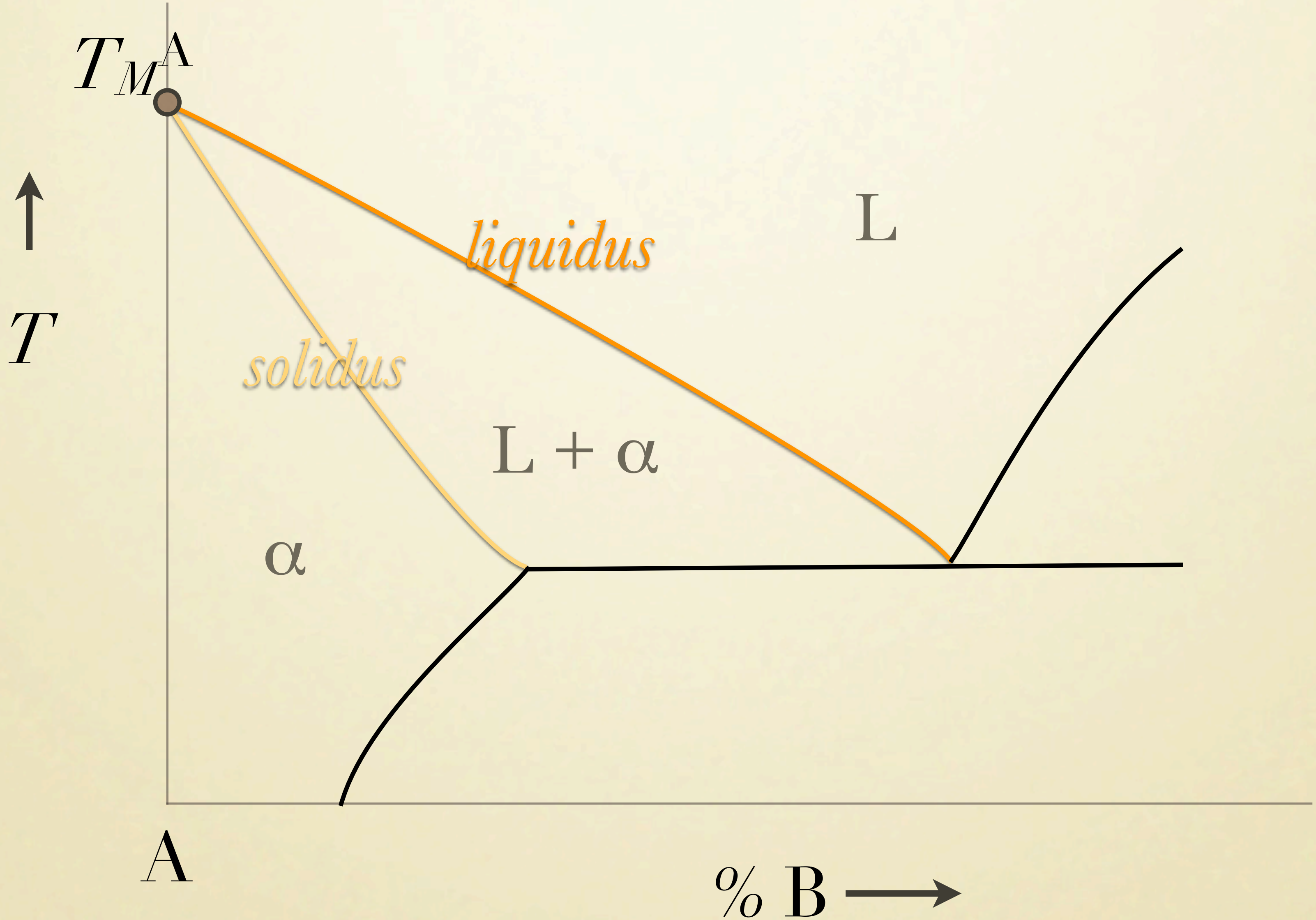
Nanomaterials Synthesis and Processing

Solidification Processing

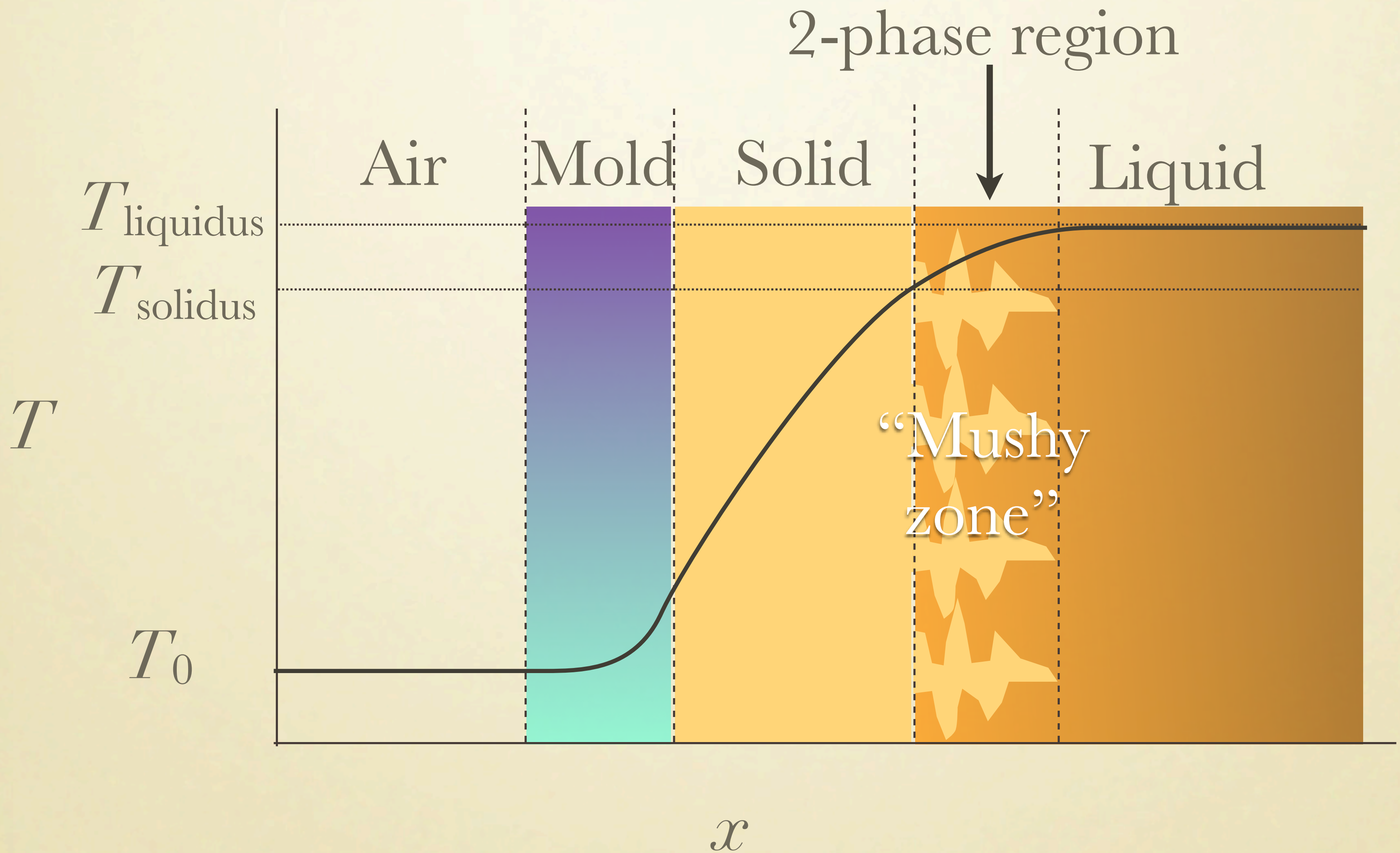
“Melting Point”

- Elements melt/solidify at a single temperature (T_M)
- Alloys melt/solidify over a range of temperatures

