EFFECT OF IMPLANTATION OF C, Si AND Cu INTO ZrNb NANOMETRIC MULTILAYERS

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Abstract

Sputter-deposited Zr/Nb nanometric multilayer films with a periodicity (L) in the range from 6 to 167 nm were subjected to carbon, silicon and copper ion irradiation with low and high fluences at room temperature. The ion profiles, mechanical proprieties, and disordering behavior have been investigated by using a variety of experimental techniques (Secondary Ion Mass Spectrometry - SIMS, nanoindentation, X-ray diffraction - XRD, and scanning transmission electron microscopy - STEM). On the STEM bright field micrographs there is damage clearly visible on the surface side of the multilayer; deeper, the most damaged and disordered zone, located close to the maximum ion concentration, was observed. The in-depth C and Si concentration profiles obtained from SIMS were not affected by the periodicity of the nanolayers. This is in accordance with SRIM simulations. XRD and electron diffraction analyses suggest a structural evolution in relation to L. After irradiation, Zr (0002) and Nb (110) reflexions overlap for L=6 nm. For the periodicity L> 6 nm the Zr (0002) peak is shifted to higher angles and Nb (110) peak is shifted to lower angles.

Keywords: Zr/Nb multilayers, ion irradiation, strain, XRD, SIMS

1. INTRODUCTION

Materials under extreme environments have received significant attention recently in the context of next-generation energy, defense, and transportation technologies. These applications require materials to perform at ‘‘extremes’’ of stress, temperature, irradiation dose, and corrosive environments [1]. The next-generation of nuclear power reactors require structural materials capable of withstanding elevated temperatures and radiation fluxes in highly corrosive environments for long periods of time without failure [1,2].

For that reason, a deeper understanding of materials behavior in extreme environments is essential to mitigate all radiation-induced defects improving the reliability, lifetime, and integrity of structural materials in advanced reactors. Materials containing a high concentration of interfaces promise to offer high resistance to radiation damage accumulation [3]. Enhanced radiation performance is due to grain boundaries and interfaces between incoherent nanoscale metallic multilayers (NMMs) that act as effective sinks for defect recombination at intersections between misfit dislocations [4].

The majority of previous studies focused on fcc/bcc multilayer systems such as Cu/Nb [5], Ag/V [6], Cu/W [7], Cu/Fe [8], and Ni/Fe [9] because the large lattice parameter mismatch of fcc/bcc interfaces enhances defect storage capability of multilayers [10]. Unfortunately, when high neutron-induced radioactivity is considered, only a few fcc metals could be used in nuclear reactors [10].

Recently, hcp-based NMMs started to attract some attention and cases of hcp-based NMMs are: Mg/Nb [11], Zr/Nb [12,13], Co/Mo [14], Cu/Zr [15], etc. Most of the studies on hcp-based NMMs focused on the structure strength relationship of pristine NMMs, while no relevant investigations were performed to assess their behavior after ion irradiation. Only a few numbers of studies were conducted to assess the structural evolution of interfaces subjected to heavy ion irradiation [16]. Callisti et al. [16] investigated the structural stability and mechanical properties of sputter-deposited Zr/Nb nanoscale multilayers subjected to Si-ion irradiation in relation to the individual layer thickness. It was shown that the interface density distribution played a major role in the nature and amount of accumulated radiation damage. Our study focuses on the strain evolution of Zr/Nb NMMs with different periodicities (L) due to different heavy ions (C, Si, Cu) irradiation.

