Modelling the growth of transition metal nitrides

S Mahieu\textsuperscript{1}, D Depla, R De Gryse
Ghent University, Department of Solid State Sciences, Krijgslaan 281/S1, 9000 Ghent, Belgium

E-mail: stijn.mahieu@ugent.be

Abstract. Due to its unique physical properties, and its wide use in industrial applications, the growth of TiN has been extensively investigated and reported in literature. Since the final film properties are known to be influenced by the film microstructure and crystallographic orientation, much effort has been made to understand the fundamental phenomena determining the film growth process. However, several controversial growth models have been published. As an attempt to gain more insights in the growth of TiN and to have a better control on the development of the microstructure and crystallographic orientation, a general growth model is discussed. It will be shown that this growth model enables to understand the influence of several deposition parameters such as the film thickness, ion-to-atom ratio, and \textit{N}_2-flow on the resulting microstructure and orientation of TiN films deposited by reactive magnetron sputtering.

1. Introduction
A tremendous amount of papers discusses the growth of TiN films by reactive magnetron sputtering. Such TiN thin films are widely used as optical coatings, as diffusion barriers in Al and Cu interconnects, as biocompatible overlayers, and for sure for their enhanced mechanical properties. It has been described in literature that all these final film properties not only depend on the microstructure, but also on the crystallographic orientation of the TiN films \text[1-5]{1}. As such, there is a need for a model allowing us to understand the development of the structure and orientation of the TiN films. Many authors have observed that this microstructure and orientation is strongly influenced by the used deposition conditions. Also some of them proposed a model in an attempt to understand the film growth. However, most of these models focused on the influence of one specific deposition parameter on the microstructure and/or the orientation, while neglecting or ignoring the possible influence of many other deposition parameters. Moreover, some models seem to be in contradiction to each other.

This paper will start with an overview of most commonly described models, together with some own results of the authors (section 2). In section 3, a new growth model will be discussed. The proposed model should be able to relate the resulting microstructure and orientation with the fundamental growth phenomena, i.e. nucleation, diffusion, and recrystallization during grain growth, and thus also to interpret the results of other authors as published in literature. This new model is mainly based on the extended structure zone model (ESZM), described in ref 6.

2. Observed influences of specific deposition parameters, as published in literature.

\textsuperscript{1} To whom any correspondence should be addressed.
Since there is such a tremendous amount of papers reporting the growth of TiN films, deposited by reactive sputter deposition, not all these publications can be summarized or even referred to. A good overview of literature results has been given by Kajikawa et al. [7]. Here, the authors will limit themselves to the –in their point of view- most fundamental parameters influencing the growth of TiN. The transition from a [200] to a [111] orientation with decreasing N2-flow is often reported [1, 8-12]. The same transition in the crystallographic orientation is also reported for increasing film thickness [13-17], for decreasing substrate temperature [12, 18, 19], and for decreasing ion to atom ratio [20,21]. Also the influence of the ion energy on the orientation has been investigated [14,23-25].

2.1. Influence of the film thickness.

Several groups reported a cross-over of the TiN film orientation with increasing film thickness [13-17]. For a thickness \( h < 1 \text{nm} \) an amorphous structure was observed. Increasing the thickness up to a 5-10 nm resulted in a thin film with a dominant [200] orientation, while a gradual change in preferred orientation from [200] to [111] starts at a thickness of 20-50 nm and is completed at 200-300 nm. This cross-over in preferred orientation with increasing film thickness was often explained with the “minimization of the overall energy”.

First Pelleg et al.[17] and later Oh and Je [14,15] considered the overall energy \( W \) of a film as the summation of the strain energy and the surface energy \( S \). The total strain energy is expressed by the elastic strain energy \( E \) multiplied by the film thickness \( h \). Later on, Zhao extended the overall energy model by also taking into account the energy delivered by the impingement of energetic ions on the growing film and called this the stopping energy \( I \) [13]. Then the overall energy is written as: \( W = S + Eh + I \). In case that the mobility during the thin film growth is large enough to aim for the thermodynamic most favourable situation, the film will aim for the lowest overall energy \( W \). Thus the growing film not only has a driving force to lower the surface energy, but also other driving forces to minimize the strain energy and the stopping energy. According to Oh, Je and Zhao, the competing planes in the TiN film are the (200) plane with the lowest surface energy, the (111) plane with the lowest strain energy and the (220) plane with the lowest stopping energy. However, it was calculated by Zhao that the stopping energy should only be taken into account when the energy of the bombarding particles exceeds 400 eV [13]. As such, in most conditions the influence of the stopping energy can be ignored.

According to this model, a TiN film should have a [200] orientation as long as the strain energy is small. This strain energy increases with increasing film thickness and thus exceeding a critical thickness a [111] orientation should develop. If the film is bombarded by particles of at least 400 eV, a [200] orientation should develop.

However, Abadias et al. [25] has shown by means of \( \sin^2 \psi \) XRD measurements and a triaxial stress model that the stress in [111] oriented grains exceeds the stress in [200] oriented grains, in contradiction to the former model. Also Patsalas et al. [19, 26] has shown that there is no relation between stress and final film orientation.

2.2. Influence of the ion-to-atom ratio.

The research groups of Greene [20] and Hultman [21] reported an influence of the ion-to-atom ratio on the preferred orientation during reactive magnetron sputter deposition. They observed a [111] preferred orientation for an ion-to-atom ratio of 1, and a [200] preferred orientation for an ion-to-atom ratio higher than 3.5 à 5. The ions were \( \text{N}_2^+ \) ions of about 20 eV.

Gall et al. [27] calculated by ab initio calculations that this transition from a [111] to [200] preferred orientation can be explained by a difference in diffusion rates of the Ti adparticles on the (111) and (200) planes with increasing N/Ti flux. In case that the N/Ti particle flux towards the substrate is below 20/1, the Ti adparticles have a higher mobility on the (200) planes compared to the mobility on the (111) planes. He also reasoned that the grains with a lower mobility plane parallel to the substrate will overgrow the other grains, due to a higher perpendicular growth rate. This explains the observed [111] preferred orientation at low ion-to-atom ratio. The ab initio calculations showed that as soon as
the N/Ti flux exceeds 20/1, the (111) planes offer the highest mobility, causing a transition to a [200]
orientation, i.e. the [111] oriented grains are overgrown.

However, this model based on the ab initio calculations seems to be in contradiction to the
experimental observations of Greene and Hultman. Since their depositions were carried out in pure N
at a pressure of 2.7 Pa and at rather high ion-to-atom ratio, the flux of atomic N towards the growing
film is expected to be high. No details about their plasma composition were reported, but assuming a
dissociation degree of about 0.5% in the plasma (based on the measurements of Petrov et al. [22]) and
knowing the ion-to-atom ratio, it was calculated that they observed a [111] orientation even in the
presence of a flux of atomic N which is 60 times higher than the Ti adatom flux. Hence, if the ab initio
model of Gall was right, even at low ion-to-atom ratios they should have observed a [200] orientation
instead of a [111] orientation. Moreover, Greene and Hultman didn’t observe an overgrowth
mechanism in the [200] oriented films, but rather a zone II structure (see 3.1).

2.3. Influence of the N$_2$-flow.

Finally, results of our group [6] show that the orientation of TiN films, deposited by reactive
magnetron sputtering, changes from random to [111] and finally to [200]. The transition from a [111]
to a [200] orientation with increasing N$_2$-flow is also reported by other research groups [1, 8-12].

3. Proposed model based on the extended structure zone model.

An extended structure zone model (ESZM), modelling the film growth, the resulting microstructure
and the orientation as a function of the fundamental growth phenomena has been described in [6]. This
ESZM will be briefly summarized in 3.1. In 3.2, it will be shown that this model is not only able to
explain the influence of the N$_2$-flow, but also the influence of the film thickness and the ion-to-atom
ratio on the film orientation.

3.1. Brief summary of the ESZM, focusing on TiN.

3.1.1. Zone Ia&b. In case that a deposition is carried out at conditions where the energy flux towards
the substrate is very low or negligible, the impinging adatoms will have nearly no mobility and will
stick at the first place where they hit the substrate or the growing thin film. Such deposition conditions
will result in a nearly amorphous film. Since this paper focuses on the development of a preferred
orientation, zone Ia&b conditions are of no further interest here.