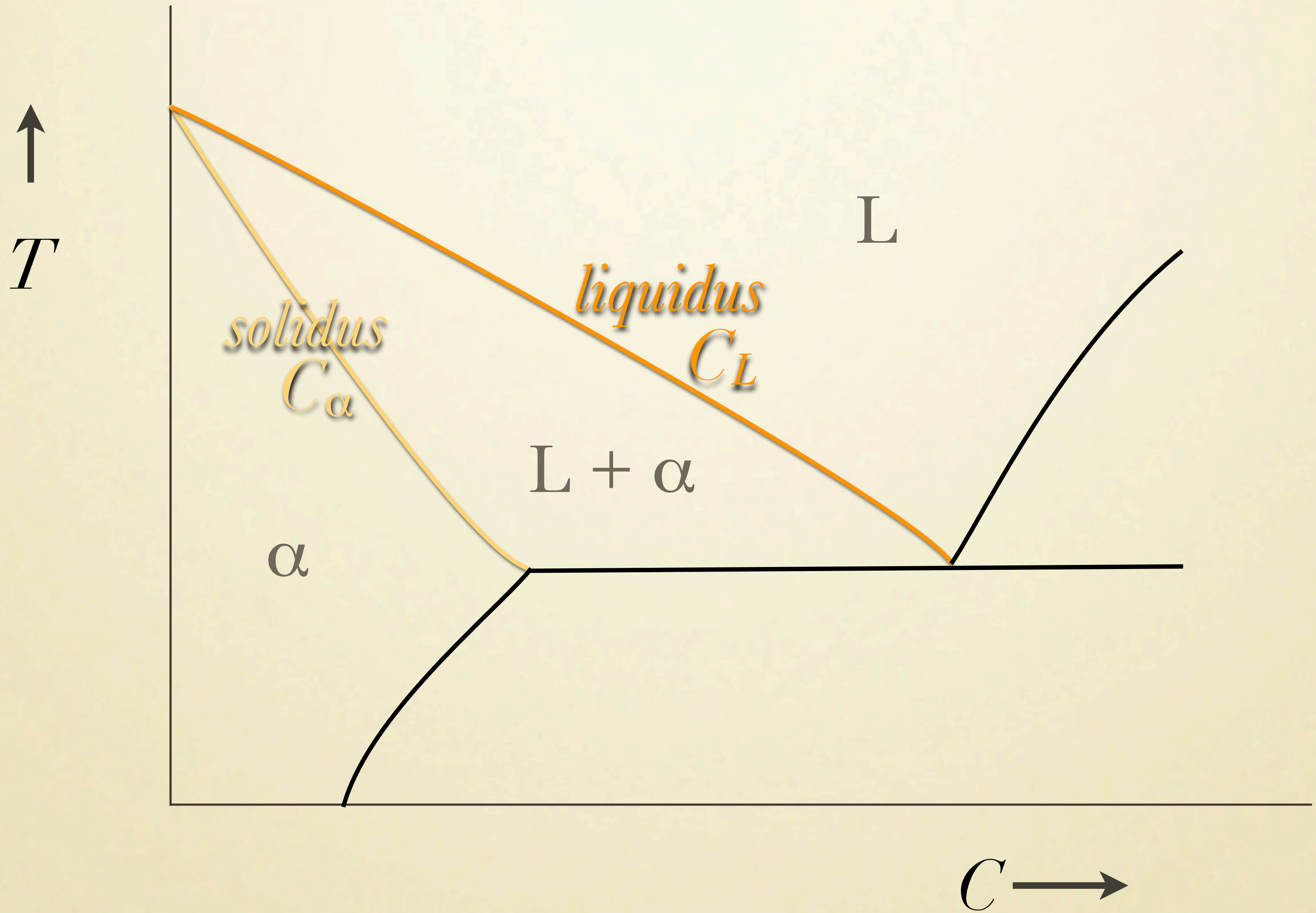
"Two-Phase" Field

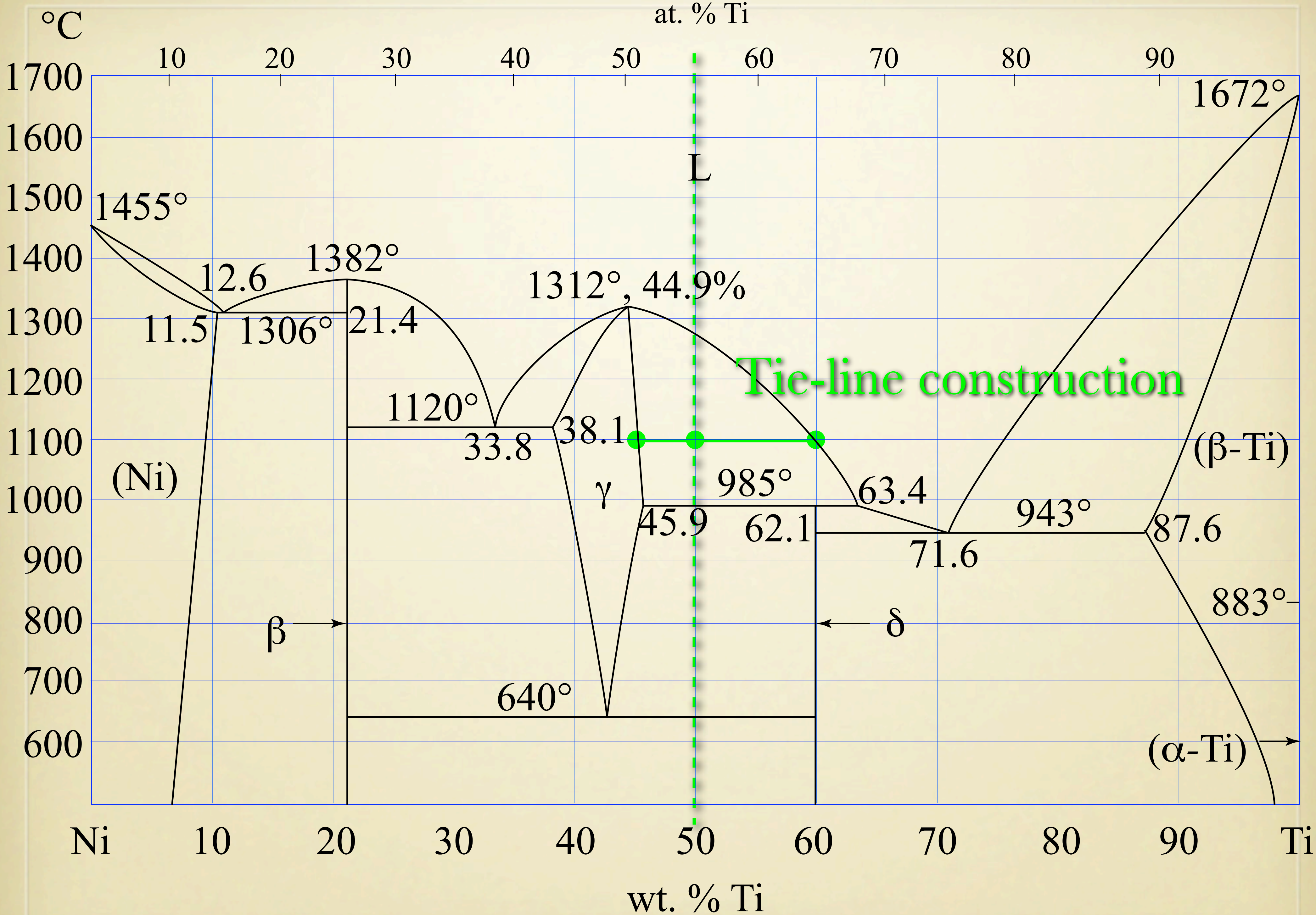


Alloy Solidification

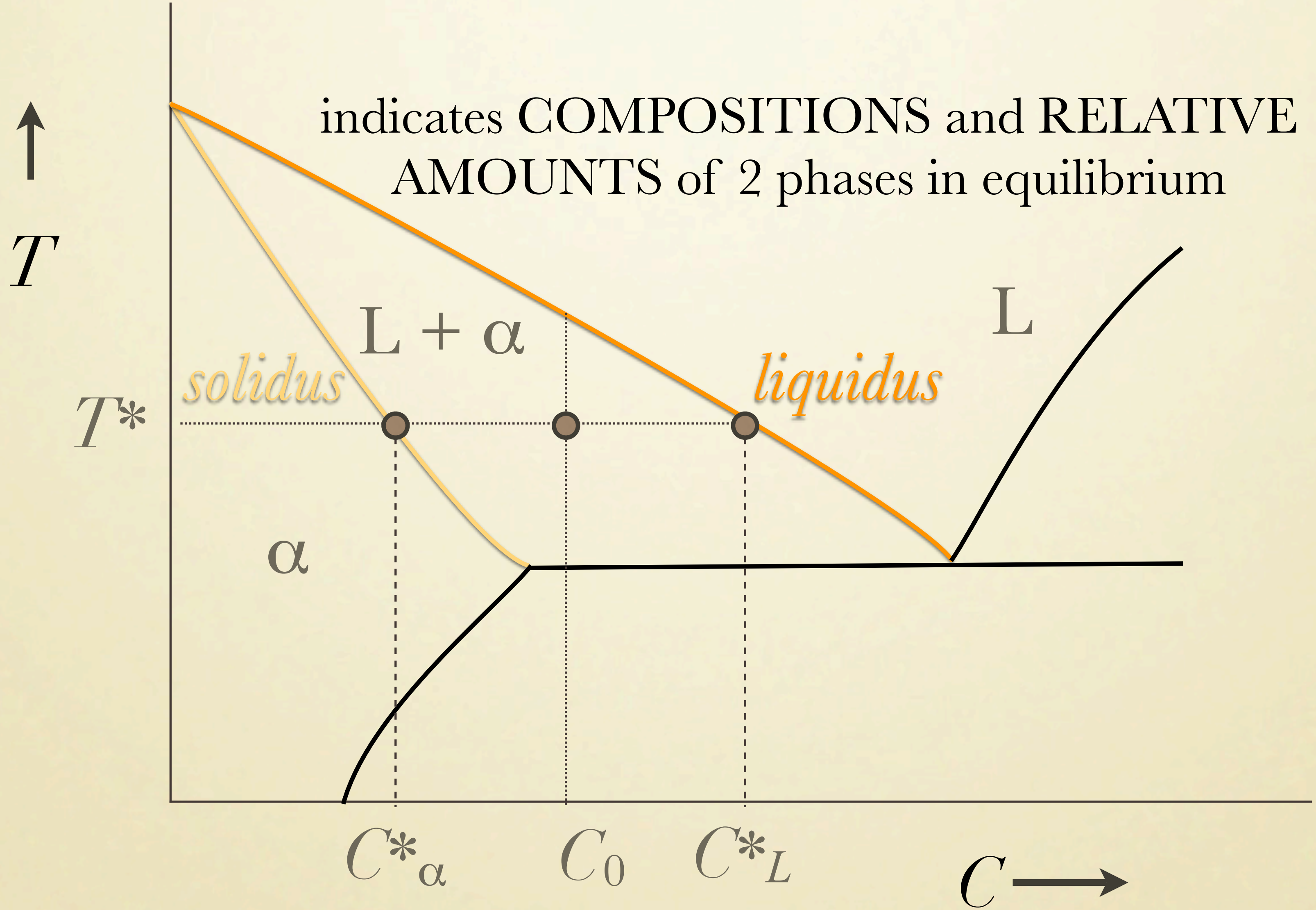


Solute Partitioning

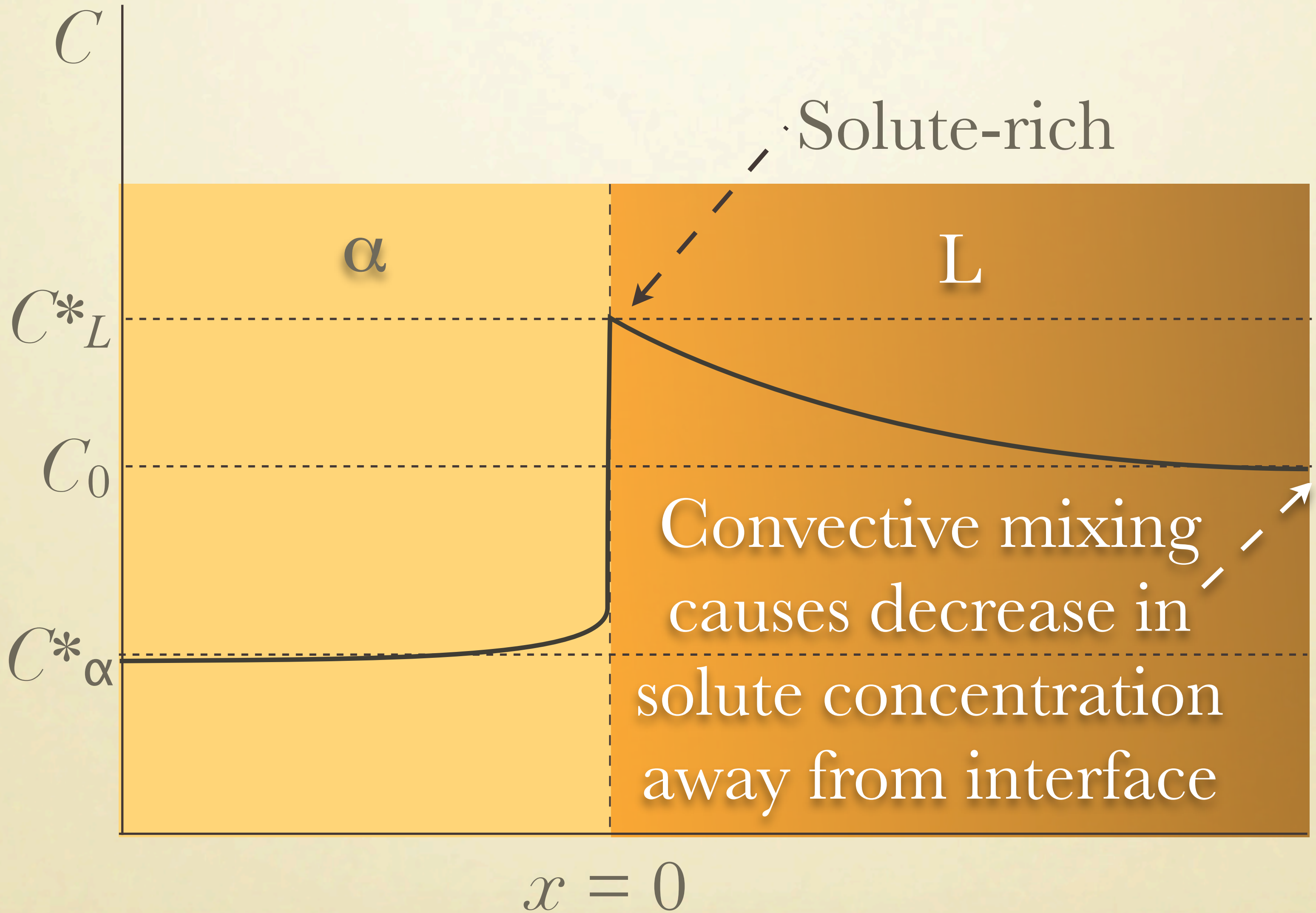



°C
at. % Ti
10
20
30
40
50
60
70
80
90
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
L
1672°
1455°
1382°
12.6
1312°, 44.9%
11.5
1306°
21.4
Tie-line construction
1120°
38.1
33.8
(β-Ti)
(Ni)
γ
985°
63.4
943°
45.9
62.1
87.6
71.6
883°
β
δ
640°
(α-Ti)
Ni
10
20
30
40
50
60
70
80
90
Ti
wt. % Ti

