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Stress and Hardness of CrN$_x$ films

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ABSTRACT

Chromium nitride films CrN$_x$ with x ranging form 0 to 1 were deposited by reactive PVD. Both stress and hardness in the films are a function of the composition. The growth stress and hardness for the majority of the films can be related through the Hall Petch relation. It is shown that the hardest films fall outside this relation. It is also shown that the hardest films are nanocrystalline. It is argued that the hardness of these films is a consequence of the nanocrystallinity of these films.

INTRODUCTION

Chromium nitride coatings are succesfully applied in tribological systems where corrosion, oxidation and intense wear are expected [1]. Hardness of the coating is one of the key parameters to the succesful performance of the coating. Wear and corrosion resistant coatings are preferably in a state of compressive stress. The stress in the films at room temperature is the sum of the tensile growth stress generated at the column boundaries, the compressive growth stress generated by the ion bombardment on the growing film, and the thermal stress.

Typically deposition conditions are chosen such that the compressive stress from the ion bombardment is larger than the tensile stress from the columnar growth, leading to corrosion and wear resistant films. In the work reported in this paper however conditions were chosen such that the tensile stress is still visible. It turns out that growth stress and hardness can be related through the Hall-Petch relation for most CrN$_x$ films. The hardest films obtained in this work fall outside that relation, indicating that the deformation mechanism for these films is different.

EXPERIMENTAL

Chromium nitride films were deposited on ball bearing steel and silicon in a Hauzer HC 139 PVD machine by reactive sputter deposition. The base pressure in the system was always below 1×10^{-6} mbar. In all experiments an argon flow of 115 sccm was led into the reaction chamber. The chamber was pumped by a 2200 l/s turbomolecular pump resulting in an argon partial pressure of 3×10^{-3} mbar. By sputter deposition in an argon/nitrogen mixture CrN$_x$ films are deposited, with x depending monotonically on the nitrogen flow. The nitrogen flow was varied from 0 to 150 sccm, resulting in films ranging from pure chromium to CrN. All depositions were done at 180°C.

The samples performed a planetary motion in the chamber; i.e. the substrate table rotated around its axis and the samples were mounted on rods on the substrate table, which also rotated about their axes (Fig.1). All depositions were carried out for 75 minutes. The thickness of the resulting film decreases monotonically with increasing nitrogen flow during deposition. Pure chromium films were 1.7 micron thick, CrN films were 1.1 micron thick.
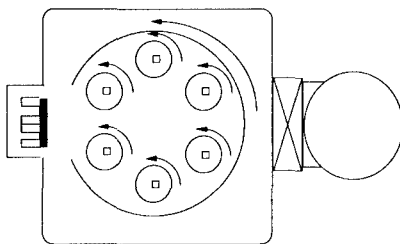
Fig.1. Schematic lay out of the PVD installation. On the left is shown the target with magnet assembly and plasma in front of the target. In the middle the planetary system, on the right the turbomolecular pump.

The microstructure of the film was studied by X-ray diffraction both for films deposited on ball bearing steel and on Si wafers. The composition of the films was measured by EPMA. The film for which the EPMA yielded $CrN_{0.48}$ was also the film with the sharpest X-ray peak for Cr_2N. In accordance with the accuracy of the EPMA of 2 at%. The hardness and the reduced modulus; $E_Y/(1-v^2)$ were measured by nano-indentation on a Hysitron/Digital Instruments nano-indenter on samples deposited on polished ball bearing steel. The stress in the films was studied by wafer curvature measurements from films deposited on 100 mm Si-wafers <100>.

RESULTS

All films showed a columnar structure in cross sectional SEM, with columns of increasing diameter over the film thickness. The final width of the columns at the surface was on the order of 100 nm. A TEM micrograph of the $CrN_{0.43}$, i.e. chromium rich Cr_2N film, on ball bearing steel is shown in Fig. 2. The hardness, reduced modulus and stress in the films are reported in Figs. 3, 4, and 5. For the $CrN_{0.43}$ film a maximum in hardness of 18 GPa was obtained. A second but lower maximum in the hardness of 9 GPa was obtained at a composition of $CrN_{0.73}$ i.e. chromium rich CrN. In contrast, the hardness of stoichiometric Cr, Cr_2N, and CrN films is only 5, 7 and 4 GPa respectively. The reduced modulus exhibits a broad maximum at stoichiometric Cr_2N.
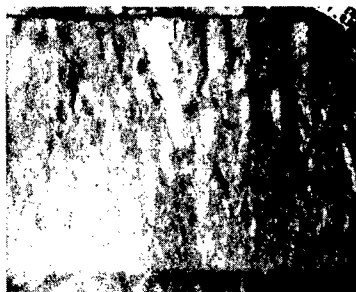

