ION IRRADIATION TOLERANCE OF AlN/TiN MULTILAYERED NANOCOMPOSITES

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ABSTRACT

This paper reports on ion irradiation tolerance of AlN/TiN multilayered system, which is known to exhibit high mechanical strength and the components are highly immiscible. Structures consisting of 10-50 alternate AlN and TiN layers (individual layer thickness ∼ 5-32 nm) were deposited by reactive sputtering on Si wafers. Total thickness of deposited structures was ∼ 250-270 nm. Irradiations were performed with a variety of ions and doses: 30 keV He (1-4x10^{17} ions/cm^{2}), 180-200 keV Ar (1-8x10^{16} ions/cm^{2}), 400 keV Xe (1-4x10^{16} ions/cm^{2}) and 166 MeV Xe (5x10^{14} ions/cm^{2}). The keV energy was selected to give the ion projected range around mid-depth of the structures, while in case of swift Xe ions the projected range was deep into the Si substrate. The applied wide range of experimental parameters enabled to distinguish between the contributions of the dominant processes that affect the structure. The multilayered structures were preserved up to relatively high irradiation doses, depending on the ion mass. Atomic collision cascades induce a low level of inter-layer mixing, which is on the predicted level of ballistic mixing, while electronic excitations contribute only to lateral grain growth within the isolated individual layers. Large amounts of implanted He accumulate at the multiple interfaces between the layers, inducing blistering at the highest doses.

KEYWORDS

Radiation tolerance, AlN/TiN multilayers, ion irradiation, TEM analysis

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1. INTRODUCTION

High strength nano-scaled multilayers of immiscible metals or ceramics have emerged as prosperous radiation tolerant materials. Multiple interfaces enhance mechanical strength of such systems, which suppresses slip and swelling of the material, and enable fast diffusion paths for accumulation and release of radiation induced point defects [1,2]. On the other hand, mutual immiscibility of components restraints inter-layer mixing, which can be significant at high irradiation doses, and can lead to degradation of the multilayered structure. Application of ion accelerators is suitable to study radiation tolerance of materials, as many parameters can be adjusted to simulate a radiation environment. Using this technique, radiation tolerance was demonstrated on a number of immiscible metallic multilayered systems, such as Cu/Nb, W/Ni, Cu/W, Mo/Cu, Ta/Ti and Ag/Ni [1-7]. Recent developments report on the synthesis of 4 mm thick radiation tolerant multilayered Cu/Nb nanocomposite [8]. Another class of potentially interesting materials are multilayered ceramics, such as AlN/TiN [9], CrN/AlTiN [10] (Ti-Al)N/Ti$_2$AlN$_x$ [11] or metal-ceramic combinations, as WZrO$_2$ [12].

This paper reports a study of ion irradiation stability of AlN/TiN multilayered nanocomposites, for varied individual layer thicknesses and upon varied irradiation conditions. Wide ranges of experimental parameters were used in order to clarify between the main processes involved in ion beam modification of this material. For example, irradiation with light (He) ions in keV range and swift heavy (Xe) ions in the MeV range simulates a nuclear fission fragment environment. Most of the results obtained for particular experimental sets were published earlier [9,13-16], while here they are referred to in a summarized form, including some additional findings and conclusion. The AlN/TiN system is known to exhibit high hardness and strength, good corrosion resistance, high temperature stability, up to 1000°C, and the constituents are immiscible, with a high positive reaction enthalpy [17] Apart from this, ceramic materials in general are resistant to radiation induced amorphization and swelling [18]. Such properties make AlN/TiN multilayered system a promising candidate for the development of radiation tolerant materials.

