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Characterisation of reactive unbalanced magnetron sputtered chromium oxynitride thin films with air

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Abstract

The aim of this work is to study the stoichiometry of chromium oxynitride thin films deposited by reactive magnetron sputtering in presence of air with various relative humidities. Rutherford backscattering spectroscopy and resonant nuclear reaction (RNRA) were used to determine the thickness and the composition of the films. Hydrogen and nitrogen profiles were obtained by RNRA. The chemical bonds were investigated by X-ray photoemission spectroscopy and low energy electron induced X-ray spectroscopy. The chromium metallic and chromium compound concentrations were measured vs. the flow and relative humidity of the air. During sputtering in metallic mode, Cr_2O_3 stoichiometry is observed with low contents of CrN, CrO_2 and $(\text{CrO}_2)_3\text{-N}$, whereas in compound mode the CrO_2 stoichiometry predominates.

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Keywords: Chromium oxynitride; Rutherford backscattering spectroscopy; RNRA; Low energy electron induced X-ray spectroscopy; X-ray photoemission spectroscopy

1. Introduction

Chromium nitride and chromium oxide are very good candidates for protection of steels and decorative applications due to their distinct colors. Like TiN, CrN has good mechanical properties [1,2] and improves the corrosion protection [1,3] because it has high oxidation resistance and a good chemical stability. Like CrN, the Cr_2O_3 thin films also present interesting properties such as: a higher hardness [1,4] and beautiful colors intended for decoration [1,5]. Furthermore, other chromium compounds like chromium oxynitride possess promising industrial applications. Chromium oxynitride thin films present various colors that vary with thickness and composition. In comparison with Cr_2O_3 , the chromium oxynitride has a higher corrosion resistance and the layer has a better adhesion and a uniform structure [6]. Collard et al. [1] have synthesized the Cr–N–O thin films by reactive sputtering in an atmosphere containing two gases, nitrogen and oxygen. Gautier and Machet [7] have applied electric arc method for the deposition of Cr–N–O. The chromium oxynitride films prepared by

these two methods (sputtering and electric arc) contain two different phases: CrN and Cr_2O_3 . Suzuki et al. [8] have produced Cr–N–O thin films using another deposition technique based on a laser beam pulsed in nitrogen and residual oxygen atmosphere. According to the works reported on the Cr–N–O films, it is interesting to produce chromium oxynitride thin films using reactive plasma with air containing various concentrations of water vapor. The aim of the present work is to study the influence of relative humidity of air on deposition rate, the composition of chromium oxynitride thin films deposited by reactive PVD on carbon and to characterize the different phases present in it by electronic spectroscopic techniques such as low energy electron induced X-ray spectroscopy (LEEIXS) and X-ray photoemission spectroscopy (XPS).

2. Experimental details

2.1. Deposition conditions

The chromium oxynitride films were produced by DC reactive sputtering using an unbalanced magnetron system in an Ar and air gas mixture. The vacuum chamber (0.25 m³) is equipped with a chromium (99.99% purity)

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Table 1
Cr, O, N and H concentration in chromium oxynitride thin films obtained by different techniques (RBS, LEEIXS, XPS and RNRA)

Sample	Element	± 5 at.% (RBS)	± 10 at.% (LEEIXS)	± 5 at.% (XPS)	± 5 at.% RNRA	Thickness (nm)
Cr–N–O/C 5 sccm dry air	Cr	42	46	38.5		240
	O	46	44	55.5		
	N	12	10	6	14	
	H				1	
Cr–N–O/C 10 sccm dry air	Cr	39	40.5	38.9		240
	O	55	53	59.3		
	N	6	6.5	1.8	4	
	H				2	
Cr–N–O/C 5 sccm air at 65% RH	Cr	40	41	36		240
	O	48	47	61		
	N	12	12	3	17.5	
	H				2.5	
Cr–N–O/C 10 sccm air at 65% RH	Cr	34	34.3	36.8		120
	O	64	62.7	61.7		
	N	2	3	1.5	3	
	H				11	
Cr–N–O/C 5 sccm air at 95% RH	Cr	38.5	42.3	36.9		240
	O	48	46.2	59.5		
	N	13.5	11.5	3.6	15.5	
	H				6	
Cr–N–O/C 10 sccm air at 95% RH	Cr	33.5	35	36.9		120
	O	62	60	61.9		
	N	4.5	5	1.2	3	
	H				11	

