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ACCEPTED MANUSCRIPT

## On the correlation between the TiN thin film properties and the energy flux of neutral sputtered atoms in direct current magnetron discharge

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# On the correlation between the TiN thin film properties and the energy flux of neutral sputtered atoms in direct current magnetron discharge

Abderzak el Farsy<sup>1,2,\*</sup>, Jean-François Pierson<sup>1</sup>, Thomas Gries<sup>1</sup>, Ludovic de Poucques<sup>1</sup>, Jamal Bougdira<sup>1</sup>

<sup>1</sup> Université de Lorraine, CNRS, IJL, F-54000 Nancy, France.

<sup>2</sup> Université Paris-Saclay, CNRS, Laboratoire de Physique des Gaz et des Plasmas, 91405 Orsay, France.

\*Corresponding author: abderzak.el-farsy@universite-paris-saclay.fr

## Abstract:

In this study, the energy flux of sputtered atoms on a substrate was correlated to the properties of titanium nitride (TiN) films deposited using direct current magnetron sputtering (dcMS) under mixed Ar and N<sub>2</sub> atmospheres. The neutral titanium sputtered atoms velocity distribution functions (AVDFs) were measured by tunable diode-laser induced fluorescence (TD-LIF), and the flux of particles and their energy were derived. Mass spectrometry was used to characterize the energy-resolved flux of the ions. It was found that the neutral sputtered atoms flux and deposition rate were in good agreement, indicating that the flux of the neutral titanium ground state represents the number of deposited atoms. Moreover, TiN films were deposited at different gas pressures and at various Ar/N<sub>2</sub> gas mixtures close to the conditions where stoichiometric TiN was formed, without bias voltage and heating of the substrates. The energy flux of the sputtered neutral Ti into the substrate was calculated from TD-LIF measurements. At a relatively low magnetron discharge pressure of 0.4 Pa, we demonstrated that the energy of sputtered neutral Ti impinging on the substrate is higher than the energy flux of ionized particles corresponding mainly to Ar<sup>+</sup>. Thus, the influence of the energy flux of the sputtered atoms on the texture and microstructure of the films is revealed. The (200) texture was obtained at 0.4 Pa when the energy flux of the sputtered atoms was higher than the ion energy flux. At 1.3 Pa where the sputtered atoms energy flux is one order lower compared to 0.4 Pa the (111) texture was obtained. The high-energy flux of the ground state of Ti sputtered atoms seems to allow stress removal in the films.

**Keywords:** dcMS, diode laser-induced fluorescence spectroscopy, TiN microstructure and texture.

## I. Introduction

In magnetron sputtering (MS), the growth of polycrystalline thin films begins with vapor condensation on the substrate surface, which nucleates into islands and consolidates to form a continuous film. Thin films and coatings are used in a wide range of technological applications including microelectronics, optical devices, and surface protection. The performance of thin films and coatings depends on their physical properties, which are governed by film morphology and phase composition. These properties depend on the interactions of the particles with the substrate. Thus, the energy and flux of atoms and ions arriving at the substrate are of major importance for tailoring the forming film properties, such

1  
2 1 as microstructure, stress, adhesion, electrical resistivity, stoichiometry, and crystalline properties. Ti-  
3 2 titanium nitride (TiN) was used in this study because of its excellent mechanical and optical properties,  
4 3 and it has been used in several applications, such as decorative and wear-resistance [1,2].  
5 4

6 5 Magnetron sputtering is a physical vapor deposition technique that can be operated with different  
7 6 power supplies: direct current magnetron sputtering (dcMS) to sputter conductive targets, radiofre-  
8 7 quency magnetron sputtering primarily used to deposit dielectric materials, and high-power impulse  
9 8 magnetron sputtering (HiPIMS) [3,4]. In the dcMS process, most of the sputtered species remain in a  
10 9 neutral state, and their energy is controlled by the degree of thermalization, i.e., the number of colli-  
11 10 sion events between the sputtered species and the processing gas. The number of collisions can be  
12 11 directly controlled by the deposition pressure and the target-to-substrate distance [5]. Their energy  
13 12 ranges from the energy they gain in the sputtering process and at virtually no collisions ( $\sim 3.2$  eV in  
14 13 average) to fully thermalized species at a larger number of collisions ( $\sim 0.1$  eV in average). Over the last  
15 14 two decades, HiPIMS has been intensively studied because of its ability to generate sputtered atoms  
16 15 with a high ionization rate (a few tens of percent). Such pulsed plasma discharges work at a peak  
17 16 current of approximately two orders of magnitude (low duty cycle: 1 % and low repetition frequency:  
18 17  $< 5$  kHz) compared with dcMS.  
19 18

20 19 In conventional dcMS to deposit nitride thin films, the ion flux on the substrate mainly contains buffer  
21 20 gas ions ( $\text{Ar}^+$  and  $\text{N}_2^+$ ), whereas the sputtered species are mainly in a neutral state. For titanium nitride  
22 21 (TiN) deposition, the energy flux on the substrate, i.e., the product of particle flux and incident particle  
23 22 energy determines the growth mode. The TiN grains are preferentially oriented along the [111] direc-  
24 23 tion for low energy flux, while [200] preferred orientation is observed for high energy flux [1,2,6,7].  
25 24 Compared with ions, it is challenging to characterize energetic neutral-sputtered atoms. Their energy  
26 25 flux can be measured by mass spectrometry, a retarding field analyzer, and a Faraday cup, but the  
27 26 atoms must be ionized for detection [8]. Other devices have been developed and proposed to measure  
28 27 the energy flux towards the substrate surface without the ionization of incoming species as calorimet-  
29 28 ric probes [9–11]. In addition, both ions and neutral metallic flux towards the substrate were simulated  
30 29 by Mahieu and Depla [12] using the Monte Carlo approach of the SIMTRA code.  
31 30

32 31 Tunable diode laser-induced fluorescence (TD-LIF) is a powerful technique for diagnosing neutral sput-  
33 32 tered atoms with high spatial and spectral resolution, and the plasma remains practically unperturbed  
34 33 in terms of temperature and density [5,13–16]. Moreover, these measurements have numerous ad-  
35 34 vantages compared to other optical diagnostics: (1) they allow probing of the ground state of the  
36 35 sputtered atoms in dcMS, (2) they are highly space and spectrally resolved, and (iii) they allow meas-  
37 36 urement of the flux and energy of sputtered atoms at the substrate position in front of the target.  
38 37 Other optical plasma diagnostics can be found in the literature, allowing the sputtered atom velocity  
39 38 distribution function (AVDFs) description [17–19].  
40 39

41 40 Many previous works have studied TiN coatings deposited using either dcMS [1] or HiPIMS processes  
42 41 [6,7,20–22], and most of these studies investigated the impact of ion flux on the properties of TiN  
43 42 films. The present study aims to correlate the energy flux of neutral sputtered atoms on a substrate  
44 43 with the properties of TiN thin films (film texture, microstructure, and morphology) grown in dcMS  
45 44 discharges where the sputtered particles are mainly neutral. To achieve this goal, we used a balanced  
46 45 magnetron to reduce the ion flux on the substrate without bias and without intentional substrate  
47 46 heating. Thus, simultaneous measurements of TD-LIF and mass spectrometry of magnetron discharge  
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under different gas mixtures (Ar/N<sub>2</sub>) were performed to characterize the energy flux of neutral sputtered Ti atoms and the ion energy flux, respectively.

