Calibration of nitrogen content for GDOES depth profiling of complex nitride coatings

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Quantitative GDOES studies in protective coating materials (oxides, nitrides, oxynitrides, *etc.*) are severely limited by the lack of certified standards containing known amounts of oxygen and/or nitrogen. In this work, we propose an alternative method for nitrogen quantification using as calibration samples, a series of deposited nitride coatings whose composition is pre-established by absolute quantitative measurements with Rutherford backscattering spectrometry. This calibration approach was successfully applied to the study of different complex nitride systems as nanometric multilayers or nanocomposite, and to enlarge the application of GDOES to a wider range of practical applications.

Introduction

Glow discharge optical emission spectroscopy (GDOES) has proven to be, in the last years, a useful technique to perform depth profiling studies on thin films in an accurate and fast way.[1–8] However, there are still severe limitations of the technique regarding quantitative analysis of nitride, oxide or carbide coatings. The study of these types of coatings is an important technological issue, due to their extensive use either as hard protective coatings for mechanical parts and tools, as optical coatings for lenses and architecture glass panels, barrier contacts for microelectronics, or in biomedical prosthesis. The major problem for obtaining quantified analysis in such materials resides in the lack of reference materials containing light elements such as H, N, O and C. Therefore, any advance in the preparation of reference materials with known composition or in the development of quantification standards would be considered a major improvement in the applicability of GDOES. Recently, two papers have been published regarding this issue. Hodoroaba *et al.*[9] have carried out a very interesting round robin exercise in the frame of the EC Thematic Network on Glow Discharge Spectroscopy for Spectrochemical Analysis (GDS-Net)[10] to analyze nitride layers. Baunack *et al.*[11] have compared results of GDOES and Auger electron spectrometry (AES) to quantify the nitrogen content of Ta–N, Ta–Si–N and Cr–N systems.

In the present work, we propose a simple method to quantify nitride layers by GDOES. In a first step, we have prepared by magnetron sputtering deposition a series of chromium nitride coatings with different nitrogen content to be used as calibration samples. There is a list of prerequisites for a coating to be considered a good standard.[9,12] First, it must be rigid and present a flat and smooth surface. Moreover, the film must support the operational conditions, mainly in terms of thermal stability. Finally, homogeneous composition, both laterally and in depth, is desirable as well as a minimum coating thickness to ensure reaching a plateau in the intensity voltage. This minimum thickness would therefore depend on the erosion rate of the material. In order to quantify the nitrogen content in the coatings, we have performed Rutherford backscattering spectrometry (RBS) experiments on the samples. RBS is a non-destructive technique that is commonly employed for in-depth compositional analysis of metal and metal nitride layers. The technique presents a high elemental sensitivity for heavy elements in a light matrix (<1 at%), a depth resolution in the nm range ($\sim$5–10 nm) and it provides absolute quantification without standards. Once the nitrogen content of the samples is established by RBS, we used some of the coatings to improve the nitrogen calibration line of GDOES. Finally, we have applied such calibration to GDOES nitrogen content quantification in a series of complex nitride systems, proving that the method works fine both for thick (>100 nm) and thin (<100 nm) layers.

Sample preparation by sputtering magnetron

Chromium nitride coatings (CrN_x) were deposited on single-crystal Si(100) wafers by DC planar magnetron sputtering. It consists of a circular planar cathode, 7.5 cm diameter, placed in front of the substrate holder, at a distance of 6.5 cm. The base pressure of the chamber was 2×10^{-4} Pa, approximately, and the working pressure was in the range 0.16–0.23 Pa. Other details of the sputtering system have been described previously.[13] Prior to deposition, 20 min of pre-sputtering was performed in order to remove the metal–nitride layer of the cathode, due to previous deposits and to achieve steady plasma conditions. The chromium target is a commercial target of purity 99.95%. A mixture of Ar (99.999%) an N_2 (99.9992%) gases was introduced in the vacuum chamber. The N_2 relative flow rate f_N = $[N_2]/[N_2 + Ar]$ was varied by changing simultaneously both Ar and N_2 flow rates. As can be observed in Table 1, the relative nitrogen flow ranges from 2%

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Table 1 List of deposited CrN_x samples and data of RBS analysis. The thicknesses of the coatings were obtained by SEM measurements

Sample	N_2 flow (%)	Thickness/nm	Cr (at%)	X = N : Cr
#0	2	1466	100 ± 1	0.00
#1	5	1398	99 ± 1	0.01
#2	10	1393	96 ± 1	0.04
#3	15	1239	83 ± 1	0.20
#4	20	1278	82 ± 1	0.22
#5	25	1193	75 ± 1	0.33
#6	30	1092	71 ± 1	0.41
#7	40	964	60 ± 1	0.67

(sample #0) to 40% (sample #7) of the total flow rate (f_{tot} = 11 sccm). The thickness of the layers was obtained by cross-sectional observation using a Hitachi S-2700 scanning electron microscope.

