



Structural changes induced by argon ion irradiation in TiN thin films

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Abstract

In this work, the effects of 120 keV Ar⁺ ion implantation on the structural properties of TiN thin films were investigated. TiN layers were deposited by d.c. reactive sputtering on Si(100) wafers at room temperature or at 150°C. The thickness of TiN layers was ~240 nm. After deposition the samples were irradiated with 120 keV argon ions to the fluencies of 1×10^{15} and 1×10^{16} ions/cm². Structural characterisation was performed with Rutherford backscattering spectroscopy (RBS), cross-sectional transmission electron microscopy (XTEM), grazing angle X-ray diffraction (XRD) and atomic force microscopy (AFM). It was found that the argon ion irradiation induced the changes in the lattice constant, mean grain size, micro-strain and surface morphology of the TiN layers. The observed micro-structural changes are due to the formation of the high density damage region in the TiN thin film structure.

Keywords: TiN, ion implantation, TEM, AFM

I. Introduction

The use of thin, hard and wear resistant nitride coatings has been successfully explored in the last decades due to its unique combination of physical and chemical properties. Among the nitrides, titanium nitride (TiN) has been the most widely studied because of a good electrical and thermal conductivity, high hardness, good heat resistance and chemical stability [1,2]. Because of these properties, TiN is a material that can be used in various applications such as coatings for corrosion and wear resistance, hard coatings [3,4], diffusion barriers in device processes and as a contact material in silicon devices [5], decorative and biocompatible coatings [6,7]. The most commonly used technique for the deposition of TiN thin films appears to be reactive sputtering from Ti target using Ar and N₂ as a sputtering and reactive gases. The microstructure (including grain size, crystallographic orientation, lattice defects, surface morphology, phase composition) of reactively sputter deposited TiN thin films has been varied by changing the deposition conditions. Additionally, more interest has been directed towards the

possibilities of using ion beam techniques to modify the properties of thin films [8]. The precise control of irradiation parameters offers several advantages, such as precise control of the impurity concentration and depth distribution of the ions [9]. Many studies have been carried out on the effect of the ion implantation of noble gas [10], metal ions [11] carbon and nitrogen ions [12] into TiN. The ion implantation has shown to considerably improve the mechanical and tribological properties of the TiN coatings.

In this paper, TiN thin films were deposited using d.c. reactive sputtering at room temperature and at 150°C on silicon substrate. After deposition the samples were irradiated with argon ions. The effects of argon ion irradiation and substrate temperature on the microstructural changes of TiN layers, such as lattice constant, mean grain size and micro-strain, were analyzed.

II. Experimental

Thin films of titanium nitride were deposited on Si(100) wafers by d.c. reactive sputtering in a Balzers Sputtron II system. A pure Ti target (purity 99.99%) was sputtered with argon ions, while nitrogen was used as the reactive gas. The partial pressure of Ar during deposition was 1×10^{-3} mbar, and partial pressure of N₂ was 3×10^{-4} mbar. During the deposition, the substrates were held at room temperature (RT) or at

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150°C. Before deposition the substrates were cleaned in HF solution and in deionized water. In order to obtain better adhesion of the TiN thin films to the substrate, a ~ 10 nm of pure Ti buffer layer was first deposited. TiN films (~ 240 nm) were deposited at a typical growth rate of ~ 8 nm/min with a base pressure of approximately 1×10^{-6} mbar. Samples were then irradiated with 120 keV Ar⁺ ions at room temperature, to the fluencies of 1×10^{15} ions/cm² and 1×10^{16} ions/cm². The ion beam was uniformly scanned over a target area of 2.5×2.5 cm². The beam current was kept at ~ 1 μ A/cm² to avoid heating of the samples. Calculations by SRIM2003 code [13] gave a projected ion range of $R_p \sim 70$ nm and straggle $\Delta R_p \sim 30$ nm, meaning that practically all implanted ions were stopped within layers. Structural characterisation of as deposited and irradiated samples was performed with Rutherford backscattering spectrometry (RBS), cross-sectional transmission electron microscopy (XTEM), grazing angle X-ray diffraction (XRD) and atomic force microscopy (AFM). For RBS analysis 900 keV He⁺⁺ ion beam was used with two Si surface barrier detectors positioned at 165° scattering angle, at the IONAS facility [14]. Experimental spectra were analyzed with WinDF code [15]. Cross-sectional TEM was done on a JEOL 100CX microscope, and we also used microdiffraction (MD) technique to study the crystalline structure. Cross-sectional samples were prepared by mechanical polishing followed by ion milling on a Gatan PIPS-691. All the samples were analyzed by X-ray diffraction at low angle incidence of 1°, with CuK α emission, using a Bruker D8 Advance Diffractometer. The surface topography of the samples, before and after irradiation was analyzed by means of atomic force microscopy (AFM) using a Quadrex Multimode III e (Veeco Instruments Inc). Data were taken in ambient air in tapping mode.

