SAND2019-14557PE

Microstructure Morphology of Bicontinuous Nanocomposites Thin-Films During Physical Vapor Deposition (PVD)

Remi Dingreville, CINT, Sandia National Laboratories

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Multi-disciplinary & Collaborative Research

- **Graduate students**

  M. Powers (Ph.D., U. Michigan), E. Hermann (UNC)

- **Postdocs**

  J. Stewart (SNL), D. Montes de Oca Zapiain (SNL)

- **External Collaborators**

  A. Misra (U. Michigan), K. Baldwin (LANL), N. Li (LANL)

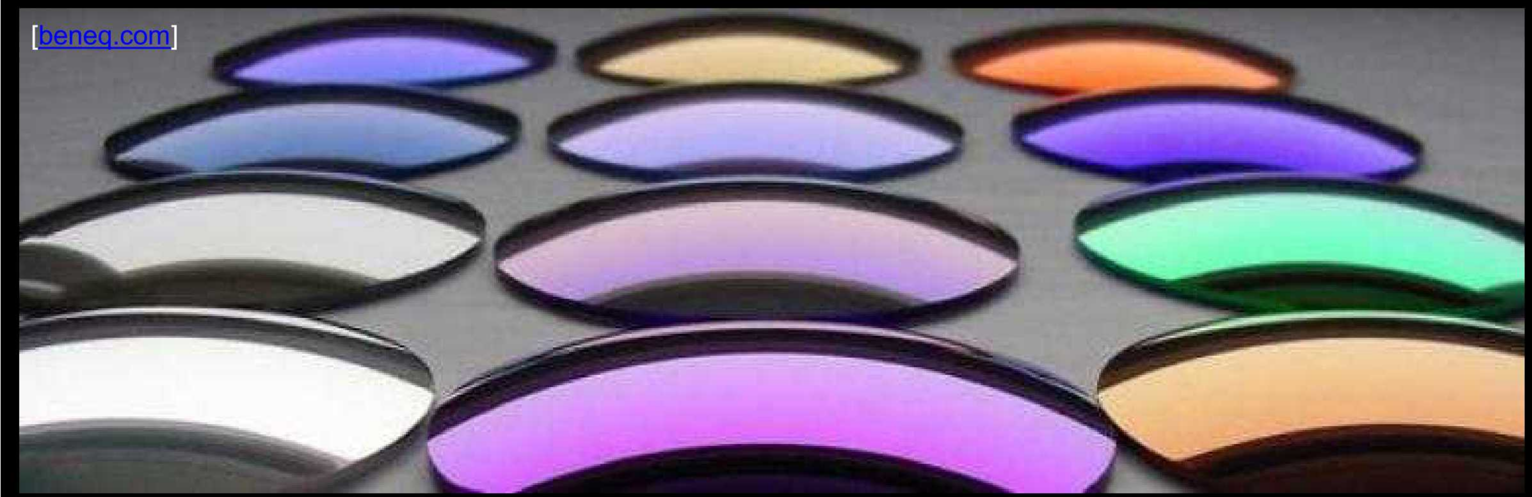
- **Funding**

  Center for Integrated Nanotechnologies (CINT)

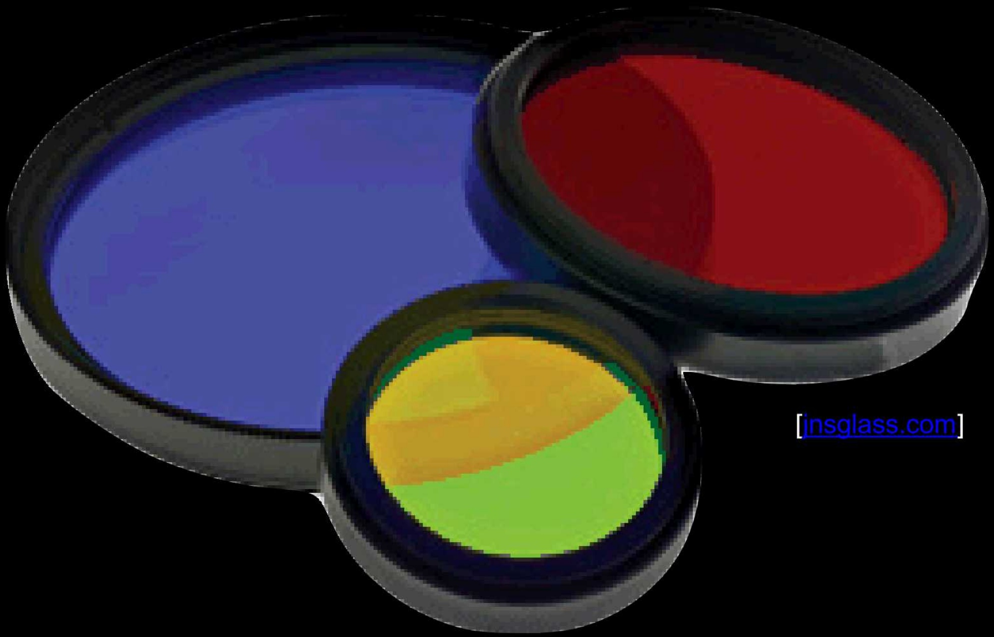
  LDRD — Laboratory Directed Research & Development