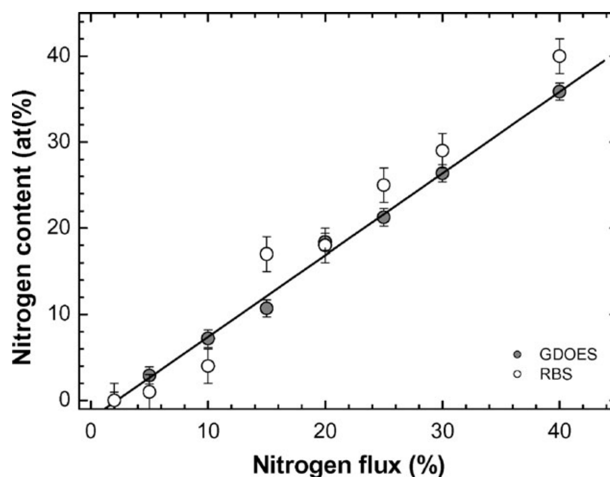

Fig. 2 Nitrogen incorporated in the CrN_x samples (in atomic%) *versus* the nitrogen flux inside the deposition chamber. The open symbols represent RBS results and the closed symbols GDOES results.

Nitrogen content quantification by RBS

The series of CrN_x samples deposited by magnetron sputtering were analyzed by means of RBS using 1.7 MeV He^+ ions at a scattering angle of 170°. The measurements were performed with the 5 MV HVEE Tandetron at the Centro de Micro-Análisis de Materiales[14] of Universidad Autónoma de Madrid. Fig. 1 shows the acquired spectra for representative samples. A monotonous reduction of the Cr content in the samples, with increasing nitrogen flux present in the deposition, can be observed. These results were quantified using the program SIMRA[15] and are presented in Table 1, together with the nitrogen content expressed in terms of the ratio between the nitrogen and chromium concentrations (X = N : Cr). It is well known that RBS presents high sensitivity to heavy elements and a lower cross-section for light elements. Therefore, the N content is derived here from the deficiency of Cr. This approach is not valid in the presence of other light elements like oxygen. In our case, the growth is done in a clean environment and the eventual incorporation of oxygen has been ruled out, at least up to the detection limits of the technique (<1 at%). Note that the sample grown under the lowest N_2 flow (2%) is 100% Cr.

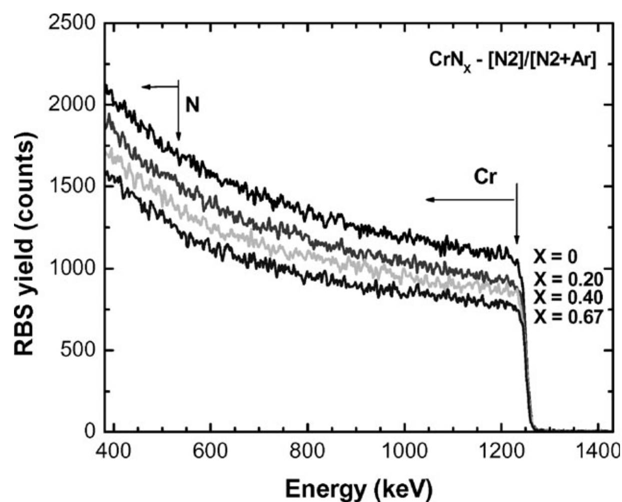

Fig. 1 RBS spectra of CrN_x deposited samples with x = 0, 0.2, 0.4 and 0.67. Experiments were performed at 1.7 MeV He^+ ions and at a scattering angle of 170°.

In Fig. 2, the nitrogen content, as derived from RBS measurements, is plotted (open circles) *versus* the relative nitrogen flux. A linear relation of practically 1 : 1 was found between the nitrogen introduced in the deposition chamber and the nitrogen incorporated in the nitride coatings. As we will describe below, the same relationship is obtained after the calibration of nitrogen by GDOES (closed circles in Fig. 2).

