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Quantification of a Ti(C_xN_{1-x}) based multilayer by Auger Electron Spectroscopy

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ABSTRACT

Auger Electron Spectroscopy (AES) is an analytical technique sensitive to the surface of materials and providing elemental and chemical composition of conductive samples. The excellent spatial resolution and its quantification possibilities, even for light elements, make AES a commonly used technique to investigate surface and interfaces.

TiN-like materials have a wide range of applications depending on their stoichiometry, but their composition is still complex (or at least not straightforward) to determine because of a strong overlapping of the Ti LMM with the N KLL Auger transitions. This quantification problem can be circumvented using computerised calculations as target factor analysis (TFA) to estimate the different nitrogen and titanium contributions in this peaks overlap. However, a more simple method, based on the study of Ti LMM and Ti LMV area ratio of pure TiN and TiC reference samples, is described in this paper and can be used to obtain the atomic composition of any titanium nitride based compound, whatever the complexity of the material. This method is an alternative to easily quantify TiN-like compounds by AES.

As an illustration, a Ti(C_xN_{1-x}) based multilayer deposited on a hardmetal substrate was investigated. This quantification method was successfully used to evidence three different layers and the diffusion phenomenon at the interfaces between the layers. This study was completed with a quantitative SIMS depth profile that the high sensitivity and depth resolution allowed to measure the small variations of composition lower than the uncertainty of AES.

1. Introduction

Carbide and nitride compounds are materials that have a wide range of applications in high technology devices. TiC and TiN coatings are commonly deposited as thin films to improve the properties of use, the hardness and the corrosion resistance of cutting tools [1,2] as well as diffusion barrier layers in microelectronic devices [3–5]. The physical properties of these compounds are mainly dependent on the stoichiometry, thus it is highly important to determine precisely their true composition. XPS and AES spectroscopy are often used to analyse such samples because they provide quantitative and chemical information on the first layers of the surface and allow to determine the evolution of the composition of a sample depending on depth if they are associated with an in situ sputtering [6–9].

However, in the case of thick samples a lengthy ion bombardment with high current density increases the roughness and decreases the depth resolution. It can also be the origin of mixing effects and preferential sputtering. This effect in the TiN_x compound has already been discussed by many authors [10–16]. It results in the modification of the elemental and the chemical composition of the sample. In order to avoid such a modification of the concentration during the sputtering, the study of the interfaces and of the composition of the different layers was not realised with a depth profile but with a bias preparation. This kind of preparation allows to observe the different layers directly at the surface of the sample and the depth information is then distributed along the surface of the specimen. A linescan along this new surface gives access to the composition of the different layers. AES was preferred to XPS to perform the linescan because the high lateral resolution of this technique is suitable for the analyses of the interfaces between the different layers.

However, the overlapping of the Ti LMM peaks (between 380 and 390 eV) and the N KLL one (at 378 eV) considerably complicates the determination of the concentration of TiN_x sample with AES. Indeed, whereas the concentration of carbon and titanium in the Ti(C_xN_{1-x}) sample can be obtained directly from the area of the C KLL peak (at 265 eV) and from Ti $L_3M_{2,3}V$ peak (at 419 eV), corrected with the appropriate sensitivity factor, the nitrogen amount should be extracted from the overlapping of the

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nitrogen $KL_{2,3}L_{2,3}$ and the titanium $L_3M_{2,3}M_{2,3}$ and $L_2M_{2,3}M_{2,3}$ peaks at 384 and 389 eV. This can be achieved using target factor analyses (TFA) and linear and non-linear least squares fitting [9,17]. TFA and NLLSF are mathematical methods simplifying the interpretation of multi-level data set and allow the extraction of meaningful information from sputter depth profile or linescan involving complex peak shape [18–20]. Nevertheless, TFA assumes that the experimental spectra are composed of a sum of different and common spectral components (whose contribution is varying with the analysed point) without any chemical interaction that could change the line shape. Moreover, the inelastic background in electron spectra varies with the in-depth composition profile and should be taken into account too [21,22].

To complete the study of this $Ti(C_xN_{1-x})$ multilayer, the sample was investigated with Secondary Ion Mass Spectrometry (SIMS). The excellent sensitivity, high dynamic range and good depth resolution make SIMS an extremely powerful technique for the analysis of surfaces and thin films. However, SIMS suffers from one major drawback that gives rise to very significant problems with quantification, known as the matrix effect. Indeed, the ionisation yield of a given sputtered element may vary by several orders of magnitude depending on the composition of the matrix in which it is incorporated and prevent SIMS to be quantitative except when dealing with ideal samples.

The Cation Mass Spectrometer (CMS), which has been developed in the Science and Analysis of Materials (SAM) department, is a unique instrument specially dedicated to the quantification by the SIMS technique and has already been fully described in previous work [26–38]. It associates a simultaneous deposition of neutral Cs to the ion bombardment in order to optimise the useful yield of MCs_x^+ or M^- secondary ions and thus allows quantification of the measurements.

In this study, a multilayer was grown on a polished WC/Co substrate. $Ti(C_xN_{1-x})$ layers with different compositions (x ranging from 0 to 0.6) were obtained by varying the experimental deposition settings of the CVD process. These layers are about 100 nm thick and they were deposited directly on the substrate. However, they are buried in a more complex multilayer system (the uppermost layers are not of interest in this study) with a total thickness of several micrometers. The aim of this work was to characterise the interfaces and to determine the composition of the first three layers closest to the substrate (Fig. 1) with composition close to TiN, $Ti(C_xN_{1-x})$ and $Ti(C_{x'}N_{1-x'})$ respectively.

2. Experimental details

2.1. Samples elaboration

Four reference samples, TiC, TiN, $Ti(C_{50}N_{50})$ and $Ti(C_{70}N_{30})$, were used in this study to determine the area ratio of Auger peaks and to validate the concentration calculation method proposed in this paper. They were all synthesized by hot pressing of nitride, carbide and carbonitride titanium powders provided by HC Starck and containing less than 1% of oxygen. The multilayer sample was grown by chemical vapour deposition using H_2, N_2, CH_4, CH_3CN and $TiCl_4$ gases as precursors, a temperature ranging from 1173 to 1273 K and a pressure of 160, 75 and 60 mbar for the successive $Ti(C_xN_{1-x})$. The elaboration conditions to tune the composition of this stack of three $Ti(C_xN_{1-x})$ layers are summarized in Table 1.

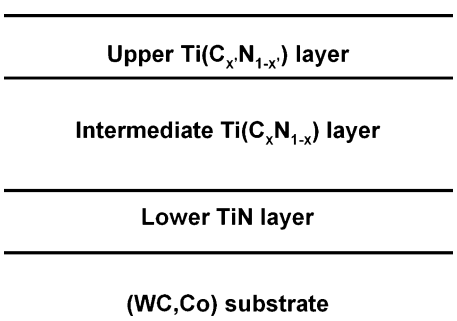

Fig. 1. Schematic description of the multilayered coating.

Table 1
Elaboration conditions of the $Ti(C_xN_{1-x})$ based multilayer.

	T (K)	P (mbar)	H_2 (slm)	N_2 (slm)	CH_4 (slm)	CH_3CN (sccm)	$TiCl_4$ (sccm)
Lower TiN layer	1173	160	16.8	11.2			1.35
Intermediate $Ti(C_xN_{1-x})$ layer	1173	75	18	9.5		0.25	1.85
Upper $Ti(C_{x'}N_{1-x'})$ layer	1273	60	20	6	0.8		1

2.2. Sample preparation

The depth composition was investigated thanks to a bias preparation of the sample realised by polishing the surface of the specimen with a very small angle in order to observe all the layers composing the coating on the top surface of the sample. The polishing was realised by a classic mechanical method with a Tripod Polisher® (model 590W) using a 1 μm diamond tray and a very slow rotation speed to avoid damaging too much the coating by tearing. The polishing was performed with a varying angle along the surface to enlarge the dimension of the layers. Thus, they appear longer on the surface to be analysed but no correlation between their dimension on the bias preparation and their thickness can be deduced.

2.3. AES analyses

The Auger analyses were carried out with a Thermo Electron Microlab350 apparatus using a Spherical Sector Analyser. All spectra were recorded in direct mode and with a 10 keV and 1 nA primary beam. With these analysis conditions, a lateral resolution of 40 nm was achieved. The angle of incidence of the primary electrons beam and of escaping electrons was 30° with respect to the surface normal. The energy resolution of the spectrometer was fixed to 0.2%. The samples were slightly sputtered with an Ar^+ ion gun (E = 1 kV, I = 500 nA on a 1 mm^2 rastered area) prior to the analysis in order to remove contamination from the surface. The compositions were obtained using relative sensitivity factors experimentally determined on TiN and TiC reference samples analysed exactly in the same conditions as the multilayer. The areas for the Auger peaks used for the quantification were obtained after the removal of a linear background. The region boundaries were 366–396, 402–427, 245–285, 160–180 and 500–525 eV respectively for the $TiL_{2,3}M_{2,3}M_{2,3}$ and N KLL transitions, Ti $L_{2,3}M_{4,5}M_{4,5}$, C KLL, W and O KLL peaks.

2.4. CMS analyses

The CMS Cs^+ ion gun was operated at an energy of 8.5 keV and delivered currents ranging from 26 to 33 nA. The sample was positioned at a distance d = 2.5 mm from the extraction nose and polarised to +4500 V. These conditions result in an angle of incidence of the primary ions (defined with respect to the surface normal) of θ = 74° with an impact energy of E = 4 keV. The primary beam was raster-scanned across a rectangular area varying from 240 μm × 150 μm to 380 μm × 230 μm. Secondary ions were accepted from a circular area on the sample surface limited to a