We Use Thin-Film Coatings to Achieve Targeted Technological Functionalities

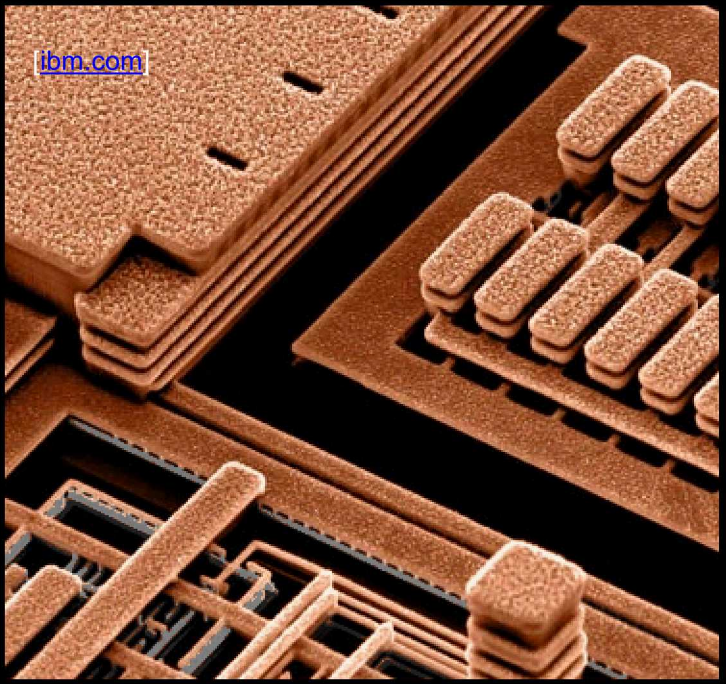
Decorative



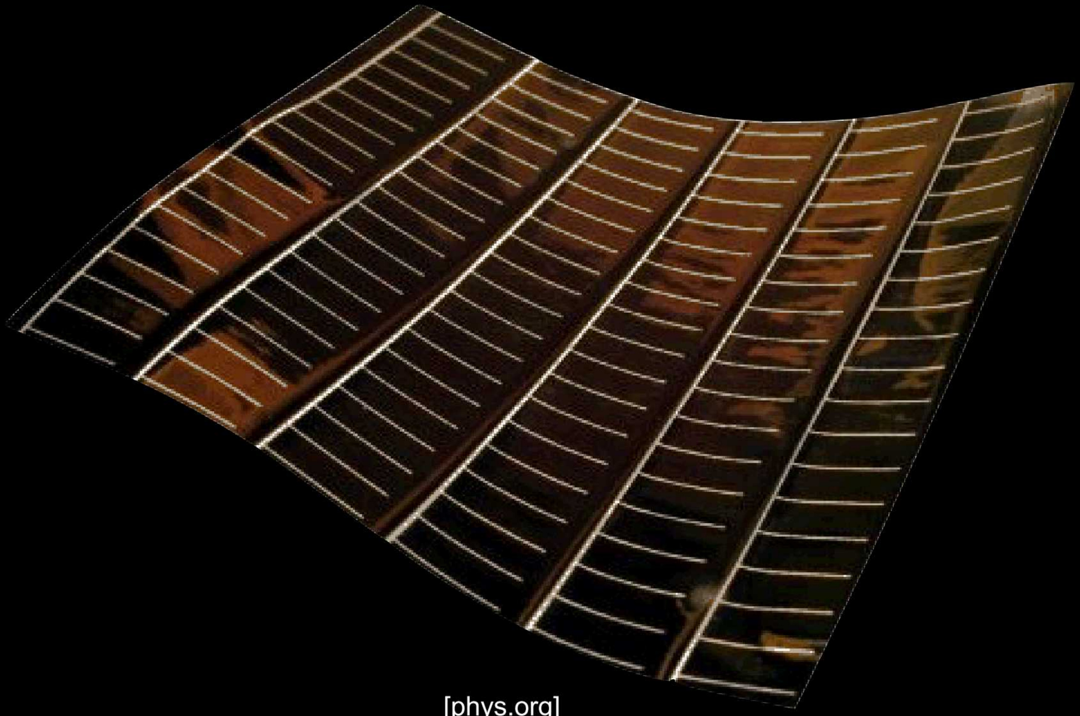
Optical



Mechanical

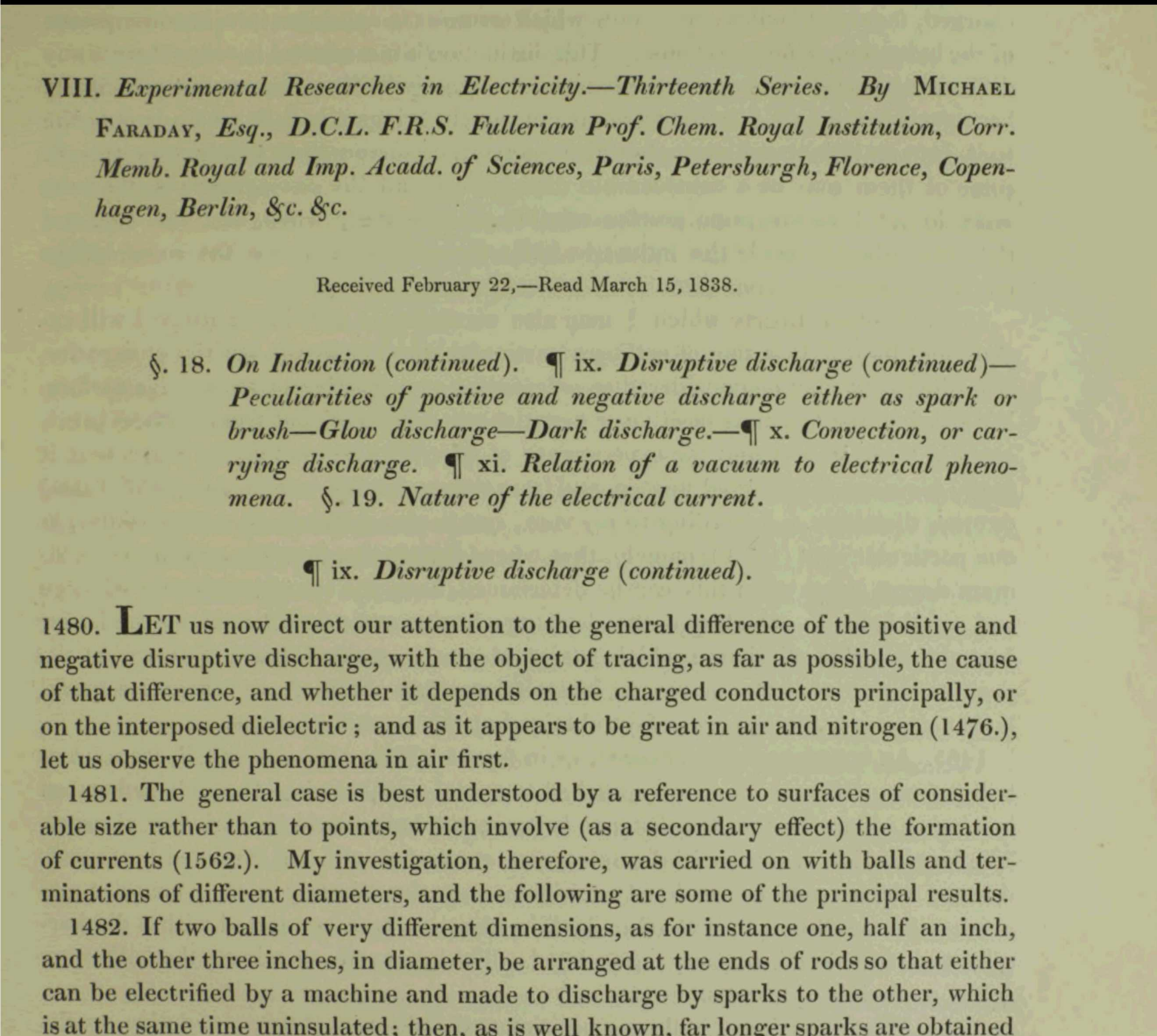


Microelectronic



Photovoltaic

The History of PVD is Closely Linked to the Discovery of Electricity and Magnetism


VIII. *Experimental Researches in Electricity.—Thirteenth Series. By* Michael Faraday, *Esq., D.C.L. F.R.S. Fullerian Prof. Chem. Royal Institution, Corr. Memb. Royal and Imp. Acadd. of Sciences, Paris, Petersburgh, Florence, Copenhagen, Berlin, &c. &c.*

Received February 22,—Read March 15, 1838.

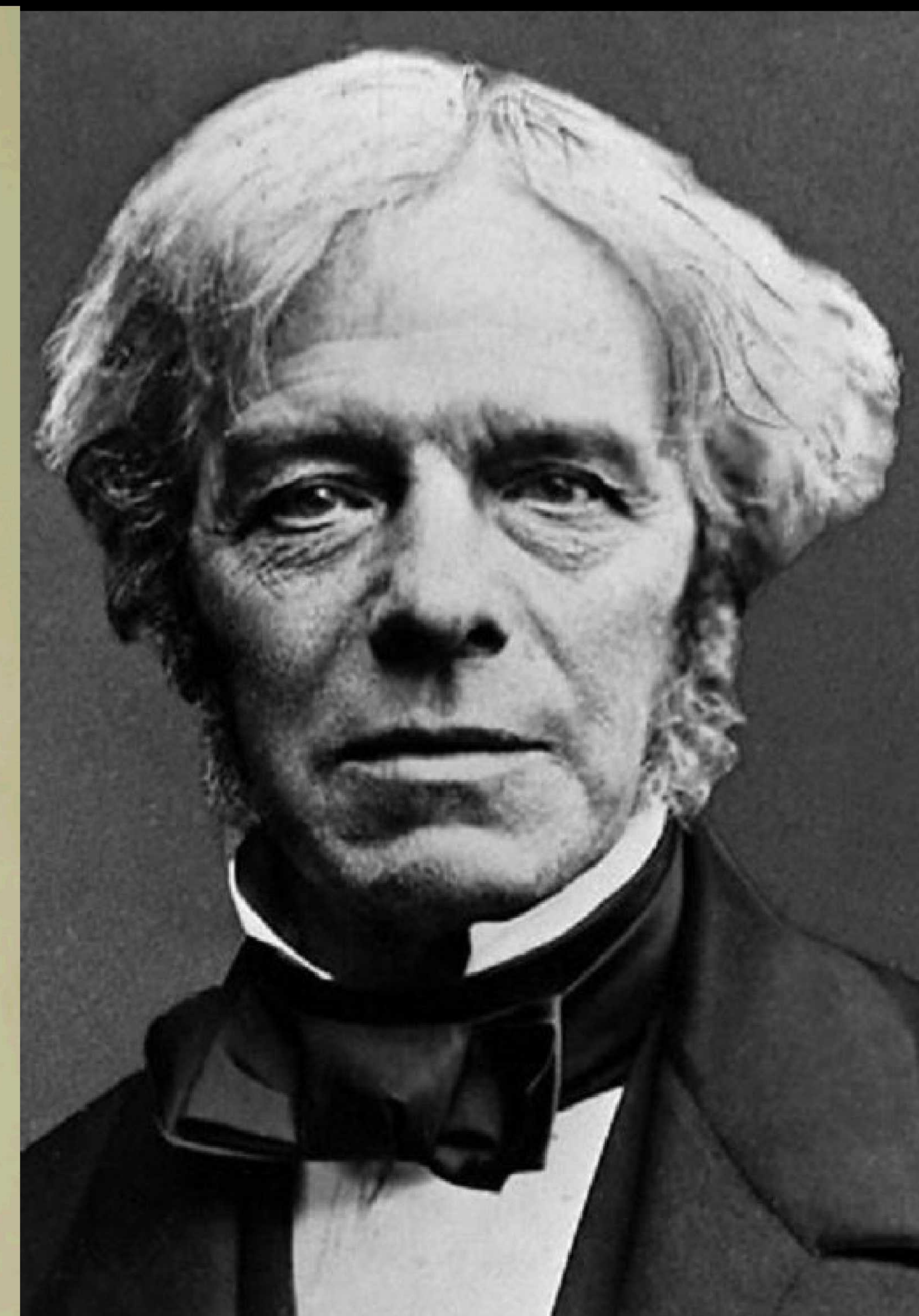
§. 18. *On Induction* (*continued*). ¶ ix. *Disruptive discharge* (*continued*)—*Peculiarities of positive and negative discharge either as spark or brush—Glow discharge—Dark discharge.*—¶ x. *Convection, or carrying discharge.* ¶ xi. *Relation of a vacuum to electrical phenomena.* §. 19. *Nature of the electrical current.*

¶ ix. *Disruptive discharge* (*continued*).

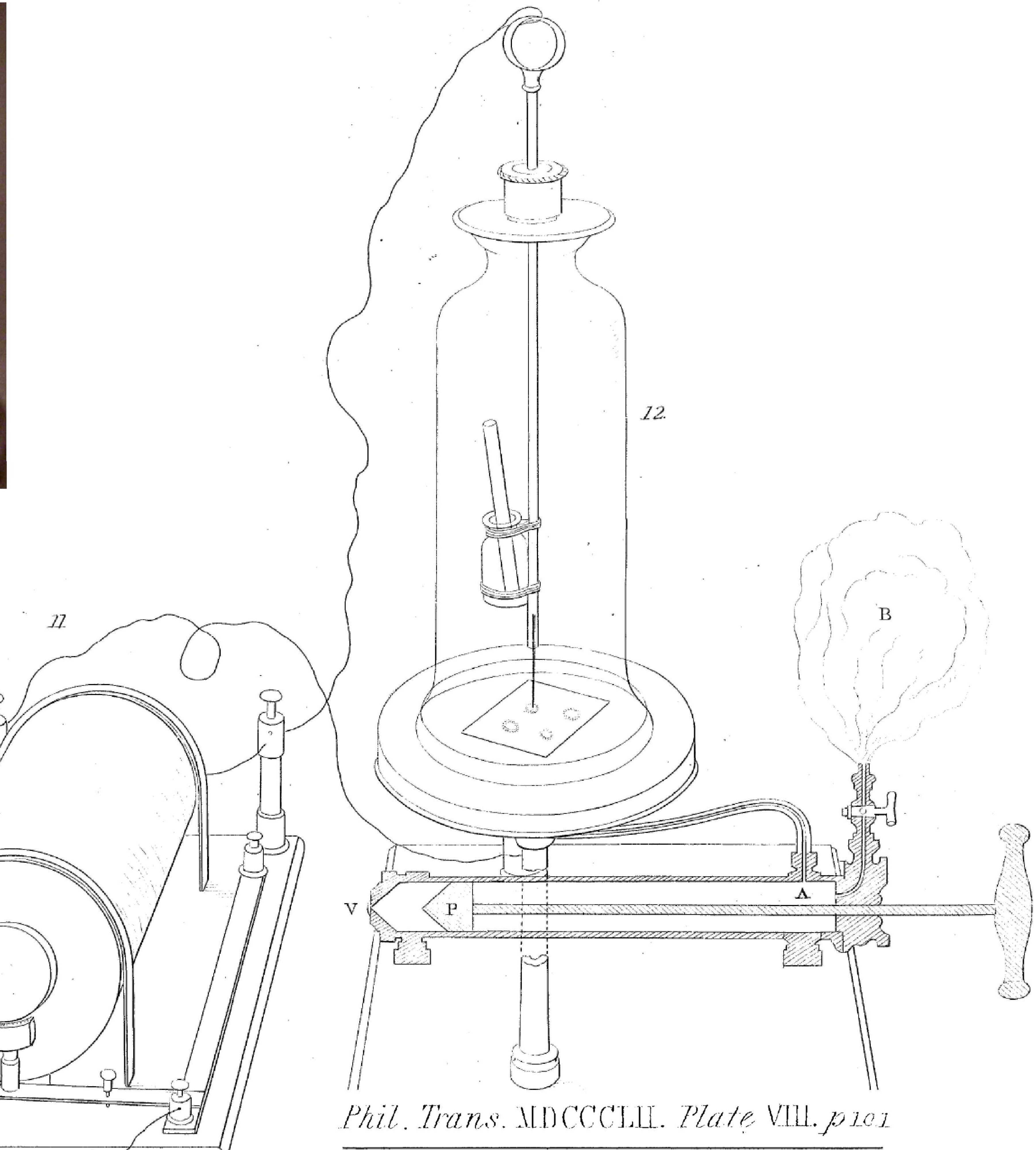
1480. Let us now direct our attention to the general difference of the positive and negative disruptive discharge, with the object of tracing, as far as possible, the cause of that difference, and whether it depends on the charged conductors principally, or on the interposed dielectric; and as it appears to be great in air and nitrogen (1476.), let us observe the phenomena in air first.