2. EXPERIMENTAL DETAILS

Multilayered AlN/TiN structures were deposited by reactive sputtering of 99.9% pure Al and Ti targets, using 1.5 keV Ar ions, with a controlled introduction of high purity nitrogen into the deposition chamber. Three different sets of samples were prepared, with 5, 15 and 25 AlN/TiN bilayers, individual layer thickness ranging from 5-32 nm. The substrates used were (100) Si wafers, cleaned by standard HF etching and a dip in deionized water before mounting in the chamber, and by back-sputtering prior to thin film deposition. The first layer deposited on the substrate was TiN, and the outermost AlN, the Si-substrates being held at room temperature during deposition. The thickness of the deposited structures was measured with a profilometer and confirmed by TEM. Ion irradiations of samples were done at normal incidence, with 30 keV $^4$He$^+$, 180 and 200 keV $^{40}$Ar$^{1+}$, 400 keV $^{132}$Xe$^{1+}$, and 166 MeV $^{132}$Xe$^{27+}$ ions. All implantations were performed at room temperature, with a uniformly scanned beam over a target area of 2x2 cm$^2$, or 1x1 cm$^2$ in case of MeV energy Xe. Evaluations of the projected ion range, distribution of recoils, energy loss and displacements per atom (dpa) were done using the SRIM code [19]. Table I. lists a description of the sets of samples prepared, number of layers, individual layer thickness, total structure thickness, and ion irradiations performed on each set. Table II. gives a list of ions used for irradiation, the ion energy, projected range, irradiation dose, and evaluated values of dpa for each case.

Structural and compositional characterizations of the samples were done by transmission electron microscopy (TEM), Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), and time of flight elastic recoil detection analysis (TOF-ERDA). TEM contrast imaging and electron diffraction analyses were done on Philips EM 400T and CM 200 microscopes, operated at 120 and 200 kV, respectively. The samples were prepared for cross-sectional analysis by ion beam thinning.
For RBS characterization 1 and 1.5 MeV He$^+$ ion beams were used, the spectra being collected with two detectors (149° and 172° scattering angles), at normal incidence and 45° tilt to the sample surface. XPS analyses were carried out on the PHI-TFA XPS spectrometer produced by Physical Electronics Inc. Ion sputtering was performed with a 3 keV Ar$^+$ ion beam scanned over an area of 4 x 4 mm$^2$. The analyzed area was 0.4 mm in diameter. XPS spectra were excited by X-ray radiation from an Al-standard source. During depth profiling the samples were rotated to improve the depth resolution. TOF-ERDA analyses were done with a 20 MeV iodine beam at incidence angle of 20° to the target surface, and the spectrometer was set at an angle of 37.5° to the beam line. Nano-hardness of the samples was measured by the Vicker's method.

### Table I. List of prepared samples, giving the layer thickness and ion irradiations performed

<table>
<thead>
<tr>
<th>Multilayered structure</th>
<th>Number of layers</th>
<th>AlN thickness</th>
<th>TiN thickness</th>
<th>Total thickness</th>
<th>Irradiations performed</th>
</tr>
</thead>
<tbody>
<tr>
<td>(AlN/TiN)x5</td>
<td>10</td>
<td>~22.0 nm</td>
<td>~32.0 nm</td>
<td>~270 nm</td>
<td>200 keV Ar 166 MeV Xe</td>
</tr>
<tr>
<td>(AlN/TiN)x15</td>
<td>30</td>
<td>~8.0 nm</td>
<td>~9.3 nm</td>
<td>~260 nm</td>
<td>30 keV He 180 keV Ar 400 keV Xe 166 MeV Xe</td>
</tr>
<tr>
<td>(AlN/TiN)x25</td>
<td>50</td>
<td>~5.0 nm</td>
<td>~5.0 nm</td>
<td>~250 nm</td>
<td>180 keV Ar 400 keV Xe 166 MeV Xe</td>
</tr>
</tbody>
</table>

### Table II. Ion species, energy, projected range, irradiation dose and evaluated dpa

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy</th>
<th>$R_p \pm \Delta R_p$ (nm)</th>
<th>Dose (cm$^{-2}$)</th>
<th>AlN (dpa)$_{max}$</th>
<th>TiN (dpa)$_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4$He$^{1+}$</td>
<td>30 keV</td>
<td>155 ± 46 nm</td>
<td>(1-4) x 10$^{17}$</td>
<td>4-18</td>
<td>6-24</td>
</tr>
<tr>
<td>$^4$Ar$^{1+}$</td>
<td>180 keV</td>
<td>109 ± 34 nm</td>
<td>(1-8) x 10$^{16}$</td>
<td>11-92</td>
<td>16-127</td>
</tr>
<tr>
<td>$^4$Ar$^{1+}$</td>
<td>200 keV</td>
<td>127 ± 39 nm</td>
<td>(1-4) x 10$^{16}$</td>
<td>11-42</td>
<td>16-63</td>
</tr>
<tr>
<td>$^{129}$Xe$^{3+}$</td>
<td>400 keV</td>
<td>93 ± 25 nm</td>
<td>(1-4) x 10$^{16}$</td>
<td>40-159</td>
<td>55-218</td>
</tr>
<tr>
<td>$^{132}$Xe$^{3+}$</td>
<td>166 MeV</td>
<td>19.6 ± 0.6 μm</td>
<td>5x10$^{14}$</td>
<td>0.03</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### 3. RESULTS AND DISCUSSION

