

Nanostructured Ti thin films by magnetron sputtering at oblique angles

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Abstract.-

The growth of Ti thin films by the magnetron sputtering technique at oblique angles and at room temperature is analysed from both experimental and theoretical points of view. Unlike other materials deposited in similar conditions, the nanostructure development of the Ti layers exhibits an anomalous behaviour when varying both the angle of incidence of the deposition flux and the deposition pressure. At low pressures, a sharp transition from compact to isolated, vertically aligned, nanocolumns is obtained when the angle of incidence surpasses a critical threshold. Remarkably, this transition also occurs when solely increasing the deposition pressure under certain conditions. By the characterization of the Ti layers, the realization of fundamental experiments and the use of a simple growth model, we demonstrate that surface mobilization processes associated to a highly directed momentum distribution and the relatively high kinetic energy of sputtered atoms are responsible for this behaviour.

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I.- Introduction

The oblique angle configuration is a useful geometrical arrangement to promote the vacuum growth of nanostructured layers with high porosity and large specific surfaces [1]. The main feature of evaporation techniques operating under this configuration is the oblique arrival of sublimated species at a substrate and their subsequent condensation in the form of tilted columnar structures with diameters in the order of few tens nanometers [2]. This geometrical arrangement has also been tested with magnetron sputtering (MS) techniques [3-8] obtaining films with diverse columnar and porous structures and outstanding properties for applications in medicine, photovoltaics, microfluidics, catalysis or sensors, among others [1]. For example, in a recent work, we prepared by this technique operated at oblique angles (MS-OAD) a nanostructured coating made of Ti nanocolumns that exhibited opposite behavior towards cell or bacteria proliferation, a property that makes this film suitable for medical applications [9].

MS is a widespread growth method fully scalable for mass production and widely employed in research and industry [10]. Unlike electron beam evaporation method working in full vacuum conditions, MS-OAD utilizes a powered target placed in a reactor chamber that contains an inert gas (usually argon) at low pressures. Thanks to the propagation of an electromagnetic signal, this gas turns into plasma [11], resulting in the acceleration of positive ions towards the target and the sputtering of atoms with kinetic energies around 10 eV in a preferential direction perpendicular to the target surface [10]. These species pass through the plasma and are deposited on a tilted substrate where they give rise to a nanostructured film. Therefore, in contrast with the evaporation technique, the MS-OAD introduces particular features that may strongly influence the growth of the films: i) the plasma species may interact with the film during the deposition [12], ii) some

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3 sputtered species may collide with heavy particles in the plasma and gradually loss their
4 kinetic energy and preferential direction before being deposited (this phenomenon is
5 called thermalization) [13], and iii) the kinetic energy of sputtered particles may be high
6 enough to induce atomic mobilization processes at the film surface (dubbed hyperthermal
7 processes) that may alter the film morphology [14-16].

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10 In a recent work [17] we have analyzed the MS-OAD of Au thin films with the idea of
11 expanding the well-known Thornton's Structure Zone Model (SZM) [18-19],
12 incorporating the tilt angle of the substrate as an additional degree of freedom. In
13 agreement with numerous experiments at low temperatures, we concluded that four
14 generic nanostructures can develop depending on the plasma gas pressure and the tilt
15 angle of the substrate [8, 17]. Remarkably, the growth of these gold nanostructures could
16 be accurately explained by just considering the collisional transport of sputtered particles
17 in the plasma gas and their subsequent deposition, disregarding any hyperthermal
18 mobilization process on the film surface. Moreover, the same model was found adequate
19 to describe the MS-OAD of TiO₂ thin films [20], thus suggesting that hyperthermal
20 processes might not be efficient to produce noticeable changes in the final film
21 nanostructures, at least in these two reported cases. However, the comparison between
22 the nanostructures appearing in these Au or TiO₂ films with those in the nanocolumnar
23 Ti coating mentioned above [9], strongly suggests that additional mechanisms may play
24 a relevant role in this latter case. In fact, while the porous gold nanostructure found at low
25 pressures and high deposition angles consisted of densely packed columnar arrays tilted
26 more than 50° with respect to the vertical, the nanostructure of Ti coatings prepared
27 under similar experimental conditions presented a well-spaced and almost perpendicular
28 nanocolumnar structure. In the present work, we have carried out a systematic study on
29 the growth of nanostructured Ti films by MS-OAD, exploring a wide range of

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3 experimental deposition conditions. Through the characterization of the obtained
4 nanostructures, the analysis of fundamental experiments performed under selected
5 conditions and the help of a simple growth model, the main processes governing the
6 growth of these Ti layers have been identified and general insights gained that may likely
7 be extended to understand the growth and nanostructure development of other materials.
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17 **II.-Experimental conditions**

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20 We have deposited a series of Ti thin films by MS-OAD at different pressures and
21 deposition angles. A 5 cm diameter Ti target was employed with argon as sputter gas and
22 a base pressure in the chamber in the mid 10^{-7} Pa range. A flat 1 cm^2 Si (100) substrate
23 (with surface roughness below 0.5 nm) cleaned in an ultrasonic bath, was placed at 0.22
24 m from the target and tilted at different angles with respect to its normal (see figure S1).
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26 The argon pressure, p_g , was set to 0.15, 0.5, 1 and 1.5 Pa, whereas the tilt angle of the
27 substrate, σ , was set to 0° , 45° , 60° , 70° , 80° and 85° in the case of $p_g = 0.15 \text{ Pa}$, and 0° ,
28 45° , 60° in the higher pressure cases. The DC electromagnetic generator was set at a
29 constant power of 300 W, conditions at which the visible plasma glow covers a volume
30 extending up to 7 cm from the target and remains more than 15 cm away from the film.
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32 A cylindrical metallic chimney with 5 cm radius and 9 cm long was placed besides the
33 target to collimate the ballistic flux of material and to trap the sputtered species that stay
34 thermalized in the plasma phase (see ref. [21] for more details). The film temperature
35 was always below 350 K during the sputtering process, whereas the deposition times
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58 Films were characterized by field emission scanning electron microscopy (FESEM) from
59 two different perspectives, Δ and Π , defined in figure 1. Rutherford Backscattering
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3 Spectroscopy (RBS) was employed to assess the areal density of the films: experiments
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5 were carried out in the 3 MV tandem accelerator of the National Center for Accelerators
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7 (Seville, Spain) with a beam of 1.5 MeV alpha particles and a passivated implanted planar
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9 silicon (PIPS) detector located at 165° scattering angle, with accumulated doses about 1.5
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11 μC , and ~ 1 mm beam spot diameter. The RBS spectra were simulated with the SIMNRA
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13 code [22], whereas the density of each film was calculated by dividing the areal density
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15 by the thickness, as obtained from the cross-sectional FESEM image. Moreover, for
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17 comparison purposes, a Ti thin film was deposited by the electron beam-assisted physical
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19 vapour deposition at a zenithal deposition angle of 85° using the experimental set-up
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21 described in reference [23].
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28 Crystal quality and texture of the films were assessed by X-ray diffraction (XRD) in a
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30 Bragg-Brentano configuration. A XRD diffractometer with 4-angle goniometer (Bruker,
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32 D8 Advance) was used to explore the preferential orientation of the crystal domains in
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34 the films by means of pole figure analysis of different reflections in a wide range of tilt
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36 angles, $\chi=0-70^\circ$.
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42 **III.-Growth Model**

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47 Following the same approach than in previous works [17, 23, 24], our growth model
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49 selects the minimum set of processes that may explain the most outstanding
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51 nanostructural features observed in the films upon variation of experimentally
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53 controllable quantities. We consider the deposition of Ti atoms on a two-dimensional flat
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55 substrate that defines the x-y plane of coordinates, whereas the z axis is defined by the
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57 direction perpendicular to it. The three dimensional space is divided into a $N_L \times N_L \times N_H$
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59 cubic grid, where each cell has the value 1 if it contains a deposited Ti atom and 0
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3 otherwise. Each cell, with an estimated size equivalent to the typical atomic volume in
4 the material ($\sim 0.4 \times 0.4 \times 0.4$ nm), represents an atom in the network. The Ti atoms are
5 sputtered from the cathode with a momentum distribution $F(\vec{p})$, where \vec{p} is the lineal
6 momentum, and experience different scattering events in the plasma gas, arriving at the
7 film with a momentum distribution function, $f(\vec{p})$. Then, the deposition process is
8 described as follows: once the Ti atoms approach the film surface, they follow a straight
9 trajectory with momentum \vec{p} until they hit the surface, where the following hyperthermal
10 processes are taken into account (see figure 2a and 2b for a scheme):
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25 *Kinetic energy-induced mobility.* This process is well documented in the literature and
26 considers that upon deposition vapour atoms may transfer part of its kinetic energy and
27 momentum to a surface atom, breaking the bonds and inducing a preferential mobility in
28 the direction defined by the lineal momentum of the vapour atom [14-16, 25]. The
29 dynamics of such collision is quite complex and, for simplicity reasons, we assume the
30 following mechanism: if the energy involved in the collision, $\varepsilon = p^2 / 2M_{Ti}$ (M_{Ti} is the
31 mass of the Ti atom) is above certain energy threshold, ε_K , the target atom breaks its
32 bonds and both atoms are allowed to relax to an available next neighbor position within
33 a cone region aligned with the momentum of the incoming particle (see figure 2a).
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49 *Biased diffusion:* If the kinetic-energy induced mobility process is inefficient, either
50 because the energy involved is below ε_K or because there are no free next neighbour sites
51 available for the target atom to relax, we assume that the incident atom may keep part of
52 its momentum in the direction parallel to the surface, p_{\parallel} , and slide over it until it becomes
53 deposited by sticking at an obstacle site (see figure 2b). As stated in ref. [15-16, 26], this
54 process takes place if the energy associated to that momentum, $p_{\parallel}^2 / 2M_{Ti}$, is above a
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3 certain value, ε_{BD} , and the angle of incidence above certain angular threshold with respect
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6 to the normal to the surface, θ_{BD} .
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9 If none of the abovementioned processes takes place, the arriving atom is deposited just
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11 at the landing position. Consequently, the difference between this growth model and those
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13 previously employed in references [17, 20] is the addition of hyperthermal processes. In
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15 order to discuss the results, we specifically make use of the concept of thermalization
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17 degree of sputtered particles, usually named Ξ , which is a non-dimensional quantity
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19 deduced in ref. [21] for the MS-OAD of Ti thin films as $\Xi \approx 13.2 \times p_g L \text{ Pa}^{-1} \text{ m}^{-1}$, with L
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21 the distance between the target and the film. The value of Ξ accounts for the
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23 thermalization degree at the substrate position of sputtered particles by interaction with
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25 the plasma gas: when $\Xi \ll 1$ the deposition flux is highly energetic and directional,
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27 whereas $\Xi \gg 1$ implies that particles are thermalized and possess low energy and no
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29 preferential directionality.
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37 The model is solved by knowing $F(\vec{p})$, $f(\vec{p})$, ε_K , ε_{BD} and θ_{BD} . $F(\vec{p})$ has been
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39 calculated by using the SRIM code [27], through which the function $f(\vec{p})$ was obtained
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41 using the well-known and tested SIMTRA code [28-29]. The value of ε_K was taken as
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43 the heat of sublimation of Ti, $\varepsilon_K = 4.9 \text{ eV}$, whereas the biased diffusion energy and
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45 angular thresholds have been estimated using molecular dynamics simulations and the
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47 Kalypso code [30]. By this calculation, we have thrown numerous Ti atoms with different
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49 energies and angles onto a Ti flat surface and found the values $\varepsilon_{BD} \sim 1 \text{ eV}$ and $\theta_{BD} \sim 30^\circ$
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57 , which are quite similar to those reported in ref. [26] for Cu.
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3 It is worth noticing that other physical interactions and processes involved in the thin film
4 growth have not been included in the model. This is the case of thermally-activated
5 mobility processes that, due to the low value of the film temperature during growth
6 $\sim 0.15 \times T_m$ (T_m is the melting film temperature), can be reasonably discarded. This
7 coincides with the deductions derived from the well-known structure zone model [31], in
8 the sense that surface shadowing dominates over thermally activated processes when the
9 growth temperature remains below $0.3 \times T_m$. In addition, we have not introduced re-
10 sputtering processes because they play a minor role in the absence of negative ion species
11 [32]. Argon ion bombardment effects are also neglected because of two reasons: i) the
12 plasma glow is separated from the film more than 15 cm and, ii) the Ar plasma is
13 maintained by a DC electromagnetic signal, implying that plasma ions possess low kinetic
14 energy when arriving at the film surface [20, 33].

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33 To prove the reliability of the model, we have calculated the density of the simulated
34 films. In general, these possess three different regions as a function of height: a first
35 accommodation layer ~ 10 nm thick close to the substrate, a second bulk region where the
36 nanostructure is clearly defined, and a third region corresponding to the film surface.
37 When the film is thick enough, the bulk region represents by far the largest part of the
38 film, and thus, the overall density would tend to the bulk value. For this reason, in our
39 calculations we have taken the local density in the bulk region as equivalent to that of the
40 whole film. i.e., the number of occupied cells in one slice of material at a given height in
41 the bulk divided by the number of cells in the slice.

52 53 54 55 56 57 **IV.-Experimental Results** 58 59 60

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3 The nanostructural and crystallographic features of the films have been analysed as a
4 function of the tilt angle of the substrate, σ , for a given thermalization degree of sputtered
5 particles, Ξ . A series of FESEM images along the Δ and Π directions are presented in
6 figures 3 and 4, respectively, for $\Xi=0.4$ ($p_g = 0.15 Pa$) and increasing values of σ .
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8 There, it is clear that the layers deposited for $\sigma = 0^\circ$, 45° and 60° depict rather compact
9 structures, whereas for $\sigma=70^\circ$ a columnar morphology is formed made of vertically
10 aligned and well-separated columns with diameters ranging from 50 to 100 nm.
11 Remarkably, for $\sigma=80^\circ$ and $\sigma=85^\circ$, the structure is rather similar, being the columns
12 almost vertically aligned in both cases, a quite different behaviour to that reported for Au
13 or TiO_2 thin films prepared by MS-OAD at low pressures. In these latter cases, the tilting
14 degree of the columnar structures progressively increased with σ , up to $\sim 50^\circ$ with
15 respect to the vertical when $\sigma = 85^\circ$ [17, 20]. Another significant difference in the present
16 case of Ti is the remarkable abrupt transition from compact to columnar morphologies
17 when the deposition angle varies between $\sigma=60^\circ$ and $\sigma=70^\circ$, a phenomenon we dub
18 *columnar breakdown*. This behaviour is quite different from that observed for Au or TiO_2
19 thin films, where a smooth shift from compact to tilted nanocolumnar structures took
20 place for angles between $\sigma=60^\circ$ and $\sigma=80^\circ$ [17]. Interestingly, the columnar breakdown
21 involves a sharp variation of films' density as reported in Figure 5a where we plot the
22 relative density of the Ti films, in comparison with a fully dense layer, as a function of
23 σ . There, it is clear that, with a density above 80%, films are quite compact for $\sigma < 70^\circ$
24 whereas the abrupt change in morphology for $\sigma=70^\circ$ translates into a noticeable density
25 drop that reaches a value of 30% when $\sigma=85^\circ$.

