Compositional depth profiling analysis of thin and ultrathin multilayer coatings by radio-frequency glow discharge optical emission spectroscopy

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Abstract

In most of the industrial applications of multilayer coatings, a detailed knowledge of the interlayer structure and the interfaces is needed. In comparison with standard surface analysis techniques (SIMS, XPS, AES, etc.), depth profiling by radio-frequency glow discharge optical emission spectroscopy (rf-GDOES) provides rapid information, with a high depth resolution, about the multilayer composition. In rf-GDOES analysis, the depth resolution mainly depends on the roughening induced during the sputtering, the resulting crater geometry and sputtering of material re-deposited on the crater wall. In this work, we have isolated the contribution of these effects in the depth resolution of metal and metal nitride multilayer coatings.

The importance of these effects has been firstly tested on multilayer stacks consisting of three alternating metal or nitride layers, typically of 500 nm each. The profiles of materials with high sputtering rate become less affected than material with low sputtering rate due to lower mixing of the layers. The contribution of these factors increased during the analysis of thinner multilayer coatings (~ 100 nm). After reversing the order of the layer elements, completely different profiles were measured, confirming the role of the differences in sputtering rate and crater shape.

Finally, in order to evaluate the depth resolution function of the GDOES technique, ultrathin metal chromium and aluminium nitride layers of 5 nm have been buried at different depths in a metal titanium and chromium nitride matrix, respectively, up to a thickness of 2 μm. The markers were properly resolved both near the surface and deeply embedded in the matrix, demonstrating the excellent capabilities of the GDOES technique to detect very thin films in the nanometric range.
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1. Introduction

Metal nitride coatings have been investigated since long due to their outstanding characteristics, such as high chemical stability, high hardness and wear resistance, good adhesion to metal substrates, metallic lustre, etc., which turn them into excellent candidates for many technological applications (protective and decorative coatings, anti-diffusion barrier for microelectronic contacts, etc.). More recently, these materials are deposited in complex multilayer structures (superlattices) in order to obtain hardness values in the range of the so called 'super-hard' materials (i.e., hardness >40 GPa). The achievement of these hardness values entails strict requirements regarding the nature of the materials (with different elastic

constants), the thickness of the individual layers (in the range of a few nanometres) and the crystalline coherence and abruptness of the interfaces [1,2]. Under this concept, hardness values close to diamond have been reported for multilayers stacks of TiN/NbN, TiN/VN, etc., with super-lattice period of some 5–10 nm [3].

In the synthesis process, the analysis of the individual layers and interfaces of these materials, with nanometric resolution is essential to attain the expected hardness properties of the coatings. Surface analytical techniques, namely X-ray photo-electron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS), can be used to obtain the compositional profile of these multilayer structures. Although they can offer detailed chemical information at atomic level, the major difficulty with these techniques is the long time of analysis, associated to the need of ultrahigh vacuum as well as to the low sputtering rates. Alternatively, glow discharge optical emission spectroscopy

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(GDOES) [4,5] can be used advantageously for depth profiling of nanometric multilayer systems since it combines the ability to provide the atomic composition of the layers [6–11] with a high depth resolution (better than 10 nm) [12–16]. Since GDOES operates in the glow discharge regime, the discharge pressure is relatively high (0.2 Pa) and the sputtering process is very fast (more than 1 μm min^{-1}).

Despite of these advantages, GDOES is not exempt of problems, particularly those associated to the mixing of layers as a consequence of the special shape of the crater produced by the sputtering of the substrate during the depth profiling [17]. As discussed in previous papers for the case of metal coatings [18,19], three different factors may contribute in a greater or lesser extent to the degradation of the depth and interface resolution in monolithic and very thin multilayer systems: (a) the surface roughness of the crater bottom, (b) the edge well around the crater and (c) the re-deposition at the crater wall of the previous sputtered material. All these effects are dependent on the sputtering parameters, particularly the sputtering rate of the material under study, and they are magnified with the depth of the analysed layer. This problem has been found to seriously affect the profiles of the thin multilayer coatings made of different metals (Ti, Cr and Al), giving rise to a strong degradation and mixing of the oscillating signals of the individual metals as we penetrate deep into the layers.