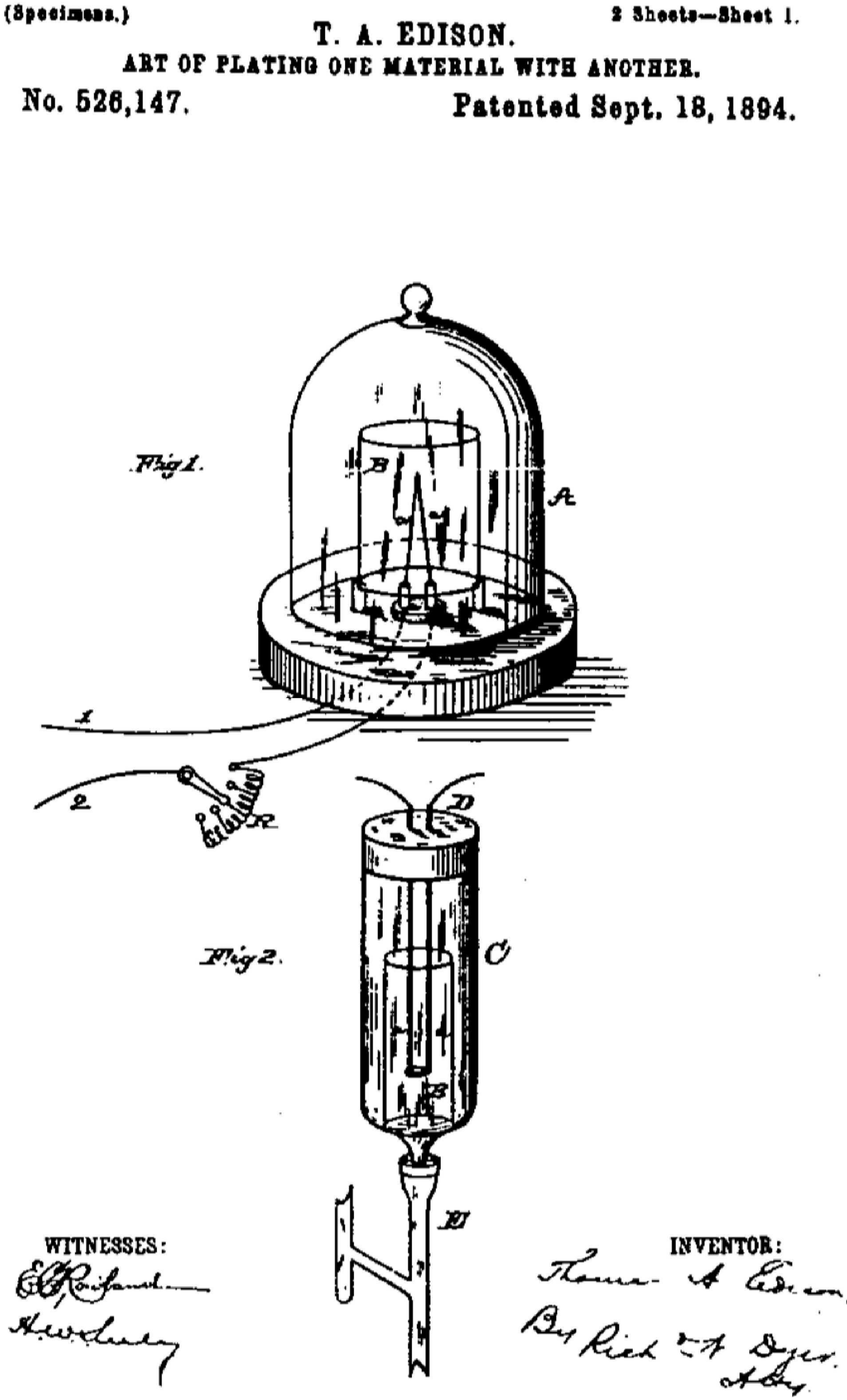
1481. The general case is best understood by a reference to surfaces of considerable size rather than to points, which involve (as a secondary effect) the formation of currents (1562.). My investigation, therefore, was carried on with balls and terminations of different diameters, and the following are some of the principal results.

1482. If two balls of very different dimensions, as for instance one, half an inch, and the other three inches, in diameter, be arranged at the ends of rods so that either can be electrified by a machine and made to discharge by sparks to the other, which is at the same time uninsulated; then, as is well known, far longer sparks are obtained



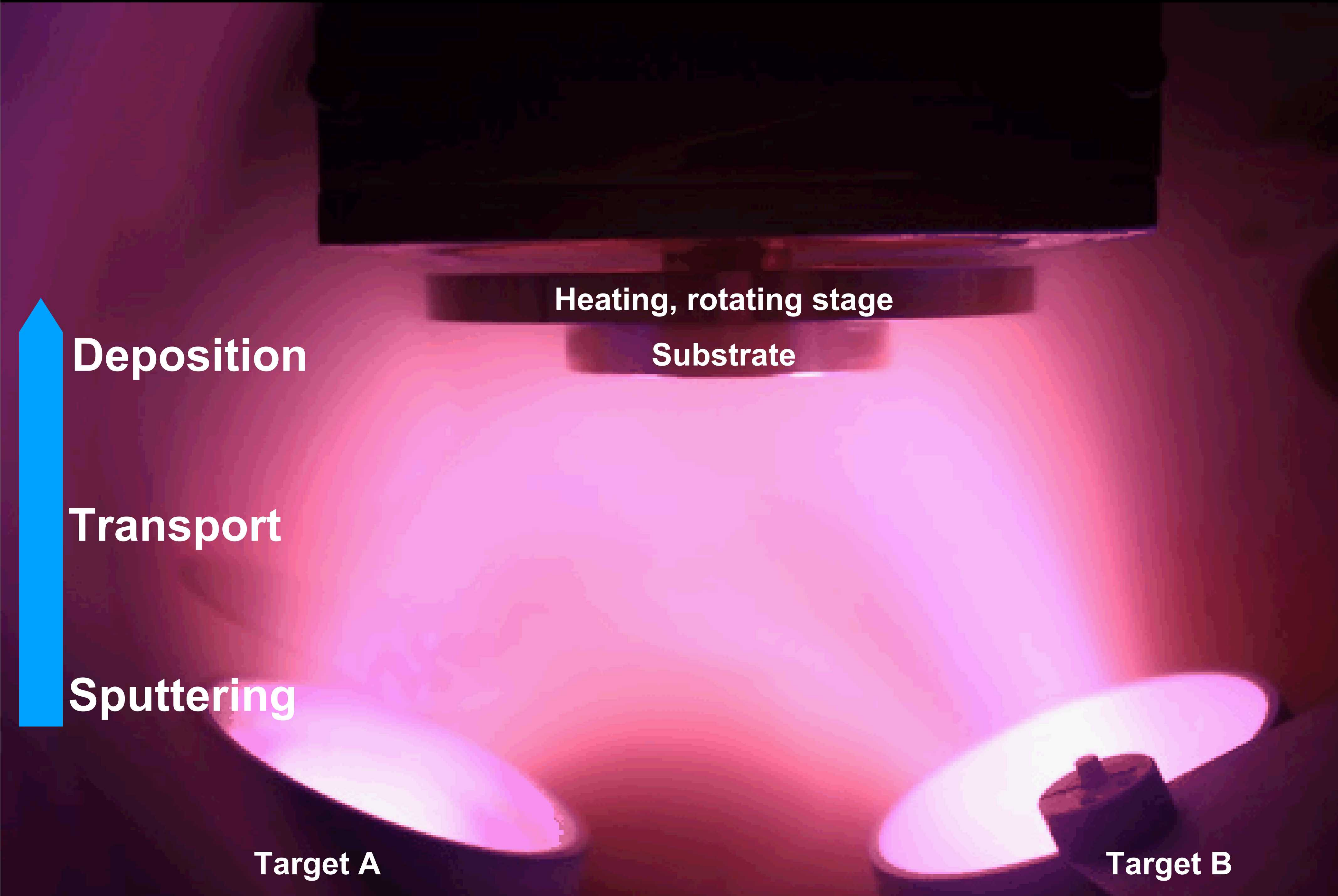
William Robert Grove




(Specimens.)
2 Sheets—Sheet 1.
T. A. EDISON.
ART OF PLATING ONE MATERIAL WITH ANOTHER.
No. 526,147.
Patented Sept. 18, 1894.
Fig 1.
Fig 2.
WITNESSES:
INVENTOR:

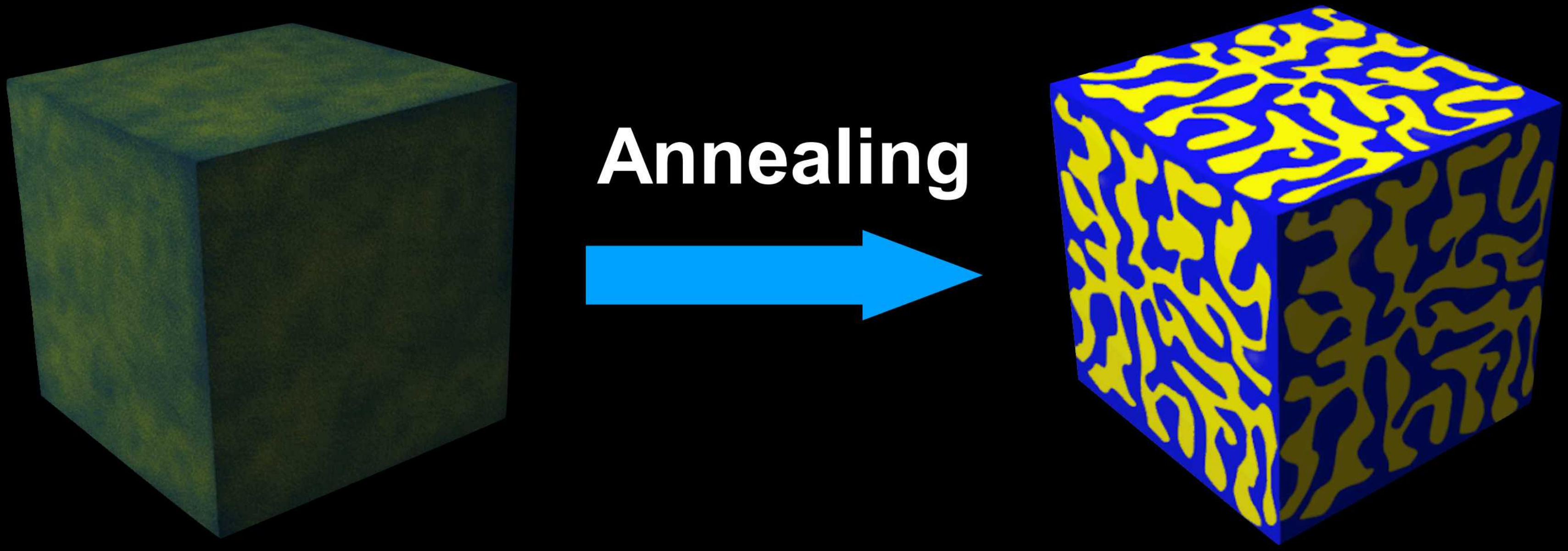

THE EDISON
NEW STANDARD
PHONO-GRAPH.
PRICE $20 COMPLETE
Produces the same results as the other famous models of the GENUINE EDISON PHONOGRAPH, using the same records and the same reproducer. Simplest, most durable, and cheapest talking-machine.
EDISON NEW STANDARD, - $20.00
" Home Phonograph - 30.00
" Spring Motor " - 75.00
" Electric " " - 75.00
ALL GENUINE PHONOGRAPHS bear this signature:
TRADE
Thomas A. Edison
MARK
Send for free Catalogue No. 18, our latest edition.
NATIONAL PHONOGRAPH CO.,
St. James Building, Broadway and 26th Street, New York.
Edison Records 50 cents each, $5.00 per dozen.