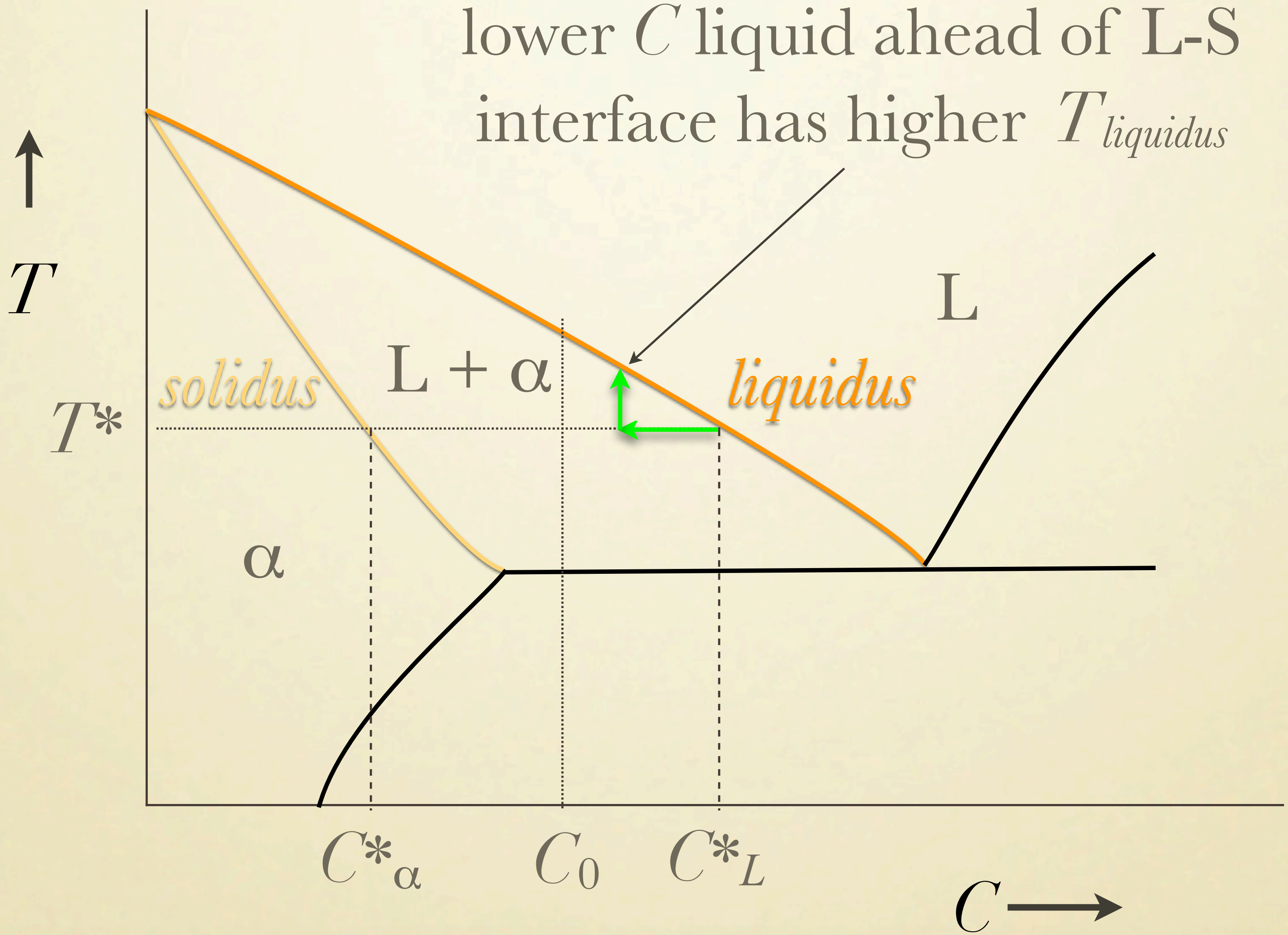
Tie-Line Construction



Boundary Layer

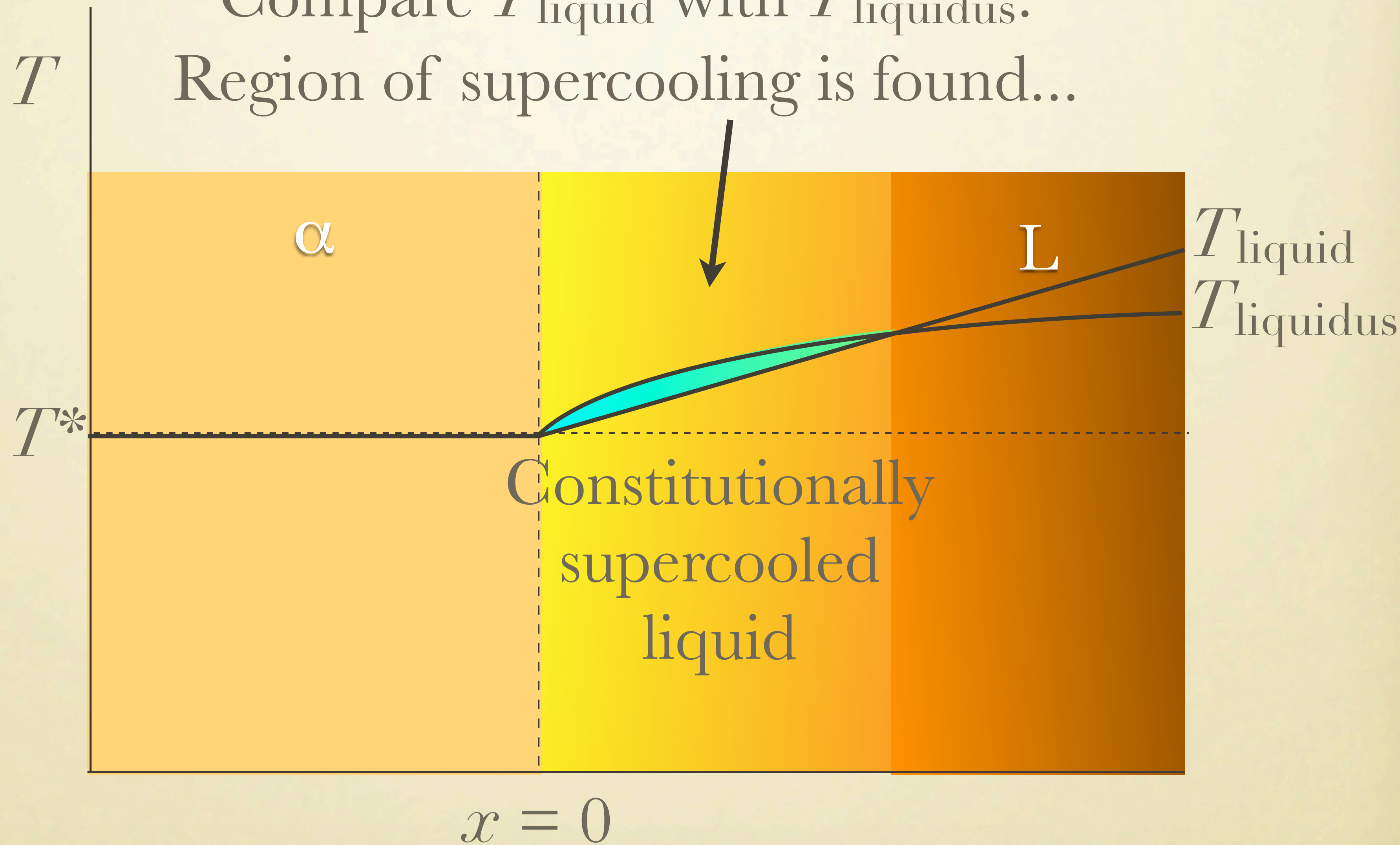


Effective Liquidus



Supercooling

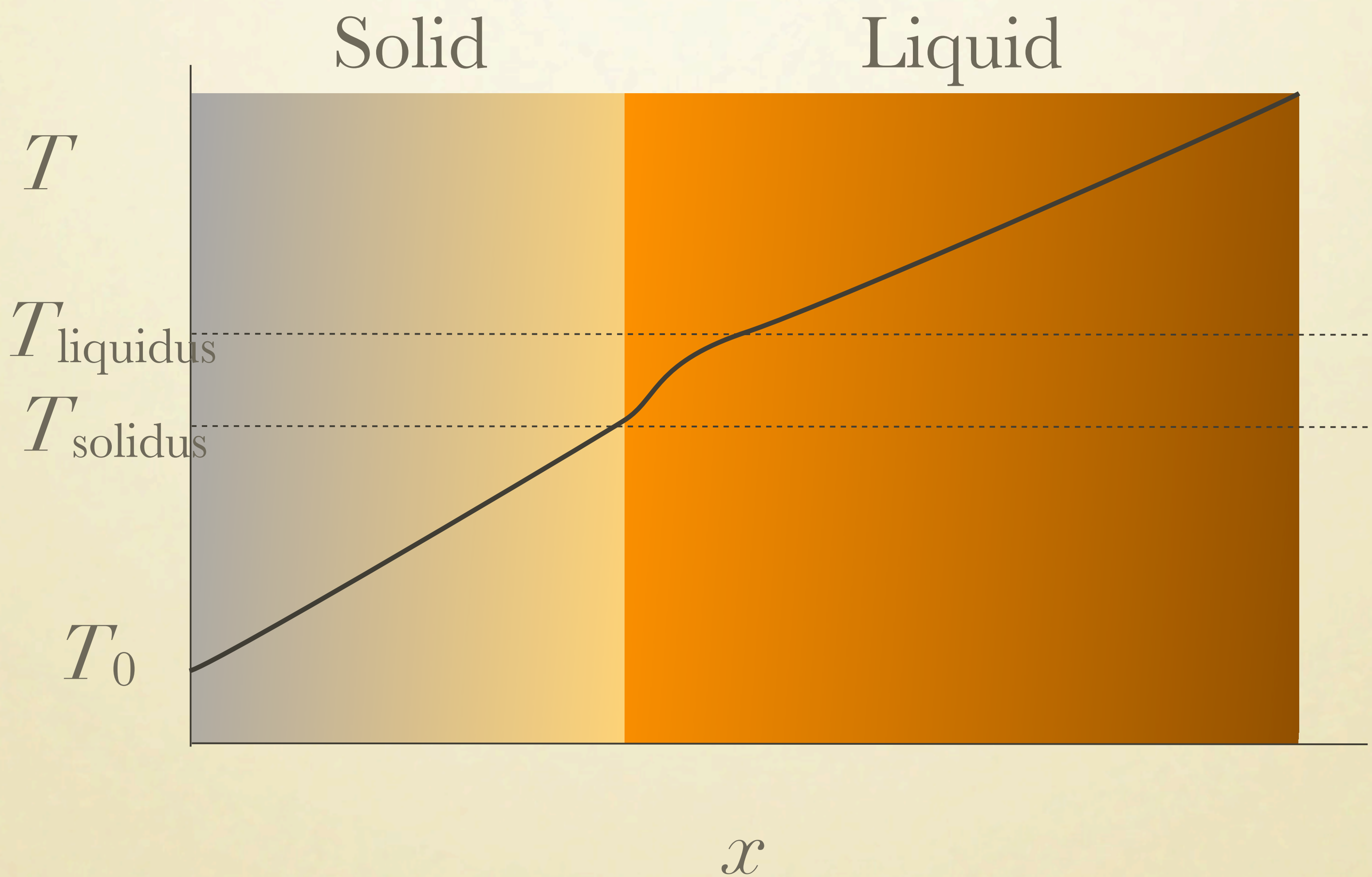
Compare T_{liquid} with T_{liquidus}.
Region of supercooling is found...



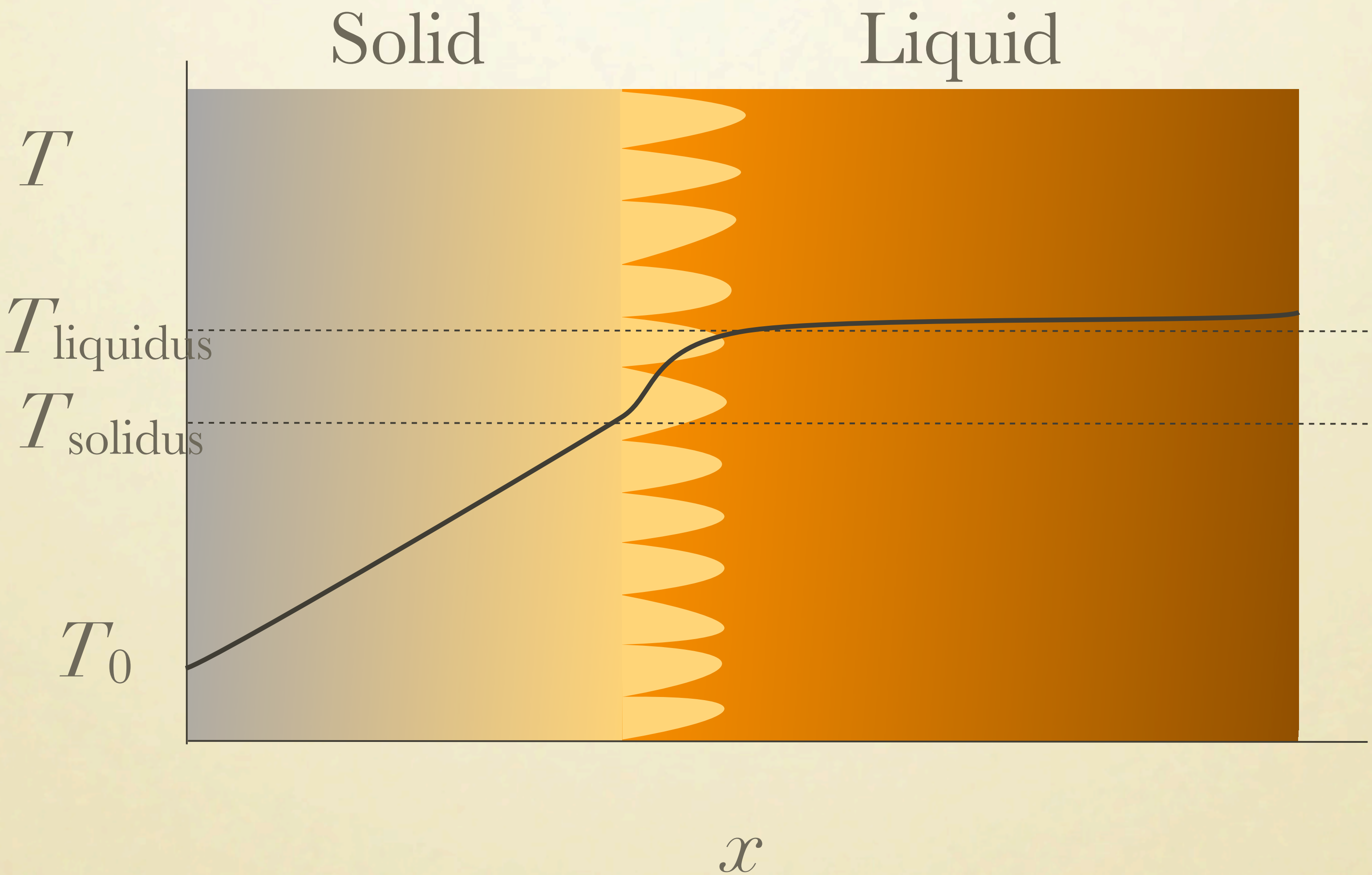
Interface Morphology

- At slow growth rates, L-S interface can be “planar.”
- As growth rate increases, L-S interface becomes “cellular.:
- At high growth rate, L-S interface is “dendritic.”
- Dendritic growth directions are preferred crystallographic directions

