



## Ion-beam irradiation effects on reactively sputtered CrN layers

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### Abstract

This paper presents a study of microstructural changes induced in CrN layers by irradiation with 120 keV argon ions. The layers were deposited on (100) Si wafers, at different nitrogen partial pressures ( $2 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  mbar), to a total thickness of 260–280 nm. During deposition the substrates were held at 150°C. After deposition the samples were irradiated with argon ions to the fluences of  $1 \times 10^{15}$  and  $1 \times 10^{16}$  ions/cm<sup>2</sup>, under the vacuum of  $7 \times 10^{-6}$  mbar. Characterisation of the samples structure and morphology were performed by X-ray diffraction (XRD) analysis and cross-sectional transmission electron microscopy (XTEM), and the concentration profiles were determined by Rutherford backscattering (RBS) spectrometry. It was found that the layer composition strongly depends on the nitrogen partial pressure during deposition. A pure stoichiometric CrN phase was achieved for the highest nitrogen partial pressure ( $5 \times 10^{-4}$  mbar). Argon ions irradiation induces microstructural changes in the CrN layers such as variation of the lattice constants, micro-strain and mean grain size.

**Keywords:** CrN; ion implantation; thin films; TEM analysis

### 1. Introduction

Chromium-nitride coatings have been studied extensively due to their remarkable mechanical properties, such as high hardness [1], high corrosion and wear resistance [2], as well as high temperature oxidation resistance [3,4]. Compared to TiN, the most widely used coating material, CrN layers exhibit close values of surface hardness, but better corrosion and oxidation resistance. A number of reports on the growth of chromium-nitrides employing the PVD and CVD techniques are available in the literature [1,5,6]. In these studies reactive sputtering from Cr target in an Ar-N<sub>2</sub> atmosphere is frequently used. By varying the composition of the working gas, i.e. the partial pressures of Ar and N<sub>2</sub>, films with different stoichiometries and phase compositions are obtained [7,8]. Namely, chromium-nitride possesses two types of chemical structures: Cr<sub>2</sub>N (hexagonal structure, space group *P-31m*) and CrN (cubic structure, space group *Fm-3m*).

In recent years, investigations have turned towards more complex nitride compounds, multilayered films and also the modification of films by ion irradiation. Ion implantation of hard coating materials was proven as a very powerful technique for improving their tribological properties [9,10]. As a non-equilibrium process ion implantation can produce amorphous, metastable and stable crystalline phases. The microstructure and phase composition of irradiated surface layers are controlled by the implantation parameters (ion energy, dose rate and processing temperature), which can be maintained easily and precisely. It is also observed that the use of carbon, nitrogen or metal ions may improve the tribological properties, oxidation behaviour and hardness of the hard coatings [11,12] and led by these considerations, we have carried out a series of experiments, in which CrN/Si bilayers were irradiated at room temperature with 120 keV Ar ions.

In this study our interest was to investigate the effects of ion implantation on the structure of CrN layers. The layers were deposited by reactive ion sputtering on Si substrates and subsequently irradiated with 120 keV Ar ions. It has been found that the microstructural changes induced by heavy ion irradiation are due to the highly damaged region formed inside the CrN layer.

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## II. Experimental

Chromium-nitride films were deposited by reactive ion sputtering in a Balzers Sputtron II system, having a base pressure in a low  $10^{-6}$  mbar region. We used high purity chromium target (purity 99.9%), which was sputtered with argon ions in a nitrogen ambient. The Ar partial pressure was  $1 \times 10^{-3}$  mbar, while the nitrogen partial pressure was set either at  $2 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$ , or  $5 \times 10^{-4}$  mbar. The layers were grown on (100) Si wafers, at a rate of  $\sim 10$  nm/min, to a thickness of 260–280 nm. The thickness of the films was determined by a surface profilometer. During deposition the substrates were held at  $150^\circ\text{C}$ .

After deposition the samples were implanted with 120 keV Ar ions, to the fluences of  $1 \times 10^{15}$  and  $1 \times 10^{16}$  ions/cm<sup>2</sup>. Implantations were performed under the vacuum of  $7 \times 10^{-6}$  mbar. During irradiation the samples were held at room temperature and the ion beam was scanned uniformly over an area of  $2.5 \times 2.5$  cm<sup>2</sup>. The beam current was kept at  $\sim 1 \mu\text{A}/\text{cm}^2$ , in order to avoid heating of the samples. Irradiation energy was chosen in such a way that the projected range of ions and energy deposition density were in CrN side of the CrN/Si bilayers, according to simulation made with the SRIM 2003 code [13]. The projected ion range ( $R_p$ ) and straggle ( $\Delta R_p$ ) values for 120 keV Ar ions in CrN are 70 nm and 30 nm, respectively.