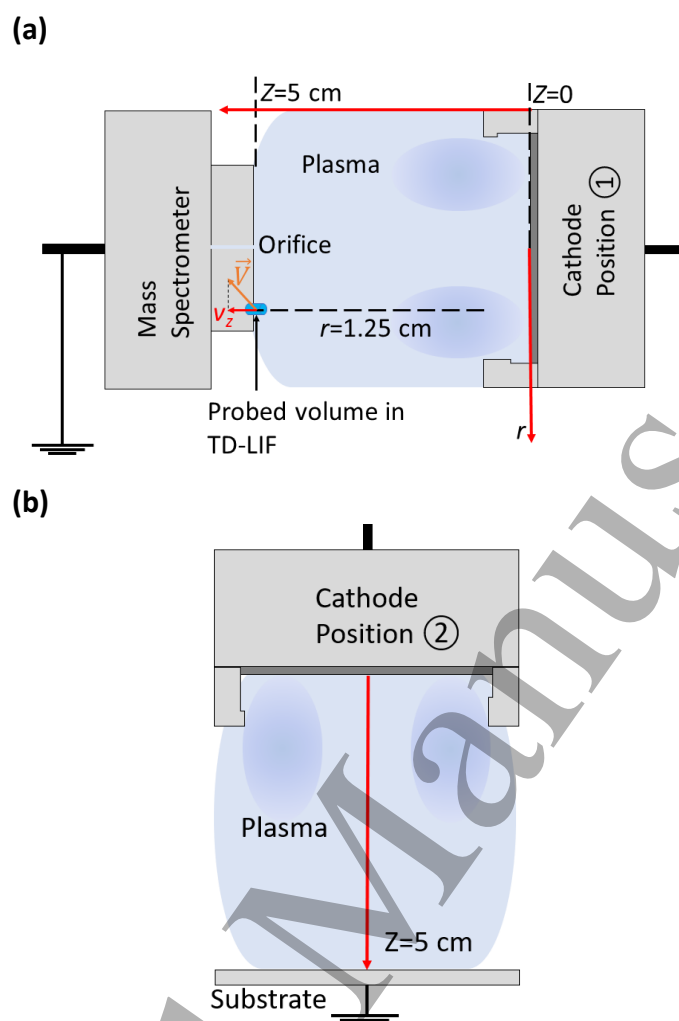
## II. Experimental details

The growth of TiN thin films and plasma diagnostics were carried out in a stainless-steel cylinder, 30 cm in diameter and 35 cm in height. Using mechanical and turbomolecular pumps, the base pressure obtained was approximately  $2 \times 10^{-4}$  Pa. A titanium target, 50 mm in diameter, 3 mm in thickness, and 99.99 % pure, was installed on a 2-inches balanced magnetron cathode cooled by water. The power source was a MELEC SIPP 2000 power supply ( $U_{\max} = 1$  kV;  $I_{\max\_peak} = 200$  A). The reactive gas mixture (Ar and N<sub>2</sub>) was added to the chamber at various N<sub>2</sub>/(Ar+N<sub>2</sub>) flow rate ratios, and the total flow rate was maintained at 18 sccm. We investigated the gas mixture range of 2 % to 5 % N<sub>2</sub> where quasi stoichiometric TiN films were formed as shown latter by the measurements of the chemical composition of the films, the same conditions were found in early work with another deposition system [23]. For all the results presented in this work, the average power was fixed at 5 W cm<sup>-2</sup> (100 W for the target area). In addition, all plasma measurements and thin film depositions were performed at a target-to-substrate distance of 5 cm (figure 1).

Plasma diagnostics and film depositions were performed in the same reactor, and the (100)-oriented Si substrates were installed using configuration 2, where the magnetron cathode was installed atop the chamber [figure 1 (b)]. No substrate bias or external heating was applied to the substrate during the film growth. The energy source on the substrate comes only from the deposited species, which are characterized by the diagnostic methods described below. Prior to deposition, all the substrates were ultrasonically cleaned in acetone for 10 min and ethanol for 10 min. Table 1 summarizes the deposition conditions.

**Table 1.** Summary of deposition conditions for the various realized coatings: reactive gas mixture, pressure, cathode voltage and film thickness.

% N <sub>2</sub>		2 %	3 %	5 %
Deposition duration: 2 hours	0.4 Pa	345 V 3400 nm	340 V 3000 nm	351 V 2700 nm
	1.3 Pa	285 V 2600 nm	280 V 2800 nm	340 V 2300 nm



**Figure 1.** Schematic of the experimental setup. The cathode magnetron is in position ① to measure titanium neutral AVDFs and IEDFs, while it is moved to position ② atop the chamber to deposit thin films. The schemes are to scale. The measured atoms velocity by TD-LIF technique is the component  $v_z$ , for the sake of simplicity it is mentioned  $v$  in the text.

The velocity distribution functions of the neutral sputtered atoms were measured using the tunable diode laser-induced fluorescence technique (TD-LIF). The reader can refer to Desecures *et al.* [15] for a detailed description of the TD-LIF experimental setup. The laser source used in this study was a tunable diode laser (Toptica Photonics DL 100), which was accorded to probe the transition from  $3d^2s^2 (^3F_2)$  to  $3d^2 (^3F) 4s4p (^1P^o)$  of the ground state of neutral titanium sputtered atoms ( $\lambda_0=398.17\text{ nm}$ ). The diode laser was tuned to scan a 9 pm wavelength range with a locked single-mode, and the spectral resolution was 0.005 pm, enabling an accurate description of the Doppler broadening profile. The typical scanning frequency for measurements was 50 Hz. The probed volume in the TD-LIF measurements was approximately  $3\text{ mm}^3$  above the racetrack center, that is, at  $r=1.25\text{ cm}$  and  $z = 5\text{ cm}$  (figure 1(a)). The combination of high spectral and spatial resolutions accurately measures the flux and energy of the deposited species.

