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3 **Chemical vapor deposition of titanium nitride thin** 4 **films: kinetics and experiments**

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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 (H₂) as carrier gas on single crystal c-plane sapphire (Al₂O₃), 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.

24 **Keywords:** TiN; Chemical Vapor Deposition; Supersaturation; Decorative and functional coatings.
25

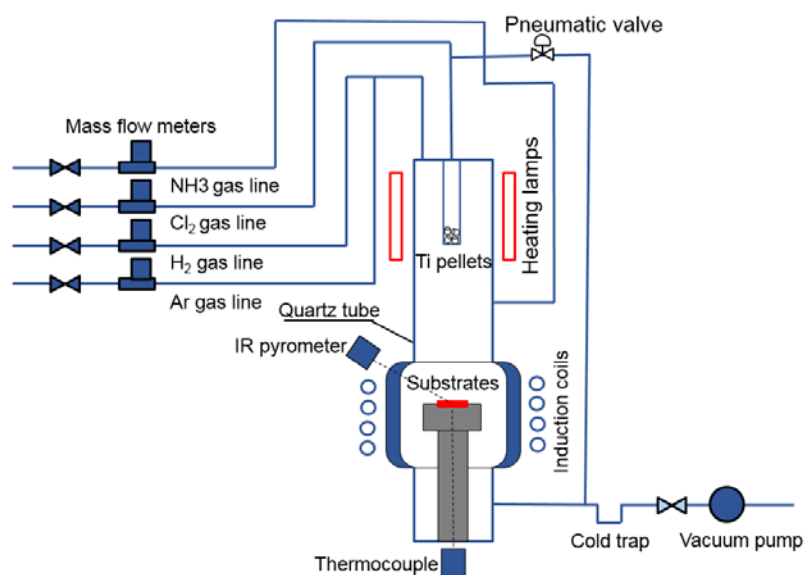
26 **1. Introduction**

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, TiCl₄-N₂-H₂ and TiCl₄-NH₃-H₂, 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 TiCl₄-N₂-H₂ system and by Jiang et al. [20] for the TiCl₄-NH₃-H₂ 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 H₂, N₂, and NH₃ partial pressures but a positive to negative
41 dependence of growth rate to increasing TiCl₄ partial pressure is observed in literature [17,21]. It
42 results from the formation of a non-reactive complex, TiCl₄NH₃ 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 $\text{TiCl}_4\text{-N}_2\text{-H}_2$ system was proposed in Ref. [17,21]. A
 46 detailed kinetic mechanism and reaction pathways were built for the $\text{TiCl}_4\text{-NH}_3\text{-H}_2$ 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_4 and
 52 TiCl_3 [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 $\text{TiCl}_x\text{-}$
 54 $\text{NH}_3\text{-H}_2$ 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 μm). Stainless steel and graphite are finished with 1- μm (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_3 (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_2 (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



77
 78 **Figure 1.** The cold wall experimental system for TiN CVD growth.

79 At the beginning of each run, 200 sccm of H₂ 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). NH₃ 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.

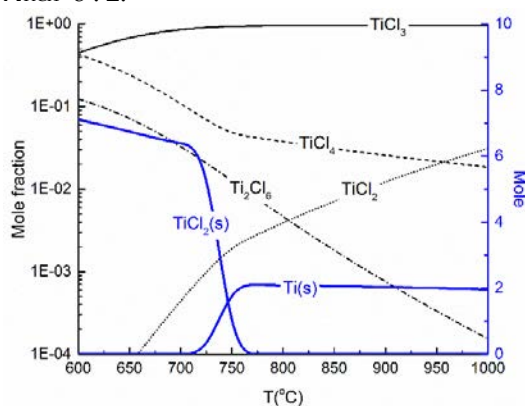
87 In the present study, $\theta/2\theta$ scans are made with a PANalytical X'Pert Pro MPD two-circle
 88 diffractometer (θ - θ , CuK α , acceleration voltage of 45 kV and current of 40 mA from a sealed x-ray
 89 tube) equipped with a 1D linear detector. Field Emission Gun-Scanning Electron Microscope (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).

