

Modeling of metastable phase formation diagrams for sputtered thin films

Keke Chang, D. Music, M. to Baben, D. Lange, H. Bolvardi, J.M. Schneider

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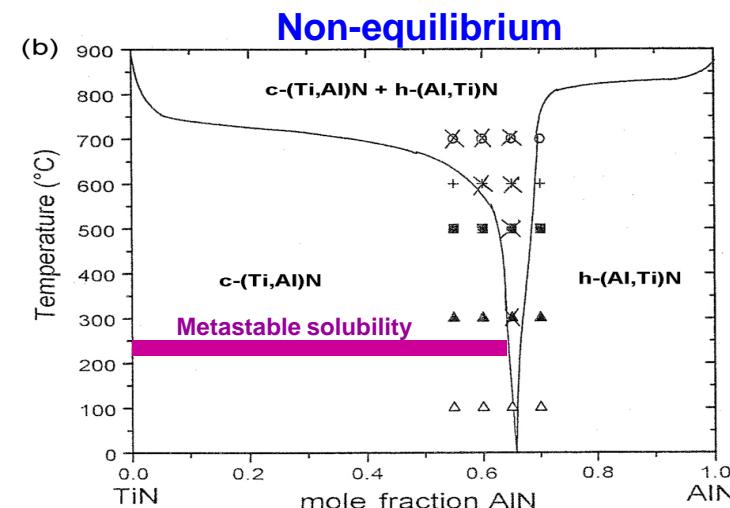
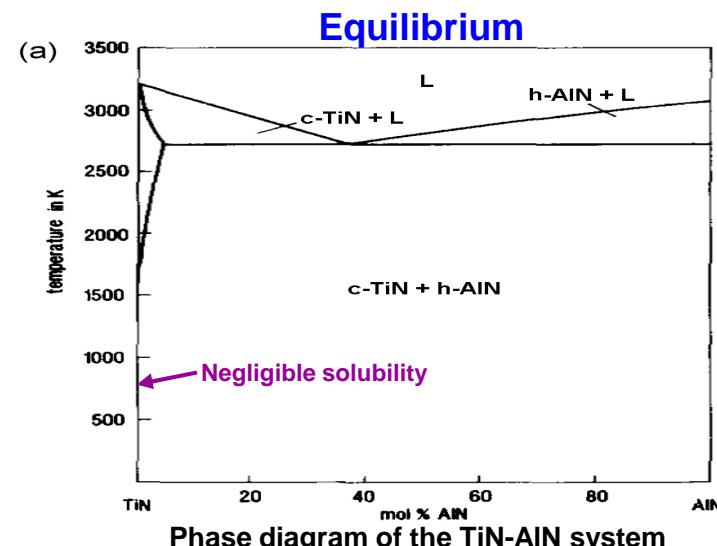
Materials Chemistry, RWTH Aachen University

Outline

- **Background**
- **Surface diffusion**
- **Research strategy**
 - Experiments: thin film synthesis and characterization
 - *Ab initio* calculations
 - Thermodynamic description using CALPHAD approach
 - Modeling of metastable phase formation diagrams
- **Outlook**



Wide application of nitride coatings



$$X = \sqrt{2D_s t}$$

by Einstein

Eq. (1)

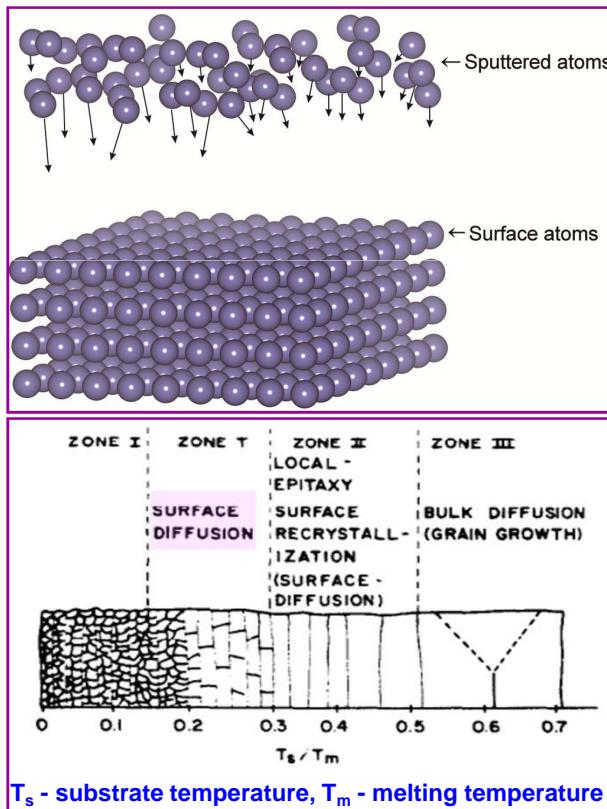
A. Einstein, Z. Elektrochem. 14 (1908) 235.