sputtering target disc of 19.6 cm² area and a 400-l/min turbomolecular pump. The pressure in the chamber before starting the sputtering process was less than 5×10^{-5} Pa. The deposition working pressure and plasma power density were maintained, respectively, at 0.56 Pa and 5.86 W/cm². The temperature of the substrate during the sputtering process was always less than 100 °C. Prior to the introduction of the carbon substrate in the deposition chamber, they were polished down to a surface roughness of less than 10 nm and cleaned with distilled water and acetone. Before deposition, pure argon plasma was used to clean the chromium target. The carbon substrate was etched for 4 min in a pure argon plasma atmosphere. High-purity argon and dry air were used and both gas flows were controlled. The reactive gas (air with various relative humidities) and argon were admitted separately through an MKS flow control system, keeping a constant total gas flow of 35 sccm (60 Pa l/s) for all deposition runs. The reactive gas flow varied from 0 to 25 sccm.

2.2. Analysis methods

The thickness and composition of chromium oxynitride thin films were measured by Rutherford backscattering spectroscopy (RBS) and RNRA techniques at LARN using 2-MV Tandemron accelerator. The RBS technique was performed with 2-MeV α -particles. The nitrogen

and hydrogen profiles were measured by using narrow resonance nuclear reaction: the $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ reaction at $E_p = 429$ keV for nitrogen and $\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction at 6.385 MeV for hydrogen profiling. The 4.43 MeV γ -radiation of $^{12}\text{C}^*$ was measured with a NaI detector as a function of the incident particles energy. The chemical bond and the composition of the films formed were studied by LEEIXS and XPS. The LEEIXS is based on the ionization of the inner-shell of the analyzed element by electrons of a 5 keV, the gas pressure is 0.23 Torr and the current is 0.12 mA: in this work we investigate the intensity of the Cr L α with a TAP crystal ($2d = 2.575$ nm). The thickness of the samples analyzed was in between 120 and 240 nm. The XPS measurements were recorded with a SSX-100 spectrometer using the monochromatised X-ray Al K α (1486.4 eV) at LISE (Laboratoire Interdépartmental de Spectroscopie Electronique) at FUNPD.

3. Results and discussion

The LEEIX spectroscopy results have shown, during sputtering in metallic mode, that the Cr₂O₃ stoichiometry is in majority with a small percentage of CrN and CrO₂. This can be explained by the fact that enthalpy of formation of Cr–N at 25 °C is -29.8 kcal/g mol, very low value in comparison with that of Cr₂O₃ -269.7 kcal/g mol [9]. When air flow and relative humid-