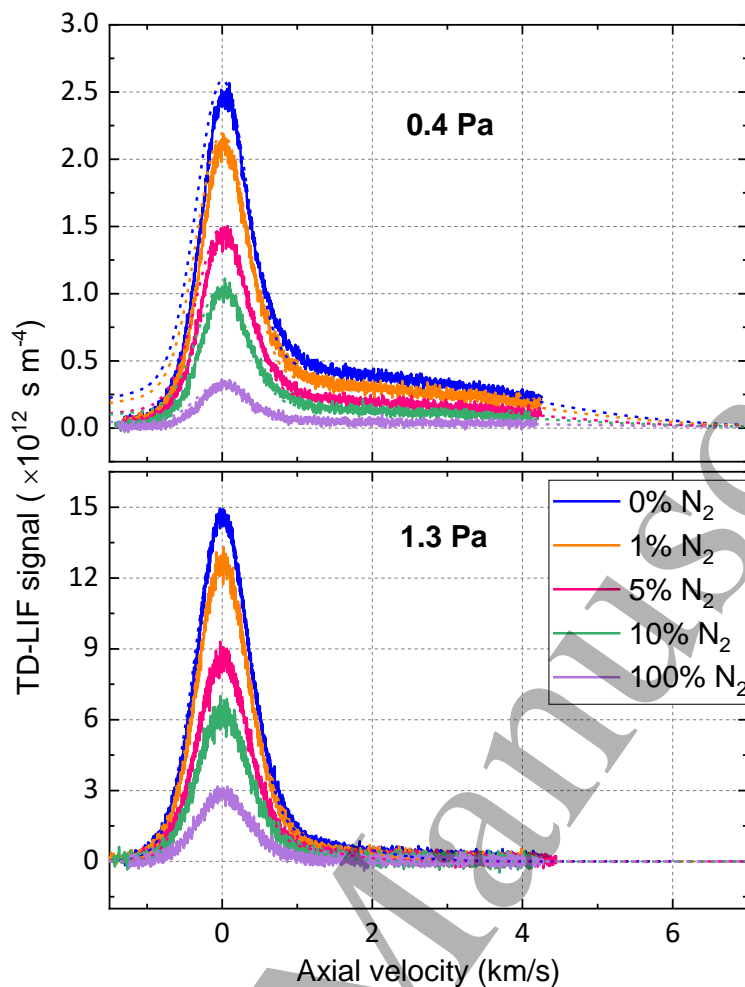
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2 1 The ion energy distribution functions (IEDFs) of  $\text{Ar}^+$  and  $\text{N}_2^+$  were measured using a HIDEN EQP 300  
3 2 instrument. The plasma was sampled by a grounded orifice of a 100  $\mu\text{m}$  diameter mass spectrometer  
4 3 installed in the virtual position of the substrate (figure 1(a)). Because the mass spectrometer signal  
5 4 depends on the differences in the acceptance angle for different ion energies and the unknown trans-  
6 5 fer function of the mass spectrometer, the measurements do not represent the absolute values of the  
7 6 ion flux; therefore, we discuss only the qualitative signal variations. Herein, only the qualitative  
8 7 changes in terms of energy are discussed. However, owing to the reactor geometry, mass spectrometry  
9 8 measurements were only performed in front of the target center at  $r = 0$  cm (see figure 1).  
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12 9 The deposition rate was measured *via* scanning electron microscopy using a cross-sectional view of  
13 10 the specimens. The microstructure (crystallite size) and preferred orientation of the films were char-  
14 11 acterized by X-ray diffraction (XRD) analysis (Brüker D8 Advance with  $\text{Cu K}\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ ) in  
15 12 Bragg-Brentano geometry ( $\theta$ - $2\theta$ ). This mode allows for the identification of planes parallel to the thin-  
16 13 film surface. The chemical composition of the films was determined by wavelength dispersive X-ray  
17 14 spectroscopy (WDS), also known as electron probe microanalysis (EPMA), using a JEOL JXA-8530F in-  
18 15 strument. Ti,  $\text{Fe}_4\text{N}$ , and  $\text{MgO}$  were used as standards to measure the Ti, N, and O concentrations,  
19 16 respectively. For each sample, the reported chemical composition was obtained by averaging 50 dif-  
20 17 ferent spots measured on the surface ( $\sim 200 \times 200 \mu\text{m}^2$ ). The topography and RMS roughness of the  
21 18 TiN films were investigated in resonant mode using a nano-observer atomic force microscope (AFM)  
22 19 developed by CSInstruments.  
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### 31 20 III. Results and discussion

#### 32 21 III-1. Correlation between the deposited flux and deposition rate

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35 22 Figure 2 shows the neutral Ti ( $^3\text{F}_2$ ) AVDFs in dcMS discharge at 0.4 and 1.3 Pa, for the different gas  
36 23 mixtures ( $\text{N}_2/\text{Ar}$ ). We used the resonance fluorescence signal ( $\lambda_{\text{laser}} = \lambda_{\text{lif}} = 398.17 \text{ nm}$ ), which signifi-  
37 24 cantly improved the TD-LIF signal compared with previous studies [5,16]. Then, the AVDF profiles and  
38 25 the atoms populations are accurately described: thermalized (centered at  $v = 0 \text{ km/s}$ ) and energetic [ $v$   
39 26  $> 1 \text{ km/s} \approx 1 \text{ eV}$  for titanium atoms] [5] are separated at relatively low and high magnetron pressures  
40 27 ( $p = 0.4$  and  $1.3 \text{ Pa}$ ). The dashed curves represent fitting of the TD-LIF signal. The measured velocity  
41 28 field is the axial component (component perpendicular to the target surface as shown in figure 1 (a)),  
42 29 and two Gaussian functions were used to fit the experimental signal, which corresponded to the ther-  
43 30 malized and energetic atoms populations. Because the measurements were carried out 5 cm away  
44 31 from the target, sputtered atoms undergo collision with the buffer gas, inducing the energetic popu-  
45 32 lation to be better fitted by a Gaussian function instead of the commonly known Thompson function  
46 33 [24]. The fitting by these two Gaussians results in some discrepancy for negative velocity ( $v < 0$ ), espe-  
47 34 cially at low pressure (0.4 Pa, top panel of figure 2). The main goal of the fitting is to better calculate  
48 35 the flux and energy of the atoms with momentum towards the substrate (positive velocity) to correlate  
49 36 with the film properties. Only the measurements performed at the substrate position are shown at a  
50 37 distance  $z = 5 \text{ cm}$  from the target. For a detailed description of the AVDFs' fitting and titanium sput-  
51 38 tered atoms transport characterization combined with PIC Monte Carlo modeling in argon gas, the  
52 39 reader is referred to Revel *et al.* [5].  
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**Figure 2.** TD-LIF signal of the neutral Ti( $J=2$ ) atoms as a function of the percentage of  $N_2$  in gas mixture at  $P_{DC}=5 \text{ W/cm}^2$ ,  $r=1.25 \text{ cm}$ ,  $z=5 \text{ cm}$  and  $p=0.4 \text{ Pa}$  (top) and  $p=1.3 \text{ Pa}$  (bottom). Dashed curves are the fitting of the measured signal.

The addition of nitrogen to the argon discharge completely altered the sputtering process.  $N_2$  molecules react with the target surface material, forming a nitride layer that induces variations in secondary electron emission, electron temperature, and cathode voltage, but also induces variations in the ions striking the cathode, that is,  $Ar^+$ ,  $N_2^+$ , and  $N^+$  allowing sputtering instead of only  $Ar^+$  in pure Ar gas. Figure 2 shows that the TD-LIF signal at the substrate positioned at a distance  $z=5 \text{ cm}$  from the target decreased progressively with increasing  $N_2$  content. This decrease was observed for all atoms regardless of their energy. This is due to two main changes: (i) poisoning of the target surface in which the binding energy of Ti-N (8.04 eV [25]) is higher than that of Ti-Ti ones (6.6 eV [26]) and (ii) plasma variation in which the  $N^+$  and  $N_2^+$  ions can be less efficient for sputtering compared to the  $Ar^+$  ion [27]. TD-LIF measurements performed near to the target surface ( $z=1.1 \text{ cm}$ ) at low pressure of 0.4 Pa show that the surface nitridation affects the surface binding energy, we measured an average energy of  $4.0 \pm 0.2 \text{ eV}$  at nitride mode and  $3.2 \pm 0.2 \text{ eV}$  in metallic mode (100% Ar). The gas mixture does not affect the temperature of thermalized sputtered atoms since they are in thermal equilibrium with the buffer gas. In terms of the energy of the sputtered atoms, an expected difference can be observed when the gas pressure is increased; thermalized atoms are increased at a relatively high pressure ( $p=1.3 \text{ Pa}$ )



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3 1 compared to the energetic atoms. Indeed, the sputtered atoms leaving the target with an average  
4 2 energy of  $4.0 \pm 0.2$  eV (nitride mode,  $3.2 \pm 0.2$  eV in metallic mode) towards the substrate [5] undergo  
5 3 more collisions than at 0.4 Pa, efficiently transfer their energy to argon and nitrogen particles, and are  
6 4 more thermalized when they reach the substrate position at  $p=1.3$  Pa.

