Surface Chemical Changes Induced by Low Energy Ion Bombardment in Chromium Nitride Layers

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Introduction

Chromium nitride CrN is an example of hard coatings providing high wear resistance combined with good tribological properties and excellent corrosion resistance. Therefore, it is one of the most universal tribological coating systems frequently used for forming and casting applications. Results on reactively sputtered CrN_x coatings have been reported in many papers.

It is known that by varying the N_2 flow-rate in magnetron sputtering, coatings containing Cr, Cr(N) solid solution, Cr_2N and CrN phases can be deposited. Determination of the crystallographic phases present in these films is usually done by X-ray diffraction, which allows the identification of the overall crystalline phases. However, in the case of dual-phase film structures or very low grain sizes the exact determination of the individual phases by XRD can be ambiguous due to overlapping peaks or peak broadening. Thus, the aim of this work is to evaluate the composition and the chemical state of the elements in CrN_x films, deposited by magnetron sputtering at varying $N_2/(N_2+Ar)$, using X-ray photoelectron spectroscopy. Implications of the effect of ion bombardment on the composition and structure of the CrN films have been clearly demonstrated recently. This oriented our attention towards investigations of the effect of Ar^+ and N_2^+ bombardment on the CrN_x layers of different composition and structure. Conclusions were made upon the possible alterations of the Cr_2N and CrN stoichiometry by these bombarding ions.

Aims

In this work three types of CrN_x layers, one close to Cr_2N, the other to CrN composition and a third with high nitrogen content CrN_{1+y}, were prepared by reactive magnetron sputtering. The samples were subjected to bombardment by Ar^+ and N_2^+ ions applied in sequence. The relative atomic concentration and the chemical states of the elements in the surface layer were determined by X-ray photoelectron spectroscopy.

Deposition parameters ($N_2/(Ar+N_2)$ flow rate; ion energy, E_i; ion/atom flux ratio, J_i/J_a; coating thickness, t) **and dominant crystallographic phases determined by XRD and their average grain sizes** (d)

Coating	$N_2/(Ar+N_2)$	E_i [eV]	J_i/J_a	t [µm]	Phases	d [nm]
$CrN_{0.52}$	0.20	87	0.41	3.0	Cr_2N	16
$CrN_{0.98}$	0.31	32	0.61	3.3	CrN	60
$CrN_{1.00}$	0.53	32	0.84	3.2	CrN	18
CrN_{1+x}	0.71	32	1.32	3.2	CrN	10
CrN_{1+y}	0.83	32	1.32	5.5	CrN	9

Experimental

Film Deposition

***Substrates*:** silicon (100), molybdenum, austenitic stainless steel
Unbalanced DC magnetron Cr target (99.99 %) at 9 cm, Ar + N_2 (99.999 %) substrate temperature 300 °C. Base pressure ≤ 8×10^{-4} Pa, working pressure, 0.4 Pa. Sputtering power density 3 W cm^{-2}
The plasma parameters measured using a Hiden ESP Langmuir wire probe.

Sample Analysis

Film thickness: spherical abrasion test
***Chemical composition*:** Microspec WDX-3PC wavelength-dispersive electron-probe microanalysis (EPMA)
XRD: Siemens D500 (Bragg-Brentano mode), Cu Ka, Pseudo-Voigt profile function

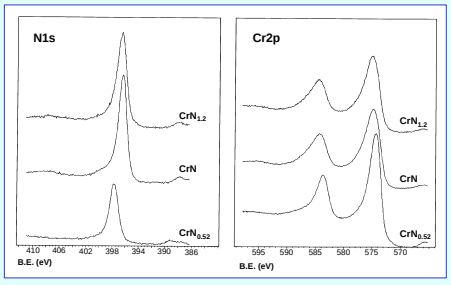
Ion Bombardment

Kratos MacroBeam and Technorg Linda ion guns
0.5-5 keV, doses up to 10^{18} ions/cm^2
99.999 % N_2 and Ar