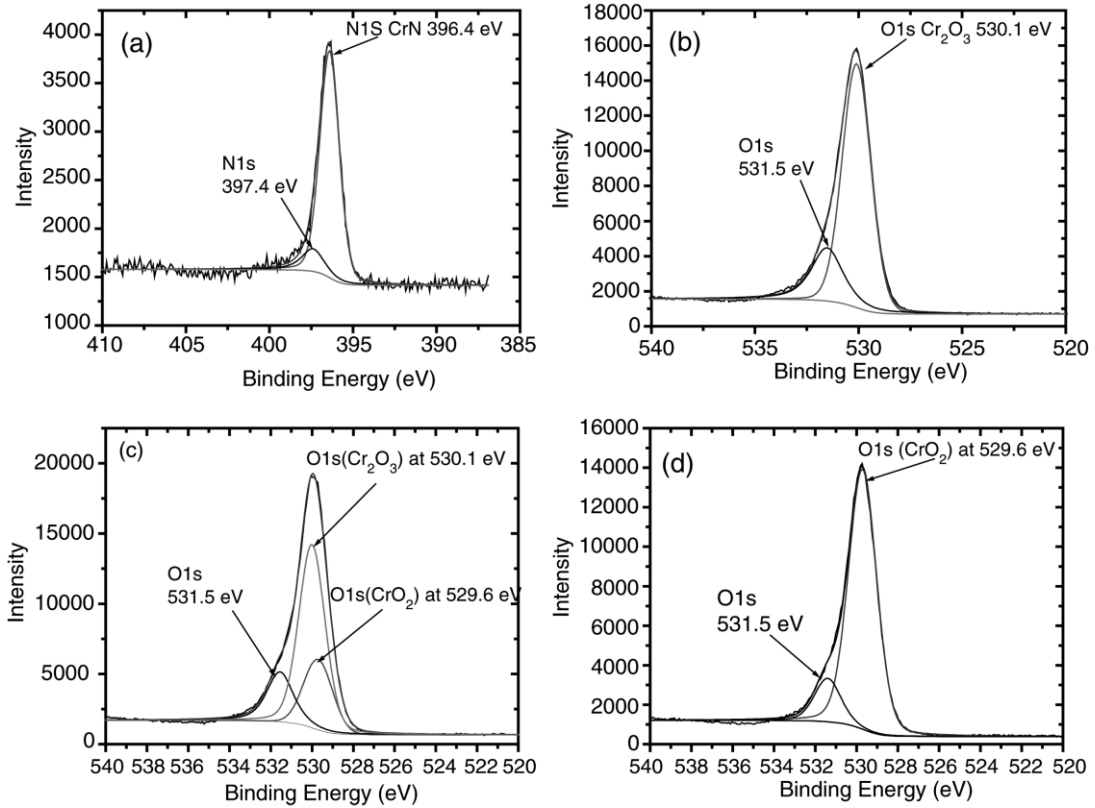


Fig. 1. N 1s and O 1s XPS spectra for chromium oxynitride sample deposited with 5 sccm dry air flow (a and b); 5 sccm (c) and 10 sccm (d) of air at 65% RH.

ity are increased the content of CrO₂ increases while the Cr₂O₃ concentration decreases. During sputtering in the compound mode, we have observed the existence of

two different compounds CrO₂ and CrN. In this mode of sputtering, relative humidity does not affect the proportions of the compounds formed and CrO₂ (90%)

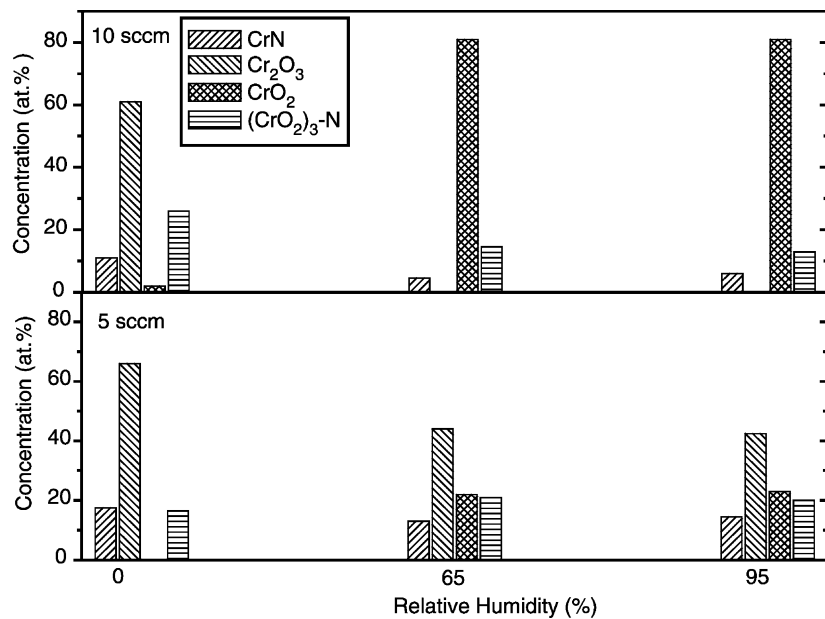


Fig. 2. Evolution of Cr and compound content determined by LEEIX spectroscopy and XPS as air flow and relative humidity.