95 Table 1 summarized the experiments performed for this study. Experimental as well as
 96 modeling results are summarized in this table and will be discussed in next sections. To obtain the
 97 surface activation energy, the last 5 experiments in Table 1 are designed to vary the deposition
 98 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 equilibrium and gas-phase kinetic analysis

102 For the traditional TiN coating system, TiCl₄ 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, Cl₂ gas passes over Ti pellets, solid TiCl₂ 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 TiCl₂ during chlorination process, that reacts in a second time with
 109 Cl₂. Figure 2 presents the thermodynamic equilibrium of 10 mol TiCl₂(s) and 2 mol Cl₂(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 TiCl₃(g) and TiCl₄(g) in equilibrium
 114 with solid-phase TiCl₂(s). Additionally, the deposition of a purple powdered films on the quartz tube
 115 is an indication of the presence of TiCl₃(g) (see Figure S1 in supplementary material). The mole
 116 fraction ratio is around $X_{\text{TiCl}_3} : X_{\text{TiCl}_4} = 8 : 2$.



117

118

Figure 2. Mole fraction at equilibrium of a mixture of 2 mol Cl₂ (g) and 10 mol TiCl₂ (s) at 1000 Pa.

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

Temperature °C	Pressure (Pa)	Scm NH ₃	Scm Cl ₂	N/Ti in gas phase	Measured growth rate ($\mu\text{m}\cdot\text{h}^{-1}$)	Theoretical growth rate ($\mu\text{m}\cdot\text{h}^{-1}$)	Log ₁₀ (surface supersaturation)	Main texture (T _c %) on c- plane sapphire	Main texture (T _c %) 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#
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. Continued.

Temperature °C	Pressure (Pa)	Scm NH ₃	Scm Cl ₂	N/Ti in gas phase	Measured growth rate ($\mu\text{m}\cdot\text{h}^{-1}$)	Theoretical growth rate ($\mu\text{m}\cdot\text{h}^{-1}$)	Log ₁₀ (surface supersaturation)	Main texture (T _c %) on c- plane sapphire	Main texture (T _c %) 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 [‡]
680	1000	5	5	1.5	0.4	0.6	12.16	-	200& (100%)	golden [‡]
750	1000	5	5	1.5	0.6	0.84	10.21	-	200& (69%)	brown [‡]
800	1000	5	5	1.5	0.7	1.02	8.96	-	200& (69%)	brown [‡]
1400	1000	5	5	1.5	3.8	3.1	-0.135	111 (100%)	111 [#] (62%)	Dark brown*#

122 For the traditional $\text{TiCl}_4\text{-NH}_3$ system, Umanskii et al. [27] studied the reaction pathways
 123 involving complex formation (TiCl_xNH_3). It was concluded that, in typical CVD conditions, only
 124 TiCl_4NH_3 is formed in substantial amount at low temperature. Grujicic et al. [24] took into account
 125 the presence of non-reactive complex formation. As $\text{TiCl}_4(\text{g})$ concentration is increased, it causes
 126 additional $\text{NH}_3(\text{g})$ 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 $\text{NH}_3(\text{g})$ 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 $\text{TiCl}_4(\text{g})$. 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_x ($x=1, 2, 3, 4$), 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_x can be, TiCl_x 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_2 , 8% TiCl_3 and 2%
 147 TiCl_4 since $X_{\text{TiCl}_3} : X_{\text{TiCl}_4} = 8 : 2$ from thermodynamic equilibrium in chlorination tube. It can be seen that
 148 the mole fraction of TiCl_2 is increasing and the mole fraction of TiCl_4 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_3 is however almost stable, indicating that the decomposition and formation of TiCl_3 are almost
 151 kinetically balanced. Figure 3 further illustrates that TiCl_3 and TiCl_4 only should be considered for
 152 surface reactions and TiCl_2 can be ignored, because the mole fraction of TiCl_2 is negligible in typical
 153 CVD conditions.

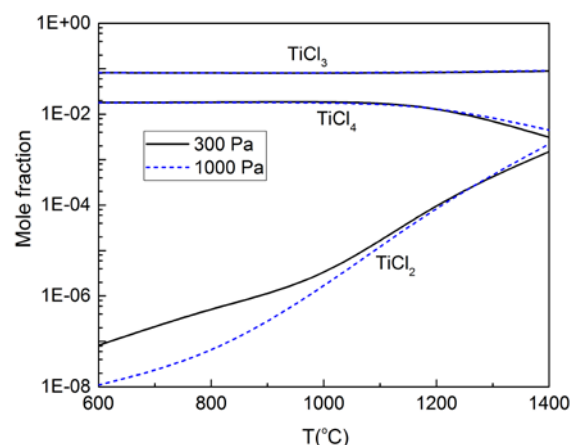
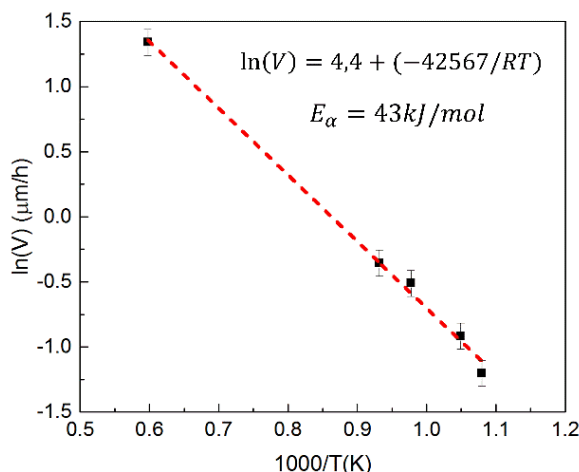