Surface diffusion distance - X

$$X = \sqrt{2\nu \frac{a}{r_D} \cdot a \cdot \exp\left(-\frac{Q_s}{2kT}\right)}$$

by Cantor and Cahn

Eq. (2)



ν - vibrational frequency, a - lattice parameter, r_D - deposition rate, Q_s - activation energy for surface diffusion, k - Boltzmann constant, T - substrate temperature

B. Cantor, R. Cahn, Acta Metall. 24 (1976) 845.

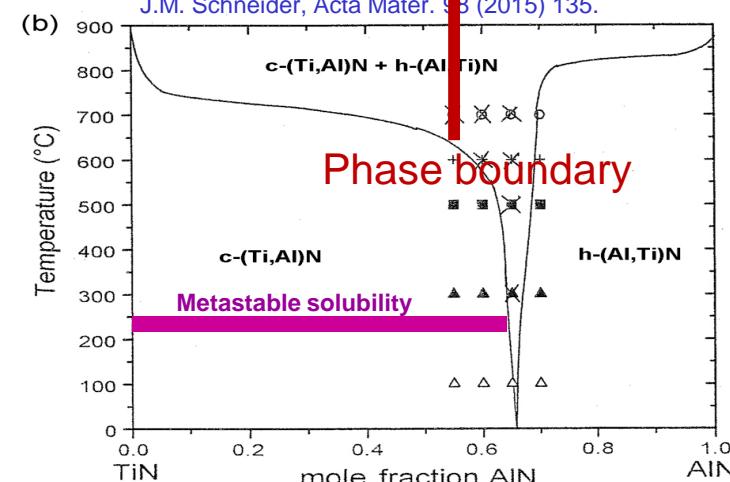
Critical diffusion distance - X_c

$$X_c = \sqrt{2\nu \frac{a}{r_{Dn}} \cdot a \cdot \exp\left(-\frac{Q_s}{2kT_c}\right)}$$

Eq. (3)

T_c - critical temperature

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Metastable phase formation diagram for sputtered (Ti,Al)N thin films

P. Spencer, Z. Metallkd. 92 (2001) 10.

Surface diffusion

Critical diffusion distance - X_c

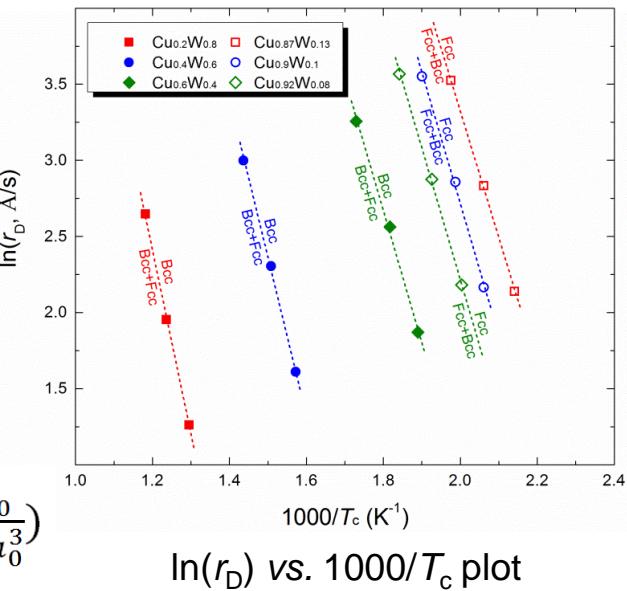
$$X_c = \sqrt{2\nu \frac{a}{r_{Dn}} \cdot a \cdot \exp\left(-\frac{Q_s}{2kT_c}\right)}$$

Eq. (3)

$$X_{c0} = \sqrt{2\nu \frac{a_0}{r_D} \cdot a_0 \cdot \exp\left(-\frac{Q_{s0}}{2kT_c}\right)}$$