PVD is a Synthesis Route to Deposit and Engineer Thin-Films One Atom at a Time

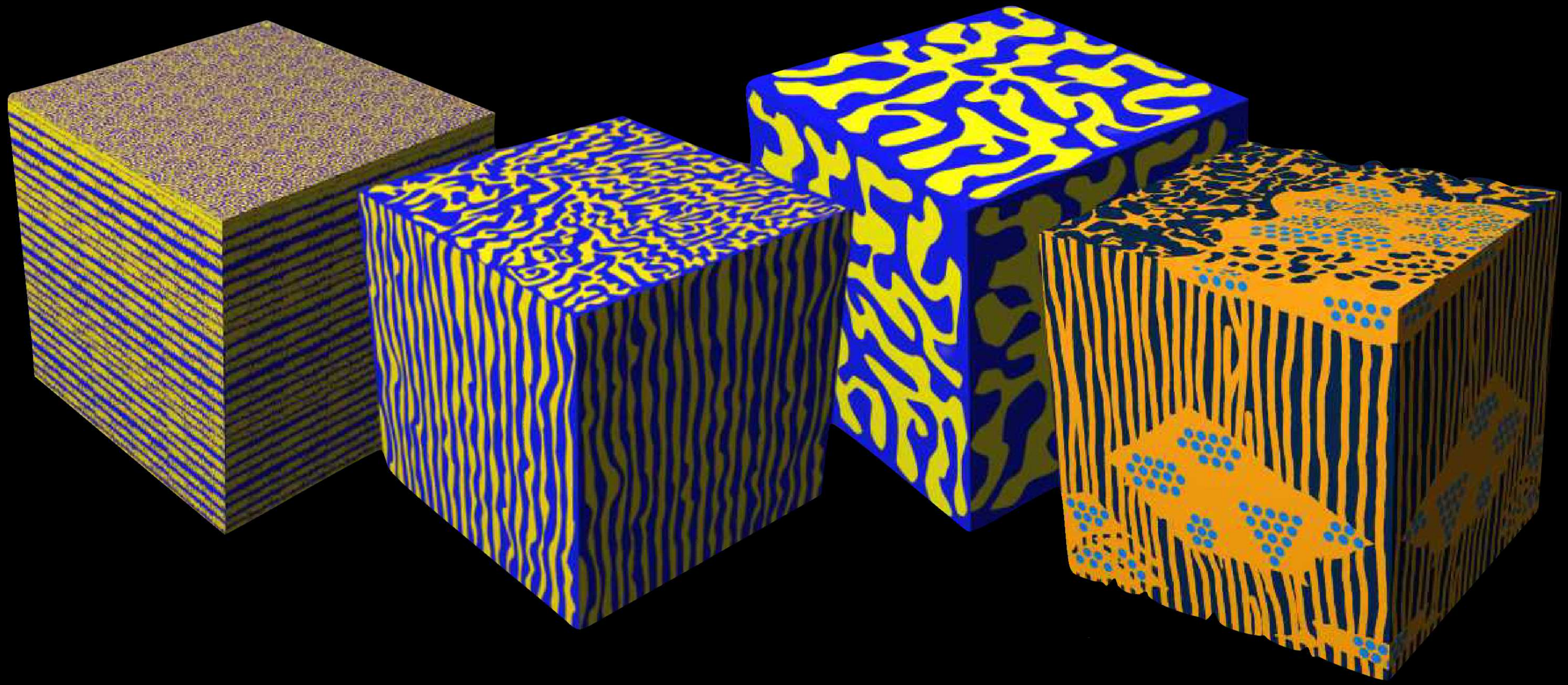


Diffrent PVD Synthesis Routes Enable (some) Control of the Morphology

RT deposition + Annealing

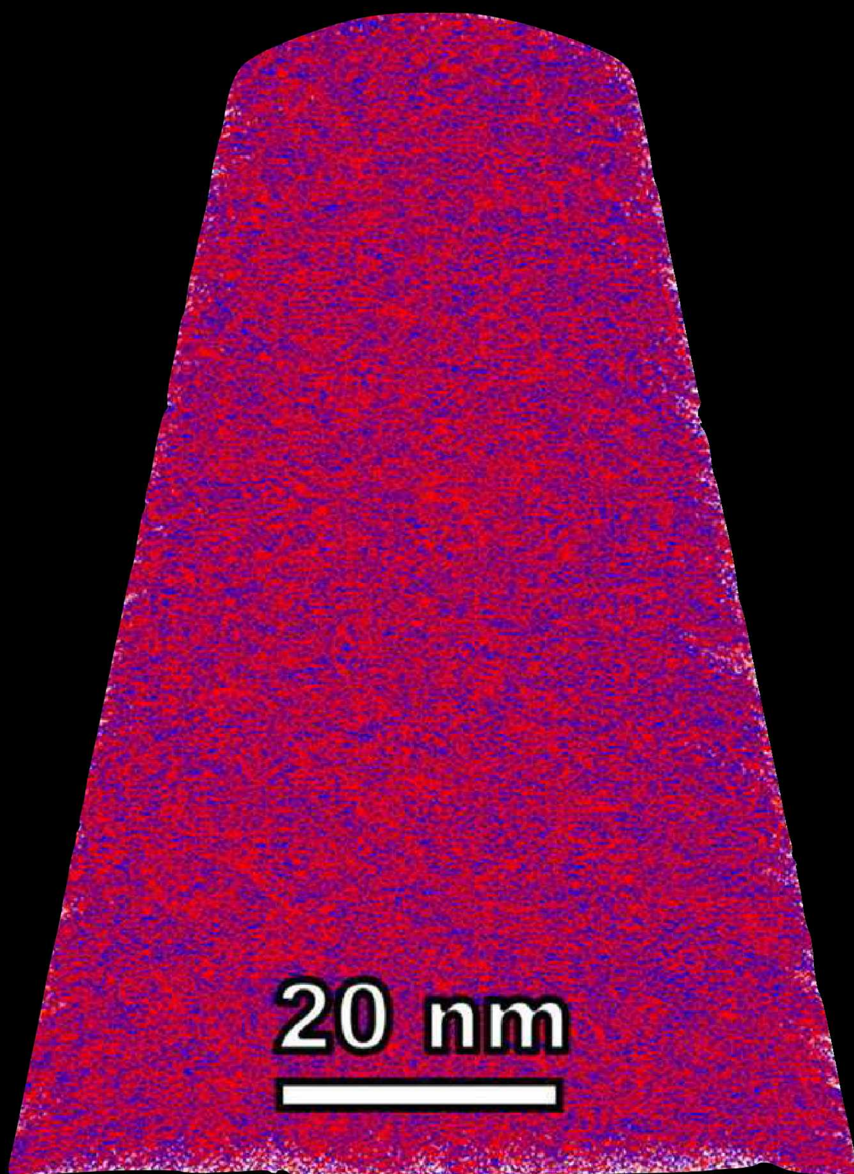


Heating during deposition

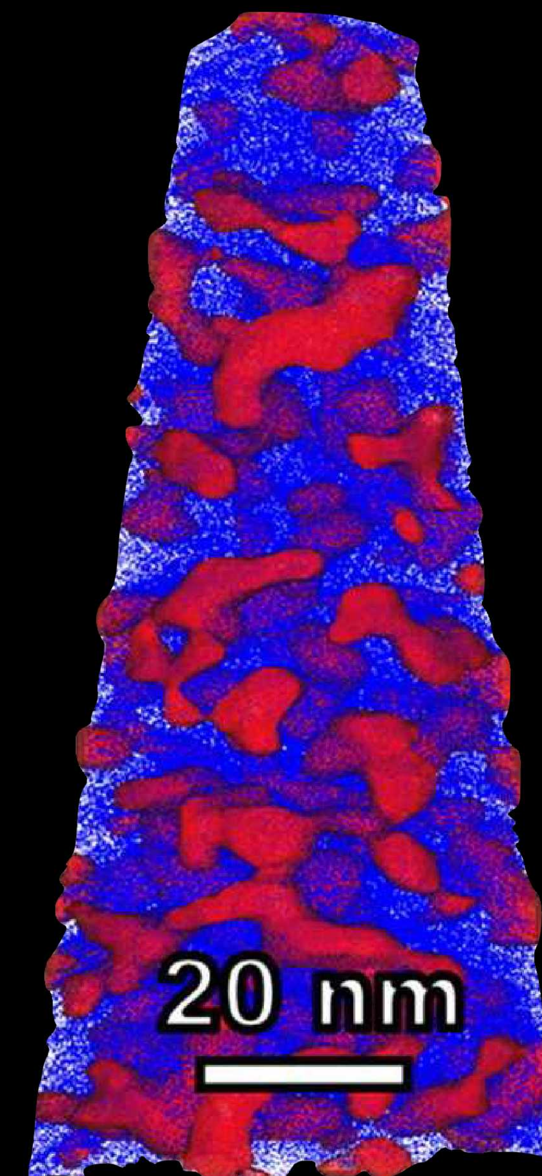


[courtesy of B. Derby]

Example 1: Phase Separation in Cu-Ta Due to Co-deposition followed by Annealing

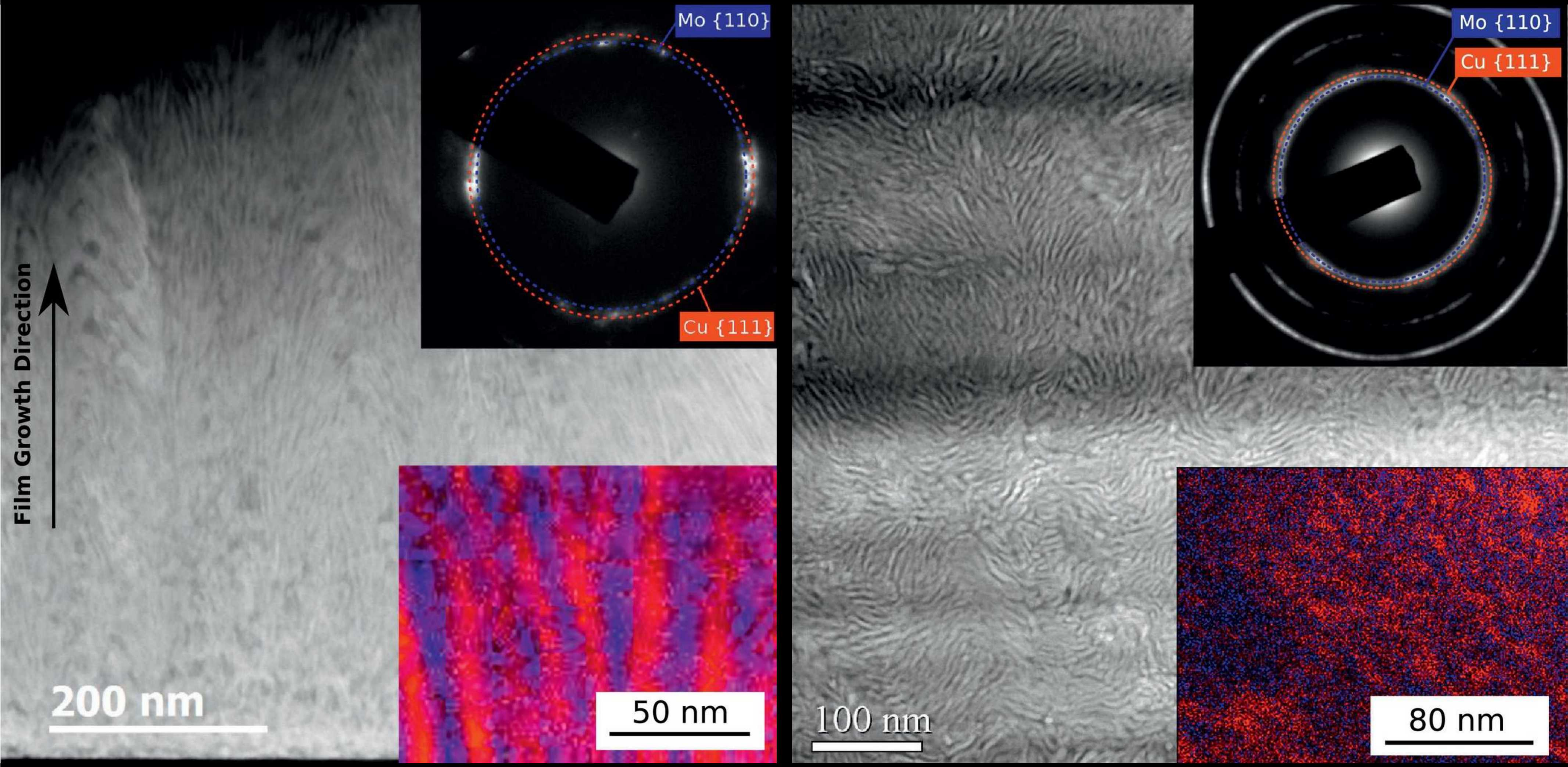


Annealing at
400 C
for 30 min



[Muller et al. Acta Mater., 2015]