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28 Changes in morphology and density are accompanied by significant modifications in the
29 films crystallographic structure. The XRD diagrams in Figure 6a show that all the Ti films
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3 are crystalline, although the relative intensities of the (100), (002) and (101) diffraction
4 peaks of the hcp structure vary significantly with the deposition angle. This change in the
5 peaks intensities clearly points to a certain texture evolution: the high intensity XRD
6 peaks for the (002) and (100) reflections in the film deposited at $\sigma = 0^\circ$ indicates a mixed
7 *a/c* preferential orientation, a situation that evolves to an almost pure *c*-axis orientation
8 for the films deposited at $\sigma = 45^\circ$. Above this deposition angle, the samples show much
9 weaker diffraction peaks suggesting a loss of preferential orientation, as well as a lower
10 crystal quality (see figure 6a). This transition is in perfect correspondence with the
11 morphology and density changes associated to the transition from compact morphology
12 for $\sigma \leq 60^\circ$ to a highly porous microstructure when $\sigma > 60^\circ$. To further assess the
13 evolution of thin film texture, polar plots have been obtained to study the preferential
14 orientation of crystal domains as a function of deposition angle. Figure 6b shows the pole
15 figures for the (002) reflections in the films deposited at different angles. The areas with
16 maximum intensity correspond to the stereographic projection of the orientation
17 distribution of *c*-axis oriented domains. Films grown with $\sigma = 0^\circ$, 45° and 60° show that
18 (002) reflections approach the zenith position $\chi = 0^\circ$ indicating a *c*-axis orientation very
19 close to the vertical direction. The enlargement of the region around $\chi = 0^\circ$ (in the insets)
20 reveals a slight tilt of the *c*-axis of about $\chi = 2^\circ$ and 2.5° away from the vertical direction
21 towards the incident flux of material for the $\sigma = 45^\circ$ and 60° samples, respectively. Films
22 grown at $\sigma = 70^\circ$, 80° and 85° still reveal a certain preferential orientation of crystallites,
23 although with a very broad distribution of *c*-axis orientations and a progressive tilt from
24 $\chi = 35^\circ$, to 45° and 50° , respectively.

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Films deposited at a higher pressure of 0.5 Pa ($\Xi = 1.45$) show rather compact structures
for tilt angles between $\sigma = 0^\circ$ and $\sigma = 45^\circ$ (see figures 7 and 8) and the evolution of a

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3 clearly defined columnar structure for $\sigma = 60^\circ$. This result contrasts with the rather
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5 compact microstructure obtained when $\sigma = 60^\circ$ and $\Xi = 0.4$ (figures 3 and 4), which
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7 suggest that, remarkably, the sole increase of the argon gas pressure has induced a
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9 columnar breakdown for $\sigma = 60^\circ$. This behaviour is again quite different to that reported
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11 for Au or TiO₂, where the lower directionality of the deposition particles due to the
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13 increase of the argon pressure leads to less defined columnar microstructures [17]. We
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15 will come back to this point when discussing the results of the growth model.
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21 Increasing the pressure also induces changes in the film density (see figure 5b), with
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23 values around 80% and 70%, for $\Xi = 1.45$ and $\sigma = 0^\circ$ and $\sigma = 45^\circ$, respectively. An
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25 abrupt drop to a density below 50% in the $\sigma = 60^\circ$ case confirms the columnar breakdown
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27 taking place under those conditions. Titanium thin films deposited at even higher
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29 thermalization degrees, $\Xi = 2.9$ ($p_g = 1 Pa$) and $\Xi = 4.3$ ($p_g = 1.5 Pa$) (images shown
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31 in the supplementary information file S2) possess a density almost independent of σ , in
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33 all cases around 50% of that of a compact material (see figure 5b). This result suggests
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35 that sputtered particles have lost their preferential directionality and arrive at the film
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37 surface according to an isotropic angular distribution function, independent of σ .
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45 VI.- Growth simulation and Discussion

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48 The results presented in the previous section indicate that the nanostructural development
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50 of Ti thin films deposited by MS-OAD is rather different from that of Au or TiO₂
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52 deposited in similar conditions. This suggest that additional fundamental processes,
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54 besides the collisional transport of sputtered particles through the plasma gas and the
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56 surface shadowing mechanism, must be at play during the growth of the former. In
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58 particular, we propose that hyperthermal processes may explain the nanostructural
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60 transitions reported above, and that the well-tested model to describing the growth of Au

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3 and TiO₂ films must be extended accordingly. We will show that, by comparing the
4 solutions of the model and the experimental results, we are able to draw relevant
5 conclusions on the growth of Ti by MS-OAD.
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11 *Low pressure cases* ($\Xi=0.4$, $p_g = 0.15Pa$)
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15 The growth model has been solved under different conditions for $N_L = 2000$ and different
16 values of N_H , so that the simulated thin films possess the same thickness than the
17 experimental ones. Simulations for $\Xi=0.4$ ($p_g = 0.15Pa$) and different values of σ are
18 presented besides the experimental FESEM images in figures 3 and 4, evidencing the
19 existence of a good agreement in all studied cases, except for $\sigma = 70^\circ$ which will be
20 discussed later. Primarily, for $\sigma = 0^\circ$ and $\sigma = 45^\circ$, the obtained compact structures
21 reflect the low efficiency of surface shadowing effects at these low incidence angles [17]
22 and the relatively high energy that sputtered particles carry prior to their deposition, a
23 situation that favours the mobilisation of surface atoms by hyperthermal processes. Figure
24 3 and 4 also shows that the rather compact structures simulated for $\sigma=60^\circ$ and $\sigma = 70^\circ$
25 evolve into a vertically oriented columnar nanostructure for $\sigma = 80^\circ$ and 85° . To
26 understand the columnar breakdown and explain how the vertical columns are formed,
27 we show in Figure 9 the magnitude of the average displacements per deposited atom
28 caused by hyperthermal processes as a function of σ , differentiating those that take place
29 either vertically or horizontally with respect to the substrate. This figure shows that, for
30 low incident angles, the arrival of energetic atoms mainly causes downwards
31 displacements, likely contributing to densify the films and remove any emerging pattern.
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33 However, when $\sigma > 70^\circ$, displacements are mainly horizontal in the Δ direction due to
34 both, the glancing incidence of sputtered species and the appearance of new surfaces (the
35 side of the columns), in a process we dub *dragging mechanism*. In fact, the dragging
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3 mechanism strongly influences the columnar growth: equivalent simulations in Figure 10
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5 in the absence of hyperthermal processes show that nanocolumns would naturally tilt
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7 towards the sputtered flux (see figure 10a), i.e., in the direction opposite to Δ , as it was
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9 previously reported for Au and TiO₂ thin films. Therefore, and regarding the almost
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11 vertical alignment of the columns in the Ti cases, it seems that when $\sigma > 70^\circ$, the
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13 dragging mechanism is responsible for mobilizing surface atoms in the Δ direction,
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15 compensating the natural tilt of the columns and straightening them up. This is illustrated
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17 in figure 11, where we show how the dragging mechanism affects the otherwise tilted
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19 columnar growth, straightening the columns up, and making them cast a larger shadow
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21 over the substrate. This makes columns grow more separated, promoting the growth of
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23 films with lower densities.
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30 The dragging mechanism does not only explain why columns remain almost vertical no
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32 matter the value of σ , but also the sharp columnar breakdown found at low pressures. In
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34 fact, and according to classical growing concepts accounting for the appearance of tilted
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36 nanocolumns in evaporated thin films at glancing angles [1], their formation is promoted
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38 by the appearance of slightly taller surface nuclei in the first stages of growth that become
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40 larger and turn into columns thanks to surface shadowing mechanisms. Our model
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42 indicates that this picture still holds for MS-OAD, although the incorporation of the
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44 dragging mechanism contributes to straighten these nuclei up as soon as they emerge and
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46 to enhance the surface shadowing processes thanks to their larger projected shadow. All
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48 these factors combined are responsible for promoting the growth of vertically aligned and
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50 very spaced columns, as well as for a sharp transition between compact and columnar
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52 morphologies.
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3 Experimental evidence on the existence of the dragging mechanism can be concluded by
4 comparing the reported nanostructures in figures 3 and 4 with that of a Ti thin film
5 deposited by the electron beam-assisted evaporation technique at low temperatures
6 (details on the deposition method appear in refs. [23, 34]), where the low kinetic energy
7 of evaporated species when arriving at the film surface ($\sim 0.1-0.2$ eV) should preclude
8 any dragging mechanism. In a remarkably good agreement with the simulations in
9 absence of hyperthermal processes (Figure 10a), the cross-sectional FESEM image of this
10 film (in Figure 10b) shows that the Ti nanostructures appear tilted towards the vapour
11 flux. This result clearly demonstrates that the dragging mechanism, and thus the
12 hyperthermal processes, have a direct influence on the formation of vertically aligned
13 columns.
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30 As mentioned before, the simulations for $\sigma = 70^\circ$ and $\Xi = 0.4$ do not match well with
31 experiments in figures 3 and 4: while a columnar arrangement is experimentally obtained,
32 the model predicts a rather compact structure. We think that this disagreement is caused
33 by the sharpness of the transition and the simplified vision of the hyperthermal
34 mechanisms employed in our model, which renders a threshold angle for the columnar
35 breakdown of $\sigma \sim 75^\circ$, instead of the experimental value $\sim 70^\circ$. In any case, the good
36 agreement between simulations and experiments can be quantitatively confirmed by
37 comparing measured and calculated film densities in figure 4a, which again shows a good
38 concordance. Unfortunately, no predictive assessment can be extracted from the model
39 on the film texture evolution (c.f., Figure 6), since no crystalline planes can be made out
40 from simulations. Yet, it seems quite remarkable that the texture of the films experiences
41 a drastic modification for $\sigma > 60^\circ$, i.e., when the dragging mechanism emerges as a
42 dominant nanostructuring process, suggesting a possible link between both. However, the
43 extension of this possible relation to other materials or conditions has to be taken
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3 carefully: in references [35-36], for instance, highly crystalline Al thin films grown by
4 evaporation were obtained, thus suggesting that efficient thermally-activated relaxation
5 processes (associated to the lower melting point of Al in comparison to that of Ti) may
6 promote the formation of crystal planes at room temperature in absence of dragging
7 processes.
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10 11 12 13 14 15 16 17 18 19 20 *Film morphology at higher pressures*