Once the composition of the coatings is characterized by RBS, we proceed to introducing these samples as calibration samples in the nitrogen calibration line of GDOES. We must note that such a procedure requires a constant matrix independent emission yield. The constant emission yield approach has been extensively discussed in a recent review by Bengston *et al.*[16] The depth of that discussion exceeds the aim of this technical note.

GDOES calibration of nitrogen

A commercial Jobin Yvon RF GD Profiler[17] was used for the GDOES analysis of the samples. The setup was equipped with a 4 mm diameter anode, operating at a typical radio frequency discharge pressure of 650 Pa and power of 40 W. A collection rate of 200 points s^{-1} was fixed to measure all the samples. Quantified profiles were obtained automatically using the standard QUANTUM Intelligent Quantification (IQ) software.[17] The setup was calibrated using standard materials of known composition. The calibration lines represent the intensity measured by GDOES for an element i (I_i), as a function of the element concentration (c_i), multiplied by the sputtering rate of the standard (q).[6,18] The IQ software calculates the sputtering rate (sputtered mass per time), of the materials from the erosion rate (sputtered depth per time) and the material density. In order to simplify the procedure, the sputtering rate is commonly replaced by the relative sputtering rate ($q_{relative}$).[19]

Table 2 List of samples used in the nitrogen multi-matrix calibration

Standard	Mayor element (wt%)	Nitrogen content (wt%)
12MB.S.CA2A	Iron 97%	0.015
A/8	Iron 99%	0.0
CE 650	Aluminium 38%	0.27
HS3K	Iron 59%	0.019
NSC3S	Iron 62%	0.61
RH18/17	Iron 67%	0.0
RH32/6	Iron 33%	0.15
TiN coating	Titanium 77%	23

The relative sputtering rate is defined as the ratio of the absolute sputtering rate of the measured standard and the sputtering rate of a reference standard (pure iron in our case).

$$I_i = f(c_i q_{\text{relative}})$$

$$q_{\text{relative}} = \frac{q}{q_{\text{ref}}}$$

Initially, a multi-matrix calibration line using the standards described in Table 2 was applied. However, it was clear that such a set of standards mainly covered nitrogen weight contents below 1%. Only the stoichiometric TiN coating gave high nitrogen content calibration data of 23 wt% (or 50 at%). This last material was provided by the company CERATIZIT and although it is not a certified reference material, they have a precise procedure to manufacture in a reproducible manner the correct values of composition and density (5.30 g cm^{-3}).

In order to use the CrN_x coatings as intermediate nitrogen content samples in this calibration, the relative erosion rate (in μm min^{-1}) and the density of the samples are required. The absolute erosion rate of the CrN_x coatings can be derived straightforwardly, once the thickness of the layer is measured (see Table 1). After performing a GDOES experiment on each sample, the thickness of the layer divided by the time needed to sputter the whole layer provides the absolute erosion rate of the coatings. On the other hand, the density of the samples is directly estimated by the algorithms of the IQ software. The basis of the algorithm is described in the paper of Payling *et al.*[20] In short, the main idea behind the algorithm is that the sample contains pure elements and compounds with their own density. Using information about the electronegativity of the elements, the algorithm seeks compounds and, subsequently, introduces them in the density equation as individual elements. Both the erosion rate and the calculated density are plotted *versus* the nitrogen in Fig. 3.

The density decreases linearly with the nitrogen flux from a value of 7.19 g m^{-3} obtained for sample #0 (Cr_{100}), to a value of 6.3 g cm^{-3} for sample #7 ($Cr_{60}N_{40}$). This linear decrease predicts a density of 6.05 g cm^{-3} for stoichiometric CrN. The density values for pure Cr and CrN are 7.14 and 5.9 g cm^{-3}, respectively.[21] Therefore, the algorithms of the IQ software correctly compute the density of the deposited nitrides. The absolute erosion rate follows the same trend, decreasing with increasing nitrogen flux. Finally, as we mentioned above, the relative erosion rate is defined as the ratio of the absolute

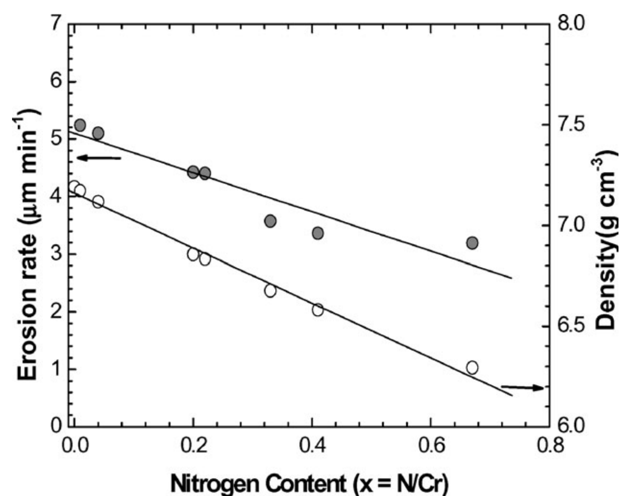

Fig. 3 Absolute erosion rate and density of the CrN_x deposited samples as a function of the nitrogen flux in the deposition chamber.

erosion rate q and the erosion rate of a reference standard (pure iron in our case with q_{ref} = 5.65 μm min^{-1}).