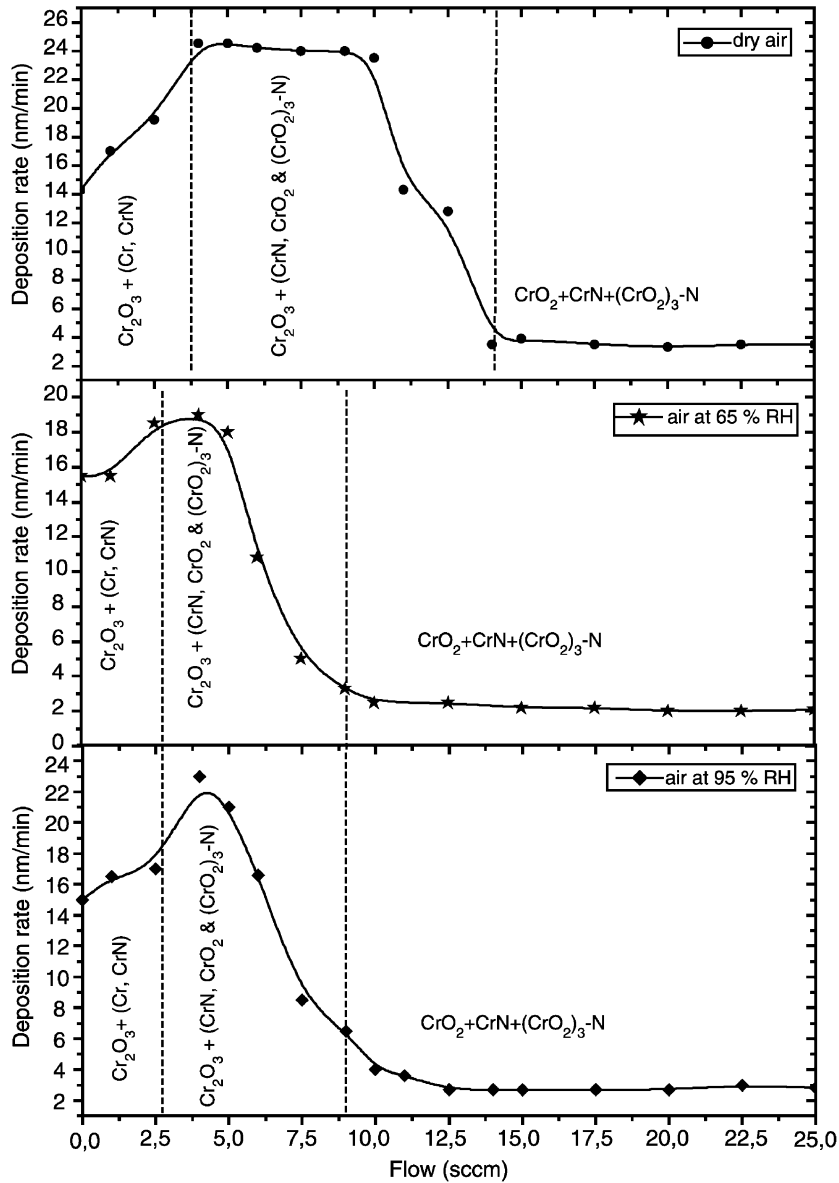


Fig. 3. Deposition rate of chromium oxynitride thin films vs. flow of dry air, air at 65 and 95% RH.

stoichiometry predominates in coexistence with low contents of CrN (10%). The Cr, O, N and H contents obtained by various techniques are given in Table 1.

The LEEIXS results are completed by XPS measurements of O 1s and N 1s peaks. In Fig. 1a and b, we present N 1s and O 1s XPS spectra from chromium oxynitride film deposited with 5 sccm of dry air flow and O 1s XPS spectra of the samples deposited with 5 sccm (Fig. 1c) and 10 sccm (Fig. 1d) of air at 65% RH. In Fig. 1a, the decomposition of N 1s peak clearly shows the existence of two components: a major component at 396.4 ± 0.1 eV attributed to N 1s from CrN in agreement with the literature value 396.6 ± 0.2 eV [10] and a second component at 397.4 ± 0.1 eV. Furthermore, the decomposition of O 1s peak (Fig. 1b)

reveals the presence of two peaks, the first at 530.1 ± 0.1 eV which corresponds to the O 1s from Cr_2O_3 also in agreement with the literature value of 530.2 ± 0.2 eV [10] and the second peak at 531.5 ± 0.1 eV.