In this paper, we have extended our research work to alternating layer structures consisting of two metal nitrides, CrN and AlN, deposited by sputtering magnetron on silicon substrates. The materials have been chosen because they are used typically in protective and decorative coatings where depth resolution is a major issue [20]. We have analysed the above crater effects on the interface resolution, both in thick coatings (trilayers of about 400 nm each) and in very thin multilayers coatings (up to 50 bilayers of 10 nm). The results are compared to those obtained on the corresponding pure metal coatings, with a more simple composition. To our knowledge, no systematic studies have been carried out to date on this problem.

2. Experimental

The deposition of the multilayers was performed in a conventional balanced planar DC magnetron sputtering system using two sputtering sources, placed at 6.5 cm away from the substrate holder. The holder can be rotated to face the sample to each sputtering source and is provided with automatic position controller in order to control the deposition time for each layer. The deposition rates of the specimens were 125 Å min^{-1} for

Table 1
Description of the studied coating systems

Coating	Thickness
Cr/Al/Cr	450 nm/400 nm/450 nm
CrN/AlN/CrN	380 nm/470 nm/380 nm
Multilayers Ti/Cr	10×(70 nm Ti/150 nm Cr)
Multilayers CrN/AlN	10×(40 nm CrN/90 nm AlN)+100 nm Cr
AlN markers in CrN	10×5 nm AlN in 2 μm CrN+100 nm Cr

All coatings were deposited onto (100) silicon.

Table 2
Sputtering rates of the different studied coatings

Coating	Sputtering rate (μm min^{-1})
Chromium	5.3
Aluminium	5.4
Titanium	3.5
Silicon	3.4
Chromium nitride	4.2
Aluminium nitride	2.5

titanium, 250 Å min^{-1} for chromium and aluminium, 135 Å min^{-1} for chromium nitride and 50 Å min^{-1} for aluminium nitride. Details of the sputtering system have been described previously [21]. The base pressure was approximately 2×10^{-4} Pa and the working pressure was in the range 0.16–0.23 Pa. The cathode power was held constant at 100 W. No bias voltage was applied to the substrate holder by a DC power supply. Prior to deposition, 20 min of pre-sputtering have been performed in order to remove the metal-nitride layer of the cathodes due to previous deposits. The metal targets used were commercial targets of very high purity. A mixture of Ar (99.999%) and N_2 (99.9992%) gases was introduced in the vacuum chamber. The N_2 relative flow rate (fr$_{N2}$) was fixed to be 70% of the total flow rate (f_{tot}=11 sccm) by changing simultaneously both Ar and N_2 flow rates. The multilayer nitride coatings used to study the bias influence were deposited with an interlayer of Cr, 100 nm thick, to improve the adherence. Table 1 gives a summary of the coatings studied in this work. The coatings were all deposited onto silicon (100) substrates.

GDOES depth profile analysis of the coatings was completed using a Jobin Yvon RF GD Profiler [22] equipped with a 4 mm diameter anode and operating at a typical radio frequency discharge pressure of 650 Pa and power of 40 W. Table 2 shows the sputtering rates (SR) of the elements used in the study. The discharge settings (power and pressure) were changed during the experiments to investigate the influence of the discharge parameters on the GDOES crater. Quantified profiles were obtained automatically using the standard Jobin Yvon QUANTUM Intelligent Quantification (IQ) software. The setup was calibrated using standard materials of known composition. The shape and depth of the crater and the coating thickness were measured by profilometry utilizing a Dektak 3030 surface profilometer.

3. Results and discussion

Fig. 1a shows a GDOES profile of a metal multilayer system consisting on three layers of approximately 500 nm thick, two of chromium and an intermediate layer of aluminium. The composition of the multilayer is clearly observed. The first Cr layer presents a very squared profile, but the interface with the Al intermediate layer is very broad. This effect cannot be attributed to a loss in depth resolution of the GDOES experiment but to the deposition conditions, non-optimized for the aluminium layer. Profilometry measurements on single Al layer deposited on silicon resulted on roughness of more than 100 nm. The interface width (calculated as the measured
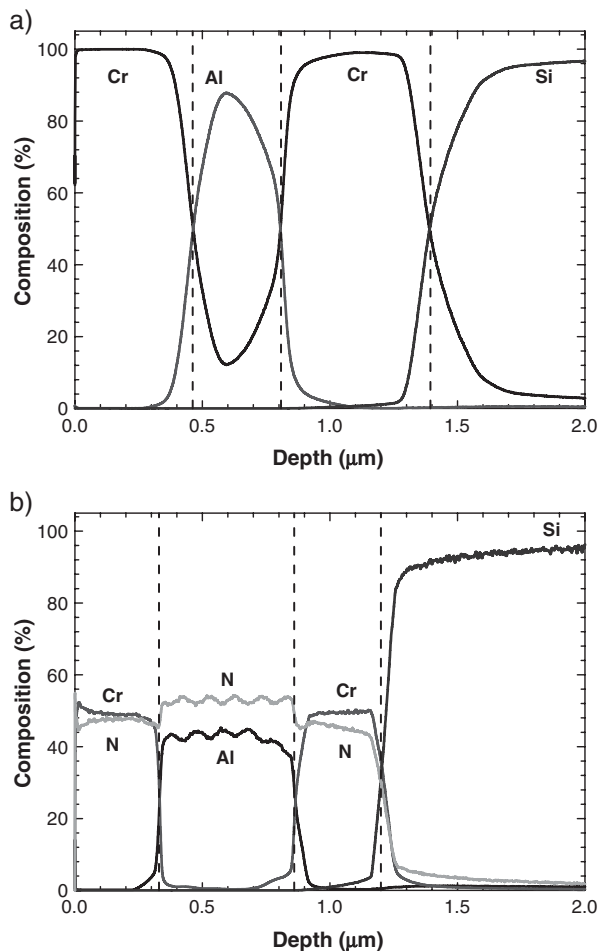
Fig. 1. Quantified GDOES depth profile of multilayer (a) Cr/Al/Cr coating and (b) CrN/AlN/CrN deposited on silicon. The dashed lines delimitate the different layers.

sputtered depth over which the signal of an element decreases from 84% to 16% [23,24]) in the Cr/Al interface was measured to be of 140 nm, that is much larger than Ti/Cr and Cr/Ti interfaces previously measured [18]. Strengthening the hypothesis of a rough Al layer, the following Al/Cr interface, although deeper, was measured to be narrower (85 nm). Finally, the width of the Cr/Si interface was determined to be of 230 nm, that is, similar to the one measured for the Cr/Si interface at the Cr/Ti/Cr/Si multilayer system studied in [18] at the same depth. In such study, we determined a variation of the interface width with depth for different metal multilayer coatings (Cr/Ti/Cr/Si, Ti/Cr/Ti/Si, Ti/Si and Cr/Si). The width of Cr/Ti and Cr/Si interfaces linearly increases 154 ± 46 nm per each micron the interface is buried in. The Ti/Cr interfaces widths gave a lower value of 56 ± 30 nm/μm and the Ti/Si interfaces widths results in an intermediate value of 72 ± 7 nm/μm. We attributed this different behaviour to the dissimilar values of the sputtering rates of the elements present before and after the interface. The broadening is wider in interfaces where the top metal (e.g. Cr) has a higher sputtering rate than the underneath metal or substrate (e.g. Ti or Si).

In order to check the behaviour of nitride multilayers, we deposited a system consisting of two CrN layers and an intermediate AlN one (see Fig. 1b). The total thickness of the coating was measured to be of 1220 nm by profilometry and scanning electron microscopy observations revealed the individual layer thicknesses (380 nm, 470 nm and 380 nm, respectively). Such thicknesses correlate very well with the one obtained by GDOES (350, 490 and 370 nm). The first CrN layer has a homogeneous stoichiometric composition 50–50 all over the coating thickness. This composition was confirmed by RBS experiments. The oscillations observed in the AlN layer are not due to an inhomogeneous deposition as RBS experiments derived a constant (and also stoichiometric) composition of the coating. We are tempted to believe that it is likely associated to interference effects during the sputtering process due to the transparent nature of AlN. Similar profile was obtained for a 600 nm monolithic AlN layer deposited on silicon. The last CrN layer has again a stoichiometric composition, but the N content decreases with depth while the silicon signal increases. This initial rise of the silicon content is due to the well at the edge of the crater that reaches the silicon substrate before the bottom of the crater (see below in Fig. 2). The reason why this crater edge effect only affects the nitrogen and not the chromium signal is still unclear. Regarding the interface widths, the first CrN/AlN interface was measured to be of 23 nm, increasing up to 52 and 61 nm for the following AlN/CrN and CrN/Si interfaces, respectively. Such interface widths are considerably lower than the ones obtained for metal multilayers, probably due to a lower sputtering rate of the compounds involved, as observed in Table 2. Further experiments were performed on the reversed system AlN/CrN/AlN/Si (with similar individual layer thicknesses). The widths of the interfaces resulted to be 27, 32 and 62 nm for AlN/CrN, CrN/AlN and AlN/Si interfaces, respectively. Merging all these experiments, we can estimate a linear increase of the nitride interfaces with depth of 57 ± 2 nm/μm for the AlN/CrN interface and of 23 ± 1 nm/μm for the CrN/AlN one. Therefore, the loss of resolution with depth during GDOES experiments appears to be much lower in nitride multilayers than in metals. Furthermore, and contrary to what we observed
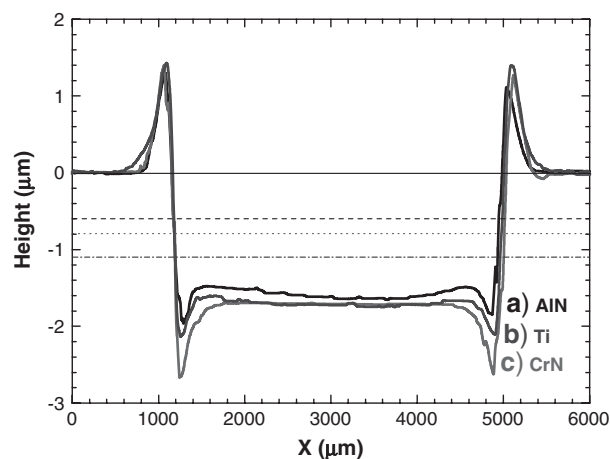

Fig. 2. Crater shape after a GDOES experiment performed for 30 s on single layers of (a) 600 nm AlN, (b) 1.1 μm titanium and (c) 800 nm CrN deposited on silicon. The solid line represents the original surface. The dashed, dotted and dash-dotted lines represent the interfaces of AlN, titanium and CrN, respectively.

in metal multilayers, there is a larger degradation of the interface when the top nitride (e.g. AlN) has a lower sputtering rate than the underneath nitride (CrN). These results indicate that not only the sputtering rate is important to determine the interface width measured by GDOES. The shape of the crater before and after the interface is also crucial. Fig. 2 shows the crater shape after 30 s of GDOES sampling on (a) 600 nm AlN, (b) 800 nm CrN and (c) 1100 nm Ti deposited on silicon. It can be clearly observed how both the Ti and CrN craters have a more pronounced crater edge effect and, what is more important for depth resolution, a very flat bottom. On the other hand, the AlN crater presents a more concave shape that seems to be determinant in the worsening of the interface.