In (AlN/TiN)x5 set of samples irradiated with 200 keV Ar and 166 MeV Xe no significant inter-layer mixing or redistribution of elements were detected [9,14]. Bright field cross-sectional TEM images taken from as-deposited sample and samples implanted with 4x10$^{16}$ Ar/cm$^2$ and 5x10$^{14}$ Xe/cm$^2$ are shown in Figure 1. Bright contrast corresponds to AlN and dark to TiN, showing well separated layers with flat and sharp interfaces. The as-deposited layers grow in form of very fine columnar nanocrystalline grains (~10 nm), stretching across the entire depth of individual layers. Argon irradiation caused an increased width of the columnar grains (up to ~20 nm) within the top 3 AlN/TiN bilayers, approximately to a depth that coincides with the projected Ar range. Individual layers preserve clear separation and interface planarity. Sample irradiated with swift heavy Xe ions exhibits an increased width of the crystalline columns throughout the multilayered AlN/TiN structure (roughly up to ~20 nm as in Ar-implanted sample), and again the surface and interface planarity is preserved. However, elemental depth profiling indicated a low level (up to 5%) migration of Ti into AlN layers within the affected zone upon Ar...
irradiation, and absence of any elemental redistribution upon swift Xe irradiation. Nano-hardness increased with Ar implantation, suggesting an enhanced strength of the structure. Analysis of the results implies that the detected intermixing is due to atomic collision cascades generated by high dose Ar implantation, while thermal spikes generated via electronic excitations contribute only to lateral grain growth within isolated individual layers [14].

Figure 1. Cross-sectional TEM analysis of (AlN/TiN)x5 samples: as-deposited and irradiated with 200 keV Ar to $4 \times 10^{16}$ ions/cm$^2$, and 166 MeV Xe to $5 \times 10^{14}$ ions/cm$^2$.

In case of thinner individual layers (AlN/TiN)x15 and two times higher Ar irradiation dose (180 keV $8 \times 10^{16}$ ions/cm$^2$), the multilayered structure suffered a considerable intermixing [15]. For this very high irradiation dose, which introduces up to ~8 at.% of Ar species in the structure, the original TiN layers appear to become thicker and the AlN layers become thinner. The intermixing occurs due to a high contribution of collision cascades, enhanced by the process of TiN grain growth, which is influenced by the generated thermal spikes. In this mixing process the growing TiN grains consume the adjacent AlN layers, transforming partly to (TiAl)N phase. However, despite of intermixing and grain growth, a multilayered structure with a relatively flat surface and interfaces remains preserved. An example of cross-sectional TEM analysis of such structures, irradiated with 180 keV Ar and 400 keV Xe, both to the same dose of $1 \times 10^{16}$ ions/cm$^2$, is shown in Figure 2. It can be seen that Ar implantation to this dose does not affect the structure significantly, while implantation with heavy Xe ions yields a similar effect that was observed for a much higher Ar dose (180 keV Ar, $8 \times 10^{16}$ ions/cm$^2$) [15].

Figure 2. Cross-sectional TEM analysis of (AlN/TiN)x15 samples: irradiated with 180 keV Ar to $1 \times 10^{16}$ ions/cm$^2$, and 400 keV Xe to $1 \times 10^{16}$ ions/cm$^2$. 
Interesting results were obtained upon irradiating (AlN/TiN)x15 structures with 30 keV He, to very high doses of 1-4x10^{17} ions/cm^2, which introduce 10-40 at.% of helium within the structure [16]. An example of TEM analysis is shown in Figure 3. Implanted He segregates in form of bubbles at the AlN/TiN interfaces, and causes blistering, but does not induce any detectable inter-layer mixing, even for these very high irradiation doses. However, a closer analysis shows lateral grain growth within isolated layers in the affected region (up to the He ion range), suggesting the influence of thermal spikes. Also shown in the figure is the same structure irradiated with 166 MeV Xe to 5x10^{14} ions/cm^2, where again a lateral grain growth is observed, and no inter-layer mixing. Depth profiling of these samples showed that the He content coincides with the implanted doses of 1x10^{17} and 2x10^{17} ions/cm^2, while for the highest dose of 4x10^{17} ions/cm^2, the gas is partially released from this highly destructed structure [16].

