High Ion Irradiation Tolerance of Multilayered AlN/TiN Nanocomposites

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Abstract. Structural stability of nanocrystalline (AlN/TiN)x5 multilayers upon argon ion irradiation was investigated. The layers were deposited on (100) Si wafers, to a total thickness of ~270 nm. Argon ions were implanted at 200 keV, to the fluences from $5x10^{15}$ to $4x10^{16}$ ions/cm^2. For comparison, metallic (Al/Ti)x5 multilayers were also deposited to similar thickness and irradiated with argon ions under the same conditions. It was found that (AlN/TiN)x5 multilayers exhibit a remarkable ion irradiation stability. Ion irradiation induces a slight increase of the mean grain size in individual layers, and small local density changes. Apart from this, no distinct intermixing of the layers was observed, the interfaces remaining flat and sharp. On the other hand, a pronounced interface mixing was observed in (Al/Ti)x5 multilayers, and formation of intermetallic phases for the highest irradiation fluence. The results suggest that immiscible metal-nitride multilayers should attract further attention as radiation tolerant materials.

1. Introduction

Multilayers of metals and metal-nitrides, with individual layer thickness from a few to a few tens of nanometers, are interesting due to their unique properties. As hard coating materials they offer numerous advantages over single component coatings, such as much higher hardness and strength due to a large number of interfaces, possibilities to form super lattices, graded composition, more dense and less porous structures. [1-4] High strength nanolayered structures are also interesting as radiation protective materials, because of a large number of interfaces that act as sinks for radiation induced damage. [5] With respect to ion irradiation stability, so far mainly multilayers of immiscible metals were investigated, such as Cu/Nb, W/Ni, Cu/W or Mo/Cu. [5-9] It was demonstrated that Cu/Nb multilayers, which are stable up to 800^{o}C, are also stable upon high fluence He^+ ion irradiation, and can be used for He storage. [5,6] For immiscible W/Ni system it was shown that the multilayered structure remains intact after irradiation with 120 MeV Au^{9+} ions, although crystallization was observed for higher fluences.[7] From compound systems, there was a report on ion irradiation stability of crystalline TiN/amorphous B-C-N multilayers, [10] and on enhanced radiation tolerance in nanocrystalline $MgGa_2O_4$. [11]

This paper reports on the stability of AlN/TiN multilayers upon Ar^+ ion irradiation, as compared to the stability of Al/Ti multilayers irradiated under the same conditions. The AlN/TiN system exhibits a high temperature stability, up to 1000^{o}C, and the constituents are immiscible. [4,12,13] These multilayers also exhibit a high hardness and strength, providing the same performance at much lower thicknesses compared to single component layers. At a very low thickness of up to ~2 nm, AlN and TiN and can form superlattices. In case of Al/Ti multilayers, the constituents are miscible. They can form solid solutions or intermetallic compounds, depending on temperature or ion beam treatments. Titanium-aluminides, based on the intermetallic γ-TiAl phase, are promising materials for high temperature wear and corrosion protection in mechanical applications. This phase can be synthesized from Al/Ti multilayers, in a solid state reaction at 600^{o}C. [14,15]

2. Experimental Details

The (AlN/TiN)x5 and (Al/Ti)x5 multilayers were deposited in a commercial Balzers Sputtron II system, using 1.5 keV argon ions and 99.9% pure Al or Ti targets. The base pressure in the chamber was around $1x10^{-6}$ mbar, and the Ar partial pressure during deposition $1x10^{-3}$ mbar. Reactive sputtering was used for preparation of metal-nitride layers, by introducing high purity nitrogen into the deposition chamber, at a partial pressure of $3x10^{-4}$ mbar. Multilayered structures were deposited in a single vacuum run, at ~0.12 nm/s for nitrides and ~0.17 nm/s for pure metals, without heating of the substrates. 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 backsputtering prior to thin film deposition. The deposited structures consisted of alternate AlN and TiN layers (Al and Ti in case of pure metals), five of each around 27 nm, giving a total thickness of ~270 nm. The first layer deposited on the substrate was TiN (Ti), and the outermost AlN (Al). The thickness of the deposited structures was measured with a profilometer and confirmed by TEM.

