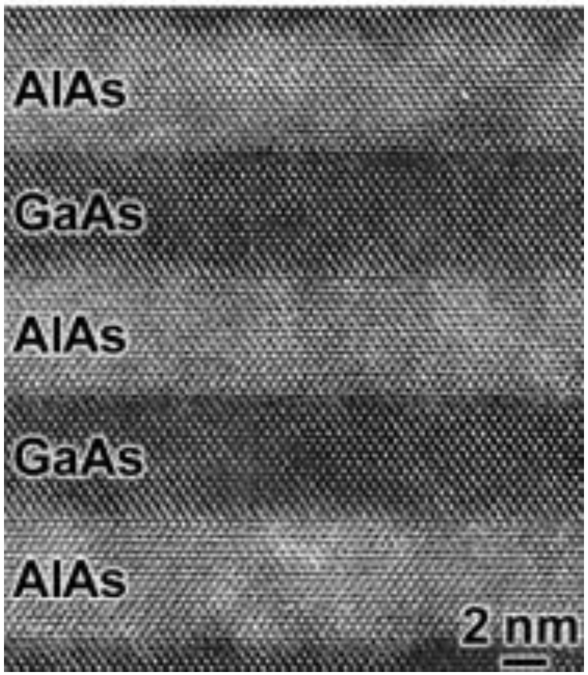
Nucleation and growth of nanostructures and films

Seongshik (Sean) Oh



Outline

Introduction and Overview

1. Thermodynamics and Kinetics of thin film growth
2. Defects in films
3. Amorphous, Polycrystalline and Epitaxial Films

Vacuum Film Deposition Techniques

1. Physical Vapor Deposition (PVD)
    - Evaporation : Thermal and Electron-Beam
    - Sputtering: RF and DC Magnetron
    - Pulsed Laser Deposition (PLD)
    - Molecular Beam Epitaxy (MBE)
2. Chemical Vapor Deposition (CVD)
    - Plasma-Enhanced CVD (PE-CVD)
    - Atomic Layer Deposition (ALD)

More about MBE

Introduction and Overview

What is a "thin film" ?

thin = less than about 1000 nm thick
film = layer of material on a substrate

Applications:

- Microelectronics - electrical conductors, electrical barriers, diffusion barriers . . .
- Sensors: magnetic sensors, gas sensors, …
- Optics - anti-reflection coatings
- Corrosion protection, Wear resistance, etc
- Tailored materials with new properties

Special Properties of Thin Films: different from bulk materials

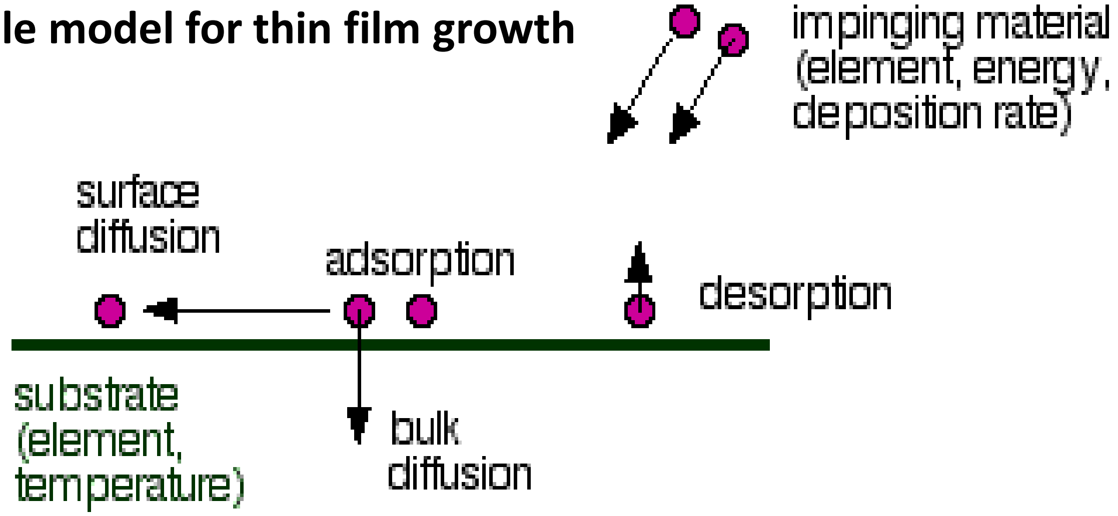
Thin films may be:

- not fully dense
- under stress
- different defect structures from bulk
- quasi - two dimensional (very thin films)
- strongly influenced by surface and interface effects

Typical steps in making thin films:

1. Emission of particles from source (heat, high voltage . . .)
2. Transport of particles to substrate
3. Condensation of particles on substrate

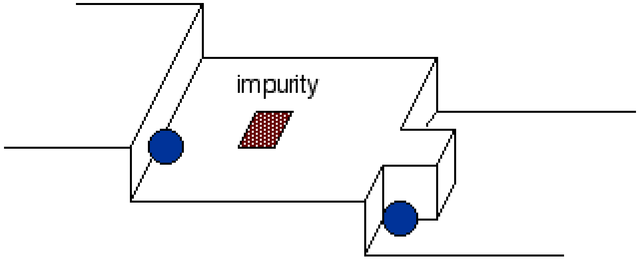
Simple model for thin film growth



Detailed Steps in Film Formation

1. thermal accommodation (substrate should be cold, and impinging material should have low energy)
2. binding (Physisorption and Chemisorption)
3. surface diffusion (Larger than bulk diffusion)
4. nucleation
5. island growth
6. coalescence
7. continued growth

Nucleation and Growth occurs mostly on step edges because of higher bonding energy



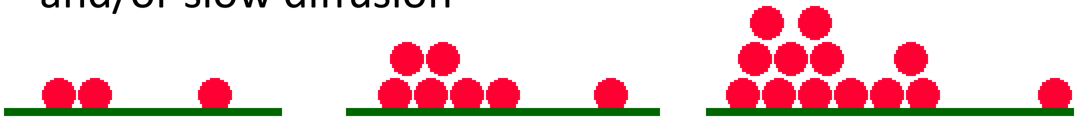
Highly ordered thin films can be grown at much lower temperatures than for bulk, because of the larger surface diffusion (Step 3 above).

Three different growth modes

1. Island growth (Volmer - Weber)

form three dimensional islands

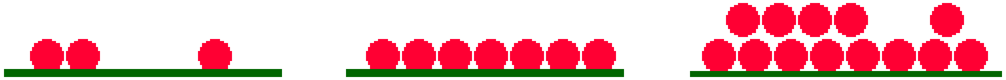
source: film atoms more strongly bound to each other than to substrate
and/or slow diffusion



2. Layer by layer growth (Frank - van der Merwe)

generally highest crystalline quality

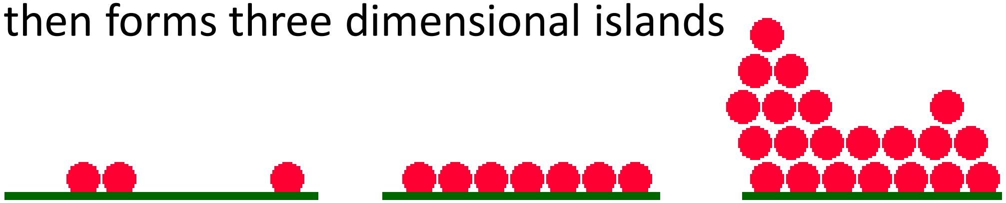
source: film atoms more strongly bound to substrate than to each other
and/or fast diffusion



3. Mixed growth (Stranski - Krastanov)

initially layer by layer

then forms three dimensional islands

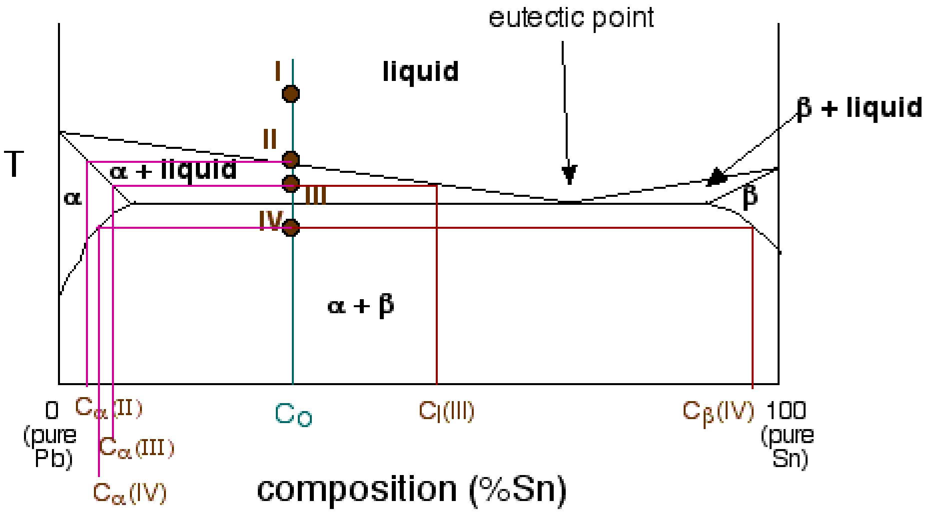


Thermodynamics and Kinetics of thin film growth:

Thin film growth is not a equilibrium process!

Two factors determining growth of thin films:

1. Thermodynamics (Equilibrium Condition, Gibbs Free Energy and Phase Diagram)
   Can the intended solid phase be formed at the growth temperature?

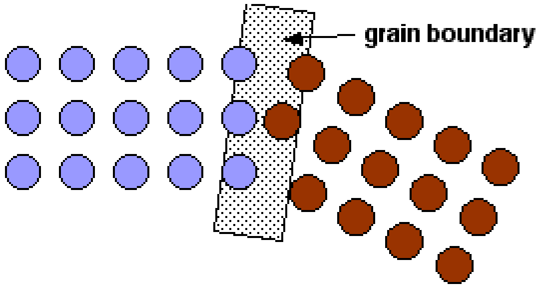


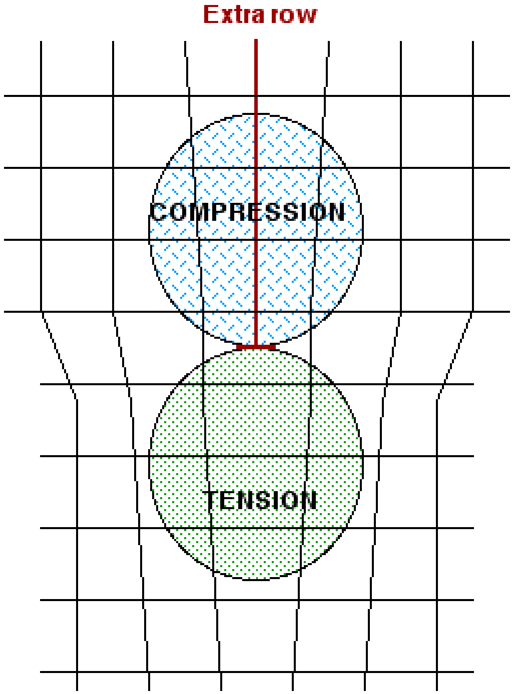
2. Kinetics (Rate and Diffusion)
   How fast are materials arriving and diffusing?

Artificial superlattice is the best example of manipulating Kinetics and Thermodynamics

Three types of crystalline defects

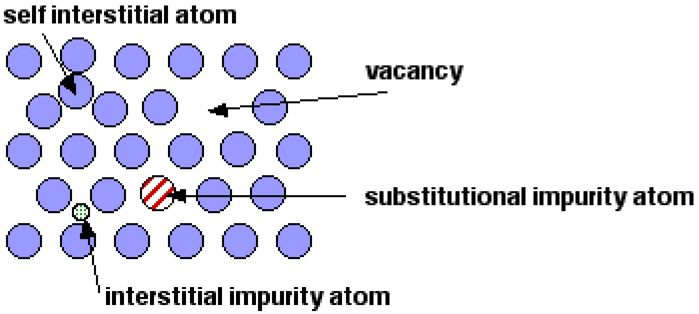
1. Planar defects: Grain boundaries: Weak link for diffusion or corrosion





2. Line defects: Dislocations:
   Causing Stress (Tension and Compression)

3. Point defects: Interstitial, Vacancy, Impurities



Thin film types based on crystallinity:

1. **Amorphous**: No-crystalline structures, so no crystalline defects: Common insulators such as amorphous SiO_2
2. **Polycrystalline**: Lots of grain boundaries: Most elemental metals grown near room temperatures
3. **Epitaxial** (Single-Crystalline): No grain boundaries: Requires high temperatures and slow growth rate: high quality thin films such as III-V semiconductor films and complex oxides

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Mean free path in vacuum

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n} \qquad \lambda = \frac{5 \times 10^{-3}}{P}$$

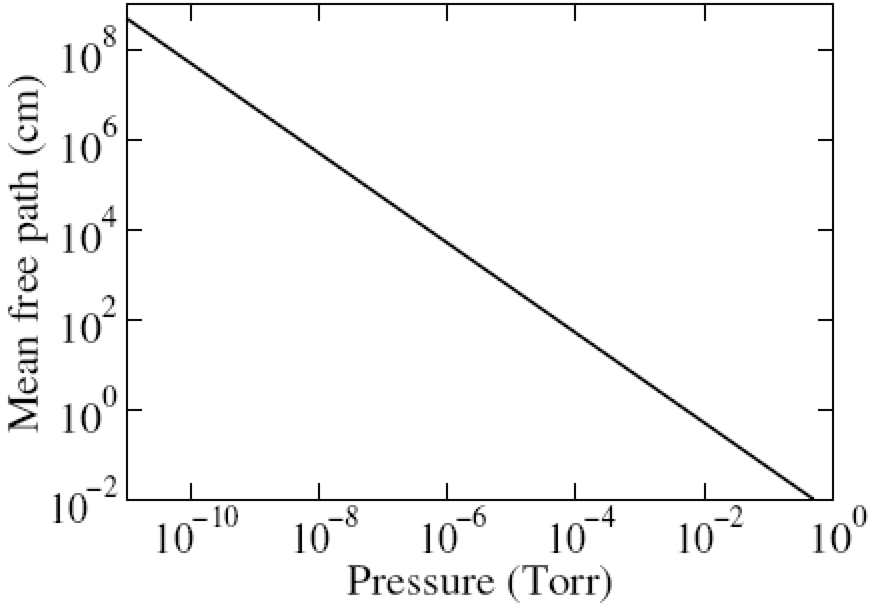


Fig. 2: Mean free path for nitrogen molecules at 300K.

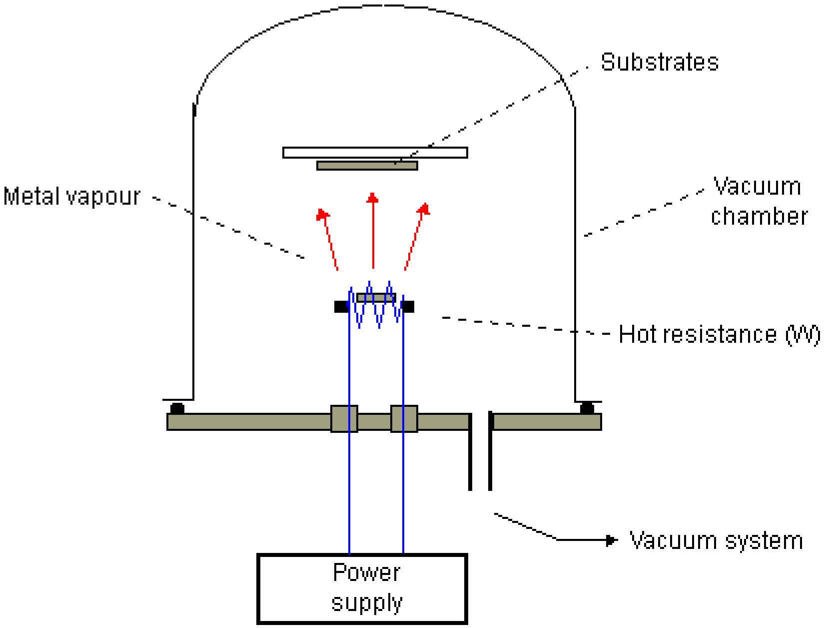
How long does it take to form a single complete layer of gas on a surface ? Assume sticking coefficient of one.