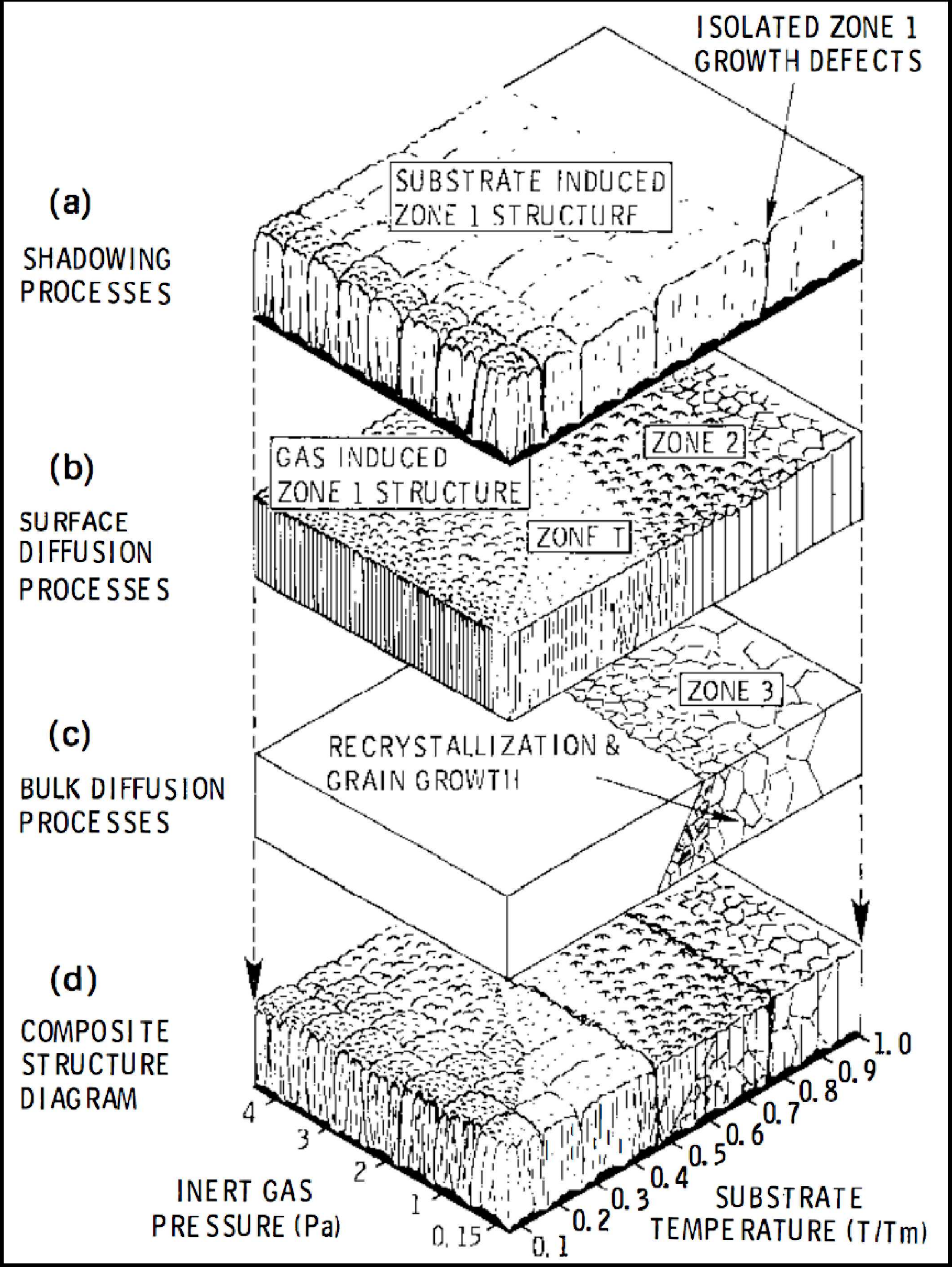
Example 2: Phase Separation in Cu-Mo By Changing the Deposition Temperature and Flux



[Derby et al. Thin Solid Films, 2018]

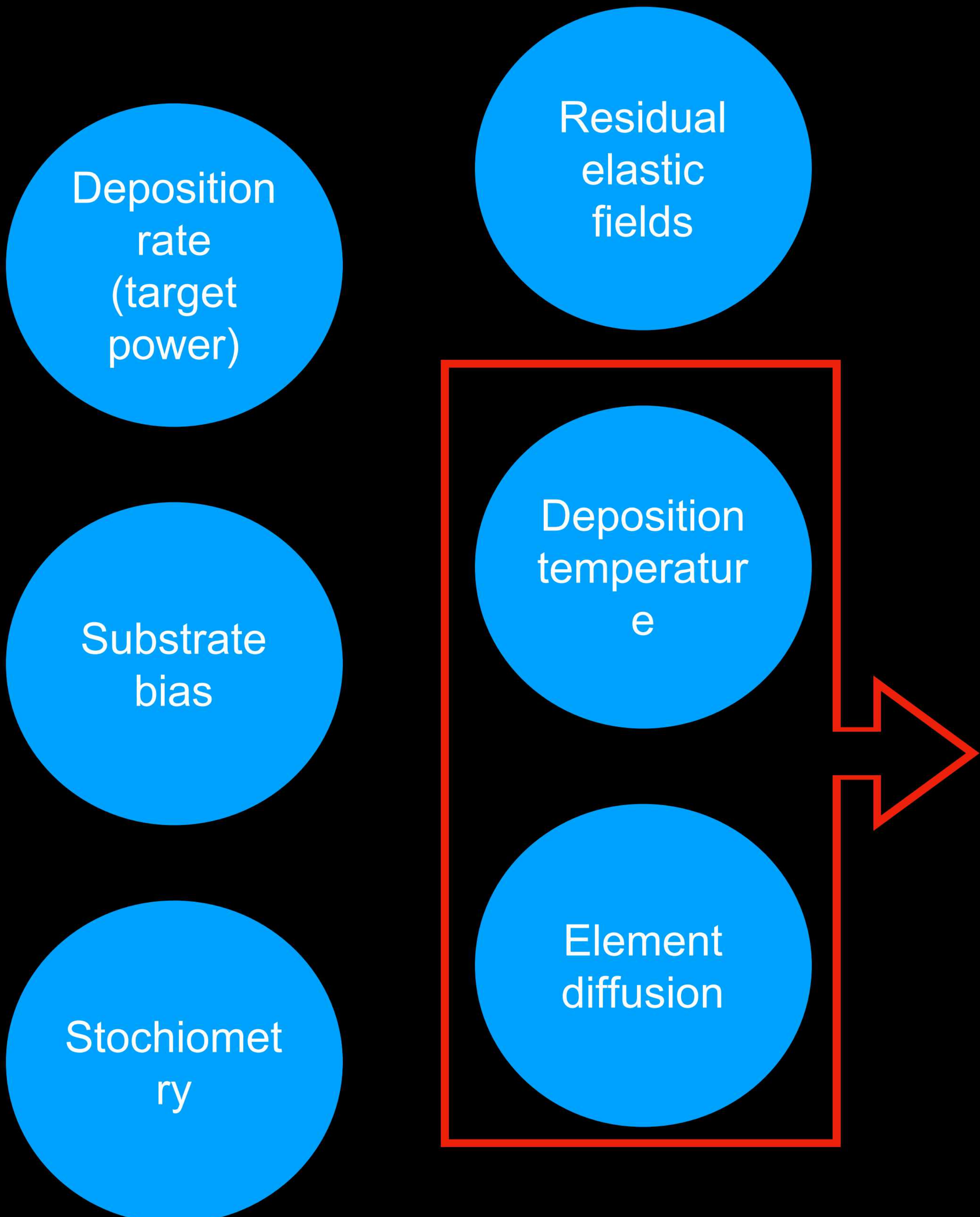
THERE ARE MULTIPLE VARIABLES AFFECTING THE RESULTING MICROSTRUCTURE

- Deposition rate (target power)
- Residual elastic fields
- Substrate bias
- Deposition temperatur e
- Stochiomet ry
- Element diffusion



[Thornton, Annu. Rev. Mater. Sci., 1977]

The Characteristic Size is Governed by the Competition Between Bulk and Surface Ordering



BULK: $\ell_{\mathrm{bulk}} = \sqrt{2D\tau}$

THIN-FILM: $\ell_{\mathrm{thin\ film}} = \sqrt{\dfrac{2D\lambda}{\nu}}$

- D **Inter-diffusivity**
- τ **Atom dwell time**
- λ **Surface layer thickness**
- ν **Deposition rate**

[Thornton, Annu. Rev. Mater. Sci., 1977] [Adams et al., J. Mater. Res., 1991]