8 5 We calculated the deposition rate from the film thickness determined from the scanning electron mi-  
9 6 croscopy images. The flux of sputtered neutral Ti atoms ( $^3F_2$ , 0 eV) was obtained from the AVDFs using  
11 7 the following formula:

$$\Phi_{J=2}(\text{cm}^{-2} \text{s}^{-1}) = \int_0^{\infty} v \text{AVDF}(v) dv, \quad (1)$$

15 9 where,  $v$  is the axial velocity. Figure 3 (a) shows that the parameters, i.e., the flux of sputtered atoms  
17 10 and the deposition rate, are in good agreement.

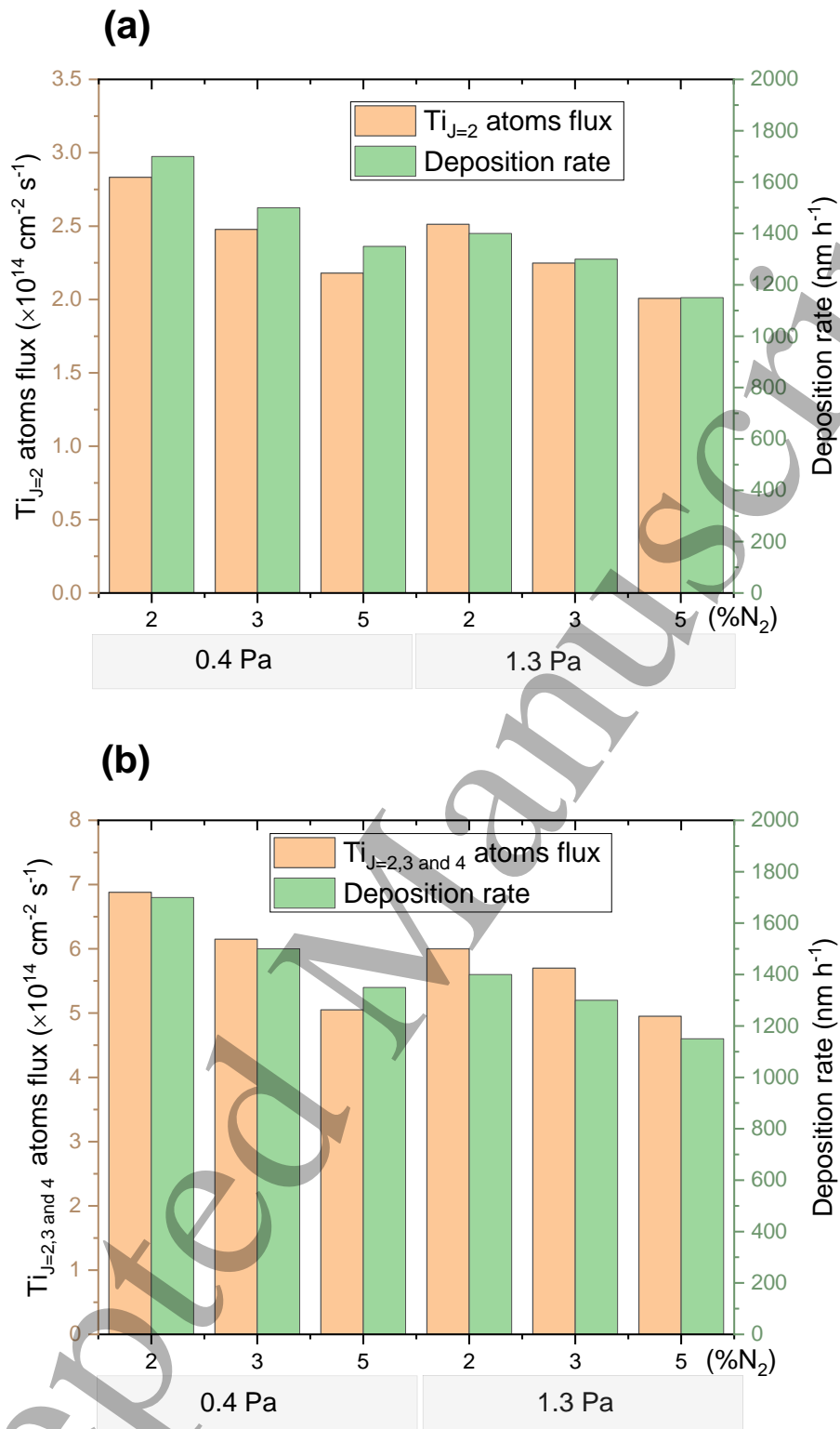
19 11 Because the TD-LIF measurements were performed on the lower level of the ground state ( $J = 2$ ), we  
20 12 assumed that neutral titanium atoms are in Boltzmann equilibrium and calculated the absolute value  
21 13 of the flux of ground-state titanium atoms as

$$\Phi_{\text{absolute}}(\text{cm}^{-2} \text{s}^{-1}) = \Phi_m \left\{ 1 + \sum_{J=1}^{m-1} \frac{g_J}{g_m} \exp\left(-\frac{E_J - E_m}{k_B T}\right) \right\}, \quad (2)$$

26 15 where  $E_J$  and  $g_J$  are the energy and statistical weight, respectively, of state  $J$  and  $k_B$  is the Boltzmann  
28 16 constant. The titanium ground state has a triplet structure, in which the levels  $J = 2, 3$ , and 4 are at  
29 17 energies of 0, 0.021, and 0.047 eV, respectively. Therefore, Eq. (2) simplifies to

$$\Phi_{\text{absolute}}(\text{cm}^{-2} \text{s}^{-1}) = \Phi_{J=2} \left\{ 1 + \frac{g_3}{g_2} \exp\left(-\frac{E_3 - E_2}{k_B T}\right) + \frac{g_4}{g_2} \exp\left(-\frac{E_4 - E_2}{k_B T}\right) \right\}. \quad (3)$$

34 19 The temperature of the thermalized atoms was used to calculate the absolute flux of the Ti atoms. The  
35 20 absolute flux and deposition rates are shown in figure 3 (b). The flux of Ti atoms reaching the substrate  
36 21 at 2 %  $\text{N}_2$  and  $p = 0.4$  Pa was  $6.8 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$  and decreased to  $5 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$  when 5 %  $\text{N}_2$  was added  
37 22 to the gas mixture. Similarly, the deposition rate decreased from 1700 to 1350  $\text{nm h}^{-1}$  when the gas  
38 23 mixture varied from 2 to 5 %  $\text{N}_2$ . By increasing the pressure  $p = 1.3$  Pa, a slight decrease in the deposi-  
39 24 tion rate and Ti atoms flux was measured compared to  $p = 0.4$  Pa. The influence of the gas mixture was  
40 25 similar at both pressures. These variations show good agreement between the flux and the deposition  
41 26 rate for the 0.4 and 1.3 Pa pressures used in this work. In fact, increasing the percentage of nitrogen  
42 27 induces poisoning of the target and decreases the number of sputtered titanium atoms, resulting in a  
43 28 corresponding decrease in the deposition rate. In the studied pressure range, the pressure variation  
44 29 slightly affected the deposition rate, whereas the sputtered atoms thermalization increased signifi-  
45 30 cantly when the pressure increased (figure 2).