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22 For higher thermalization degrees, e.g., $\Xi = 1.45$ ($p_g = 0.5 Pa$), the results of the
23 simulations also show a good agreement with experiments in figures 7 and 8. For $\sigma = 0^\circ$
24 and $\sigma = 45^\circ$, simulations render compact films, whereas for $\sigma = 60^\circ$ the structure
25 evolves into vertically aligned columns. As mentioned before, this result is puzzling
26 because it indicates that the sole increase of pressure when $\sigma = 60^\circ$ promotes a columnar
27 breakdown. According to our model, this phenomenon can be explained by considering
28 the plot in Figure 12 that shows the proportion of arriving Ti atoms that may induce
29 hyperthermal processes at the film surface, i.e. with kinetic energies above ε_K , for
30 increasing thermalization degrees (pressures). As expected, the decreasing trend obtained
31 indicates that the more thermalized sputtered atoms become, the less kinetic energy they
32 carry, and hence less hyperthermal processes are induced. Therefore, a plausible
33 explanation for this pressure-induced transition is as follows: the higher amount of
34 energetic Ti atoms at low pressures is responsible for inducing numerous hyperthermal
35 processes at the film surface which, at low deposition angles ($\sigma \leq 60^\circ$), implies the
36 removal of any emerging pattern and the promotion of a compact thin film growth. At
37 higher pressures, on the other hand, the higher thermalization degree leads to a lower
38 amount of energetic atoms, so that the occurrence of less hyperthermal processes allows
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3 for the formation of columns. In order to corroborate this result, in figure 13 we show the
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5 simulated structure for $\Xi=0.4$ ($p_g = 0.15 Pa$, low pressure) and $\sigma = 60^\circ$ in the absence
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7 of hyperthermal processes, where a clear columnar nanostructure is obtained. All this
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9 confirms that the actual compact structure found at 60° and low pressure (c.f. figures 3
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11 and 4 for $\sigma = 60^\circ$) is associated to highly efficient hyperthermal mobilization processes,
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13 and that the reported pressure-induced columnar breakdown is mediated by the different
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15 efficiency of hyperthermal processes during the film growth.
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21 The conclusions above can be further validated by comparing the calculated and
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23 measured densities of the films for increasing pressures and different values of σ . Indeed,
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25 our model does not only reproduce the film density for $\Xi=1.45$ ($p_g = 0.5 Pa$) for different
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27 values of σ , but also in the cases with $\Xi = 2.9$ ($p_g = 1 Pa$) and $\Xi = 4.3$ ($p_g = 1.5 Pa$),
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29 as depicted in figure 5b. In agreement with figure 12, when $\Xi = 2.9$ ($p_g = 1 Pa$) and
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31 $\Xi = 4.3$ ($p_g = 1.5 Pa$), the very high thermalization degree of sputtered atoms causes an
32
33 important drop of kinetic energy that inhibits hyperthermal processes. This fact together
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35 with the loss of preferential directionality of sputtered species when arriving at the
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37 substrate explains why the film density presents a very weak dependence on pressure and
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39 substrate tilt angle in these cases.
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48 All the simulations presented in this paper were performed on flat surfaces due to the 0.5
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50 nm roughness of the Si substrates experimentally used. According to our experience, the
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52 final film morphology would be the same whenever the roughness of the substrate is kept
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54 low enough. For instance, we have used medical grade Ti6Al4V substrates of 2 mm
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56 thickness (mechanically polished to a mirror finish), with a roughness of about 3 nm over
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58 a $4 \mu m^2$ area, to grow the Ti nanostructures at low pressures and with 80° tilt angle [9].
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3 In this case, the obtained nanocolumnar morphology is the same as that grown on the Si
4 substrates (depicted in figures 3 and 4). However, it is worth mentioning that if substrates
5 were seeded, different nanostructures could be developed depending on the particular
6 seed pattern and size. Indeed, these seeds could induce additional surface shadowing
7 mechanisms and surface correlations that would promote the appearance of different
8 structures. In this paper, due to the complexity and vast number of conditions associated
9 to the presence of seeds, we have focussed on the nanostructuration process in simple
10 conditions, i.e., on almost flat or low roughness substrates, demonstrating the importance
11 of hyperthermal processes in the formation of Ti nanocolumns by MS-OA. The model
12 presented here reproduces the nanostructural features of the Ti thin films grown at
13 different pressures and tilt angles of the substrate and explains the sharp columnar
14 breakdown that takes place when increasing the tilt angle at low pressures, and when
15 increasing the deposition pressure for $\sigma = 60^\circ$. Moreover, the good match between
16 experimental and calculated film densities ensures the accuracy of our model to predict
17 film densities and porosities.

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19 As a final remark, it is worth mentioning the relevance of developing a growth model
20 such as the one presented in this paper. It allows the computational analysis of the film
21 growth in different conditions and geometries, providing a first assessment on the
22 outcome of a particular experiment in a matter of hours (typical running time in an
23 average personal computer of a 100 nm x 100 nm x 100 nm simulation is less than 1
24 hour). It can be employed, for instance, to give insights on the geometrical constraints to
25 scale up the MS-OAD technique to industrial reactors and homogeneously coat large
26 substrates. As mentioned in the introduction, in ref. [9] we demonstrated that the $\sigma = 80^\circ$
27 case in figures 3 and 4, possesses a selective behavior when exposed to osteoblast cells
28 and bacteria (allowing the growth of the former, and inhibiting the proliferation of the
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3 latter) due to its particular nanostructure. These phenomena are of the utmost importance
4 for biomedical applications, since nanostructured coatings onto actual implants may
5 significantly reduce the infection rate. Such application would require not only coating
6 large surfaces (up to tens of cm^2) but also, in some cases, using strategies to deposit with
7 oblique incidence onto curved substrates. Moreover, the MS-OAD technique has also
8 proven adequate for the development of devices in small scales for numerous
9 applications, e.g., sensors, microfluidics, solar cells, plasmonics, etc. [1], for which the
10 development of growth methods on large substrates is required. This issue represents a
11 clear scientific and engineering challenge that demands the development of models like
12 the one presented here.
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29 **VII.- Conclusions**