Characterisation of the samples structure and morphology was performed by X-ray diffraction (XRD) analysis and cross-sectional transmission electron microscopy (XTEM), and the concentration profiles were determined by Rutherford backscattering (RBS) spectrometry. For RBS analysis we used 900 keV He<sup>++</sup> ion beam at normal incidence and the Si surface barrier detector at  $165^\circ$  backscattering angle. Experimental spectra were analyzed with programme WinDF code [14].

Cross-sectional TEM analysis was done on a JEOL 100CX microscope (operated at 100 kV accelerating voltage) and we also used micro diffraction (MD) technique to study the crystalline structure of the samples. XTEM specimens were prepared by mechanical polishing followed by ion milling on a Gatan PIPS-691, using two Ar ion beams with energy of 5 keV. XRD analysis was done at grazing incidence of  $3^\circ$ , using Cu K $_{\alpha}$  line with a wavelength of 0.154 nm, at a Bruker D8 Advance X-ray diffractometer. All the spectra were recorded between  $30^\circ$  and  $70^\circ$  with step  $0.02^\circ$  and the measurement time 4 s per step.

## III. Results and discussion

The RBS spectra presented in Fig. 1a were taken from the samples deposited at nitrogen partial pressures of  $2 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  mbar. The results of RBS analysis showed that chromium-nitride thin films stoichiometry strongly depends on the nitrogen partial pressure during deposition [15,16]. The layers have different thickness, but we can see uniform Cr depth profiles, while the N signal is overlapped by Si. The presented spectra clearly show that the nitrogen partial pressure determines the composition of the deposited layers, which is manifested in the decrease of the Cr-signal intensity with the increase of the N<sub>2</sub> partial pressure. For the lower nitrogen partial pressures of  $2 \times 10^{-4}$  and  $3.5 \times 10^{-4}$  mbar, the layers contain  $\sim 27$  at.% and  $\sim 39$  at.% of N, respectively. For the pressure of  $5 \times 10^{-4}$  mbar the nitrogen content is  $\sim 47$  at.%, thus hinting at the formation of a stoichiometric CrN phase. RBS analyses have also shown that all as-deposited layers contain 1–2 at.% of argon, which is incorporated during the deposition process. The spectrum of the sample deposited at the highest nitrogen pressure and then irradiated

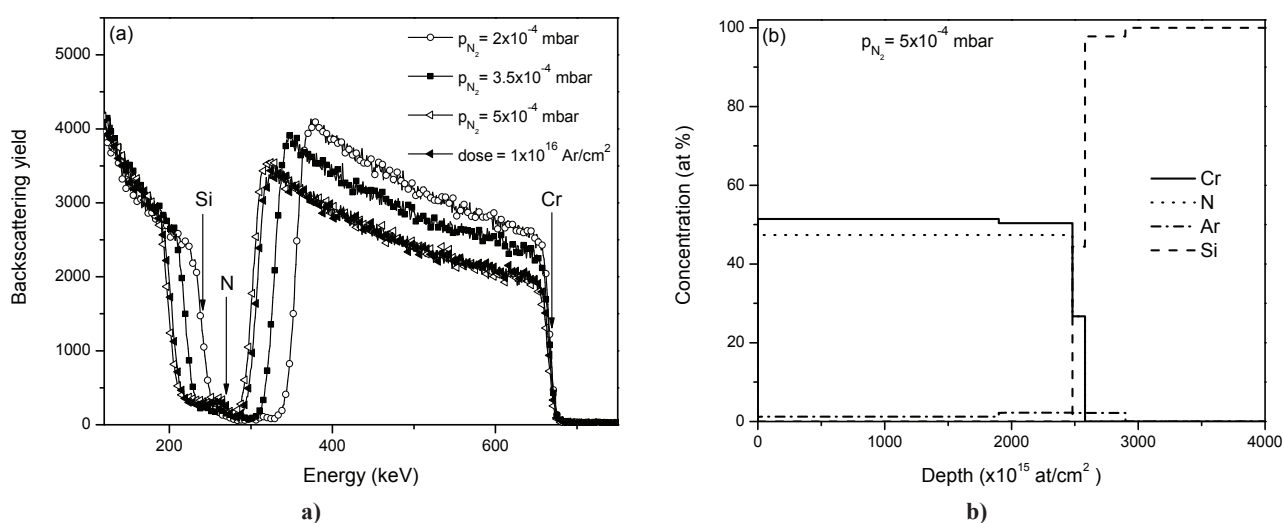


Figure 1. RBS analysis of Cr-N/Si bilayers: a) RBS spectra of samples deposited at different nitrogen partial pressures ( $2 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  mbar) and sample deposited at nitrogen partial pressure of  $5 \times 10^{-4}$  mbar and irradiated with  $1 \times 10^{16}$  Ar/cm<sup>2</sup>; b) extracted depth profiles of sample deposited at nitrogen partial pressure of  $5 \times 10^{-4}$  mbar