Figure 3. Mole fraction of TiCl_x at the substrate center as a function of the deposition temperature.

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

159 **4. Results and discussion**160 *4.1. Experimental growth rates versus modeling and the surface kinetic parameters*

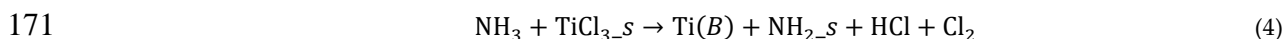
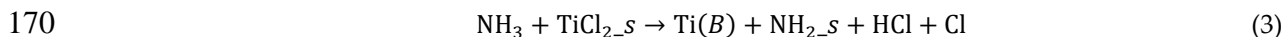
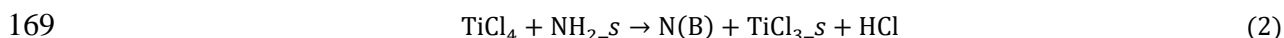
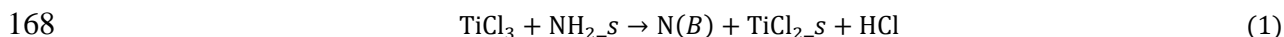
161 Arrhenius plot obtained at fixed flow rate and pressure (last five experiments in Table.1) is
 162 shown in Figure 4. It shows that the growth rate is kinetically controlled with an activation energy of
 163 43 kJ/mol.



164

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

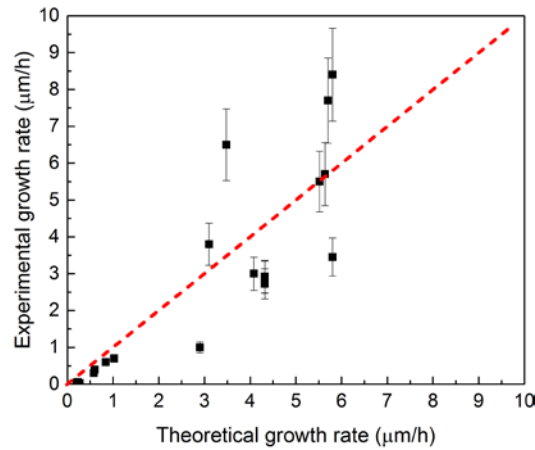
166 From the previous kinetic database[23,25], a simplified kinetic model taking into account
 167 temperature variations is assumed.



172 where three kinds of surface species on growing TiN surfaces are only considered: TiCl_{3_s} , TiCl_{2_s} and
 173 NH_{2_s} . Surface reaction rate and kinetic data can be found in supplementary materials (see Table S3
 174 in supplementary material).

175 Surface kinetic parameters have been obtained by minimizing the relative difference between
 176 experimental and simulated growth rates while maintaining kinetics from the original database [23]
 177 and varying the activation energy. It should be noted that each surface reaction conserves the total
 178 number of surface species, i.e. surface sites. In the case of the first reaction, for example, when a gas-
 179 species TiCl_3 attaches to the surface, there is one bulk phase atom added to the solid and a new surface
 180 species created. Reactions (1)-(4) are bimolecular reactions.

181 Although there are some reports of TiN deposition rates in the literature for $\text{TiCl}_4\text{-NH}_3$ system
 182 [21,23,33], the lack of detailed information makes it difficult to simulate the deposition rates
 183 published. The parity diagram between simulated and experimental growth rates from this work is
 184 presented in Figure 5. The experimental error originates from substrate temperature and thickness
 185 uncertainties.