2. MATERIALS AND METHODS

Magnetron sputtering was employed to fabricate Zr/Nb nanoscale metallic multilayers (NMMs). High-purity Zr and Nb targets were used to deposit NMMs with different periodicity (L) onto a single-crystal (111) Si substrate (L=6nm (sample 03), L=27 nm (sample 05), L=60nm (sample 06), L=96 nm (sample 07)). Some samples of the as-deposited multilayers were irradiated by Si^+ ions with an energy of 1.8 MeV and with two fluences (4.0×10^{15} Si^+/cm^2 (LF) and 1.0×10^{16} Si^+/cm^2 (HF)), others were irradiated by C^+ ions with an energy of 1.4 MeV and with low fluence (LF) ($1x10^{16}$ C^+/cm^2) and to high fluence (HF) ($5x10^{16}$ C^+/cm^2) and finally some samples were irradiated by Cu+ with an energy of 2.25 MeV and with low fluence ($1.5x10^{15}$ Cu^+/cm^2) (LF) and high fluence ($4x10^{15}$ Cu^+/cm^2) (HF). Here we report on the ion beam induced modifications of periodic Zr/Nb multilayers (NMMs) and their analysis using combined X-ray diffraction, and secondary ion mass spectroscopy (SIMS) techniques. After ion irradiation, we have found dilatation of the Nb layers (positive out-of-plane strain for L= 6, and 27 nm) and compression of Zr layers. On the other hand, for L> 27 nm, a compressive strain in the multilayers was detected. SIMS profiles of ion irradiated materials have been obtained to understand the observed effects.

3. RESULTS AND DISCUSSION

3.1. Ion distribution

The as-implanted C, and Si concentration depth profiles measured by SIMS are in agreement with Stopping Range of Ions in Matter code (SRIM) calculations (**Figure 1**). The agreement between experimental and simulated ion profiles also suggests that no long-range diffusion leading to the redistribution or escape of the implanted C, Si occurred. The second smaller peaks of C ions close to substrate (**Figures 1a, c**) are most probably due to some contamination during sputtering deposition (they do not appear on Si irradiation profiles (**Figures 1b, d**)). All experimental SIMS ion profiles show oscillations in concentration following Zr and Nb layers. These oscillations are more pronounced in the samples 05 having higher periodicity (L=27 nm - **Figures 1c, d**). From **Figure 1e**, where the C, Zr and Nb SIMS profiles are plotted together, it can be noticed that the Nb layers trap more C^+ ions than the Zr ones. This is also observed for Si^+ ions, but the amplitude of the oscillations is not so pronounced (**Figure 1d**). These oscillations are also present in SRIM profiles (**Figures 1a-d**). The difference in the trapping power of Nb and Zr is most probably due to higher Nb density (8.57 g/cm^3) over Zr (6.52 g/cm^3) and lower atomic packing factor (68 %) for bcc Nb lattice in comparison with 74 % for hcp Zr lattice. It means that there is more free void space (32 %) in bcc unit cell than in hcp unit cell (26 %). Furthermore, the ratio between the trapped ion concentration is more significant at the maximum projected range (R_p ~ 1200 nm) in **Figures 1c, e**.

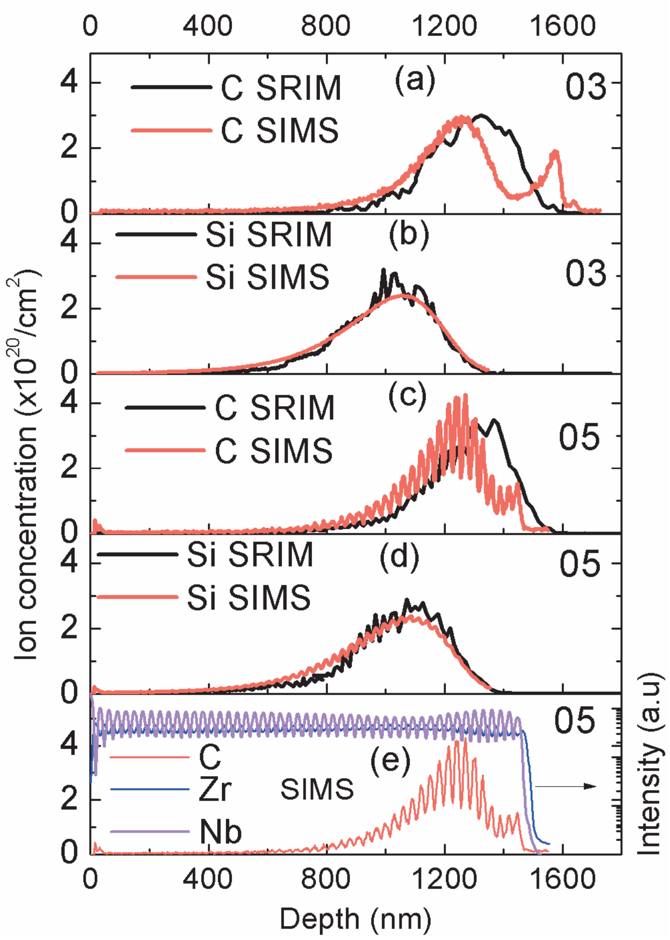

Figure 1 SIMS (red line) and SRIM (black line) profiles for C^+ and Si^+ ion irradiated samples: (a,b) - sample 03 (periodicity 6 nm), (c,d) - sample 05 (periodicity 27 nm), (e) SIMS profiles of C, Zr and Nb in the C^+ irradiatied multilayer with periodicity 27 nm (sample 05).

