Morphology and crystallography of Cr, CrN and CrAlN films - Effect of annealing temperature

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Abstract
The present study relates the influence of the annealing temperature on the morphology and crystallography of Cr, CrN and CrAlN films, deposited on silicon substrate (100) using magnetron sputtering. Annealing treatments are performed at 500°C, 600°C and 800°C for 1 hour on Cr coating samples for different thickness. At low temperatures, the results show a thermal stability of these coatings and the XRD analysis show that these films are crystallized according to the orientation (110). Annealing treatments that carried out on CrN coatings, between 500°C and 1000°C, show a thermal stability of these coatings until 700°C. Moreover, {111} texture is observed for the CrN thinner films, while texture {200} is obtained for CrN thick films. However, adding aluminum increases the oxidation resistance up to 1200°C but with lower adherence.

Keywords: Thin Films, Cr-CrN-CrAlN, Magnetron sputtering, SEM- EDX, XRD, Texture.

Introduction
CrN and Cr2N films possess high melting point, low electrical resistivity, high micro-hardness and excellent abrasive wear, corrosion as well as oxidation resistance characteristics [1]. The CrN coating realized industrially by Balzers, Hauzer and Multi-Bow [2] are stable thermicaly until 700°C. Almer and al. [3] observed that beyond 700°C, the Cr2O3 appeared in CrN films and only this oxide remains present at 900°C. The oxidation of nitrides thin films is an important mechanism leading to the degradation of the mechanical properties at high temperatures [4,5]. The chemical reaction between chromium nitride and oxygen gives the following equation:

$$2CrN + 3/2\ O_2 \rightarrow Cr_2O_3 + N_2 \qquad (1)$$

To improve the mechanical and tribological performance of CrN coatings, ternary compounds including another metal such as Al, V, Nb and Cu have been explored. Among them, CrAlN coatings results are very promising due to the formation of complex aluminium and chromium oxides which eventually suppress oxygen diffusion to the bulk [6,7].

The aim of this work is to prepare CrN and CrAlN coatings synthesized with different parameters and to study their mechanical properties and tribological performance under different condition. In addition, the thermal stability and oxidation resistance of the aforementioned films is examined.

Experiment

The CrN and CrAlN films were deposited by RF reactive magnetron sputtering. The used substrates were silicon single-crystal {100}. Before deposition, Cr target and the substrates were cleaned by etching for 5min in Ar plasma. The CrN deposition conditions are given in Table 1. The deposit films were annealed at different temperatures 600, 700, 800 and 1000°C for one hour. SEM observations and EDX (usedSEM VEGA TS5130 MM equipped with EDX-Rontec) analyses have been carried out in order to study the effect of annealing treatment on the morphology and the composition of CrN system. The texture analyses by X ray diffraction (XRD) carried out on CrN films, for different thickness, annealed in air at 600°C for 1 hour.

Table 1. CrN and CrAlN deposition conditions.

Deposition time (mn)	Voltage (-V)	Intensity (A)	Pressure Ar (Pa)	N_2 (%)	Ar (%)
7.5	364	0.5	0.3	30	70

Results

An important density of cracks is observed on the CrAlN films, whereas the CrN films remain perfectly adhesive. These observations are in agreement with those of CrN and CrAlN films deposited seen on AISI M2 steel [8].

After heating in nitrogen, the O/Cr ratio increases for CrN film (0.15 to 2.77) while this change is almost not significant for the CrAlN film (0.78 to 1.00). It clearly appears that the CrAlN film present a more elevated thermal stability compared to the CrN film. The EDX analyses on CrN and CrAlN films, deposited on steel and annealing up to 500°C and 800°C, showed that the CrAlN film have an oxidation resistance more elevated than CrN film [8].

Figure 1 shows the XRD texture analyses that carried out on CrN films annealed in airat 600°C, for different thickness. The textures formed can be adjusted in plan between {111} and {200}.The {111} texture is observed for the CrN thinner films, while texture {200} is obtained for CrN thick films. The fiber orientations depend on methods and deposition conditions (time and temperature).

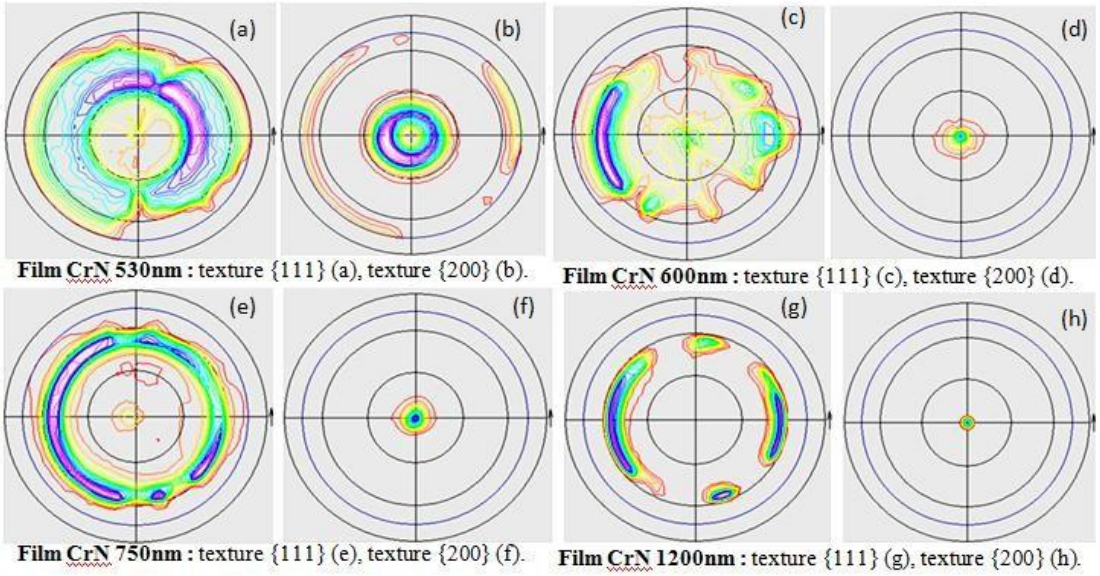

Figure 1. XRD analyses of CrN films annealed in air at 600°C, for different thickness.

Conclusion

We were interested in this work to the thermal stability and adhesion of CrN and CrAlN thin films, deposited on silicon (Si) substrate**.** The influence of the annealing temperature on the morphological characterization films was considered.

From 700°C, there is apparition of oxygen in CrN films, until 1000°C, nitrogen is replaced by the oxygen. The CrN phase disappears and transforms on Cr_2O_3 phase. Chromium nitride films are thermally stable until about 700°C.

The SEM analyses show that the CrN film present a better adhesion to 700°C than the CrAlN film but the EDX analyses show that the CrAlN film presented higher thermal stability compared to CrN film.

The XRD analyses show the {111} texture for the CrN thinner films and {200} texture for CrN thick films.

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