Figure 3. Cross-sectional TEM analysis of (AlN/TiN)x15 samples: irradiated with 30 keV He to 2x10^{16} and 4x10^{16} ions/cm^2, and 166 MeV Xe to 5x10^{14} ions/cm^2.

Thinner layered (AlN/TiN)x25 structure was found to be even more sensitive to 180 keV Ar and 400 keV Xe irradiation, as shown in Figure 4. Already for 2x10^{16} Ar/cm^2 the structure becomes considerably intermixed, and for 1x10^{16} Xe/cm^2 it is fully mixed. This analysis illustrates the role of individual layer thickness on radiation resistance of this system upon medium and heavy ion irradiation.

Figure 4. Cross-sectional TEM analysis of (AlN/TiN)x25 samples: as-deposited, irradiated with 180 keV Ar to 2x10^{16} ions/cm^2, and 400 keV Xe to 1x10^{16} ions/cm^2.
In order to compare the experimental data with theoretical predictions, full cascade SRIM calculations were performed for each of the structure and the ions used for irradiation. Figure 5 (a) plots the evaluated dpa values for selected experimental parameters. Compared to experimental findings, the highest intermixing or destruction of the structures occurred for the cases of highest dpa. As elaborated in detail previously [9,14], the detected amount of ion beam mixing in the investigated AlN/TiN system is at the low level of ballistic mixing due to atomic collision cascades. SRIM evaluations of the final recoil distribution after irradiation with a particular ion species, energy and dose give a good estimate of inter-layer mixing due to ballistic effects. An example of evaluated final depth distribution of recoiled Al and Ti atoms in (AlN/TiN)x15 structure after irradiation with 400 keV Xe to 1x10¹⁶ ions/cm² is given in Figure 5(b). It predicts that for this set of parameters the layers suffer 10-15 % mixing already in the initial atomic collision stage, and this is in reasonable agreement with the experimental findings for this case. Similar evaluations show that thicker individual AlN and TiN layers undergo a much lower amount of knocked-on atomic species that cross over the interfaces, and accordingly, the observed inter-layer mixing is much lower in that case.

![Figure 5. SRIM evaluations: (a) displacements per atom for different sets of parameters; (b) final distribution of Al and Ti recoils for Xe irradiation of (AlN/TiN)x15.](image)

4. CONCLUSIONS

The investigated AlN/TiN multilayered structures exhibit a good radiation tolerance up to relatively high Ar doses, which introduce 4-8 at% of foreign species. They suffer a low level of mixing, due to ballistic processes in collision cascades, while chemical driving forces maintain the low level of mixing. Thinner layers suffer more crossed over knocked-on atomic species, resulting in higher intermixing. Heavier ions (Xe) are much more efficient than light ions (He) of similar projected range. Generated thermal spikes contribute only to lateral grain growth and not to interface mixing. Mechanical strength increases with initial intermixing of up to ~5 at.% (concentration of implanted inert gas species is up to ~ 4 at%) but starts to deteriorate at around 15-20 at% mixing (implanted species reach above 8 at%). In the mixing process TiN grains grow in size, consuming the adjacent AlN layers and transforming to Al deficient (TiAl)N phase of the same crystalline structure as TiN. Degradation of the multilayered structure occurs when AlN layers are fully consumed. Light He ions give a negligible contribution to inter-layer mixing, but at high implanted concentration of 20-40 at% agglomerate and cause blistering and splitting at AlN/TiN interfaces. Further developments of this system should consider structures with much thinner...
TiN and thicker AlN layers, where a possible transformation of mixed (TiAl)N phase form Al deficient to Ti deficient could yield a higher ion irradiation tolerance.

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