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NANOSTRUCTURED AlN/TiN FILMS GROWN BY REACTIVE SPUTTERING OR ION IMPLANTATION OF Al/Ti MULTILAYERS

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Abstract: *A comparative study of AlN/TiN multilayers, grown by reactive sputtering of AlN and TiN, and by implantation of nitrogen into metallic Al/Ti multilayers, is presented. The (AlN/TiN)x5 and (Al/Ti)x5 multilayers with a total thickness of ~270 nm were deposited on Si(100). The Al/Ti structures were implanted with 200 keV* N_2^+*, to* $1x10^{17}$ *and* $2x10^{17}$ *at/cm*^{2}*, and AlN/TiN were irradiated with argon ions. It was found that sputter deposited AlN/TiN multilayers are well separated, with sharp interfaces and a nanocrystalline structure, remaining stable after argon ion irradiation. Nitrogen implantation of Al/Ti induced a pronounced intermixing, resulting in a graded multilayered structure, with different content of Al, Ti and N. In all cases nano-hardness increased with ion implantation fluence.*

Keywords: *AlN/TiN multilayers, reactive sputtering, ion irradiation, graded composition, nanocrystalline structure, nano-hardness*

1. INTRODUCTION

Nano-scaled multilayered coatings of metals and metal-nitrides 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, denser 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 obstacles to slip and sinks for radiation induced defects [5,6]. Multilayers composed of AlN/TiN provide the same performance at much lower thickness compared to thick single layers such as TiN or (Al,Ti)N, and have microstructural stability up to 1000°C [7-9]. For very low thicknesses of individual layers (a few nm), these multilayers can form superlattices [8].

The use of ion beam processing in fabrication of thin film structures can be beneficial towards achieving better adhesion to the substrate, relaxing the interface stresses, increasing the film density and decreasing porosity. In this work we have studied the properties of TiN/AlN multilayers grown by reactive sputtering, and the changes induced upon irradiation with argon ions. We have also studied the formation of graded (AlTi)N multilayers by high fluence nitrogen ion implantation into Al/Ti multilayered structures.

2. EXPERIMENTAL DETAILS

Multilayered AlN/TiN and Al/Ti structures were deposited on Si(100) wafers, in a Balzers Sputtron II system, using 1.5 keV argon ions and 99.9% pure Al or Ti targets. The starting structures consisted of (AlN/TiN)x5 and (Al/Ti)x5, with a total thickness of ~270 nm. Depositions were done in a single vacuum run for each of the analyzed systems, switching from one target to the other. The base pressure in the chamber was around $1x10^{-6}$ mbar, and the argon partial pressure $1x10^{-3}$ mbar. For preparation of metal-nitride layers we used reactive sputtering, introducing high purity nitrogen in the vacuum chamber at a partial pressure of $3x10^{-4}$ mbar.

The (Al/Ti)x5/Si structures were implanted with 200 keV N_2^+ ions, to the fluences of $1x10^{17}$ and $2x10^{17}$ at/cm^2. The (AlN/TiN)x5/Si were irradiated with 200 keV Ar^+, to $5x10^{15}$ - $4x10^{16}$ ions/cm^2. All implantations were done at room temperature, with a beam current of ~ 1 μA/cm^2, to avoid beam heating of the samples The projected ion range in both cases was around mid-depth of the deposited structures, as calculated by TRIM [10].

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 [11]. Random RBS spectra at normal incidence to the sample surface were collected. The experimental data were analyzed with the NDF code [12]. 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. The step was 0.05^o and the time interval 10 s per step. 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.

Nano-hardness measurements were done by the Vicker's method, using a pyramidal indenter with the top angle of 136^o. The applied load was 5 mN, so the indenter penetrates to around mid-depth of the multilayered structures. Due to a high influence of the substrate, the measured values of nano-hardness should be considered as relative.

3. RESULTS AND DISCUSSION

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. 1. 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.