with  $1 \times 10^{16}$  Ar/cm<sup>2</sup> is also presented in Fig. 1a. It can be seen that after irradiation the spectrum remains essentially the same, indicating that Ar ions irradiation does not change significantly the composition of the as-deposited layer. The depth profiles of the components (Cr, N, Si and Ar) extracted from the RBS spectrum of the sample deposited at nitrogen partial pressure of  $5 \times 10^{-4}$  mbar, are presented in Fig. 1b. These profiles confirm the homogenous and stoichiometric nature of the deposited CrN layer.

Information of the phases appearing in the samples was obtained from the X-ray diffraction measurements. Figure 2 shows the grazing angle incidence XRD spectra of the samples deposited at nitrogen partial pressures of  $2 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  mbar, and spectrum of sample deposited at highest partial pressure and irradiated with 120 keV Ar ions. It can be seen that layers deposited at lower nitrogen partial pressures ( $2 \times 10^{-4}$  and  $3.5 \times 10^{-4}$  mbar) are fine-grained structures and contain a mixture of Cr, Cr<sub>2</sub>N and CrN phases and that amount of Cr<sub>2</sub>N phase increases in sample deposited at  $3.5 \times 10^{-4}$  mbar, which is visible through the appearance of the peaks around 68°. When the nitrogen partial pressure was increased to  $5 \times 10^{-4}$  mbar, the formation of a pure stoichiometric CrN phase was achieved, as seen in Fig. 2c. The spectrum shows a well-defined 200 CrN peak and two broad peaks corresponding to 111 CrN and 220 CrN. After Ar ions irradiation to  $1 \times 10^{16}$  ions/cm<sup>2</sup> a broadening of the characteristic 200 CrN line suggests that the crystalline grains decrease in size. Values of mean grain size, calculated by Sherrer's equation [17], show that crystallites decreases from ~17 nm to ~9 nm when increasing

ion fluence. It is clear that the observed changes are influenced by ion irradiation, which induces local structural rearrangements and defects formation.

In Fig. 3, the calculated values of lattice constants and micro-strain are shown as a function of Ar ions fluence. As it can be seen the lattice constants of as-deposited sample are found in agreement with values reported in the literature (~0.414 nm) [18]. The lattice constants increase when increasing ion fluence to  $1 \times 10^{15}$  ions/cm<sup>2</sup>. Then, the lattice constants start to slightly decrease along crystallographic directions [200] and [220] after irradiation with the higher ion fluence of  $1 \times 10^{16}$  ions/cm<sup>2</sup>. At the same time the constant along crystallographic direction [111] does not change. It is very likely that the pronounced ion induced damage accumulated in the CrN films may cause an increase in the lattice constants. When the irradiated fluence was increased to  $1 \times 10^{16}$  ions/cm<sup>2</sup> the stress relaxation is larger along crystallographic directions [200] and [220], suggesting that the relief of point defects is the predominant mechanism. Micro-strain is related to the distortions of the structure and the increase of the micro-strain could be assigned to the high concentrations of irradiation induced defects and dislocations.

Cross-section TEM analysis confirmed the microstructural changes of chromium-nitride layers occurring during deposition and subsequent irradiation with 120 keV Ar ions. Figure 4 shows typical XTEM bright field images and corresponding MD patterns of the layers deposited at different values of nitrogen partial pressures. Results of XTEM analysis of sample deposited at partial pressure of  $5 \times 10^{-4}$  mbar and then irradiated to  $1 \times 10^{16}$  Ar/cm<sup>2</sup> are also presented in Fig. 4. We can see that nitro-

