

# Chemical vapor deposition of titanium nitride thin films: kinetics and experiments

Juan Su, Rapahel Boichot, Elisabeth Blanquet, Frederic Mercier, Michel Pons

## ► To cite this version:

Juan Su, Rapahel Boichot, Elisabeth Blanquet, Frederic Mercier, Michel Pons. Chemical vapor deposition of titanium nitride thin films: kinetics and experiments. CrystEngComm, 2019, 21 (26), pp.3974-3981. 10.1039/C9CE00488B . hal-02315144

## HAL Id: hal-02315144 https://hal.science/hal-02315144

Submitted on 13 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

- 1 CrystEngComm, Royal Society of Chemistry, 2019, 21 (26),
- 2 pp.3974-3981. (10.1039/C9CE00488B)

# Chemical vapor deposition of titanium nitride thin films: kinetics and experiments

5 Juan Su<sup>1</sup>, Raphaël Boichot<sup>1,\*</sup>, Elisabeth Blanquet<sup>1</sup>, Frédéric Mercier<sup>1</sup>, and Michel Pons<sup>1</sup>

<sup>1</sup> Univ. Grenoble Alpes, CNRS, Grenoble INP\*, SIMaP, F-38000 Grenoble, France. \* Institute of Engineering
 Univ. Grenoble Alpes; juan.su@grenoble-inp.fr; elisabeth.blanquet@grenoble-inp.fr;

8 frederic.mercier@grenoble-inp.fr; michel.pons@grenoble-inp.fr

9 \* Correspondence: raphael.boichot@grenoble-inp.fr; Tel.: +33-476826537

10 Received: date; Accepted: date; Published: date

11 Abstract: Titanium nitride (TiN) films were grown by CVD (Chemical Vapor Deposition) from 12 titanium chlorides generated in situ by direct chlorination of titanium metal, ammonia (NH3) and 13 hydrogen (H<sub>2</sub>) as carrier gas on single crystal c-plane sapphire (Al<sub>2</sub>O<sub>3</sub>), cemented carbides (WC-Co), 14 stainless steel (AFNOR Z150CDV12) and amorphous graphite substrates. Kinetic pathways 15 involving four surface reactions has been proposed to simulate the growth rate. The proposed 16 model has been validated by experiments performed at different temperatures (650-1400 °C), 17 pressures (300-1000 Pa), with different amount of precursors (N/Ti ratio in gas phase) and on 18 different substrates. The study shows that on polycrystalline materials, the crystal orientation 19 depends on supersaturation while (111) preferred orientation is forced by underlying c-plane 20 sapphire whatever the supersaturation. The low N/Ti ratio in gas phase leads to low growth rate 21 and dense TiN film which is the key to obtain golden TiN. The high growth rate corresponds to 22 brown TiN. Globally, the study shows that golden color is independent from texture and is just the 23 natural aspect of a dense stoichiometric TiN layer.

- Keywords: TiN; Chemical Vapor Deposition; Supersaturation; Decorative and functional coatings.
- 26 1. Introduction

27 Thin films of titanium nitride (TiN) have been widely applied as wear resistant coatings for tools 28 [1-6], diffusion barrier layers [7-10], decorative layers [11,12] and for its high hardness, thermal and 29 chemical stability and good electrical conductivity. Chemical Vapor Deposition (CVD) [13] is a 30 common technique for the growth of TiN thin films [5,6,12,14-16]. Particularly, two major chemical 31 systems for the thermal CVD of TiN coatings, TiCl<sub>4</sub>–N<sub>2</sub>–H<sub>2</sub> and TiCl<sub>4</sub>–NH<sub>3</sub>–H<sub>2</sub>, are used [17]. The 32 temperature range for the first system is 900–1200 °C due to the low reactivity of nitrogen [18]. The 33 temperature range for the second system can be easily lowered to 550–750 °C [12]. The effects of 34 process parameters on the growth rate of CVD TiN coatings have been studied by Kuo et al. [19] for 35 the TiCl<sub>4</sub>–N<sub>2</sub>–H<sub>2</sub> system and by Jiang et al. [20] for the TiCl<sub>4</sub>–NH<sub>3</sub>–H<sub>2</sub> system. Due to the complexity 36 of the process parameters, their experiments were only focused on process parameters such as partial 37 pressure, temperature and the N/Ti ratio in gas phase. To the date, it is still difficult to predict which 38 process conditions will lead to a certain texture or visual aspect in TiN due to discrepancies in the 39 effect of parameters according to different authors and scattered data. In general, the growth rate is 40 positively affected by increasing H<sub>2</sub>, N<sub>2</sub>, and NH<sub>3</sub> partial pressures but a positive to negative 41 dependence of growth rate to increasing TiCl<sub>4</sub> partial pressure is observed in literature [17,21]. It 42 results from the formation of a non-reactive complex, TiCl<sub>4</sub>NH<sub>3</sub> in the gas phase. In this work, 43 comprehensive link between supersaturation, temperature and growth rate will be presented

44 combining experiments with CFD simulation.

45 A global kinetic model of TiN growth from TiCl<sub>4</sub>-N<sub>2</sub>-H<sub>2</sub> system was proposed in Ref. [17,21]. A 46 detailed kinetic mechanism and reaction pathways were built for the TiCl4-NH3-H2 system by Larson 47 et al. and Allendorf et al. [22,23], but only for a temperature of 630°C. They estimated the growth rate 48 by a series of surface reactions considering 4 gases, 10 surface sites and 2 bulk species. Grujicic et al. 49 [24] applied this mechanism for multi-length scale modeling and showed that the grain size increased 50 with increasing coating thickness. The thermodynamics and kinetics of gas-phase reactions in the Ti-51 Cl-H system was studied by Teyssandier et al. [25], the rate coefficients of decomposition of TiCl<sub>4</sub> and 52 TiCl<sub>3</sub> [25] were confirmed by experiments at high temperature (1000-1200 °C) in Ref. [26]. The aim of 53 this study is: (1) to assess simplified reaction pathways for the simulation of TiN growth with TiClx-54 NH3-H2 system based on the study of Larson and Allendorf [22] and extend it to a broad range of 55 process temperature; (2) to improve the understanding of the relationships between growth rate, 56 temperature, supersaturation, preferred orientation and morphology on ideal single crystal (c-plane 57 sapphire) and polycrystalline materials (WC-Co, Stainless steel Z150CDV12, and amorphous 58 graphite); (3) to figure out the main process parameters and the key feature for obtaining golden TiN.