3.2. Microstructural evolution of irradiated Zr/Nb multilayers

Figure 2 shows the X-ray diffraction curves of four Zr/Nb NMMs with different periodicities (L) before and after irradiation. The diffraction patterns for the as-deposited NMMs with L>6nm (samples 05, 06, 07) appear with two peaks at Bragg angles θ_B = 35.66° and θ_B = 38.37°, representing Zr (0002) and Nb (110) crystal planes, respectively [12]. In the case of the lowest periodicity (L=6 nm, sample 03) the main Bragg peaks disappear and satellite peaks become even more prominent because of the increased degree of interfacial coherency between the layers. (for further details see Refs. [12,16]). After ion irradiation, all XRD peaks shift to higher angles except for L=6 nm, and L=27 nm, where the (110) Nb peak shifts to lower angles. This peak shift is characteristic of the lattice strain in the direction normal to the sample surface. Dilatation of the crystal lattice introduces shifts towards $\theta < \theta_B$ (to the left). Conversely, compression of the crystal lattice introduces shifts towards $\theta > \theta_B$ (to the right).

Both the lattice parameters of the as-deposited Zr and Nb layers ($d_{\text{as-dep layer}}$) and of the implanted layer ($d_{\text{impl layer}}$) follow Bragg's law, and so we can calculate strain from the difference of the as deposited Bragg angle ($\theta_{B,\text{ as-dep}}$) and the corresponding Bragg angle of irradiated samples with shift $\Delta\theta$ ($\theta_{B,\text{ as dep}} + \Delta\theta$). The out-of-plane (normal) strain ε is expressed by equation:

$$\varepsilon = \frac{d_{\text{impl layer}} - d_{\text{as-dep layer}}}{d_{\text{as-dep layer}}} = \frac{\sin(\theta B,\text{as-dep})}{\sin(\theta B,\text{as-dep}+\Delta\theta)} - 1 \qquad (1)$$

The results of the calculations are summarized in **Table 1**. For L=27 nm (sample 05) the shift of the peaks to the lower angle is corresponding to an out-of-plane lattice compression. The magnitude of out-of-plane strain is enhanced in multilayers with increasing of the ion fluence and reaches the largest value with Cu irradiation (3 % - blue curve in **Figure 2b** - sample 05, first Nb column in **Table 1**). On the other hand, Zr undergoes compression increasing with tensile strain in Nb layers. The highest value of -1.3 % out-of-plane lattice compression is reached with copper irradiation and high fluence (first Zr column in **Table 1**).