From the series of CrN_x deposited samples, we have selected the lowest nitrogen content sample (#0), two intermediate nitrogen content samples (#4 and #5) and the highest nitrogen content sample (#7) to be added to the nitrogen calibration line. For all the deposited samples, a homogeneous intensity of nitrogen within the coating was observed. This constitutes a prerequisite for such samples in order to be used as calibration samples. As can be observed in Fig. 4, the four selected CrN_x coatings nicely matches with the certified standards in a linear calibration curve, with a correlation coefficient r^2 = 0.9963.

The remaining CrN_x deposited coatings were also measured by GDOES, in order to corroborate in a first stage this calibration. In Fig. 2, it can be appreciated how all the GDOES results on the CrN_x coatings (closed symbols) are very close to the ones obtained by RBS. A linear 1 : 1 relation between the nitrogen flux in the deposition chamber and the nitrogen incorporated in the films is again obtained.

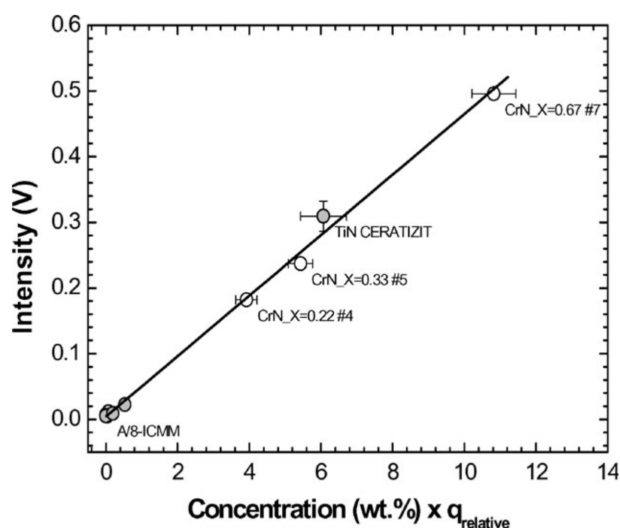

Fig. 4 Calibration lines for nitrogen. The closed circles represent certified standard materials and the open circles the CrN_x coatings.

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As reported in ref. 22, this linear relation holds until 40% nitrogen flux, reaching saturation for higher fluxes. It is important to note that no significant signal of oxygen was detected during GDOES experiments, supporting the approach of estimating the N content from the deficiency of Cr in the RBS profiles.

Application of the calibration to complex nitride systems

As a final step, we have tested the above proposed nitrogen calibration, based on CrN_x coatings, to the study of more complex nitride systems. These coatings were presented and discussed in previous work,[8] comparing the results with those obtained by RBS. In Fig. 5a, a trilayer CrN–AlN–CrN deposited on a silicon substrate is shown. The quantified CrN layers were estimated to be stoichiometric (Cr = N = 50%) while the intermediate AlN was slightly over-stoichiometric (N = 56%). Both results were confirmed by RBS measurements performed after the GDOES experiments, within a 5 at% accuracy. Within the AlN layers, the waving behaviour of the nitrogen and aluminium profiles is due to interference phenomena as described in ref. 8. It is very interesting to note that the nitrogen quantification can also be properly applied to nanometric nitride layers. In Fig. 5b, the quantified GDOES profile of a multilayer system, consisting on 50 bilayers of 10 nm AlN and 10 nm CrN, is also shown. Every single layer can be detected by the oscillations of the metal intensities. Although the amplitude of the oscillations of the signals of both metals decay with depth and saturate at a value of ~25 at%, the nitrogen concentration properly remains at the correct value of ~50 at%. The small oscillations in the nitrogen content are related to the changes in the stoichiometry of CrN and AlN films, as observed in Fig. 5a. Finally, we show a quantified result on a nitride coating not based on CrN_x structures. The quantified profile of a $TiSi_xN$ ternary coating, deposited using the filtered cathodic arc technique, is presented in Fig. 5c. The stoichiometry of the deposited film, as measured by X-ray photoelectron spectroscopy (XPS), was found to be of 10 at% Si and 42 at% N, while after the calibration the GDOES analysis returned 10 at% Si and 48 at% N, at a depth of 100 nm. The lower nitrogen content measured by XPS is related to a higher oxygen contribution from the outmost surface. A pre-sputtering of the sample was performed to remove surface contamination but some oxygen remains in the coating.