Ion irradiation of samples was done in a 500 kV ion implanter, using a 200 keV Ar^+ ion beam, at normal incidence. The beam was uniformly scanned over a target area of 2.5x2.5 cm^2 and the implanted fluences were in the rage from $5x10^{15}$ to $4x10^{16}$ ions/cm^2. Implantations were performed at room temperature, the beam current being maintained at ~1 $\mu A/cm^2$ to avoid beam-heating of the samples. The projected range of the implanted argon species, calculated with TRIM, [16] is around mid-depth of the multilayered structures.

Structural and compositional characterizations of the samples were done by Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). For RBS analysis a 1.5 MeV He^+ ion beam, generated by a 2 MV Tandetron accelerator from HV Europe was used. Random RBS spectra at normal incidence to the sample surface were collected. The experimental data were analyzed with the NDF code [17,18]. XPS photoelectron spectroscopy 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. For XRD analysis Cu K_α X-ray diffraction patterns were collected by Bruker D8 Advance Diffractometer. TEM imaging was done on a Philips EM 400T microscope at 120 kV, the samples being prepared for cross-sectional analysis by ion beam thinning.

3. Results and Discussion

Experimental RBS spectra, taken from an as-deposited (AlN/TiN)x5/Si sample, and a sample implanted to $2x10^{16}$ ions/cm^2, are shown in Fig. 1. A relative shift is seen in the spectrum taken from the implanted sample, which is assigned to a change in the local density induced by implantation of argon, and a possible build up of oxides at the surface during ion irradiation. Also plotted are separated spectra from Al and N, deduced from the as-deposited sample. It is seen that the innermost Ti peak coincides with the first Al peak. Hence, the change in its intensity is due to a relative movement of these two peaks. Apart from a small shift, the extracted depth profiles showed no ion irradiation induced interface broadening. [19]

Elemental depth profiles obtained by XPS analysis of as-deposited (AlN/TiN)x5/Si sample and a sample implanted with argon to $4x10^{16}$ ions/cm^2, are shown in Fig. 2. Both depth profiles show well separated Al and Ti signals. The TiN layers are stoichiometric and the AlN

layers are nitrogen rich, as was also determined by RBS. A build up of surface oxide is registered in the implanted sample. Ion irradiation causes an increased concentration of Ti in the second and third AlN layer up to about 5 at% and consequently decreases the concentration of Al and N in the same region. This suggests that some migration of Ti atoms occurred only in these AlN layers, located in the region where the highest radiation damage is deposited by the impact ions. Apart from this, the AlN and TiN layers remain well separated after ion irradiation.

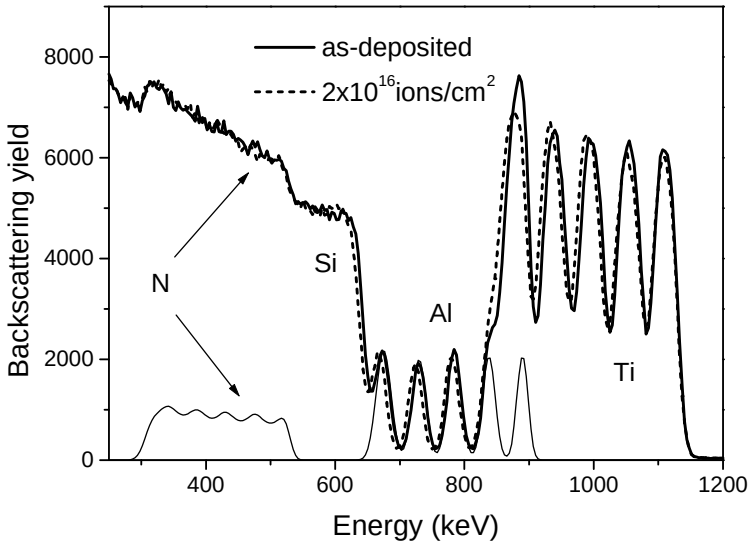

FIG. 1. Experimental RBS spectra from an as-deposited (AlN/TiN)x5/Si sample, and a sample implanted to $2x10^{16}$ ions/cm^2.