**Figure 3.** Variation of the flux of neutral Ti atoms [(a)  $J=2$  level, (b) the absolute flux of neutral Ti] and the deposition rate under dcMS discharge as a function of the percentage of  $N_2$  in the background gas at  $z = 5$  cm,  $P_{DC} = 5 \text{ W cm}^{-2}$ , and  $p = 0.4$  and  $1.3$  Pa.

### III-2. Influence of deposited energy on the film microstructure, texture, and morphology

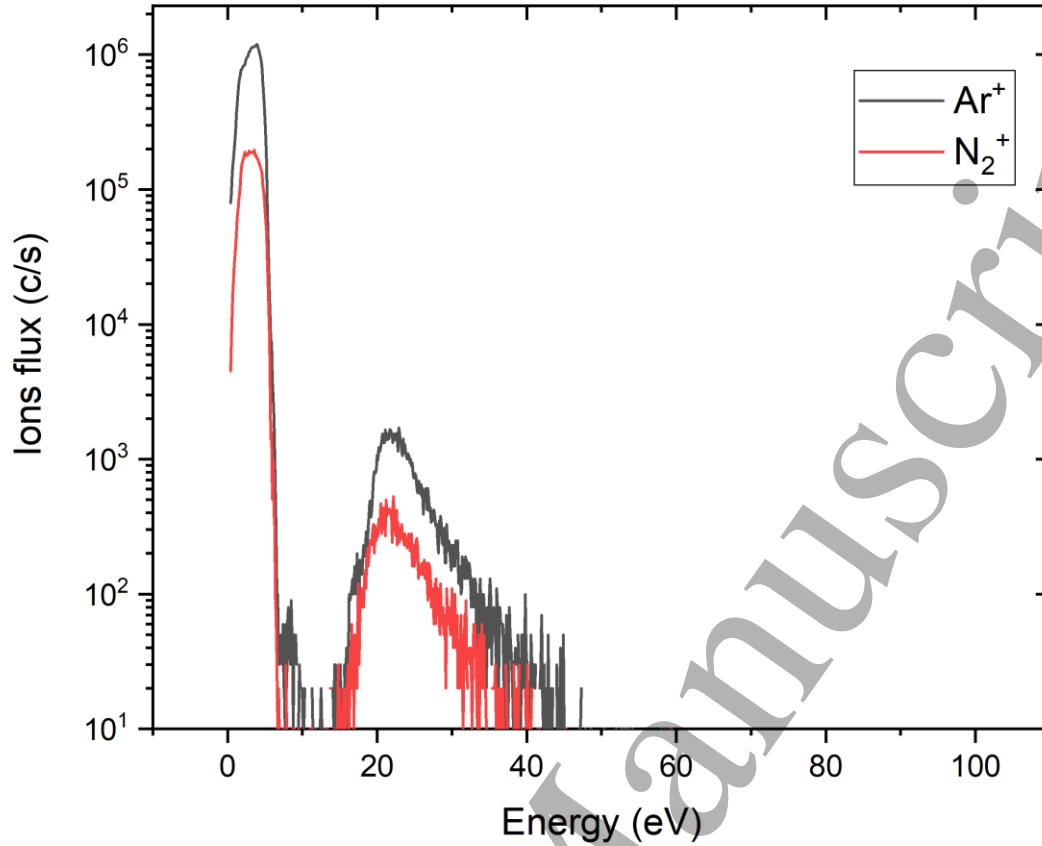
As mentioned in the experimental section, TiN films were deposited in the dcMS discharge without any heating or bias of the substrate. The Ar gas temperature was measured as a function of the distance from the target using tunable diode laser absorption spectroscopy. It reaches a high temperature of 1400 K near the target ( $z = 1.3$  cm), but a low temperature of approximately 500 K was measured at  $z = 5$  cm [5]. Under these conditions, the total energy flux towards the substrate is the sum of the different contributions due to the kinetic energy of different deposited species. This section reports the different contributions.

In dcMS using a balanced magnetron, the plasma is trapped close to the target surface, in which the ion flux into the substrate decreases [4]. Figure 4 shows the IEDFs of  $\text{Ar}^+$  and  $\text{N}_2^+$  at 0.4 Pa and 3 % $\text{N}_2$  in gas mixture. The mass spectrometer signal represents the flux of ions, and two groups of ions arrive at the substrate: the low-energy group ( $E < 6$  eV) and high-energy group ( $E$  around 20 eV). The low-energy group of ions is thermalized with the buffer gas. The high-energy group has been studied in many works, especially in HiPIMS discharge [28–30], and is generally attributed to ion acceleration inside spokes in magnetron plasma. As shown in figure 4, the signal magnitude of this high-energy group is three orders of magnitude lower than that of the thermalized ions. Thus, to calculate the energy flux towards the substrate, only low-energy ions were considered. In an early study of Ar/ $\text{N}_2$  magnetron discharge, Petrov *et al.* [23] demonstrated that  $\text{Ar}^+$  ions are the primary ions incident on the substrate in Ar- $\text{N}_2$  dcMS discharges, with a flux accounting for more than 92 % of the total ion flux when the percentage of  $\text{N}_2$  was lower than 15 %. It worth to mention herein that ours mass spectrometer measurements are not calibrated. Thus, the corresponding ion energy flux to the substrate is calculated using the following expression [31]:

$$\Phi_{energy, \text{Ar}^+} (\text{mW cm}^{-2}) = \frac{1}{4} e n_i v_i V \quad (4)$$

where  $n_i$  and  $v_i$  are the ion density and thermal ion velocity,  $e$  is the electron charge and  $V$  is the voltage drop in the substrate sheath. Bradley *et al.* [32] measured the ions density in dcMS with a cathode of 15 cm in diameter, 0.26 Pa argon pressure, and a dc power of about  $1.5 \text{ W cm}^{-2}$ , they found an ions density of about  $10^{16} \text{ m}^{-3}$  at  $z = 5$  cm. In ours deposition system at  $z = 5$  cm away from the target and  $P_{DC} = 5 \text{ W cm}^{-2}$ , we assumed an ion density of  $2 \times 10^{16} \text{ m}^{-3}$  and an ion temperature of 600 K [5]. Based on our mass spectrometer measurements of the thermalized ions (figure 4), the voltage drop at the substrate sheath was estimated to be 3 V. For these plasma parameters, the energy flux corresponding to the ion contributions (equation 4) is approximately  $0.075 \text{ mW cm}^{-2}$ .

Regarding the energy flux of the electron contribution, the energetic secondary electrons accelerated in the cathode sheath are trapped near the cathode surface for ionization by the magnetic field, and only thermalized electrons can reach the substrate. Our substrate was grounded, and because the plasma potential at  $z = 5$  cm was positive, the thermalized electrons were pushed away from the substrate. Therefore, their energy flux contributions can be neglected.