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

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

191

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

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193

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

194

$$T_{c_hkl} = \frac{\frac{I_{hkl}}{I_{0,hkl}}}{\frac{1}{N} \cdot \sum_1^N \frac{I_{hkl}}{I_{0,hkl}}} \quad (3)$$

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in which $N=4$ is the peak amount of TiN, I_{hkl} and $I_{0,hkl}$ 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.

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

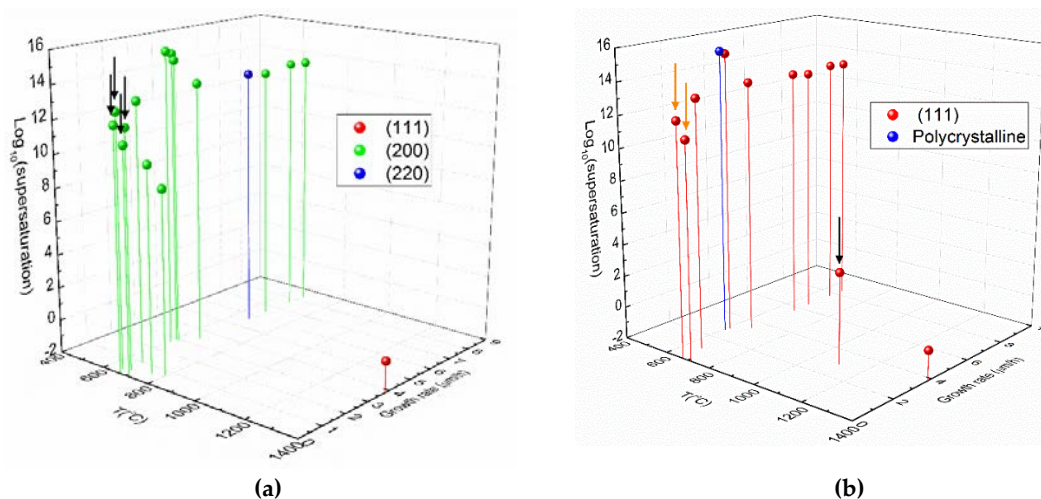


Figure 6. Relationships among preferred orientations, growth rates, supersaturation and deposition temperatures. (a) Substrates are WC-Co, stainless steel and graphite without preferred orientation. (b) Substrate is (0001) sapphire. Black arrows show TiN films with golden color and orange arrows show 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 $0.4 \mu\text{m/h}$). On (0001)
 219 sapphire, silver and golden TiN films prefer low growth rate (less than $3 \mu\text{m/h}$). 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 $2 \mu\text{m/h}$.
 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 $8 \mu\text{m/h}$ 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 $0.4 \mu\text{m/h}$. 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 $0.1 \mu\text{m/h}$, 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 $3 \mu\text{m/h}$, TiN film with shining golden color is obtained once. The brown TiN films are
 238 obtained when the growth rate is above $3 \mu\text{m/h}$ or N/Ti ratio is above 2. In conclusion, golden TiN
 239 films on non-orientated substrates are determined by a low growth rate ($\leq 0.4 \mu\text{m/h}$) while on
 240 sapphire film should be thick enough ($\approx 3 \mu\text{m}$) and not columnar (dense).

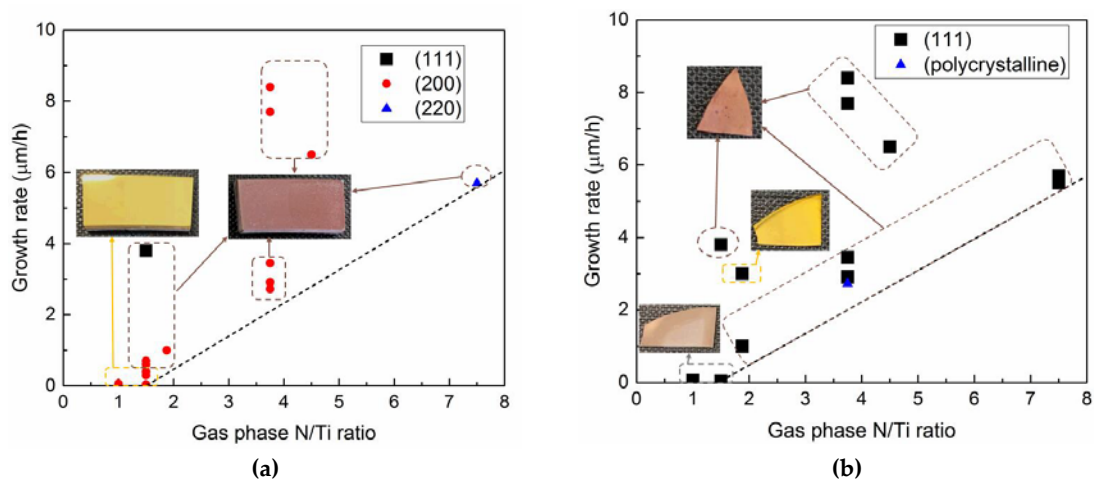


Figure 7. TiN growth rate versus N/Ti ratio on (a) non-orientated substrates and (b) (0001) sapphire. The figure also indicates the preferred orientation and color of TiN.