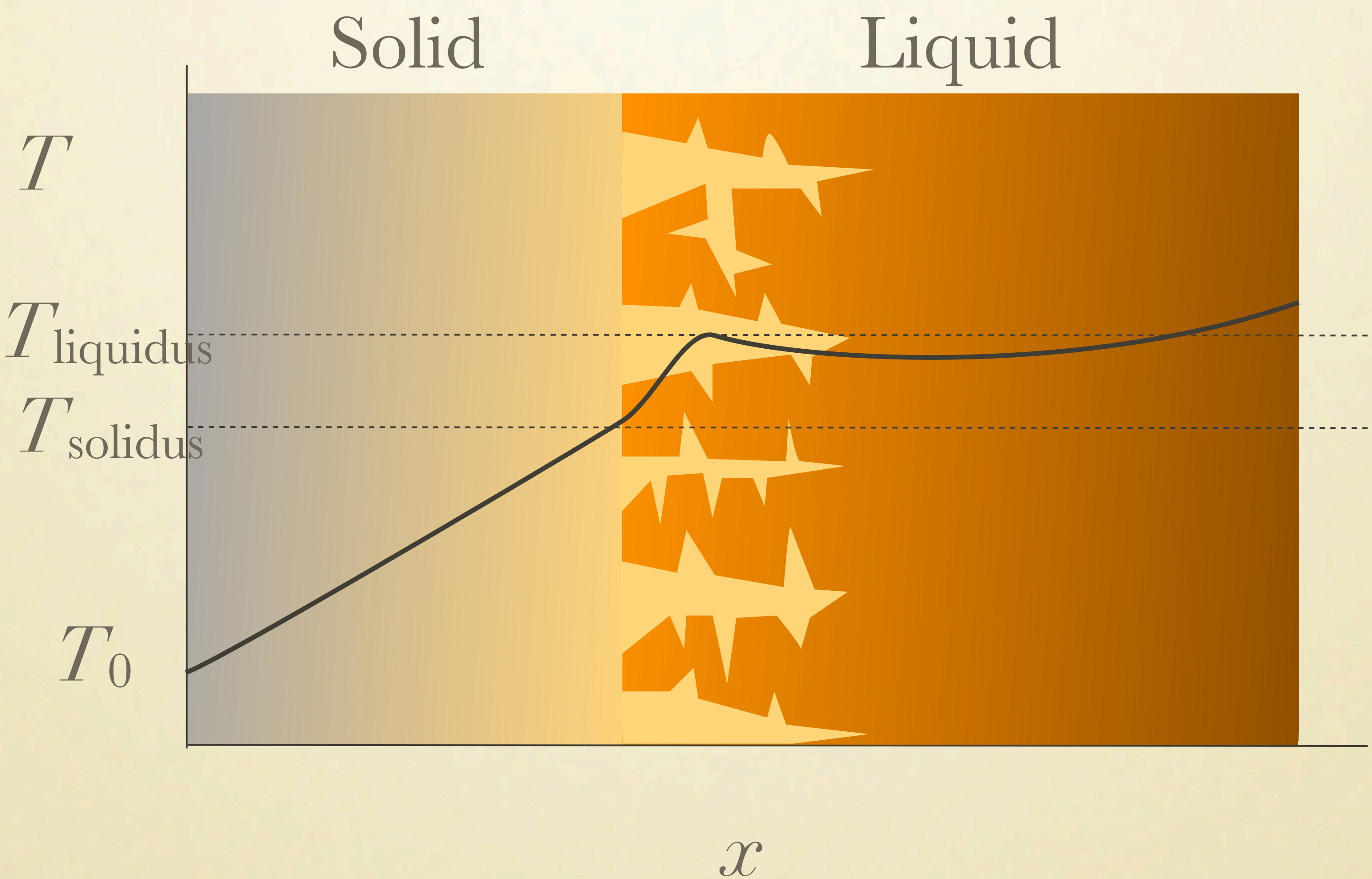
Planar Growth

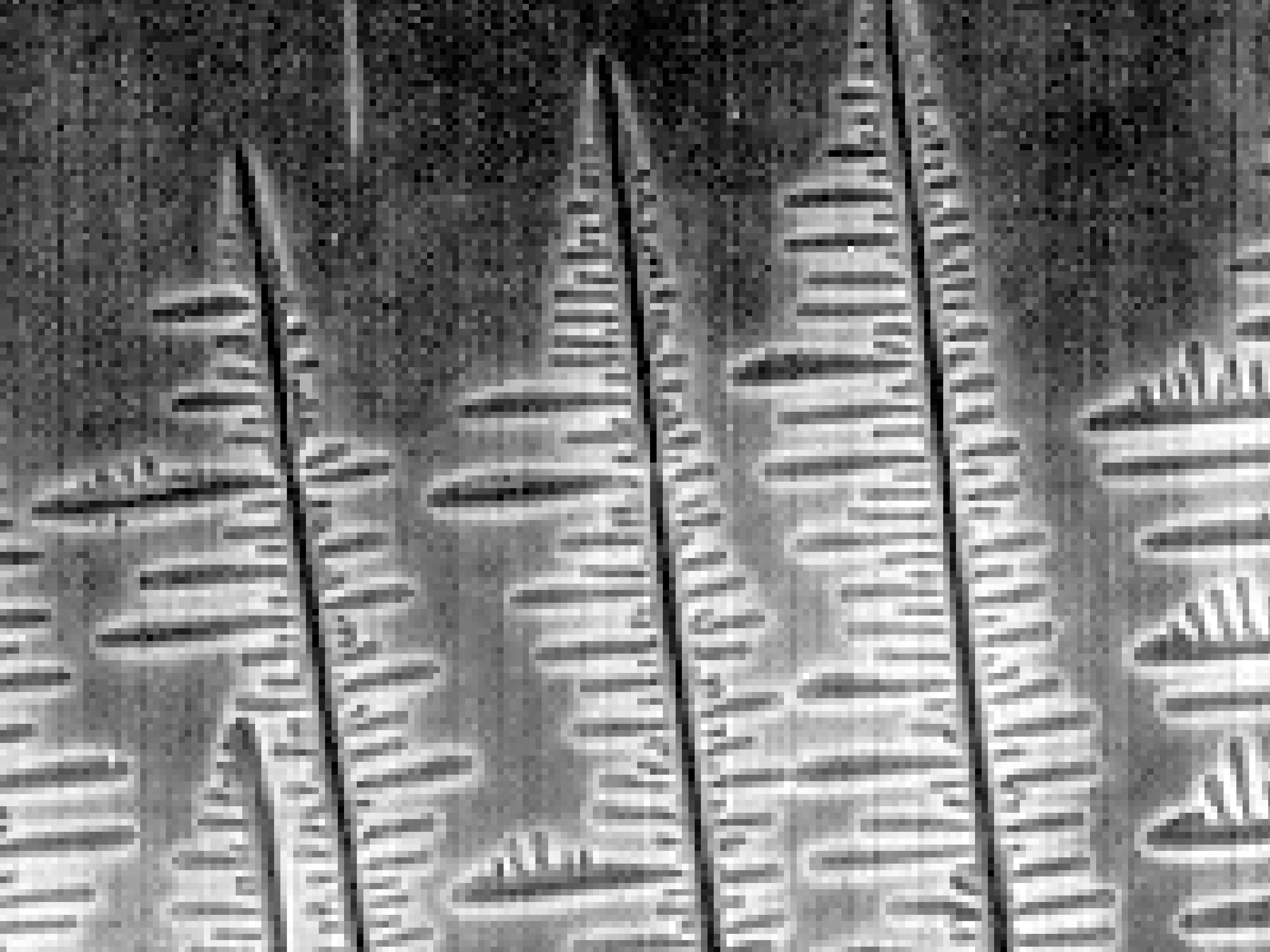


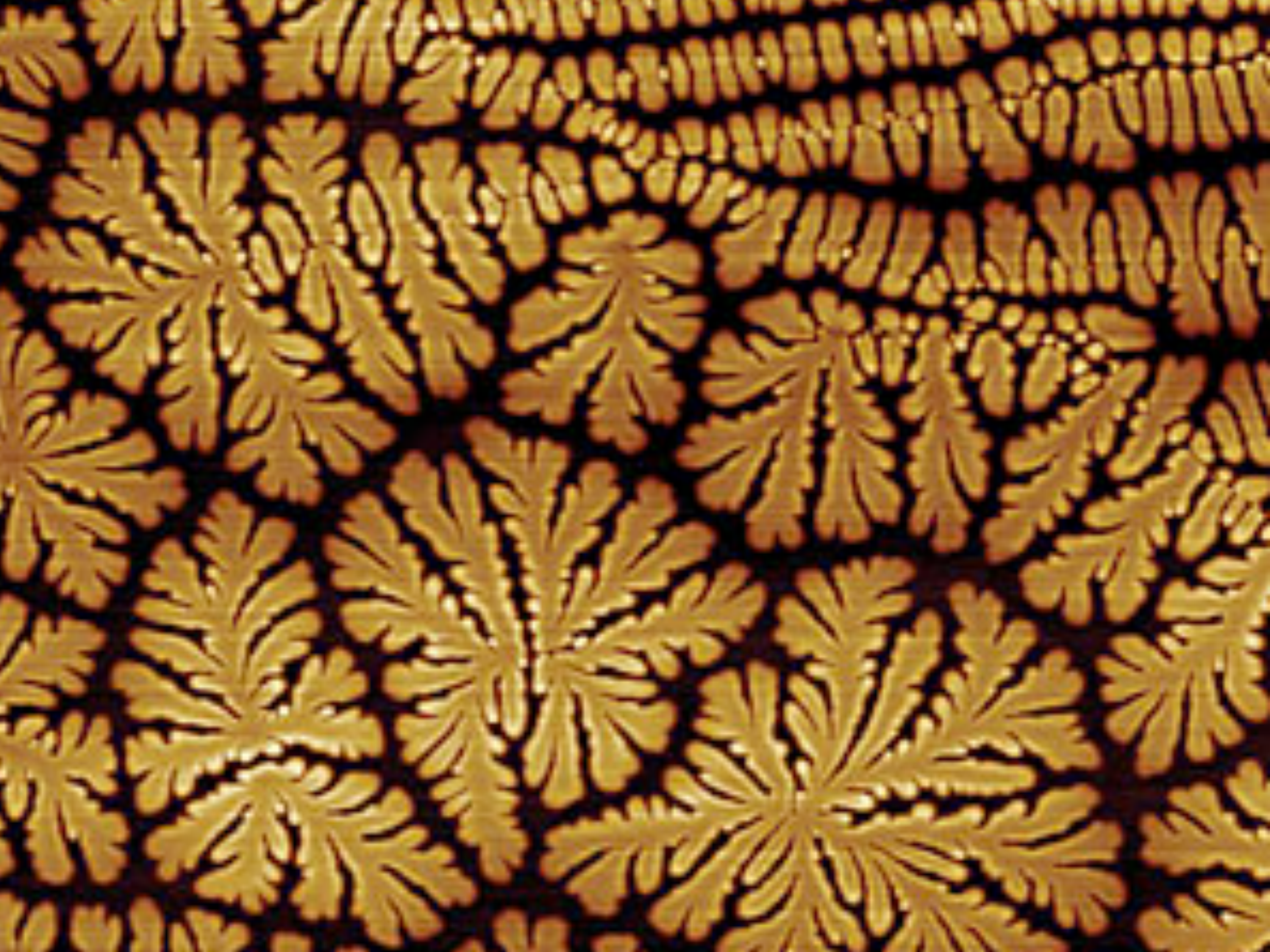
Cellular Growth



Dendritic Growth



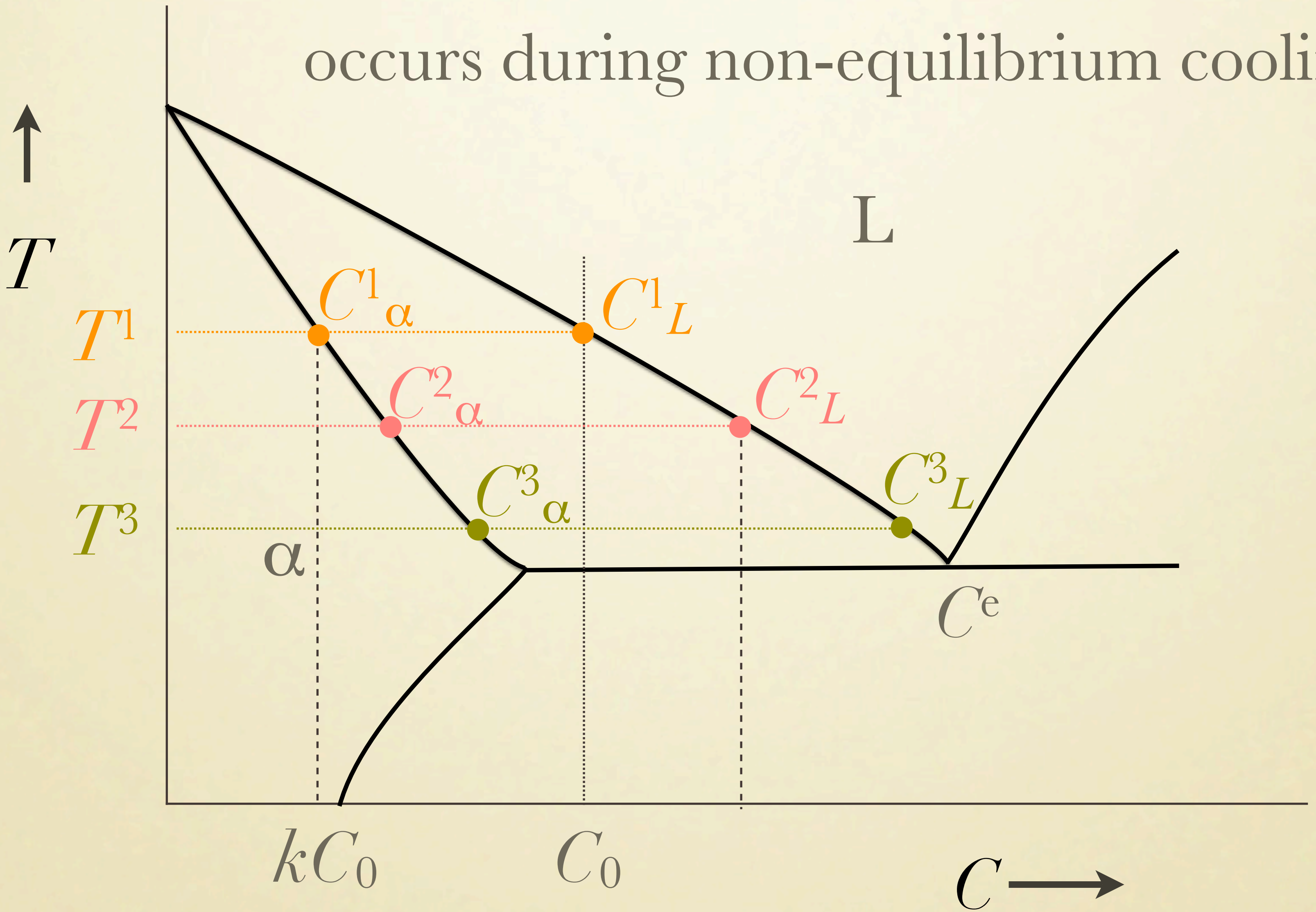




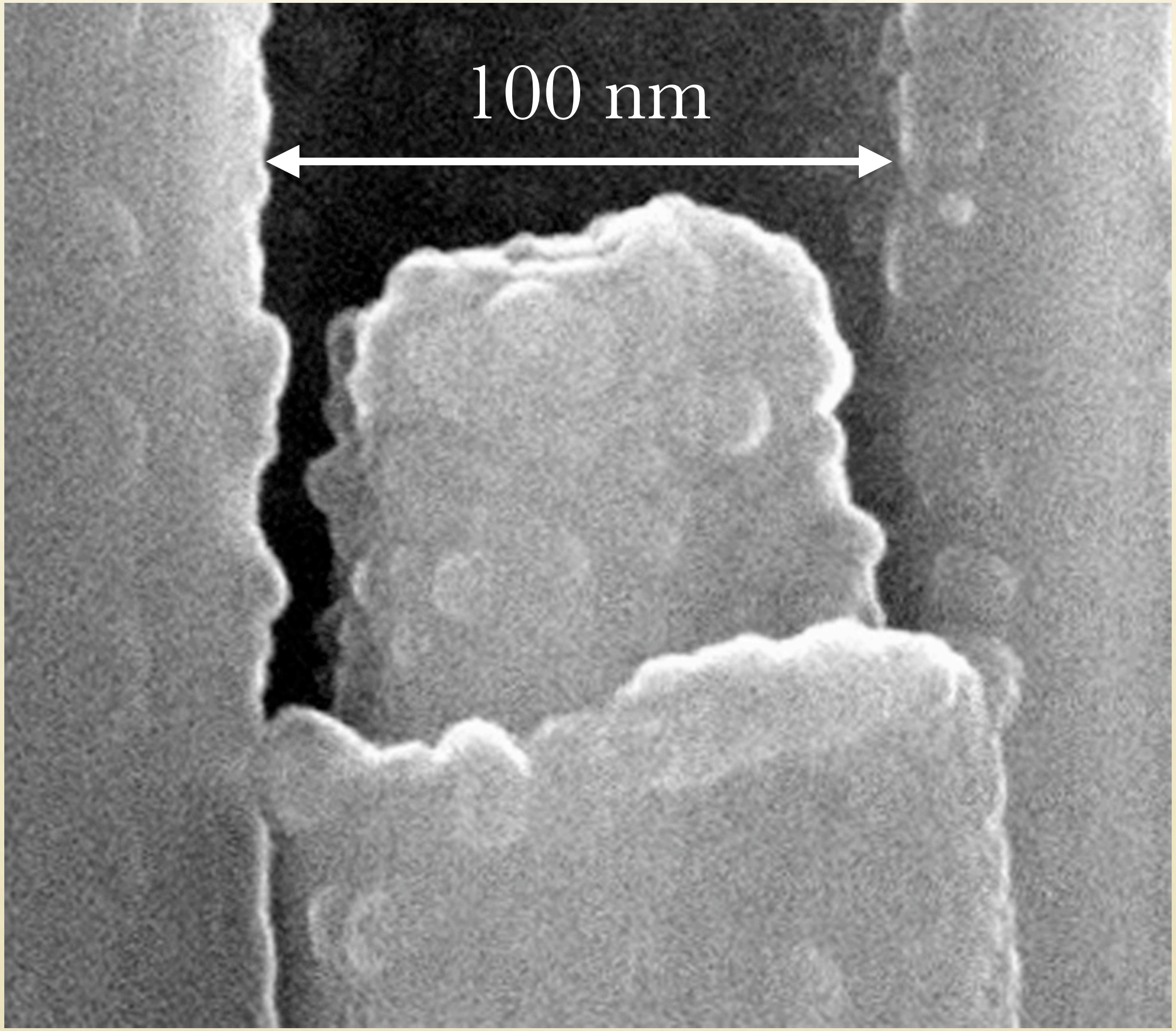

30 µm

Solute Partitioning

occurs during non-equilibrium cooling



Core & Shell

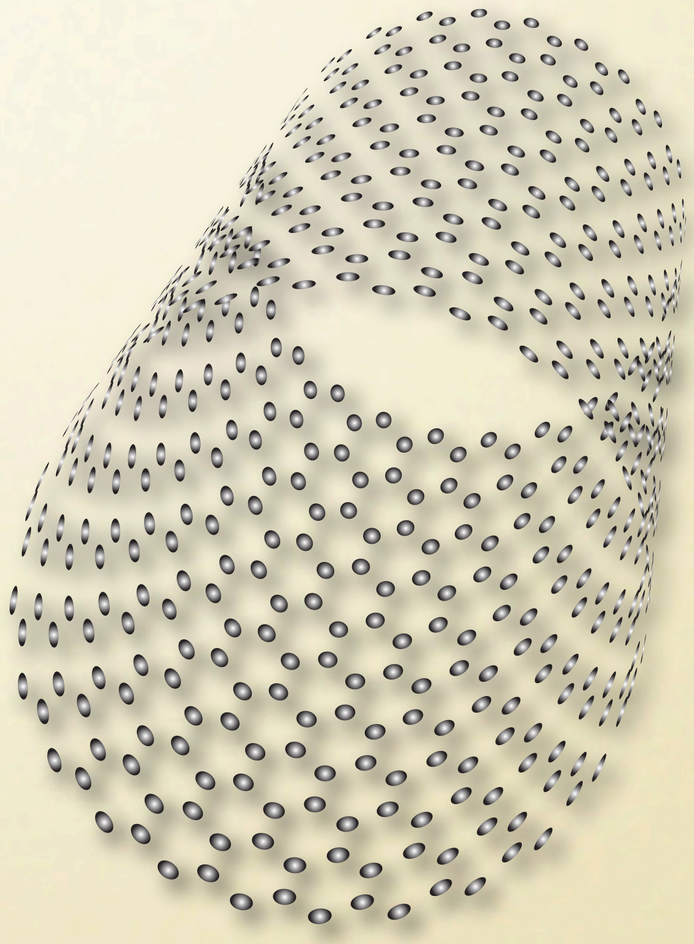


$CoSb_3$

Nano Synthesis

Nanotube Synthesis

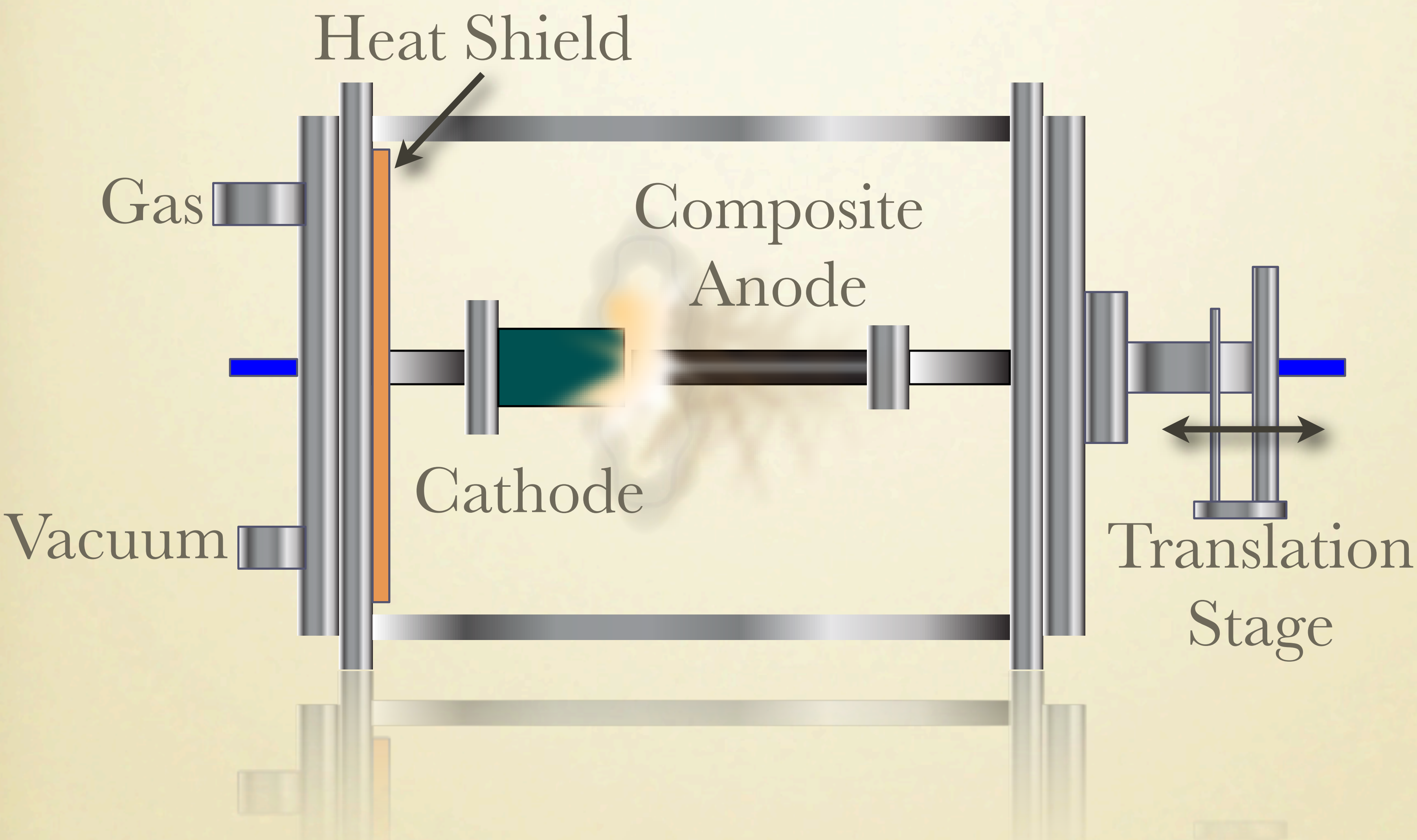
- High aspect ratio fullerenes (nanotubes) synthesized by two primary methods
    - Sublimation + condensation of graphite
    - Decomposition of carbon-containing compounds



MWNT

- T.W. Ebbesen and P.W. Ajayan, "Large scale synthesis of carbon nanotubes," *Nature* **358**, 220 (1992)
- M. Cadek *et al*., "Optimization of the arc-discharge production of multi-wall carbon nanotubes," *Carbon* **40**, 923 (2002)

Arc-Discharge Method



SWNT

- C. Journet, *et al.*, "Large-scale production of single wall carbon nanotubes by the electric-arc technique," *Nature* **388**, 756 (1997)
- Z. Shi *et al.*, "Mass production of single wall carbon nanotubes by arc-discharge method," *Carbon* **37**, 1449 (1999)
- M. Takizawa *et al.*, "Change of tube diameter distribution...ratio of Ni and Y catalysts," *Chem. Phys. Lett.*, **326**, 351 (2000)