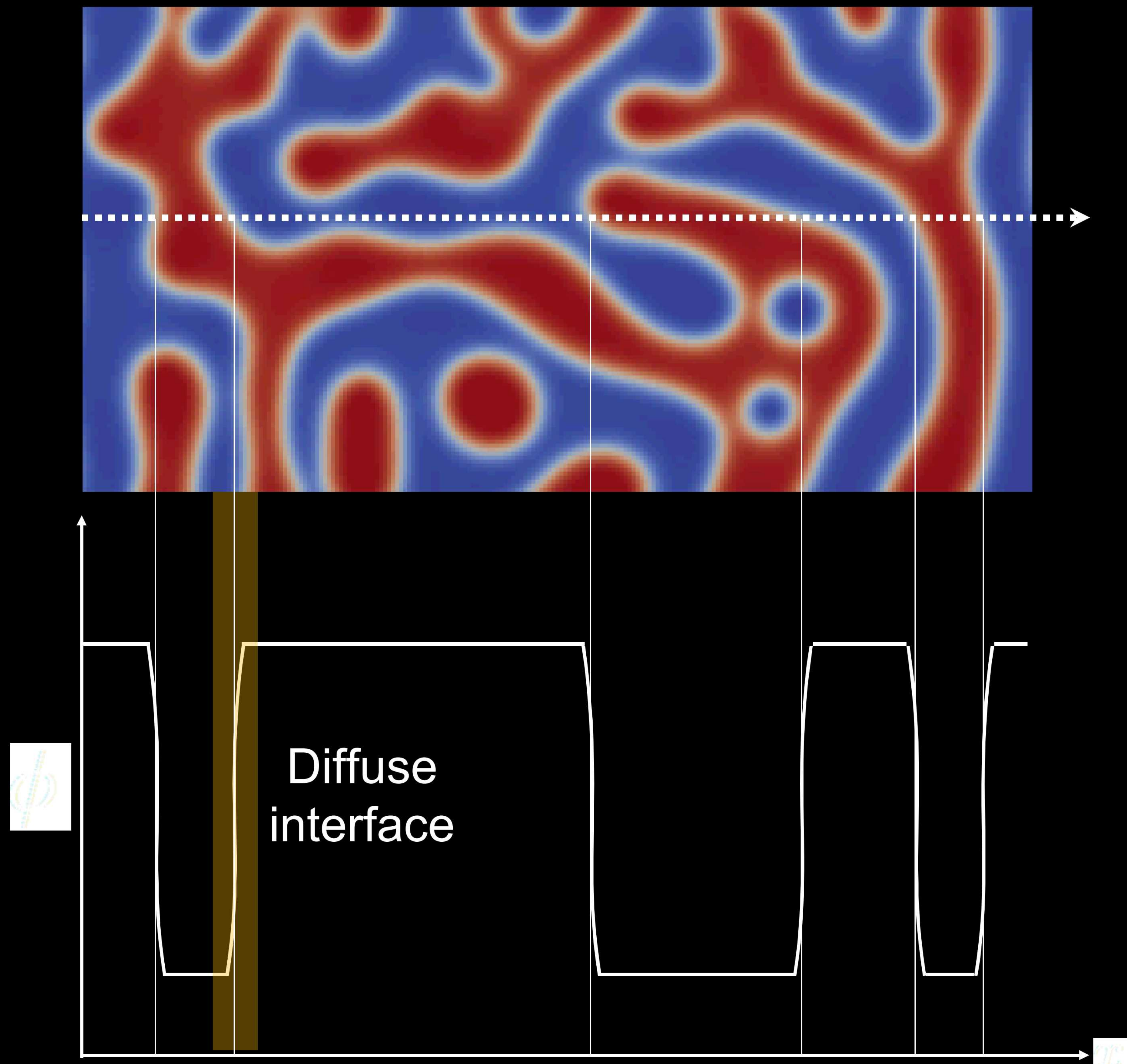
The Synthesis Challenge

- **Broad range of deposition conditions**
  - Target Power
  - Temperature
  - Shadowing

- **Broad range of species**
  - Surface vs. Bulk diffusion

- **Beyond single phase systems**
  - Competition in Phase Ordering
  - Elastic mismatch

Phase Field 101: Modeling Microstructure Evolution



Phase Field 101: Modeling Microstructure Evolution

$$F = \int \left[f(\eta_1, \ldots, \eta_p, c_1, \ldots, c_q) + \sum_{i=1}^{n} \alpha_i (\nabla c_i)^2 + \sum_{i,j=1}^{3} \sum_{k=1}^{p} \beta_{ij} \nabla_i \eta_k \nabla_j \eta_k \right] d\Omega$$

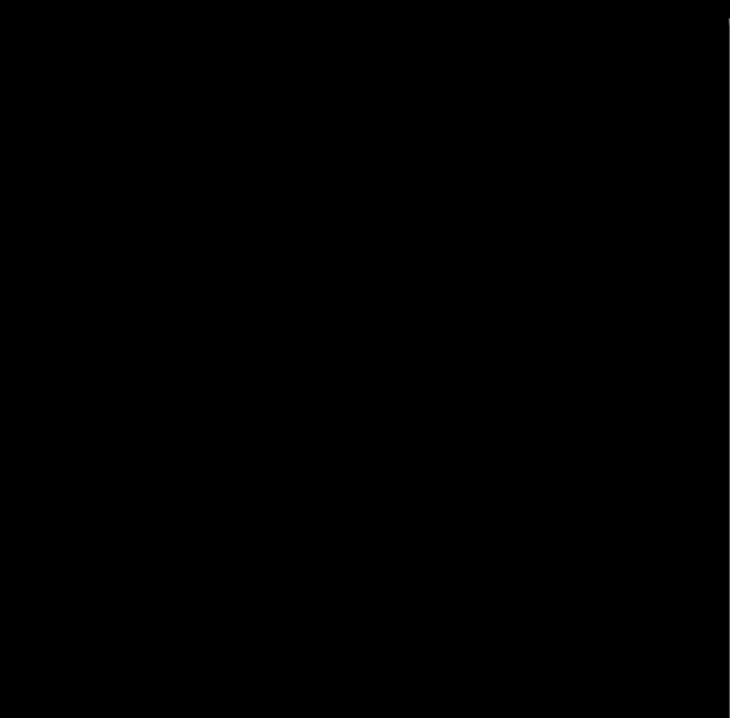
Allen-Cahn:
Non-conserved

$$\frac{\partial \eta_p}{\partial t} = -M_{pq} \frac{\delta F}{\delta \eta_q}$$

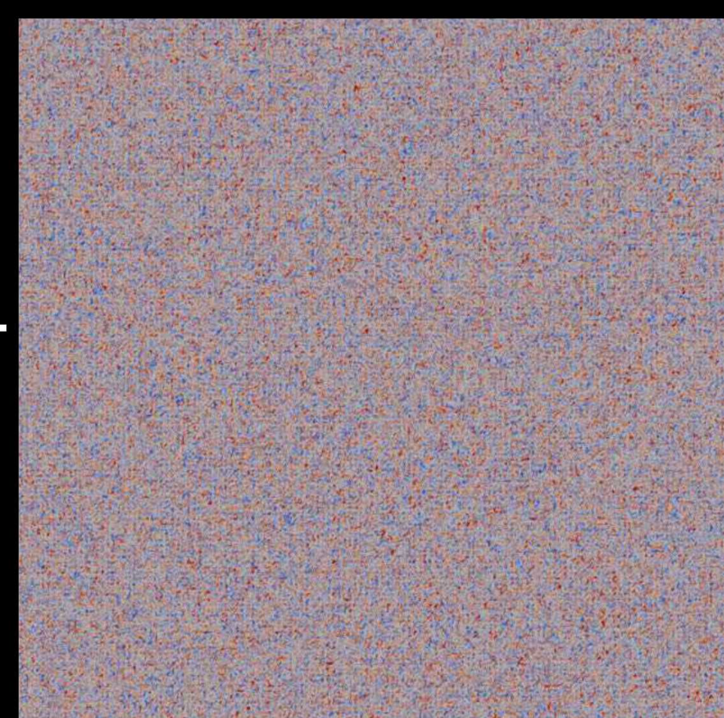
Cahn-Hillard:
Conserved

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left(M_{ij} \nabla \frac{\delta F}{\delta c_j} \right)$$

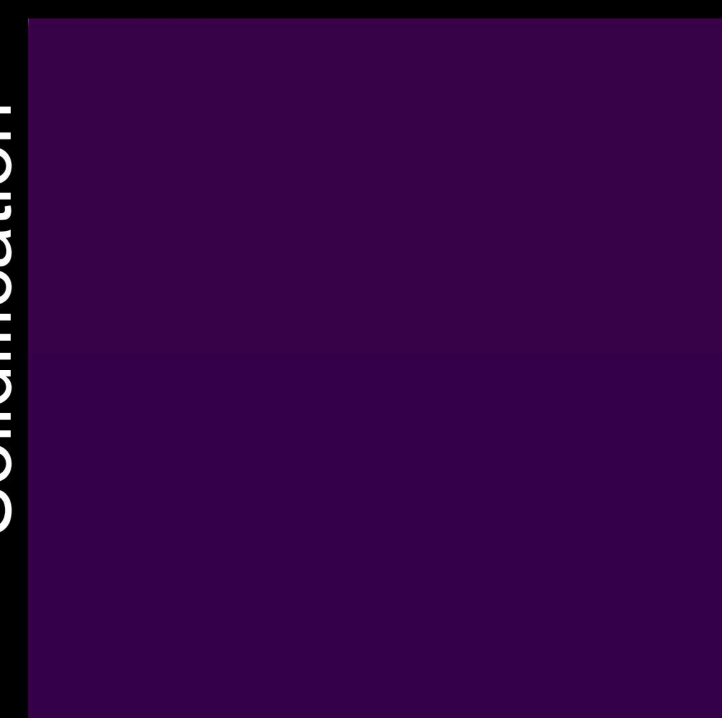
Grain growth



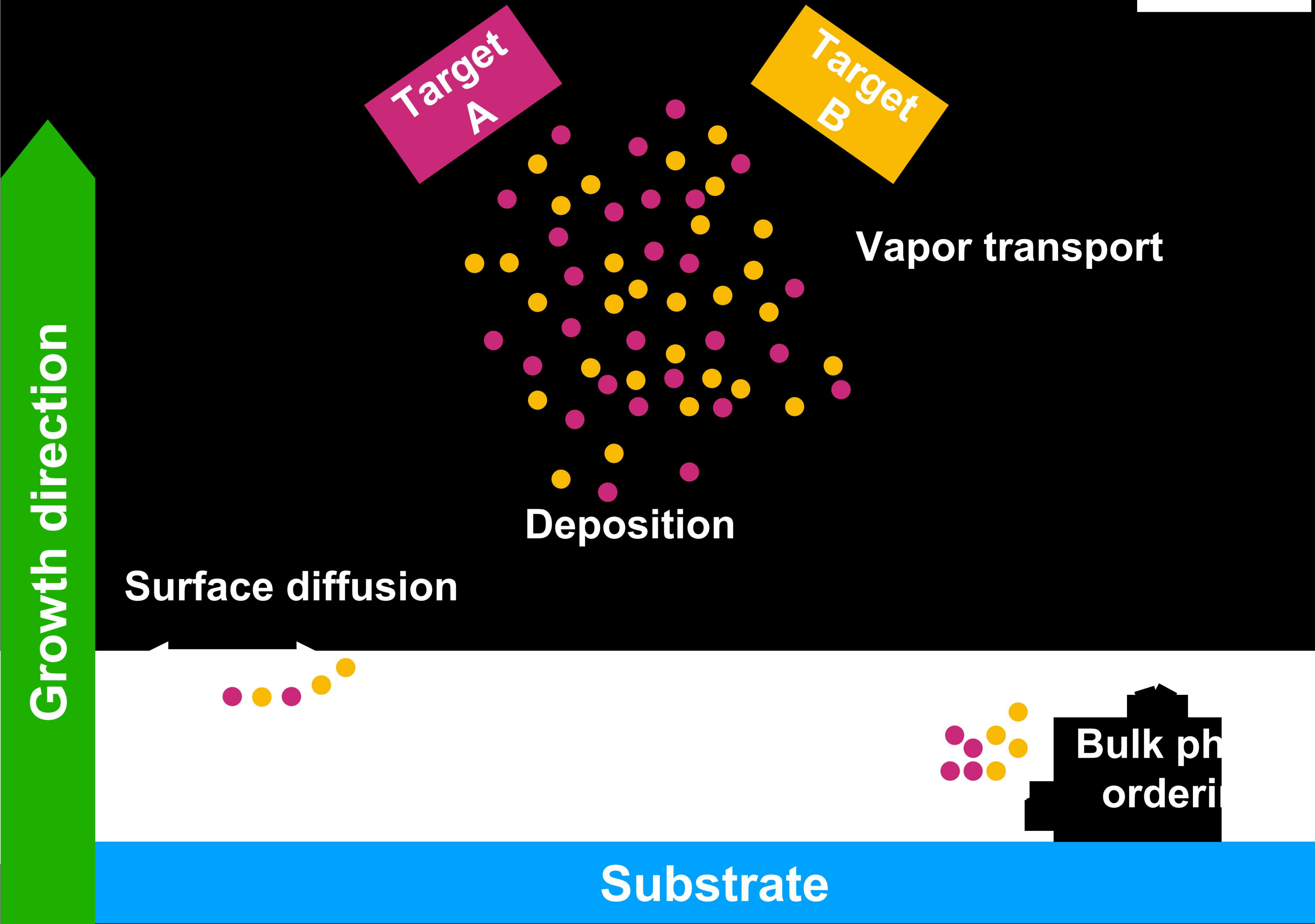
Spinodal decomposition



Solidification



Modeling Vapor Deposition with Phase Field



Modeling Vapor Deposition with Phase Field

$$F = \int \left[f_\phi + \frac{\kappa_\phi^2}{\cdots} \cdots + s(\phi) \left(f_c \cdots + \frac{\kappa_c^2}{2} (\nabla c)^2 \right) \right] d\Omega$$