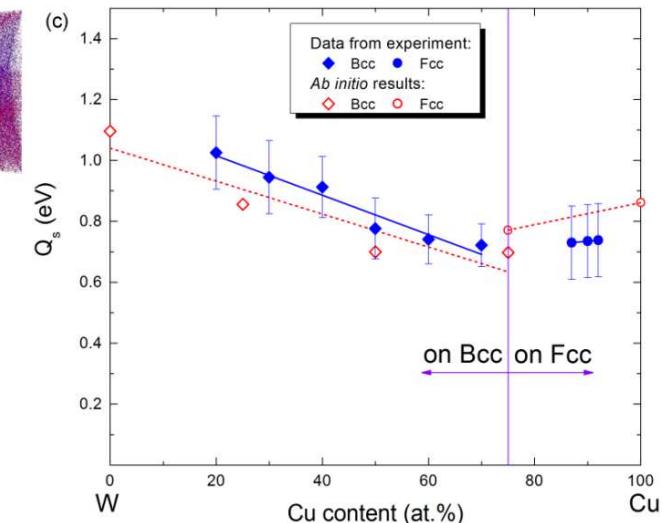
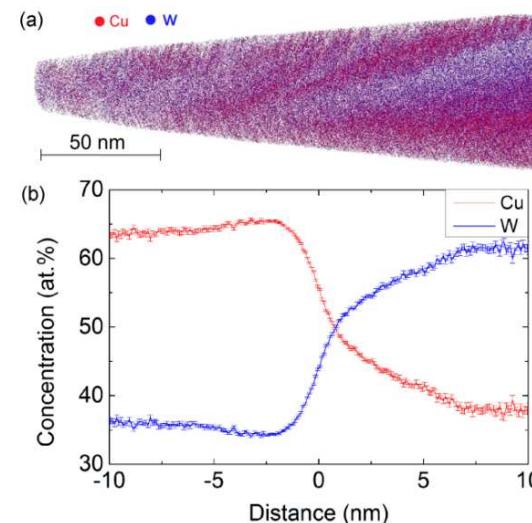
$$\ln r_D = -\text{constant1} \cdot \frac{1}{T_c} + \text{constant2}$$

$$\ln r_D = -\frac{Q_{s0}}{k} \cdot \frac{1}{T_c} - \ln\left(\frac{X_{c0}^2}{2\nu a_0^3}\right)$$



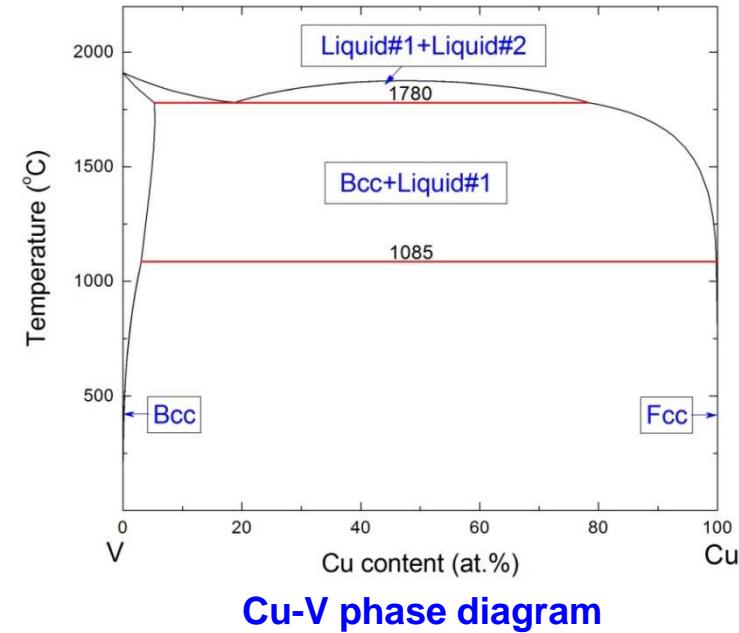
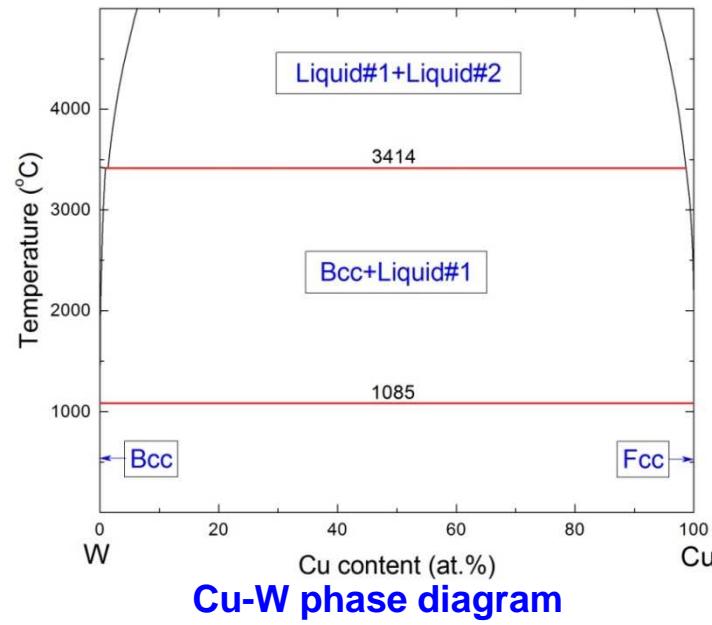
A proposed method to obtain activation energy- Q_s

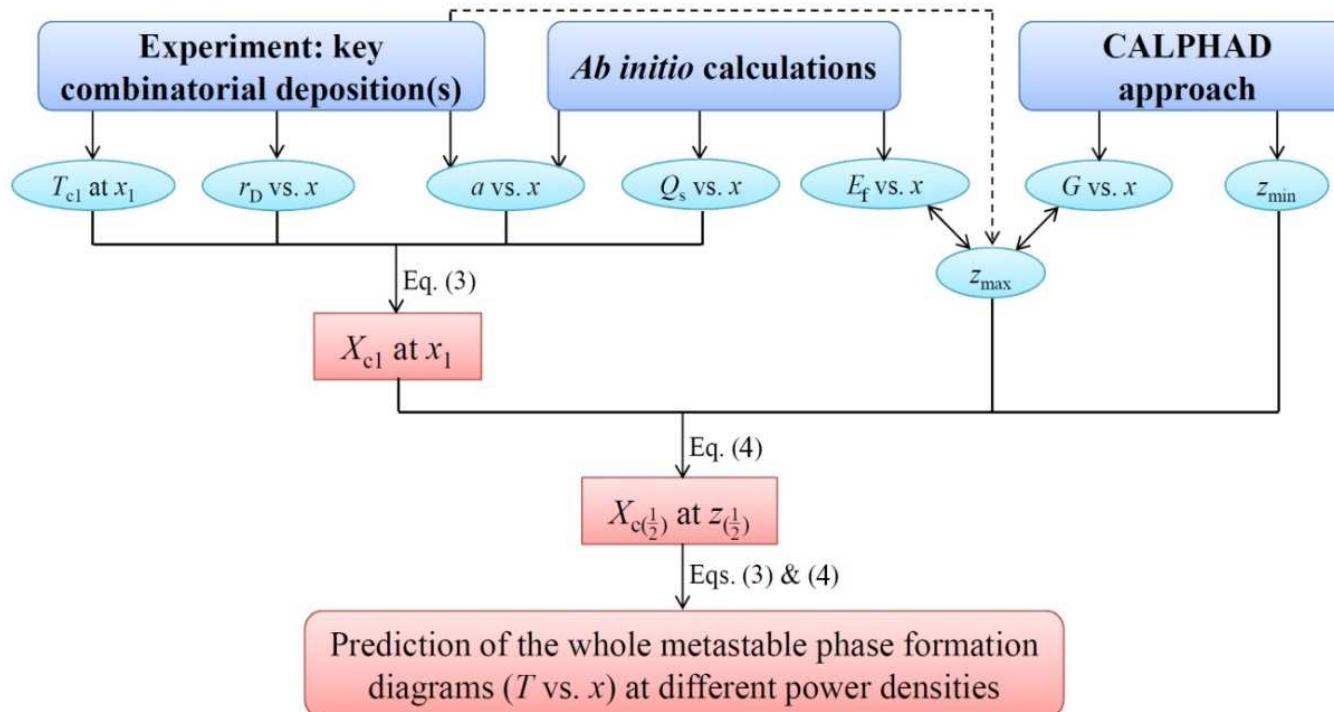
K. Chang, M. to Baben, D. Music, D. Lange, H. Bolvardi, J.M. Schneider, Acta Mater. 98 (2015) 135.



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- **Summary and outlook**





Critical diffusion distance - X_c

$$X_c = \sqrt{2\nu \frac{a}{r_{Dn}} \cdot a \cdot \exp\left(-\frac{Q_s}{2kT_c}\right)} \quad \text{Eq. (3)}$$

T_c - critical temperature

ν - vibrational frequency, a - lattice parameter, r_{Dn} - deposition rate, Q_s - activation energy for surface diffusion, k - Boltzmann constant

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A proposed equation to describe X_c

$$X_c = X_{c(\frac{1}{2})} \cdot \sqrt{\frac{z_{\max} - z}{z - z_{\min}}} \quad \text{Eq. (4)}$$

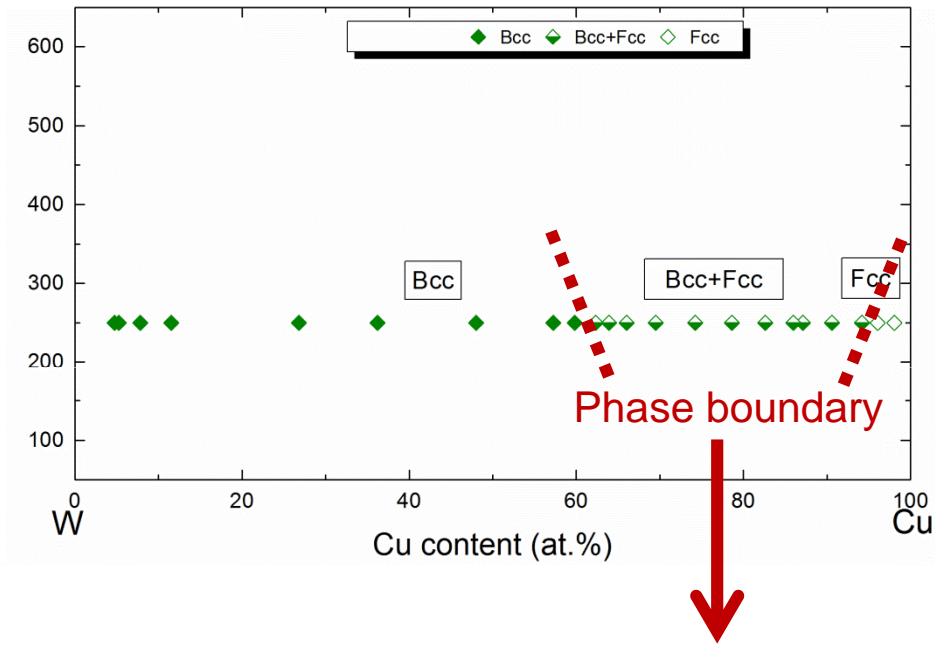
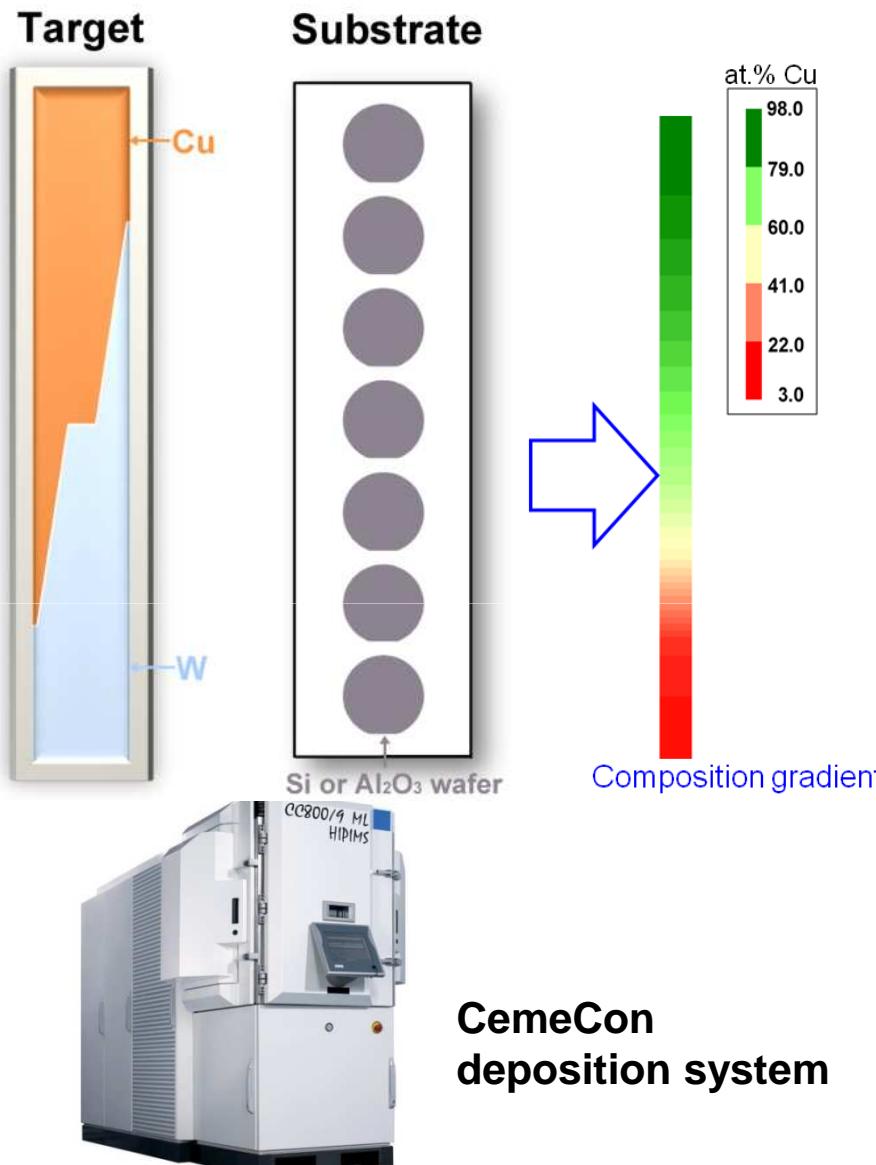
z - solid solubility

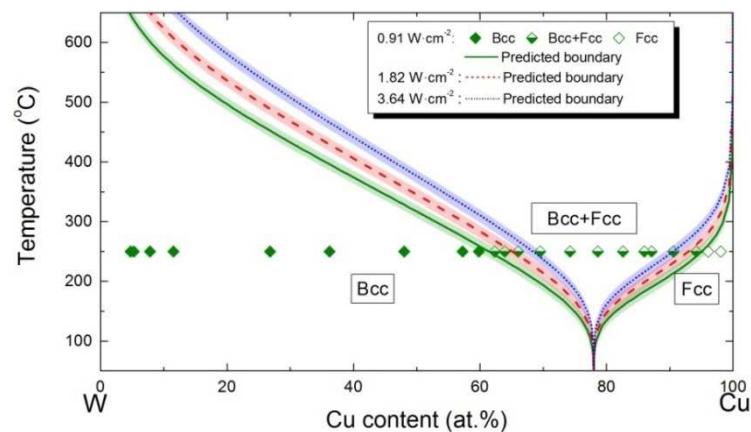
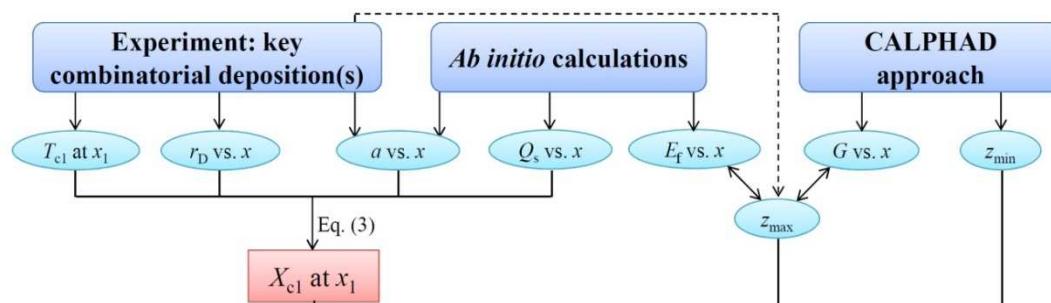
z_{\max} - maximum metastable solid solubility

z_{\min} - stable solid solubility from the equilibrium phase diagrams

$X_{c(\frac{1}{2})}$ - critical diffusion distance at half metastable solid solubility

K. Chang, D. Music, M. to Baben, D. Lange, H. Bolvardi, J.M. Schneider, Sci. Tech. Adv. Mater. 17 (2016) 210.





Prediction of the metastable phase formation diagrams for sputtered Cu-W thin films (power density – temperature –composition)

$$X_c = \sqrt{2\nu \frac{a}{r_{Dn}} \cdot a \cdot \exp\left(-\frac{Q_s}{2kT_c}\right)}$$

Eq. (3)

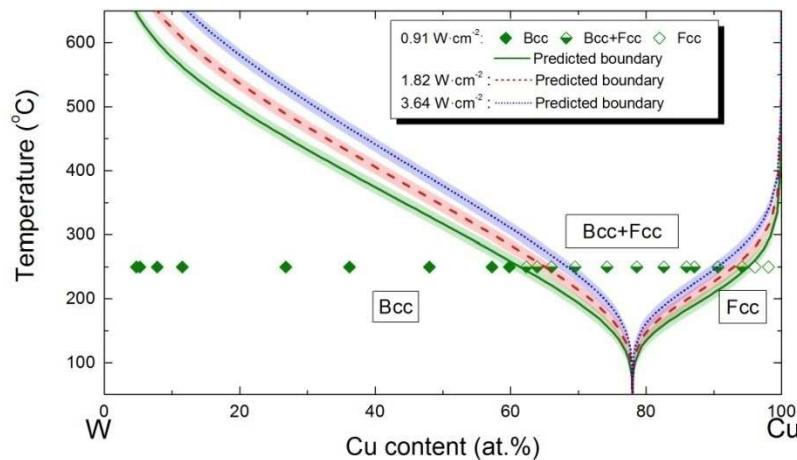
$$X_c = X_{c(\frac{1}{2})} \cdot \sqrt{\frac{z_{\max} - z}{z - z_{\min}}}$$

Eq. (4)

Condition	Phase formation
Where $x < 0.78$, if $T < T_c$, then $X < X_c$	Bcc metastable solid solution
Where $x < 0.78$, if $T \geq T_c$, then $X \geq X_c$	The Bcc metastable solid solution decomposes into Bcc and Fcc phases
Where $x > 0.78$, if $T < T_c$, then $X < X_c$	Fcc metastable solid solution
Where $x > 0.78$, if $T \geq T_c$, then $X \geq X_c$	The Fcc metastable solid solution decomposes into Bcc and Fcc phases

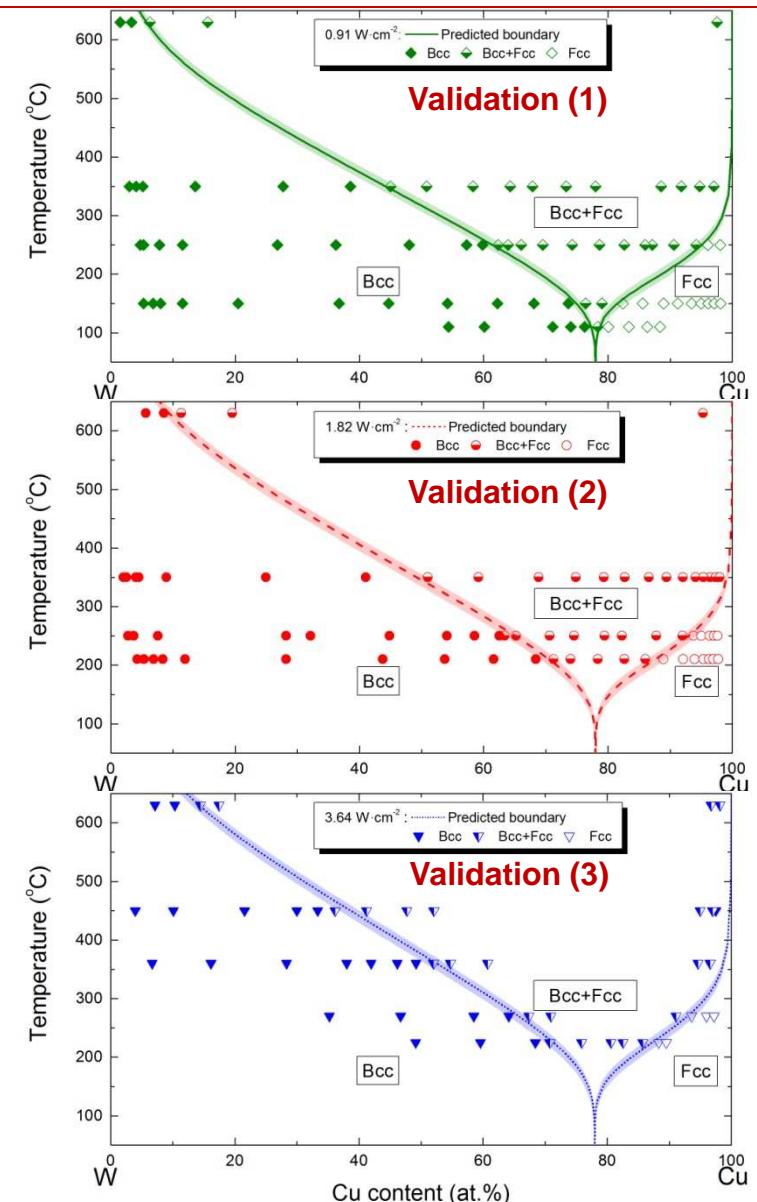
Structure evolution for $\text{Cu}_x\text{W}_{1-x}$ thin films at a certain deposition rate (T_c : critical temperature; X_c : critical surface diffusion distance)

One key experiment + *ab initio* calculations + CALPHAD



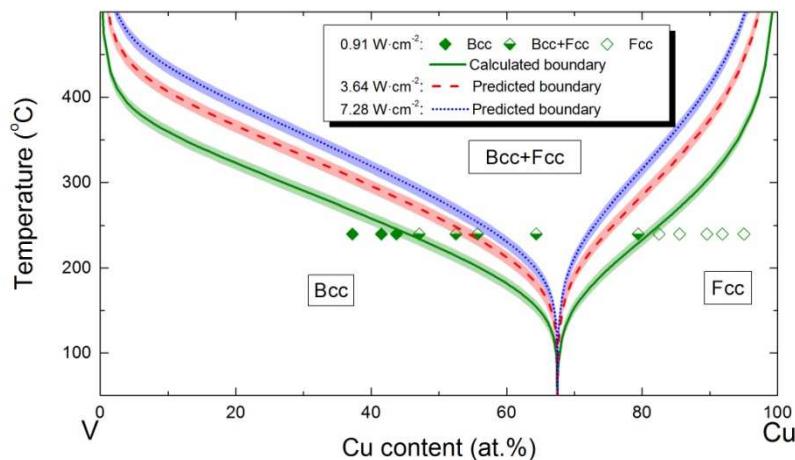
Prediction of the metastable phase formation diagrams for sputtered Cu-W thin films (power density – temperature –composition)

