X-RAY EMISSION STUDIES OF CERAMIC THIN FILMS OBTAINED BY LOW-PRESSURE MAGNETRON SPUTTERING

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ABSTRACT

This work deals with spectroscopic characterization of ceramic thin films (chromium oxides and nitrides) deposited onto low-carbon steel by reactive magnetron sputtering. Among the x-ray emission methods, Low-Energy Electron Induced X-ray Spectrometry (LEELXS) was used to point out the composition and stoichiometry variations in the films and the possible concentration gradients when the deposition experimental conditions change. It allowed to show that over-stoichiometric oxides are formed when high oxygen flow rates are sent in the reactor. Other analytical methods were used to fully characterize these films. Under these conditions, it was possible to point out their complementarity and limitations. Particularly, chromium nitride deposits identified as CrN by x-ray diffraction, have shown that they always contain high proportions of oxygen.

INTRODUCTION

During the last decade, rapid development has occurred in the field of thin film technology due to the introduction of PVD techniques and especially of magnetron sputtering. Let us recall that:

(i) magnetron sputtering consists in removing the surface atoms from a solid target by means of ionic bombardment \((Ar^+)\) generated by a plasma. In such a standard, non reactive mode, the target material and the deposited film are, from a chemical point of view, virtually similar. Addition of a reactive gas in the reactor allows compounds of variable stoichiometry to be deposited on the substrate;

(ii) the corresponding process has specific advantages to obtain corrosion-resistant, wear-resistant, hard and decorative coatings at low substrate temperature.

Intimate relationships do exist between deposition parameters (gas nature, reactive/sputtering gas flow rate proportions, working pressure, power density, substrate bias) and film morphology, composition and properties. In order to establish such relationships, appropriate analytical techniques have to be used. In this field, the main characterization techniques commonly used are XRD for structure determination [1-3], XRFS and SEM for thickness evaluation [2, 3], XPS and AES for surface stoichiometry estimation [3-6] and, in some cases, RBS [7] and GDOS [6] for bulk composition determination and in-depth elemental profile obtention.

In the present work, film deposition was performed on low-carbon steel substrates by using a metallic target of chromium and a reactive atmosphere \((O_2, \text{ air, } N_2)\). The thickness of the films obtained in various experimental conditions was estimated mostly by XRFS and the
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characterization (chemical composition, stoichiometry) was investigated by LEEIXS. Such measurements were made in the short and long-wavelength regions by detecting Cr, Fe and Ni Kα radiations (XRFS), Cr and Fe Lαβ, O, C and N Kα radiations (LEEIXS). In both cases, x-rays were wavelength-dispersed by using appropriate analysing crystals (LiF, TIAP, OHM) or multilayer mirrors (OV 45). Depth probed by LEEIXS was controlled in the 5-100 nm range by varying the incident electron beam energy between 1 and 4 keV. Complementary data about film composition were obtained by XPS, AES and RBS and structural information by XRD.

EXPERIMENTAL.

* Thin film deposition

The deposition chamber is a home-made reactor [8] consisting mainly of (i) a AJA 320 magnetron equipped with a metallic target (Cr) and with a system allowing the sputtering gas (Ar) to enter into the chamber in the vicinity of the target, (ii) a gas entrance for reactive gases located nearby the substrate, (iii) a substrate-holder which may be polarized in the range from -100 to +150 V, the target to substrate distance being 100 mm. The reactor is pumped down to a base pressure of 1.5 \(10^{-6}\) Torr and the working pressure is comprised between 1 and 5 \(10^{-2}\) Torr. High purity nitrogen (99.998 %) and oxygen (99.999 %) were used as reactive gases.

* Film characterization

Film structure was determined by XRD with a Philips diffractometer equipped with a Cu anode tube and film thickness by XRFS with a Philips spectrometer using a Mo anode tube and a LiF (200) crystal. In this work, film thicknesses were estimated by considering for each film a density adjusted to its composition.