pressure	t_m
1 atm	2×10^{-9} sec
10^{-6} torr	2 seconds
10^{-9} torr	31 minutes

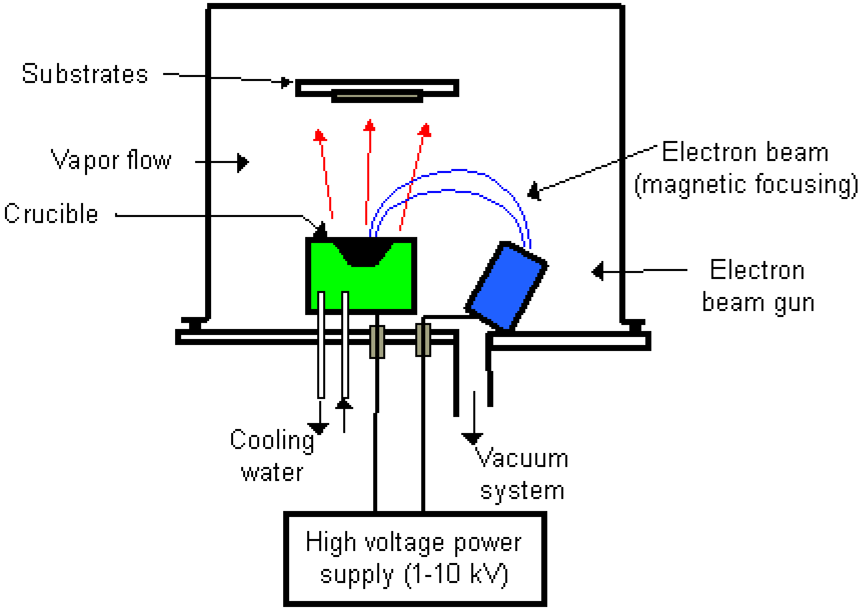
➔ We need good vacuum for thin film growth

Evaporation (Pbase < ~10^{-6} Torr)

Thermal Evaporation for non-refractory materials

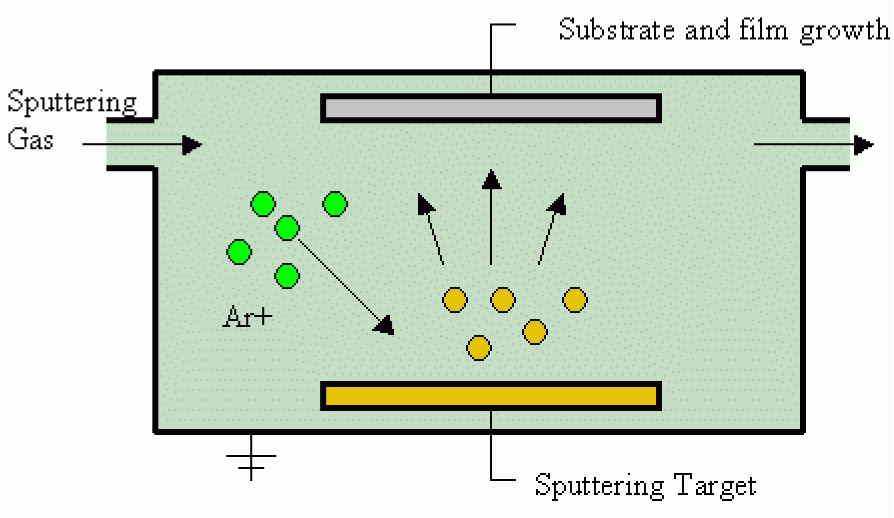


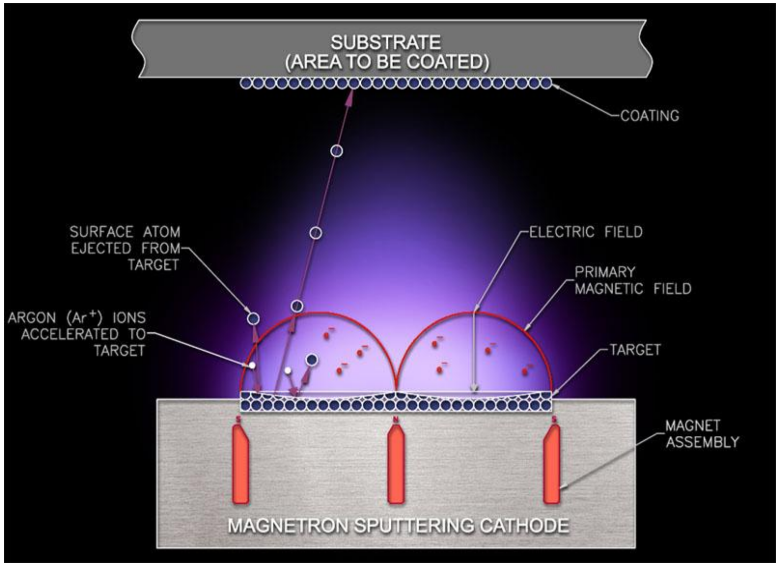
E-beam Evaporation for refractory materials



Sputtering: (1~10 mTorr of Ar)

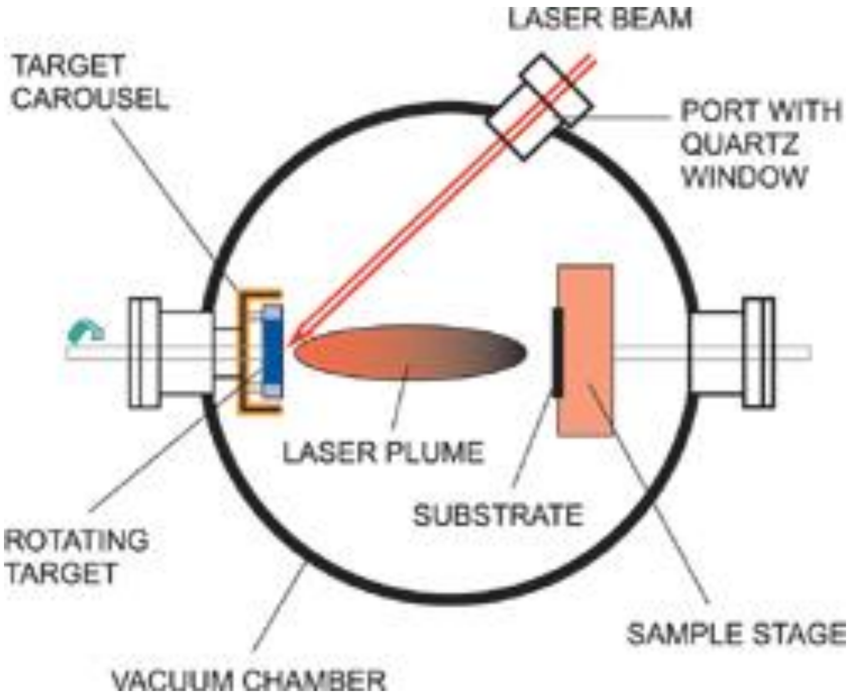
- DC for conducting materials
- RF for insulating materials
- Magnetron sputtering is most popular due to high rate and low operation pressure





Magnetron sputtering for high density of plasma near target

Pulsed Laser Deposition (PLD)
Good for multielemental materials (Pgas < 1 Torr)



Molecuar Beam Epitaxy (MBE)

Most sophisticated growth method (Pbase < 10^{-8} Torr)