#### 59 2. Experimental details

60 TiN is grown on single crystal (0001) sapphire (The Roditi International corporation Ltd., 61 London, UK), stainless steel (AFNOR Z150CDV12: 1.5%C, 12%Cr, 1%Mo and 1%V), WC-Co with 6 62 wt.% Cobalt (Hyperion, Grenoble, France) and amorphous graphite (Graphitech company, Saint 63 Martin d'Hères, France). Due to the high hardness, WC-Co is first polished with diamond discs and 64 finished by diamond suspension (1  $\mu$ m). Stainless steel and graphite are finished with 1- $\mu$ m (2400 65 grit) silicon carbide paper. These substrates are at the center of the graphite susceptor of 55 mm 66 diameter. Deposition temperature is measured by a thermocouple (20-700 °C) or an infrared 67 pyrometer (700-1400°C). The cold-wall experimental system used is shown in Figure 1. Ammonia 68 NH<sub>3</sub> (99.999%) gas is injected from the side of the quartz tube to minimize gas-phase reactions before 69 deposition. The others gases are injected from the top of reactor. Chlorine gas Cl<sub>2</sub> (99.999%) is injected 70 into a chlorination tube which contains high purity titanium pellets (Goodfellow company, 71 Coraopolis, PA, USA, purity of 99.98%). Lamps at the top of the quartz tube allow the chlorination 72 reactions. Induction coils (20 kHz) are used to heat the graphite holder. The temperature of cooling 73 water for the quartz tube is fixed at 85°C to minimize species condensation on walls. All the samples 74 except graphite are cleaned by acetone, ethanol and isopropanol successively in an ultrasonic bath. 75 Each cleaning procedure takes 5 minutes.

76



Figure 1. The cold wall experimental system for TiN CVD growth.

79 At the beginning of each run, 200 sccm of H<sub>2</sub> are injected into the chlorination tube to clean the 80 titanium pellets at 650 °C for 20 minutes (removing of carbon contamination on the surface). The 81 substrates are then heated under 1000 sccm of H2 with a 30 K/min ramp to reach the working 82 temperature, followed by a 10 min plateau (thermal stabilization). NH<sub>3</sub> is injected into the reactor 1 83 min before chlorine to reduce the etching of substrates by chlorides, especially when substrates are 84 WC-Co (cobalt is particularly sensitive to chlorine). At the end of the experiment, the chlorine gas is 85 switch off 1 min before NH3. The H2 flow is then replaced by 1000 sccm of N2. The substrates are 86 cooled down with a 37 K/min ramp.

87 In the present study,  $\theta/2\theta$  scans are made with a PANalytical X'Pert Pro MPD two-circle 88 diffractometer ( $\theta$ - $\theta$ , CuK $\alpha$ , acceleration voltage of 45 kV and current of 40 mA from a sealed x-ray 89 tube) equipped with a 1D linear detector. Field Emission Gun-Scanning Electron Microscope (ZEISS 90 Ultra-55) is used to characterize TiN layers surface morphology and texture. Thermodynamic 91 analysis of the gas-phase chemistry is made using Factsage 7.2 thermodynamic software and the 92 thermodynamic database FactPS. For the modeling of TiN deposition, heat transfer, mass transport 93 and gas flow dynamics are solved using the CFD-ACE+ multiphysics software package (2017 94 version).

Table 1 summarized the experiments performed for this study. Experimental as well as modeling results are summarized in this table and will be discussed in next sections. To obtain the surface activation energy, the last 5 experiments in Table 1 are designed to vary the deposition temperature while the N/Ti ratio and pressure in the reactor are fixed at 1.5 and 1000 Pa, respectively.

99 All the experiments in Table 1 are used to develop numerical modeling and simulation of TiN growth.

#### 100 3. Modeling and simulation

#### 101 3.1. Thermodynamic equilibrum and gas-phase kinetic analysis

102 For the traditional TiN coating system, TiCl<sub>4</sub> is generated by dosing and vaporizing its liquid 103 phase. This solution necessitates handling liquid TiCl4, a particularly corrosive product with a high 104 vapor pressure. Teyssandier and Allendorf [25] have shown that TiCl4 is stable and remains the most 105 important Ti-containing species when the temperature is below 900 °C. In the chlorination system 106 used here, Cl<sub>2</sub> gas passes over Ti pellets, solid TiCl<sub>2</sub> is theoretically the only chlorination product by 107 thermodynamic calculation (large excess of titanium versus chlorine). This means that the titanium 108 pellets are surrounded with solid TiCl<sup>2</sup> during chlorination process, that reacts in a second time with 109 Cl<sub>2</sub>. Figure 2 presents the thermodynamic equilibrium of 10 mol TiCl<sub>2</sub>(s) and 2 mol Cl<sub>2</sub>(g) at 1000 Pa 110 in the 600-1000 °C temperature range, conditions close to our chlorination process. Some experiments 111 are also carried out at around 300 Pa in this study, but the thermodynamic calculation shows that the 112 total pressure does not affect the mole fraction of gaseous species. At 650 °C (chlorination 113 temperature in the present work), the main gaseous species are TiCl<sub>3</sub>(g) and TiCl<sub>4</sub>(g) in equilibrium 114 with solid-phase TiCl<sub>2</sub>(s). Additionally, the deposition of a purple powdered films on the quartz tube 115 is an indication of the presence of  $TiCl_3(g)$  (see Figure S1 in supplementary material). The mole 116 fraction ratio is around XTIC13 : XTIC14=8 : 2.



**Figure 2.** Mole fraction at equilibrium of a mixture of 2 mol Cl<sub>2</sub>(g) and 10 mol TiCl<sub>2</sub>(s) at 1000 Pa.

Temperature °C	Pressure (Pa)	Sccm NH3	Sccm Cl <sub>2</sub>	N/Ti in gas phase	Measured growth rate (μm·h <sup>-1</sup> )	Theoretical growth rate (μm·h <sup>-1</sup> )	Log10 (surface supersaturation)	Main texture (Tc%) on c- plane sapphire	Main texture (Tc%) on WC-Co(*), graphite(#), steel(&)	Color on sapphire(*) and non-orientated substrates(#)
663	1000	25	20	1.875	1	2.9	13.4	111 (94%)	200* (100%)	brown*#
663	1000	50	20	3.75	7.7	5.7	13.63	111 (83%)	200* (100%)	brown*#
662	1000	50	10	7.5	5.7	5.64	13.57	111 (91%)	220* (93%)	brown*#
1100	1000	10	8	1.875	3	4.08	3.68	111 (100%)	-	golden*
710	310	5	7.5	1.0	0.06	0.228	11.39	111 (100%)	200* (100%)	silver*, golden <sup>#</sup>
673	310	5	5	1.5	0.04	0.2	12.39	111 (100%)	200* (100%)	silver*, golden#
665	1000	50	20	3.75	8.4	5.8	13.57	111 (73%)	200* (100%)	brown*#
604	1000	50	20	3.75	2.724	4.32	15.60	111 (57%), 200 (34%)	200* (100%)	brown*#

Table 1. Summary of the growth parameters. To calculate texture coefficient T<sub>c</sub>, 4 main diffraction peaks are taken into account: (111), (200), (220) and (420).