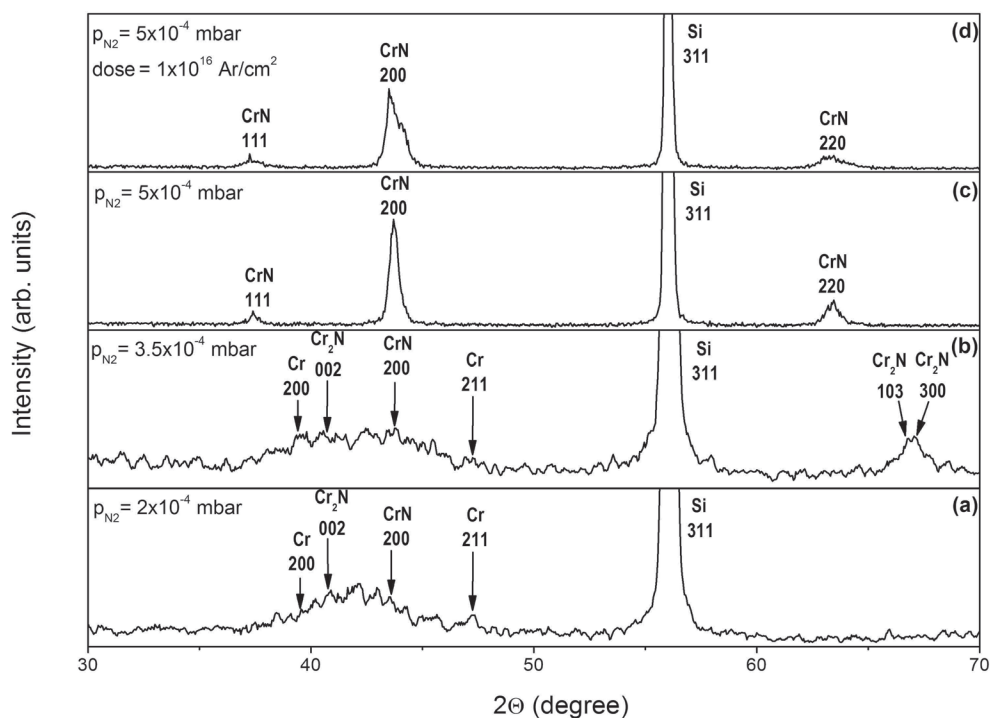


Figure 2. XRD spectra of chromium-nitride layer deposited at nitrogen partial pressure: a)  $2 \times 10^{-4}$  mbar; b)  $3.5 \times 10^{-4}$  mbar; c)  $5 \times 10^{-4}$  mbar and d)  $5 \times 10^{-4}$  mbar and irradiated to  $1 \times 10^{16}$  Ar/cm<sup>2</sup>

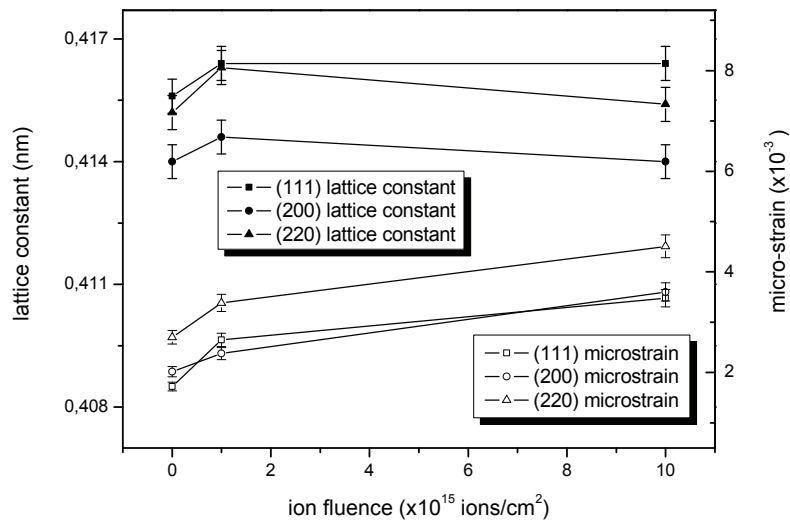


Figure 3. Variation of the lattice constant and micro-strain with Ar ion fluence for CrN layer deposited at nitrogen partial pressure  $5 \times 10^{-4}$  mbar.