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31 In this paper we have studied the fundamentals of the growth of Ti thin films by
32 magnetron sputtering at oblique angles. For this purpose, we have explored a wide range
33 of deposition conditions and characterized the obtained Ti nanostructures as a function of
34 the deposition angle and working pressures. The substantial differences found between
35 the Ti nanostructures and those obtained for Au and TiO_2 grown in similar conditions
36 indicate that processes other than the collisional transport of sputtered species in the
37 plasma and surface shadowing mechanism must be at play. To account for the different
38 observations, we have obtained that kinetic energy-induced hyperthermal processes have
39 a relevant influence on the development of the Ti nanostructures: a simple growth model
40 accounting for these mechanisms has been developed that qualitatively explains the main
41 morphological features of the Ti thin films as well as the nanostructural changes observed
42 when varying the experimental conditions. Moreover, a quantitative agreement has been
43 also found when comparing the density of the experimental and simulated layers.
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3 Overall, the results presented in this paper indicate that hyperthermal processes play a
4 fundamental role in the growth of Ti thin films by MS-OAD, either by removing the
5 columnar structure due to vertical displacements, or by straightening the columns up
6 whenever they emerge thanks to the, so-called, dragging mechanism. Moreover, we have
7 proved the existence of a transition from a compact to a columnar morphology by solely
8 increasing the background pressure, a phenomenon that has been explained by the lower
9 efficiency of hyperthermal processes when deposition species undergo numerous
10 collisions in the plasma gas and arrive at the film surface with lower kinetic energies. The
11 results presented herein do not only shed some light on the main processes governing the
12 growth of Ti thin film by the magnetron sputtering technique at oblique angles, but also
13 provide general insights that may likely be extended to understand the growth and
14 nanostructure development of different materials.
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31 32 **Acknowledgements**

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38 29081) for financial support.
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Figure Caption

Figure 1.- Definition of the Π and Δ directions

Figure 2.- Hyperthermal processes considered in the model. a) Kinetic energy-induced mobility, b) biased diffusion.

Figure 3.- View from the Π direction of the obtained nanostructures for the Ti thin films for $\Xi=0.4$ ($p_g = 0.15Pa$), and different tilt angles of the substrate. The FESEM images of the films are displayed in the left column, whereas in the right column the corresponding results of the simulations are presented.

Figure 4.- View from the Δ direction of the same Ti thin films presented in figure 3. The FESEM images of the films are displayed in the left column, whereas in the right column the corresponding results of the simulations are presented.

Figure 5.- Experimental density of the films as a function of the substrate angle, together with the results of the simulations. a) $\Xi=0.4$ ($p_g = 0.15Pa$), and b) $\Xi=1.45$ ($p_g = 0.5 Pa$), $\Xi = 2.9$ ($p_g = 1Pa$) and $\Xi = 4.3$ ($p_g = 1.5Pa$).

Figure 6. a) XRD peaks of the films grown at $\Xi=0.4$ ($p_g = 0.15Pa$), for different values of the substrate angle. b) Pole figures of the 002 reflection for the films grown for $\Xi=0.4$ ($p_g = 0.15Pa$). The tilt angle χ varies from 0 to 90° and the rings correspond to steps of 10°. The insets correspond to close up of the $\chi=0-10^\circ$ region.

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3 Figure 7.- View of the obtained nanostructures for the Ti thin films in the Π direction for
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5 $\Xi = 1.45$ ($p_g = 0.5 Pa$), and different tilt angles of the substrate. The FESEM images of
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7 the films are displayed in the left column, whereas in the right column the corresponding
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9 results of the simulations are presented.
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14 Figure 8.- View of the obtained nanostructures for the Ti thin films in the Δ direction for
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16 $\Xi = 1.45$ ($p_g = 0.5 Pa$), and different tilt angles of the substrate. The FESEM images of
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18 the films are displayed in the left column, whereas in the right column the corresponding
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20 results of the simulations are presented.
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25 Figure 9. Vertical and horizontal lateral mobility processes caused by hyperthermal
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27 processes per deposited particle, for $\Xi = 0.4$ ($p_g = 0.15 Pa$) and different substrate angles.
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31 Figure 10.- a) Result of the model in absence of hyperthermal processes for $\Xi = 0.4$ and
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33 $\sigma = 85^\circ$, b) FESEM image of a Ti thin film grown by evaporation at an oblique angle of
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35 85° for the sake of comparison.
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40 Figure 11.- Scheme on the influence of the dragging mechanism in the columnar growth.
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43 Figure 12.- Calculated proportion of Ti atoms with kinetic energy above ε_K when
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45 arriving at the substrate as a function of the thermalization degree.
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49 Figure 13.- Image of a simulated film in the conditions $\Xi = 0.4$ and $\sigma = 60^\circ$ when
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51 hyperthermal processes are inhibited.
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Figure 1