The relevance of the GDOES technique was tested when studying thin and ultrathin nitride layers and comparing them with the results on metal coatings obtained in [18,19]. Fig. 3 shows the GDOES profiles of metal and metal nitride multi-layers with individual thickness in the order of 100 nm. In the multilayer metal system consisting of 10 bilayers of 70 nm titanium and 150 nm chromium (Fig. 3a), the different effects affecting the mixing of the signals during a GDOES experiment can be clearly observed. As discussed in [19], although the

Fig. 4. GDOES depth quantified profile of the multilayer coating consisting on 5 nm AlN layers embedded in a CrN matrix deposited on silicon. The dashed lines follow the variation of the AlN peak intensities with depth. The inset graphs show a zoom in of the profiles down to the first 100 nm. The panel below the graph schematically represents the system studied.

structure of the multilayer coating is well resolved, there is a high mixing of the thin titanium layers as compared to the thin chromium layers. It has to be noted that, for the last titanium layers, a higher signal of chromium is detected. Similar results are obtained for the case of the 10 bilayers of 40 nm CrN and 90 nm AlN (Fig. 3b). In the first six bilayers, the AlN profile keeps a very square profile without a great loss of resolution (the maximum content decreases less than 4%). In the same range, the intensity of the CrN signal decreases approximately a 35%. This behaviour resembles the results observed for the metal multilayers of Fig. 3a. However, as the nitride coatings are approximately 40% thinner, we can assert that the profile
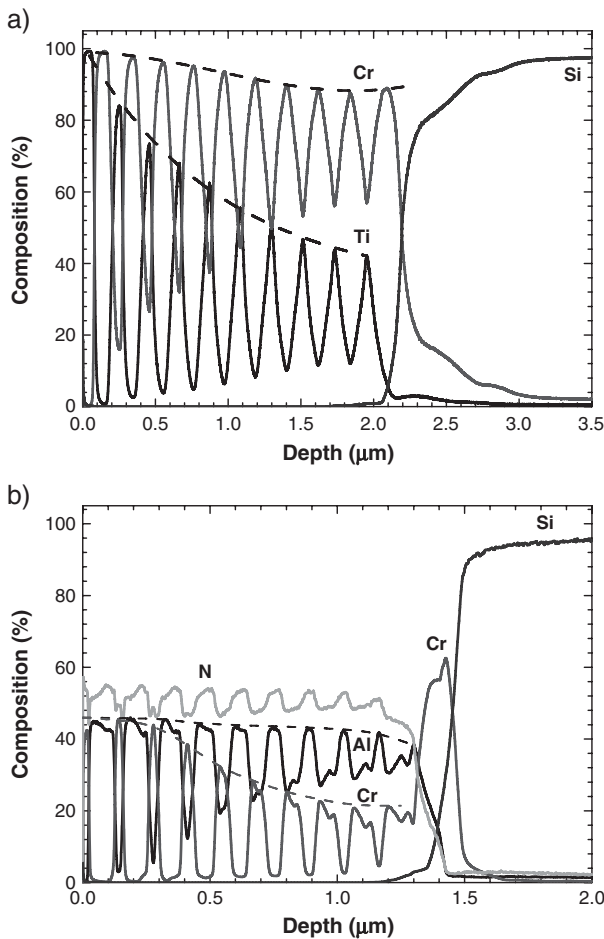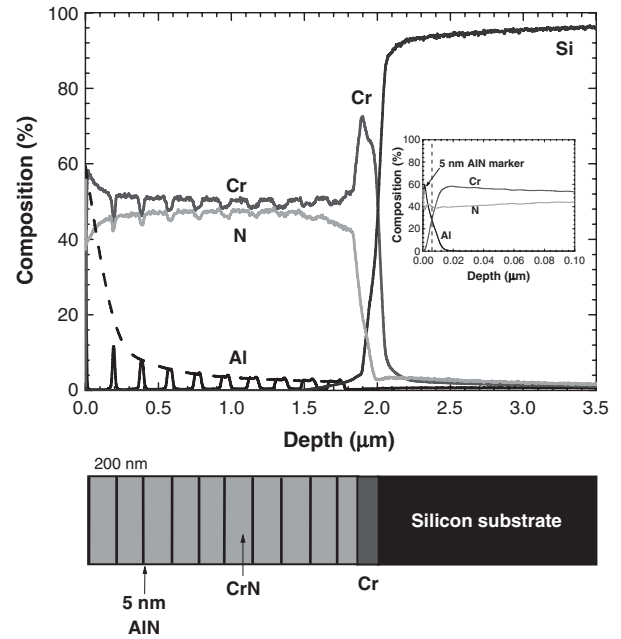
Fig. 3. GDOES depth quantified profile of (a) 10×(70 nm titanium/150 nm chromium) and (b) 10×(40 nm CrN/90 nm AlN) multilayer coatings deposited on silicon. The dashed lines follow the variation of the metal peak intensities with depth in both systems.
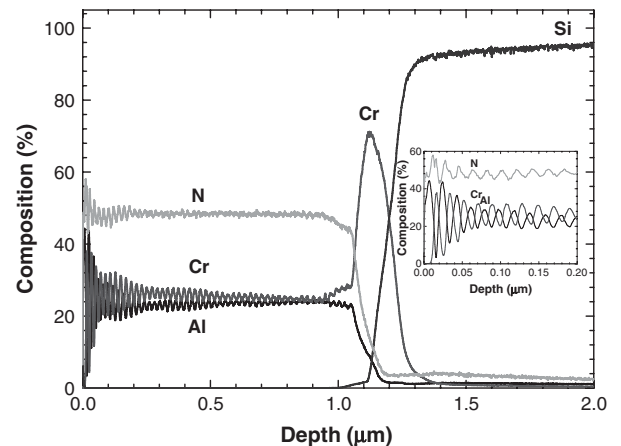
Fig. 5. GDOES depth quantified profile of (a) 50×(10 nm CrN/10 nm AlN) multilayer coatings deposited on silicon. The inset graphs show a zoom in of the profiles down to the first 200 nm.