Fig.2. Cross sectional TEM micrograph of a 1.3 micron thick $CrN_{0.43}$ film on ball bearing steel. Apart from a columnar structure faults inside the columns can be seen.
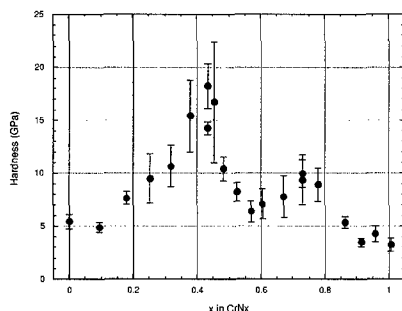
Fig.3. Hardness of CrN_x films versus composition. The hardest films are chromium rich Cr_2N films.

In Fig.6 the X-ray diffraction spectra for the $CrN_{0.43}$ and $CrN_{0.48}$ films are presented, these films resulted from deposition in an Ar/N_2 mixture with respectively 30 and 35 sccm nitrogen. A small difference in nitrogen flow leads to a large difference in microstructure of the film as is witnessed by the X-ray spectrum.
A crystallite size of 8 nm was estimated from the broadness of the diffraction peaks for the $CrN_{0.43}$ films, using the Scherrer equation [2]. This is not in correspondence with the width of the columns, as observed in SEM. Close inspection of the TEM micrograph (Fig.2) showed two length scales: the width of the colums that develop in the film and the size of unfaulted regions within the columns. Apparently the intra-columnar length scale causes the diffraction line broadening.
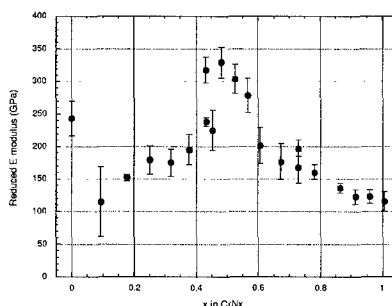

Fig.4. Reduced modulus of the CrN_x films versus composition. The modulus shows a broad peak for stoichiometric Cr_2N.
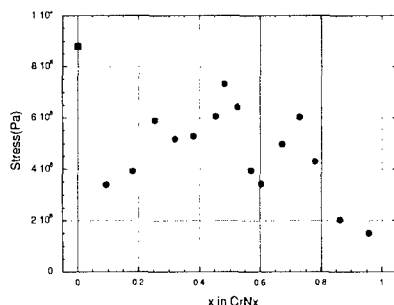
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Fig.5. Stress in Cr (square) and CrN_x films (dots) versus composition.
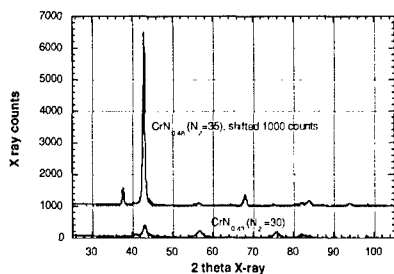

Fig.6. X-ray diffraction spectra taken on films deposited at 30 sccm N_2 flow and 35 sccm N_2 flow. Although the composition differs only slightly, the microstucture is considerably different.

DISCUSSION

In none of the films a mixture of phases was observed. This is particularly intruiging for $CrN_{0.43}$, the composition of the hardest films. Only Cr_2N peaks with pronounced broadening were identified in the X-ray spectrum taken on the $CrN_{0.43}$ film. No bcc Cr was observed in the $CrN_{0.43}$ films indicating the absence of Cr crystals. Assuming that the excess Cr in these films is located at the grain boundaries of 8 nm crystallites, we calculate the thickness of the chromium at the grain boundaries to be less than one atomic layer. Apparently, during deposition the mobility of the excess chromium is so small that this growth mode prevails over the growth of a two phase mixture, thereby forcing the growth of a nanocrystalline material.

