Nitrogen effect and thermal stability of Cr and CrN thin films deposited by HiPIMS

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Keywords

HiPIMS, Chromium, Chromium nitride (CrN), thin films, reactive sputtering, annealing treatment.

Introduction

The chromium nitride thin films are studied since several years and are widely use in mechanical applications as corrosion barrier. It has already been established that magnetron sputtering can improve by many ways the chromium nitride properties such as hardness, adhesion, oxidation resistance. A new development of this process, named HiPIMS (High Power Impulse Magnetron Sputtering), allows enhancing coating properties.

In the first part, the objective of this study is to check the influence of the nitrogen content in the gas mixture on the CrN thin film (on the structure, the morphology). And next, the annealing treatment was investigated to study their behavior at high temperature.

Experimental

Chromium and chromium nitride thin films were deposited by reactive magnetron sputtering from a pure chromium target (99,99 %). The nitrogen content in the gas mixture was varied between 0 and 50%. Cr and CrN were deposited using HiPIMS generator (HIP3 Solvix 5K) at floating potential without heating during deposition. The on-time was set at 30 µs and the frequency was 1000Hz. To obtain films with the same thickness, deposition time was adjusted with nitrogen content injected in the gas mixture.

The thickness of the film was measured by profilometry. The film crystallinity was analyzed by X-ray diffraction. From the XRD diagrams, the crystallite size is calculated using the Scherrer formula.

In order to study the thermal stability, we performed annealing tests from 400°C to 900°C in heater for 1 hour in air.

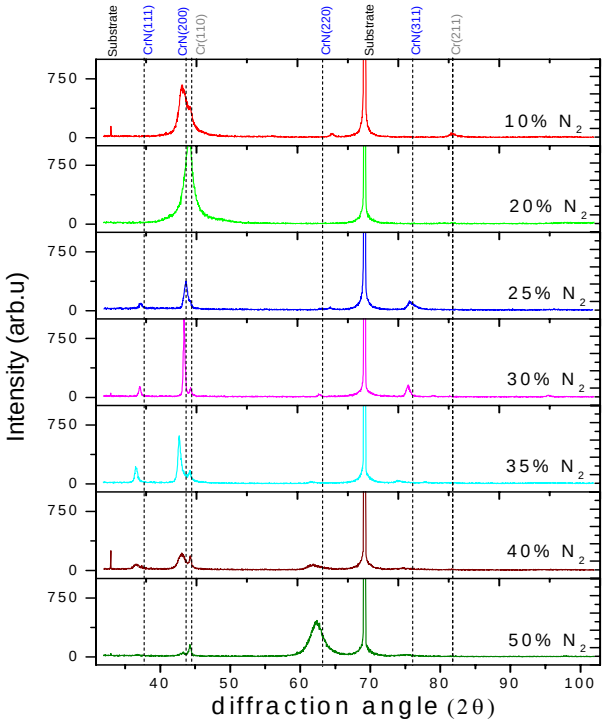

Figure 1, *XRD pattern of CrN thin films with different discharge nitrogen contents*

Results

In this part, the amount of nitrogen in the discharge was varied between 0 and 50%. As we can see on Figure 1, the structure evolves from (110) Cr to (220) CrN phase.

On each diagrams, we can see a Cr peak, it comes from the adhesion layer. The introduction of small nitrogen quantity leads to formation of Cr-CrN phase, reduces the crystallinity and the peaks are broader. Face centered cubic polycrystalline CrN thin films (JCPDS 11-0065) can be obtained with 25%. As the nitrogen increases, the crystallinity increases up to 30%. At this percentage, the film presents a strong (200) preferential orientation to minimize the surface energy.

If one increase further the nitrogen content up to 50% the crystallinity declines and the preferential orientation changes from (200) to (220). In the same time, we can observe the broadening of the XRD peaks.

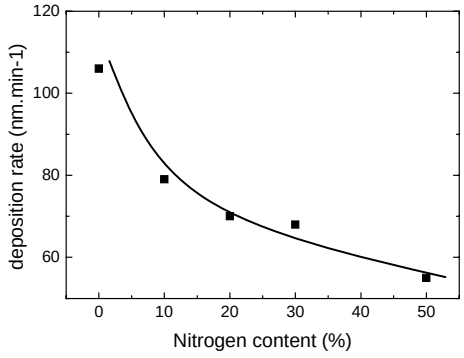

Figure 2, *Deposition rate evolution with various discharge nitrogen contents*

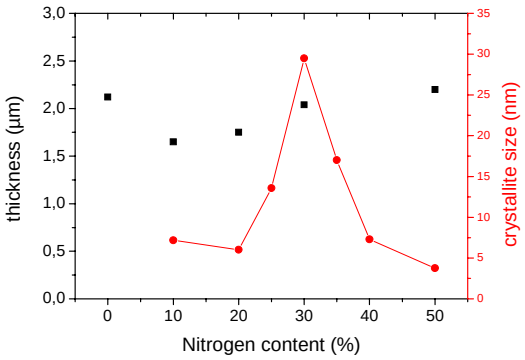

Figure 2, *Thickness and crystallite size with various discharge nitrogen contents*

With similar thickness, the calculations of the grain size from the Scherrer formula (Figure), reveals crystallite sizes around 5-10 nm except between 25% and 35% of nitrogen. In this region, their sizes reach a maximum of 30 nm at 30% of nitrogen. Below 30%, the CrN films are metal rich and above, the nitrogen tends to amorphized the layer.