III. Results and discussion

The depth profiles of Ti and Si obtained from RBS spectra taken after deposition at RT, 150°C and after implantation with 1×10^{16} Ar/cm² are presented in Fig. 1a. The presented depth profiles of Ti confirm the homogeneous Ti concentration of ~ 50 at.% over the whole layer. A uniform stoichiometric composition of TiN layers remains unchanged after argon ion irradiation. The extracted concentration profiles of Ti, N, Si and Ar for the sample deposited at RT and then irradiated to 1×10^{16} Ar/cm² show a nearly uniform stoichiometry of TiN layer (Fig. 1b). It was found that the ion implantation adds an extra up to 2 at.% of argon ions around the projected range.

Phase analyses of the as deposited and irradiated samples were carried out with X-ray diffraction measurements. Fig. 2a-c shows diffraction spectra of TiN/Si layers deposited at RT (a) and after irradiation to 1×10^{15} Ar/cm² (b) and 1×10^{16} Ar/cm² (c). Three peaks are observed for the sample deposited at RT corresponding to the diffractions of the planes (111), (200) and (220). This indicates that the TiN films with a NaCl-type FCC polycrystalline structure is formed. The spectrum of sample deposited at RT shows a more pronounced 220 TiN orientation with less 111 and 200 orientation. After irradiation of the lower fluence 220 line is still stronger than that of 111 and 200. With increasing of the ion fluence the intensity of 220 line decrease while the intensity of 111 line remain unchanged indicating partial texturing of the layer. Figure 2d shows the XRD spectra taken from the sample deposited at 150°C. At the 150°C, the 111 and 220 lines are observed, while 200 line is lost suggesting a partial texturing with respect to the substrate.

The peak position in the XRD patterns were also used for determining the lattice parameters for the TiN/Si bilayers before and after irradiation with 120 keV Ar ion irradiation. Fig. 3a shows the variation of the lat-