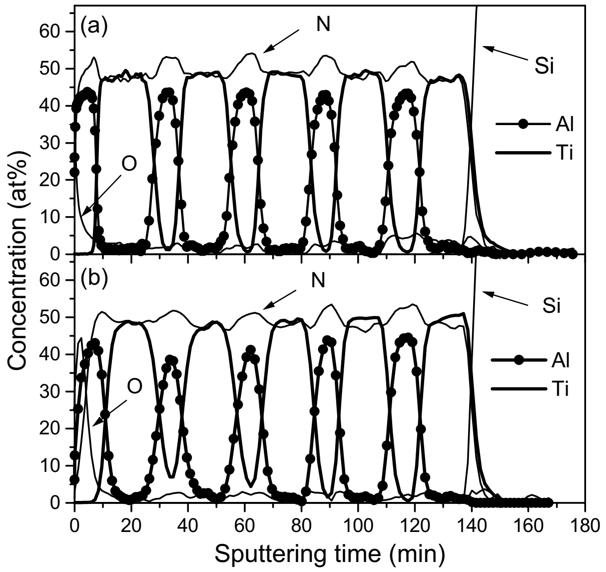

Figure 1. XPS depth profiles of (AlN/TiN)x5/Si: (a) as-deposited sample; (b) sample implanted with argon to $4x10^{16}$ ions/cm^2.

RBS analysis of (Al/Ti)x5/Si structures is presented in Fig. 2. Experimental spectra taken from an as-deposited sample and a sample implanted with nitrogen to $2x10^{17}$ at/cm^2 are shown in (a). It is seen that the initial as-deposited structure exhibits well separated Ti and Al signals from individual layers. After implantation the RBS yield arising from Ti and Al becomes lower and broader. We also observe a build up of backscattering yield arising from the implanted nitrogen, and a surface oxygen peak which increases after ion irradiation. Extracted depth profiles from sample implanted with nitrogen to $2x10^{17}$ at/cm^2 are shown in (b). The profiles show that Al and Ti become almost fully intermixed, especially at mid-depth of the structure, where a maximum concentration of nitrogen (~ 30 at%) was detected. Also, oxygen is detected at the surface, and there is a small fraction of argon, which was used as a sputtering gas and to clean the Si substrates before deposition.

XRD spectra taken from an as-deposited (Al/Ti)x5/Si, and from a sample implanted with nitrogen to $2x10^{17}$ at/cm^2, are shown in Fig. 3. Well defined Al and Ti diffraction peaks are seen in the as-deposited sample. In the implanted sample these peaks are shifted, their relative intensity is altered, and they become markedly broadened, suggesting the appearance of other phases. There is a number of possible reflections that can appear in the small 2Θ range from 35-40°, which correspond to various Al-Ti intermetallic compounds and their nitrides. We have marked in the figure the positions that correspond to AlN, TiN, Ti_2AlN, Ti_3AlN and Ti_3Al phases. It is difficult to distinguish isolated peaks for each of these phases, though this analysis is in agreement with RBS results. The layers are fully intermixed, and the possible formed phases are intermetallic Al-Ti and metal-nitrides with various composition.