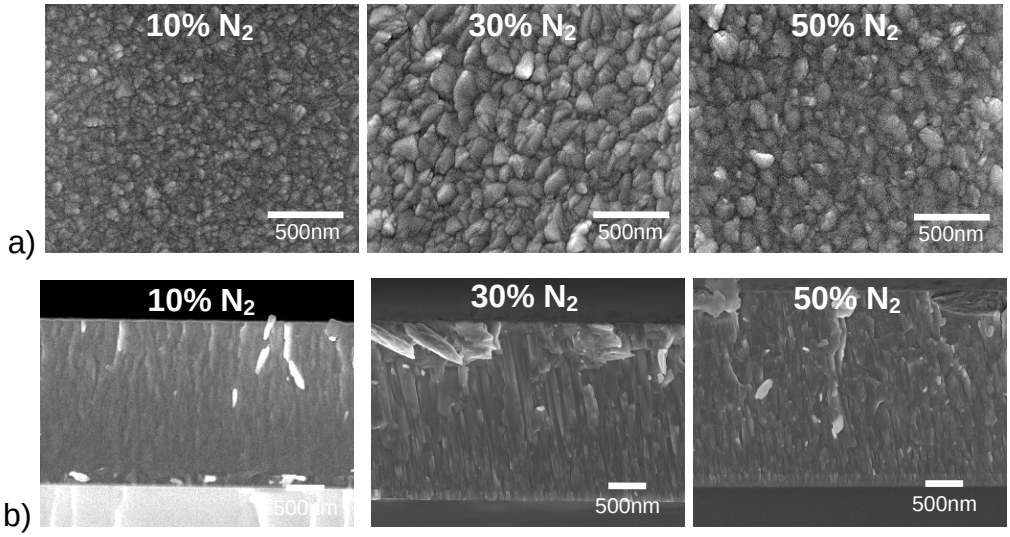

Figure 3, *a) Surface and b) cross-sectional scanning electron micrographs of CrN thin films deposited with various nitrogen contents*

The SEM micrographs show that column tops in surface tends to be bigger at 30% of nitrogen (Figure 3). This observation is in good agreement with calculations. At 10% of nitrogen, the film is featureless and very dense. At 30 and 50% of nitrogen, cross-section images reveal columnar structures. Nevertheless, with more nitrogen (50%)

the coating seems to be denser. As expected, the XRD measurements (not showed) from the chromium and the chromium nitride thin films show an increase of the crystallinity and the texture with the annealing temperature.

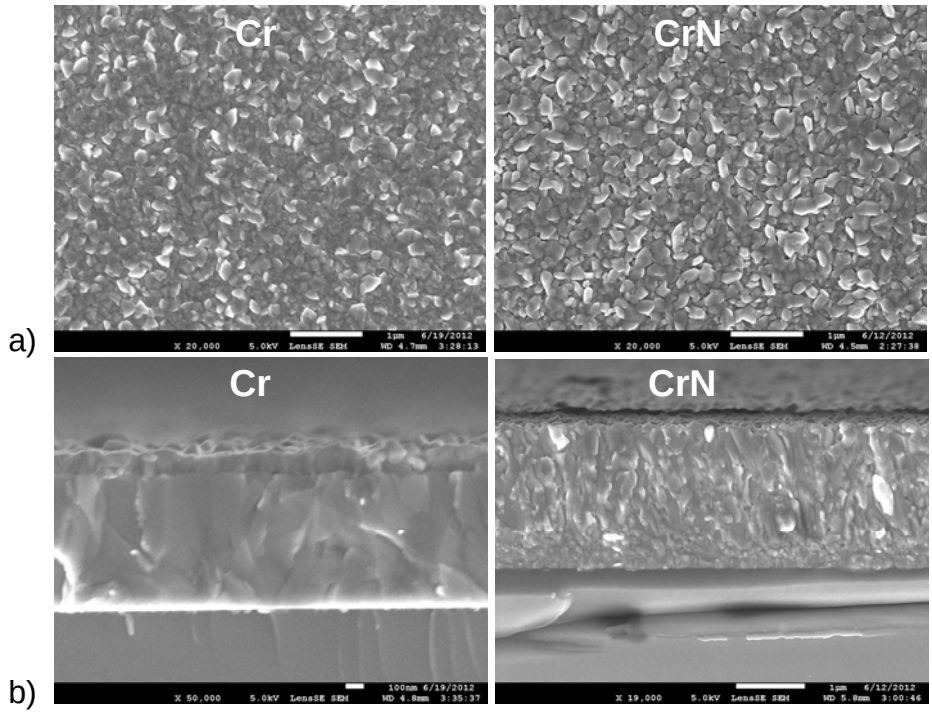

Figure 4, *a) Surface and b) cross-sectional scanning electron micrographs of Cr and CrN thin film annealed at 700°C*

The CrN was deposited with 30% of nitrogen. Film oxidation evaluated by XRD, reveals a Cr_2O_3 phase from 700°C in the two cases. The crystallite size increases continuously with the temperature. The SEM pictures from the surface and the cross-section confirm this tendency. On the other hand, the Cr_2O_3 layer in surface seems to be thicker in chromium deposition (Figure 4).

To summarize, the chromium thin films are well crystallized, stable up to 700°C with a slight change of the morphology. Whereas the chromium nitride coatings are also more crystallized but the morphology is unchanged at this temperature (stable at 900°C).

Acknowledge

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