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 seen that thin and dense TiN layers present golden color while TiN films with thick columnar
 244 structure present brown color.

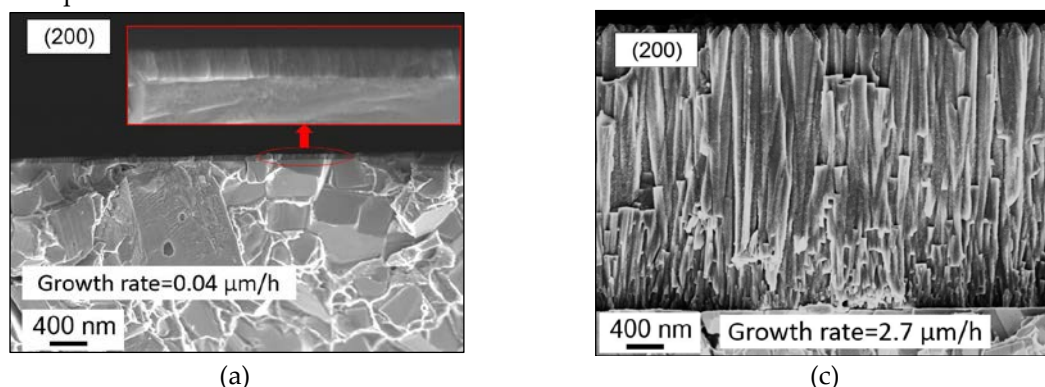
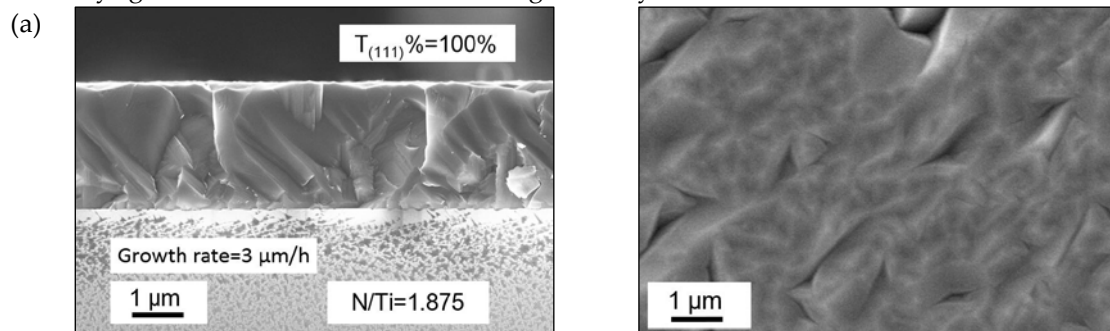


Figure 8. Cross-sectional morphology of (a) golden TiN on WC-Co (b) brown TiN on WC-Co. The figure also indicates preferred crystallographic direction and growth rate.

245 Three cross-sectional and surface morphology of TiN films: (a) golden, growth rate at 3 $\mu\text{m/h}$,
 246 N/Ti=1.875, (b) brown, growth rate at 3 $\mu\text{m/h}$, N/Ti=3.75 and (c) brown, growth rate at 5.7 $\mu\text{m/h}$,
 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.