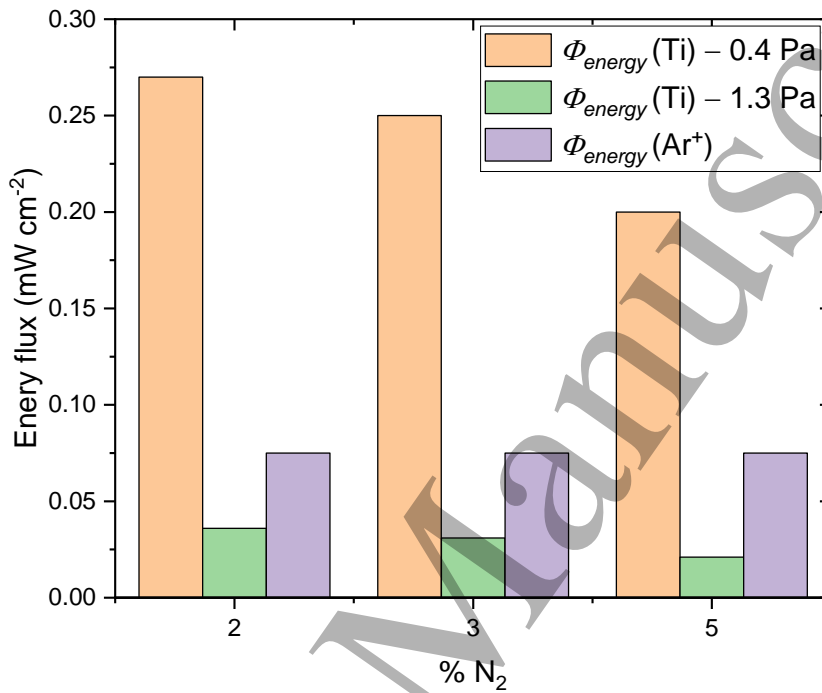
**Figure 4.** IEDFs of  $\text{Ar}^+$  and  $\text{N}_2^+$  ions at  $z = 5$  cm, 3 %  $\text{N}_2$ ,  $P_{DC} = 5$  W  $\text{cm}^{-2}$ , and  $p = 0.4$ .

For the neutral species reaching the substrate, the energy flux deposited by Ti atoms ( $J=2$ ) is obtained as follows:

$$\Phi_{energy, J=2} = \int_0^{\infty} \frac{1}{2} M v^2 v AVDF(v) dv, \quad (2)$$

where  $M$  (amu) is the atomic mass of titanium and  $v$  is the axial velocity. The total energy flux of the ground state Ti atoms was then deduced by applying equation (3). Figure 5 shows the variations in the energy flux of the ground state of the neutral Ti atoms and  $\text{Ar}^+$  ions as a function of the nitrogen percentage. At  $p = 0.4$  Pa, the energy flux gradually decreases from 0.27 to 0.20  $\text{mW cm}^{-2}$  when the nitrogen percentage increases from 2 to 5 %. This decrease was mainly due to the decrease in the number of Ti-neutral atoms reaching the substrate. However, at  $p = 1.3$  Pa, where the vapor is more thermalized, the energy flux is one order of magnitude lower than that measured at 0.4 Pa. It is on the order of 0.03  $\text{mW cm}^{-2}$ . The most important result is that the energy flux of sputtered Ti atoms is higher than that of  $\text{Ar}^+$  ions at a low magnetron pressure of 0.4 Pa. Other sputtered species, such as nitrogen atoms (N), could contribute to the energy flux towards the substrate, and its behavior as a function of pressure is expected to be similar to that of neutral Ti atoms. The knowledge of their energy flux requires further investigation. In other deposition system, Gauter *et al.* [33] used direct calorimetric probe to characterize the energy flux on the substrate during the deposition by HiPIMS

discharge with copper magnetron, they measured an averaged energy flux of  $20 \text{ mW cm}^{-2}$ . Calorimetric probe was also used by Bornholdt et al. [34] to energy flux during the deposition of ZnO by a radio-frequency discharge of  $15 \text{ W cm}^{-2}$  (3 target with  $5 \text{ W cm}^{-2}$ ), they found a total energy flux of  $30 \text{ mW cm}^{-2}$ . In those calorimetric probe experiments, the energy flux is higher than the obtained by our diagnostics because (i) their measurements consider the contributions of all species arriving to the substrate, (ii) the discharge power is higher than used in our work and (iii) the zinc and copper have higher sputtering efficiency compared to titanium.



**Figure 5.** Energy flux of neutral of the ground state of Ti sputtered atoms as function of the percentage of N<sub>2</sub> in gas mixture, calculated at the substrate distance ( $z = 5 \text{ cm}$ ), for  $p = 0.4$  and  $1.3 \text{ Pa}$ .

### A. Film composition

Measurement of the chemical composition of thin films is not an easy task when the films contain light elements, such as nitrogen. The TiN samples deposited were analyzed using EPMA, and the percentages of O, Ti, and N were obtained. The quantitative results are summarized in Table 2. For Ti and N, the films are quasi-stoichiometric for both pressures (0.4 and 1.3 Pa). The Ti and N concentrations were approximately 48 and 50 at. % at respectively for the films at 0.4 Pa. At 1.3 Pa, the Ti concentration was 48 at. % and the N concentration is 46 at. %. Concerning the oxygen contamination, EPMA measurements show that the concentration of O element increases in the films from 2 at. % at 0.4 Pa to 6 at. % at 1.3 Pa. This contamination can be attributed to the residual oxygen in the chamber. Because the amount of oxygen in the chamber is constant and weak, the increase in oxygen concentration with the pressure is due to the decrease in the deposition rate. Indeed, films that grow at a low deposition rate contain more oxygen. However, the deposition rate at 1.3 Pa is about 85% of the deposition rate at 0.4 Pa. This decrease seems rather small to explain the increase of O concentration, from 2 to 6%. The higher oxygen concentration seems induced by film density (denser at 0.4 Pa)

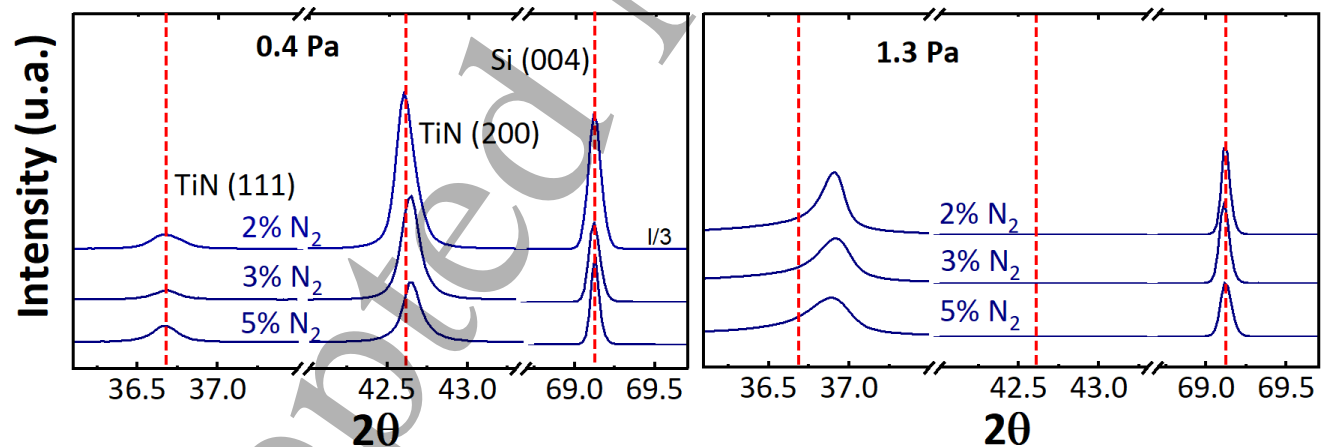
or by the plasma variation especially the electron density and temperature assuming that the oxygen atoms are produced by the dissociation of oxygen molecule by electron impact.