Bulk film composition and stoichiometry were investigated by LEEIXS. This method, less known than the preceding ones, was presented elsewhere [9-12] and will be briefly described here. It consists in bombarding the sample with a nonfocused electron beam supplied by a gas discharge tube working in the primary vacuum of the spectrometer and detecting the resulting x-rays with a conventional wavelength dispersive device. In this work, a TIAP crystal was used for dispersing O Kα, Cr Lαβ, Fe Lαβ radiations and a multilayer mirror (OV 45) for dispersing N Kα radiations. The probed depth (from 10 to 150 nm) depends on the primary electron energy (from 1 to 5 keV) and can therefore be chosen according to the chemical nature of the sample and the radiation considered. Because of the large area analysed (\(\sim 1\) cm²) the irradiated volume is large and as a consequence the method is very sensitive for detecting low energy radiations (particularly the Kα radiations of light clements: B, C, N, O, F) while using a low current density (0.2 mA·cm⁻²) to avoid sample damage.

Surface characterizations were performed by XPS or AES using either an SIA 200 RIBER or an VG spectrometer. The first one is equipped with a MAC 2 analyser, the second one with an hemispherical one (CLAM 2).
RESULTS AND DISCUSSION

* Characterization of chromium oxides

All the chromium oxide films deposited, whatever the experimental conditions used, are amorphous, which prevents from determining their structure, therefore their stoichiometry by XRD. In an attempt to solve this question, LEEIXS was used. Experiments were performed with 4 keV electrons, so that, the mean thickness probed is about 120 nm. Different chromium oxide films were deposited during identical times by progressively increasing the oxygen flow rate (expressed here as the percentage with respect to the total gas mixture (Ar and O₂) entering in the reactor) and using either a single gas entrance (a) close to the target for both Ar and O₂, or two separate gas entrances (b), the one (for Ar) close to the target, the other (for O₂) close to the substrate. Figures 1 (a) and (b) represent the variations of the O Kα / Cr Lα,β intensity ratio obtained by LEEIXS and the Cr Kα signal intensity obtained by XRFS for different chromium oxide films, as a function of the oxygen flow rate. Figures 1(a) and 1(b) concern the results obtained for single and separate gas entrances respectively. In the first case (a), the Cr Kα signal intensity which is directly proportional to the film thickness decreases dramatically while the O Kα / Cr Lα,β ratio reaches rapidly a plateau when the oxygen flow rate increases between 0 and 10 %. For very low oxygen flow rates, the target which is scarcely oxidized is easily sputtered and the films obtained correspond mainly to a mixture of metallic chromium and chromium oxide. When the target becomes more oxidized its sputtering becomes more and more difficult, the composition of the film deposited changes and its corresponding thickness decreases. Nevertheless, the thickness of the films analyzed in this study is never less than about 150 nm. When the oxygen flow rate is over 10 %, the films obtained are over-stoichiometric compared to Cr₂O₃. In the second case (b), when both gases enter separately in the reactor, target poisoning only appears when the oxygen flow rate reaches 20 to 25 % (Fig. 1 b). Indeed, in this range, the film thickness decreases dramatically and the films change abruptly from under to over-stoichiometric composition.
When dry air is used as one gas playing both roles of sputtering and reactive gas, the composition of the films deposited is constant and close to that of stoichiometric Cr$_2$O$_3$ as shown in figure 2, whatever the experimental conditions used. This figure represents the variations of the O$_{K\alpha}$/Cr$_{L\alpha,\beta}$ ratio characterizing the films themselves and of the intensity of the Fe$_{L\alpha,\beta}$ signal due to the substrate, for various films deposited during increasing times. The signal emitted by the substrate decreases rapidly when the deposition duration increases. Indeed, as the film thickness increases, the incident electrons which are absorbed by the film penetrate less and less into the substrate. The maximal electron range inside Cr$_2$O$_3$ determined from Feldman's and Reed's relations [12] is estimated on average at about 120 nm for 4 keV electrons. Under these conditions, assuming that the deposition rate is constant, the latter may be estimated, from figure 2, at about 1.2 μm/h.