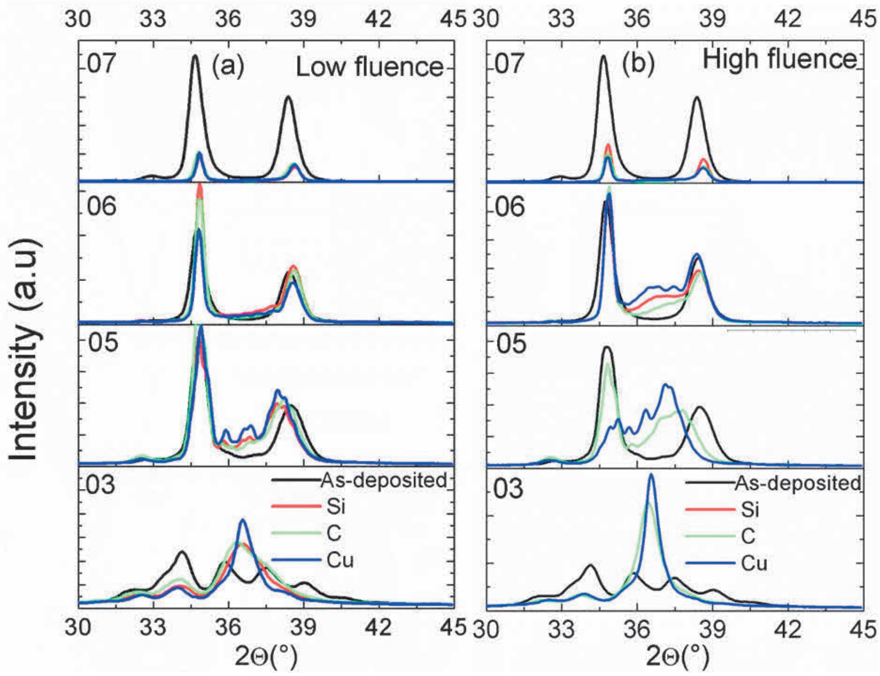

Figure 2 XRD patterns for Zr/Nb nanoscale metallic multilayers with different periodicities (sample 03 - L=6 nm, sample 05 - L=27 nm, sample 06 - L=60 nm, sample 07 - L=96 nm) before and after C, Si and Cu irradiation with (a) low fluence, (b) high fluence.

Table 1 Out-of-plane (normal) strain after irradiation

Out-of-plane strain (%)	05		06		07	
	Nb	**Zr**	**Nb**	**Zr**	**Nb**	**Zr**
C (LF)	+0.8	-0.02	-0.4	-0.2	-0.4	-0.4
Si (LF)	+0.8	-0.07	-0.4	-0.2	-0.58	-0.4
Cu (LF)	+1.3	-0.2	-0.3	-0.2	-0.58	-0.3
C (HF)	+2.1	-0.1	-0.2	-0.4	-0.6	-0.7
Si (HF)	-	-	0	-0.4	-0.6	-0.7
Cu (HF)	+3	-1.3	0.2	-0.4	-0.6	-0.7

In the case of Zr/Nb multilayers with the lowest periodicity (L=6nm - sample 03) the Zr and Nb peaks overlap with each other due to the superlattice effect in diffraction. The diffraction patterns are thus more complex. The corresponding strains were not calculated, but they can be qualitatively estimated. Only one important peak is visible after irradiation (located at 36.53°), which is sharper for Cu^+ ion irradiation with high fluence (**Figure 2b**, sample 03). In comparison with the sample 05 (L = 27 nm) the shift of the peaks follows the same trend (Nb shifts to the left, and Zr to the right). This means that Nb layers are in tension, while Zr layers are in compression. As the shift of the peaks is more significant for the sample 03, the strain should be more important than in the 05 sample (L=27), i.e. higher than +3 % out-of-plane lattice expansion in Nb and more negative than -1.3 % lattice compression in Zr layers.

For L> 27 nm, after all ion implantations, all XRD peaks shift to higher angles, corresponding to an out-of-plane lattice compression. The magnitude of the out-of-plane strain is enhanced in multilayers with increasing layer thickness and reaches the largest value for Cu^+ irradiation with high fluence. In general, factors such as isolated C, Si and Cu atoms, self-interstitials, vacancies, interstitial loops, vacancy clusters and the geometric constraint of the metal layers from the rigid Si substrate are the major contributions to lattice distortions. During room temperature implantation, isolated interstitials prefer to migrate to interfaces (particularly when the interface spacing is a few nanometers L=6 nm, and 27 nm) or to form interstitial loops (for thicker layers, L>27 nm). Hence the overall concentration of interstitials induces a compressive or tensile stress. This strain is more pronounced in Nb layers. This can be explained by higher ion concentration trapped in Nb layers (**Figure 1**).

4. CONCLUSIONS

We examined the effects of radiation damage on the structural properties of Zr/Nb nanoscale metallic multilayers with different periodicities. For the multilayer with a periodicity of 6 nm, and 27 nm, Si, C and Cu-ion irradiation led to a tensile strain of Nb layers and compressive strain of Zr layers. This strain evolution is more significant for Cu irradiation with high fluence. On the other hand, for L> 27 nm, both Zr and Nb layers exhibit compressive out-of-plane strain. The strain (tensile or compressive) is more pronounced in Nb layers due to higher trapping power of Nb with respect to Zr, which was measured by secondary ion mass spectrometry.

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