**Table 1.** Continued.

Temperature °C	Pressure (Pa)	Sccm NH3	Sccm Cl2	N/Ti in gas phase	Measured growth rate (µm·h <sup>-1</sup> )	Theoretical growth rate (µm·h <sup>-1</sup> )	Log10 (surface supersaturation)	Main texture (Tc%) on c- plane sapphire	Main texture (Tc%) on WC-Co(*), graphite(#), steel(&)	Color on sapphire(*) and non-orientated substrates(#)
609	1000	50	20	3.75	3	4.32	15.42	111 (86%)	200* (100%)	brown*#
619	1000	50	20	3.75	2.904	4.32	15.06	111 (93%)	200* (100%)	brown*#
662	1000	30	10	4.5	6.5	3.48	13.39	111 (100%)	200* (100%)	brown*#
662	1000	50	20	3.75	3.45	5.8	13.66	111(65%)	200* (100%)	brown*#
650	1000	5	5	1.5	0.3	0.58	13.0	-	200* (100%)	golden <sup>#</sup>
680	1000	5	5	1.5	0.4	0.6	12.16	-	200* (100%)	golden <sup>#</sup>
750	1000	5	5	1.5	0.6	0.84	10.21	-	200* (69%)	brown <sup>#</sup>
800	1000	5	5	1.5	0.7	1.02	8.96	-	200* (69%)	brown <sup>#</sup>
1400	1000	5	5	1.5	3.8	3.1	-0.135	111 (100%)	111# (62%)	Dark brown*#

2 of 14

122 For the traditional TiCl<sub>4</sub>-NH<sub>3</sub> system, Umanskii et al. [27] studied the reaction pathways 123 involving complex formation (TiClxNHy). It was concluded that, in typical CVD conditions, only 124 TiCl<sub>4</sub>NH<sub>3</sub> is formed in substantial amount at low temperature. Grujicic et al. [24] took into account 125 the presence of non-reactive complex formation. As TiCl4(g) concentration is increased, it causes 126 additional NH<sub>3</sub>(g) to be tied up in the complex. This complex could be either poorly reactive, either 127 with a very low vapor pressure and condensing. This decreases the concentration of NH<sub>3</sub>(g) available 128 for the CVD of TiN and, in turn, decreases the deposition rate. The effect is a very small negative 129 order of the TiN deposition rate with respect to the concentration of TiCl<sub>4</sub>(g). Teyssandier and 130 Allendorf [25] developed a gas-phase kinetic model which corresponds to our experimental range. 131 This dataset involving decomposition and formation of TiCl<sub>x</sub> (x=1, 2, 3, 4), and equilibrium reactions 132 is used to understand gas-phase transformations as a function of temperature and pressure (see Table 133 S2 in supplementary material).

134 3.2. Mass transport modeling

135 For mass transport modeling, the models and software packages already used for AlN 136 deposition are used [28]. The governing equations of multicomponent mass transport and heat 137 transfer can be found in Table S1 in supplementary material. The species properties such as diffusion 138 coefficients, mixtures viscosities and thermal conductivities are calculated using the Enskog theory 139 [29]. Lennard-Jones parameters for gaseous species are computed according to the empirical method 140 in Ref. [30]. The laminar incompressible momentum equation is used to solve the diffusion-141 convection problem since the Reynolds number in all experiments is less than 50. The mixture 142 enthalpy is calculated by a polynomial relationship with temperature by JANAF formalism [31].

143 To simplify the surface reaction model and figure out which TiCl<sub>x</sub> can be, TiCl<sub>x</sub> mole fractions 144 on the substrate as a function of temperature at 300 Pa and 1000 Pa considering the 17 gas-phase 145 reactions of the Ti-Cl-H system (see Table S2 in supplementary material) has been calculated by CFD-146 ACE as shown in Figure 3. The typical inlet gas-phase mole fractions are 90% H<sub>2</sub>, 8% TiCl<sub>3</sub> and 2% 147 TiCl4 since XTiCl3 : XTiCl4=8 : 2 from thermodynamic equilibrium in chlorination tube. It can be seen that 148 the mole fraction of TiCl<sub>2</sub> is increasing and the mole fraction of TiCl<sub>4</sub> is decreasing with temperature, 149 regardless of pressure. This conclusion is in a good agreement with Ref. [25,32]. The mole fraction of 150 TiCl<sub>3</sub> is however almost stable, indicating that the decomposition and formation of TiCl<sub>3</sub> are almost 151 kinetically balanced. Figure 3 further illustrates that TiCl<sub>3</sub> and TiCl<sub>4</sub> only should be considered for

- 152 surface reactions and TiCl<sub>2</sub> can be ignored, because the mole fraction of TiCl<sub>2</sub> is negligible in typical
- 153 CVD conditions.



Figure 3. Mole fraction of TiCl<sub>x</sub> at the substrate center as a function of the deposition temperature.

The kinetic model of surface reactions developed by Allendorf et al. [23] was first used to compare experimental and modeling results at 630°C. This model involves 14 surface reactions and successfully predicts TiN growth rates as a function of key reactor parameters including inlet reactant concentrations, reactor pressures and total gas flow rates. This model will be modified to take into

account the activation energy.

#### 159 4. Results and discussion

160 4.1. Experimental growth rates versus modeling and the surface kinetic parameters

Arrhenius plot obtained at fixed flow rate and pressure (last five experiments in Table.1) is shown in Figure 4. It shows that the growth rate is kinetically controlled with an activation energy of 43 kJ/mol.



164

165 **Figure 4.** Arrhenius plots for TiN deposition.

From the previous kinetic database[23,25], a simplified kinetic model taking into account temperature variations is assumed.

168 
$$\operatorname{TiCl}_{3} + \operatorname{NH}_{2} s \to \operatorname{N}(B) + \operatorname{TiCl}_{2} s + \operatorname{HCl}$$
(1)

169 
$$\operatorname{TiCl}_{4} + \operatorname{NH}_{2} s \to \operatorname{N}(B) + \operatorname{TiCl}_{3} s + \operatorname{HCl}$$
(2)

170 
$$NH_3 + TiCl_2 \rightarrow Ti(B) + NH_2 \rightarrow HCl + Cl$$
(3)

171 
$$NH_3 + TiCl_3 s \rightarrow Ti(B) + NH_2 s + HCl + Cl_2$$
(4)

172 where three kinds of surface species on growing TiN surfaces are only considered: TiCl<sub>3</sub>, TiCl<sub>2</sub>, and

173 NH2\_5. Surface reaction rate and kinetic data can be found in supplementary materials (see Table S3174 in supplementary material).