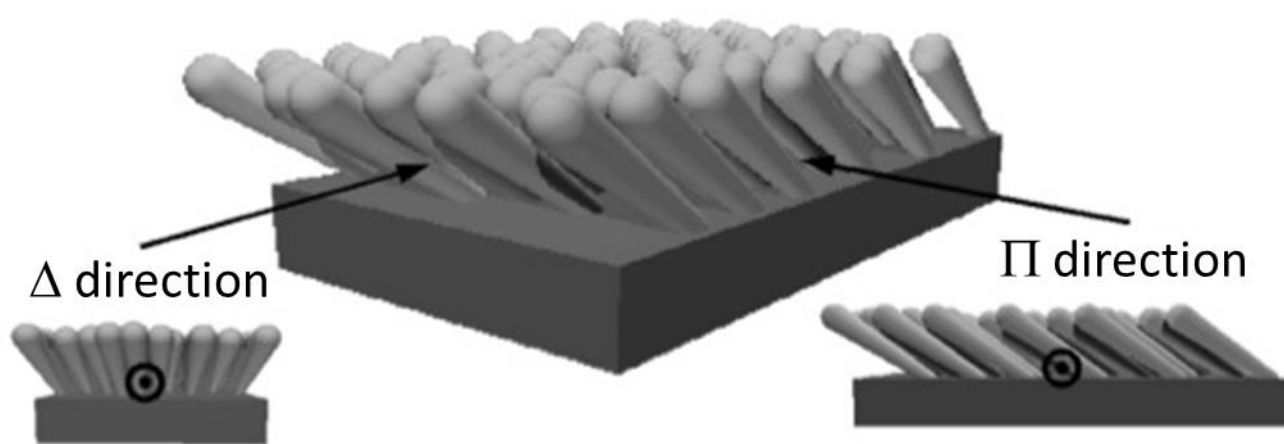


Figure 2

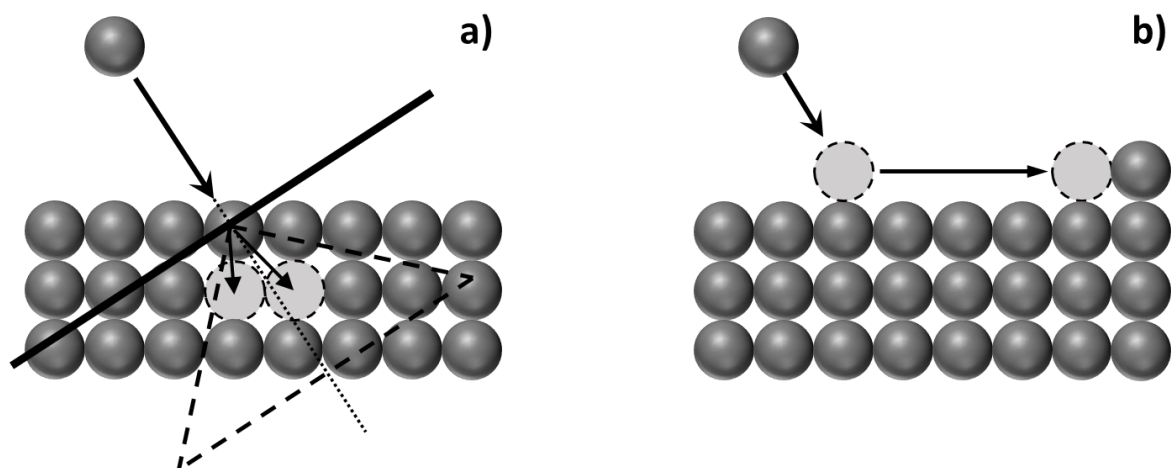


Figure 3

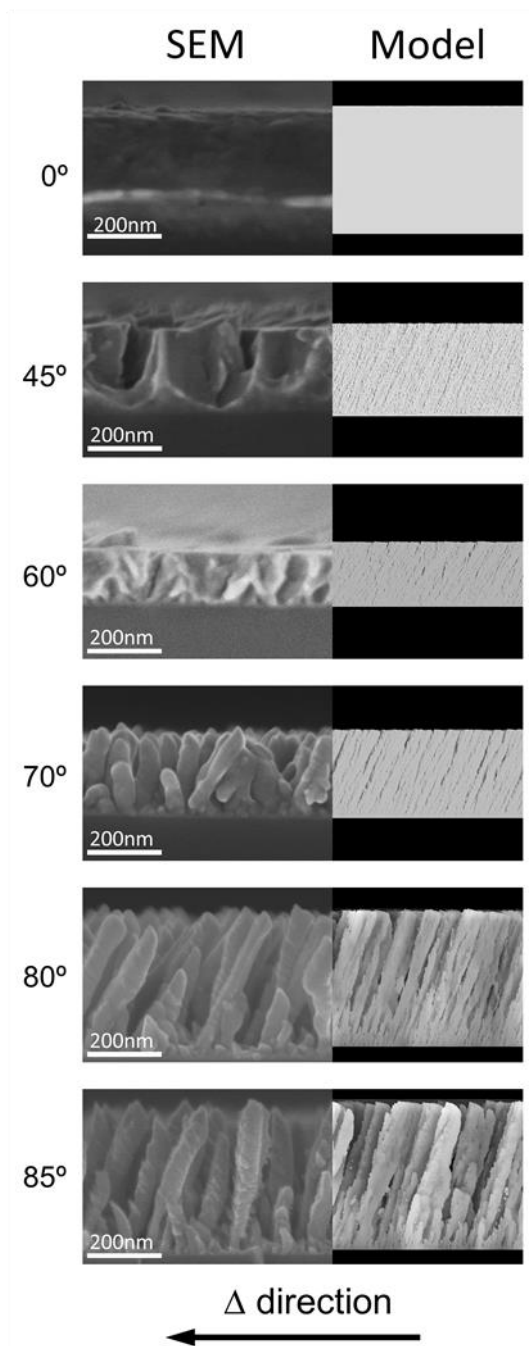


Figure 4

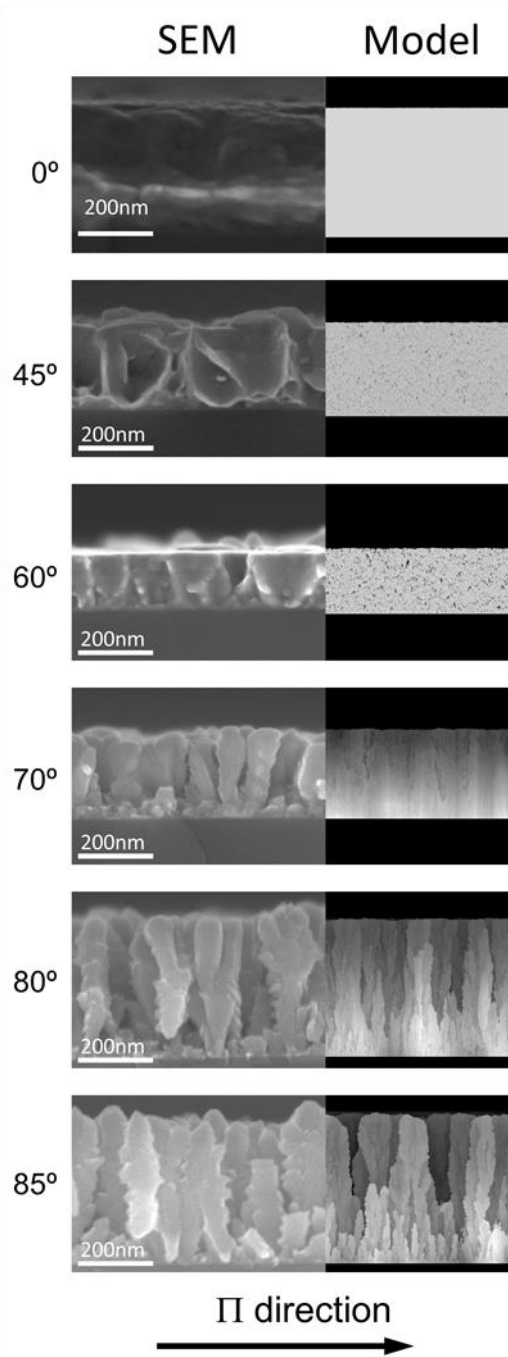


Figure 5

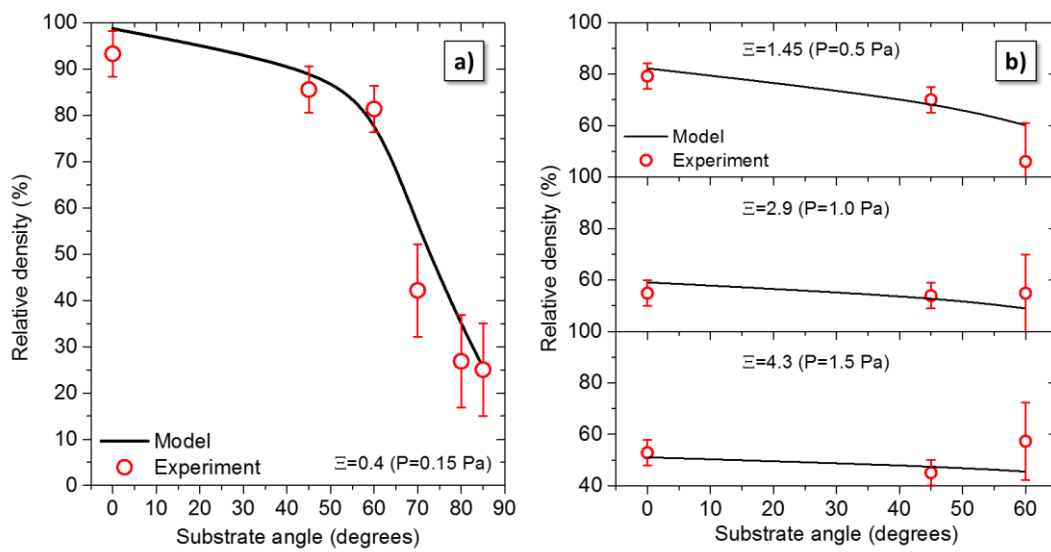


Figure 6

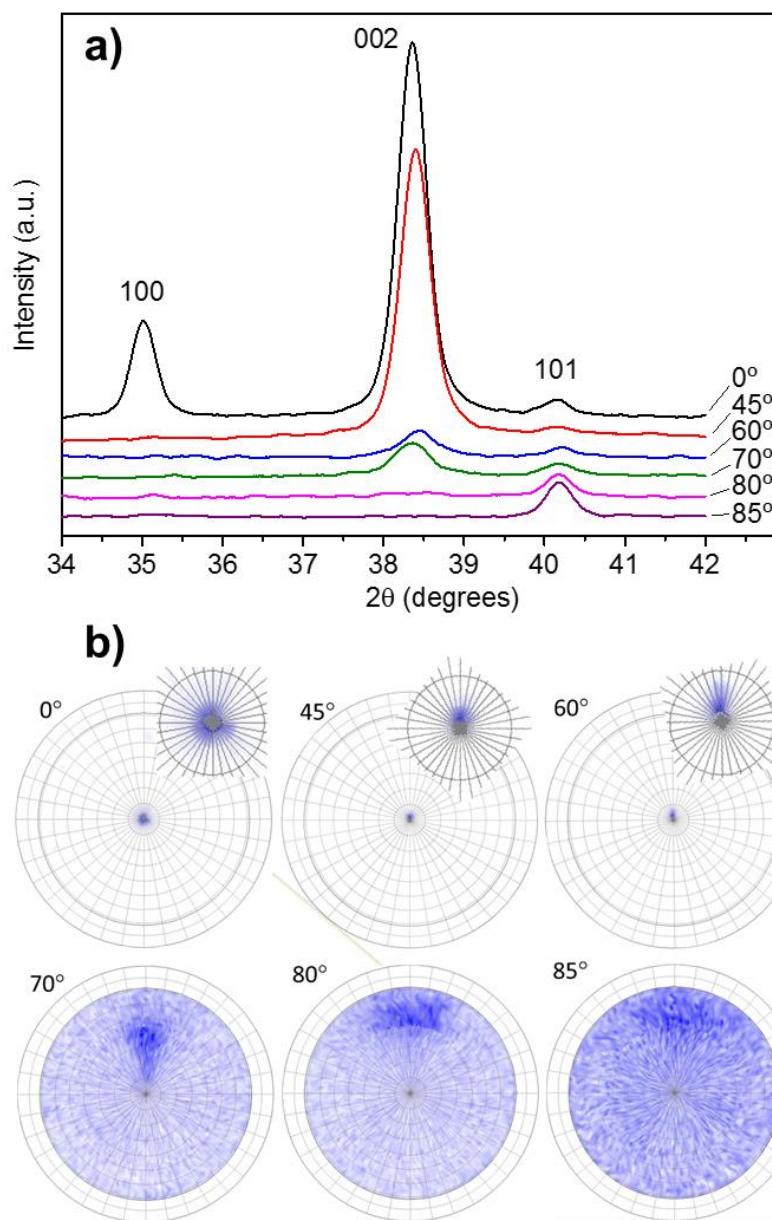


Figure 7

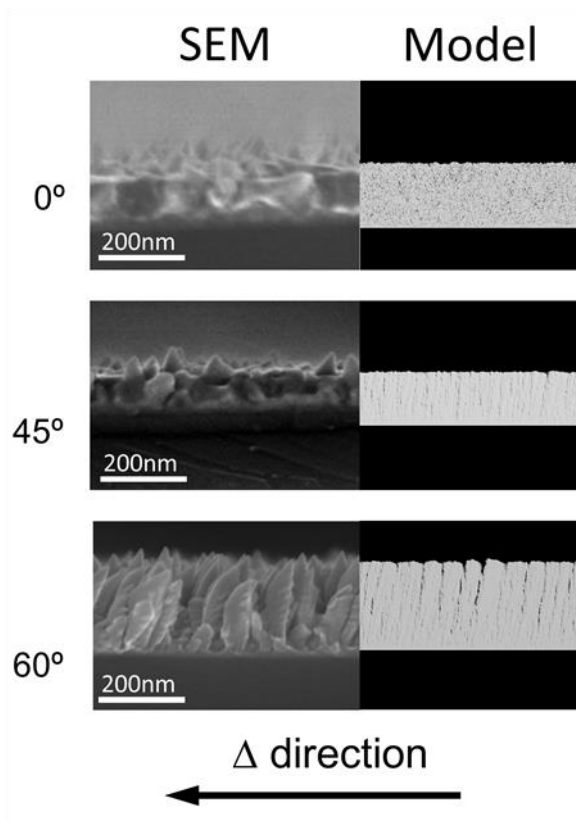


Figure 8

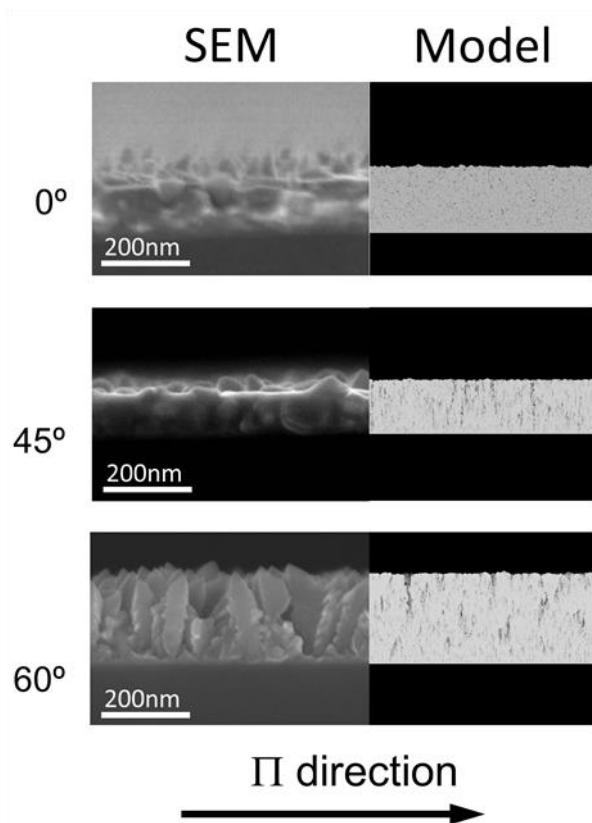


Figure 9

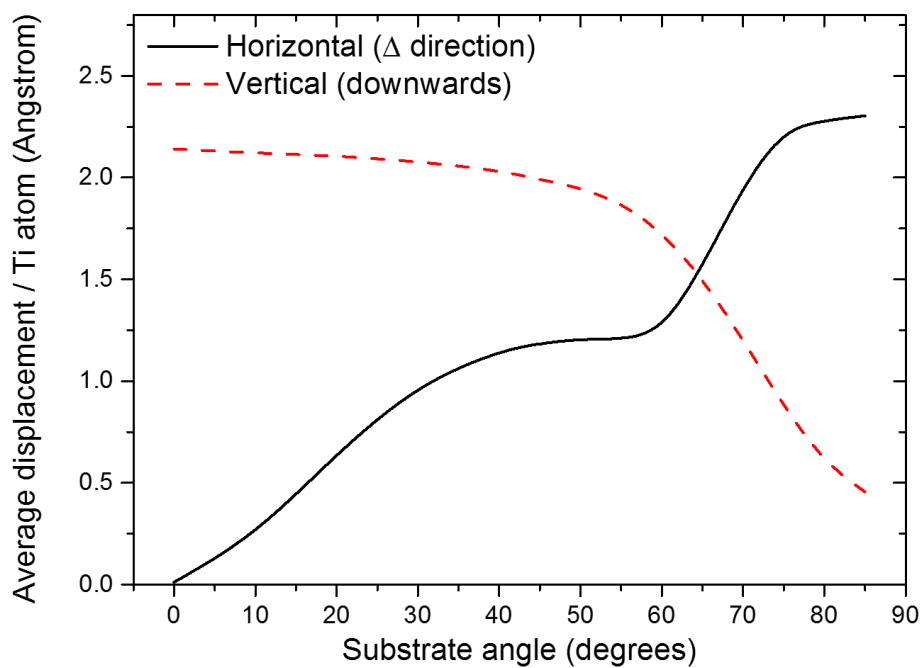


Figure 10

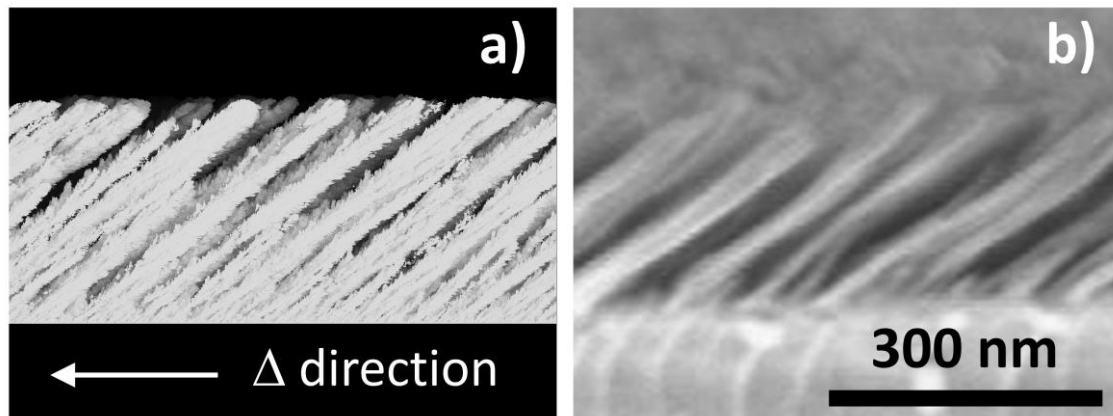


Figure 11

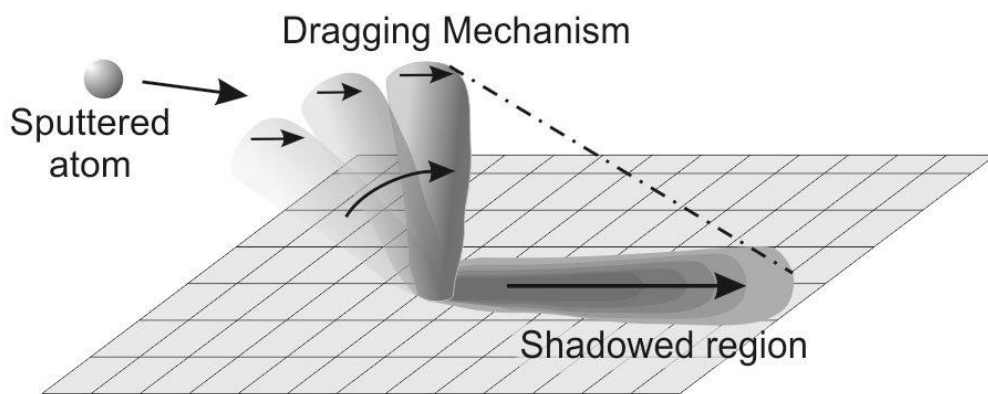
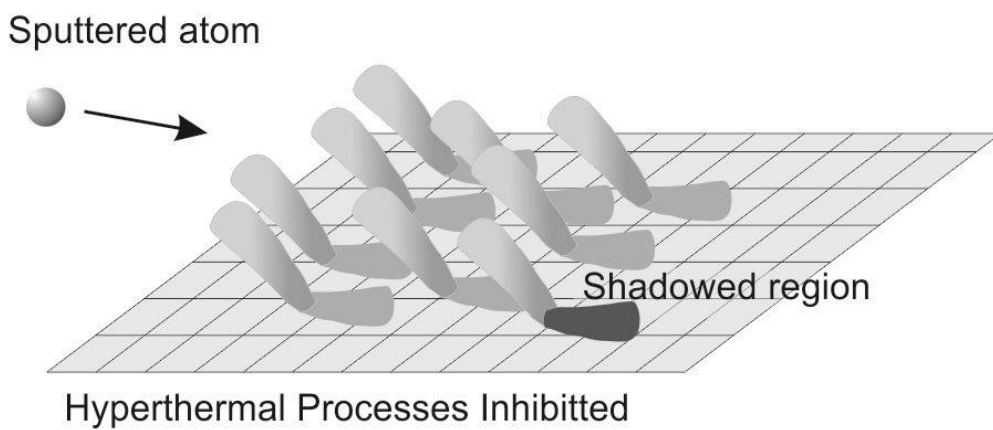


Figure 12

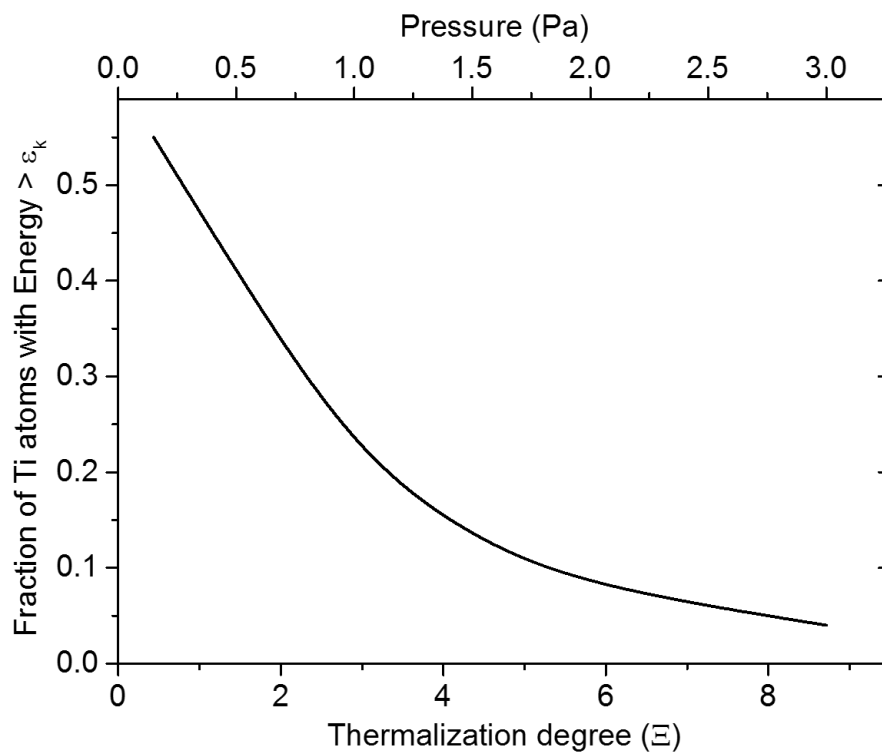