SWNT

- T. Guo *et al.*, “Catalytic growth of single-walled nanotubes by laser vaporization,” *Chem. Phys. Lett.* **243**, 49 (1995)
- M. Yudasaka *et al.*, “Single-wall carbon nanotube formation by laser ablation using double targets of carbon and metal,” *Chem. Phys. Lett.* **278**, 102 (1997)
- W.K. Maser *et al.*, “Production of carbon nanotubes: the light approach,” *Carbon* **40**, 1685 (2002) [focused solar radiation]

Laser Ablation

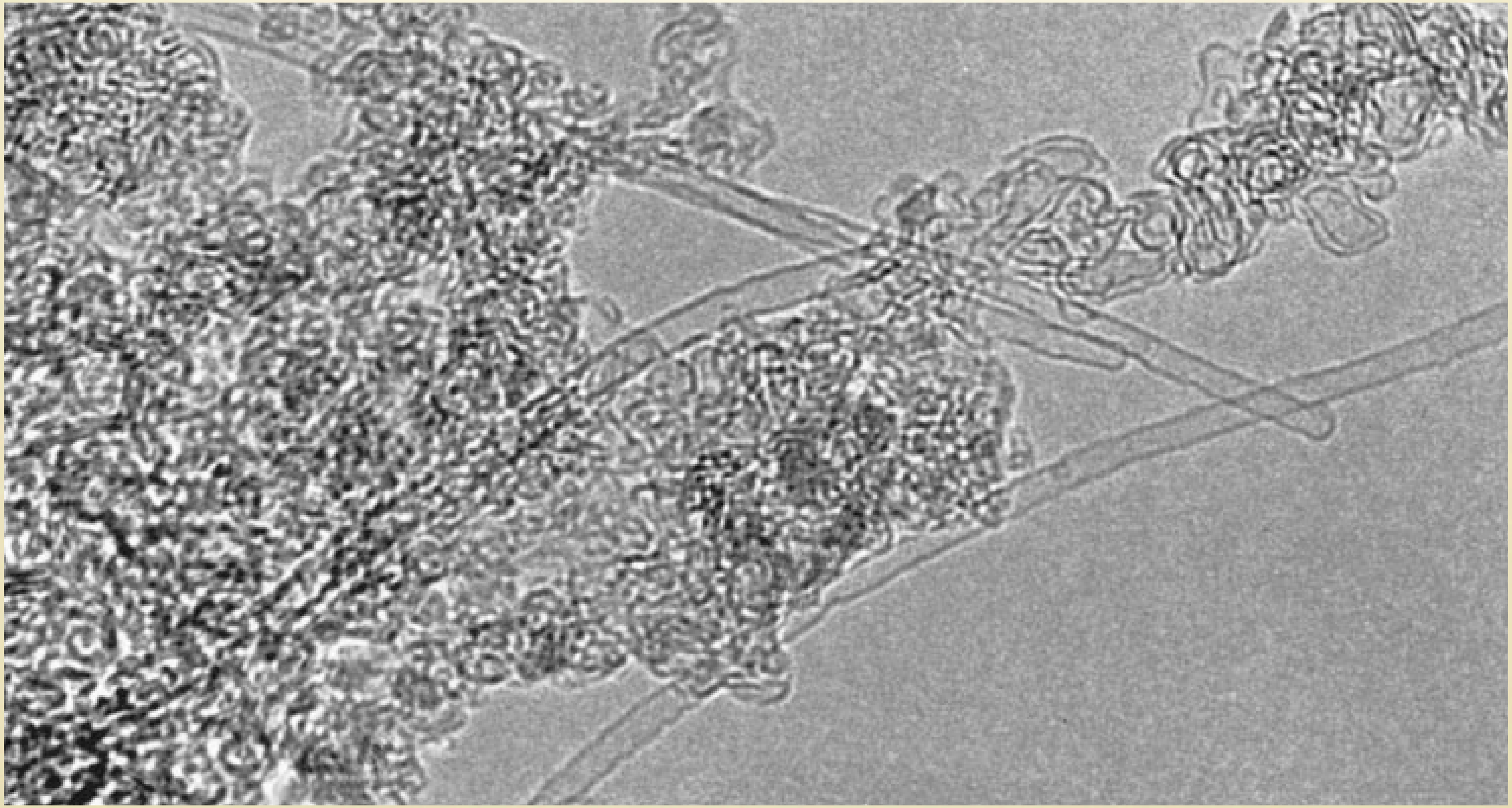
- Choose wavelength for minimum absorption depth, maximum energy deposition
- Short pulse duration maximizes peak power, minimizes thermal conduction to surrounding matter
- High pulse repetition rate minimizes heat loss between pulses

APPLIED PHYSICS LETTERS VOLUME 75, NUMBER 20 15 NOVEMBER 1999

Formation of single-wall carbon nanotubes by laser ablation of fullerenes at low temperature

Y. Zhang[a)]
Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

S. Iijima
Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501 and Department of Physics, JST International Research Project on Nanotubulites, Meijo University, Nagoya 468-8502, Japan



26 November 1999

Chemical Physics Letters 314 (1999) 16–20

CHEMICAL PHYSICS LETTERS

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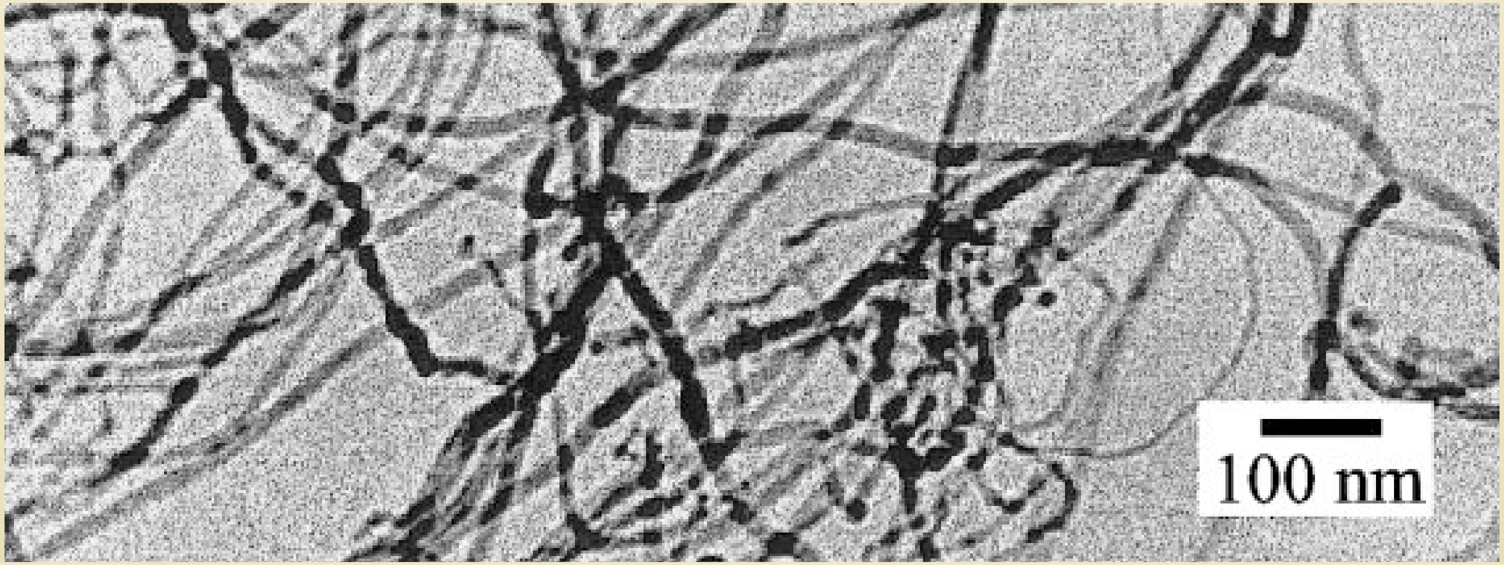
Si nanowires synthesized by laser ablation of mixed SiC and SiO_2 powders

Y.H. Tang, Y.F. Zhang, H.Y. Peng, N. Wang, C.S. Lee, S.T. Lee *

Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China



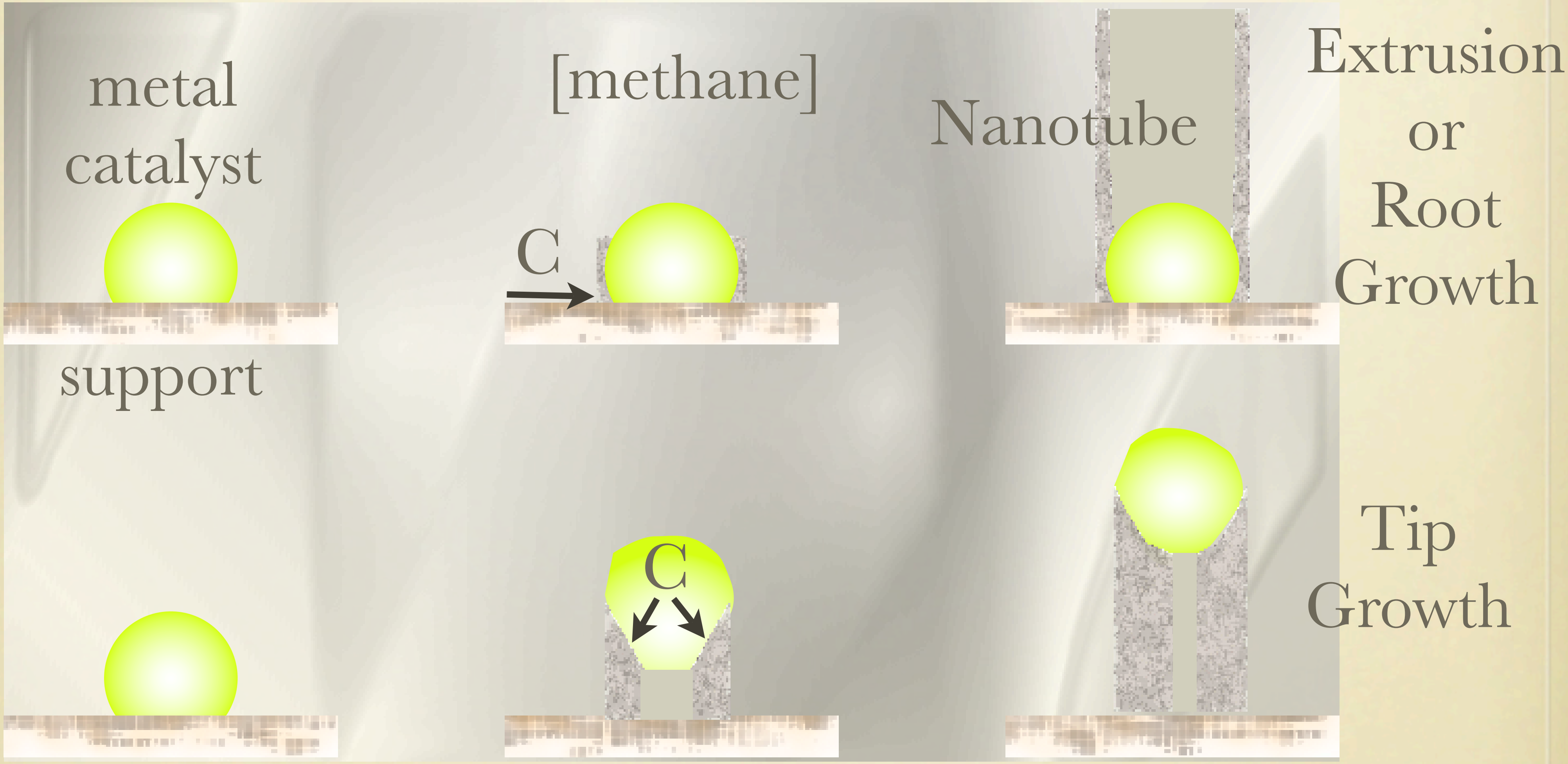
Decomposition of Carbon Compounds

- Pyrolysis of gases: chemical vapor deposition (CVD)
- Pyrolysis of solids (polymers)
- Hydrothermal synthesis from aqueous solutions [J.A. Libera and Y. Gogotski, *Carbon* **39**, 1307 (2001)]
- Organic solutions (supercritical toluene) [D.C. Lee *et al.*, *J. Am. Chem. Soc.* **126**, 4951 (2004)]

CVD

- Heat catalyst material 500-1000°C in tube furnace with flowing hydrocarbon gas (methane)
- Catalyst = Fe, Ni or Co (all have high solubility for C [see phase diagram], supported on porous alumina
- Dissociation of hydrocarbon molecules by transition metal, dissolution of C by metal, supersaturation
- Precipitation of C from particle leads to tubular carbon solids with sp^2 bonding