Surface kinetic parameters have been obtained by minimizing the relative difference between experimental and simulated growth rates while maintaining kinetics from the original database [23] and varying the activation energy. It should be noted that each surface reaction conserves the total number of surface species, i.e. surface sites. In the case of the first reaction, for example, when a gasspecies TiCl<sub>3</sub> attaches to the surface, there is one bulk phase atom added to the solid and a new surface species created. Reactions (1)-(4) are bimolecular reactions.

Although there are some reports of TiN deposition rates in the literature for TiCl<sub>4</sub>-NH<sub>3</sub> system [21,23,33], the lack of detailed information makes it difficult to simulate the deposition rates published. The parity diagram between simulated and experimental growth rates from this work is presented in Figure 5. The experimental error originates from substrate temperature and thickness

185 uncertainties.



186 187

Figure 5. Parity diagram between experimental and theoretical growth rates from this work.

188 It is now possible to calculate the actual supersaturation (see equation S6 in supplementary 189 materials for definition) just above the substrate by numerical modeling and to find relationships 190 between processing parameters and microstructural information.

#### 191 4.2. Relationship among the texture of TiN, growth rate and supersaturation

192 For each process conditions, the texture coefficient  $T_{c_hkl}$  for each (hkl) plane of the obtained film 193 is calculated as follows [34],  $I_{hkl}$ 

194 
$$T_{c\_hkl} = \frac{\frac{\overline{I_{0,hkl}}}{\overline{I_{0,hkl}}}}{\frac{1}{N} \cdot \sum_{1}^{N} \frac{I_{hkl}}{\overline{I_{0,hkl}}}}$$
(3)

in which N=4 is the peak amount of TiN, *I*<sub>hkl</sub> and *I*<sub>0,hkl</sub> are the integrated intensity of the (hkl) Bragg reflection for the studied and for a randomly oriented samples, respectively, as give in ICDD: 00-038-1420. In the present study, 4 main diffraction peaks (111), (200), (220) and (420) are taken into account. The percentage of texture coefficient  $T_{c_hkl}$ % is defined as  $T_{c_hkl}/N$  to show the preferred orientation of TiN films in the present work.

200 Figure 6 presents the relationship between the preferred orientation of TiN, growth rate, 201 supersaturation, and deposition temperature on various substrates. In CVD, high deposition 202 temperatures are generally correlated to low supersaturations. In Figure 6a, the substrates are 203 stainless steel, WC-Co or graphite which are only poorly or randomly textured. It can be seen that 204 the orientation of TiN is correlated with supersaturation. TiN film with (111) preferred orientation 205 appears at low supersaturation (high temperature) while (200) and (220) preferred orientation are 206 likely grown at high supersaturation (so low temperature), in agreement with Ref. [35]. In Figure 6b, 207 the substrates are (0001) single crystal sapphire. Due to crystallographic relationships, the (0001) 208 hexagonal lattice of sapphire imposes the (111) preferred orientation to the TiN film. High 209 supersaturation (Log<sub>10</sub> (supersaturation) >15.5) contributes to polycrystalline TiN film. It also can be 210 seen from Figure 7 that there is no clear correlation between N/Ti ratio and the crystallographic 211 orientation of TiN films.

#### 4 of 14



**Figure 6.** Relationships among preferred orientations, growth rates, supersaturation and deposition temperatures. (a) Substrates are WC-Co, stainless steel and graphite without preferred orientation. (b) Substrate is (0001) sapphire. Black arrows show TiN films with golden color and orange arrows show TiN films with silver color.

#### 213 4.3. The formation conditions and feature of golden TiN

214 Even if the color of TiN film is affected by various properties such as composition, stoichiometry 215 and thickness etc. [36], we studied color feature as function of process parameters (N/Ti gas phase 216 ratio, supersaturation) and finally cross-section morphology. In Figure 6, the black and orange arrows 217 point out the conditions for obtaining golden TiN films and silvery TiN films, respectively. On non-218 oriented substrates, golden color is obtained at rather low growth rate (less than 0.4 µm/h). On (0001) 219 sapphire, silver and golden TiN films prefer low growth rate (less than 3 µm/h). TiN films with both 220 (200) and (111) preferred orientation can have golden color. Polycrystalline TiN with golden color 221 can also be obtained (see Figure S2 in supplementary material). Therefore, the golden color of TiN is 222 clearly not related with its texture.

223 In Ref. [37], the color of TiN films was studied in a small range of growth rates, less than 2 µm/h. 224 It showed that the color of TiN films was determined by N/Ti gas-phase ratio. In our experiments, 225 the range of growth rate is from 0.03 to 8 µm/h at various N/Ti ratios on single and polycrystalline 226 substrates. So it is interesting to study TiN color according to these two parameters only. Figure 7 227 presents the influence of N/Ti on growth rate and color of TiN on non-orientated substrates (Figure 228 7a) and (0001) sapphire single crystal (Figure 7b). It can be seen that high N/Ti ratio leads to high 229 growth rate. Figure 7a shows that on polycrystalline substrates, the color of TiN is mainly influenced 230 by growth rate. The golden TiN can be obtained when the growth rate is below 0.4  $\mu$ m/h. Figure 7b 231 shows that the influence of N/Ti ratio and growth rate on the color of TiN films grown on (0001) 232 sapphire single crystal is more complicated. The sapphire substrates have an ordered structure and 233 transparent color. Golden color is difficult to obtain because TiN film with (111) crystallographic 234 orientation prefers to grow as columnar layer, not dense enough. When the growth rate is less than 235 0.1 µm/h, TiN films present a silvery color. The color of TiN films changes from silver to golden with 236 deposition time (visual observation during experiments). When the N/Ti ratio is around 2 and growth 237 rate is around 3  $\mu$ m/h, TiN film with shining golden color is obtained once. The brown TiN films are 238 obtained when the growth rate is above 3 µm/h or N/Ti ratio is above 2. In conclusion, golden TiN 239 films on non-orientated substrates are determined by a low growth rate ( $\leq 0.4 \mu m/h$ ) while on 240 sapphire film should be thick enough ( $\approx 3 \,\mu$ m) and not columnar (dense).





**Figure 7.** TiN growth rate versus N/Ti ratio on (a) non-orientated substrates and (b) (0001) sapphire. The figure also indicates the preferred orientation and color of TiN.

- 241 To show the structure difference between golden and brown TiN, Figure 8 shows cross-sectional
- 242 morphology of (a) golden TiN on WC-Co, (b) brown TiN on WC-Co. On non-orientated substrates,
- 243 it can be see that thin and dense TiN layers present golden color while TiN films with thick columnar
- 244 structure present brown color.



Figure 8. Cross-sectional morphology of (a) golden TiN on WC-Co (b) brown TiN on WC-Co. The figure also indicates preferred crystallographic direction and growth rate.