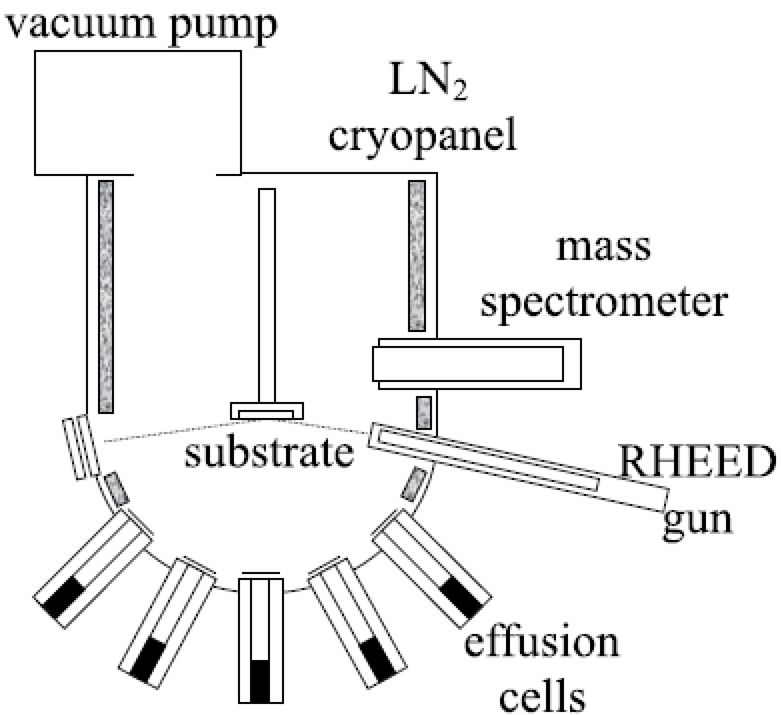
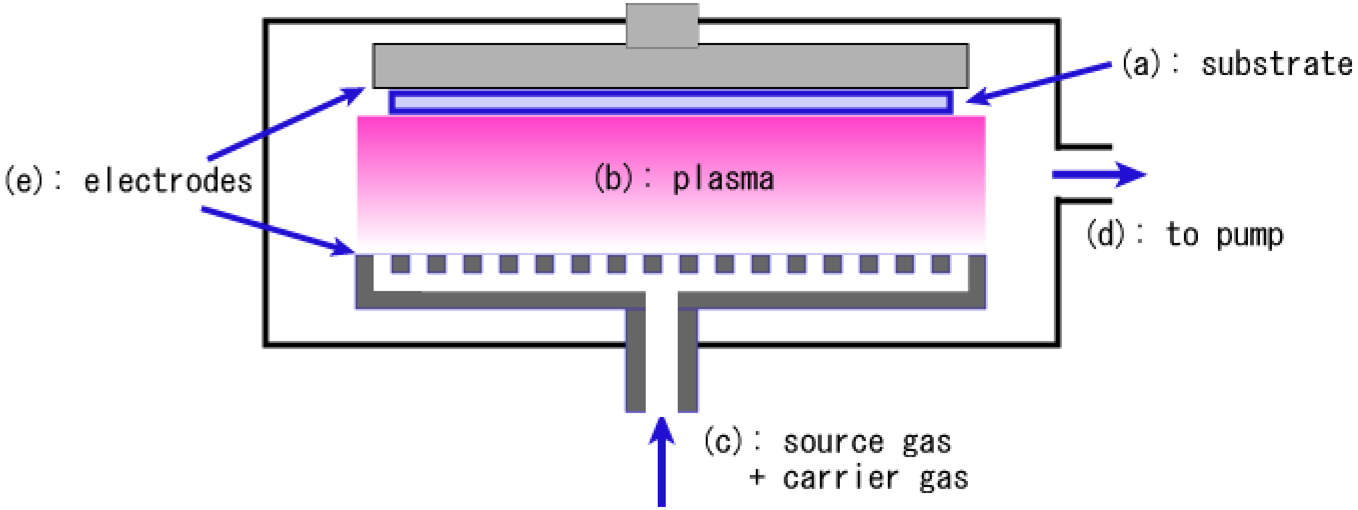


Fig. 1: A typical MBE system.

Chemical vapor deposition (CVD)

need **precursors**, which react and/or decompose on the substrate surface to produce the desired deposit.

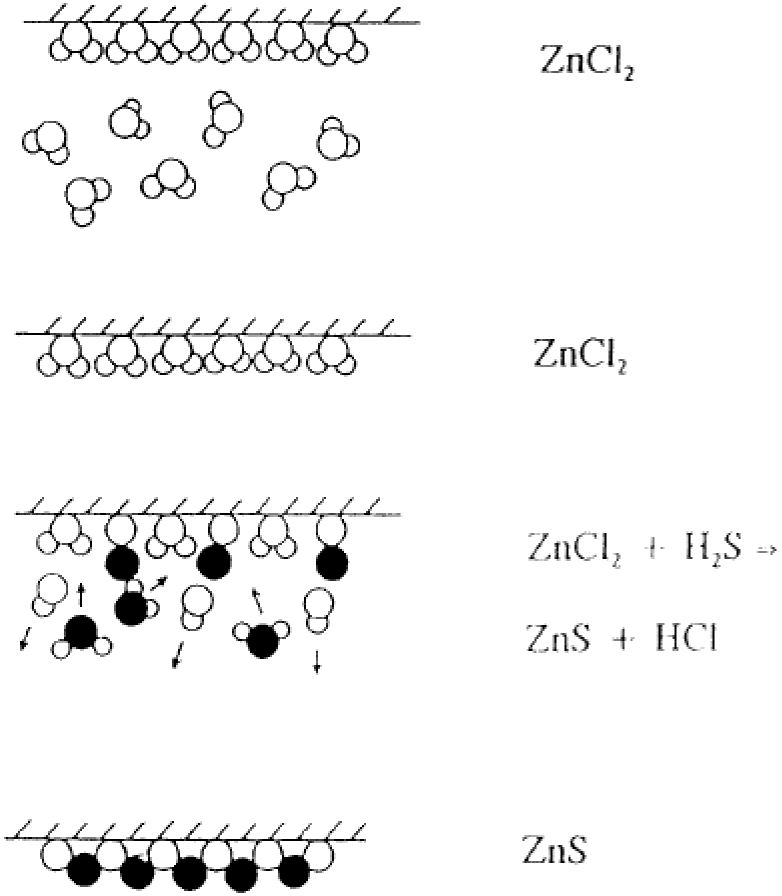
Plasma-Enhanced CVD: P<~1 Torr)



Three different precursor combinations to make SiO_2 thin film

$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$
$SiCl_2H_2 + 2N_2O \rightarrow SiO_2 + 2N_2 + 2HCl$
$Si(OC_2H_5)_4 \rightarrow SiO_2$ + byproducts

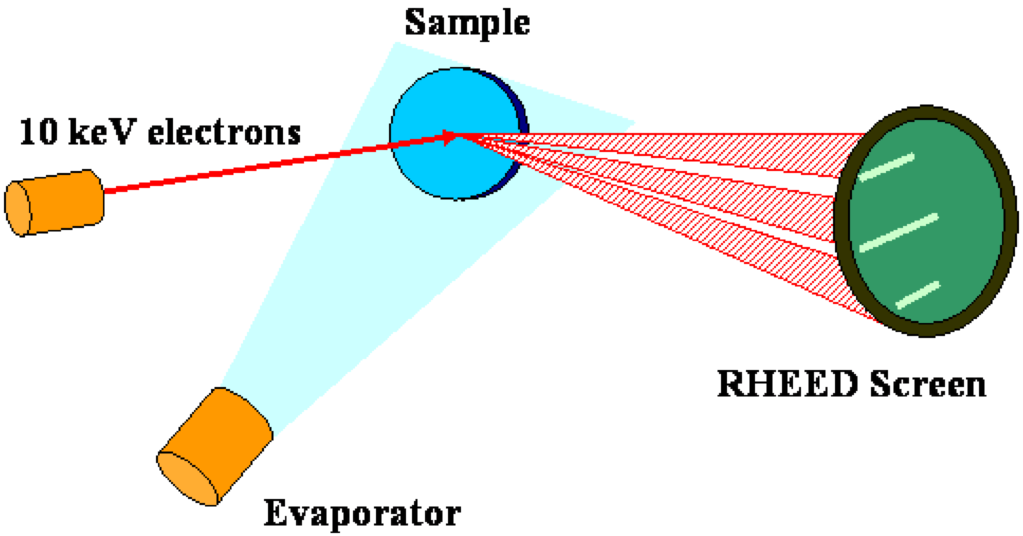
Atomic Layer Deposition: Self-limited CVD process