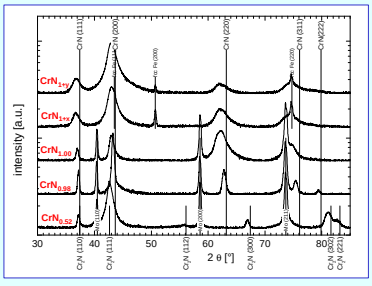
XPS Measurements

Kratos XSAM 800 spectrometer
Mg Ka radiation, base pressure 10^{-10} mbar
Fixed analyser transmission mode with 40 eV pass energy
Shirley type background subtraction
Kratos Vision 2000 and XPS MultiQuant softwares

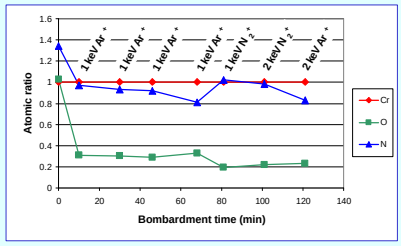
The N1s and Cr2p lines of the $CrN_{0.52}$, CrN and CrN_{1+y} ($CrN_{1.2}$) samples
after elimination of the oxidised layer by Ar^+ sputtering



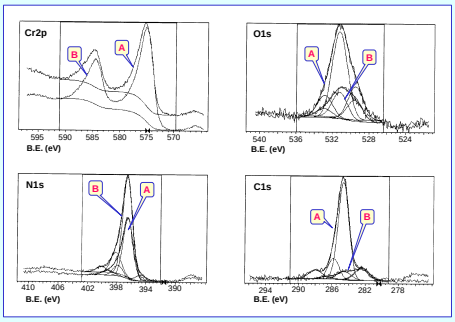
XRD patterns of the chromium nitride samples
(Lines of the substrates, molybdenum or austenitic stainless steel, are also visible.)



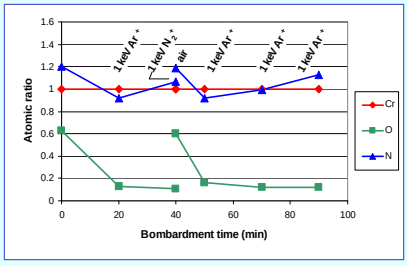
Composition changes of the CrN sample during consecutive bombardment by Ar^+ and N_2^+ ions



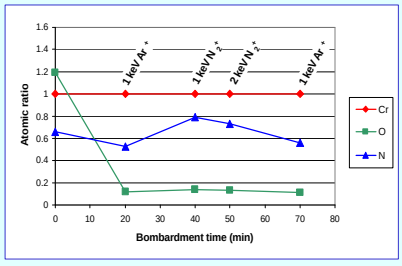
The XP spectra of the CrN_{1+y} sample: Cr2p, O1s, N1s and C1s regions with the synthetic-line components of two states,
(A) - oxidised (exposed to air), (B) - Ar^+ ion bombarded



Composition changes of the CrN_{1+y} sample during consecutive bombardment by Ar^+ and N_2^+ ions
After two steps the sample was exposed to air for 24 hours at room temperature



Composition changes of the $CrN_{0.52}$ sample during consecutive bombardment by Ar^+ and N_2^+ ions



Conclusions

- All chromium nitride samples were crystalline. The phase and chemical composition were in good agreement. The XRD lines of the super-stoichiometric samples showed a distinct peak broadening.
- Ar^+ ion bombardment could not reduce the nitrogen content of the $CrN_{0.52}$ sample while N_2^+ bombardment increased it up to $\mathbf{CrN_{0.8}}$ but complete conversion to **CrN** *could not be achieved*.
- Ar^+ ion bombardment reduced the nitrogen content of the CrN sample to $\mathbf{CrN_{0.8}}$ and N_2^+ bombardment increased it slightly **above 1:1**.
- Super-stoichiometric chromium nitride samples up to $\mathbf{CrN_{1.3}}$ composition could be prepared by the applied method. The excess nitrogen *could not be removed* by *Ar^+ ion bombardment*.