- 245 Three cross-sectional and surface morphology of TiN films: (a) golden, growth rate at 3 µm/h, 246 N/Ti=1.875, (b) brown, growth rate at 3  $\mu$ m/h, N/Ti=3.75 and (c) brown, growth rate at 5.7  $\mu$ m/h, 247 N/Ti=7.5 on sapphire are shown in Figure 9. Morphology in Figure 9(a) shows very dense TiN film 248 while there are gaps between columns in Figure 9(b) and (c). Especially (a) and (b) has the same 249 growth rate and thickness, it indicates that dense structure is the key point for the golden TiN film. 250 Increasing N/Ti ratio as shown in Figure 9(b) or increasing both N/Ti ratio and growth rate as shown 251 in Figure 9(c) leads to columnar growth and present brown color. As a conclusion, dense TiN films 252 are always golden. Low N/Ti ratio leads to high density.
  - (a)







**Figure 9.** Cross-sectional and surface morphology for TiN layers with (a) golden (b) brown (c) brown color on sapphire. The figure also indicates preferred crystallographic orientation, growth rate and N/Ti ratio.

#### 253 5. Conclusions

254 A simplified kinetic model associated with heat and mass transport for TiN film growth was 255 proposed. TiCl<sub>3</sub> and TiCl<sub>4</sub> are the most important Ti-containing gas-phase species. These species are 256 adsorbed on the growing surface with an activation energy close to 43 kJ/mol. The model has been 257 validated within a broad range of process parameters (temperature, N/Tigas-phase ratio, pressure). 258 The relationship between growth rate, supersaturation, deposition temperature and preferred 259 orientation was studied. It was shown that the orientation of TiN films on non-orientated substrates 260 is influenced by both supersaturation and deposition temperature. TiN films with (111) dominated 261 orientation are preferably grown at low supersaturation and high temperature while (200) and (220) 262 preferred orientation at high supersaturation and low temperature. On (0001) sapphire single crystal, 263 TiN thin films with (111) preferred orientation are most likely to be growing. There is no obvious 264 relationship between the golden color and texture.

Supplementary Materials: Table S1: Governing equations of multicomponent mass and heat transfer. Table S2:
 The gas phase reactions and rate constant for reaction K is represented in the standard Arrhenius form. Table
 S3: Surface reactions and correspond kinetic parameters used in the simplified model. Figure S1: Purple TiCl<sub>3</sub>
 films on the quartz tube. Figure S2: The surface morphology of polycrystalline TiN with golden color on WC Co.

Author Contributions: Conceptualization, Michel Pons, Frederic Mercier and Raphaël Boichot; Experiments,
 Juan Su; Simulation, Juan Su, Michel Pons, Elisabeth Blanquet and Raphaël Boichot. Writing-Original Draft
 Preparation, Juan Su.; Writing-Review & Editing, Michel Pons, Frederic Mercier, Elisabeth Blanquet and
 Raphaël Boichot; Project Administration, Raphaël Boichot.

Funding: This research was supported by Carnot Institute 'Énergies du Futur' for the project "AlN pour
 materiaux refractaires fonctionnels' and by the Centre of Excellence of Multifunctional Architectured
 Materials "CEMAM" [grant number ANR-10-LABX-44-01].

Acknowledgments: The authors want to thank R. Reboud for emergency management during experiments,
 M. Jaquemin for help in experiments, S. Coindeau and T. Encinas for discussions on the XRD results.

#### 283 References

- Echigoya, J.; Liu, Z.-t.; Imamura, A.; Takatsu, S. Transmission electron microscopy studies of growth and interface structure of chemically vapour deposited TiC and TiN films on WC-Co alloy substrates. *Thin Solid Films* 1991, *198*, 293-300, doi:10.1016/0040-6090(91)90347-Z.
- Prengel, H.G.; Pfouts, W.R.; Santhanam, A.T. State of the art in hard coatings for carbide cutting tools. *Surface and Coatings Technology* 1998, *102*, 183-190, doi:10.1016/S0257-8972(96)03061-7.
- 3. Matei, A.A.; Pencea, I.; Branzei, M.; Tranca, D.E.; Tepes, G.; Sfatb, C.E.; Ciovica, E.; Gherghilescu, A.I.;
  Stanciu, G.A. Corrosion resistance appraisal of TiN, TiCN and TiAlN coatings deposited by CAE-PVD method
  on WC-Co cutting tools exposed to artificial sea water. *Applied Surface Science* 2015, *358*, 572-578,
  doi:10.1016/j.apsusc.2015.08.041.
- Rebenne, H.E.; Bhat, D.G. Review of CVD TiN coatings for wear-resistant applications: deposition processes,
   properties and performance. *Surface and Coating Technology* 1994, 63, 1-13, doi:10.1016/S0257 8972(05)80002-7.
- Wagner, J.; Mitterer, C.; Penoy, M.; Michotte, C.; Wallgram, W.; Kathrein, M. The effect of deposition
  temperature on microstructure and properties of thermal CVD TiN coatings. *International Journal of Refractory Metals and Hard Materials* 2008, 26, 120-126, doi:10.1016/j.ijrmhm.2007.01.010.
- Kashani, H.; Sohi, M.H.; Kaypour, H. Microstructural and physical properties of titanium nitride coatings
  produced by CVD process. *Materials Science and Engineering A* 2000, 286, 324-330, doi:10.1016/S09215093(00)00744-9.
- Fiordalice, R.W.; Hegde, R.I.; Kawasaki, H. Orientation control of chemical papor deposition TiN film for
  barrier applications. *Journal of the Electrochemical Society* **1996**, *143*, doi:10.1149/1.1836949.
- 3048.DelaCruz, S.; Wang, Z.; Cheng, P.; Carraro, C.; Maboudian, R. TiN diffusion barrier for stable W/SiC(0001)305interfaces in inert ambient at high temperature. Thin Solid Films 2019, 670, 54-59,306doi:10.1016/j.tsf.2018.11.058.
- Sato, M.; Takeyama, M.B. Relationship between TiN films with different orientations and their barrier
   properties. *Japanese Journal of Applied Physics* 2018, *57*, 07MB01-07MB03, doi:10.7567/JJAP.57.07MB01.
- 30910.Grosso, S.; Latu-Romain, L.; Berthome, G.; Renou, G.; Coz, T.L.; Mantel, M. Titanium and titanium nitride thin310films grown by dc reactive magnetron sputtering Physical Vapor Deposition in a continuous mode on stainless311steel wires: Chemical, morphological and structural investigations. Surface and Coatings Technology 2017, 324,312318-327, doi:10.1016/j.surfcoat.2017.05.089.
- Roquiny, P.; Bodart., F.; Terwagne, G. Colour control of titanium nitride coatings produced by reactive
  magnetron sputtering at temperature less than 100°C. *Surface and Coatings Technology* 1999, *116-119*, 278283, doi:10.1016/s0257-8972(99)00076-6.
- Kafizas, A.; Carmalt, C.J.; Parkin, I.P. CVD and precursor chemistry of transition metal nitrides. *Coordination Chemistry Reviews* 2013, 257, 2073-2119, doi:10.1016/j.ccr.2012.12.004.
- 318
   13.
   Choy, K.L. Chemical vapour deposition of coatings. Progress in Materials Science 2003, 48, 57-170,

   319
   doi:10.1016/S0079-6425(01)00009-3.

