

## Supplementary materials

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

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

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

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

Reaction K	$\alpha_k$	$\beta_k$	$E_{\alpha k}$
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:

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

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]:

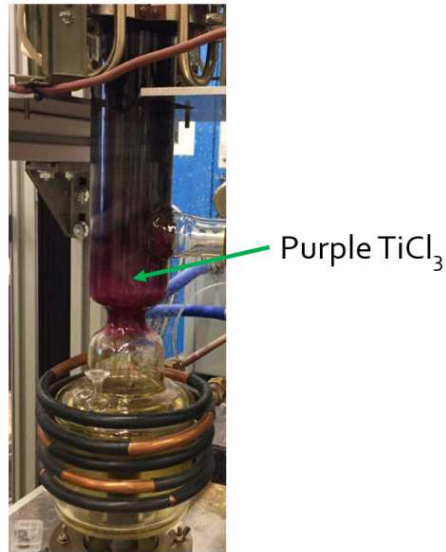
$$\beta = \frac{P_{TiCl_3} + P_{TiCl_4} + P_{NH_3}}{P_{Ti}^* + 2P_{N_2}^*} \quad (S6)$$

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  $1.8 \times 10^{-9}$  mol  $cm^{-2}$ .

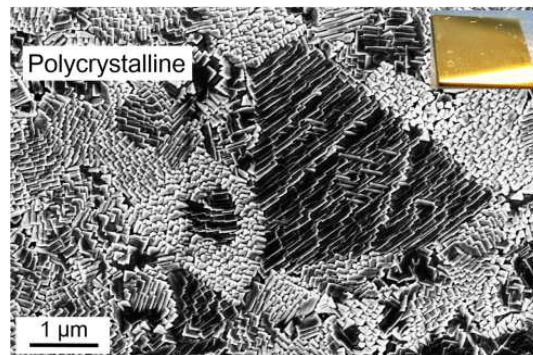
<b>Heterogeneous reaction unit CGS (cm-g-s)</b>			
<b>Surface reactions</b>	<b><math>\alpha_k</math> Pre exp. factor</b>	<b><math>\beta_k</math> Temp. exp.</b>	<b><math>E_{\alpha k}/R</math> Activ. temp. (K)</b>
$TiCl_3 + NH_{2_s} \leftrightarrow N(B) + TiCl_{2_s} + HCl$	1E+14	0.5	4900
$TiCl_4 + NH_2(S) \rightarrow N(B) + TiCl_3(S) + HCl$	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  $\text{TiCl}_3$  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.

## 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

- $R_S$  : 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

$\omega_i$	:	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
$\rho$	:	density ( $\text{kg}\cdot\text{m}^{-3}$ )
$\lambda$	:	thermal conductivity of the gas mixture ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )
$\mu$	:	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
$\rho$	:	density ( $\text{kg}\cdot\text{m}^{-3}$ )
$h$	:	advection coefficient ( $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ )
$T_{\text{amb}}$	:	ambient temperature (K)
$\sigma_{\text{st}}$	:	Stefan-Boltzmann constant ( $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$ )
$\varepsilon$	:	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 ( $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ )
$\Gamma_{\text{tot}}$	:	total surface site concentration ( $\text{mol}\cdot\text{m}^{-2}$ )
$M_A$	:	Molar mass for gaseous specie $A$ ( $\text{kg}\cdot\text{mol}^{-1}$ )
$E_{\alpha k}$	:	activation energy for reaction $k$ ( $\text{J}\cdot\text{mol}^{-1}$ )
$V_k$	:	production rate of solid surface for reaction $k$ ( $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ )