# Study by AES of the titanium nitruration in the growing of TiN thin films by PLD technique

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# Abstract

A series of different TiN<sub>x</sub> thin films were grown by PLD. The purpose for this work was to study through the AES interpretation, how the different conditions of the partial pressure of N inside the chamber during the growing of these thin films, affects the stoichiometry of the TiN<sub>x</sub> deposited. The results obtained were that the different thin films change each one through TiN<sub>x</sub> (*x*=0.88-1.33). The results were supported with XPS and EELS spectroscopy doing also an analysis of elemental ratio to show the stoichiometry and sub-stoichiometry obtained. This work concludes the adequate conditions for this experiment to obtain TiN as thin film by PLD at room temperature, supported with the results in the present work and the interpretation of the AES spectra even when Ti and N peaks overlap.

Keywords: AES; XPS; TiN; Thin films; PLD

# Introduction

Hard coatings and their applications continuously are in progress. The thin films of transition metals nitrides have a broad range of potential applications that goes from microelectronics to the metalmechanics industry or in biological implants. The research of TiN is still on in actuality for the different science branches like the above mentioned.



Different techniques are used to grow thin films. Mostly used are RF [1–5] and DC-sputtering [5–7]. But these, requires about 500 °C of temperatures for growing high purity TiN. Therefore, there is a very interest in methods for growing TiN at low temperatures or room temperatures. So, the laser ablation is very well-established technique for growing thin films at room temperature and is known as pulsed laser deposition (PLD) [8,9].

A characteristic in PLD technique is that very slightly variations in the deposition parameters (laser fluency, substrate temperature, partial pressure of a gas environment) result in a great alteration of the final film properties. And as shown in this work, slightly variations in N<sub>2</sub> atmosphere during the ablation of titanium, results in different TiN<sub>x</sub> thin films.

The results are accomplished by in situ surface analysis techniques, such as Auger electron (AES), Xray photoelectron (XPS) and electron energy loss (EELS) spectroscopies.

#### Experimental

#### Film preparation

All the thin films were deposited at room temperature in a laser ablation system, Riber LDM-32 with in situ AES, EELS and XPS spectroscopies implemented. Deposition was performed by ablating a 99.99% titanium target into an environment of high purity molecular nitrogen. Nitrogen partial pressures  $P_N$ , wer in the  $\leq P_N \geq$  70 mTorr range in steps of 5mTorr. Layers were deposited on Si(111) *n*-doped silicon wafers without any pre-cleaning process. The base pressure in the growing chamber was



maintained in the  $10^{-9}$  Torr with the aim to have a minimum or to exclude totally H<sub>2</sub>O and O<sub>2</sub> at the inner walls.

Target ablation was by means of a *KrF* excimer laser ( $\lambda$ =248nm) focused on the target at 50° off the surface normal. Laser energy, deposition time and pulse repetition rate were fixed at 200 mJ, 60 min and 5 Hz, respectively, having therefore a total of 18,000 laser pulses for each film and the substrate in constant rotation of 60 rev/min in order to improve the homogenization of the deposition. This 18,000 laser pulses are much less than other works [10,11].

# Film characterization

The spectroscopies were performed in situ by an electron energy analyzer Mac-3 from CAMECA. For the AES measurements, the incident electron beam energy was set to 3 keV and the data acquisition was performed with a resolution of  $\Delta$  *E/E*=0.3%. The incident electron beam for EELS was of 1200 eV and a resolution of 1.5 eV. XPS data were collected using an X-rays emissor with anode of Al K $\alpha$  (1486.6 eV). The energy scale was calibrated using the Cu 2p<sub>3/2</sub> and Ag 3d<sub>5/2</sub> references at 932.67 and 368.26 eV, respectively.

The elemental XPS quantification is based in Eq. (1) [12]. It is assumed that the  $TiN_x$  films are homogeneous. Then the XPS intensity for a core level k can be written as:

$$I_k \alpha I_0 n \sigma_k \lambda_{\text{MED}}(E_k) T(E_k) \tag{1}$$



Where *n* is the atomic density in the film,  $\sigma_k$  is the photo-ionization cross-section for the level *k* [13],  $\lambda_{MED}$  (E<sub>k</sub>) the mean escape depth for electrons with kinetic energy E<sub>k</sub> in the examined material, T(E<sub>k</sub>) the spectrometer transmission function [14], and I<sub>0</sub> is a constant factor dependent of the X-ray radiation intensity. The product  $\sigma_k \lambda_{MED}(E_k)T(E_k)$ is defined as the relative sensitivity factor Sr [15] for the core level *k*. All these factors were calculated for Ti 2p<sub>1/2</sub>, 2p<sub>3/2</sub> and N 1s transitions in TiN<sub>x</sub> using the electron analyzer CAMECA Mac-3 transmission function and an Al Ka X-ray source. With this scheme, the elemental ratio in the thin film can be evaluated from the XPS peak areas with good accurate.

The atomic density was determined by the collective bulk plasma oscillation measured by EELS. The maximum in the energy-loss function *Ep*, assigned to the resonant plasma condition at classical frequency  $\omega_p$ , is given by [16]:

$$E_{\rm p} = \sqrt{\frac{4\pi\hbar^2 n_{\rm e}e^2}{m_{\rm e}}}\tag{2}$$

where  $n_e$  is the number of electrons responsible for plasmon oscillations per volume unit, me the electron mass and e is the electron charge.

# **Results and discussion**

#### XPS

Fig. 1 shows the high resolution XPS spectra of the N and Fig. 2 of the Ti from where the elemental ratios were calculated. The background subtraction was made using Touggard's method [17]. Analyzing this figure, we can see a chemical shift. It



means the changing in  $P_N$  the change in stoichiometry. Elemental ratios for each one of the films were calculated from Ti  $2p_{1/2}$  and  $2p_{3/2}$  and from N 1s. At naked eye, the films at  $P_N = 20$  mTorr is of golden color, saying us is TiN. This first shut was supported with the further analysis.



Fig. 1. Here is shown the chemical shift of the nitrogen in TiN and the sample of 15 mTorr is the lower.

In XPS spectra, for carbides the peak would be at  $\cong$  455 eV [18] but here is not clear. Also, we can se the presence of other Ti compounds due to oxide at  $\cong$  458 eV [19]. The main components with binding energies of 454.0 and 459.9 eV are attributable to the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> elemental titanium peaks, respectively, while titanium nitride phases can be identified by the 2p<sub>3/2</sub> peak at 455.8 eV and the 2p<sub>1/2</sub> peak at 460.2 eV. These values were compared with [19,20].





Fig. 2. Here is shown the high resolution XPS for Ti at TiN compared with pure Ti. A chemical shift is observed.

Table 1										
Showing	the	elemental	ratio	calculated	for	each	one	of	the	grown
films										

P <sub>N</sub> (mTorr)	$C_{\rm N}/C_{\rm Ti}$				
5	0.98				
10	0.99				
15	1.00				
20	1.02				
25	1.05				
30	1.11				
50	1.32				
70	1.32				

The Table 1 shows the calculated elemental ratios from all films and it came out to

corroborate that at  $P_N = 20$  mTorr we have TiN. This table was calculated through:

$$C_i = \frac{I_i/S_i}{\sum_{i=1}^n I_i/S_i} \tag{3}$$

and  $\sigma$  at Eq. (1) to obtain S<sub>i</sub> is calculated from:



$$\sigma = \int_0^{\pi} \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} (1 - \cos\xi) \mathrm{sen}\,\xi\,\mathrm{d}\xi \tag{4}$$

From the above analysis, Table 1 is completed.

In EELS spectra (in Fig. 3) obtained in order to calculate the atomic density and a very small shoulder appears at 2–2.5 eV. These are due to a resonance and probably due to a wide background backscattered electrons of the N enlaces [21].



Fig. 3. EELS spectra obtained in order to calculate the atomic density. A very small shoulder appears at 2-2.5 eV. This is probably due to a wide background backscattered electrons of the N enlaces.

# AES

The AES spectra for each one of the series of thin films is shown in Fig. 4. The main problem in AES is that transitions of many elements, overlap partially among them, and this difficult or limits the analysis for many elements [22]. Probably for that reason, there are no many works for TiN with AES analysis. For this case of TiN, the transition  $N_{KLL}$  overlaps with transition  $Ti_{LMM}$  at 384 eV [23,24]. Fortunately, applying the second



derivative to the spectra can show both transitions slightly separated as show in same figure. The different spectra shapes through the samples show us the different TiN<sub>x</sub>. An analysis as shown in Fig. 3(a) we can conclude that the highest ratio presented (sample at 20 mTorr) could means the smallest energy state for Ti with N and therefore, the most stable system. And comparing this result with the other results in this work, again point to sample of 20 mTorr is TiN. Of course also the most stable the harder thin film [25]. And TiN is the harder of all the known existent TiN<sub>x</sub> [26].

Therefore, the AES spectra for the sample of 15 mTorr is as a finger print for TiN.



Fig. 4. (a) Shown how the c value was calculated and (b) shown all the values obtained for each one of the samples and the higher value of c is at the sample of 15 mTorr, the which one is TiN. And therefore that spectra is as finger print of the TiN.

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