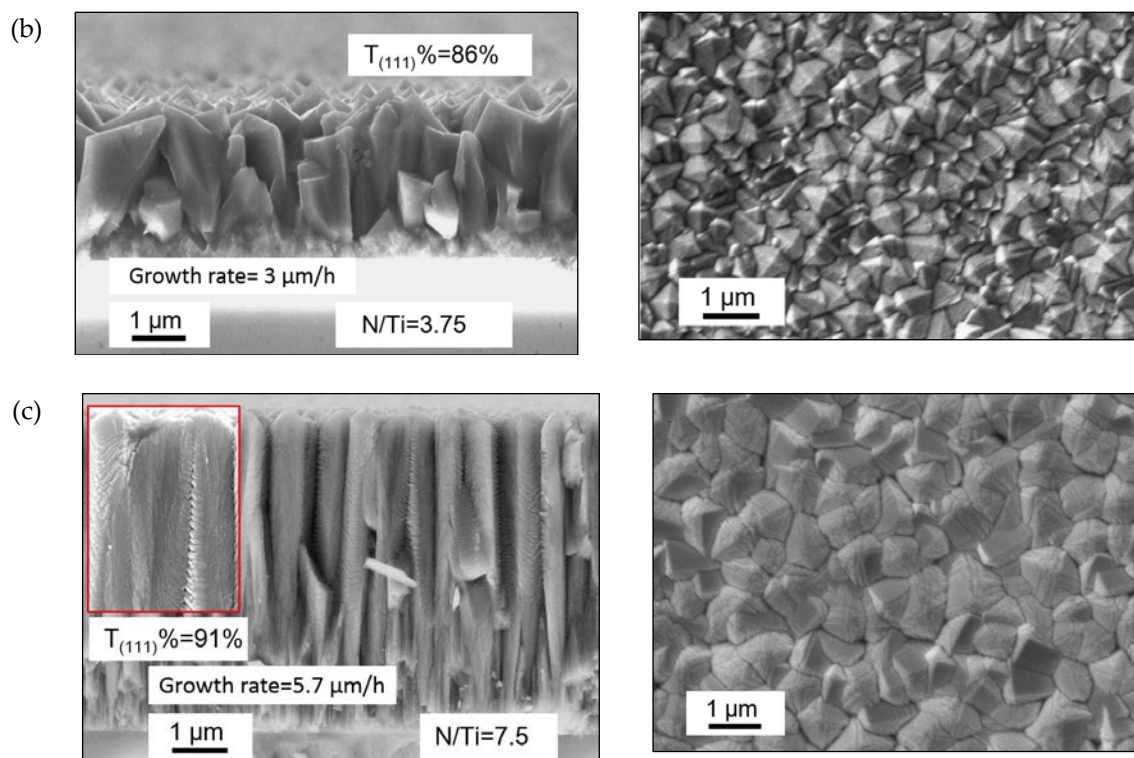


Figure 9. Cross-sectional and surface morphology for TiN layers with (a) golden (b) brown (c) brown color on sapphire. The figure also indicates preferred crystallographic orientation, growth rate and N/Ti ratio.

253 5. Conclusions

254 A simplified kinetic model associated with heat and mass transport for TiN film growth was
 255 proposed. TiCl_3 and TiCl_4 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/Ti gas-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.

265 Golden TiN films were obtained when the growth rate is lower than $0.4 \mu\text{m/h}$. Otherwise, TiN
 266 films are brown because of columnar structure. On (0001) sapphire single crystals, TiN films should
 267 be thick ($\approx 3 \mu\text{m}$) and dense enough to obtain a golden color. The main characteristic of golden TiN
 268 films is found to be a dense structure, whatever the process parameters used to get this property.

269 **Supplementary Materials:** Table S1: Governing equations of multicomponent mass and heat transfer. Table S2:
 270 The gas phase reactions and rate constant for reaction K is represented in the standard Arrhenius form. Table
 271 S3: Surface reactions and correspond kinetic parameters used in the simplified model. Figure S1: Purple TiCl_3
 272 films on the quartz tube. Figure S2: The surface morphology of polycrystalline TiN with golden color on WC-
 273 Co.

274 **Author Contributions:** Conceptualization, Michel Pons, Frederic Mercier and Raphaël Boichot; Experiments,
 275 Juan Su; Simulation, Juan Su, Michel Pons, Elisabeth Blanquet and Raphaël Boichot. Writing-Original Draft
 276 Preparation, Juan Su.; Writing-Review & Editing, Michel Pons, Frederic Mercier, Elisabeth Blanquet and
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Supplementary materials

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

Juan Su ¹, Raphaël Boichot ^{1,*}, Elisabeth Blanquet ¹, Frédéric Mercier ¹, and Michel Pons ¹

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 H₂ (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)	$\nabla \cdot (\rho \vec{v} \vec{v}) = \nabla \cdot \underline{\underline{\tau}} - P + \rho \vec{g}$ $\underline{\underline{\tau}} = \mu (\nabla \vec{v} + (\nabla \vec{v})^t) - \frac{2}{3} \mu (\nabla \cdot \vec{v}) \cdot \underline{\underline{I}}$
Energy balance (2)	$c_p \nabla \cdot (\rho \vec{v} T) = \nabla \cdot (\lambda \nabla T) + \nabla \cdot \left(RT \sum_{i=1}^N \frac{D_i^T}{M_i} \frac{\nabla x_i}{x_i} \right)$ $+ \sum_{i=1}^N \frac{H_i}{M_i} \nabla \cdot \vec{J}_i - \sum_{i=1}^N \sum_{k=1}^K H_i \nu_{ik} (\mathcal{R}_k^g - \mathcal{R}_{-k}^g)$
Species transport (3)	$\nabla \cdot (\rho \vec{v} \omega_i) = -\nabla \cdot \vec{J}_i + M_i \sum_{k=1}^K \nu_{ik} (\mathcal{R}_k^g - \mathcal{R}_{-k}^g) \quad i = 1, N$ $\vec{J}_i^c = -\sum_{j=1}^N (\rho D_{ij}) \nabla x_j \quad i = 1, N$ $\vec{J}_i^T = -D_i^T \frac{\nabla T}{T} \quad i = 1, N$
Ideal gas law (4)	$\rho = \frac{PM}{RT}$
Deposition rate (5)	$R_s = \vec{J}_i \cdot \vec{n} = \vec{J}_i^c \cdot \vec{n} + \vec{J}_i^T \cdot \vec{n} \quad i = 1, N$

Gas-phase kinetics pathways

From thermodynamic equilibrium calculation in chlorination tube, both TiCl₄ and TiCl₃ 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:

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

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 α_k are s^{-1} ; for bimolecular reactions, the units are $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$. All energies are in kJ mol^{-1} .

Reaction K	α_k	β_k	$E_{\alpha k}$
K1: $\text{TiCl}_4 \leftrightarrow \text{TiCl}_3 + \text{Cl}$	2.32 E+20	-1.17	387.9
K2: $\text{TiCl}_3 \leftrightarrow \text{TiCl}_2 + \text{Cl}$	1.02E+18	-0.742	422.6
K3: $\text{TiCl}_2 \leftrightarrow \text{TiCl} + \text{Cl}$	3.65E+20	-1.06	509.6
K4: $\text{TiCl}_4 + \text{H} \leftrightarrow \text{TiCl}_3 + \text{HCl}$	5.11E+06	2.5	12.6
K5: $\text{TiCl}_3 + \text{H} \leftrightarrow \text{TiCl}_2 + \text{HCl}$	1.11E+06	2.5	33.5
K6: $\text{TiCl}_2 + \text{H} \leftrightarrow \text{TiCl} + \text{HCl}$	3.05E+06	2.5	145.2
K7: $\text{TiCl} + \text{H} \leftrightarrow \text{Ti} + \text{HCl}$	4.09E+05	2.5	24.7
K8: $\text{H} + \text{Cl} + \text{M} \rightarrow \text{HCl} + \text{M}$	7.20E+21	-2.0	0.0
K9: $\text{HCl} + \text{M} \rightarrow \text{HCl} + \text{M}$	7.90E+25	-3.0	445.6
K10: $\text{Cl} + \text{Cl} + \text{M} \leftrightarrow \text{Cl}_2 + \text{M}$	2.00E+14	0.0	-7.5
K11: $\text{H} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2$	1.69E+13	0.0	17.2
K12: $\text{Cl} + \text{H}_2 \rightarrow \text{H} + \text{HCl}$	2.95E+13	0.0	21.3
K13: $\text{Cl}_2 + \text{H} \leftrightarrow \text{Cl} + \text{HCl}$	8.60E+13	0.0	5.0
K14: $\text{H} + \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2$	9.70E+16	-0.6	0.0
K15: $\text{H}_2 + \text{H}_2 \rightarrow \text{H} + \text{H} + \text{M}$	8.80E+14	0.0	402.1
K16: $\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$	2.20E+14	0.0	402.1
K 17: $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	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]:

$$V_k = k_k[A] \times [C(S)] \quad (S2)$$

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

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

In which,

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

$$\beta_k = 0.5 \quad (S5)$$

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]:

$$\beta = \frac{P_{TiCl_3} + P_{TiCl_4} + P_{NH_3}}{P_{Ti}^* + 2P_{N_2}^*} \quad (S6)$$

where P and P^* are calculated pressure of species ($TiCl_3$, $TiCl_4$, and NH_3) 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 1.8×10^{-9} mol cm^{-2} .

