵ ions/cm² (30 dpa), the spectrum (c) presents three noticeable new peaks emerging at 40.4°, 58.3° and 73.2° and the reduction of peak intensity for the initial five peaks. The three new peaks correspond to (1 1 0), (2 0 0) and (2 1 1) planes of α-W, respectively. It indicates a phase transformation from β-W to α-W at the fluence of 3 × 10¹⁵ ions/cm². In the spectrum (d), at the highest fluence, 1 × 10¹⁶ ions/cm² (100 dpa), all the initial five peaks belonging to β phase disappear and the reflection peaks corresponding to (1 1 0), (2 0 0) and (2 1 1) planes of α-W present, indicating that the β phase has been completely transformed into α phase in highly ion irradiated tungsten films.

The phase transformation behavior of W film from β to α phase is characterized in terms of weight ratio of the phase. If we assume β phase and α phase have the same absorption coefficient and density, the integrated peak intensity of β phase (or α phase) has linear relationship with its weight ratio. For example, if the integrated peak intensity of pure β phase is I₀β and the integrated peak intensity of α phase from the mixture phases of β and α is I₀α, then the weight ratio of β in the mixture phases is α/I₀α. Therefore, the weight ratio of α phase increases and finally reaches 100% when the phase transformation finished at the highest fluence of 1 × 10¹⁶ ions/cm².

The widths of the major peaks in Fig. 2 decrease as the ion fluence increases, indicating clear grain growth. The radiation-induced grain growth was determined by fitting the major diffraction peaks of β(2 1 0) or α(1 1 0) from the samples under different fluences and the average grain sizes of each sample were estimated by Scherrer formula [28,29]. It is noted that the average grain size determined by XRD has better statistic and lower uncertainty than that determined by TEM. Fig. 4 shows the variation of the average grain size with ion fluence deduced from the major peaks according to Scherrer formula for each sample. The estimation shows that the nanocrystallites have grown with the increase of ion fluence. The average grain size in the films increases from 10.9 nm to 18.2 nm when the ion fluence increases to 1 × 10¹⁶ ions/cm². This can be described by a power law expression, Dₙ = D₀₁₆⁻ⁿ, which relates the average grain size with the ion fluence. D₀ is the initial average grain size, φ is ion fluence (10¹⁶ ion/cm²), and K and n are constants. In this study, the values of K and n are obtained by fitting the plot of average size of the samples versus ion fluence shown in Fig. 4.

Grain growth in the irradiated samples was examined by TEM as well. Fig. 5a shows dark-field XTEM image of the as-deposited sample. Being taken from the main diffraction spots, β(2 1 0), the
discrete bright areas in the image present the fine grains with the same orientation and different sizes. Fig. 5b shows the dark-field XTEM image taken from the main diffraction spots, (110) of the sample irradiated under 3 x 10^15 ion/cm^2. The comparison of the grain size before (Fig. 5a) and after radiation (Fig. 5b) shows the significant grain growth in the radiated tungsten film. Fig. 5c presents the corresponding distribution of grain size which is obtained by measuring the size of tens of grains within HRTEM images combining with dark field XTEM images. The average size is determined as ~12.7 nm, larger than that of the as-deposited tungsten film (~8.1 nm). Fig. 5d-f shows the bright field XTEM image, SAED pattern and size distribution of the sample irradiated with 1 x 10^16 ion/cm^2, respectively. In Fig. 5d, the cross-sectional full view of the irradiated film exhibits a reduction on thickness (~8.6%) compared to the as-deposited film shown in Fig. 1a. For SAED pattern, the discrete points in Fig. 5e suggests larger grain size and more aligned orientations of pure α phase. The average size of grains is determined as ~16.8 nm as shown by the corresponding distribution in Fig. 5f. There is no radiation-induced
amorphous region observed even at the highest fluence, $1 \times 10^{16}$ ions/cm$^2$. This shows good agreement between the TEM results in Fig. 5 and the GIXRD spectra in Fig. 2.

### 3.3. Irradiation-induced defects

Atoms in target materials can be displaced by energetic incident ions and they in turn can displace other atoms when get more energy than their displacement threshold energy, creating a cascade of atomic collision events as well as the incident ions. Eventually, it may lead to a distribution of interstitials and vacancies, which may migrate, gather and form clusters even voids.