degradation of the nitride multilayers is lower than that for the case of metals. On the other hand, in the last four bilayers, there is a high mixing of both nitrides. The profiles revealed that, due to the induced roughening during GDOES experiment, several layers are being sputtered at the same time.

In a final stage, we have studied the ultimate depth resolution of GDOES for nitride coatings. To this end, ultrathin AlN coatings were embedded at increasing depths in a CrN matrix. The multilayer system consists on 10 layers of aluminium nitride (5 nm thick) buried in between chromium nitride layers. The total thickness of the coatings was measured by profilometry to be 2.1 μm. The AlN markers are placed every 200 nm from the coating surface. Fig. 4 shows the depth profile GDOES analysis together with a scheme of the system studied (bottom panel). The 10 ultrathin layers are observed, even when embedded a few microns deep in the CrN matrix. In the insert of Fig. 5, the first 250 nm of the coating is shown. The first marker, sited at the outmost surface, is clearly resolved probing the excellent resolution for a 6 nm thickness layer. However, the profile degradation of the consecutive layers is evident as we go deeper into the coating.

Finally, we have applied GDOES depth profiling to a more practical case, studying a multilayer system consisting on 50 bilayers of alternating 10 nm AlN and 10 nm CrN. In Fig. 5, it can be observed that GDOES is able to resolve all the 100 layers, although with an important mixing of the layers. Similar experiments were performed with thinner layers of 5 nm. In such case, only the first 10 bilayers could be well resolved, whereas, deep into coating thickness, the mixing of the layers is so high that the signal of Cr and Al are kept constant.

4. Conclusions

In this work, we aimed to study the application of GDOES to depth profiling of alternating thin and ultrathin layer structures consisting of two metal nitrides, CrN and AlN, deposited by sputtering magnetron on silicon substrates. Sharper interfaces were measured for nitrides as compared to those obtained on the corresponding pure metal coatings (individual layer thickness of approximately 400 nm). In thinner coatings (∼100 nm), the nitride profiles present a lower mixing than the metal ones until a depth of 500 nm. Beyond that depth, the roughening of the crater shapes provokes the detection of several layer at the same time, worsening the depth profiles. Nevertheless, multilayer

nitride coatings of 50 bilayers of alternating 10 nm CrN and 10 nm AlN were well resolved. The ultimate depth resolution of the technique was evaluated using ultrathin (5 nm) aluminium nitride markers. These results assert the superb capabilities of the rf-GDOES technique to detect nanometric films in a very short experimental time.

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