In Fig. 1c, we observe clearly the existence of three O 1s components. A first component at 529.6 ± 0.1 eV and can be attributed to the O 1s coming from CrO_2 in agreement with the literature value of 529.3 eV [11]. The second component at 530.1 ± 0.1 eV corresponds to the O 1s from Cr_2O_3 and a third component at 531.5 ± 0.1 eV. In the case of the O 1s XPS spectra obtained from sample deposited with 10 sccm of air with 65% RH (Fig. 1d), we observe the presence of two peaks, at 529.6 ± 0.1 eV characteristic of CrO_2 and a peak at 531.5 ± 0.1 eV. The presence of the two peaks

N 1s (397.4 eV) and O 1s (531.5 eV) could be attributed to a different chromium compound containing nitrogen and oxygen like $\text{Cr}_x\text{N}_y\text{O}_z$ type.

The N 1s and O 1s peak areas are used to determine the stoichiometry of $\text{Cr}_x\text{N}_y\text{O}_z$ compound and were found to be $(\text{CrO}_2)_3\text{-N}$. It obvious from three CrO_2 grouping with a nitrogen incorporation which disturbs the O–Cr bond to give a satellite peak O 1s at 531.5 eV and another satellite peak N 1s at 397.4 eV. However, it is not known if this nitrogen is close or free in the CrO_2 networks. The percentage of $(\text{CrO}_2)_3\text{-N}$ present in each of the samples could be deduced from the percentages of the satellite peaks O 1s and N 1s and the content of $(\text{CrO}_2)_3\text{-N}$ varies according to the air flow and relative humidity (Fig. 2). From the variations of the concentration in $(\text{CrO}_2)_3\text{-N}$ (Fig. 2), we note that with 5 sccm air flow, the content of $(\text{CrO}_2)_3\text{-N}$ increases with detriment of Cr_2O_3 concentration according to relative humidity and reaches a maximum when the relative humidity reaches 65% RH. At 10 sccm of air flow, the content of $(\text{CrO}_2)_3\text{-N}$ decreases according to the relative humidity whereas the content of CrO_2 increases. The variations of the content of $(\text{CrO}_2)_3\text{-N}$ can be related to the amount of CrO_2 and nitrogen in chromium oxynitride thin films. At 5 sccm of air flow, the thin films that contain CrO_2 and nitrogen (>3%) give a significant content of $(\text{CrO}_2)_3\text{-N}$, on the other hand those that contain a low nitrogen content ($\pm 1\%$) give a small proportion of $(\text{CrO}_2)_3\text{-N}$. With air as a reactive gas, the deposition rate of chromium oxynitride thin films is also influenced by the relative humidity in air (Fig. 3).

In conclusion, relative humidity accelerates the formation of CrO_2 and $(\text{CrO}_2)_3\text{-N}$ with detriment of Cr_2O_3 while the content of $(\text{CrO}_2)_3\text{-N}$ is proportional to the nitrogen content in chromium oxynitride thin films.

4. Conclusion

The LEEIXS and XPS measurements provide useful information about the nature of the formed compounds. Indeed, XPS results revealed the presence of a compound other than CrN, Cr_2O_3 and CrO_2 determinate by the LEEIXS. This compound contains nitrogen and oxygen and it has a $(\text{CrO}_2)_3\text{-N}$ stoichiometry. Currently it is not known if this nitrogen is close to or free in CrO_2 network. In a metallic mode of sputtering, when the films contain a considerable nitrogen amount (>3 at.%), relative humidity favors the formation of $(\text{CrO}_2)_3\text{-N}$ with detriment of Cr_2O_3 phase whereas the quantity of CrO_2 is comparable with that of $(\text{CrO}_2)_3\text{-N}$. When the compound mode of sputtering is installed, the nitrogen quantity is very weak, not exceeding 1.5 at.%, and the content of $(\text{CrO}_2)_3\text{-N}$ decreases whereas the content of CrO_2 increases with an increase in relative humidity and is stabilized approximately 80%, when the relative humidity reaches 65%. In this deposition mode the Cr_2O_3 compound is not observed.

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