- García, J.; Pinto, H.; Ramos-Moore, E.; Espinoza, C.; Östby, J.; Coelho, R. In-situ high temperature stress
  analysis of Ti(C,N) coating on functionally graded cemented carbides by energy dispersive synchrotron X-ray
  diffraction. *International Journal of Refractory Metals and Hard Materials* 2016, 56, 27-34,
  doi:10.1016/j.ijrmhm.2015.12.001.
- Tang, S.; Gao, S.; Wang, S.; Wang, J.; Zhu, Q.; Chen, Y.; Li, X. Characterization of CVD TiN coating at
   different deposition temperatures and its application in hydrocarbon pyrolysis. *Surface and Coatings Technology* **2014**, 258, 1060-1067, doi:10.1016/j.surfcoat.2014.07.029.
- von Fieandt, L.; Larsson, T.; Lindahl, E.; Bäcke, O.; Boman, M. Chemical vapor deposition of TiN on transition
  metal substrates. *Surface and Coatings Technology* 2018, *334*, 373-383, doi:10.1016/j.surfcoat.2017.11.063.
- 329 17. Dekker, J.P.; Put, P.J.v.d.; Veringa, H.J.; Schoonman, J. A kinetic study of titanium nitride chemical vapor
   330 deposition using Nitrogen, Hydrogen, and Titanium Tetrachloride. *Journal of The Electrochemical Society* 1994,
   331 141, 787-795, doi:10.1149/1.2054812
- 332 18. Spee, C.I.M.A.; Driessen, J.P.A.M.; Kuypers, A.D. Low temperature deposition of TiN ceramic material by
  333 metal organic and/or plasma enhanced CVD. *Le Journal de Physique IV* 1995, 05, C5-719-C715-734,
  334 doi:10.1051/jphyscol:1995587.
- Kuo, D.-H.; Huang, K.-W. Kinetics and microstructure of TiN coatings by CVD. Surface and Coatings *Technology* 2001, *135*, 150-157, doi:10.1016/S0257-8972(00)00986-5.
- Jiang, C.; Goto, T.; Hirai, T. Morphology and preferred orientation of titanium nitride plates prepared by
  chemical vapour deposition. *Journal of Materials Science* 1994, 29, 669-675, doi:10.1007/BF00445977.
- 339 21. Nakanishi, N.; Mori, S.; Kato, E. Kinetics of chemical vapor deposition of titanium nitride. *Journal of The* 340 *Electrochemical Society* 1990, *137*, 322-328, doi:10.1149/1.2086412.
- Larson, R.S.; Allendorf, M.D. *A reaction mechanism for titanium nitride CVD from TiCl<sub>4</sub> and NH<sub>3</sub>*; SAND968443 · UC-401, Sandia National Laboratories: California, May 5-10, 1996, 1996; pp 41-46.
- Allendorf, M.D.; Arsenlis, A.; Bastasz, R.; Colvin, M.E.; Evans, G.; Germann, G.; Janssen, C.L.; Larson, R.S.;
  Melius, C.F.; Osterheld, T.H., et al. *Development of a Process Simulation Capability for the Formation of Titanium Nitride Diffusion barriers*; SAND97-8235-UC-404, Sandia National Laboratories: California, 1997;
  pp 1-40.
- 347 24. Grujicic, M.; Lai, S.G. Multi-length scale modeling of chemical vapor deposition of titanium nitride coatings.
  348 *Journal of Materials Science* 2001, *36*, 2937-2953, doi:10.1023/A:1017958621586.
- 349 25. Teyssandier, F.; Allendorf, M.D. Thermodynamics and kinetics of gas-phase reactions in the Ti-Cl-H system.
  350 *Journal of the Electrochemical Society* 1998, *145*, 2167-2177, doi:10.1149/1.1838613.
- J.Herzler; Roth, P. High-temperature decomposition of TiCl<sub>4</sub> based on Cl-Concentration measurements.
   *Proceedings of the Combustion Institute* 2002, 29, 1353-1359, doi:10.1016/S1540-7489(02)80166-3.
- 353 27. Umanskii, S.Y.; Novoselov, K.P.; Minushev, A.K.; Siodmiak, M.; Frenking, G.; Korkin, A.A. Thermodynamics
  and kinetics of initial gas phase reactions in chemical vapor deposition of titanium nitride. Theroretical study of
  TiCl4 Ammonolysis. *Journal of Computational Chemistry* 2001, 22, 1366, doi:10.1002/jcc.1095.
- Boichot, R.; Coudurier, N.; Mercier, F.; Claudel, A.; Baccar, N.; Milet, A.; Blanquet, E.; Pons, M. CFD modeling
  of the high-temperature HVPE growth of aluminum nitride layers on c-plane sapphire: from theoretical
  chemistry to process evaluation. *Theoretical Chemistry Accounts* 2014, *133*, doi:10.1007/s00214-013-1419-8.
- 359 29. Bird, R.B.; Stewart, W.E.; lightfoot, E.N. *Transport phenomena, Rivesed 2nd ed.*; Wiley, J., New York, 2002.
- 360 30. Svehla, R.A. NASA technical report R-132.; 1962.
- 361 31. Chase, M.W. *JANAF Thermochemical tables, 4th ed.*; American Chemical Society; Woodbury, N.Y. : American
   362 Institute of Physics for the National Institute of Standards and Technology: Washington, D.C., 1998.

9 of 14

363	32.	Mercier, F.; Shimoda, H.; Lay, S.; Pons, M.; Blanquet, E. Reactive chemical vapor deposition of heteroepitaxial
364		Ti1-xAlxN films. CrystEngComm 2018, 20, 1711-1715, doi:10.1039/c7ce02129a.
365	33.	Kurtz, S.R.; Gordon, R.G. Chemical vapor deposition of titanium nitride at low temperatures. Thin Solid Films
366		<b>1986</b> , <i>140</i> , 277-290, doi:10.1016/0040-6090(86)90271-3.
367	34.	Consonni, V.; Rey, G.; Roussel, H.; Bellet, D. Thickness effects on the texture development of fluorine-doped
368		SnO2 thin films: The role of surface and strain energy. Journal of Applied Physics 2012, 111, 033523,
369		doi:10.1063/1.3684543.
370	35.	Pangarov, N.A. On the crystal orientation of electrodeposited metals. <i>Electrochimica Acta</i> 1964, 9, 721-726,
371		doi:10.1016/0013-4686(64)80060-8.
372	36.	Anderbouhr, S.; Blanquet, E.; Ghetta, V.; Bernard, C. TiN and (Ti <sub>1-x</sub> Al <sub>x</sub> )N films obtained by a low pressure
373		chemical vapor deposition process. In Proceedings of Proc 14th Int conf chem vap dep and EUROCVD XI,
374		Pennington, 1997; pp. 356-363.
375	37.	Nah, JW.; Kim, BJ.; Lee, DK.; Lee, JJ. Color, structure, and properties of TiN coatings prepared by plasma
376		enhanced chemical vapor deposition. Journal of Vacuum Science & Technology A 1999, 17, 463-469,
377		doi:10.1116/1.581607.
378		
379		