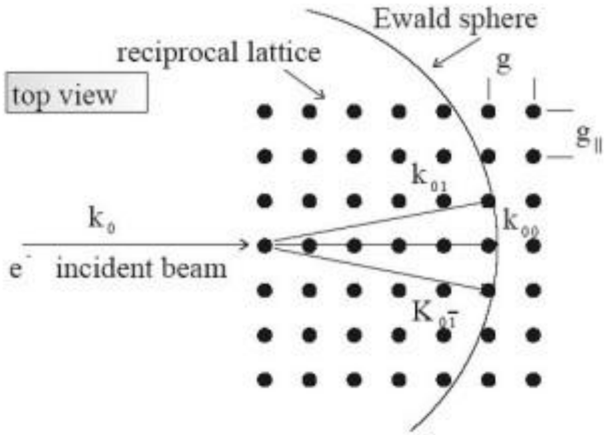


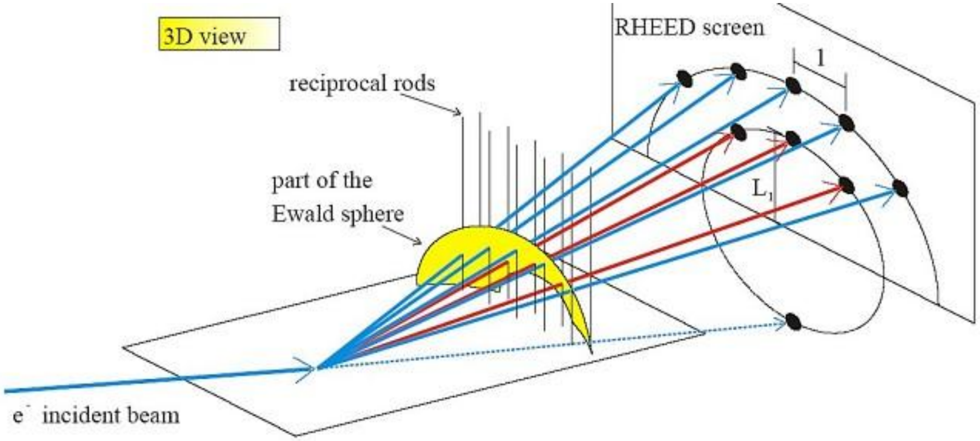
More about MBE

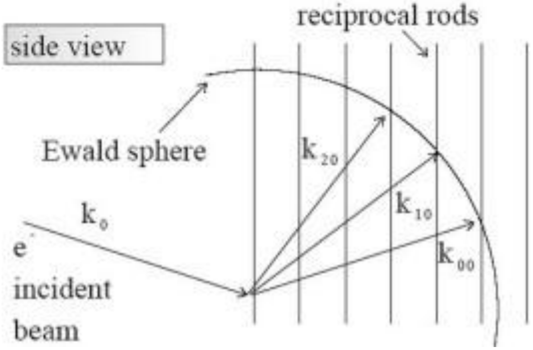
MBE is special because you can monitor and control film growth at atomic scale using RHEED

Reflection High Energy Electron Diffraction (RHEED)

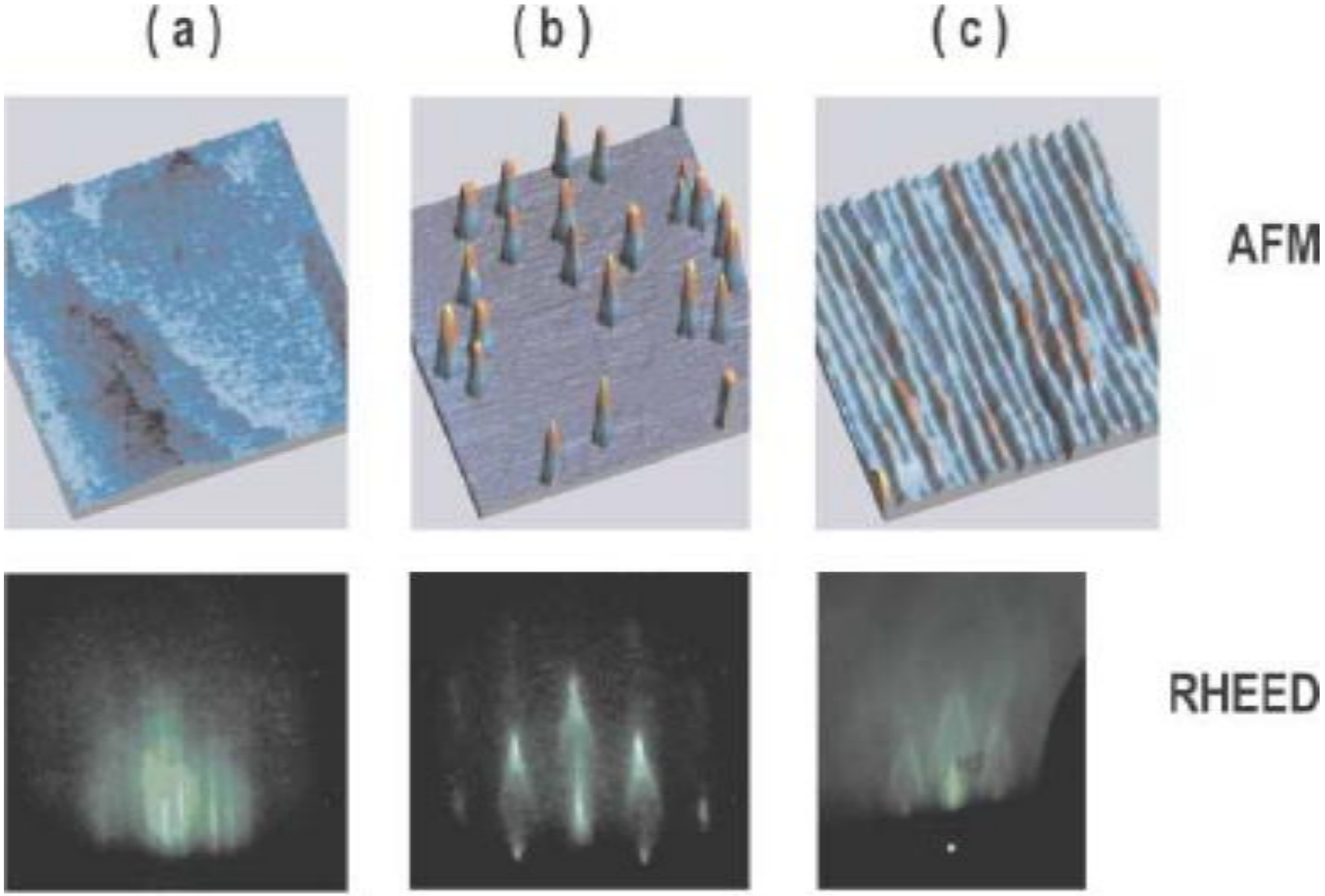




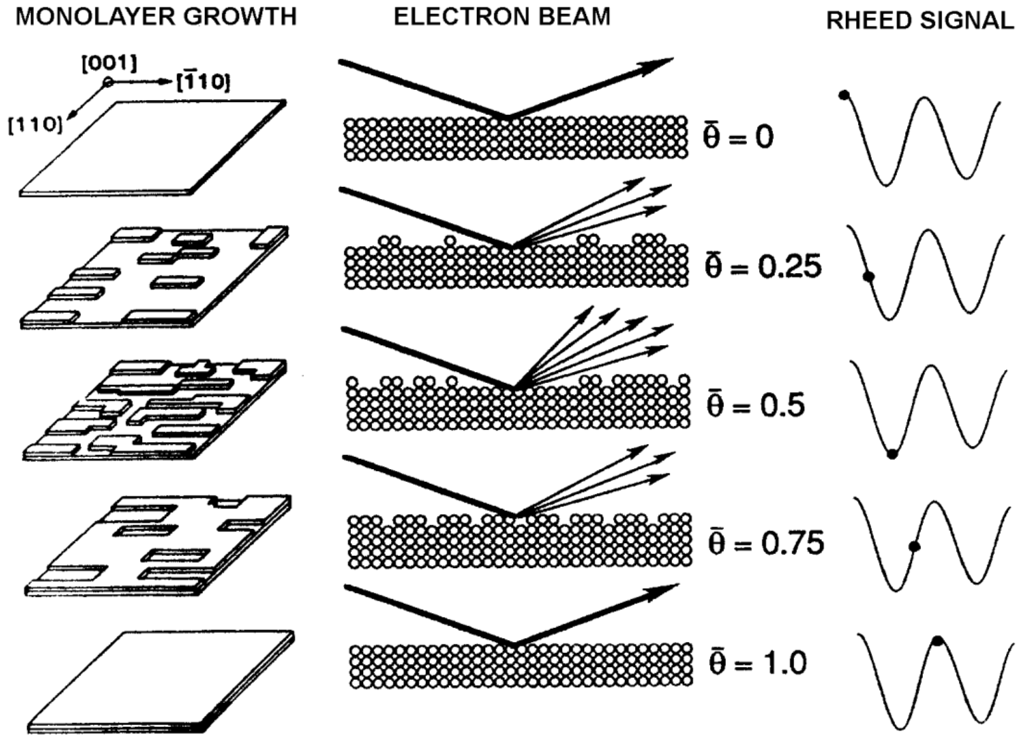




RHEED pattern gives information on real space morphology:



RHEED oscillation provides atomic-level thickness control



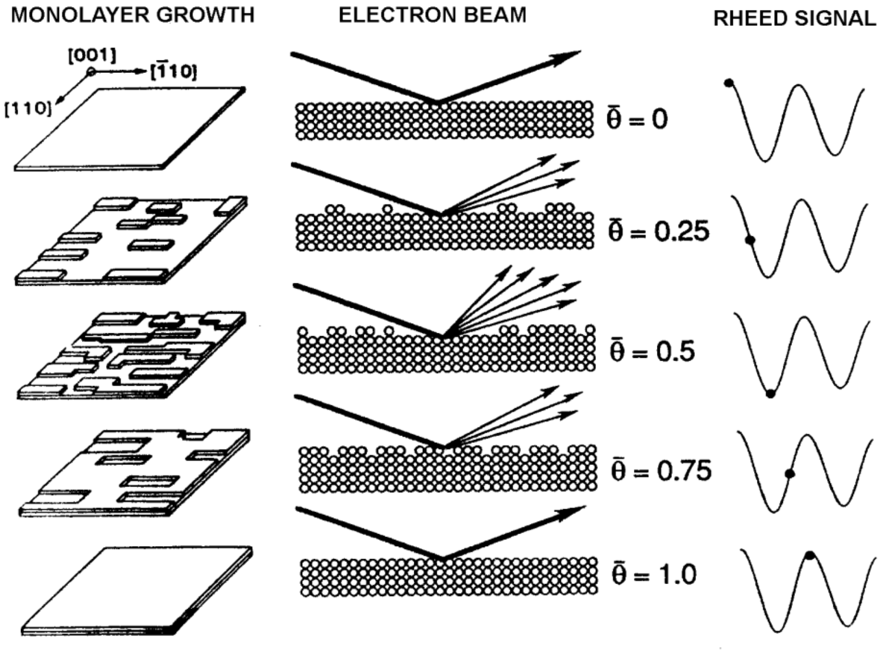
1970s: Birth of Molecular Beam Epitaxy

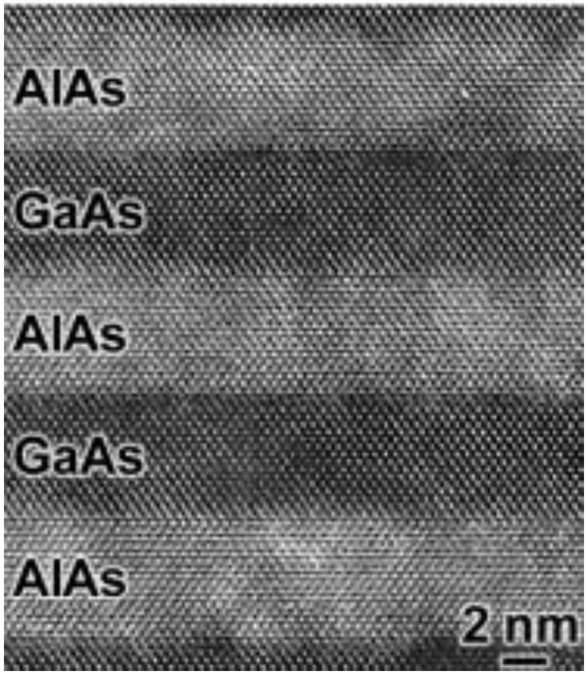
First MBE, Bell lab 1970

Modulation doping in GaAs/Al(Ga)As, Bell lab 1978

1980s: Atomic-layer engineering in III-V semiconductors

- Discovery of RHEED oscillations in Ga(Al)As growth ➔ atomic layer-by-layer growth

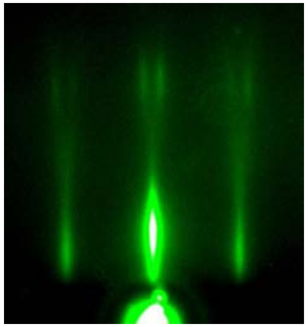




1990s: Atomic-layer engineering in complex oxides

Atomic-layer-by-layer growth of a layered superconductor

1



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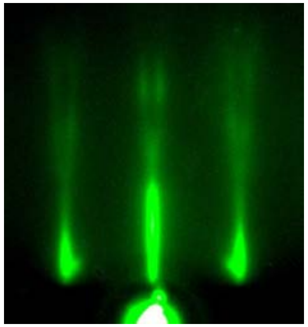
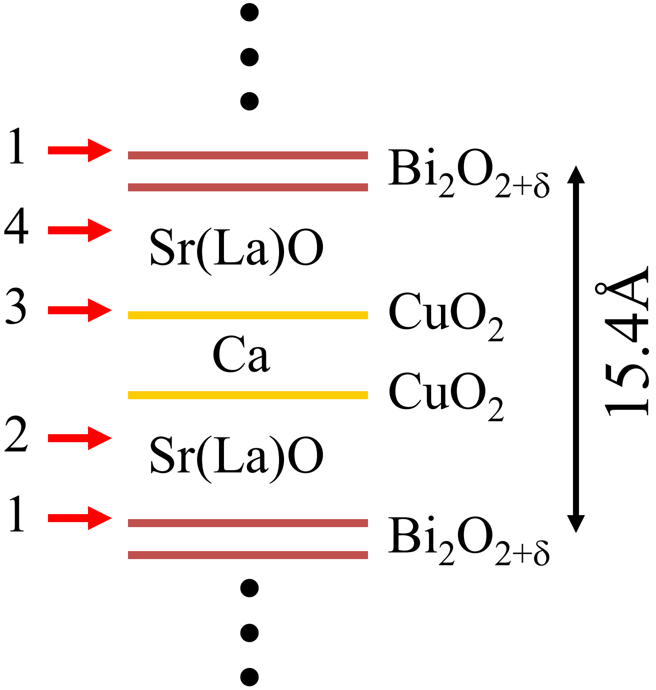