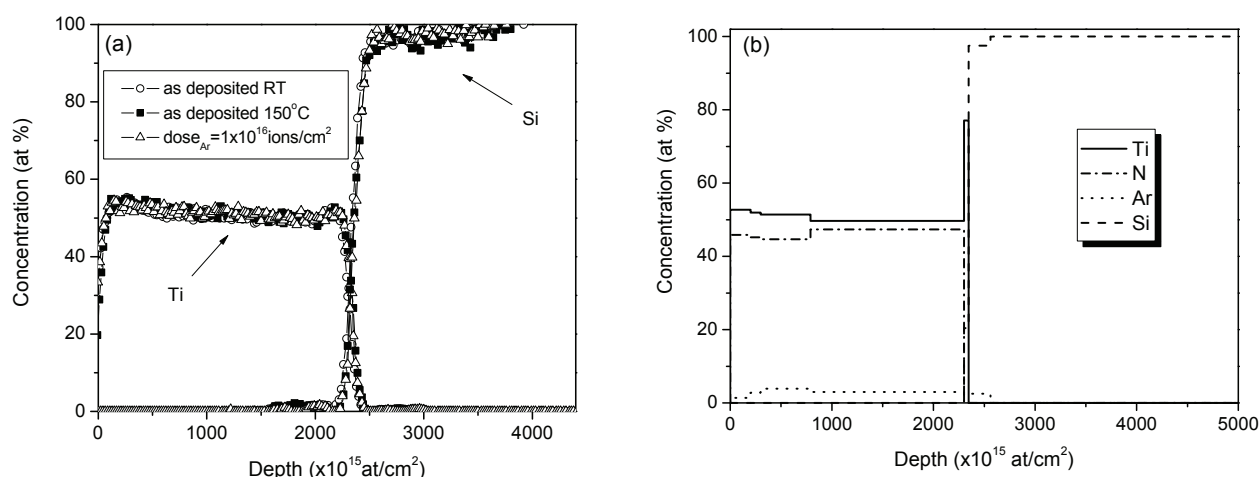


Figure 1. RBS analysis of TiN/Si layers: a) depth profiles of Ti and Si obtained from RBS spectra taken after deposition at RT, 150°C and after implantation with 1×10^{16} Ar/cm² and b) extracted concentration profiles of Ti, N, Si and Ar for the sample deposited at RT and irradiated to 1×10^{16} Ar/cm²

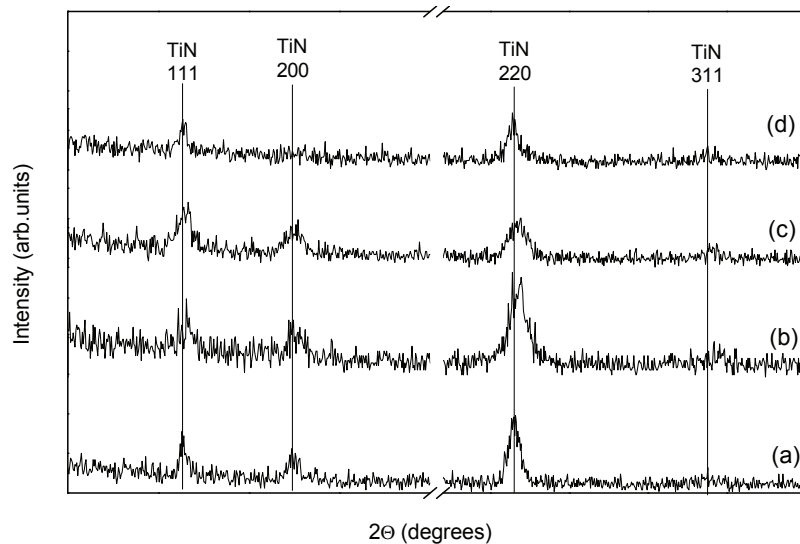


Figure 2. XRD spectra of TiN/Si sample: a) deposited at RT; b) deposited at RT and implanted to 1×10^{15} Ar/cm²; c) deposited at RT and implanted to 1×10^{16} Ar/cm² and d) deposited at 150°C

tice constant with ion fluence for the sample deposited at RT and at 150°C. It is clear that the lattice constant of (111) and (200) plane for both types of TiN/Si samples start to decrease when increasing ion fluence to 1×10^{15} ions/cm², and then slightly increase after ion irradiation with the higher ion fluence of 1×10^{16} ions/cm². At the same time the constant of (220) plane does not change after ion irradiation. When the irradiated fluence was increased to 1×10^{16} ions/cm² the stress relaxation is larger for (111) and (200) planes. This suggests that the relief of point defects is predominant mechanism for different stress relaxation. Fig. 3b shows the micro-strain of TiN layers, deposited at RT and 150°C, as a function of the irradiation fluence. It was found that the micro-strain increase with increasing ion fluence for both types of sample. Since the micro-strain is related to the distortions of the structure, the increase of the micro-strain could be assigned to the high concentration of irradiation induced defects and dislocations.

From the XRD peaks, using the Scherrer formula [16], the mean crystallite size in the TiN films was found to be ~13 nm and ~16 nm for the samples deposited at RT and at 150°C, respectively. Higher substrate temperature results in higher adatom mobilities on the surface during growth as well as increased migration of grain boundaries. Both effects lead to an increase in the grain size [1]. After argon ion irradiation the mean grain size decreased to ~7 nm for the higher ion fluence. During argon ion irradiation the number of the structural defects increase which leads to decrease of grain size. The formation of the smaller grains reflects a relatively high destabilizing effect of defects to the total free energy [17].