Film composition variations pointed out by measurement of the O$_{K\alpha}$/Cr$_{L\alpha,\beta}$ ratio may also be inferred from the chemical effects presented by the Cr$_{L\alpha,\beta}$ emission band which is associated with electron transitions from the valence band to Cr$_{L_{2,3}}$ levels. Figure 3 shows the Cr$_{L\alpha,\beta}$ band characteristic of various samples: (a) metallic chromium, (b) chromium oxy-nitride (obtained with separate gases and with a nitrogen flow rate of 20 %), (c) under-stoichiometric chromium oxide (obtained with separate gases and with an oxygen flow rate of 20 %), (d) stoichiometric oxide (obtained with air), (e) over-stoichiometric oxide (obtained with separate gases and with an oxygen flow rate of 40 %), (f) stoichiometric Cr$_2$O$_3$ thermal oxide. As can be seen, an energy shift of the band maximum occurs when chromium atoms gain a more and more electronegative surrounding. In the present case, the energy shift is larger as the number of oxygen atoms per chromium atom is larger. It is the reason the over-stoichiometric oxide presents the largest energy shift. The shape of the corresponding spectrum (e) in which the L$_\alpha$ and L$_\beta$ bands are not separated, is probably characteristic of a great structural disorder. A similar study was performed by XPS to point out the stoichiometry variations of the films according to the experimental conditions used for their deposition. Figure 4 shows Cr 2p1/2,3/2 spectra of chromium oxide films obtained with various oxygen flow rates: (a) 1 %, (b) 5 %, (c) 10 %, (d) 25 %, (e) 40 %, the sputtering and reactive gases entering into the reactor by the same way.
Spectra (a) and (b) correspond mainly to metallic chromium (574.6 eV), the shoulder at 576.7 eV is due to oxidized chromium. Such spectra correspond to oxides considered as under-stoichiometric from LEEIXS analyses. Spectra (c) and (d) have their maximum, characteristic of Cr$_2$O$_3$, located at 576.7 eV with a weak shoulder (574.6 eV) due to metallic chromium and spectrum (e) presents a single peak at 576.7 eV. According to LEEIXS results, the corresponding oxides were considered as stoichiometric (c) and over-stoichiometric (d) and (e). It may be surprising that XPS which is well-known for its sensitivity to chemical effects does not show any difference in the Cr 2p spectra between Cr$_2$O$_3$ and over-stoichiometric oxides while LEEIXS does. The only explanation is given by the large difference in depths probed by both methods (120 nm by LEEIXS, only 7 to 8 nm by XPS).

In addition, a quantification attempt was performed using over-stoichiometric samples by XPS and RBS, the latter method characterizing the bulk. As expected, the results obtained are quite different and lead respectively to the following stoichiometric formula: Cr$_2$O$_{3.8}$ (XPS results concerning the top surface) and CrO$_{4.4}$ (RBS results concerning an average composition characteristic of the whole film).

Among these spectroscopic methods, it appears, that LEEIXS is quite able to detect composition variations in a sample. Another example illustrating these capabilities concerns chromium oxides deposited for 10 min on low-carbon steel substrates using air and polarizing the substrate at different bias between -150 and +100 V. The film thickness variation estimated through the
Cr K$_{\alpha}$ signal measurement as a function of bias is shown in figure 5 a. In this same figure, the maximal range R$_p$ of electrons having a kinetic energy comprised between 1.5 and 4 keV is represented. It was determined by considering the average value calculated from Feldman's and Reed's equations [12]. All the analyses performed are represented by black points in figure 5 a. Thickness is large for films deposited with a high negative bias, then, it decreases quasi-linearly when the bias used is between -30 and +100 V. These measurements point out the very strong effect of bias towards deposition rate. Furthermore, LEEIXS studies performed with electrons of variable energy in order to probe variable thicknesses show composition variations when bias changes from -150 to +100 V. In particular, the intensity measurement of the Fe L$_{\alpha}$ signal emitted by the substrate when the samples are bombarded with electrons of 1.5; 2; 2.5; 3 and 4 keV is represented in figure 5 b. The curve corresponding to 4 keV electrons points out the presence of iron in all the samples analyzed. Indeed, such electrons are sufficiently energetic to go across the largest films and excite the substrate as indicated in figure 5 a. On the other hand, electrons of lower energy cannot all cross the oxide film and reach the substrate. Considering data of figure 5 a, it can be estimated that the analyses corresponding to black points surrounded with a circle and located on the left side or at the limit of the curve representing oxide thicknesses should not indicate the presence of iron. Now, figure 5 b shows (points surrounded with a circle) that iron is always found whatever the incident energy used for the electrons (between 1.5 and 3 keV) and whatever the sample considered, except that obtained with a bias of -150 V. These observations indicate that iron atoms migrate from the substrate towards the oxide film mainly when the substrate is positively polarized. To confirm these results, in-depth elemental AES profiles were plotted for two oxide films respectively deposited with a bias of (a) -30 V and (b) +100 V, while sputtering them with Ar$^+$ ions. Figure 6, which shows these profiles, points out a slight diffusion of iron into chromium oxide films for sample (a) and a very strong diffusion for sample (b). This confirms the LEEIXS results.
Fig. 6: AES depth profiles (Cr and Fe) plotted from chromium oxide films deposited with a bias of -30 V (a) and +100 V (b).