CVD



S. B. Sinnot *et al.*, *Chem.Phys.Lett*. **315**, 25-30 (1999)

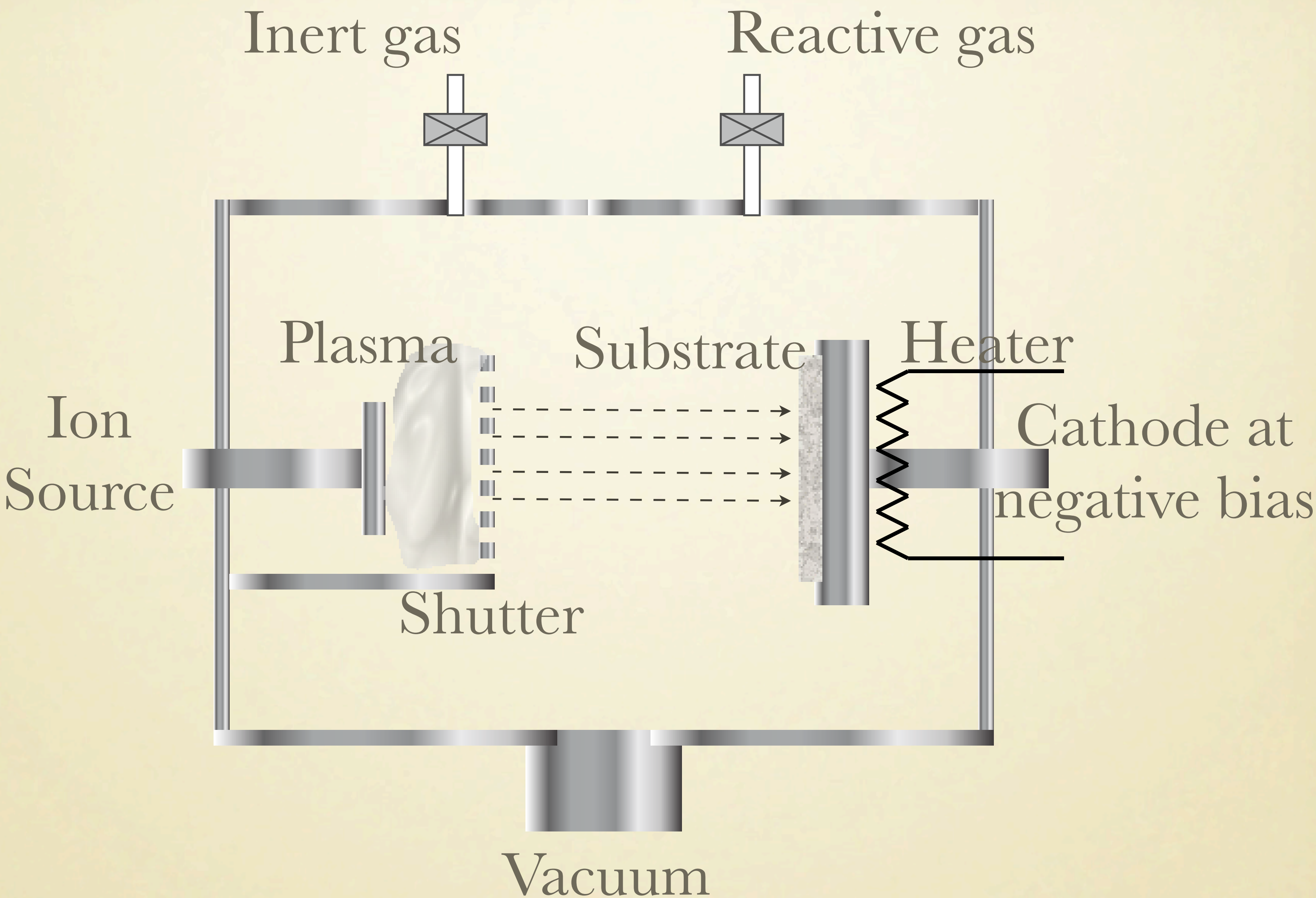
CVD

- A. Cassell *et al.*, "Directed growth of free-standing single-walled carbon nanotubes," *J. Am. Chem. Soc.* **121** 7975 (1999)
- Lithographic patterning of Si substrate to form pillars
- Contact printing transfers catalyst to tops of pillars
- Nanotubes nucleate on pillar tops, grow directionally

Nano Films

Sputtering

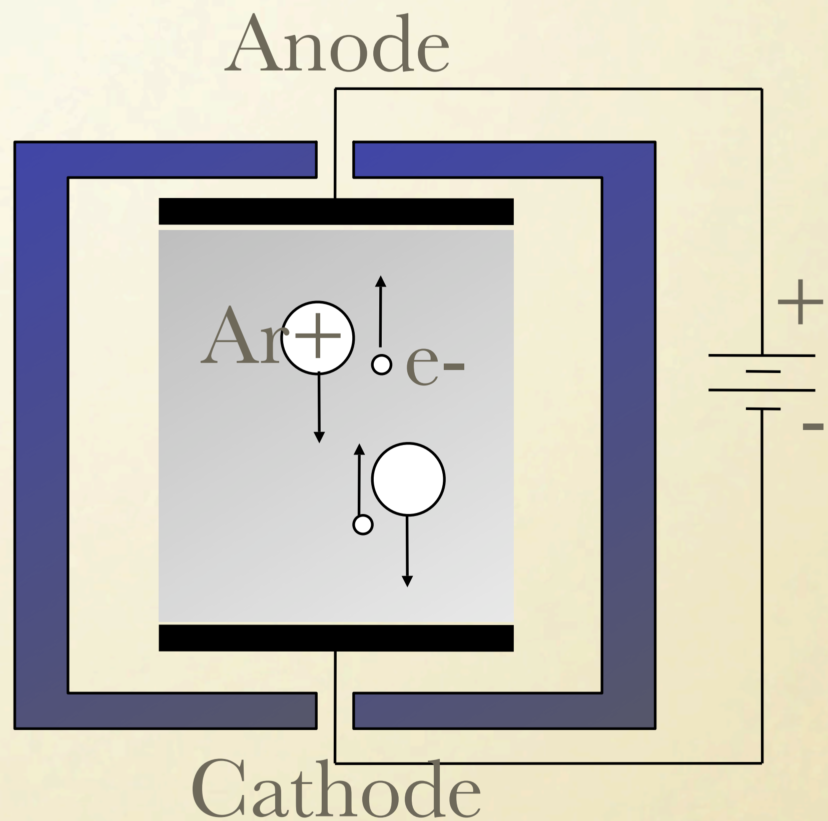
- Gas ions collide with target, sputter material from surface, deposit onto substrate
- Gas can be inert (Ar) or reactive (O_2, N_2)
- Magnetron added beneath target; magnetic field traps electrons in electron tunnel, increasing erosion by increasing gas ion collisions



Inert gas
Reactive gas
Plasma
Substrate
Heater
Ion
Source
Cathode at
negative bias
Shutter
Vacuum

Planar Diode Source

- High voltage supply ionizes small amount of gas between electrodes
- DC discharge develops, causing sputtering from cathode
- Cathode is water-cooled disk 5-10 cm diameter
- Slow process



Triode Source

- Heated filament added to a diode source: provides electrons to sustain the glow discharge, independent of target
- Discharge operates at lower gas pressures (0.5—1 mtorr), and lower target voltage
- Increased ionization efficiency, high deposition rates

Magnetron Source

- Magnetic field of 50—500 gauss parallel to target surface
- In combination with electric field causes electrons to drift in a closed circuit or “magnetron tunnel” in front of target
- Electron confinement increases efficiency, resulting in lower gas pressure

Magnetron Parameters

- Cathode current density = 20 mA / cm^2
- Voltage 250 — 800 V
- Target to substrate distance ≈ 10 cm
- Deposition rate ≈ 100 — 2000 Å/min
- Current density at cathode is peaked where magnetic field lines are tangent to surface of cathode, causing non-uniform erosion

Ion Beam Source

- Multi-aperture Kaufman ion sources commercially available (Harold Kaufman, NASA-Lewis, 1960's)
- Ar^+ ion beam up to 10 cm diameter
- 0.5-1.0 A/cm^2
- Beam energy 500-2000 eV
- Low background pressure (0.1 mtorr)

Ion Beam Sources

- Substrate isolated from ion generation
- Minimal interaction between processes at target and processes at substrate
- Control of ion impact angle and spot size
- Independent control of ion energy and current density

Metallic Films

- **Sputtering** of metals in Ar^+ gas results in easy deposition of conducting films
- Adhesion is superior to evaporation methods: energetic particles from target clean substrate and promote local rearrangements on surface
- Multicomponent targets do not always produce alloy films of same composition: different sputter yields of component species; correction is to use multiple targets ("*co-sputtering*")

Reactive Ion Sputtering

Target	Gas	Film
Si	O_2	SiO_2
Si	N_2	SiN_2
Ti	N_2	TiN_2
In/Sn	O_2	In_2O_3/SnO_2

Microstructures: Sputtered Films

- "Zone" Model widely accepted
- J.A. Thornton, *J. Vac. Sci. Tech.* **12**, 830 (1975)

Zone 1

- Zone 1
- $T/T_m < 0.3$
- Tapered columnar grains with intergranular voids

Zone 2

- Zone 2
- $0.3 < T/T_m < 0.5$
- Columnar, platelet, or whisker grains separated by dense intercrystalline boundaries

Zone 3

- Zone 3
- $T/T_m > 0.5$
- Equiaxed grains and epitaxial growth on surface

Zone T

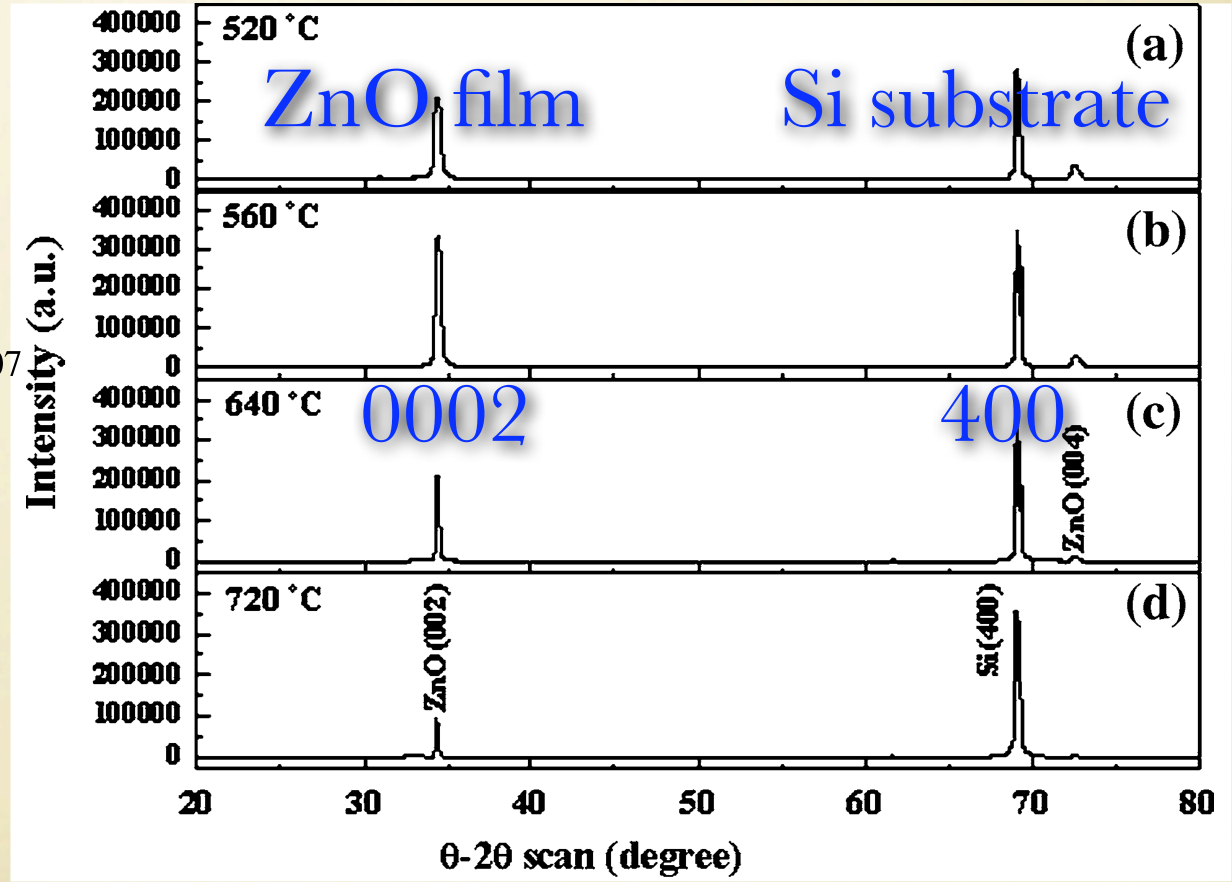
- Zone T
- "Transition" zone, resulting from bombardment-induced surface mobility
- Films that would be expected in Zone 1 can by grown with high density and smooth surface by biasing the substrate (200 V) to increase ion flux
- Bombardment causes compressive stresses in films