**Table 2.** Concentration of Ti, N, and O elements measured with EPMA (top) for the samples deposited at 3%N<sub>2</sub>.

	Ti	N	O
0.4 Pa	50 ±1 %	48 ±1 %	2 ±1 %
1.3 Pa	48 ±1 %	46 ±1 %	6 ±1 %

## B. Film texture, microstructure, and morphology

Figure 6 shows the  $\theta$ -2 $\theta$  X-ray diffractograms of TiN films deposited in dcMS discharge for different gas mixtures at pressures of 0.4 and 1.3 Pa. All films exhibited characteristic diffraction peaks corresponding to polycrystalline TiN with a cubic (NaCl-type) structure. At 0.4 Pa, the thin films exhibit a mixed orientation with the (111) and (200) planes. Other planes with negligible intensities were detected and are not shown here. At 0.4 Pa, we observed that the (111) and (200) planes co-existed, but the peak corresponding to the (200) planes was highly dominant. At 1.3 Pa, we observed that the (111) planes exhibited the highest intensity for all percentages of N<sub>2</sub> investigated. We also observed the quasi-absence of the (200) planes. The two preferred orientations have different surface energies. In fact, the family of (111) planes has an atom density greater than that of (200) planes, thus inducing a lower surface energy of the (111) planes. Therefore, we can consider that the latter are more stable and require less energy to be produced than the (200) plane. Thus, the preferred (111) orientation is the result of deposition under conditions close to equilibrium [6]. Because the TiN films were deposited at ambient temperature and without substrate bias, the texture variation could only be affected by the energy flux of the arriving species and the chemical composition of the films.

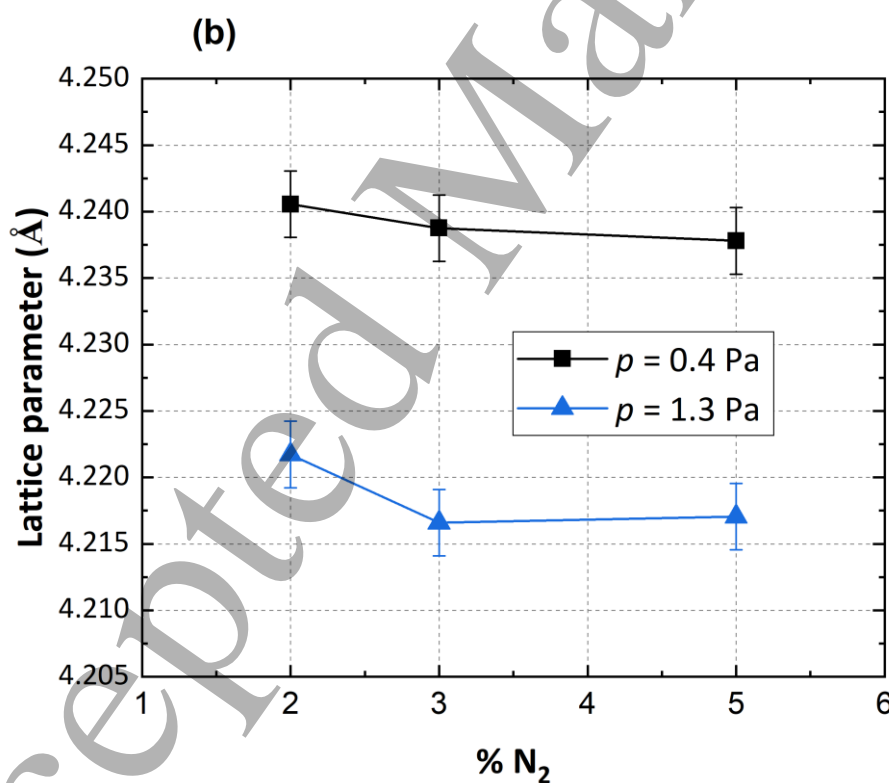
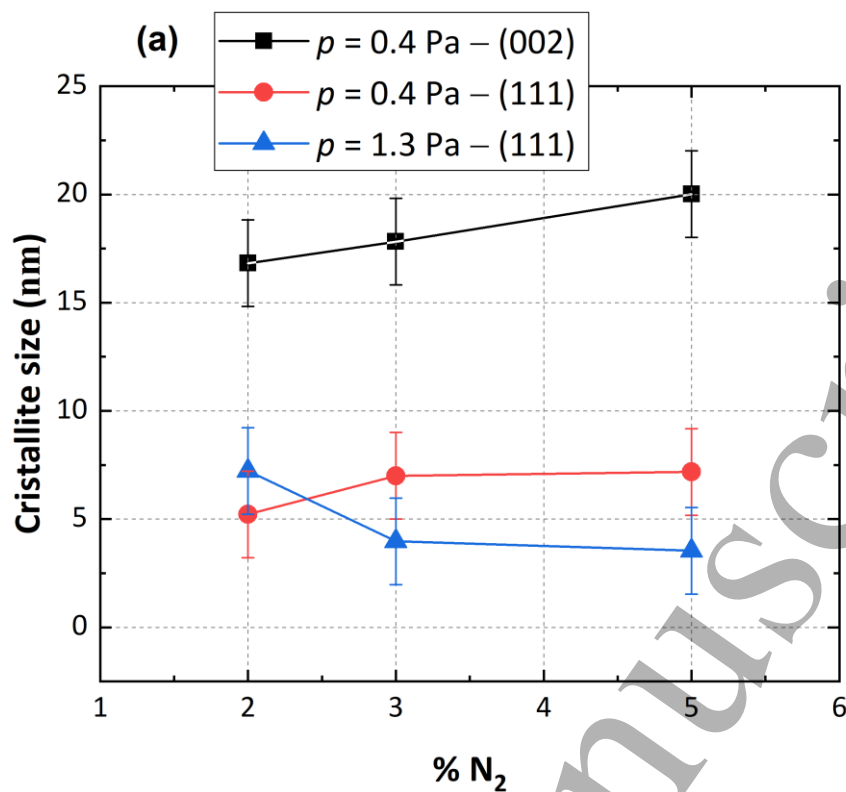


**Figure 6.**  $\theta$ -2 $\theta$  X-ray diffractograms of TiN films deposited by dcMS as a function of the percentage of N<sub>2</sub> in the gas mixture, at  $p = 0.4$  Pa (left) and 1.3 Pa (right). For films at  $p = 0.4$  Pa – 2 % N<sub>2</sub> the XRD signal was divided by a factor of 3.