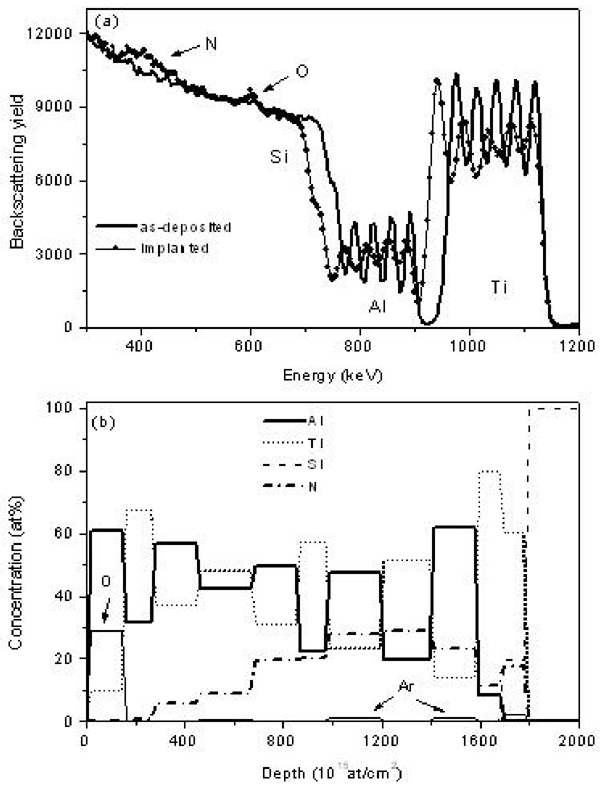

Figure 2. RBS analysis of (Al/Ti)x5/Si: (a) experimental spectra from an as-deposited sample and sample implanted with nitrogen to $2x10^{17}$ at/cm^2; (b) extracted depth profiles of the implanted sample.

The results of cross-sectional TEM analysis are shown in Figs. 4 & 5. Bright field image in (4a) was taken from as-deposited (AlN/TiN)x5/Si, and in (4b) after implantation of this structure with argon to $2x10^{16}$ ions/cm^2. Bright contrast corresponds to AlN layers and dark to TiN. In both cases the AlN and TiN layers are well separated, having a very fine nanocrystalline structure. Ion irradiation induces an 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 Ar^+ ions are being stopped. Analysis of as-deposited (Ti/Al)x5/Si is shown in (5a), and of this structure implanted with nitrogen to $2x10^{17}$ at/cm^2 in (5b). White contrast is from Al layers and dark from Ti. Here we observe that initially well separated Al and Ti layers become fully 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. However, the multilayered nature of the structure is preserved.

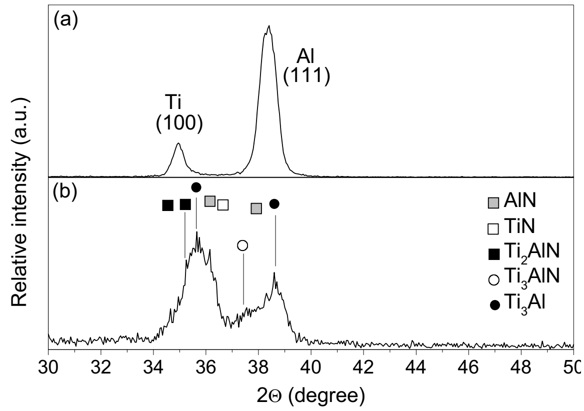

Figure 3. XRD spectra: (a) from as-deposited (Al/Ti)x5/Si; (b) sample implanted with nitrogen to $2x10^{17}$ at/cm^2.

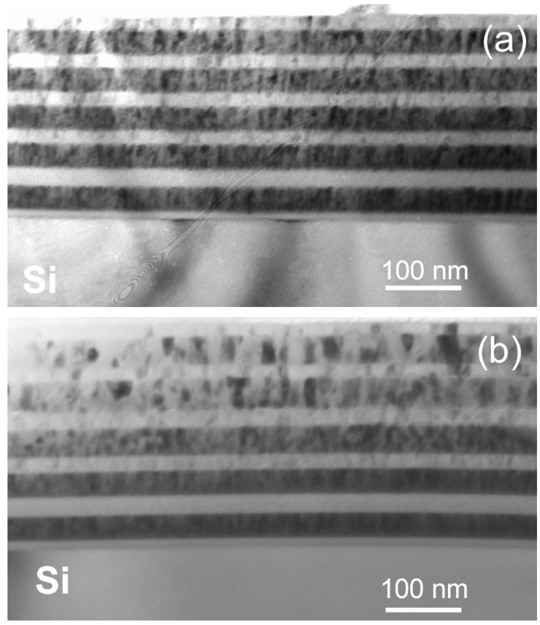

Figure 4. Bright field cross-sectional TEM images of: (a) as-deposited (AlN/TiN)x5/Si; (b) (AlN/TiN)x5/Si implanted with argon to $2x10^{16}$ ions/cm^2.

