

Characterization of Nitride Thin Films Using SEM and EDX

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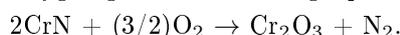
The chromium nitride thin films have become more and more popular in the last years because of their very good physical, chemical and mechanical properties. The present study relates to thermal stability of hard thin films of chromium nitride CrN, carried out physical vapour deposition. We studied the influence of the annealing temperature on the morphology of CrN films, deposited on silicon substrate using magnetron sputtering. The characterizations are examined using scanning electron microscope equipped with energy dispersive X-ray spectroscopy. Annealing treatments in N₂ at 600–1000 °C for 1 h are performed on CrN coating samples for 530 nm thickness. At low temperature, the results show a thermal stability of these coatings. The Cr₂O₃ phase is completely replaced by the CrN phase at temperature above 1000 °C. The results given by scanning electron microscopy–energy dispersive X-ray spectroscopy and X-ray diffraction are compared.

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1. Introduction

CrN and Cr₂N films possess high melting point, low electrical resistivity, high microhardness and excellent abrasive wear, corrosion as well as oxidation resistance characteristics [1]. The CrN coating realized industrially by Balzers et al. [2] are stable thermally until 700 °C. Almer et 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:



Thermal oxidation was much studied, for example, in the phase's transformations field [6] and that of the microstructures [7]. The effect of the oxidation at high temperature and on different atmospheres on the mechanical properties of CrN system was studied by Chang et al. [8]. The present study relates to thermal stability of hard thin films of chromium nitride CrN, carried out by physical vapor deposition (PVD).

We studied the influence of the annealing temperature on the morphology of CrN films deposited on silicon substrate using magnetron sputtering. The characterizations are examined using scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX). Annealing treatments in N₂ at 600–1000 °C for 1 h are performed on CrN films samples for 530 nm thickness.

2. Experimental procedure

The chromium nitride 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 5 min in Ar plasma. The deposit films were annealed at different temperatures 600, 700, 800, and 1000 °C for one hour. SEM observations and EDX analyses have been carried out in order to study the effect of annealing treatment on the morphology and the composition of CrN system.

3. Results and discussion

SEM surface observations of deposited coatings with 0.5 μm of thickness and annealed under N₂ atmosphere at 600, 700, 800, and 1000 °C during 1 h are shown in Fig. 1. The EDX analyses of these films are given in Fig. 2. All spectra reveal the presence of oxygen peak. A decrease of the nitrogen peak is observed when the annealing temperature increases, and vanishes at 1000 °C.

The transformation CrN → Cr₂O₃ is associated with nitrogen content decrease [9]. Consequently, when the annealing temperature increases, the contents of nitride and oxides in the film have to decrease and increase, respectively. Indeed, we can see the increase of oxygen peak with the increase of the annealing temperature (Fig. 2), while the nitrogen peak decreases before a complete disappearance at 1000 °C.

Our observations are in accordance with XRD spectra obtained by Lu and Chen [6]. They carried XRD analyses on CrN films annealed between 400 and 1200 °C for 2 h under air, under N₂ and under atmosphere with gas ratio N₂/H₂ = 9. These results revealed that the phase Cr₂O₃ appears over 700 °C for all the atmospheres. But, for the given temperature, its relative intensity decreases with the increase of ratio PN₂/PO₂. The CrN phase disappears completely at 1200 °C and is replaced by Cr₂O₃ phase. Their observations for annealing under air were consolidated by more recent work [8].

It is necessary to underline that this different studies use the X-ray diffraction, the results are to leave of a

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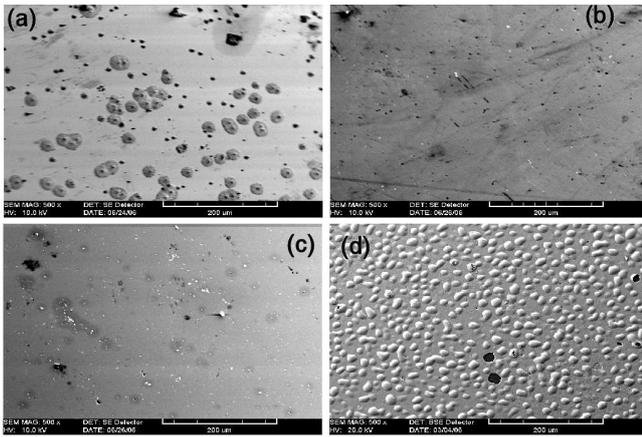


Fig. 1. SEM images of CrN films annealed during 1 h at: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 1000 °C.

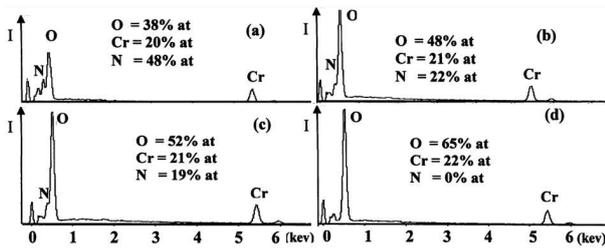


Fig. 2. EDX patterns of CrN films annealed during 1 hour at: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 1000 °C.

global characterization and suppose therefore that the replacement of the CrN phase by the Cr₂O₃ phase makes itself in homogeneous manner on the whole surface. We regrouped in Fig. 3 the X-ray microanalyses done in two different points on the CrN film of 530 nm thickness, annealed at 600 °C. We observe the oxygen peak in the two points, but the nitrogen peak exists solely for only one point.

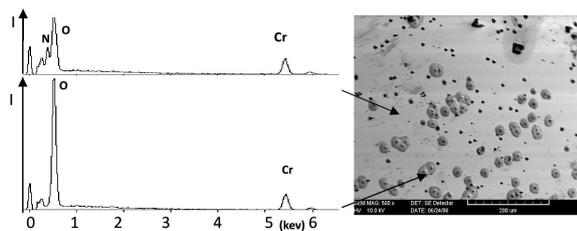


Fig. 2. EDX analyses combined with a SEM micrograph of CrN film annealed at 600 °C during 1 hour under N₂.

This difference of answers shows that the oxidation does not make itself in a homogeneous way on the whole nitride coating, that is undetectable by X-ray diffraction. This observation permits to support the fact that these are the preferential sites in the CrN microstructure for the germination of the Cr₂O₃ phase. The formation of the oxide probably starts on the grain boundaries of the

CrN phase that it replaces progressively, as it was underlined by the works of Ichumira [10].

He shows that the oxidation of CrN occurs by the very rapid diffusion of oxygen along the grain boundaries of oxide films formed on each CrN grain. The rate-determining step of the oxidation of CrN is the Cr ion diffusion through the Cr₂O₃ formed on each CrN grain.

4. Conclusion

We were interested in this work in the thermal stability of CrN thin films, deposited on silicon (Si) substrate. The influence of the annealing temperature on the morphological characterization of 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 is transformed in Cr₂O₃ phase. Chromium nitride films are stable thermally until about 700 °C. The EDX permitted to show the distribution of the phases and complete thus the XRD technique ordinarily used. The oxidization does not make itself in a homogeneous way on the whole coating of nitride, which is not detectable by X-ray diffraction. There are the preferential sites in the CrN microstructure for the germination of the Cr₂O₃ phase. Finally the XRD analysis confirms the good thermal stability of the CrN coatings. The oxidization begins at about 800 °C to become widespread at 1000 °C.

Acknowledgments

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