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ION BEAM MODIFICATION OF REACTIVELY SPUTTERED TiN THIN FILMS

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Abstract. A study of ion beam modification of structural and electrical properties of TiN thin films is presented. The layers were deposited by reactive ion sputtering on (100) Si substrates to a thickness of $\sim$ 240 nm. After deposition the structures were implanted with argon ions at 120 keV, to the fluences from 1×10^{15} – 1×10^{16} ions/cm^2. Structural analysis of the samples was performed by cross-sectional transmission electron microscopy, x-ray diffraction and Rutherford backscattering spectrometry. It was found that the as-deposited layers have a columnar structure, individual columns stretching from the substrate to the surface and being a few tens of nanometers wide. Ion irradiation rearranges their crystalline structure, which remains polycrystalline, but the columns are broken, and nanocrystals of the same phase are formed.

1. INTRODUCTION

TiN thin films have been widely used due to their high hardness, high wear resistance, low electrical resistivity, good chemical stability (Chang et al. 2004, Ma et al. 2006). TiN layers are applied as hard and protective coatings for mechanical tools and wear parts, diffusion barriers in microelectronic industry, decorative coatings. In recant years, investigations have turned towards more complex nitride compounds, multi-layered films and also the modification of films by ion implantation (Lim et al. 2003, Oda et al. 1997). Ion irradiation is a powerful tool to modify a thin film structure by a series of collision cascades induced by the impact ions.

In this work we investigate the effects of microstructural changes in TiN films induced by ion implantation. TiN layers were deposited by reactive ion sputtering on (100) Si wafers and subsequently irradiated with 120 keV Ar ions. It was found that ion irradiation induces local micro-structural changes.

2. EXPERIMENTAL PROCEDURE

Titanium-nitride thin films have been prepared on (100) Si substrates by reactive ion sputtering in a Balzers Sputtron II system. Titanium target (99.9% purity) was sputtered with argon ions in a nitrogen ambient. The base pressure in the chamber was in the low 10^{-6} mbar region, partial pressure of argon was 1×10^{-3} mbar, and partial pressure of nitrogen was 3×10^{-4} mbar. During deposition the substrates were

held at room temperature (RT). We first deposited a ∼10 nm of pure Ti buffer layer, to increase adhesion to the substrate, which was followed by deposition of ∼230 nm TiN, at 8 nm/min. A total layer thickness of ∼240 nm was measured with a Taylor-Hobson profilometer, which gives an accuracy of ±2 nm in this range.

After deposition the samples were implanted with 120 keV Ar^+ ions, to the fluences of 1×10^{15} and 1×10^{16} ions/cm^2. During irradiation the samples were held at room temperature. Calculations by TRIM (Ziegler et al. 1985) gave a projected ion range of Rp ∼ 70 nm and straggle ΔRp ∼ 30 nm, meaning that practically all implanted ions were stopped within the layers. SUSPRE (Webb 1991) gave an estimate that the applied ion fluences were above the amorphisation threshold for the system.

Structural characterization of the samples was performed with Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM) and x-ray diffraction analysis (XRD). For RBS analysis we used 900 keV He^{++} ion beam, with a detector positioned at 165° backscattering angle. We took random spectra at normal incidence and analysed the data with the Data Furnace code (Barradas et al 1997). Cross-sectional TEM analysis was done on a Philips EM 400 microscope, and we also used micro diffraction (MD) technique to study the crystalline structure. XRD analysis was done at grazing incidence of 3°, with Cu Kα emission, using a Bruker D8 Advance Diffractometer.

3. RESULTS AND DISCUSSION

Figure 1 (a-b) displays the RBS spectrum and corresponding calculated depth profiles for an as-deposited TiN layers. The experimental data could be fitted well by introducing Ti, N, Ar and Si in the Data Furnace structure file, as seen in (a). Here we also plotted separated elemental spectrum obtained from the fit. The analysis shows that argon is incorporated in the films during deposition. The extracted depth profiles (b) show a nearly uniform TiN layer stoichiometry, and 1-2 at % of Ar throughout the layer thickness. Towards the Si substrate we register an increased Ti yield, which corresponds to the thin buffer layer. RBS spectra taken from the implanted samples, are similar to the one given in Fig. 1. Ion implantation adds an extra up to 2 at % of Ar around the projected range for the higher fluence. The spectra remain essentially the same, except for a small increase in the yield that arises due to the implanted argon. RBS analysis suggests that ion irradiation does not induce any redistribution of components or intermixing at the layer/substrate interface.

TEM analysis revealed that the as-deposited layers grow in form of a polycrystalline columnar structure, with very fine crystalline grains. After ion irradiation the structure remains polycrystalline, despite the high implanted fluences, which could induce amorphisation. An example of cross-sectional TEM analysis is illustrated in Fig. 2.

The micrographs and the corresponding MD patterns were taken from an as-deposited layer (a), and from a layer implanted to 1×10^{16} ions/cm^2 (b). Bright field image in (a) shows individual columns that stretch from the substrate to the surface, and the MD pattern indicates a very fine polycrystalline structure. Micrograph in (b) shows that the polycrystalline structure of the layer is retained after ion implantation. However, the columns appear as partly broken or disconnected, and we observe randomly distributed sharp contrasts arising from nano-sized crystal grains. The corresponding MD pattern indicates a slightly finer grain structure. Compared

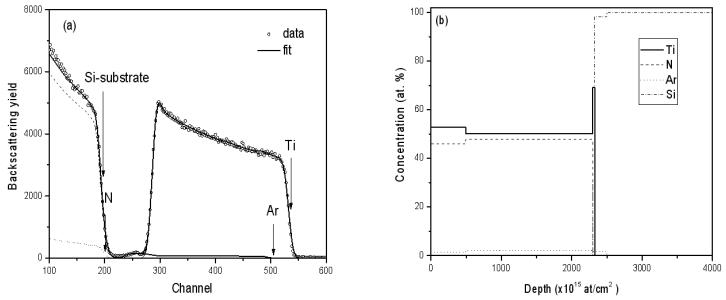

Figure 1: RBS analysis of an as-deposited sample: a) experimenta and fitted data, b) extracted depth profiles.

to the pattern shown in (a) we observe a larger number of smaller spots lying on the circles around the central spot, indicating a higher number of randomly oriented smaller grains.

The results of XRD analysis of as-deposited TiN sample, and after irradiation to 1×10^{15} and 1×10^{16} ions/cm^2, are shown in Fig. 3. We can observe a change of TiN diffraction line intensities after ion irradiation. After irradiation at the lower fluence the intensity of (111) line drops, while the intensity of (200) and (220) lines increases, suggesting a partial texturing of the layer. With further increase of the irradiation fluence the relative ratio of the diffraction line intensities remains roughly the same, but their height decreases, indicating that the mean grain size in the layers decreases.

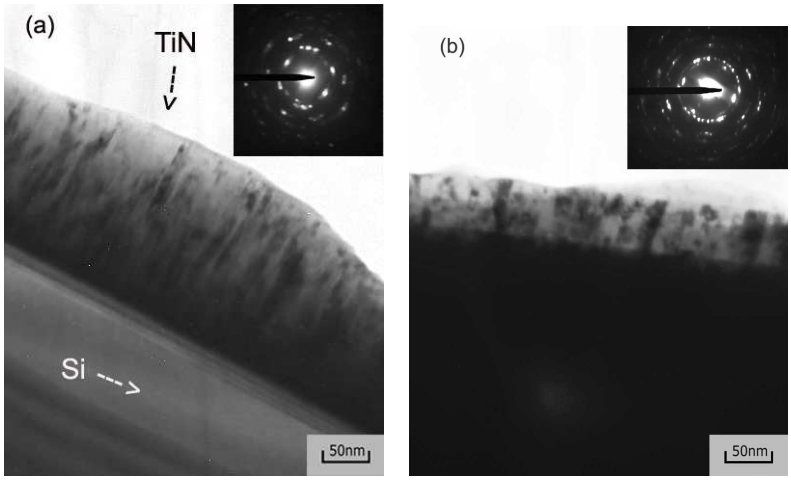

Figure 2: TEM analysis of samples: a) bright field image of as-deposited, b) bright field image of implanted to 1×10^{16} Ar/cm^2.

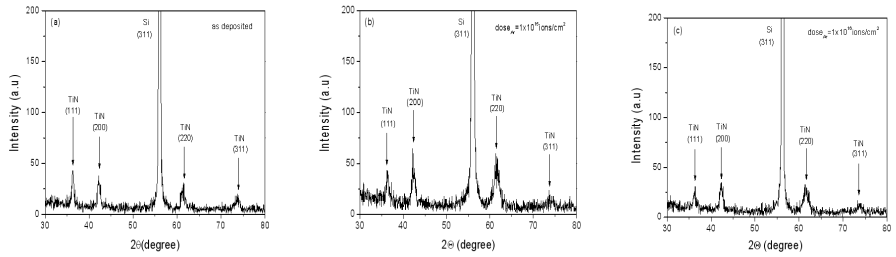

Figure 3: XRD analysis of TiN/Si samples: a) as-deposited, b) after ion irradiation to 1×10^{15} Ar/cm^2, c) after ion irradiation to 1×10^{16} Ar/cm^2.

4. CONCLUSION

We have studied the effects of Ar ion irradiation on the micro-structure of TiN films. The as-deposited layers have a columnar structure, with the mean column width of the order of a few tens of nm. Ion irradiation rearranges their crystalline structure, breaks up the columns, and induces growth of nanocrystals of the same phase.

Acknowledgements

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