Heterogeneous reaction unit CGS (cm-g-s)			
Surface reactions	α_k Pre exp. factor	β_k Temp. exp.	E_{ak}/R Activ. temp. (K)
$TiCl_3 + NH_{2_s} \leftrightarrow N(B) + TiCl_{2_s} + HCl$	1E+14	0.5	4900
$TiCl_4 + NH_2(S) \rightarrow N(B) + TiCl_3(S) + HCl$	1E+14	0.5	4900
$NH_3 + TiCl_{2_s} \rightarrow Ti(B) + NH_{2_s} + HCl + Cl$	2.4E+11	0.5	4900
$NH_3 + TiCl_3(S) \rightarrow Ti(B) + NH_2(S) + HCl + Cl_2$	2.4E+11	0.5	4900

Supplementary results

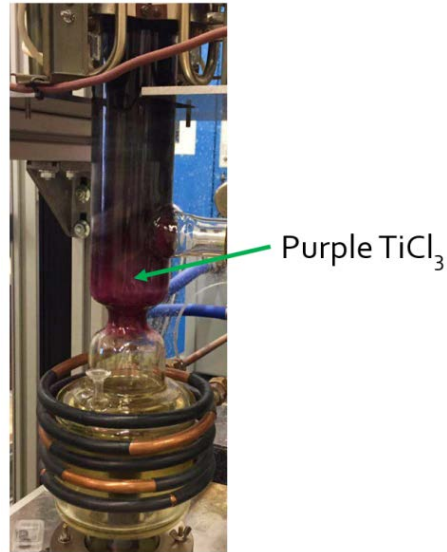


Figure S1. Purple TiCl_3 films on the quartz tube.

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.

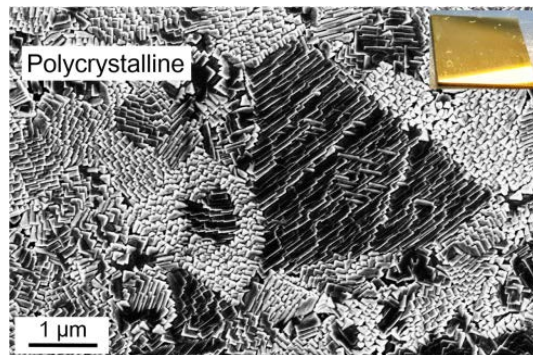


Figure S2. Polycrystalline TiN with golden color on WC-Co obtained from another CVD system in our lab.

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Notations and units

R_S	:	surface reaction rate ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
\underline{v}	:	velocity vector ($\text{m}\cdot\text{s}^{-1}$)
P	:	pressure (Pa)
x_i	:	species molar fraction of species i

ω_i	:	species mass fraction of species i
T	:	temperature (K)
\mathbf{g}	:	gravity vector ($g = 9.81 \text{ m}\cdot\text{s}^{-2}$)
\mathbf{I}	:	unity tensor
R	:	universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
M	:	molar mass of the mixture ($\text{kg}\cdot\text{mol}^{-1}$)
N	:	number of gaseous species in the mixture
ρ	:	density ($\text{kg}\cdot\text{m}^{-3}$)
λ	:	thermal conductivity of the gas mixture ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
μ	:	dynamic viscosity of the gas mixture ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$)
C_p	:	specific heat of the gas mixture ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$)
$\underline{\mathbf{n}}$:	unity vector normal
ρ	:	density ($\text{kg}\cdot\text{m}^{-3}$)
h	:	advection coefficient ($\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$)
T_{amb}	:	ambient temperature (K)
σ_{st}	:	Stefan-Boltzmann constant ($\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$)
ε	:	emissivity
\mathbf{n}	:	unity vector normal to the wall
\mathfrak{R}_{gi}	:	reaction rate of reaction i in the gas phase ($\text{kg}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$)
\mathbf{J}_i^F	:	diffusive mass flux vector ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
\mathbf{J}_i^T	:	thermo-diffusive mass flux vector ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
D_{ij}	:	multicomponent diffusion coefficients ($\text{m}^2\cdot\text{s}^{-1}$)
D_i^T	:	multicomponent thermodiffusion coefficients ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$)
Γ_{tot}	:	total surface site concentration ($\text{mol}\cdot\text{m}^{-2}$)
M_A	:	Molar mass for gaseous specie A ($\text{kg}\cdot\text{mol}^{-1}$)
E_{ak}	:	activation energy for reaction k ($\text{J}\cdot\text{mol}^{-1}$)
V_k	:	production rate of solid surface for reaction k ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)