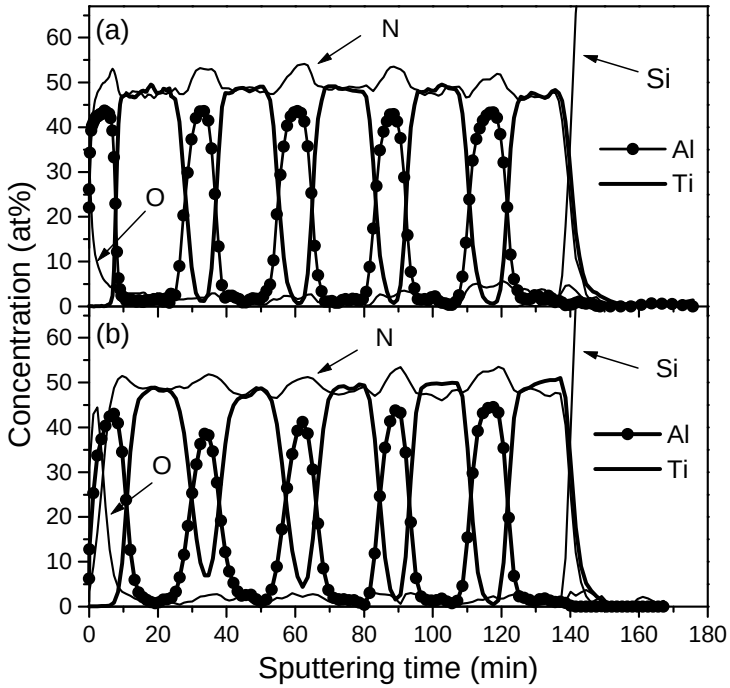

FIG. 2. XPS depth profiles of (AlN/TiN)x5/Si: (a) as-deposited sample; (b) sample implanted with argon to $4x10^{16}$ ions/cm^2.

Experimental RBS spectra taken from (Al/Ti)x5/Si samples, before and after ion irradiation with argon to $1x10^{16}$ and $4x10^{16}$ ions/cm^2, are shown in Fig. 3. It can be seen that ion irradiation induces lowering and broadening of Al and Ti peaks, indicating atomic mixing at the interfaces. For the highest irradiation fluence we see steps towards the interfaces in both Ti and Al signals, suggesting chemical interaction.

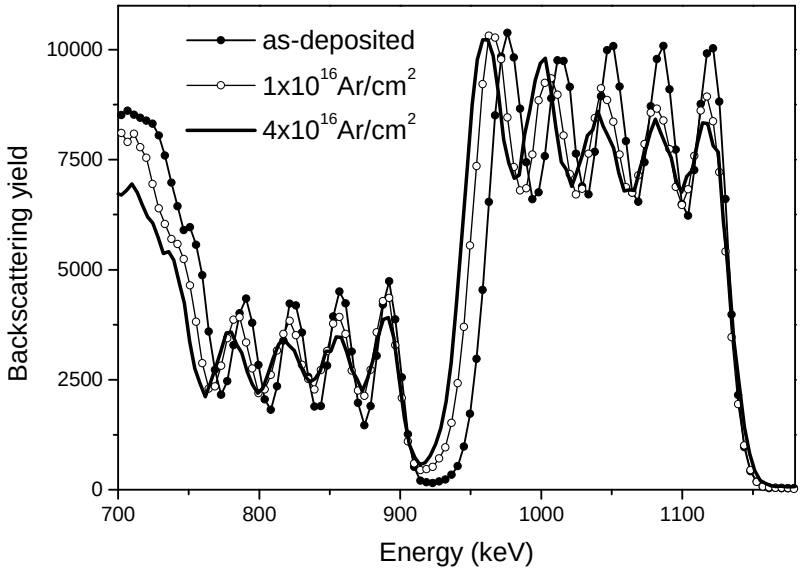

FIG. 3. Experimental RBS spectra from an as-deposited (Al/Ti)x5/Si sample, and samples implanted to $1x10^{16}$ ions/cm^2 and $4x10^{16}$ ions/cm^2.

Formation of a new phase in Al/Ti structures was confirmed by XRD analysis. Fig. 4. shows XRD spectra of as-deposited (Al/Ti)x5/Si sample (a) and sample implanted with argon to 4×10^{16} ions/cm^2 (b). It is seen that ion implantation to the highest fluence induces formation titanium reach $AlTi_3$ phase of titanium-aluminides.

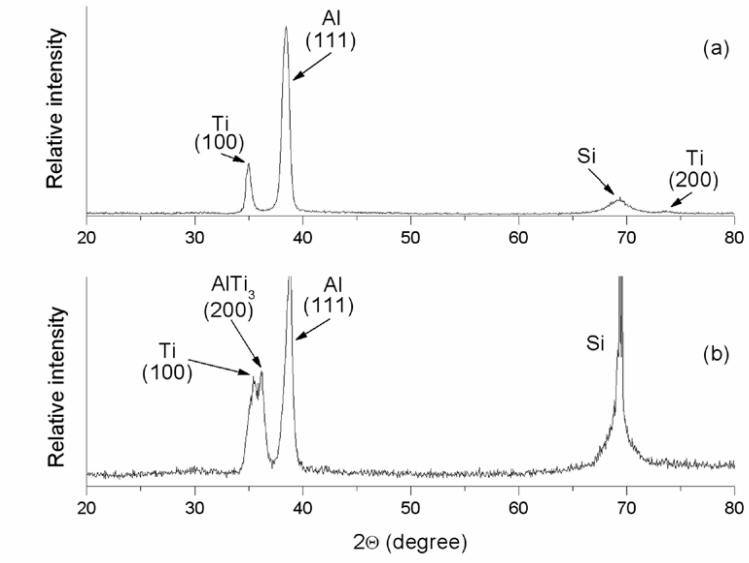

FIG. 4. XRD analysis of (Al/Ti)x5/Si samples: (a) as-deposited, and (b) sample implanted with argon to 4×10^{16} ions/cm^2.

The results of cross-sectional TEM analysis are shown in Figs. 5 & 6. Bright field image in (5a) was taken from as-deposited (AlN/TiN)x5/Si, and in (5b) after implantation of this structure with argon to $4x10^{16}$ ions/cm^2. Bright contrast corresponds to AlN layers and dark contrast corresponds to TiN. In both cases AlN and TiN layers are well separated, having a very fine nanocrystalline structure. Ion irradiation induces and enlargement of crystal grains in individual layers, from ~10 to ~20 nm. Also, some thickness increase is registered in the top three AlN/TiN bilayers, where the most damage is deposited and most of the argon ions are being stopped. This finding is in agreement with a local density change that was registered by RBS. Analysis of as-deposited (Ti/Al)x5/Si is shown in (6a), and of this structure implanted with argon to $4x10^{16}$ at/cm^2 in (6b). White contrast is from Al layers and dark contrast is from Ti. It can be seen here that initially well separated Al and Ti layers become thoroughly intermixed after ion implantation. The mean grain size in the layers increases from ~30 to ~80 nm, and the contrast becomes unified in the region where most intermixing occurred. It can be seen that in this case ion irradiation induces texturing, which results in the formation of lamellar columns, extending in length over a number of individual layers. However, the multilayered nature of the structure is preserved.

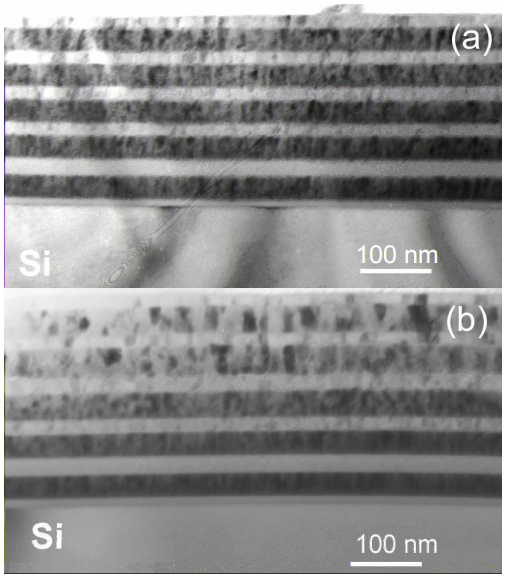

FIG. 5. Bright field cross-sectional TEM images of: (a) as-deposited (AlN/TiN)x5/Si; (b) (AlN/TiN)x5/Si implanted with argon to $4x10^{16}$ ions/cm^2.