In remainder of the text we will use the stress measurements for a discussion on the microstructure . First we discuss the tensile stress in the films. During deposition a bias voltage of 75V was applied to the substrate. A compressive stress was expected due to ion peening. The resulting tensile stress is explained in hindsight from the observation that, due to the planetary motion, the substrate is not in contact with the plasma for the major part of the time. During all

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of this time film growth takes place, unaided by ion bombardment, leading to tensile stress. We checked this hypothesis by depositing a 1.1 micron chromium film with the substrate stationary for the target. This film exhibited a compressive stress of 900 MPa. Work is in progress to deposit films in compressive stress on planetary mounted substrates.

The observed stress at room temperature is the sum of the growth stress (1), the effect of ion bombardment (2) and the thermal stress (3). The linear thermal expansion coefficients of Cr and Si are $7\times10^{-6}K^{-1}$ and $3.2\times10^{-6}K^{-1}$ respectively. Thus the thermal stress in the pure Cr film at room temperature is 140 MPa. From the measured linear thermal expansion coefficient for $CrN_{0.43}$: $\alpha = 9.3\times10^{-6}$, a thermal stress of 220 MPa is calculated [3]. This thermal stress is assumed to be present in all CrN_x samples. The compressive stress due to ion peening is assumed to be 40 MPa for all films, based on the lowest measured stress of 180 MPa for $CrN_{0.95}$ films.

Let us assume that the tensile growth stress is generated at the column boundaries of the growing film. Assuming that the average column boundary relaxes by a fixed distance, this means that the colums in the film will have to stretch by the same amount [4]. Therefore the strain in the film (ε) will be inversely proportional to the column size (d). Of course this straining of the film will have to be weighted over the film thickness, due to the evolution of the columns over the thickness. For the time being it is assumed that the column evolution is comparable for all films. Then:

$$\varepsilon = \frac{\sigma_{growth}(1-\nu)}{E_Y} \propto \frac{1}{d} \qquad (1)$$

with the Youngs modulus E_Y and Poisson ratio ν.

In many systems the Hall-Petch relation is observed. Hardness is inversely proportional to the square root of the grain size. Here we identify columns with grains for all but the nano-crystalline films.

$$Hardness \propto \frac{1}{\sqrt{d}} \qquad (2)$$

Originally this relation was proposed on the basis of dislocation pile up. However the grain boundary acting as a barrier for transfering the resolved shear stress from one grain to the next was also proposed as a mechanism [5]. In Fig.7 we plot the hardness versus $\sqrt{\varepsilon}$. The majority of the points obey the Hall Petch relation. Four points fall outside the curve. The two points with the low hardness are pure chromium and $CrN_{0.1}$. The two points with the high hardness are the points for $CrN_{0.38}$ and $CrN_{0.46}$, both nano-crystalline Cr_2N. First of all it is surprising to note that CrN_x films with x ranging from 0.17 to 1.0 obey the same Hall Petch relation. Bcc Cr for 0.18<x<0.35, hcp Cr_2N, for 0.40< x<0.65 and fcc CrN for x>0.70 all obey the same Hall Petch relation.

Now, if the plasticity of our films is indeed dislocation based we can explain the marked different behaviour of the nano-crystalline films. The width of the columns determines the stress in all films and the hardness in the "micro-crystalline" films. In the case of the nano-crystalline films the stress is still determined by the width of the columns, but the hardness is determined by the size of the unfaulted regions (8 nm).
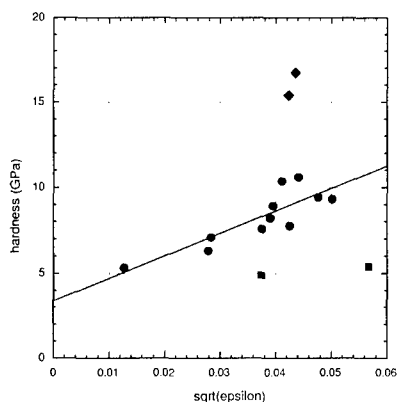
Fig.7. Hardness versus $\sqrt{\varepsilon}$. Most films obey the Hall-Petch relation (dots). Chromium films (squares) obey the Hall Petch relation with different coefficients. Nano-crystalline films (diamonds) fall outside the hall-Petch relation.

CONCLUSION

For chromium nitride films deposited by reactive sputter deposition under tensile stress the hardness depends strongly on the composition. The hardest films are chromium rich Cr_2N films. It is shown that the hardness is a consequence of the nano-crystallinity of the material. The maximum obtained hardness in our experiments was 18 GPa.

ACKNOWLEDGEMENTS

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