

## MICROSTRUCTURAL CHANGES OF CHROMIUM-NITRIDE THIN FILMS INDUCED BY ARGON ION IMPLANTATION

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**Abstract.** This paper presents a study of the structure and composition of Cr-N thin films as a function of deposition parameters and ion irradiation. Thin films were deposited by reactive ion sputtering on (100) Si substrates, to a thickness of 240-280 nm, at different nitrogen partial pressures. After deposition the samples were irradiated with 120 keV argon ions, to the fluences of  $1 \times 10^{15}$  and  $1 \times 10^{16}$  ions/cm<sup>2</sup>. Structural characterization of the samples was performed by Rutherford backscattering spectrometry, x-ray diffraction and cross-sectional transmission electron microscopy. It was found that the film composition, Cr<sub>2</sub>N or CrN, strongly depends on the nitrogen partial pressure during deposition. Ion irradiation induces local microstructural changes, formation of nanoparticles and defects.

### 1. INTRODUCTION

Chromium-nitride thin films were developed for many years as hard coatings, wear and corrosion protection materials (Nouveau et al. 2001, Wiklund et al. 1997, Komiya et al. 1997). Compared to TiN, the most widely used coating material, they exhibit close values of surface hardness, but about 1000 times better oxidation resistance (Vishnyakov 2006). In physical vapour deposition Cr-N films can grow in form of CrN or Cr<sub>2</sub>N phases, the Cr<sub>2</sub>N phase exhibiting a higher hardness. On the other hand, the CrN phase is also interesting due to its magnetic, optical and electronic properties. However, modern surface engineering involves application of ion beams in the processes such as ion implantation, plasma ion immersion, or ion beam assisted deposition. Ion beam modification of hard coating materials was found very efficient for improving their tribological properties (Sharkeev 2006).

In this study our main interest was to investigate the structure and composition of Cr-N films as a function of nitrogen partial pressure, and the effects of ion implantation on these structures. The layers were deposited by reactive ion sputtering on Si substrates and subsequently irradiated with 120 keV Ar ions. It was found that ion irradiation induces local rearrangements in the film structures.

## 2. EXPERIMENTAL PROCEDURE

Cr-N films were deposited by reactive ion sputtering in a Balzers Sputtrion II system. We sputtered a 99.99% pure Cr target with argon ions in a nitrogen ambient. The base pressure in the chamber was in the low  $10^{-6}$  mbar region, the Ar partial pressure  $1 \times 10^{-3}$  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 substrates used were (100) Si wafers, held at room temperature (RT) during deposition. The Cr-N layers were grown at a rate of  $\sim 10$  nm/min, to a total thickness of 240-280 nm.

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>. During irradiation the samples were held at room temperature, the ion beam was scanned uniformly over an area of  $2 \times 2$  cm<sup>2</sup>, and the beam current was kept at  $\sim 1$   $\mu$ A/cm<sup>2</sup>. Calculations by TRIM (Ziegler 1985) 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 the layers.

Structural characterization of the samples was performed with Rutherford backscattering spectroscopy (RBS), transmission electron microscopy (TEM) and x-ray diffraction analysis (XRD). For RBS we used 900 keV He<sup>++</sup> ion beam, with a detector positioned at 165° backscattering angle, at the IONAS ion accelerator in Goettingen (Uhrmacher 1995). We took random spectra at normal incidence and analysed the data with the WinDF code (Barradas 1997). Cross-sectional TEM analysis was done on a Philips EM 400 microscope. Micro diffraction (MD) technique was used to study the crystalline structure of the samples. XRD analysis was done at normal and grazing incidence, with Cu K $\alpha$  emission, using a Bruker D8 Advance Diffractometer.

## 3. RESULTS AND DISCUSSION

Generally, the results of RBS analysis showed that the Cr-N layer stoichiometry strongly depends on the nitrogen partial pressure during deposition. For the nitrogen partial pressures of  $2 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  mbar, the layers contain  $\sim 26$  at %,  $\sim 38$  at % and  $\sim 48$  at % of N, respectively. All as-deposited layers contain 1-2 at % of argon, which is incorporated during the deposition process.

Fig. 1 (a-c) shows the extracted depth profiles obtained from experimental RBS spectra of the samples deposited at nitrogen partial pressure of  $2 \times 10^{-4}$  mbar (a),  $3.5 \times 10^{-4}$  mbar (b) and  $5 \times 10^{-4}$  mbar (c). It can be seen that the Cr and N profiles are nearly flat, the layers containing a fraction of Ar which is distributed from the surface to the interface with Si. In (c) the concentration ratio suggests a stoichiometric CrN phase. Indeed, XRD analysis showed the dominating Cr<sub>2</sub>N peaks in the first two cases, while in the latter case we only see peaks corresponding to CrN. Ion implantation adds an extra up to 2 at % of Ar around the projected range. The RBS spectra remain essentially the same, except for a small increase in the yield arising from the implanted argon. This suggests that ion irradiation does not induce any redistribution of components or intermixing at the Cr-N/Si interface.