1 → $Bi_2O_{2+\delta}$

4 → Sr(La)O

3 → CuO_2

Ca

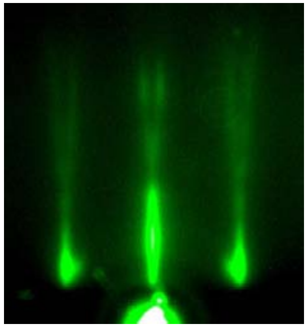
CuO_2

2 → Sr(La)O

1 → $Bi_2O_{2+\delta}$

15.4Å

2



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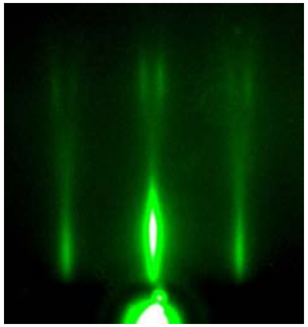
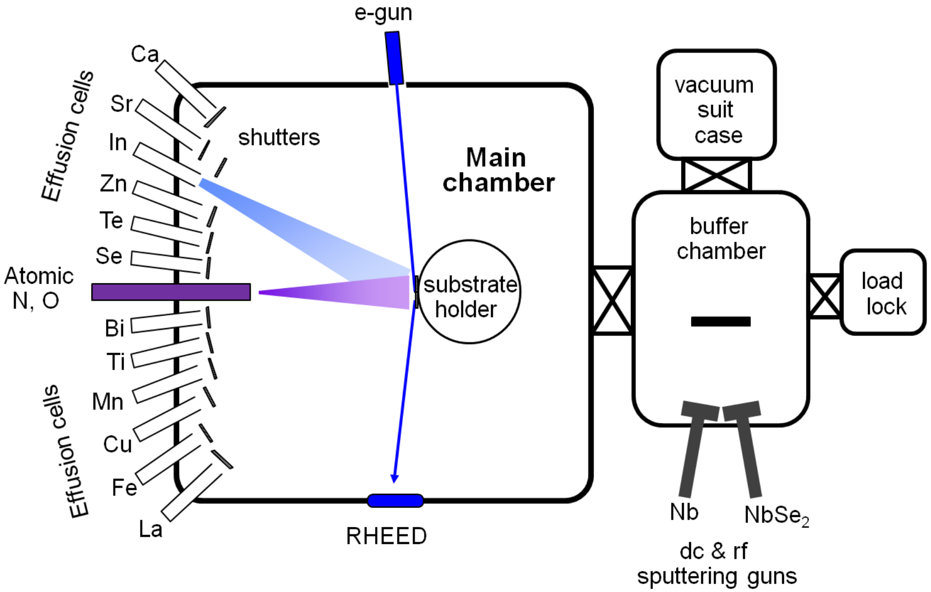


Our system (COAL MBE) (W132)



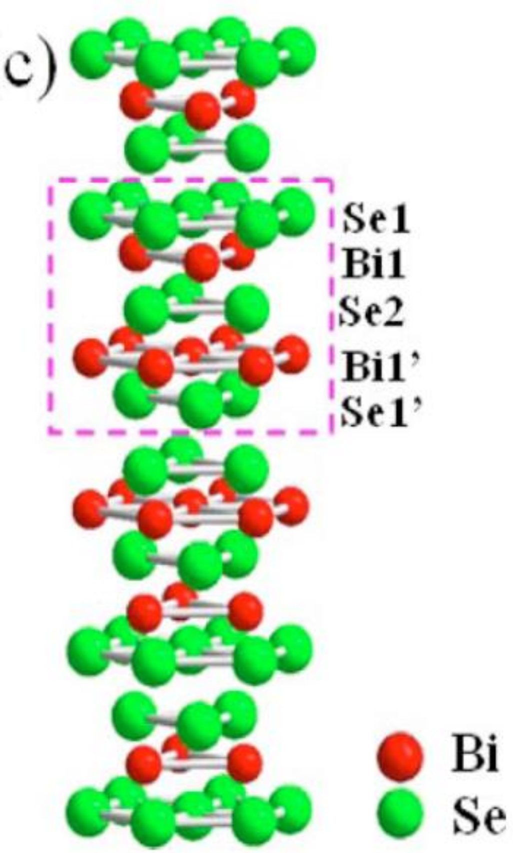
1. Flexible source to substrate distance
2. Vertical geometry and easy access to all components
3. Small source to substrate angle (good for uniformity)
4. Newly developed simple differential pumping schemes
5. Highly-optimized computer control

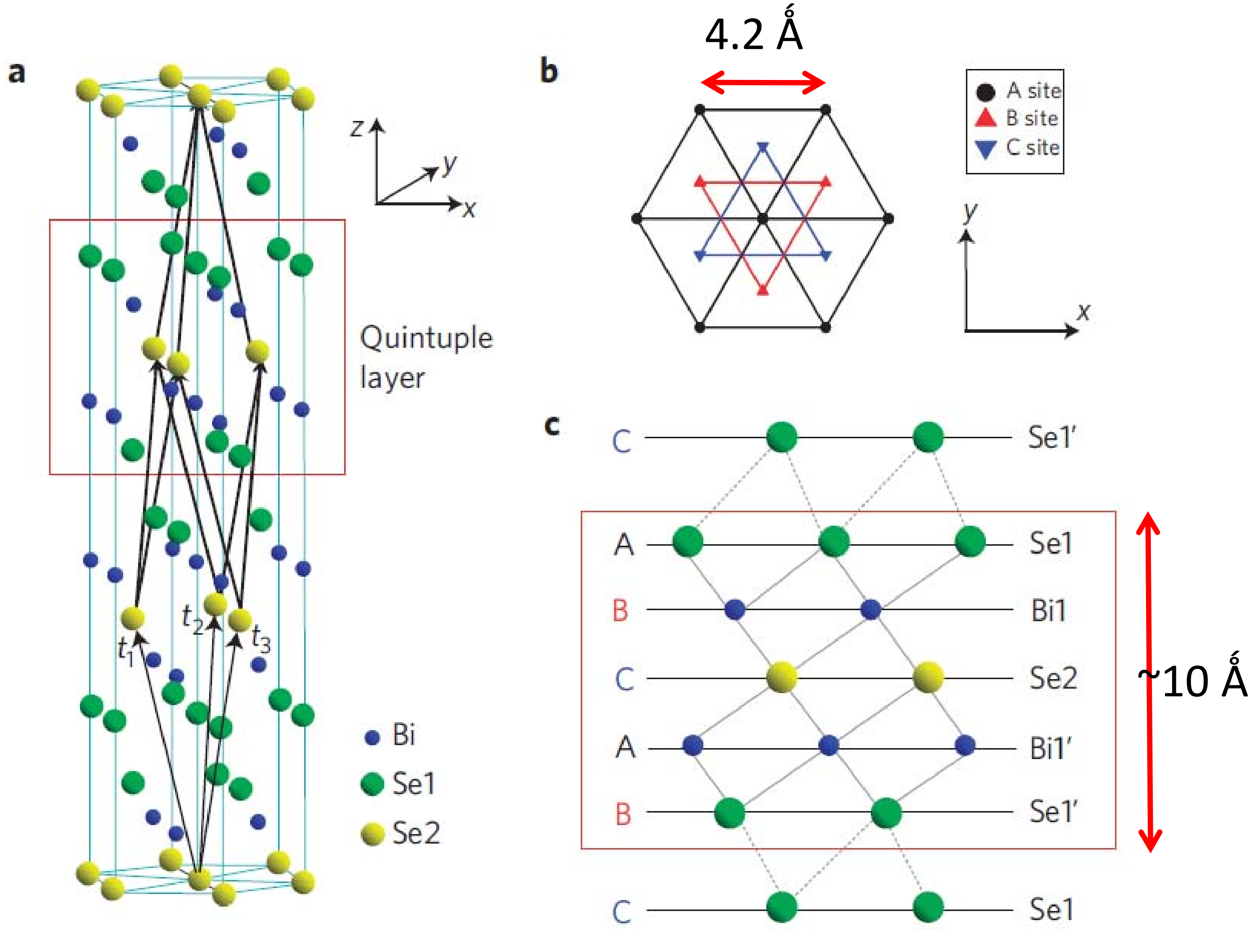
What are we working on now?