According to the calculation by SRIM code [26], the dpa profile as a function of depth, together with the atom percent of Au ion concentration resulting from radiation at $1 \times 10^{16}$ions/cm$^2$ are shown in Fig. 6. The simulation results predict that the radiation conditions used in this study lead to a damage peak of 100 dpa at the depth of 170 nm. Au ion implantation results in quasi Gaussian distribution in its concentration profile. The maximum concentration of Au ion is about 0.65 at.% at the depth of 260 nm. No gold particle or other alloyed precipitate is detected by both GIXRD and TEM characterizations due to such low Au concentration in the radiated films. However, it is worthy to notice that the actual ion range and damage region may be broader than that predicted by SRIM because of the continual atom diffusion in the actual radiation condition at room temperature while the SRIM code just takes 0 K into consideration, which can be well confirmed by observation via TEM technique.

HRTEM images in Fig. 7 show the high damage regions (at the depth of $\sim$300 nm from surface) of samples irradiated at $3 \times 10^{15}$ (a–b) and $1 \times 10^{16}$ (c–e) ions/cm$^2$. They are subjected to a damage level of 30 and 100 dpa, respectively. There is no clear defect observed in the irradiated sample at 30 dpa. Fig. 7a shows a boundary between two grains with $\beta$ (200) and $\alpha$ (200) planes. It indicates the tungsten film is in the process of the phase transition from $\beta$ to $\alpha$ and a good consistence with the pattern (c) in Fig. 2. Fig. 7b shows a coarsened grain with $\alpha$ (110) plane without any defects. When the fluence reaches up to $1 \times 10^{16}$ ions/cm$^2$, a large number of small voids with $\sim$1 nm in size are observed, as the white round dots indicated by the arrows in Fig. 7c–d which are taken in under-focus condition ($\sim 500$ nm). According to Fresnel contrast analysis, the small voids in over-focus condition will exhibit black contrast, as shown in Fig. 7e which is taken in over-focus condition ($\sim 500$ nm) and corresponds to that in Fig. 7d. No larger voids are observed. In the regions near the grain boundaries, it seems that lower number of voids is observed. It could be attributed to the role of grain boundaries as sinks.
4. Discussion

Before irradiation, all the samples had been annealed at 550 °C under mixture gas environment of argon and hydrogen for 2 h to release stress. The film structure kept stable under the annealing process, without phase transformation and grain growth. The beam current was kept at 300 nA during radiation process and the temperature increase of the sample during radiation was measured to be less than 20 °C due to beam heating. Hence, the phase transformation and the grain growth in this work were induced by radiation of 4 MeV Au ions at room temperature instead of thermal activation.

For tungsten, the thermodynamically stable phase under normal pressure and temperature is body-centered-cubic (bcc) \( \alpha \)-W. The metastable simple cubic \( \beta \) phase W is always presenting in the films prepared by sputtering, evaporation, gas condensation, and hydrogen reduction of tungsten-oxides \([30,31]\). These two phases have different properties: for example, resistivity reported in \( \beta \)-W film is one order higher than that in \( \alpha \)-W film \([32]\). Radiation induced phase transformation has been widely studied in previous work. For example, zirconia is suggested to transform from monoclinic to tetragonal under radiation by swift heavy ions \([14,15]\) when the electronic energy loss exceeds 13 keV/nm. Clear phase transformation was also observed in the radiation with low energy heavy ions \([13,16,17]\) when the nuclear stopping power is predominant. In this work, the nuclear energy and electronic energy loss of the 4 MeV Au ions impacting into W films are comparative in value, especially in the deeper region from surface. It can be suggested that the radiation-induced phase transformation of W from the simple cubic form to the bcc form is due to two effects, thermal spike and ion-induced point defects. The high temperature in local regions resulting from thermal spike makes regions thermally capable of transforming. On the other hand, the internal stresses due to trapped interstitials might cause a collapse of the lattice to the smaller volume and a closer packing \([33]\). In this work, when the ion fluence reaches up to \( 1 \times 10^{16} \) ions/cm\(^2\), the as-deposited film with \( \beta \) phase has completely transformed to \( \alpha \) phase with higher atomic packing factor (APF) due to the resolidification of W atoms under ion irradiation. For \( \beta \)-W, the lattice constant \( a = 5.05 \) Å, the number of atoms per unit cell is 1; for \( \alpha \)-W, \( a = 3.164 \) Å and the number of atoms per unit cell is 2. After complete transition to pure \( \alpha \)-W, the APF increases (0.52 for \( \beta \)-W and 0.68 for \( \alpha \)-W) due to the change of crystal structure. The relative difference of the APF is up to 30.8%. As a result, a prominent

Fig. 6. SRIM calculated profiles of dpa and Au ions concentration under radiation at \( 1 \times 10^{16} \) ions/cm\(^2\).