* Characterization of chromium nitrides

Chromium nitride films were deposited after baking out the reactor for 24 h at 180°C to desorb water vapour chemisorbed on the walls. Nitrogen was used as reactive gas and entered into the reactor close to the substrate. XRD characterization of the films deposited shows that they correspond to well-crystallized CrN (Fig. 7). As the film thickness is about 1 μm, the peaks characteristic of the substrate (Fe) are also detected.

Fig. 7: XRD spectrum characteristic of a chromium nitride film deposited onto low-carbon steel.
However, LEEIXS analyses point out the presence of oxygen in all the CrN samples analyzed, while no oxidized chromium phase is detected by XRD. Figure 8 represents the film thickness variations determined by XRFS through the Cr K$_\alpha$ signal measurement and the variations of the N K$_\alpha$ / Cr L$_{\alpha,\beta}$ and O K$_\alpha$ / Cr L$_{\alpha,\beta}$ ratios determined by LEEIXS as a function of the nitrogen flow rate. As in the case of the chromium oxide formation, the deposition rate slows down when nitrogen flow rate increases and a jump is observed in the 20-30% range. This slowing down is also due to cathode poisoning. The N K$_\alpha$ / Cr L$_{\alpha,\beta}$ ratios show a nitrogen saturation of the film beyond 20% of reactive gas introduced in the reactor, while the O K$_\alpha$ / Cr L$_{\alpha,\beta}$ ratios indicate a constant introduction of oxygen in the films.

![Graph showing film thickness variations and intensity ratios](image)

Oxygen presence in chromium nitride films deposited by reactive sputtering appears to be unavoidable as far as the limit pressure inside the reactor is not in the UHV range. In the experimental conditions used, oxygen presence in the films is due to the dissociation in the discharge of water vapor physisorbed on the reactor walls and to the very high reactivity of oxygen compared to that of nitrogen. Even if oxygen presence in nitride films is scarcely mentioned in the literature [13], it might be a general phenomenon. Indeed, we have analyzed by LEEIXS, then by XPS a silicon sample coated with TiN for microelectronics applications, the latter being deposited by reactive sputtering. Whatever the analytical method used, we have found oxygen in this sample. Figure 9 shows XPS spectra of the Si/TiN sample, (b) as received and (c) etched for 2 hours by Ar$^+$ sputtering inside the XPS spectrometer until oxygen concentration is stabilized. As a comparison, spectrum (a) corresponds to CrN deposited in the laboratory and etched in the spectrometer for 2 hours. On all these spectra, a significant oxygen peak appears. In the case of the (c) sample it corresponds to 25 at. % oxygen.

![Figure 8: Thickness variation (Cr K$_\alpha$ measured by XRFS), O K$_\alpha$ / Cr L$_{\alpha,\beta}$ and N K$_\alpha$ / Cr L$_{\alpha,\beta}$ intensity ratios (LEEIXS) versus nitrogen flow rate percentage, Ar and N$_2$ getting in the reactor through 2 separate entrances.](image)
CONCLUSION

The analytical examples given in this work show the particular capabilities of the LEEIXS method. As the sample excitation is very efficient, partly because of the large volume irradiated, the method is quite efficient for analysis of elements emitting long-wavelength radiations and particularly light elements (B to F). When the dispersive system uses a multilayer mirror, nitrogen detection is rather easy despite the strong absorption of N Kα radiation by the counter window. One of the major interests of the method consists in probing intermediary depths (100 to 200 nm depending on the sample nature) between the top surface and bulk. Finally, by varying the incident electron energy it is possible to change the depth probed and to gain information about composition gradients inside the sample analysed.

REFERENCES