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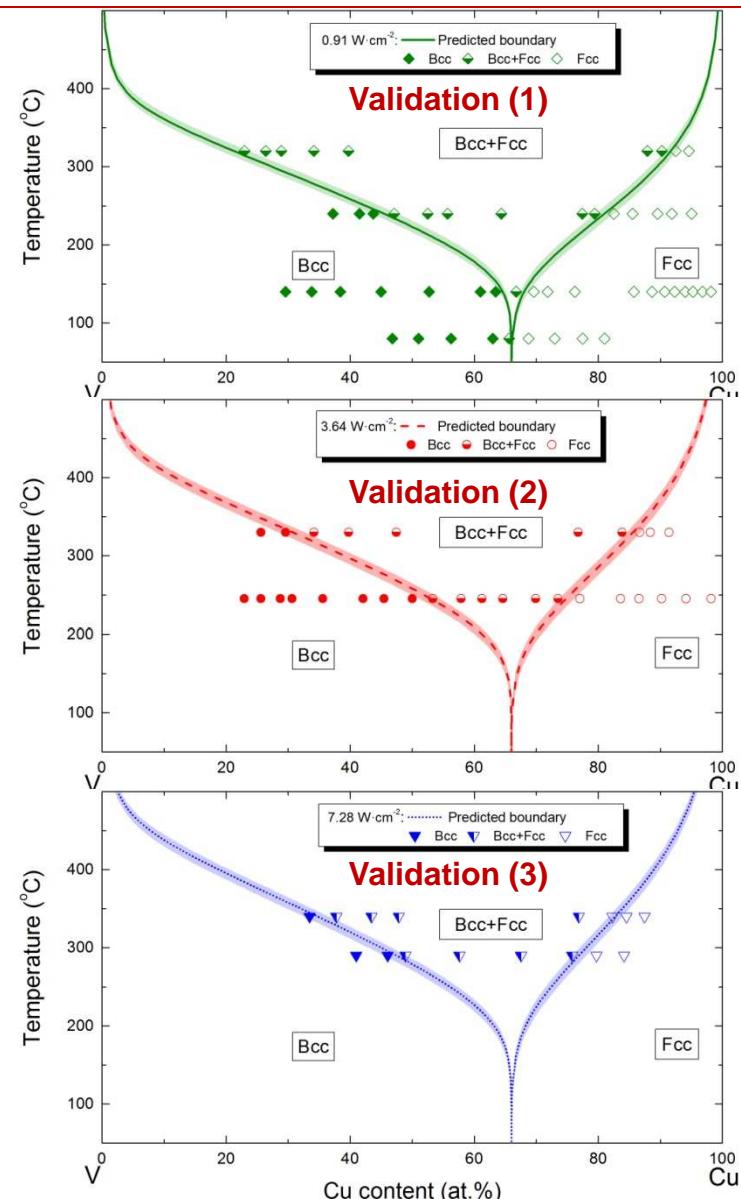
✓ The methodology also works for the Cu-V system.

One key experiment + *ab initio* calculations + CALPHAD



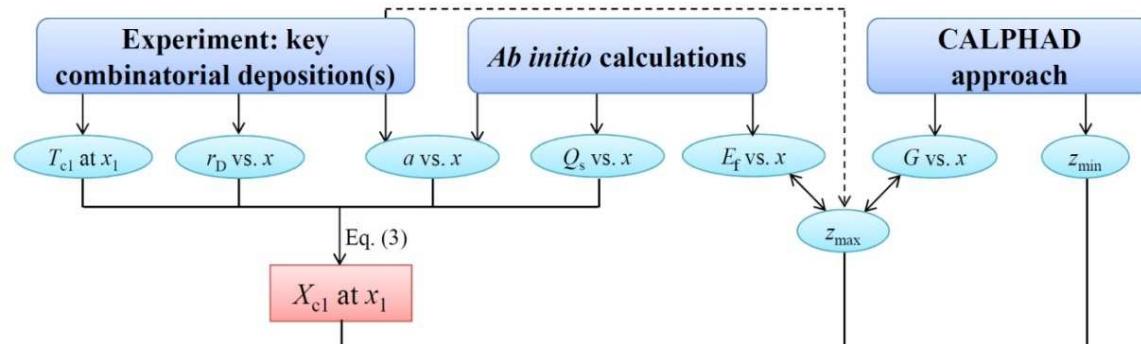
Prediction of the metastable phase formation diagrams for sputtered Cu-V thin films

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Summary

- ✓ A method to model metastable phase formation diagrams
- ✓ Composition-structure-property high-throughput screening
- ✓ A general strategy also applicable to other systems



Outlook

- ❑ Amorphous phase
- ❑ More complex systems
- ❑ Further development/improvement

Prediction of the whole metastable phase formation diagrams (T vs. x) at different power densities

Acknowledgement:



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GTT - TECHNOLOGIES



Thank you for your attention!