As deposited and ion irradiated TiN layers were examined by cross-section TEM to study the microstructure evolution due to the ion irradiation. The results of cross-sectional TEM analysis of TiN/Si sample deposited at 150°C and sample implanted to 1×10^{16} Ar/cm² with corresponding MD patterns are presented in Fig. 4.

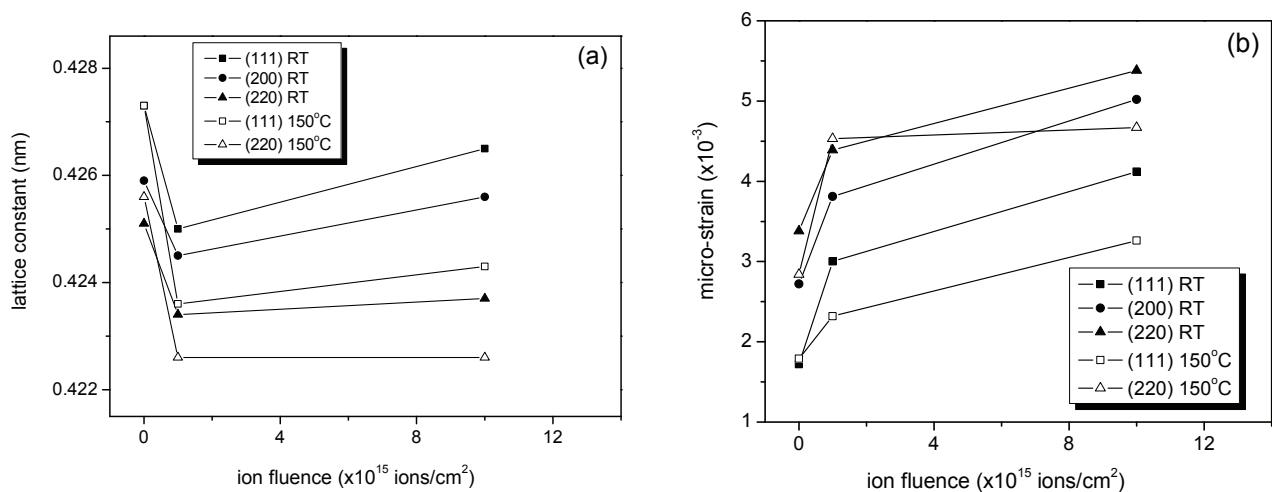


Figure 3. Variation of the lattice constant (a) and micro-strain (b) of the TiN layers deposited at RT and at 150°C with argon ion fluence

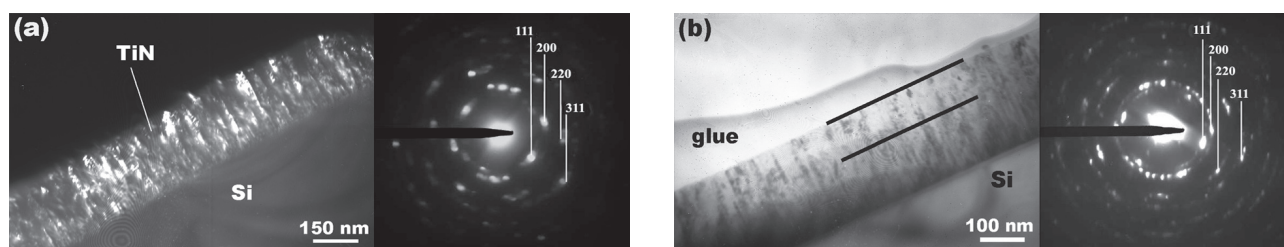


Figure 4. TEM analysis and corresponding MD patterns of TiN/Si bilayers deposited at 150°C: a) dark field image of as deposited sample and b) bright field image of the sample implanted to 1×10^{16} Ar/cm²

Dark field image taken from the as deposited layer (Fig. 4a) exhibits a very fine columnar structure. The width of columns is in the range of ~ 30 nm. Bright field image taken after irradiation with 120 keV argon ions with a fluence to 1×10^{16} ions/cm² is presented in Fig. 4b. The XTEM analysis indicates that a damage region of ~ 100 nm at the surface of the TiN films was formed. The columns appear as partly broken or disconnected after argon ion irradiation. MD patterns taken from the as deposited and irradiated samples show diffraction rings which correspond to 111, 200, 220 and 311 reflections from TiN films. The MD patterns showed that the as deposited TiN layer is polycrystalline comprising small grains of different orientations. The polycrystalline structure is retained even after higher fluence of argon ions. Compared to the MD pattern taken from the as deposited sample we observe a larger number of smaller spots indicating a higher number of randomly oriented smaller grains.