The gas composition and total pressure influence the number of sputtered Ti neutral atoms reaching the substrate position (figure 3) and substantially affect the energy flux of neutral-sputtered Ti atoms (figure 5). It should be noted that films with similar chemical compositions have different preferred

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2 1 orientations. The preferred orientation has been studied in many previous works on dcMS under dif-  
3 2 ferent energetic ion bombardment conditions [6,35–37], and it is well known that by increasing the ion  
4 3 energy at the substrate, the preferred orientation switches from [111] to [200]. As shown in figure 5,  
5 4 at a low pressure (0.4 Pa) we found that the energy flux of the ion contribution towards the substrate  
6 5 is negligible, and the primary deposited energy that can affect the adatom is the energy flux of the  
7 6 ground state of neutral Ti sputtered atoms. As the switching of preferred orientation from the [200]  
8 7 to the [111] one occurs by switching the pressure from 1.3 to 0.4 Pa, we deduce that the energy flux  
9 8 of the neutral sputtered species (Ti and N) enables the growth of films with [200] orientation. The  
10 9 (200) preferred orientation is characterized by high hardness compared with the [111] orientation  
11 10 [7,20].  
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17 11 Using X-ray diffractograms, the (111) and (200) peaks were adjusted using a Lorentzian function, and  
18 12 the full width at half maximum (FWHM) was determined to estimate the crystallite size based on the  
19 13 Scherrer formula [38]. The (111) peaks at 1.3 Pa were fitted with two Lorentzian functions because of  
20 14 the asymmetry on the left of the peak, and the crystallite size was calculated from the FWHM of the  
21 15 Lorentzian with the highest amplitude. The results are shown in figure 7 (a). There are two groups of  
22 16 crystallites according to their size. A group of sizes of approximately  $18 \pm 2$  nm corresponding to the  
23 17 crystallites oriented in the [100] direction normal to the substrate existing in the films at 0.4 Pa. The  
24 18 second group had a crystallite size of approximately  $5 \pm 2$  nm among the remaining crystallites.  
25 19 Recently, Viloan *et al.* [20] reported a high hardness of TiN crystallites with a large crystallite size. This  
26 20 type of crystallite is obtained when the energy flux of the sputtered neutral is higher than the energy  
27 21 flux of the ion contribution (figure 5).  
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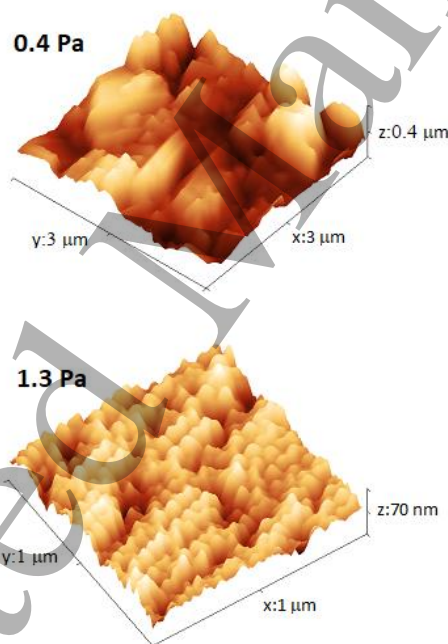
**Figure 7.** Variations of crystallite size (a) and lattice parameter (b) as function of the percentage of N<sub>2</sub> in the gas mixture, in dcMS process.

Similarly, peak fitting was used to calculate the lattice parameter, considering the shift in the



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3 1 diffraction angle in the Bragg equation [figure 7 (b)]. This was possible because the calibration of the  
4 2 XRD instrument was performed using the (004) diffraction peak observed from the Si substrate for all  
5 3 samples (figure 6). The films deposited at 0.4 Pa exhibit a lattice constant around 4.24 Å. The lattice  
6 4 constant of bulk TiN is 4.24 Å in the absence of stress. An increase in the nitrogen ratio in the gas  
7 5 mixture from 2 % to 5 % induced a slight decrease in the lattice constant from 4.240 Å to 4.235 Å. This  
8 6 decrease may be related to a slight variation in the concentration of N in the film, which was not  
9 7 detected by EPMA. However, for the films deposited at 1.3 Pa the lattice parameter was approximately  
10 8 4.215 Å, suggesting the presence of tensile stress in the films. As shown in figure 4, the energy flux of  
11 9 sputtered Ti atoms at 0.4 Pa is one order of magnitude higher than at 1.3 Pa. Therefore, the high-  
12 10 energy flux of Ti atoms seems to allow stress removal in films at low pressures.  
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17 11 AFM measurements were performed to determine the morphology and roughness of the film surfaces  
18 12 (figure 8). The films deposited at 0.4, 1.3 Pa, and 3 % N<sub>2</sub> with approximately similar thicknesses (~ 2.9  
19 13 μm) were characterized. The film deposited at low pressure exhibited a very high roughness (RMS  
20 14 surface roughness = 67 nm). The surface of this film showed large faceted grains, in agreement with  
21 15 the XRD results. On the other hand, the film deposited at 1.3 Pa show a lower roughness (RMS surface  
22 16 roughness = 11 nm) and small grains. Once again, the difference in the film surface morphology may  
23 17 be explained by the high energy flux of sputtered Ti atoms at 0.4 Pa.  
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51 20 **Figure 8.** AFM images of the surface of the samples deposited in dcMS, at 2 % N<sub>2</sub> in the gas mixture and  $p = 0.4$   
52 21 Pa (top) and 1.3 Pa (bottom).  
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#### 56 22 **IV. Conclusion**

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59 25 The neutral titanium sputtered atoms velocity distribution functions (AVDFs) at the substrate position  
60 26 were measured by a tunable diode laser induced fluorescence (TD-LIF) technique in direct current

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3 1 magnetron sputtering (dcMS) discharge and correlated to the TiN thin film properties. The measured  
4 2 velocity was perpendicular to the substrate (axial velocity in a planar circular magnetron). The flux of  
5 3 the sputtered particles was then calculated and correlated with the deposition rate. Their evolutions  
6 4 as a function of the N<sub>2</sub> content in the gas mixture are in good agreement. TiN thin films were deposited  
7 5 at 0.4 and 1.3 Pa, for different gas mixtures Ar/N<sub>2</sub> close to the conditions where stoichiometric TiN was  
8 6 formed, without bias voltage and heating of the substrates. Their microstructure, texture, and chem-  
9 7 ical composition were characterized using X-ray diffraction, EPMA. The films deposited at a low  
10 8 pressure (0.4 Pa) show a [200] preferred orientations. For 1.3 Pa, the films were oriented along the  
11 9 [111] direction and tensile stress was observed. Because the film growth was carried out without bias  
12 10 and heating of the substrate, we studied the influence of the energy flux (i.e., the product of particle  
13 11 flux and incident particle energy) of sputtered atoms deduced from TD-LIF measurements on the film  
14 12 properties. At a relatively low magnetron discharge pressure of 0.4 Pa, we found that the energy of  
15 13 the ground state of sputtered neutral Ti impinging on the substrate is higher than the energy flux of  
16 14 ionized particles corresponding mainly to Ar<sup>+</sup>. This high energy flux of sputtered neutral atoms allows  
17 15 the growth of TiN oriented along the [111] direction. In addition, it allows stress removal in the films.  
18 16 At 1.3 Pa where the sputtered atoms energy flux is one order lower compared to 0.4 Pa the (111)  
19 17 texture was obtained.  
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25 30 Lamour is also acknowledged for the access to the X-ray diffractometers.  
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