TEM analysis revealed that the as-deposited layers grow in form of a polycrystalline columnar structure, with very fine crystalline grains. The column width is of the order of a few tens of nm. 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. In all cases we present micrographs

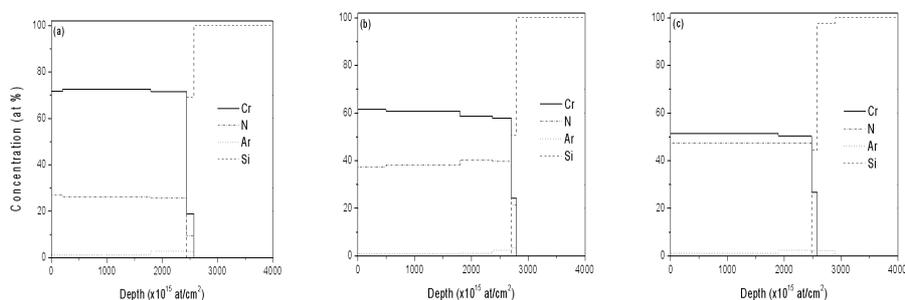


Figure 1: Extracted depth profiles from RBS analysis of as-deposited samples at nitrogen partial pressure of: (a)  $2 \times 10^{-4}$  mbar; (b)  $3.5 \times 10^{-4}$  mbar; (c)  $5 \times 10^{-4}$  mbar.

from the layers deposited at nitrogen partial pressure of  $5 \times 10^{-4}$  mbar, when CrN is formed. Inset in the micrographs are the corresponding MD patterns taken from the layers using a beam spot that covers a sample area of  $\sim 50$  nm in diameter.

Bright field image in (a) is from an as-deposited sample, showing individual columns stretching to the surface, and the MD pattern indicates a very fine polycrystalline structure. Micrographs shown in (b) and (c) are from the sample implanted to  $1 \times 10^{15}$  ions/cm<sup>2</sup>. Bright field image in (b) shows that the initial columns formed in as-deposited layers become broken after ion implantation. Besides that, the polycrystalline structure is retained, the MD pattern indicating slightly larger grains. Dark field image in (c) shows a presence of nano-particles of the same phase, which are either isolated or imbedded in larger grains.

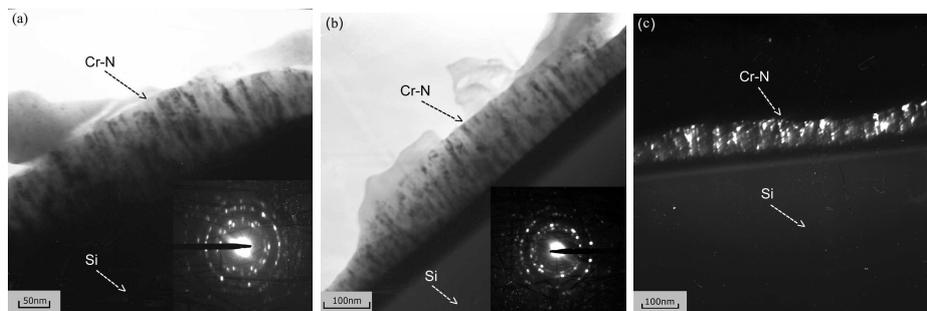


Figure 2: TEM analysis of samples deposited at nitrogen partial pressure of  $5 \times 10^{-4}$  mbar: (a) bright field image of as-deposited; (b) bright field image of implanted to  $1 \times 10^{15}$  Ar/cm<sup>2</sup>; (c) dark field image of implanted to  $1 \times 10^{16}$  Ar/cm<sup>2</sup>.

#### 4. CONCLUSION

Composition and the phases grown in the investigated Cr-N films strongly depend on the nitrogen partial pressure during deposition. At the two lower pressures of  $2 \times 10^{-4}$  and  $3.5 \times 10^{-4}$  mbar the grown phase is  $\text{Cr}_2\text{N}$ , while the highest pressure of  $5 \times 10^{-4}$  mbar yields the formation of stoichiometric CrN phase. The layers grow in form of a columnar structure. The column width is of the order of a few tens of nm.

Ion irradiation induces only local atomic rearrangements. The applied fluences were above the amorphisation level for the system, but the displaced Cr and N atomic species had sufficient mobility to recombine in a crystalline structure. The resulting effects are induced point defects in larger grains and nucleation of imbedded nanoparticles of the same phase.

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