## Supplementary materials

#### Chemical vapor deposition of titanium nitride thin films: kinetics and experiments

Juan Su<sup>1</sup>, Raphaël Boichot<sup>1,\*</sup>, Elisabeth Blanquet<sup>1</sup>, Frédéric Mercier<sup>1</sup>, and Michel Pons<sup>1</sup>

#### Heat and Mass transport model

The governing equations describing flow dynamics, heat and mass transfer are shown in Table S1. Precursors are very diluted in H<sub>2</sub> (more than 90% in mole fraction of the gaseous phase), so values of the transport properties can be calculated by the kinetic theory of dilute gas[1].

The boundary conditions for heat transfer are:  $T = T_m$  on the surface of substrate and  $T = T_c$  on the cooling wall ( $T_m$  is measured from IR pyrometer and  $T_c$  is controlled by a heating and cooling system); the temperature for initial gas-phase species are room temperature. The boundary conditions for mass transfer are: the velocity on the wall is 0; the velocity at the inlet is varied to satisfy the calculated flow rates matching the experimental conditions. Outlet condition is zero pressure (compared to the reference working pressure).

Table S1. Governing equations of multicomponent mass and heat transfer (notations are at the end of the document).

Continuity	$\nabla \cdot \rho \vec{v} = 0$
Momentum balance (1)	$\nabla \cdot \left(\rho \vec{v} \vec{v}\right) = \nabla \cdot \underline{\vec{\tau}} - P + \rho \vec{g}$
	$\underline{\tau} = \mu \left( \nabla \vec{v} + (\nabla \vec{v})^t \right) - \frac{2}{3} \mu \left( \nabla \cdot \vec{v} \right) \cdot \underline{I}$
Energy balance (2)	$c_{p}\nabla\cdot\left(\rho\vec{v}T\right) = \nabla\cdot\left(\lambda\nabla T\right) + \nabla\cdot\left(RT\sum_{i=1}^{N}\frac{D_{i}^{T}}{M_{i}}\frac{\nabla x_{i}}{x_{i}}\right)$
	$+\sum_{i=1}^{N}\frac{H_{i}}{M_{i}}\nabla\cdot\vec{J}_{i} -\sum_{i=1}^{N}\sum_{k=1}^{K}H_{i}\upsilon_{ik}\left(\boldsymbol{\mathcal{R}}_{k}^{g}-\boldsymbol{\mathcal{R}}_{-k}^{g}\right)$
Species transport (3)	$\nabla \cdot \left(\rho \vec{v} \omega_{i}\right) = -\nabla \cdot \vec{J}_{i} + M_{i} \sum_{k=1}^{K} \upsilon_{ik} \left(\boldsymbol{\mathcal{R}}_{k}^{g} - \boldsymbol{\mathcal{R}}_{-k}^{g}\right) i = 1, N$
	$\vec{J}_i^c = -\sum_{j=1}^N \left(\rho D_{ij}\right) \nabla x_j  i = 1, N$
	$\vec{J}_i^T = -D_i^T  \frac{\nabla T}{T}  i = 1, N$
Ideal gas law (4)	$\rho = \frac{PM}{RT}$
Deposition rate (5)	$R_s = \vec{J}_i \cdot \vec{n} = \vec{J}_i^c \cdot \vec{n} + \vec{J}_i^T \cdot \vec{n}  i = 1, N$

#### Gas-phase kinetics pathways

From thermodynamic equilibrium calculation in chlorination tube, both TiCl<sub>4</sub> and TiCl<sub>3</sub> should be considered for the gas-phase reactions. The gas-phase kinetic model involves unimolecular

dissociation reactions (K1-K3) and bimolecular reactions (K4-K17) is summarized in Ref[1] (Table S2). The rate constant for reaction  $k_k$  in this work is represented in the standard Arrhenius form:

$$k_k = \alpha_k T^{\beta_k} \exp\left(-\frac{E_{\alpha k}}{RT}\right) \tag{S1}$$

**Table S2**. The rate constant for reaction K is represented in the standard Arrhenius form:  $k_k = \alpha_k T^{\beta_k} \exp\left(-\frac{E_{\alpha k}}{RT}\right)$ . For unimolecular reactions, the units of  $\alpha_k$  are s<sup>-1</sup>; for bimolecular reactions, the units are cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. All energies are in kJ mol<sup>-1</sup>.

Reaction K	α <sub>k</sub>	$\beta_k$	$E_{\alpha k}$
K1: TiCl <sub>4</sub> <-> TiCl <sub>3</sub> + Cl	2.32 E+20	-1.17	387.9
K2: TiCl <sub>3</sub> <-> TiCl <sub>2</sub> + Cl	1.02E+18	-0.742	422.6
K3: TiCl <sub>2</sub> <-> TiCl + Cl	3.65E+20	-1.06	509.6
K4: TiCl <sub>4</sub> + H <-> TiCl <sub>3</sub> + HCl	5.11E+06	2.5	12.6
K5: TiCl <sub>3</sub> + H <-> TiCl <sub>2</sub> + HCl	1.11E+06	2.5	33.5
K6: TiCl <sub>2</sub> + H <-> TiCl + HCl	3.05E+06	2.5	145.2
K7: TiCl +H <-> Ti + HCl	4.09E+05	2.5	24.7
K8: H+Cl+M -> HCl + M	7.20E+21	-2.0	0.0
K9: HCl + M -> HCl + M	7.90E+25	-3.0	445.6
K10: Cl + Cl + M <-> Cl <sub>2</sub> + M	2.00E+14	0.0	-7.5
K11: H + HCl -> Cl + H <sub>2</sub>	1.69E+13	0.0	17.2
K12: Cl + H <sub>2</sub> -> H + HCl	2.95E+13	0.0	21.3
K13: Cl <sub>2</sub> + H <-> Cl + HCl	8.60E+13	0.0	5.0
K14: H + H + H <sub>2</sub> -> H <sub>2</sub> + H <sub>2</sub>	9.70E+16	-0.6	0.0
K15: $H_2 + H_2 -> H + H + M$	8.80E+14	0.0	402.1
K16: H <sub>2</sub> + M -> H + H + M	2.20E+14	0.0	402.1
K 17: H + H + M -> H <sub>2</sub> + M	6.53E+17	-1.0	0.0