The results of nano-hardness measurements as a function of the irradiation fluence for both structures are plotted in Fig. 6. As a reference we have given the measured value for a single component TiN layer, deposited to a similar thickness. It is seen that in all cases the nano-hardness increases with the irradiation fluence. Nitrogen implanted Al/Ti structures do not reach the value measured for the TiN layer, obviously because the concentration of nitrogen was not sufficient for a complete formation of metal-nitrides. On the other hand, nano-hardness of the starting AlN/TiN structures is close to that of TiN, and for higher argon fluences it increases above the TiN reference value.

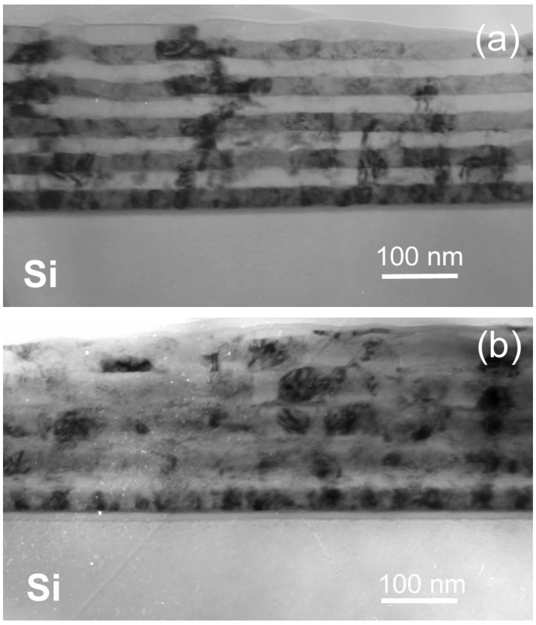

Figure 5. Bright field cross-sectional TEM images of: (a) as-deposited (Al/Ti)x5/Si; (b) (Al/Ti)x5/ implanted with nitrogen to $2x10^{17}$ at/cm^2.

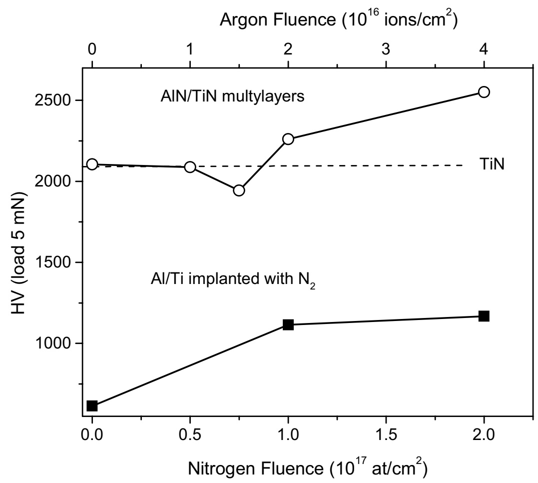

Figure 6. Nano-hardness as a function of the irradiation fluence for both (AlN/TiN)x5/Si and (Al/Ti)x5/Si structures.

There is a pronounced difference in the behavior of the two systems upon ion irradiation. The AlN/TiN layers are immiscible and stable at high temperatures [7-9]. Argon ion irradiation induced only minor structural changes, although their nano-hardness increased. The Al/Ti system is soluble and can form intermetallic compounds. Even much lighter nitrogen ions induced a totally intermixed structure. Implanted nitrogen can also interact with the target material and form metal nitrides. Multilayered structure is preserved after nitrogen implantation, but the layers have a graded composition, with different content of Al, Ti and N. The highest nitrogen concentration is around the projected ion range, while in the inner and outer regions mainly Al and Ti intermix. Because of a thorough intermixing, the resulting layers are tightly bound to each other. The measured nano-hardness did not reach the value of single component TiN, but it can be presumed that these tightly bound multilayers have a high friction and wear resistance.

4. CONCLUSION

The comparative study of sputter-deposited AlN/TiN multilayers and of nitrogen implanted Ti/Al multilayers showed a substantially different resulting structures. The sputter-deposited AlN/TiN multilayers are well separated, with a very fine nanocrystalline structure, and remain stable upon argon ion irradiation. Nitrogen implantation of Al/Ti system resulted in heavily intermixed graded multilayered structure, with different content of Al, Ti and N. In all cases nano-hardness increased with the ion implantation fluence.

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