As a conclusion, in this work we propose a relatively easy way of calibrating GDOES for nitrogen analysis to be applied in a wide number of systems of technological interest. We estimated that an accuracy of 5 at% could be obtained for the systems studied, when an error below 10% would be considered acceptable in practical use. The method is based on the deposition of nitride coatings as calibration samples[23] and a comparative analysis with an absolute technique, such as RBS. A similar calibration could be used to study oxides or carbides. The major problem in this case would be the inaccuracy in the calculation of the density of the materials. Quantification of H using hydrogen-containing samples could be more difficult.

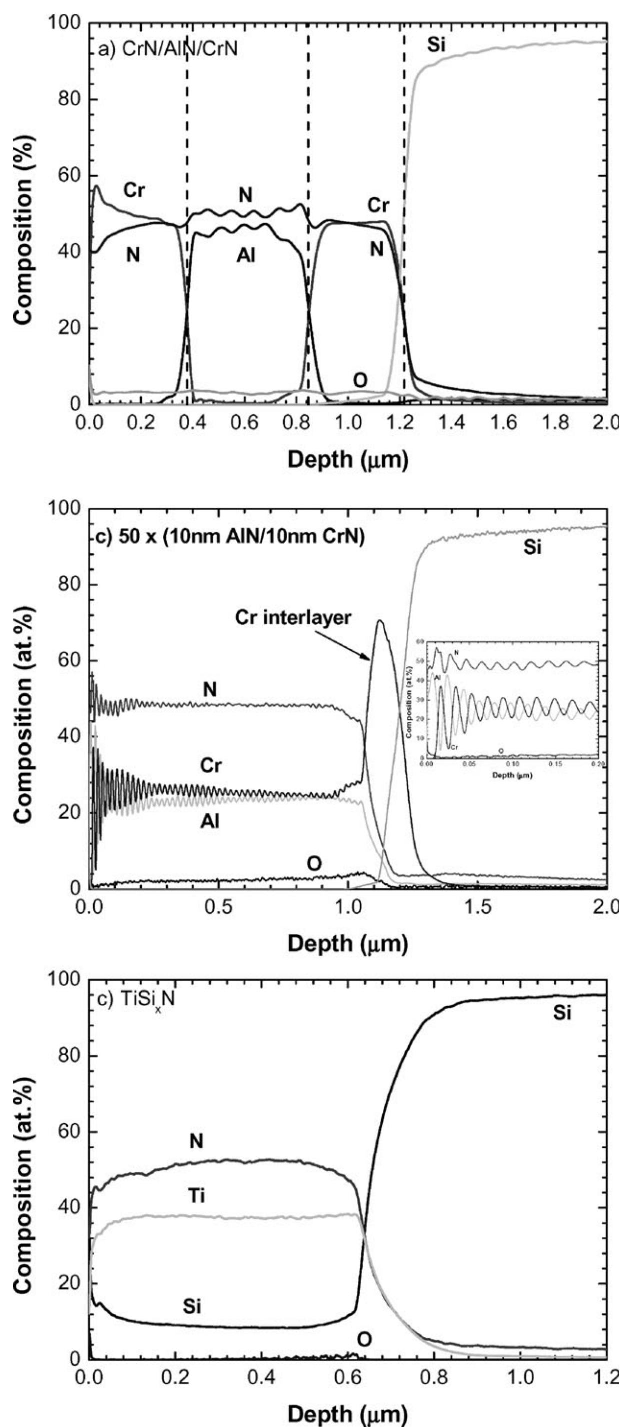

Fig. 5 Quantified GDOES depth profiles of (a) trilayer CrN–AlN–CrN, (b) multilayer 50 × (10 nm AlN–10 nm CrN) and (c) $TiSi_xN$ coatings.

Firstly, due to the well known effects of hydrogen on the emission lines in GD spectra,[24] and secondly because in that case RBS is not suitable and a combination of GDOES with elastic recoil detection analysis (ERDA) techniques would be needed. Other quantification alternatives, such as the layer mode proposed by Nelis *et al.*,[25] would be of great interest to be compared with our calibration method.

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