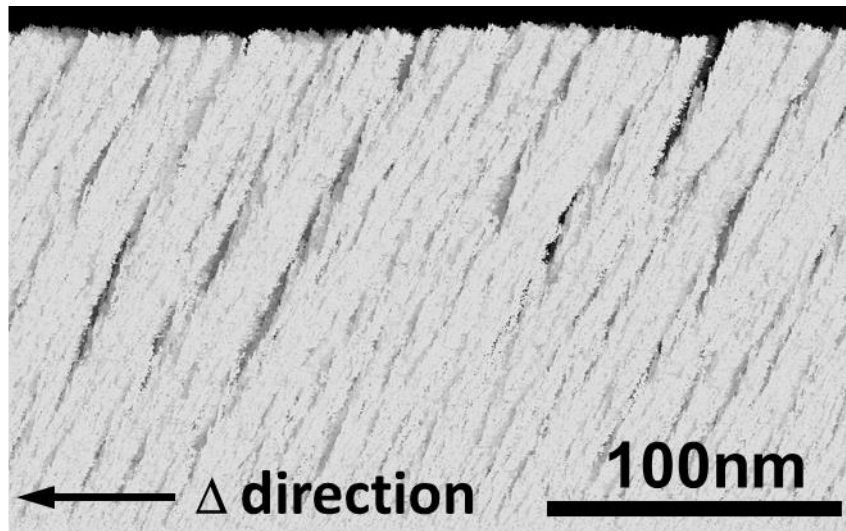


Figure 13



Supplementary information

Figure S1: Experimental Setup

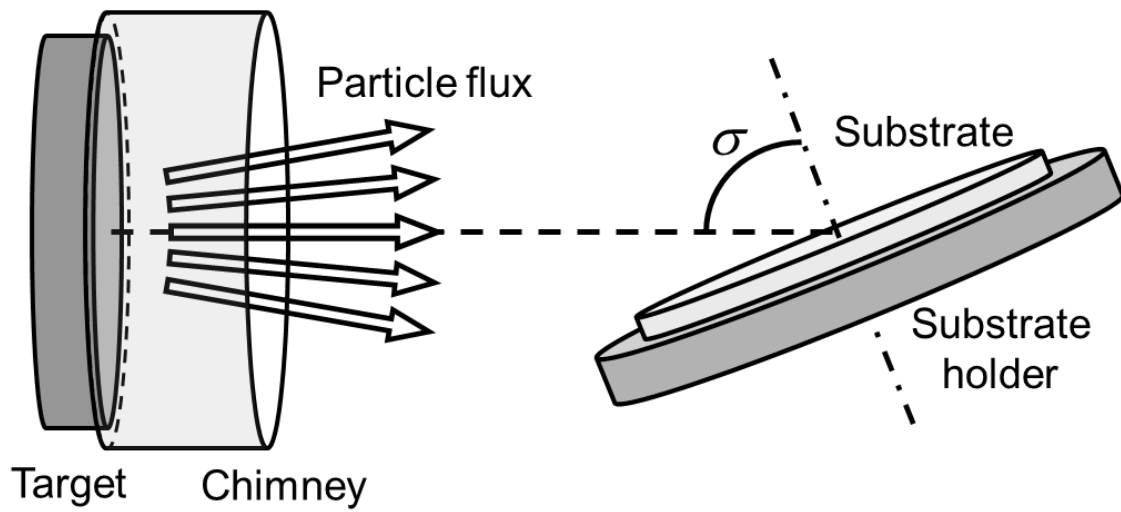


Figure S2: FESEM images of the Ti thin films grown at 0°, 45° and 60°, at higher thermalization degrees: $\Xi=2.9$ ($p_g=1$ Pa) and $\Xi=4.3$ ($p_g=1.5$ Pa).