Studies of ion beam mixing in immiscible metallic multilayered systems distinguish two competing processes: ballistic effects introduce both species into the other, while thermodynamic effects induce demixing. [8] For Cu/Nb multilayers irradiated with He^+ ions it was demonstrated [6] that the mixing rate is lower then predicted by the ballistic model. [20] In immiscible Cu/W multilayered system, irradiated with He^+ or Kr^+ ions, the mixing was saturated at a concentration of ~15% for both components into each other, due to chemical driving forces. [8] Thermal spikes [21] generated in Cu enhanced demixing during irradiation with heavy Kr^+ ions. Irradiation of Mo/Cu multilayers with Xe^+ ions induced a formation of Mo-Cu metallic glasses and metastable Cu-based alloys only within a narrow range around the interfaces. [9] Swift heavy ion irradiation of W/Ni multilayers, using 120 MeV Au^{9+} ions, induced crystallization in Ni layers and coarsening of the interfaces, but the layer separation was preserved. [7] The results presented here demonstrate a remarkable ion irradiation stability of nanocrystalline AlN/TiN multilayers. The applied argon ion fluences were

sufficient to induce a marked intermixing in normally soluble or chemically reactive materials, as compared here with the metallic Al/Ti system. In a previous publication we have shown that in the AlN/TiN system there is no interface broadening upon ion irradiation, while in the Al/Ti system we have found a linear increase of the interface variance for the lower ion fluences that do not induces chemical interaction. [19] In the AlN/TiN system ion irradiation induces a small change in the local density, and some enlargement of crystal grains in the region where the most damage energy is deposited by the impact ions. There is also a low level of Ti migration into the AlN layers in this region, probably be due to excess nitrogen in AlN layers, which can attract some of the knocked on Ti atoms. However, what is crucial for the stability of multilayered structures, the AlN and TiN layers are well separated and the interfaces remain sharp.

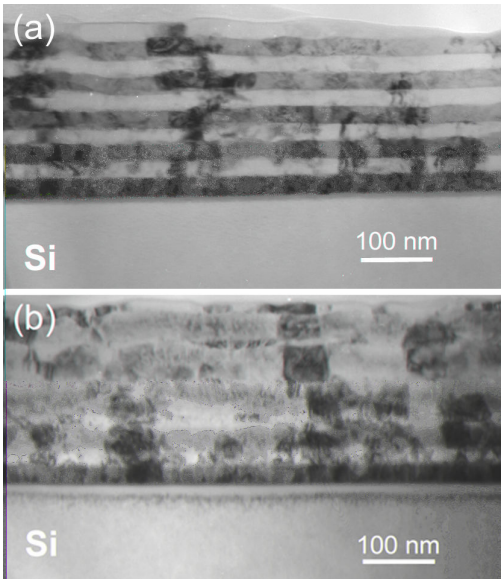

FIG. 6. Bright field cross-sectional TEM images of: (a) as-deposited (Al/Ti)x5/Si; (b) (Al/Ti)x5/Si implanted with argon to $4x10^{16}$ ions/cm^2.

4. Conclusions

The presented results demonstrate that AlN/TiN multilayered system exhibits a much higher stability when exposed to argon ion irradiation compared to the Al/Ti system. In Al/Ti multilayers we observe a progressed intermixing with increasing the ion fluence and intermetallic phase formation for the highest fluence. Ion irradiation induces an increase in the mean grain size, and growth of lamellar columns, extending in length over a number of individual layers. In AlN/TiN system no interface mixing is registered for any of the applied irradiation fluences. The layers preserve sharp interfaces and a very fine columnar polycrystalline structure. Different behaviour of the two systems is assigned to different chemical reactivity of the multilayer constituents and different cohesive energy of atomic species within individual layers. The results suggest that immiscible metal-nitride multilayers should attract further attention as radiation tolerant materials.

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