Target A

Target B

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (D(\rho) \nabla \rho) - \nabla \cdot (\rho \vec{u}) - S(\vec{n})$$

Vapor transport

Vapor-to-solid

Vapor density (background pressure)

Deposition ve

Shadowing ef

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left(M(\phi) \nabla \frac{\delta F}{\delta \phi} \right) + S(\vec{n})$$

Deposition

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(D(c) \nabla \frac{\delta F}{\delta t} \right)$$

Surface diffusion

$$M_c(\phi, c) = M^{\text{Bulk}} + M^{\text{Surf}}$$

$\phi = -1$

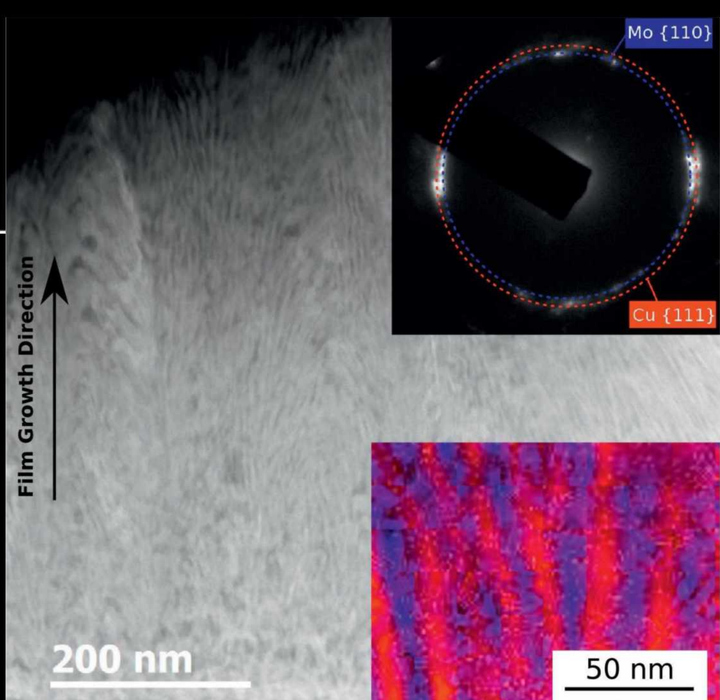
$\phi = 1$

Bulk phase orderin

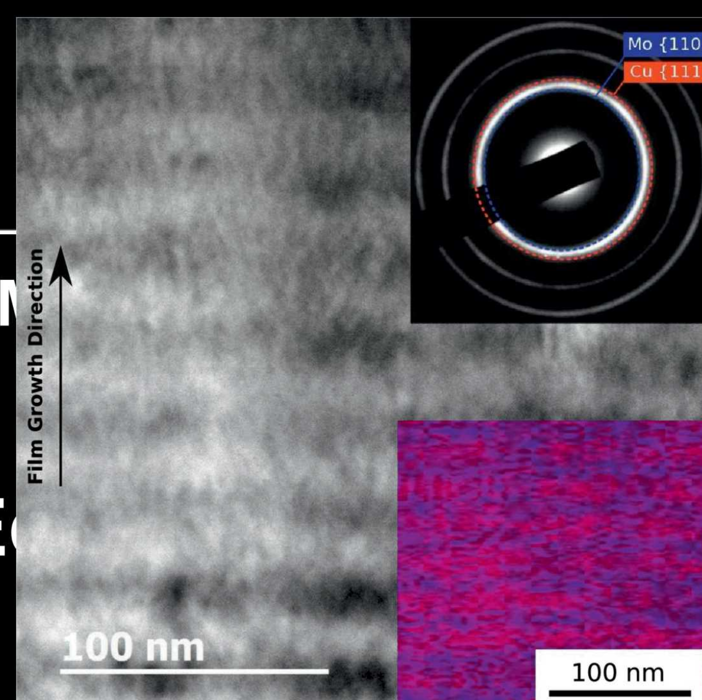
Substrate

Synthesis Routes Enable Access to at Least Four Classes of Concentration Modulations

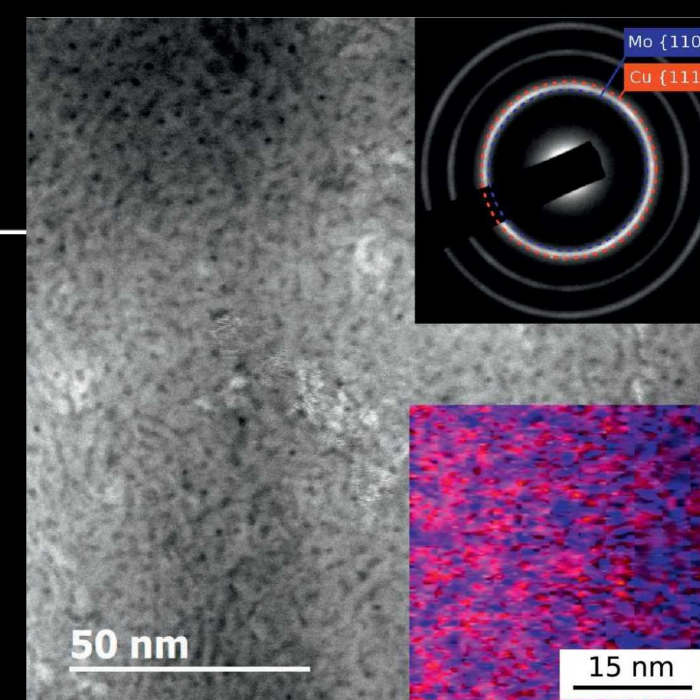
Lateral (LCM)



Vertical (VCM)



Random (RCM)



[Derby et al. Thin Solid Films, 2018]

Synthesis Routes Enable Access to at Least Four Classes of Concentration Modulations

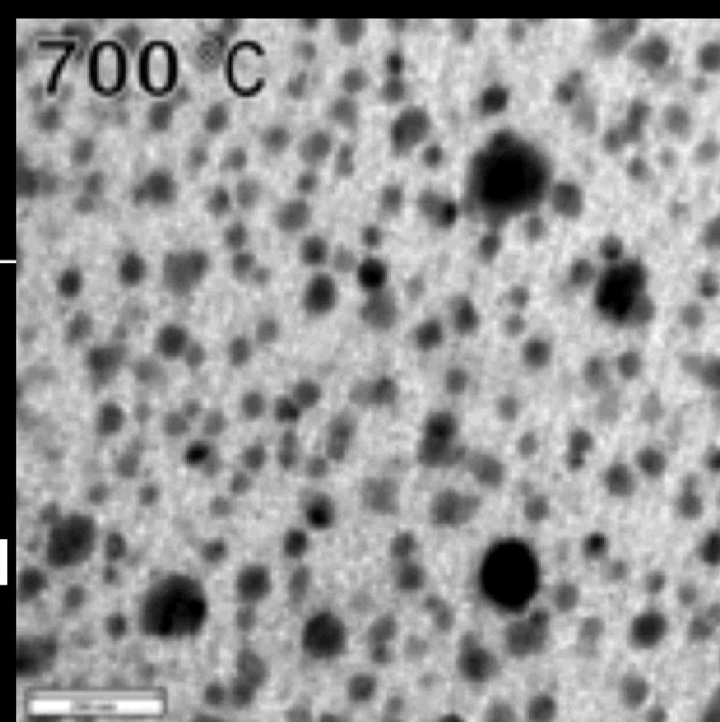
Raft-like lateral structure

Nanoprecipitates (NPCM)

Hybrid (NPCM/LCM)

Slow deposition rate

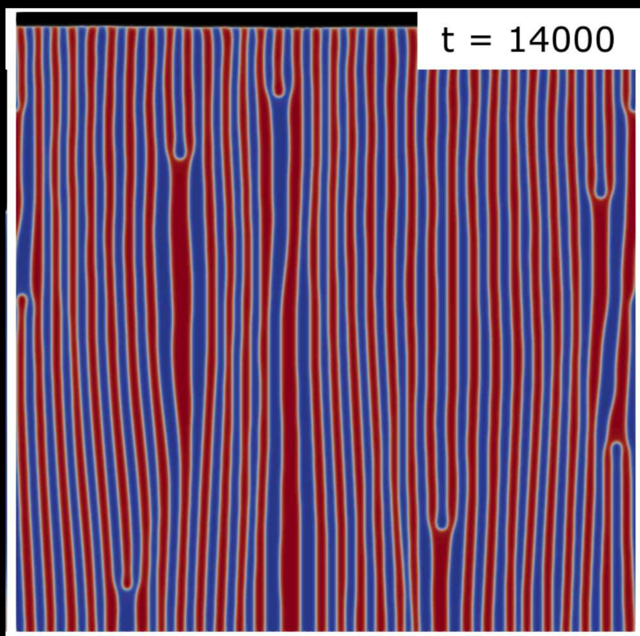
High deposition rate



UN … **TION**

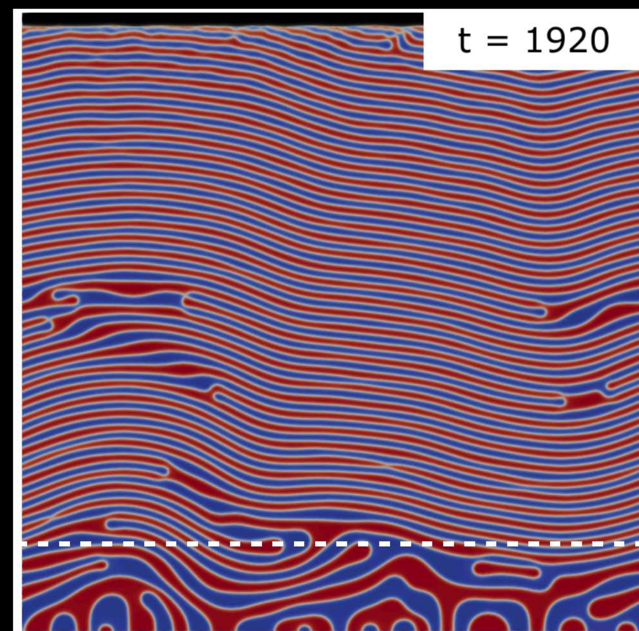
The Formation and Evolution of These Morphologies Stem From Complex Competitions

