This presentation is based on the following paper:
Moritz to Baben, Marcus Hans, Daniel Primetzhofer, Simon Evertz, Holger Ruess & Jochen M. Schneider (2016): *Unprecedented thermal stability of inherently metastable titanium aluminum nitride by point defect engineering*, Materials Research Letters, http://dx.doi.org/10.1080/21663831.2016.1233914

Thermodynamic Modelling of Physical Vapor Deposition (PVD)

M. to Baben[1,2], M. Hans[2], D. Primetzhofer[3], J.M. Schneider[2], K. Hack[1]

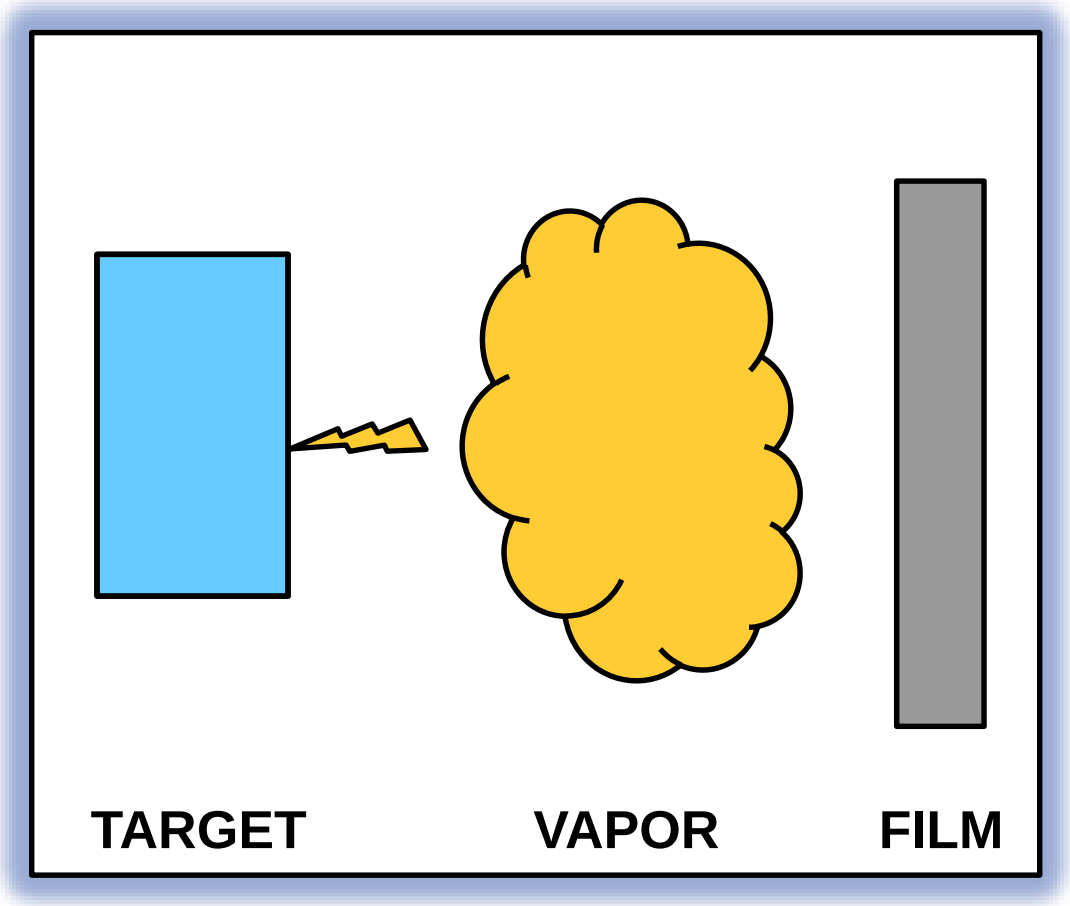
1: GTT-Technologies
2: Materials Chemistry, RWTH Aachen University
3: Applied Nuclear Physics, Uppsala University

GTT User Meeting, 29.6.2016

CONTENT

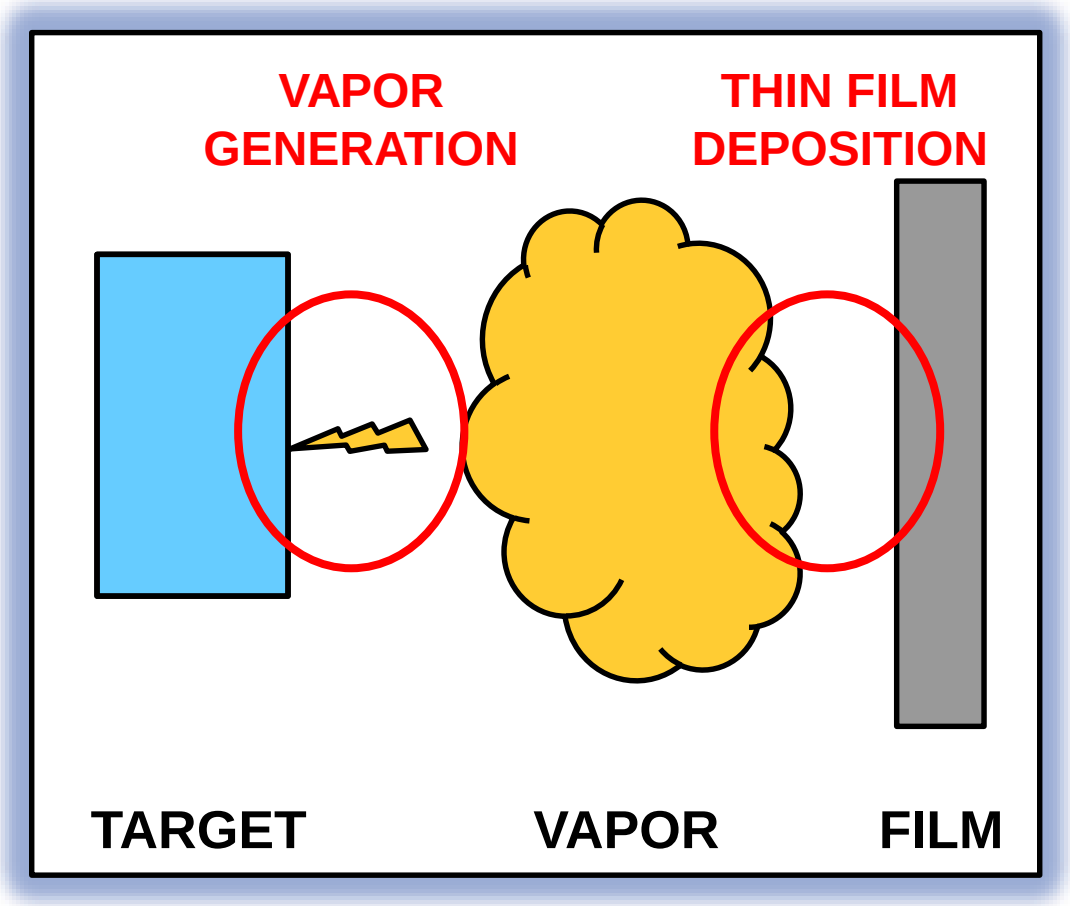
- BACKGROUND
- VAPOR GENERATION
- THIN FILM DEPOSITION
- APPLICATION

BACKGROUND: Physical Vapor Deposition



- Thermal evaporation
- Electron beam evaporation
- Cathodic arc evaporation
- Pulsed laser depositon
- Sputtering

BACKGROUND: Physical Vapor Deposition



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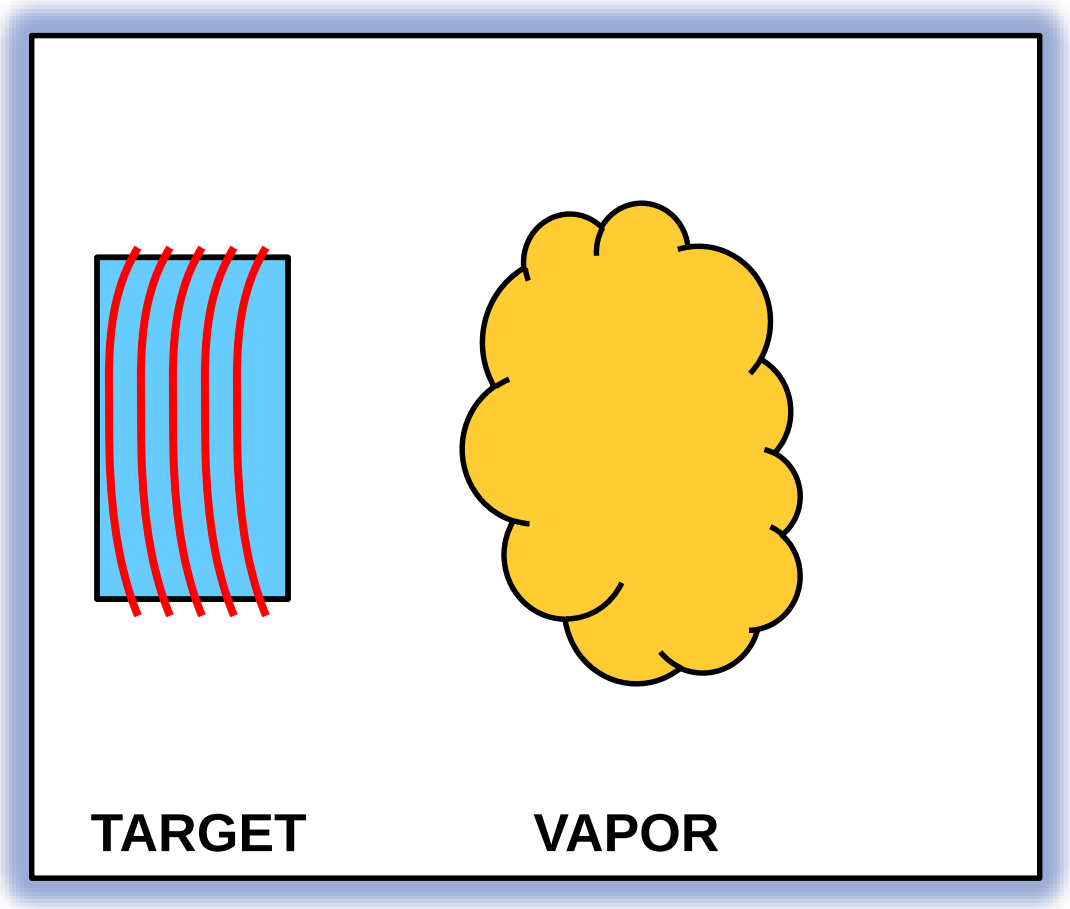
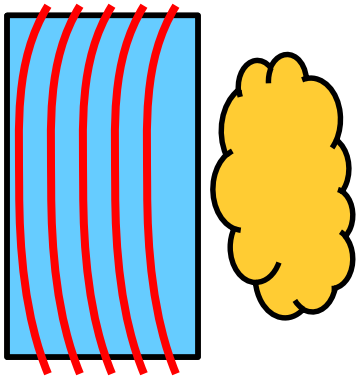
BACKGROUND: Physical Vapor Deposition



- Thermal evaporation

VAPOR GENERATION: Composition of vapor

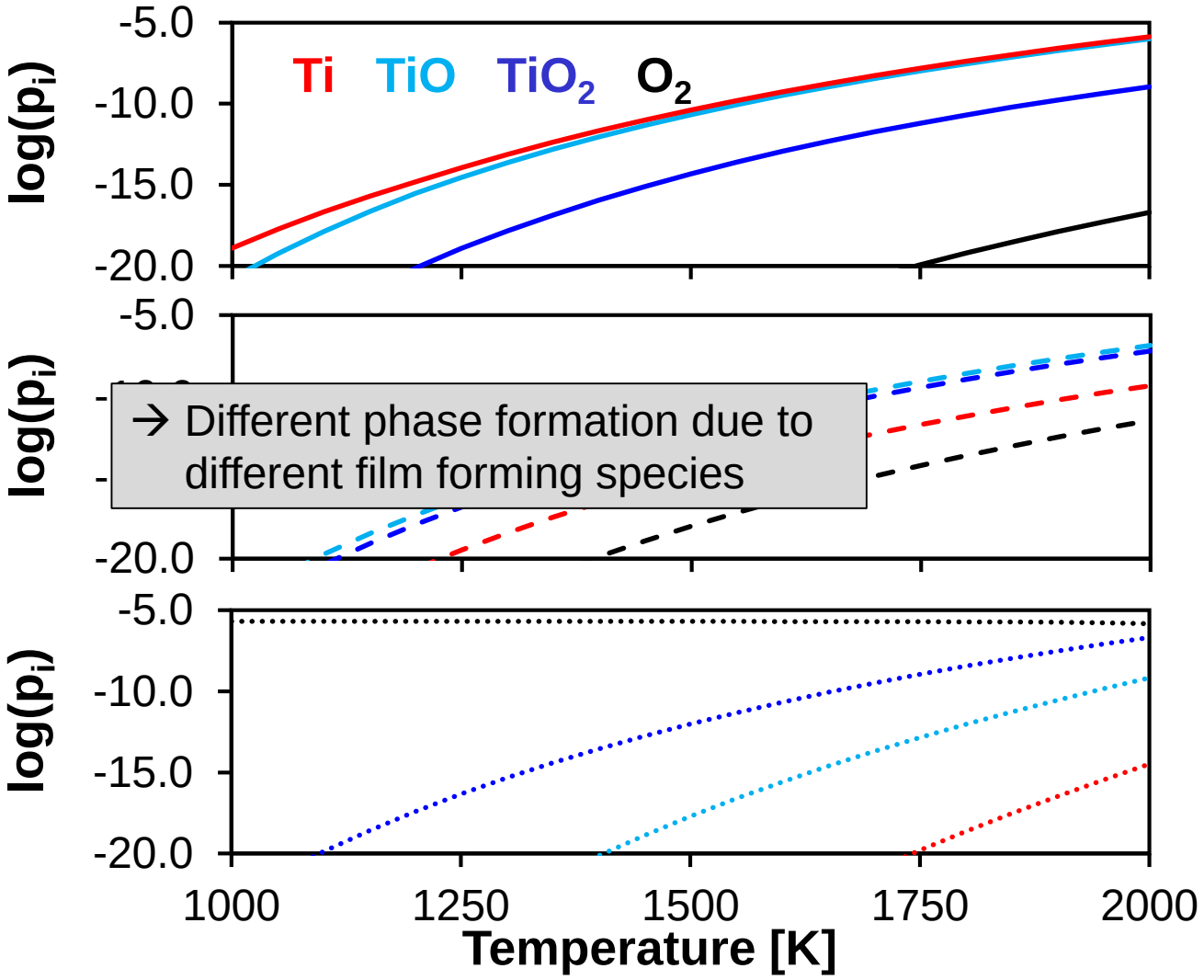
Thermal evaporation



Ti-TiO

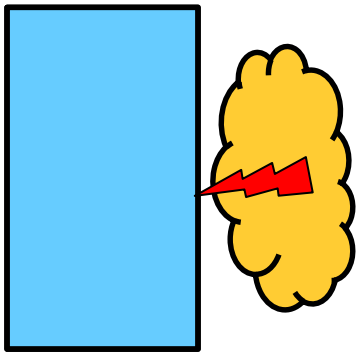
TiO-TiO_2

TiO_2-O_2

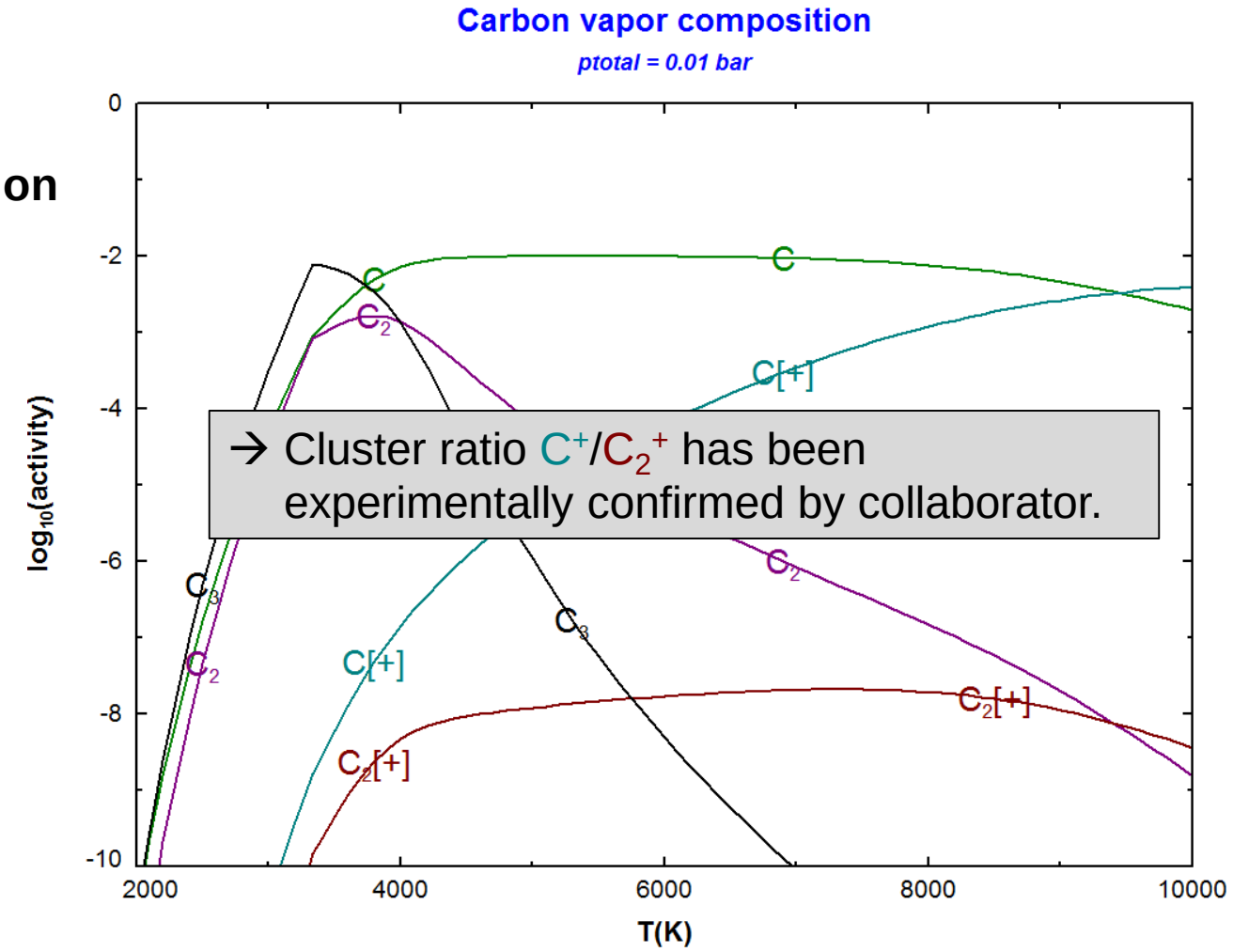


VAPOR GENERATION: Composition of vapor

Cathodic arc evaporation

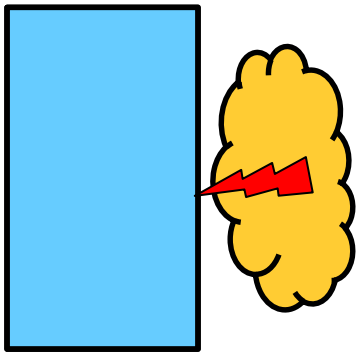


Carbon→DLC

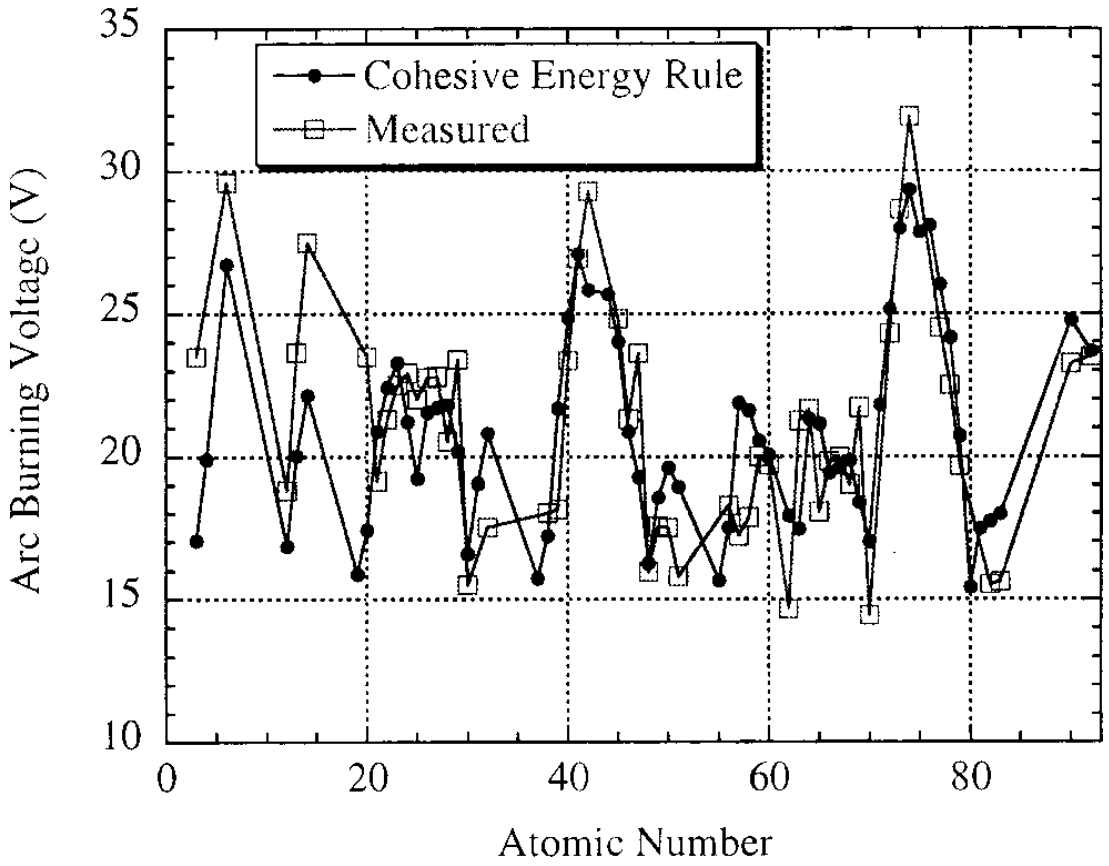


VAPOR GENERATION: Cohesive energy rule

Cathodic arc evaporation



Carbon→DLC

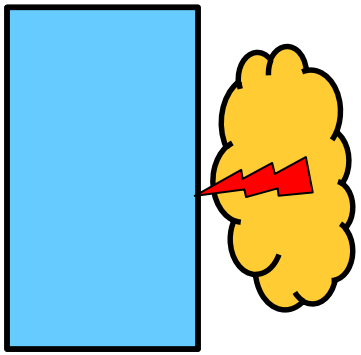


Cohesive energy (CE) rule for the burning voltage V: $V = V_0 + A^*E_{CE}$ [1].

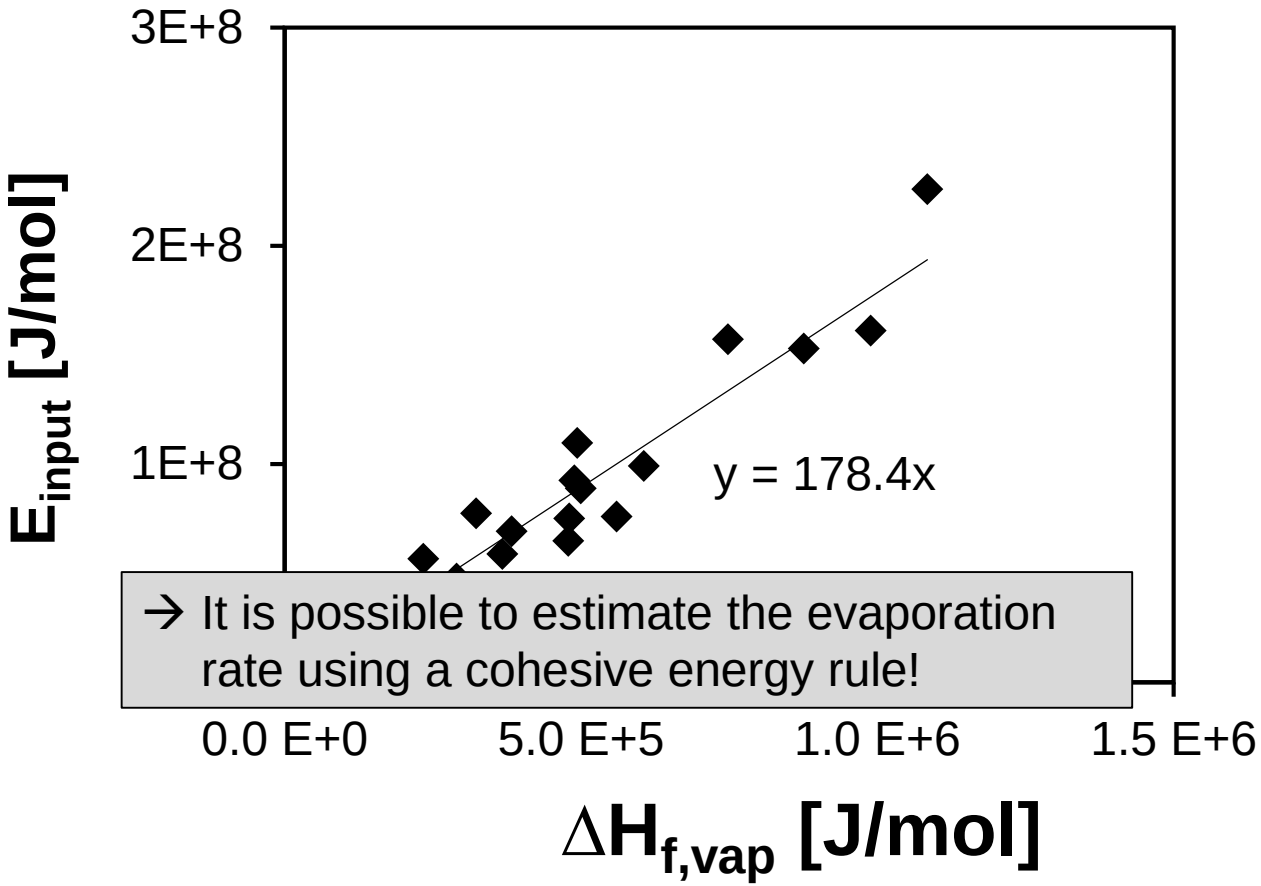
[1] Anders et al., JAP 89 (2001) 7764.

VAPOR GENERATION: Cohesive energy rule

Cathodic arc evaporation



Carbon→DLC



Cohesive energy (CE) rule for the power input: $E_{input} = 178 * \Delta H_{f,vap}$. Experimental data from [2].

[2] Anders et al., Proc. ISDEIV (2004) 272.

CONTENT

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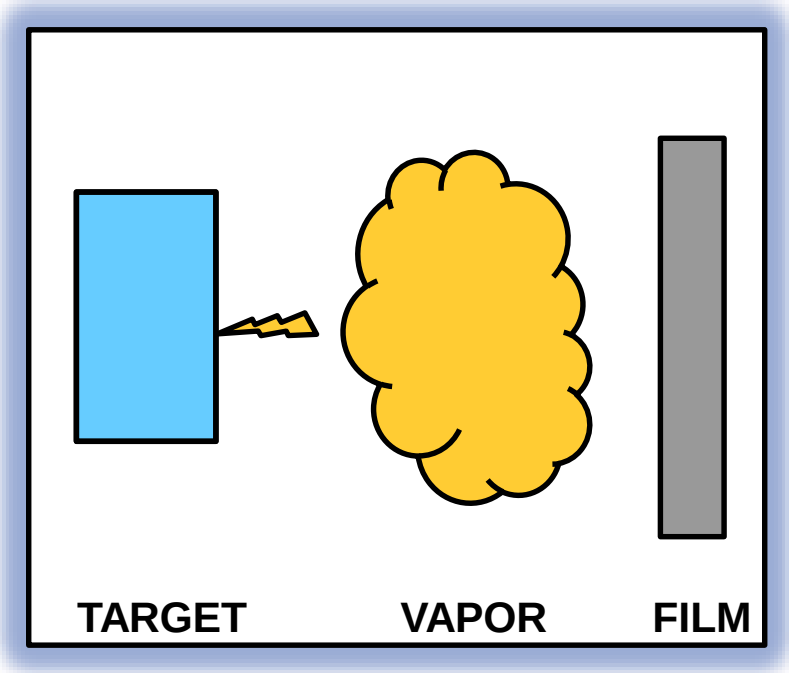
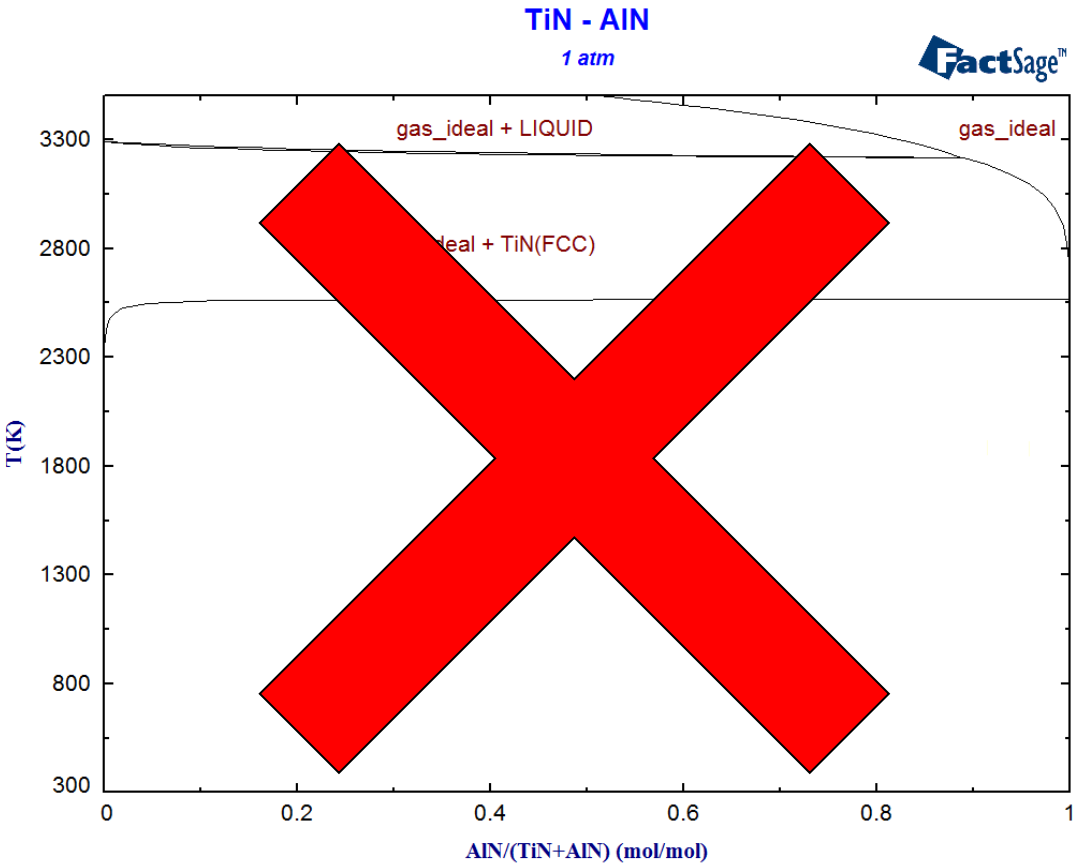
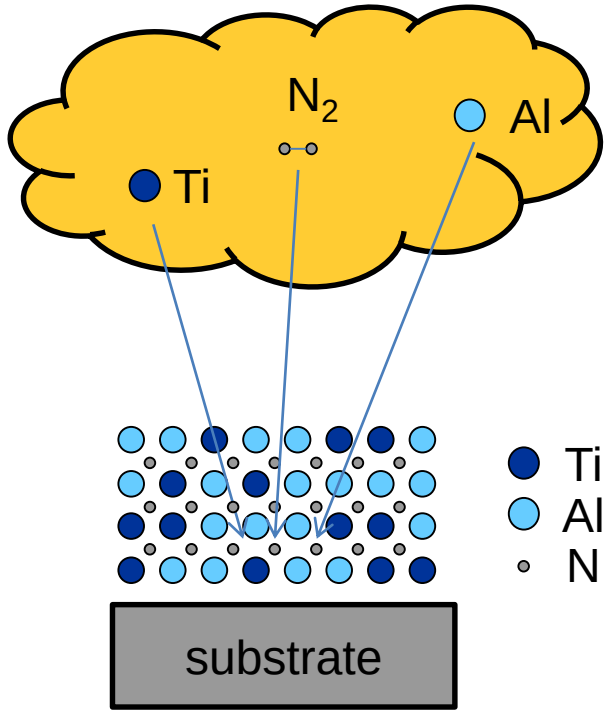
- **THIN FILM DEPOSITION**
- APPLICATION



THIN FILM DEPOSITION: Theory Example: (Ti,Al)N



Cooling rate ~10^{15} K/s!!!



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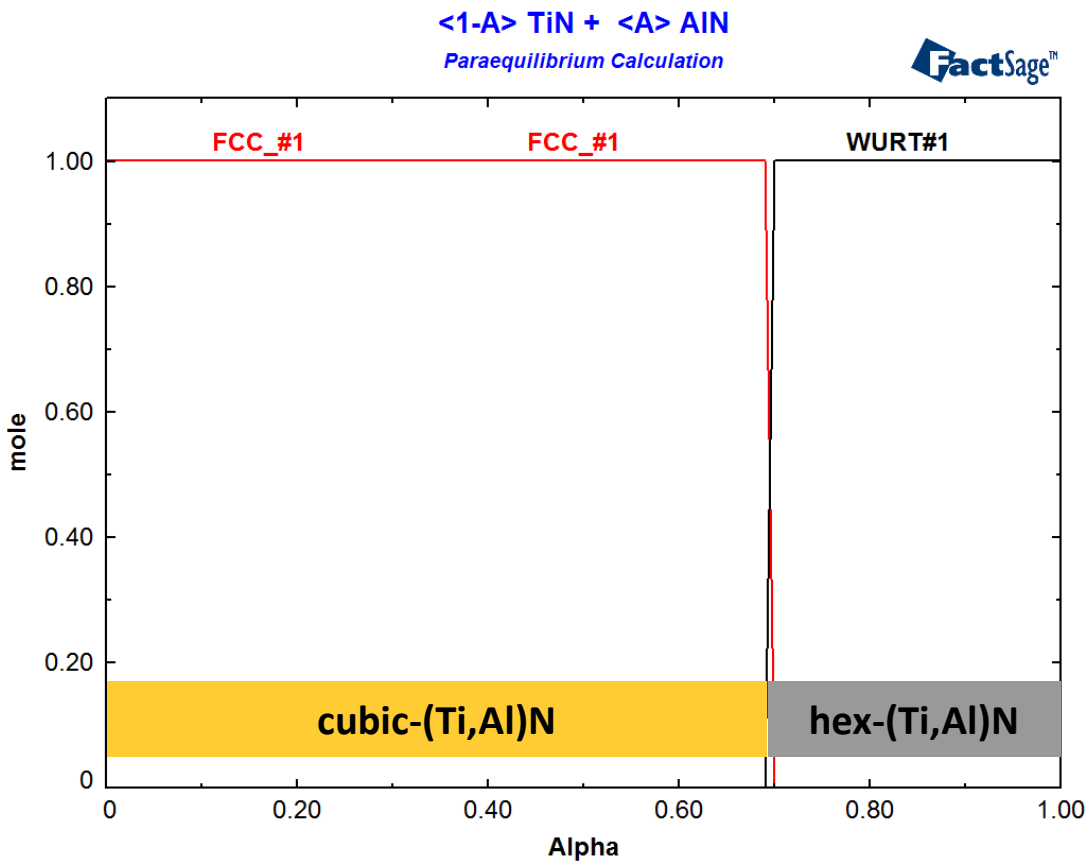
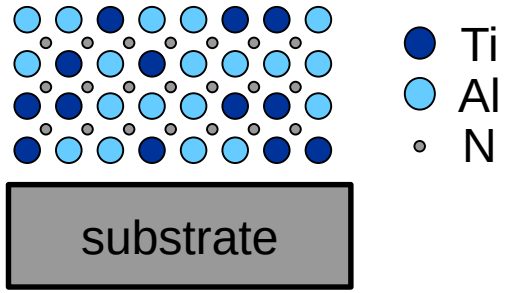
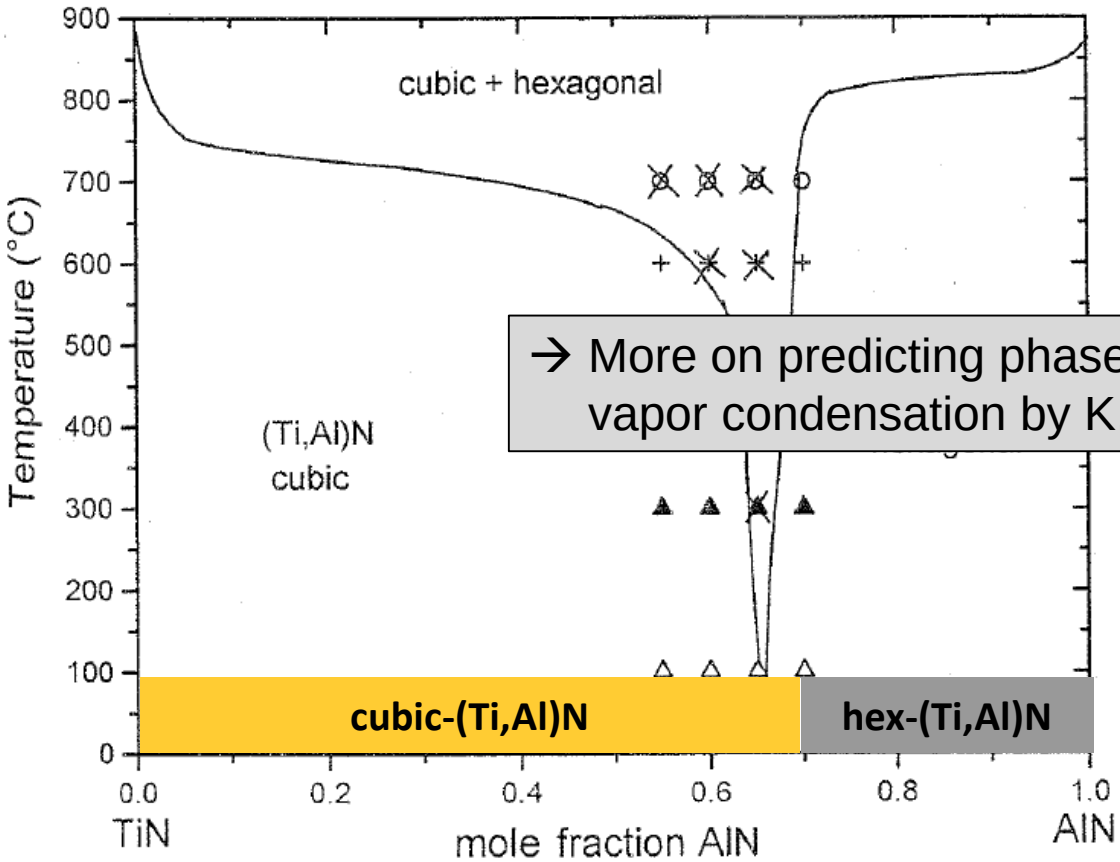


Cooling rate ~10^{15} K/s!!!

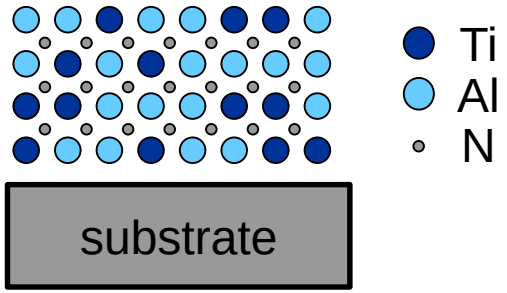


THIN FILM DEPOSITION: Theory Example: (Ti,Al)N



Cooling rate ~10^{15} K/s!!!

→ More on predicting phase formation during vapor condensation by K. Chang!



Experimental TiN-AlN phase formation diagram [3].

[3]: Spencer, Z. Metallk. 92 (2001) 10.

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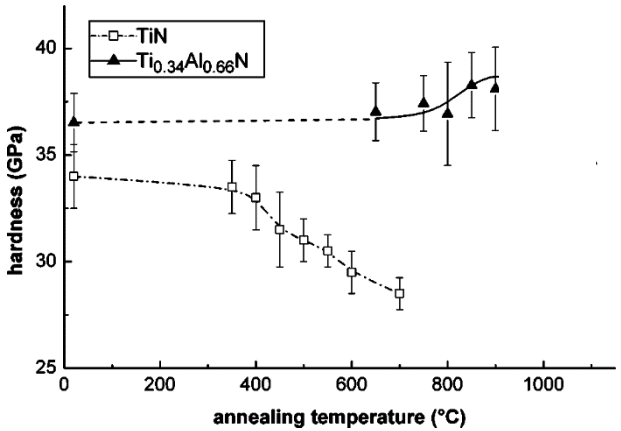
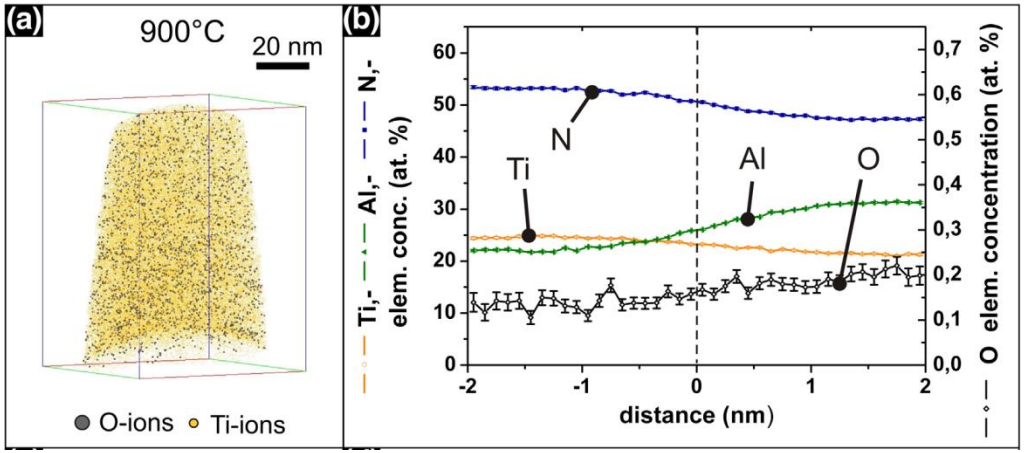
APPLICATION

Example: $(Ti,Al)N_x$



Mayrhofer et al., APL 83 (2003) 2049.



c-TiAlN
~800°C → c-TiN + c-AlN
~1000°C → c-TiN + w-AlN

Rachbauer et al., Surface & Coatings Technology 204 (2010) 1811.

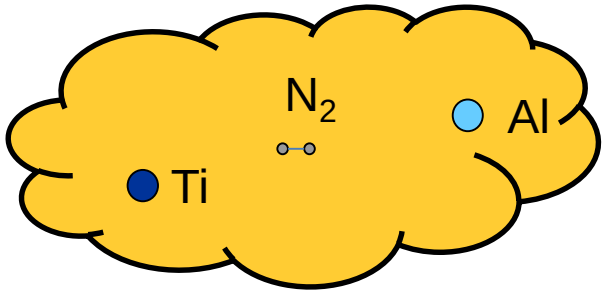
APPLICATION Stoichiometry prediction?

flux(reactive gas) >> flux(metals)

Example (Ti,Al)N:

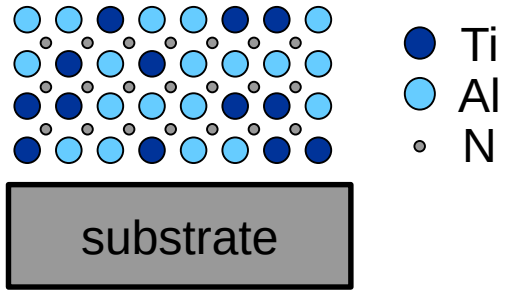
flux(N_2) = $3*10^{17}$ molecules/s*cm²

flux(Ti+Al) = $4*10^{15}$ atoms/s*cm²



Equilibrium:

? $Ti_{0.5}Al_{0.5} + \frac{x}{2}N_2 \leftrightarrow Ti_{0.5}Al_{0.5}N_x$?



APPLICATION Modelling FCC-(Ti,Al,Va)(N,Va)

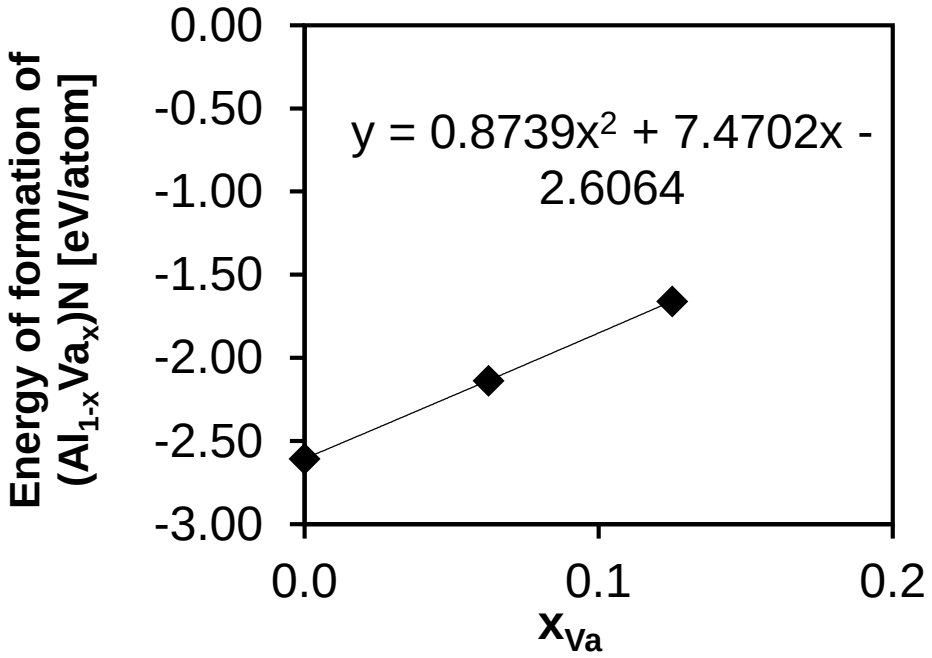
Thermodynamic Property	How modelled?
G(Ti : Va)	SGTE Solutions Database
G(Ti : N)	SGTE Solutions Database
G(Al : Va)	SGTE Solutions Database
L(Al,Ti : Va;0)	SGTE Solutions Database
L(Al,Ti : Va;1)	SGTE Solutions Database
L(Al,Ti : Va;2)	SGTE Solutions Database
L(Ti : N,Va;0)	SGTE Solutions Database
L(Ti : N,Va;1)	SGTE Solutions Database

Thermodynamic Property	How modelled?
G(Al : N)	*ab intitio*
G(Va : N)	*ab intitio*
G(Va : Va)	*ab intitio*
L(Ti,Al : N;0)	*ab intitio*
L(Ti,Va : N;0)	*ab intitio*
L(Al,Va : N;0)	*ab intitio*
L(Ti,Al,Va : N;0)	*ab intitio*
L(Ti,Al : N,Va;0)	*ab intitio*
L(Al : N,Va;0)	*ab intitio*
L(Al : N,Va;1)	*ab intitio*

APPLICATION Modelling FCC-(Ti,Al,Va)(N,Va)

- *16 ab initio* calculations using VASP (Vienna ab initio simulation) package
- 64 atom unit cell
- Energy of formation as f(composition)

→ ΔH^{298K}, *L*



Thermodynamic Property	How modelled?
G(Al : N)	ΔH^{298K} = -2.61 eV/atom
G(Va : N)	
G(Va : Va)	*ab intitio*
L(Ti,Al : N;0)	*ab intitio*
L(Ti,Va : N;0)	*ab intitio*
L(Al,Va : N;0)	ΔH^{298K} = -0.874 eV/atom
L(Ti,Al,Va : N;0)	*ab intitio*
L(Ti,Al : N,Va;0)	*ab intitio*
L(Al : N,Va;0)	*ab intitio*
L(Al : N,Va;1)	*ab intitio*

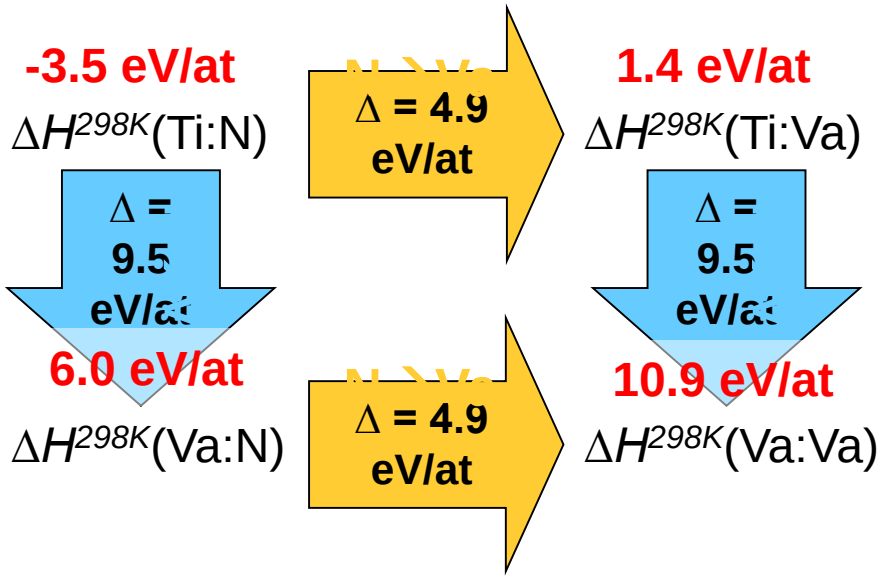
APPLICATION Modelling FCC-(Ti,Al,Va)(N,Va)

Extrapolated from $(Al_{1-x}Va_x)N$
→ ΔH^{298K}(Va:N) = 5.74 eV/atom
Extrapolated from $(Ti_{1-x}Va_x)N$
→ ΔH^{298K}(Va:N) = 6.23 eV/atom

Thermodynamic Property	**How modelled?**
G(Al : N)	ΔH^{298K} = -2.61 eV/atom
G(Va : N)	ΔH^{298K} = 5.98 eV/atom
G(Va : Va)	*ab intitio*
L(Ti,Al : N;0)	*ab intitio*
L(Ti,Va : N;0)	*ab intitio*
L(Al,Va : N;0)	ΔH^{298K} = -0.874 eV/atom
L(Ti,Al,Va : N;0)	*ab intitio*
L(Ti,Al : N,Va;0)	*ab intitio*
L(Al : N,Va;0)	*ab intitio*
L(Al : N,Va;1)	*ab intitio*

APPLICATION Modelling FCC-(Ti,Al,Va)(N,Va)

ΔH^{298K}(Va:Va) from "alchemical" interpretation of Hess's law:



Thermodynamic Property	How modelled?
G(Al : N)	ΔH^{298K} = -2.61 eV/atom
G(Va : N)	ΔH^{298K} = 5.98 eV/atom
G(Va : Va)	
L(Ti,Al : N;0)	*ab intitio*
L(Ti,Va : N;0)	*ab intitio*
L(Al,Va : N;0)	ΔH^{298K} = -0.874 eV/atom
L(Ti,Al,Va : N;0)	*ab intitio*
L(Ti,Al : N,Va;0)	*ab intitio*
L(Al : N,Va;0)	*ab intitio*
L(Al : N,Va;1)	*ab intitio*

APPLICATION Modelling FCC-(Ti,Al,Va)(N,Va)

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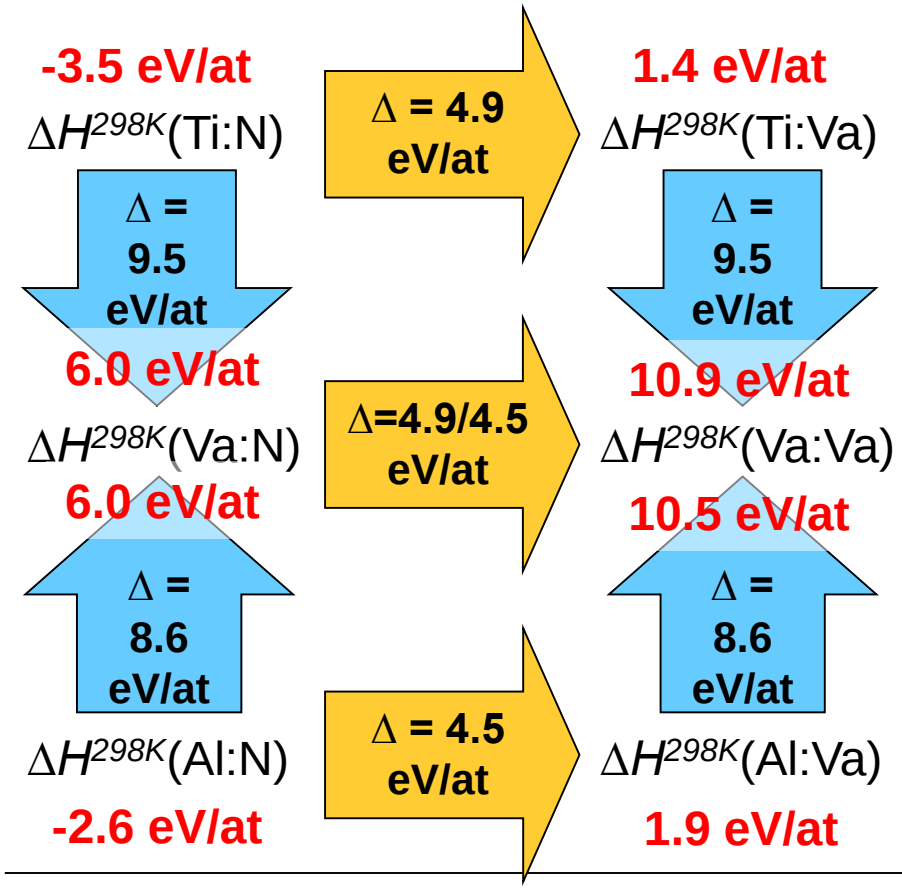

Thermodynamic Property	How modelled?
G(Al : N)	ΔH^{298K} = -2.61 eV/atom
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G(Va : Va)	
L(Ti,Al : N;0)	*ab intitio*
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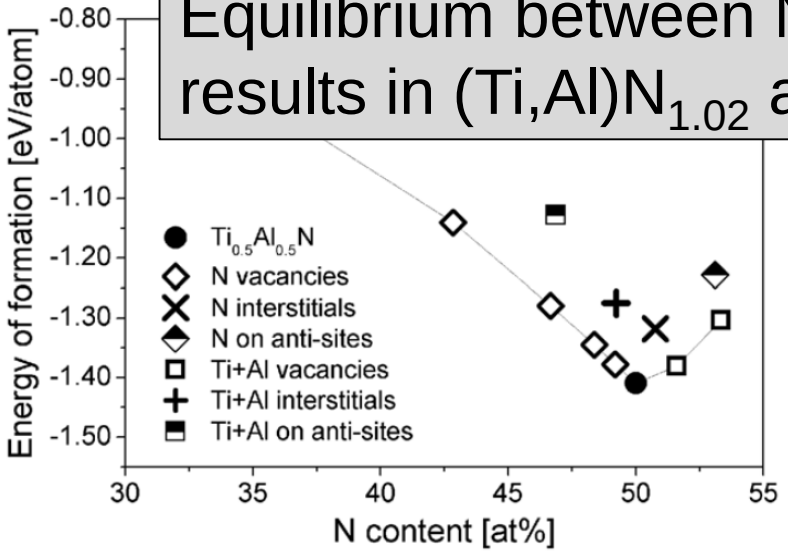
L(Al,Va : N;0)	ΔH^{298K} = -0.874 eV/atom
L(Ti,Al,Va : N;0)	*ab intitio*
L(Ti,Al : N,Va;0)	*ab intitio*
L(Al : N,Va;0)	*ab intitio*
L(Al : N,Va;1)	*ab intitio*

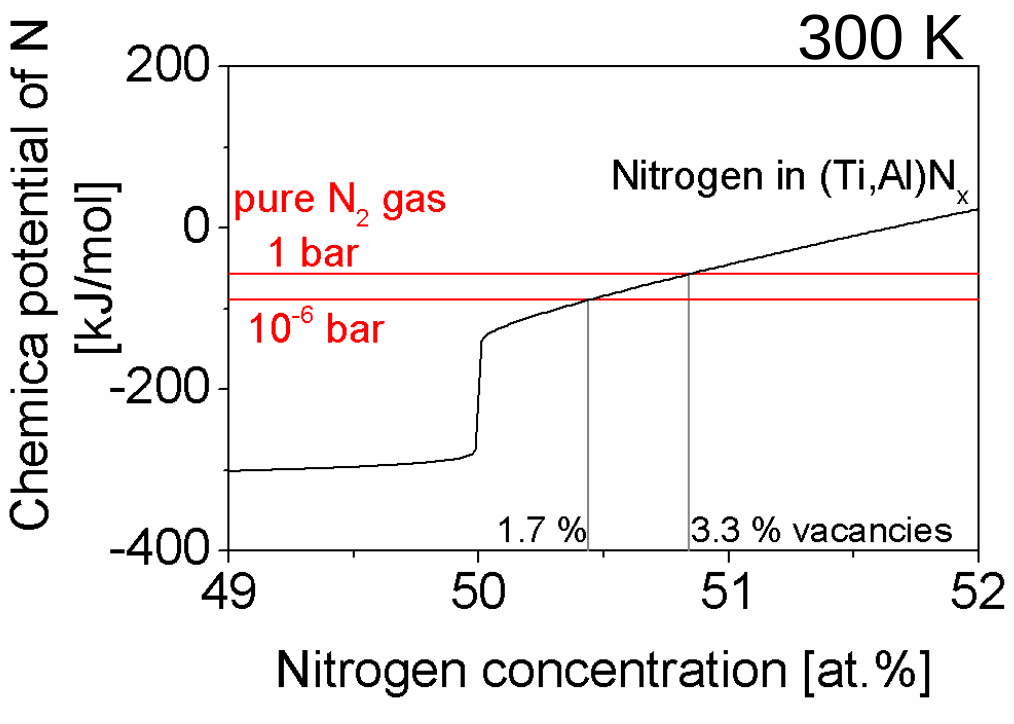
APPLICATION Stoichiometry prediction?

Equilibrium between N in the gas and the solid phase results in $(Ti,Al)N_{1.02}$ and hence in metal vacancies!



to Baben et al., JPCM 24 (2012) 155401.

Input in FactSage™



APPLICATION Diffusivity as f(stoichiometry)

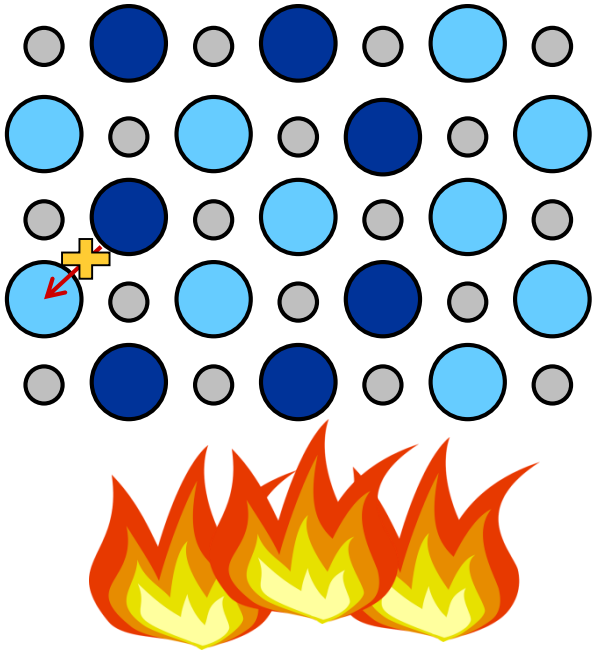
$(Ti,Al)N_1$

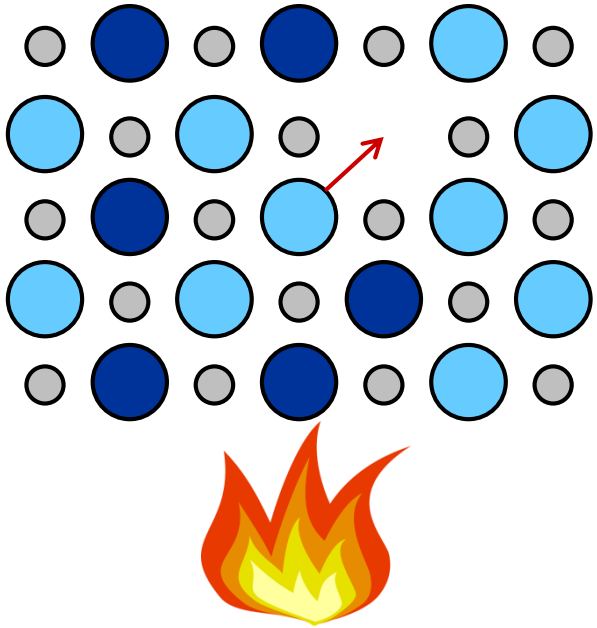
$c_{M\text{-}vac} = c_{Schottky}$

$(Ti,Al)N_{1.02}$

$c_{M\text{-}vac} = 2\ \%$

ΔE





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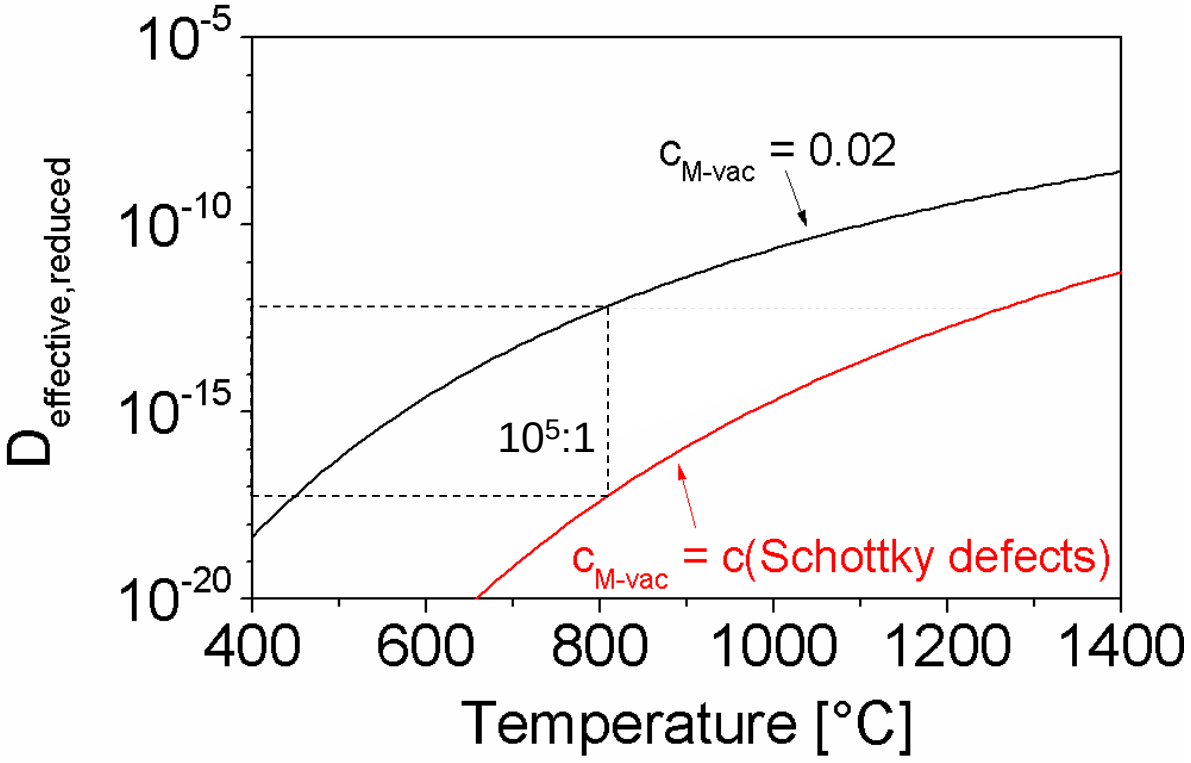


(Ti,Al)$N_{1.02}$

$c_{M\text{-}vac}$ = 2 %

(Ti,Al)N

$c_{M\text{-}vac} = exp(-E_{Schottky}/2kT)$

$E_{Schottky}$ = 2.9 eV

$$D_{reduced} = c_{vac} * exp(-E_A/kT)$$

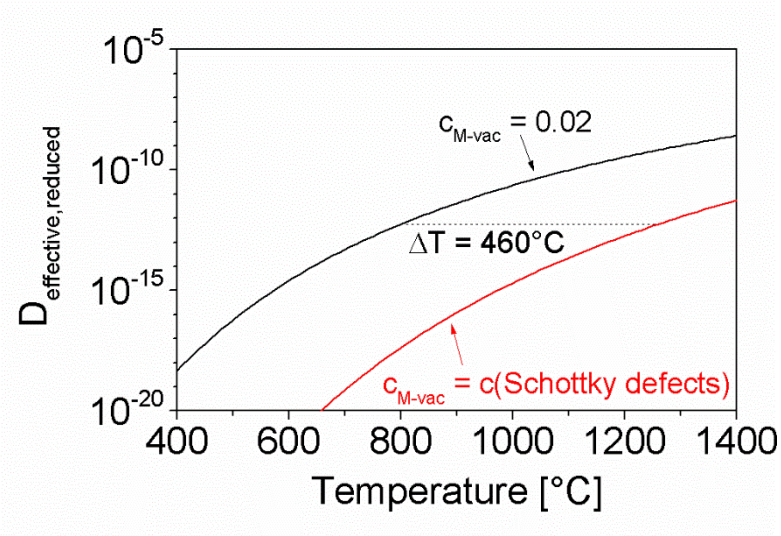
APPLICATION Diffusivity as f(stoichiometry)

Equilibrium:

$$Ti_{0.5}Al_{0.5} + \frac{x}{2}N_2 \leftrightarrow Ti_{0.5}Al_{0.5}N_x$$

→ ***(Ti,Al)$N_{1.02}$ → $c_{M\text{-}vac}$ = 2 %***

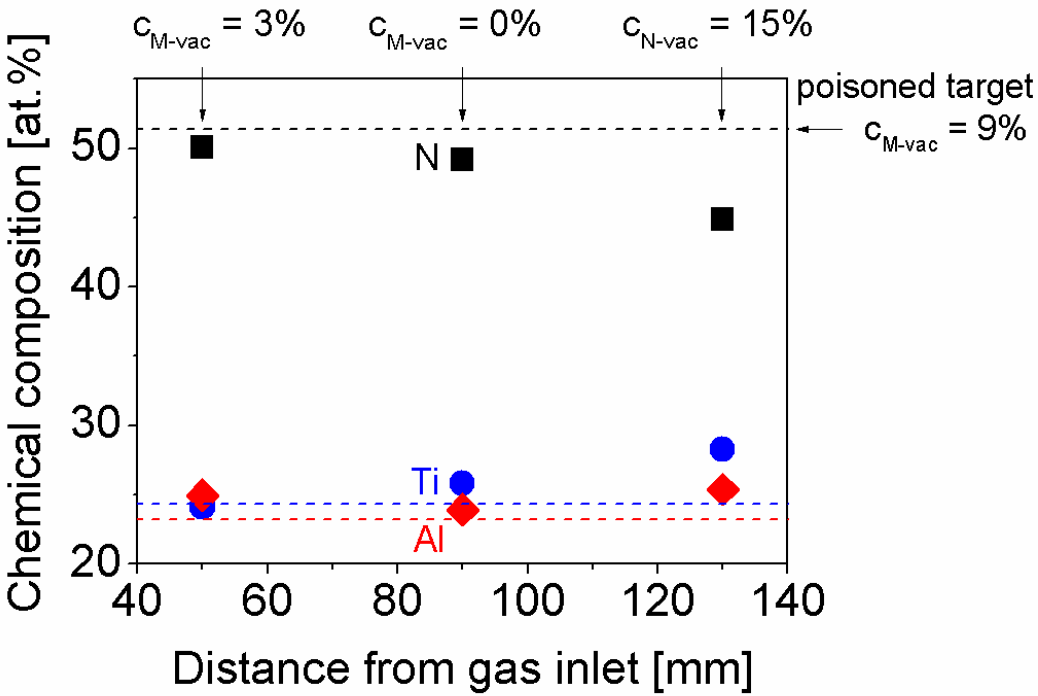
?



(Ti,Al)$N_{1.02}$ → (Ti,Al)N
→ ΔT = 460°C

?

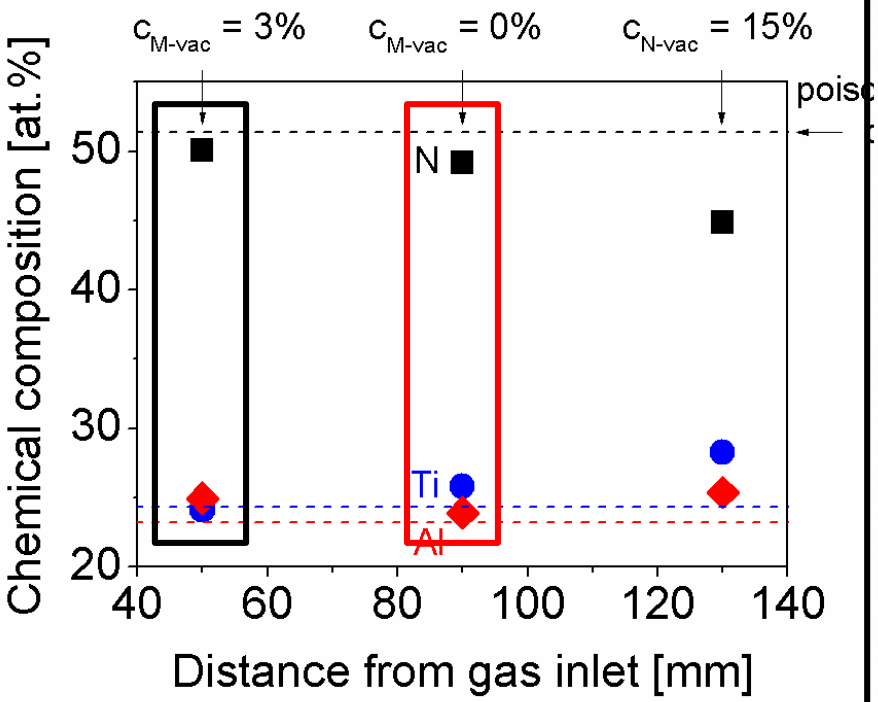
APPLICATION Diffusivity as f(stoichiometry)

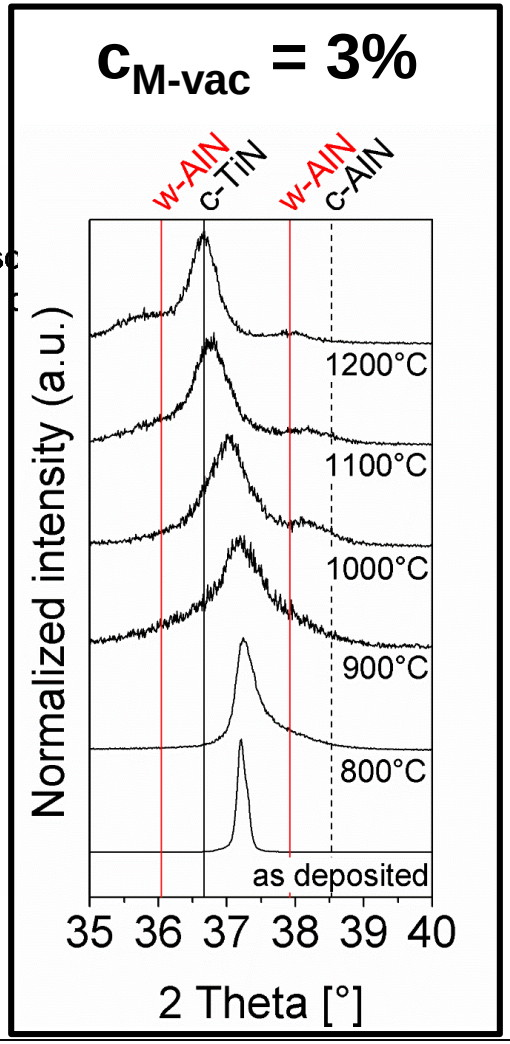


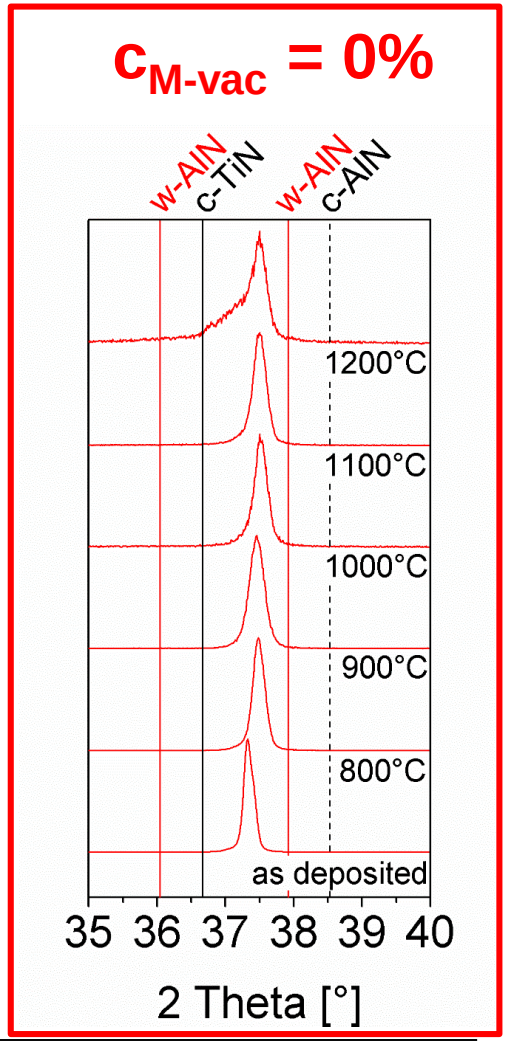
Cemecon CC800/9

APPLICATION

Diffusivity as f(stoichiometry)

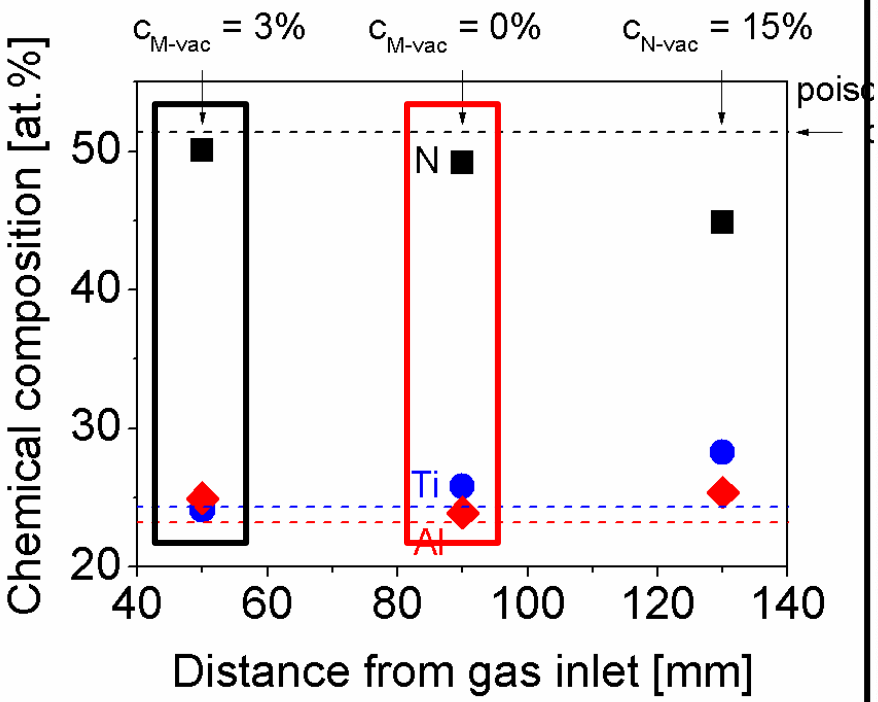


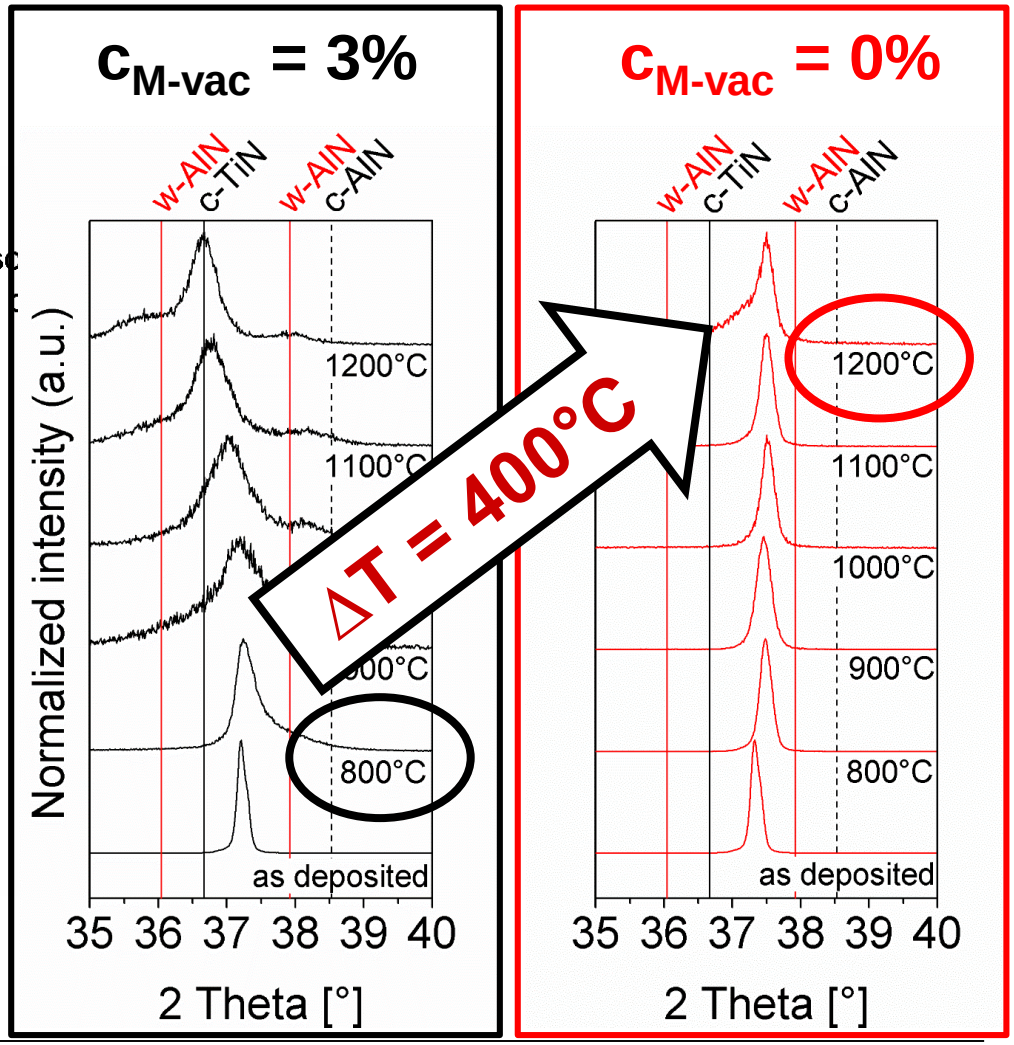




APPLICATION

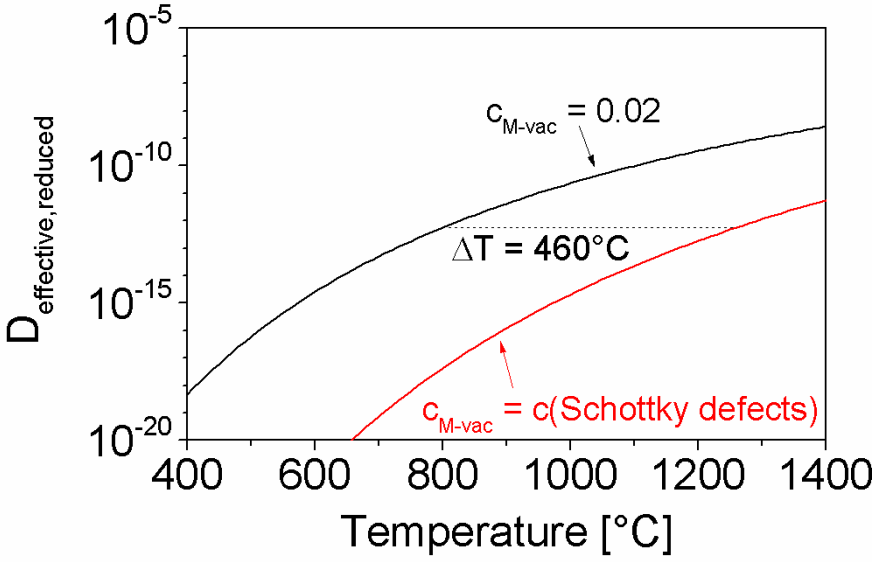
Diffusivity as f(stoichiometry)

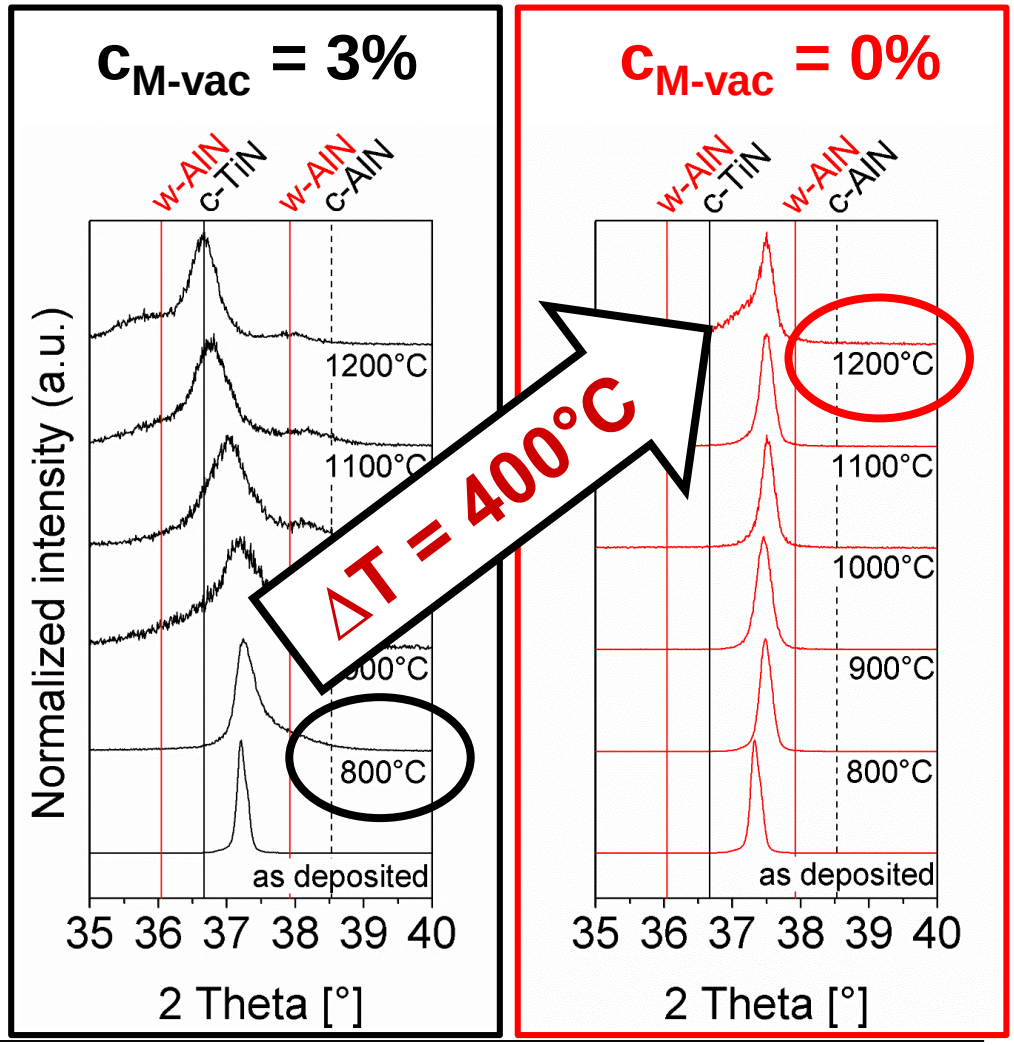




APPLICATION

Diffusivity as f(stoichiometry)



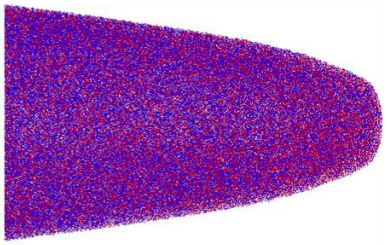


Ti
Al

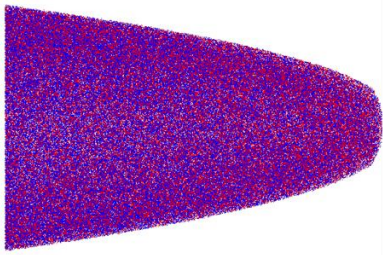
Ti/(Ti+Al) > 0.6
Al/(Ti+Al) > 0.7

as deposited

$c_{M\text{-}vac}$ = 9% (poisoned target)



$c_{M\text{-}vac}$ = 0%



40 nm

APPLICATION

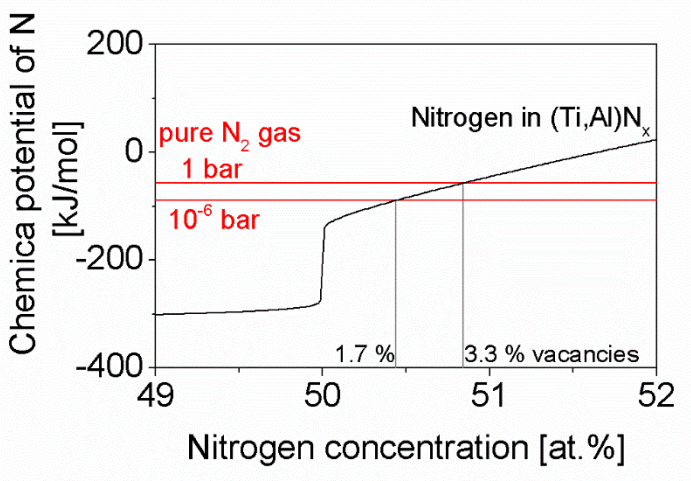
Conclusion 1/3

Thermodynamic Property	How modelled?
G(Al : N)	*ab intitio*
G(Va : N)	*ab intitio*
G(Va : Va)	*ab intitio*
L(Ti,Al : N;0)	*ab intitio*
L(Ti,Va : N;0)	*ab intitio*
L(Al,Va : N;0)	*ab intitio*
L(Ti,Al,Va : N;0)	*ab intitio*
L(Ti,Al : N,Va;0)	*ab intitio*
L(Al : N,Va;0)	*ab intitio*
L(Al : N,Va;1)	*ab intitio*

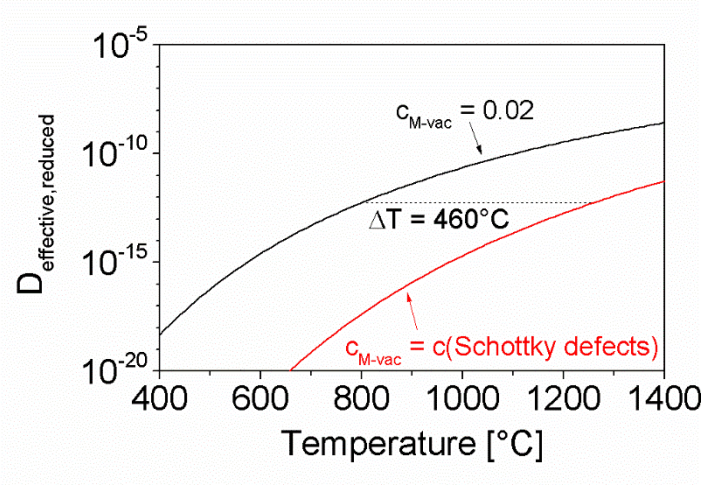
Ab initio calculations can be used to extract thermodynamic data efficiently (16 calculations → 10 thermodynamic parameters).

Vacancies can be modelled on both sublattices without computational difficulties.

APPLICATION Conclusion 2/3



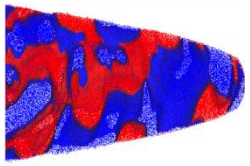
Thermodynamic equilibrium between the growing film and N_2 leads to metal vacancies.



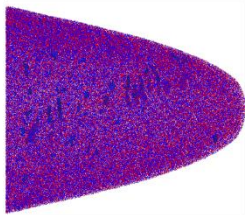
Metal vacancies lead to low thermal stability of $(Ti,Al)N_x$.

APPLICATION Conclusion 3/3

$c_{M\text{-}vac}$ = 9%



$c_{M\text{-}vac}$ = 0%



Point defect engineering increases thermal stability of $(Ti,Al)N_x$ by ~400°C.

Change name of commercially available coatings to „Titanium-Aluminium-Vacancy Nitride“?

THANK YOU FOR YOUR ATTENTION!

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