3.1.2. Zone Ic. Increasing the energy flux towards the substrate will allow the incoming adparticles to
diffuse around on the substrate, and to nucleate into crystalline islands. An adparticle arriving on such
an island will be able to diffuse around on this island. Since the deposition is a continuous process, the
islands will grow and will aim for a specific growth shape. Taking into account the different growth
rate of various crystallographic planes, the islands will be terminated or faceted by the
crystallographic planes of lowest perpendicular growth rate, since the planes with higher growth rate
will extinguish themselves.

In case that the diffusion of the adparticles is limited to one island, i.e. the adparticles are not allowed
to diffuse from one island to another one, neighbouring islands or grains will not be able to interact or
compete with each other. As such, the final film will consist of straight columns, faceted at their top,
but having a random orientation, because the nucleation process happened randomly.

3.1.3. Zone T. Further increasing the energy flux towards the substrate will allow the adparticles to
diffuse from one grain to another, i.e. intergrain diffusion is allowed. This allows neighbouring islands
or grains to interact and compete with each other. As described by van der Drift [28], this competition
will results in an evolutionary selection of the fastest growing grains. Hence, the resulting preferred
orientation will correspond to the orientation with fastest geometric growth rate. The resulting thin
film will be characterized by V-shaped columns, all facetted, and having a preferred orientation, i.e. the geometric fastest growing direction.

It was shown in ref. 6 that the geometric fastest growing direction, so the resulting preferred orientation, depends on the faceting of the grains. In case that the grains are {200} facetted, the [111] direction has the largest geometric growth rate, while the [200] direction has the largest geometric growth rate when the grains are {111} facetted. It was also shown in ref. 6 that the grains are {200} facetted in case that the reactive gas acts as molecular N$_2$ gas, while the grains will be {111} facetted when the reactive gas acts as atomic N. This atomic N can originate from N$_2$ dissociated in the gas phase, or from N$_2^+$ ions accelerated towards the substrate and having undergone collisional induced dissociation. The reactive gas is treated to act as atomic N gas, in case that the flux ratio N/Ti is high enough. Gall [27] calculated that weakly bond N atoms, i.e. N atoms which found only one or two nearest neighbours, are not stable on the surface but are thermodynamically driven to desorb again from the surface and recombine to N$_2$ in the gas phase. Therefore, an atomic N arriving at the growing film will not chemisorb to that surface, but only adsorb, diffuse some time around and then desorb again. It was calculated that such an N atom will only chemisorb on the growing surface when it encounters a Ti adatom during its diffusion process. Hence, the TiN depositions can only be carried out in the atomic reactive gas situation if the atomic N flux is so high that the steady state coverage of diffusing N adatoms is high enough to bond all Ti adatoms.

In conclusion, TiN depositions in zone T conditions will have a preferred orientation that corresponds to the geometric fastest growing direction, in its turn depending on the faceting of the grains. This faceting depends on the state of the reactive gas (N$_2$ or N).

### 3.1.4. Zone II

In case that the energy flux is so high that even recrystallization during grain growth may happen by ripening, island diffusion or grain boundary migration, the whole film will aim for its lowest surface energy, i.e. the (200) plane parallel to the substrate. Therefore, [200] oriented grains will consume other oriented grains, and straight, non-facetted, [200] oriented columns without any overgrowth will form the film.

![Diagram](image.png)

Figure 1: An overview of the relation between the energy flux and preferred crystallographic orientation in different zones of the ESZM for TiN.

### 3.2. Comparison with results from literature

#### 3.2.1. Substrate temperature

It is obvious that increasing the substrate temperature can induce a transition from zone T to zone II. In case that the deposition in zone T are performed at the molecular N$_2$ conditions, one can understand the observed transition from preferred [111] to [200] orientation [12, 18, 19].

#### 3.2.2. Film thickness

By means of in-situ XRD, TEM and corresponding SAED patterns, Oh and Je [15,16] observed that the transition from preferred [200] to [111] orientation occurred at a film
thickness of about 150 nm and that no recrystallization during grain growth happened, i.e. the deposition were performed at zone T conditions. Assuming that the reactive gas acts as molecular N\(_2\) (unfortunately, no data about their plasma composition has been published), it has been discussed in 3.1 that the [111] direction will have the largest geometric growth rate, while the [200] direction the lowest crystallographic growth rate. This [200] direction has the lowest crystallographic perpendicular growth rate, because the [200] plane offers the highest mobility to the Ti adatoms [29], meaning that the [200] oriented grains will have initially the largest lateral growth rate. Hence, due to the anisotropy in lateral growth rate, a random out-of-plane nucleated film will evolve as shown in figure 2.

Initially the [200] oriented grains have a larger diameter than all other grains, since they offered the largest lateral growth rate. Proceeding the thin film deposition, the [111] oriented grains will slowly envelop the other grains, because they have the largest geometric growth rate. It can be concluded that initially the volume fraction of [200] oriented grains is the largest, while the volume fraction of the [111] oriented grains becomes dominant as soon as they have overgrown the other grains. This exactly corresponds with the observations of Oh and Je, since an XRD \(\theta/2\theta\) spectrum represents the volume fraction of grains with a specific orientation. The transition height of about 150 nm at which the orientation changed from [200] to [111] as observed by Oh and Je, corresponds very well with the observed film thickness in their depositions at which the microstructural overgrowth was completed [14].

![Figure 2: Evolution of the initial growth of a random nucleated film in zone T conditions with the situation of N\(_2\) molecular gas. The dark grains are [200] oriented while the [111] oriented grains are white.](image)

3.2.3. \(\text{N}_2\)-flow. In ref. 6, it has been shown that an increasing \(\text{N}_2\)-flow results in an increasing energy flux per deposited Ti particle, mainly due to a decreasing deposition rate. Hence, the transition from random, to [111] and finally to [200] oriented thin films could be understood as a transition from zone Ic, to zone T (molecular \(\text{N}_2\) gas), and zone II conditions. SEM and TEM results indicated that the observed microstructures correspond to the expected microstructures of the different zones [6].

3.2.4. Ion-to-atom ratio. It is straightforward that increasing the ion-to-atom results in an increased mobility on the growing surface. Hence, the observed transition from [111] to [200] orientation with increasing ion-to-atom ratio can be understood as a transition from zone T (molecular \(\text{N}_2\) gas) to zone II conditions. This statement also fits with the experimental observation since an overgrowth mechanism was observed for the [111] oriented films, i.e. a zone T growth, while no overgrowth was noticed for the [200] oriented films, i.e. a zone II growth [20,21].

Since most deposition conditions, the ion-to-atom ratio and also the deposition rate was mentioned in their publications [20,21], the energy flux towards the growing film could be estimated. Their depositions were done on an electrically floating substrate, repelling nearly all electrons, but attracting the positive ions by the potential difference \(|V_p-V_{fl}|\) of 20 eV. The energy released during the formation of a TiN compound is 8.4 eV. The kinetic energy delivered from the sputtered Ti atoms can be ignored since most sputtered particles will be thermalised before reaching the substrate (total pressure = 2.7 Pa and target-substrate distance of 6.5 cm). Calculating the energy flux towards the substrate for the deposition at an ion-to-atom ratio of 3.5, an energy flux of \((8.4+20\times3.5) = 78.4\) eV per deposited Ti atom is obtained, as the critical value to have a transition from zone T to zone II. As
reported in ref. 6, this value corresponds very well with the needed energy per deposited Ti particle to obtain a transition from zone T to zone II growth with increasing N₂-flow.

4. Conclusions.
From above discussion, it can be concluded that the influences of the film thickness, ion-to-atom ratio, substrate temperature, and the N₂-flow during deposition on the preferred orientation of reactively sputtered TiN films can be understood by means of the presented ESZM. The most important conclusion of this ESZM is that the energy flux towards the substrate has a determinant impact on the film growth and thus also on the resulting microstructure and orientation. Future research should focus on a quantitative determination of this energy flux as a function of different deposition parameters, and its correlation with the transitions between different zones of the ESZM.

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