LCM



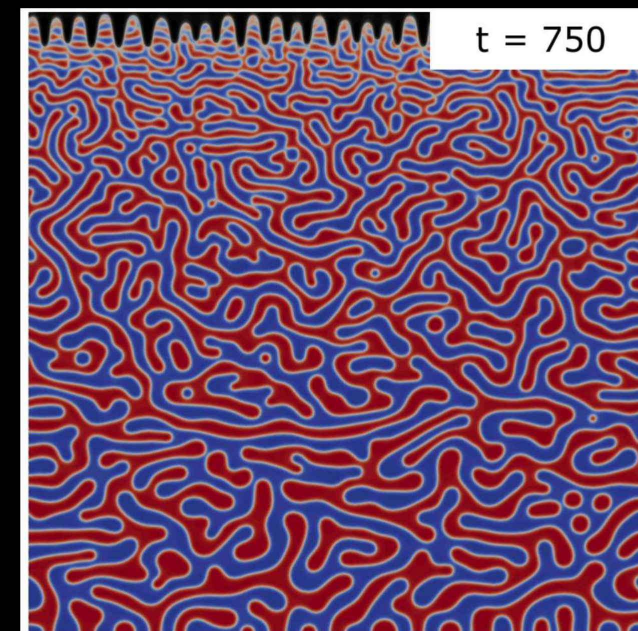
- Surface and bulk ordering much faster than slow deposition
- Deposited material diffuses further and faster along surface before being buried by “next” layer of deposited material

VCM



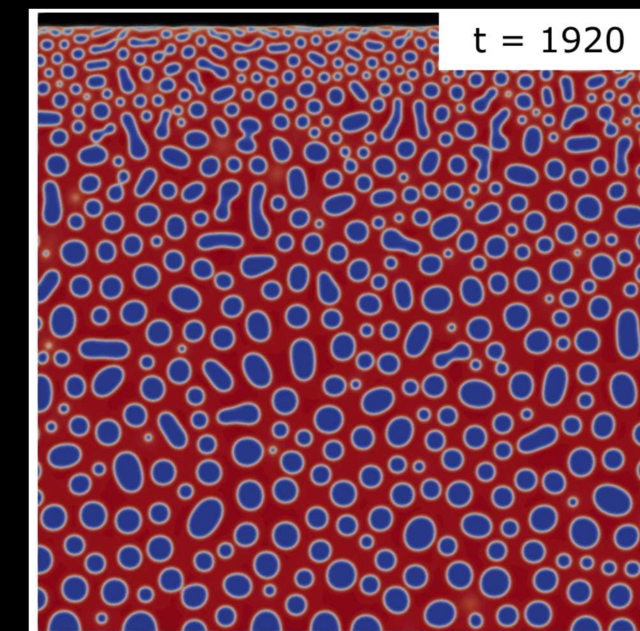
- Critical thin thickness above which interfacial contribution is energetically favored
- “Frozen” bulk approximation

RCM



- Rapid transition to “bulk” regime
- Classical spinodal decomposition
- Formation of hillocks and surface roughness due to continuous perturbation of free surface

NPCM



- Interparticule diffusion interactions (Ostwald ripening)
- Broader range of deposition conditions for unequal phase fraction

Phase Kinetics Has an Impact on the Resulting Concentration Modulation

Majority species with faster kinetics

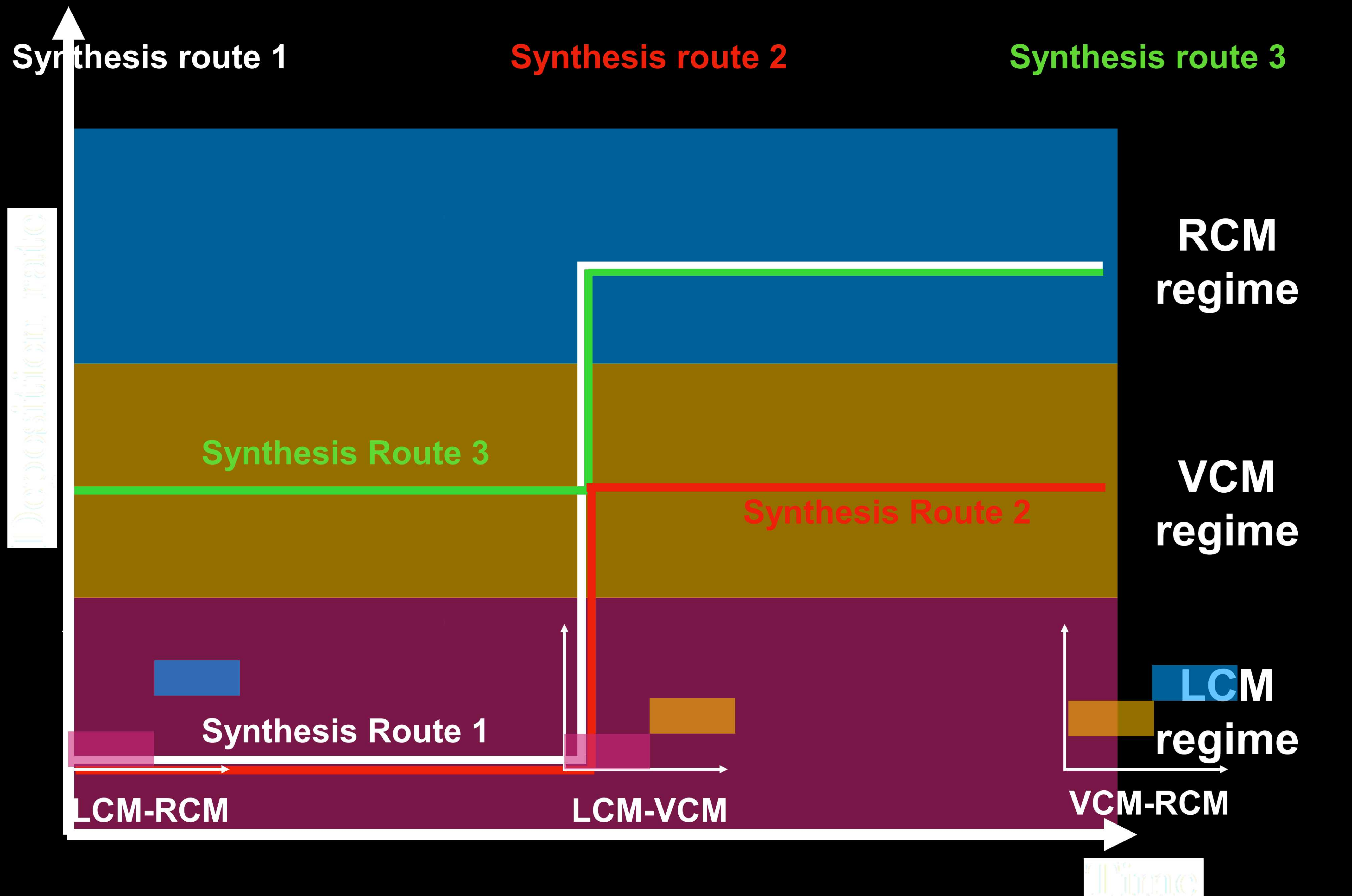
Equivalent kinetics between species

Minority species with faster kinetics

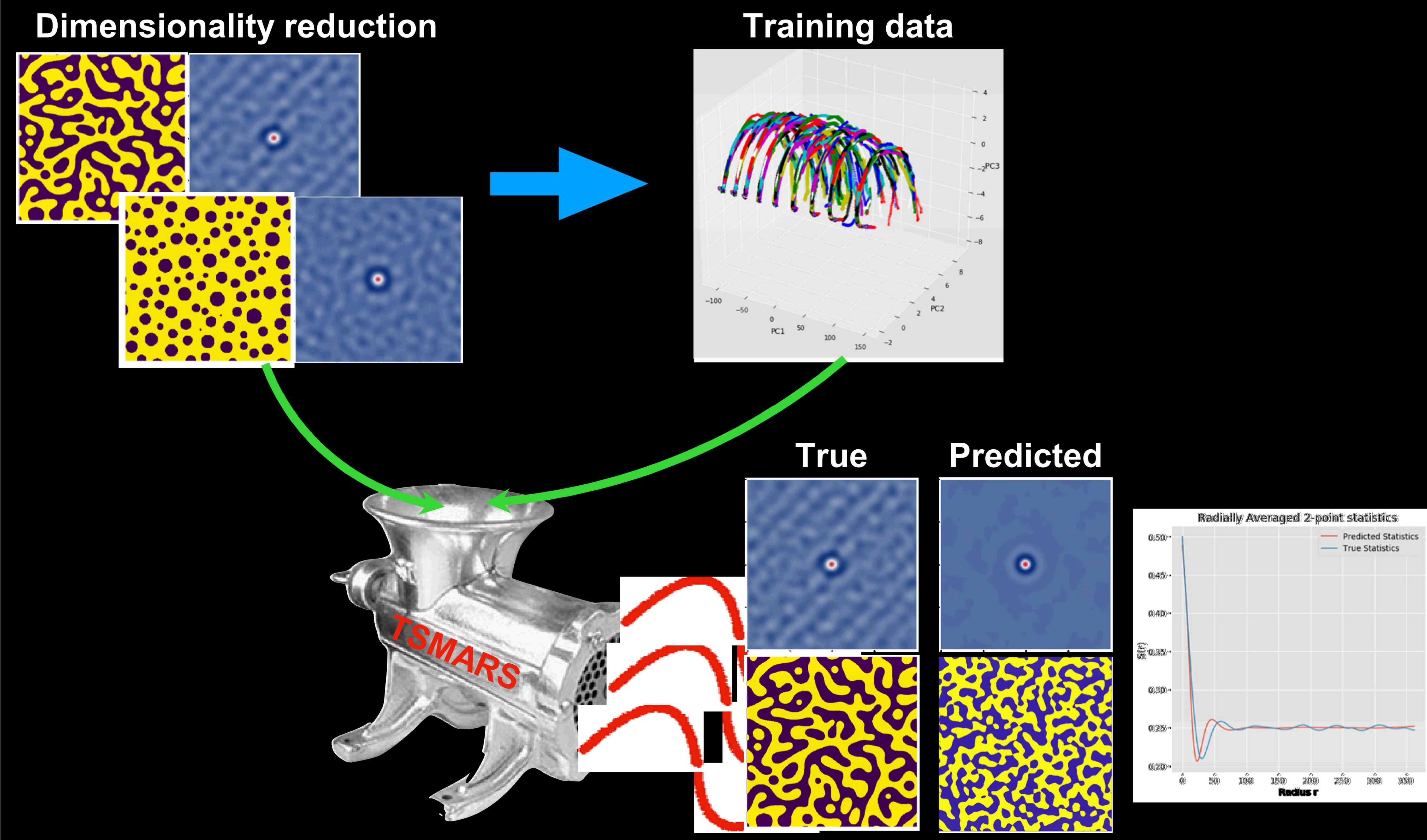
Elastic Effects Can Have an Impact on the Size and Shape of the Phase Ordering

Majority species is soft | **No elasticity** | **Majority species is hard**

Going Beyond Simple Synthesis Routes…
Multi-modulation morphologies



Going Beyond Phase Field Modeling… Machine-Learned Enabled Process-Structure Predictions



Concluding Remarks

- **Modeling of the growth of bicontinuous nanocomposites thin-films during PVD**
  - Generalized phase field model.
    - MEMPHIS: CINT user phase-field capability
  - Transport, surface diffusion, chemo-mechanical coupling during phase ordering
- **Insights into competing formation mechanisms**
  - Lateral, vertical, random, nanoprecipitate morphologies through specific combinations of deposition rate, phase fraction and phase properties
  - Guiding the choice of alloy species and deposition conditions to obtain specific nanostructured morphologies
  - Advanced regression/machine learning models to reverse engineering deposition conditions

BIG SCIENCE AT THE NANOSCALE

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– an Office of Science national user facility –

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Research areas:

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- Nanophotonics and Optical Nanomaterials
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- Soft, Biological, and Composi

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