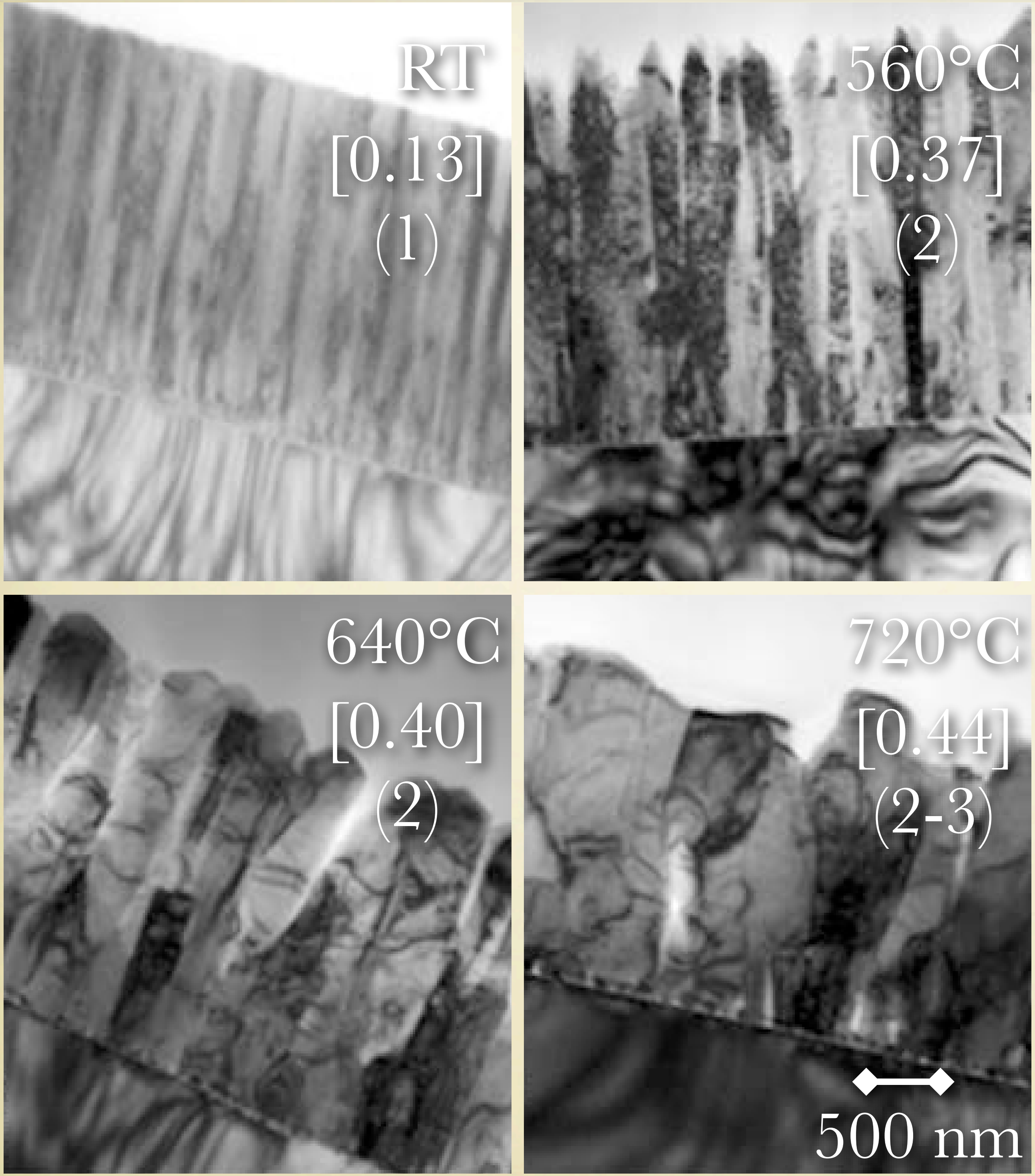
J Mater Sci: Mater Electron
DOI 10.1007/s10854-007-9402-6

Temperature dependence of ZnO thin films grown on Si substrate

Y. Y. Kim · C. H. Ahn · S. W. Kang · B. H. Kong · S. K. Mohanta · H. K. Cho · J. Y. Lee · H. S. Kim

Received: 14 May 2007 / Accepted: 30 August 2007





Key: $[T/T_s]$
(Zone)

ZnO

$T_{sublimation}$ = 1975°C
= 2248 K

1) $T/T_m < 0.3$
2) $0.3 < T/T_m < 0.5$
3) $T/T_m > 0.5$

Modifications

Gas Pulsing

- Periodic pulsing of reactive gas during reactive sputtering process
- Forms alternating layers of metal and dielectric
- Suppresses columnar growth, results in smooth surface finish
- Also stabilizes metallic mode: periodically switching off reactive gas inhibits nucleation of compounds; only metallic constituent nucleates

Modifications

Low frequency sputtering

- In the 60 — 100 kHz range, reactive magnetron sputtering is facilitated
- Deposition rate increases up to 80%
- Ions are accelerated by full voltage modulation rather than just self-bias voltage

Technical Considerations

Targets

- Fabricated by mechanical, sintering, and casting methods, sometimes at very high cost...
- Target utilization can be increased by flattening the magnetic field lines parallel to the target surface

Technical Considerations

Film Uniformity

- Deposition rate profile depends upon
  - geometry and size of the source,
  - operating pressure
  - target-to-substrate distance

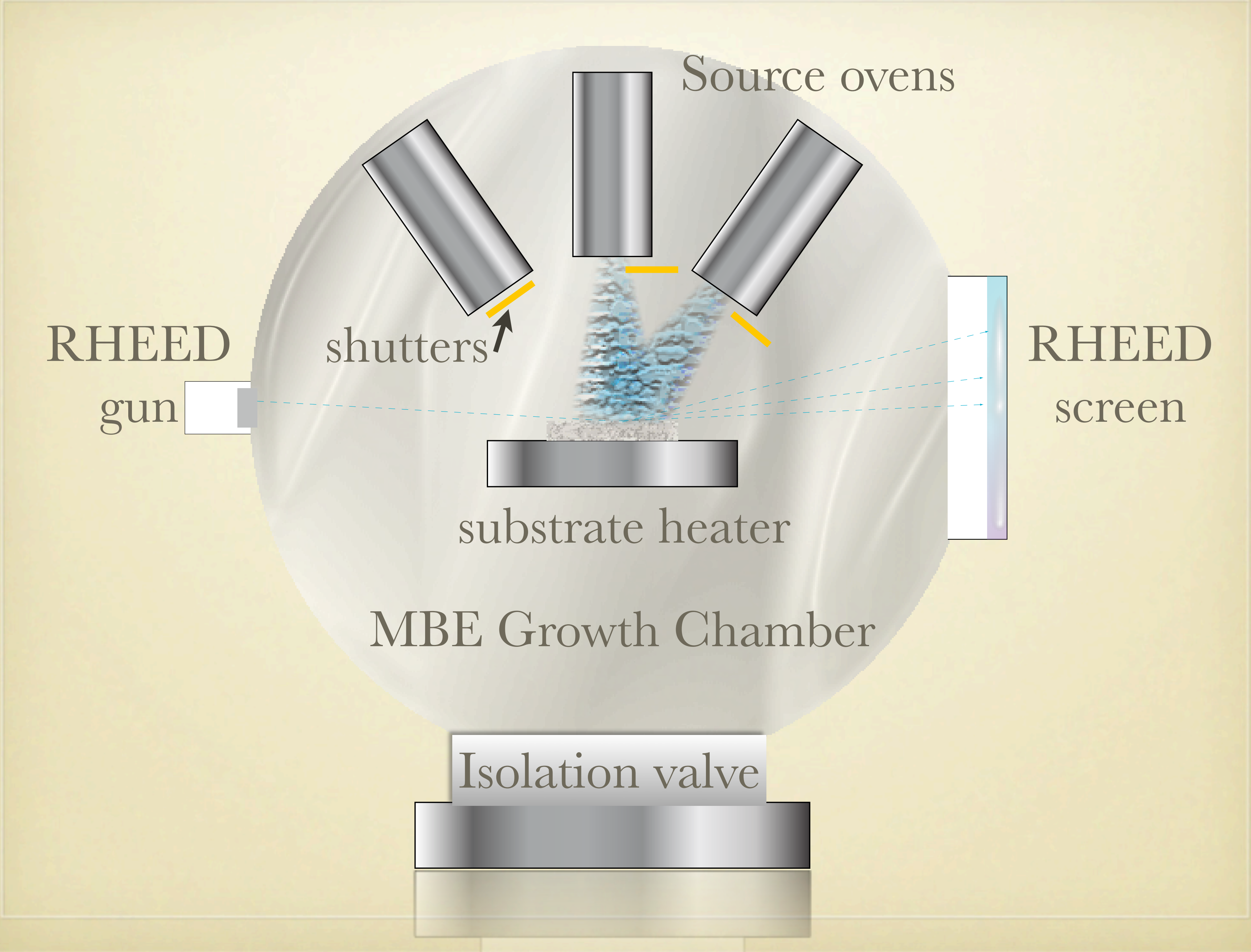
Technical Considerations

Substrate Preparation

- Glow discharge cleaning favors adhesion
- Vacuum interlocks prevents contamination

Molecular Beam Epitaxy

- A. Cho and J.R. Arthur, “Molecular Beam Epitaxy,” *Prog. Solid State Chem.* **10**, 157 (1975)
- Epitaxial film growth
- Ultrahigh vacuum conditions
- Real time analysis of surface and environment



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Journal of Crystal Growth 289 (2006) 381–386

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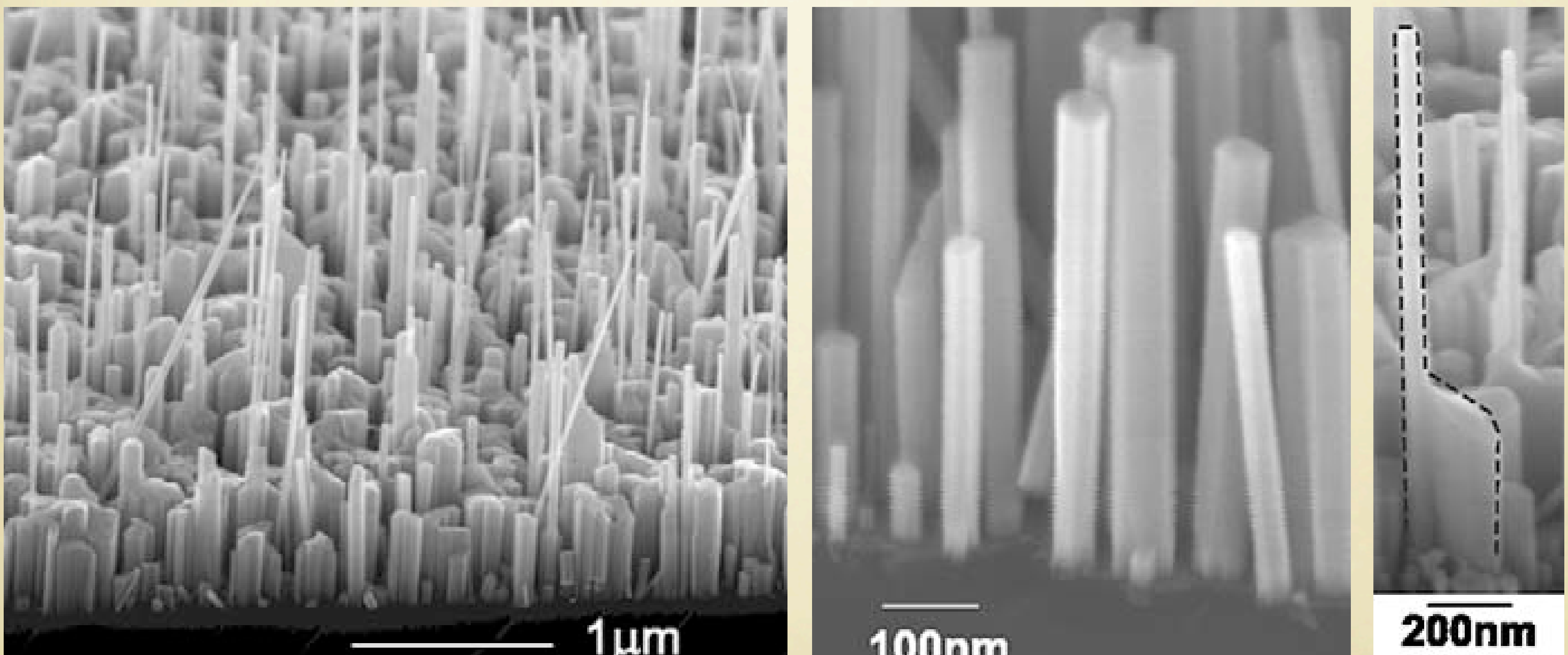
GaN-nanowhiskers: MBE-growth conditions and optical properties

R. Meijers*, T. Richter, R. Calarco, T. Stoica, H.-P. Bochem, M. Marso, H. Lüth

Institute of Thin Films and Interfaces (ISG1) and cni-Center of Nanoelectronic Systems for Information Technology, Research Centre Jülich, 52425 Jülich, Germany



Summary

- Solidification from liquid phase: control of porosity, shrinkage, constitutional supercooling, solute partitioning (can be used to advantage)
- Deposition from vapor phase: CVD, Sputtering, PLD for production, MBE for scientific evaluation

End

Lecture 08