#### Surface kinetics pathways

The surface reaction rate for adsorbed species  $C_s$  which absorb the gas-phase molecules A is expressed as [2]:

$$V_k = k_k[A] \times [\mathcal{C}(S)] \tag{S2}$$

The rate constant for reaction  $k_k$  in this work is represented in the standard Arrhenius form:

$$k_k = \alpha_k T^{\beta_k} \exp\left(-\frac{E_{\alpha k}}{RT}\right) \tag{S3}$$

In which,

$$\alpha_k = \sqrt{\frac{R}{2\pi M_A}} \frac{1}{[\Gamma_{tot}]}$$
(S4)

$$\beta_k = 0.5 \tag{S5}$$

The local gas supersaturation near the growing surface has been defined as the sum of the reactants pressure divided by the sum of the species at equilibrium pressure [3]:

$$\beta = \frac{P_{\text{TiCl}_3} + P_{\text{TiCl}_4} + P_{\text{NH}_3}}{P_{\text{Ti}}^* + 2P_{\text{N}_2}^*}$$
(S6)

where *P* and *P*<sup>\*</sup> are calculated pressure of species (TiCl<sub>3</sub>, TiCl<sub>4</sub>, and NH<sub>3</sub>) contributing to TiN growth near the growing surface and the equilibrium vapor pressure of gases in a closed volume at the same temperature calculated with Factsage 7.1.

**Table S3.** Surface reactions and correspond kinetic parameters used in the simplified model. \_s is a surface site and (*B*) is the bulk phase. The surface density is  $1.8 \times 10^{-9}$  mol cm<sup>-2</sup>.

Heterogeneous reaction unit CGS (cm-g-s)					
Surface reactions	$\alpha_k$ Pre exp. factor	$eta_k$ Temp. exp.	$E_{\alpha k}/R$ Activ. temp. (K)		
$\operatorname{TiCl}_3 + \operatorname{NH}_2 s \leftrightarrow \operatorname{N}(B) + \operatorname{TiCl}_2 s + \operatorname{HCl}$	1E+14	0.5	4900		
$\operatorname{TiCl}_4 + \operatorname{NH}_2(S) \to \operatorname{N}(B) + \operatorname{TiCl}_3(S) + \operatorname{HCl}$	1E+14	0.5	4900		
$\mathrm{NH}_3 + \mathrm{TiCl}_2 s \rightarrow \mathrm{Ti}(B) + \mathrm{NH}_2 s + \mathrm{HCl} + \mathrm{Cl}$	2.4E+11	0.5	4900		
$\mathrm{NH}_3 + \mathrm{TiCl}_3(S) \rightarrow \mathrm{Ti}(B) + \mathrm{NH}_2(S) + \mathrm{HCl} + \mathrm{Cl}_2$	2.4E+11	0.5	4900		

Supplementary results



Figure S1. Purple TiCl<sub>3</sub> films on the quartz tube.

Figure S1 shows the purple powdered films deposited on the quartz after experiments. In fact, the color of the quartz varied from light purple, dark purple to black with deposition time because the thickness increase.



Figure S2. Polycrystalline TiN with golden color on WC-Co obtained from another CVD system in our lab.

#### References for the supporting information

- 1. Teyssandier, F.; Allendorf, M.D. Thermodynamics and kinetics of gas-phase reactions in the Ti-Cl-H system. *Journal of the Electrochemical Society* **1998**, *145*, 2167-2177, doi:10.1149/1.1838613.
- 2. Coltrin, M.E.; Kee, R.J.; Rupley, F.M.; Meeks, E. *Surface chemkin*; SAND96-8217·UC-405, Sandia National Laboratories: Livermore, California, 1990.
- 3. Boichot, R.; Coudurier, N.; Mercier, F.; Claudel, A.; Baccar, N.; Milet, A.; Blanquet, E.; Pons, M. CFD modeling of the high-temperature HVPE growth of aluminum nitride layers on c-plane sapphire: from theoretical chemistry to process evaluation. *Theoretical Chemistry Accounts* **2014**, *133*, doi:10.1007/s00214-013-1419-8.

### Notations and units

- $R_{\rm S}$  : surface reaction rate (kg.m<sup>-2</sup>.s<sup>-1</sup>)
- $\underline{v}$  : velocity vector (m.s<sup>-1</sup>)
- P : pressure (Pa)
- x<sub>i</sub> : species molar fraction of species i

ω <sub>i</sub>	:	species mass fraction of species i
Т	:	temperature (K)
g	:	gravity vector (g = 9.81 m.s <sup>-2</sup> )
I	:	unity tensor
R	:	universal gas constant (8.314 J.mol <sup>-1</sup> .K <sup>-1</sup> )
М	:	molar mass of the mixture (kg.mol <sup>-1</sup> )
Ν	:	number of gaseous species in the mixture
ρ	:	density (kg.m <sup>-3</sup> )
λ	:	thermal conductivity of the gas mixture (W.m <sup>-1</sup> .K <sup>-1</sup> )
μ	:	dynamic viscosity of the gas mixture (kg.m <sup>-1</sup> .s <sup>-1</sup> )
Сp	:	specific heat of the gas mixture (J.kg <sup>-1</sup> .K <sup>-1</sup> )
<u>n</u>	:	unity vector normal
ρ	:	density (kg.m-3)
h	:	advection coefficient (W.m <sup>-2</sup> .K <sup>-1</sup> )
$T_{amb}$	:	ambient temperature (K)
$\sigma_{\text{st}}$	:	Stefan-Boltzmann constant (W.m <sup>-1</sup> .K <sup>-4</sup> )
3	:	emissivity
n	:	unity vector normal to the wall
$\mathfrak{R}_{_{gi}}$	:	reaction rate of reaction i in the gas phase (kg.m <sup>-3</sup> .s <sup>-1</sup> )
$\mathbf{J}_i^F$	:	diffusive mass flux vector (kg.m <sup>-2</sup> .s <sup>-1</sup> )
$\mathbf{J}_i^T$	:	thermo-diffusive mass flux vector (kg.m <sup>-2</sup> .s <sup>-1</sup> )
$D_{ij}$	:	multicomponent diffusion coefficients (m <sup>-2</sup> .s <sup>-1</sup> )
$D_i^T$	:	multicomponent thermodiffusion coefficients (kg. m <sup>-1</sup> .s <sup>-1</sup> )
Γ <sub>tot</sub>	:	total surface site concentration (mol m <sup>-2</sup> )
M <sub>A</sub>	:	Molar mass for gaseous specie A (kg mol <sup>-1</sup> )
E <sub>αk</sub>	:	activation energy for reaction $k$ (J mol <sup>-1</sup> )
$V_k$	:	production rate of solid surface for reaction $k \pmod{m^{-2} s^{-1}}$