Surface topography before and after irradiation was measured using atomic force microscopy. The images shown in Fig. 5 were taken from the surface of a sample deposited at RT, and sample irradiated to 1×10^{16} ions/cm². AFM measurements showed that the as deposited TiN thin films exhibit smooth surface morphology with an rms value of $\sim 0.5 \pm 0.03$ nm. Here, surface roughness is the standard deviation of all height points analyzed within the scanned area on the surface. The roughness of irradiated sample decreased to $\sim 0.3 \pm 0.02$ nm. AFM

measurements also showed that the average grain size is about 13 ± 2 nm for the sample deposited at RT. After argon ion irradiation with the higher fluence the mean grain size decreased to $\sim 7 \pm 0.02$ nm which is in a good agreement with XRD measurements.

IV. Conclusions

The microstructural changes of polycrystalline TiN thin films induced by 120 keV Ar ions irradiations were investigated in the present work. Even after irradiation at the higher fluence of 1×10^{16} ions/cm² a uniform stoichiometric composition (~ 1.0) of the TiN layers remains unchanged. But, irradiation resulted in decrease of the lattice constant and increase of the micro-strain of the TiN films. Irradiation also resulted in decrease of the mean grain size after irradiation with 120 keV Ar ions. XTEM results exhibit a columnar structure of the as deposited TiN layer. The columnar structure partially disappeared with increasing ion fluence. The results of the AFM analysis showed that the roughness of implanted samples is smaller than that for the as deposited sample. The observed variations of the structural parameters are mainly due to the induced damage region, accumulated inside of ~ 100 nm at the surface of the TiN layer.

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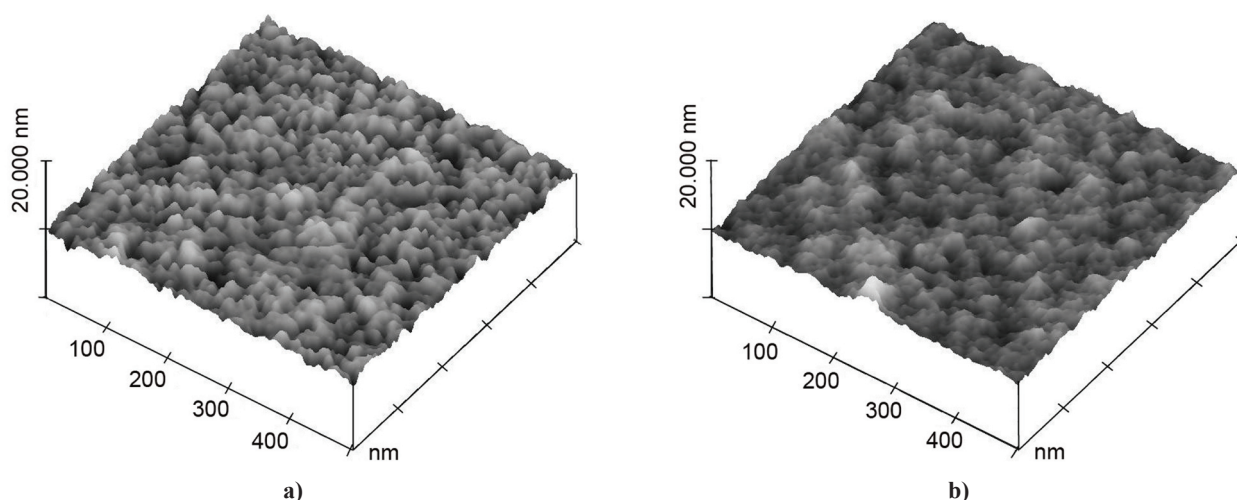


Figure 5. Three-dimensional AFM images of the TiN/Si samples: a) deposited at RT and b) irradiated with 120 keV Ar⁺ ions to 1×10^{16} ions/cm²

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