Fig. 7. HRTEM images taken within (a) a grain with both \( \alpha \) and \( \beta \) phase and (b) a coarsened grain with \( \alpha \) phase at 30 dpa; (c and d) small voids taken from the interior region of a coarsened grain in under-focus condition (500 nm) and (e) in over-focus condition (~500 nm) at 100 dpa, respectively.
reduction in volume is caused by the dramatically increasing of atomic density. On the contrary, the large number of small voids induced by radiation essentially causes swelling at the same time. As a result of the combination of phase transition and void swelling, the film thickness reduces by ~8.6% according to the step measurement.

Grain growth has been observed under both thermal annealing [34] and ion irradiation in previous work [12,18,19,35–37]. They have shown that radiation induces an exponential growth of the grain size as a function of irradiation dose and the correlation is described by a power law expression of $D_n = D_0 n^k$, where the constants $k$ and $n$ may be characteristic to a material system [12,18,38]. Comparative study on nanostructurally stabilized cubic zirconia under radiation by heavy ions and electrons indicates that the grain growth is not due to thermal activation. Instead, defect-stimulated is the dominated mechanism [18]. Hence, the nuclear energy loss dominates the radiation induced grain growth by the 4 MeV Au ions into W films although the electronic energy loss is comparable to the nuclear energy loss. Upon ion irradiation, individual target atoms can be displaced, creating an atomic collision cascade. On the other hand, energy transfer to target electrons can also enhance defect and atomic diffusion. In such non-equilibrium processes, the enhanced defect diffusion promotes grain-boundary migration and results in reducing interface curvature by atomic jumps of the radiation-induced defects across the grain boundaries, which further leads to grain growth and defect removal. The defect-activated mechanism is supported by molecular dynamics simulation on Ni [21]. It reveals when the cascade volume is exceeding the grain size or overlapping the grain boundary area, radiation-induced grain growth occurs in adjacent grains resulting from atoms recrystallization during cooling and shrinking of the cascade.

Interaction of energetic ion with nanomaterials can modify the chemical, thermodynamic, and physical properties of the materials. On the other hand, ion irradiation creates a non-equilibrium condition that may lead to increase in free energy and affect the nanostructure and phase stability. Under the combinations of radiation conditions such as temperature, fluence, ion species and energy, the determination of the dominated mechanisms of microstructure evolution such as phase transition, grain growth and voids formation under ion irradiation requires further in-depth investigation, especially for nanocrystalline materials.

5. Conclusions

The microstructure evolution of nanocrystalline tungsten with simple cubic structure is studied under radiation with 4 MeV Au ions at room temperature. The grains grow with the increase of ion fluence and it follows a power law. The enhanced defect diffusion promotes grain-boundary migration and results in reducing boundary curvature by atomic jumps and further leads to grain growth. Phase transformation occurs at the same time. The simple cubic tungsten begins to transform into bcc structure at $3 \times 10^{12}$ ions/cm² (30 dpa) instead of amorphization. At $1 \times 10^{16}$ ions/cm² (100 dpa), since phase transformation to pure α-W completes, a noteworthy reduction in film volume is mainly caused by the dramatically increasing of atomic density. Meanwhile, radiation induced small voids are clearly observed in the interior of coarsened grains and voids could induce the swelling. However, the void swelling could be canceled by the volume reduction because of complete phase transformation. Thus, as a result of the combination of decrease of volume caused by phase transformation and void swelling induced by radiation, the film thickness reduces. Nanostructured material is indeed more sensitive under the non-equilibrium state created by ion irradiation. The microstructure evolution and stability under irradiation is of great significance to further understand the radiation effect and to develop better radiation tolerant materials.

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