gen pressure during deposition have significant influence on the microstructure of the layers. The layers deposited at partial pressure of nitrogen of  $2 \times 10^{-4}$  and  $3.5 \times 10^{-4}$  mbar have a dense morphology with less developed columns. The presence of few different phases (according to the XRD analysis) and very small grains enabled the indexing of their diffraction patterns. The layers with highest content of nitrogen exhibit a pronounced columnar structure, as shown in Fig. 4c. The columns extend over the whole film thickness, with width of the order of few tens of nanometers and the MD pattern indicates a very fine polycrystalline structure. One of the reasons for changes in the morphology is the different bombardment of the growing film during deposition. As shown by Hones *et al.* [19] at low values of nitrogen partial pressure significantly more  $\text{Cr}^+$  ions exhibit a higher kinetic energy and a higher flux than at high values. These high-energy and flux ions compact the film and lead to densely packed morphology. The initial columns formed

in the layer deposited at highest nitrogen partial pressure become broken or disconnected after irradiation to the fluence of  $1 \times 10^{16}$  Ar/cm<sup>2</sup>. This damage region extends to  $\sim 100$  nm, as labeled in Fig. 4d. This can be due to the fact that considerable amount of irradiation damage accumulates inside of  $\sim 100$  nm at the surface of the CrN layer, as predicted by SRIM calculations. MD pattern shows that the polycrystalline structure of the layer is retained after ion implantation. However, compared to the pattern shown in Fig. 4c we observe a larger number of smaller spots lying on the circles around the central spot, indicating a higher number of randomly oriented nanoparticles of the same phase.

#### IV. Conclusions

Using reactive ion sputtering method, chromium-nitride thin films with different content of nitrogen could be prepared by changing the  $\text{N}_2$  partial pressure. At lower nitrogen pressures ( $2 \times 10^{-4}$  and  $3.5 \times 10^{-4}$  mbar)

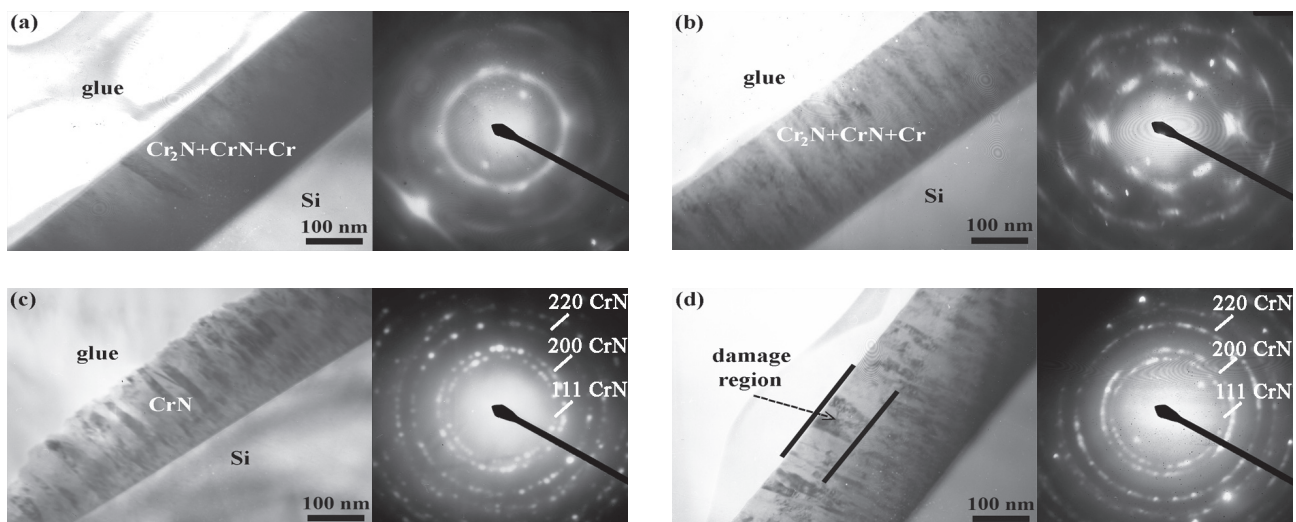


Figure 3. Variation of the lattice constant and micro-strain with Ar ion fluence for CrN layer deposited at nitrogen partial pressure  $5 \times 10^{-4}$  mbar.



the layers have densely packed morphology and contain a mixture of Cr, Cr<sub>2</sub>N and CrN phases. The highest pressure of  $5 \times 10^{-4}$  mbar yields the formation of a pure CrN phase, with a pronounced columnar structure. Argon ions irradiation does not induce any redistribution of components in the CrN layer. Even after irradiation at the higher fluence to  $1 \times 10^{16}$  Ar/cm<sup>2</sup>, the concentration ratio was found to be Cr : N ≈ 1 : 1. But, irradiation resulted in change of lattice constant, micro-strain and grain size of the CrN layers. The observed variations are due to the induced damage region, accumulated inside of ~100 nm of the CrN layer.

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