Growth of a topological insulator (Bi_2Se_3)

Crystal structure of Bi_2Se_3

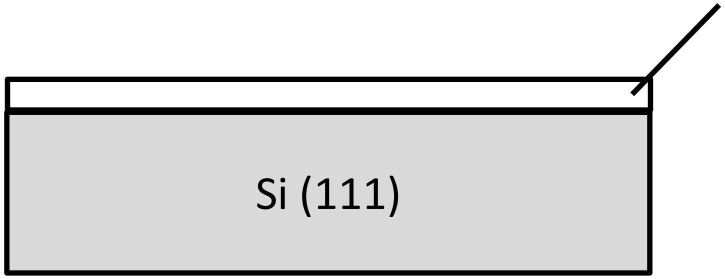
Van der-Waals bonding between Se bi-layers





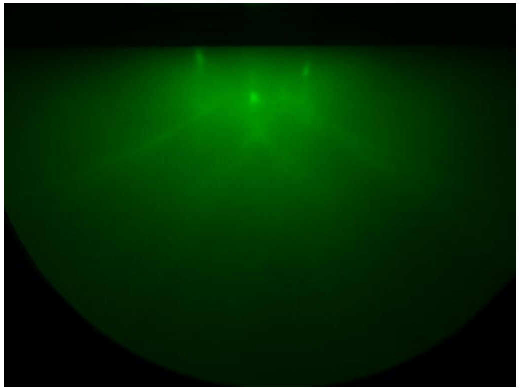
Si(111) Substrate Preparation

SiO_2 free Si surface (thermal heating)

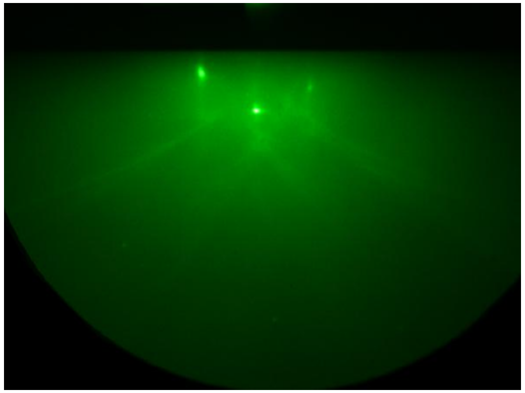


Needs to remove amorphous native oxide

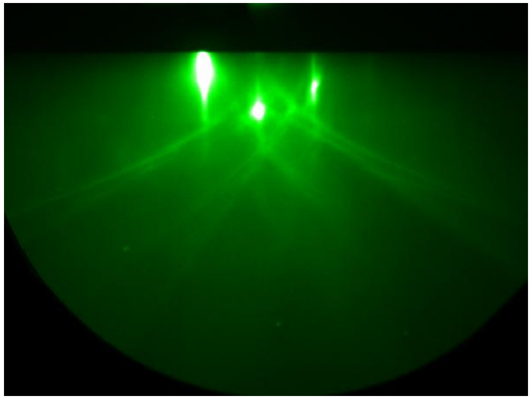
Si (111)



20˚C < T < 700 ˚C



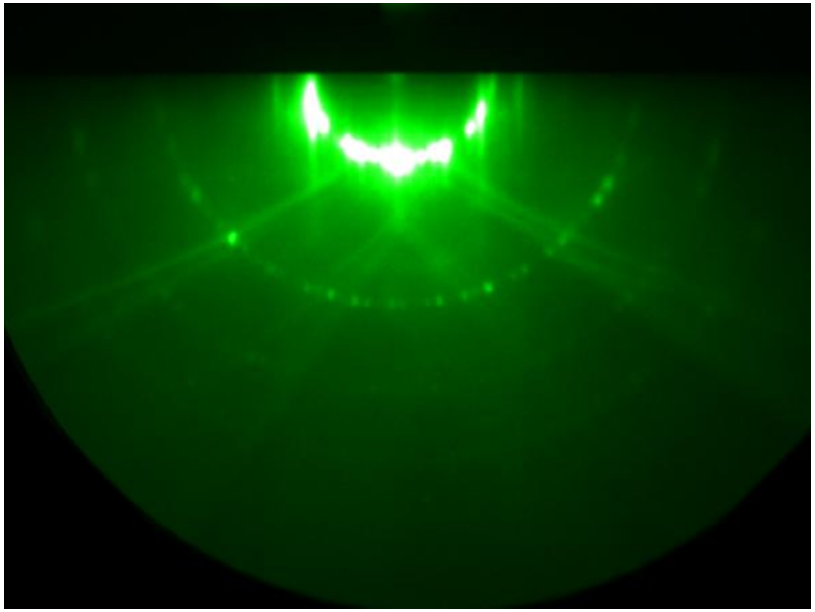
700˚C < T < 860 ˚C



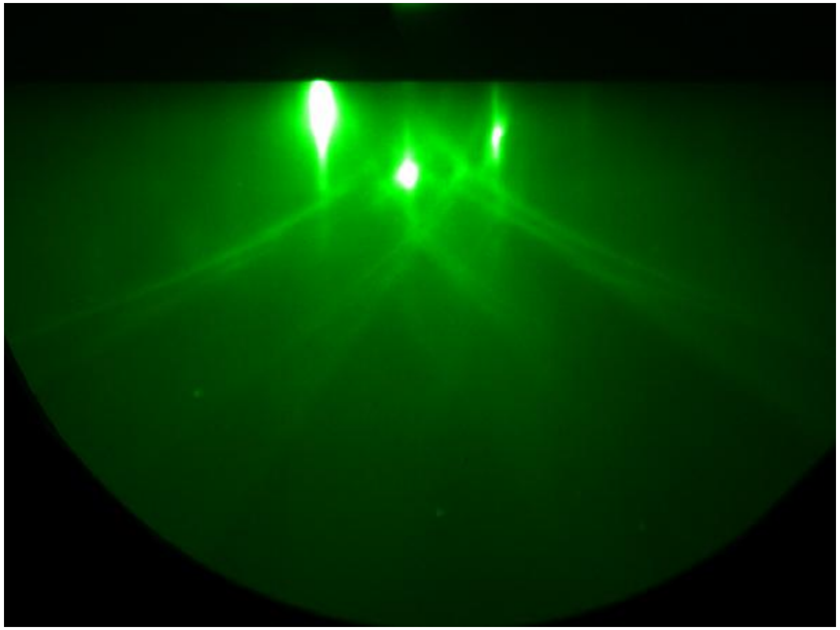
T > 860 ˚C

(7x7) to (1x1) of Si(111) surface

(7x7) occurs only if the native oxide is completely removed



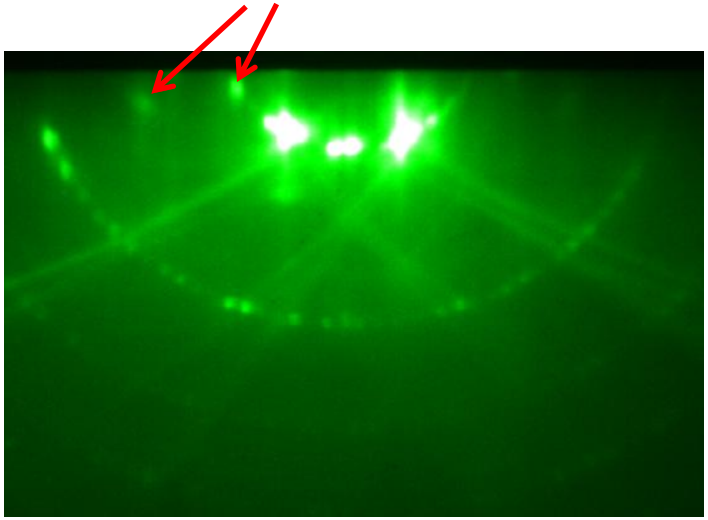
(7x7) T < 860 ˚C



(1x1) T > 860 ˚C

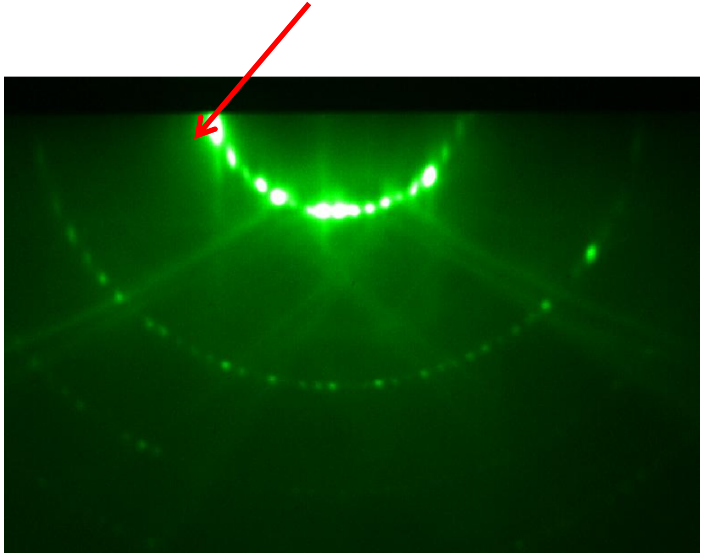
Dirty surface results in SiC clusters

STM image (SiC clusters)



Extra spot: Carbon contamination

No UV Ozone cleaning

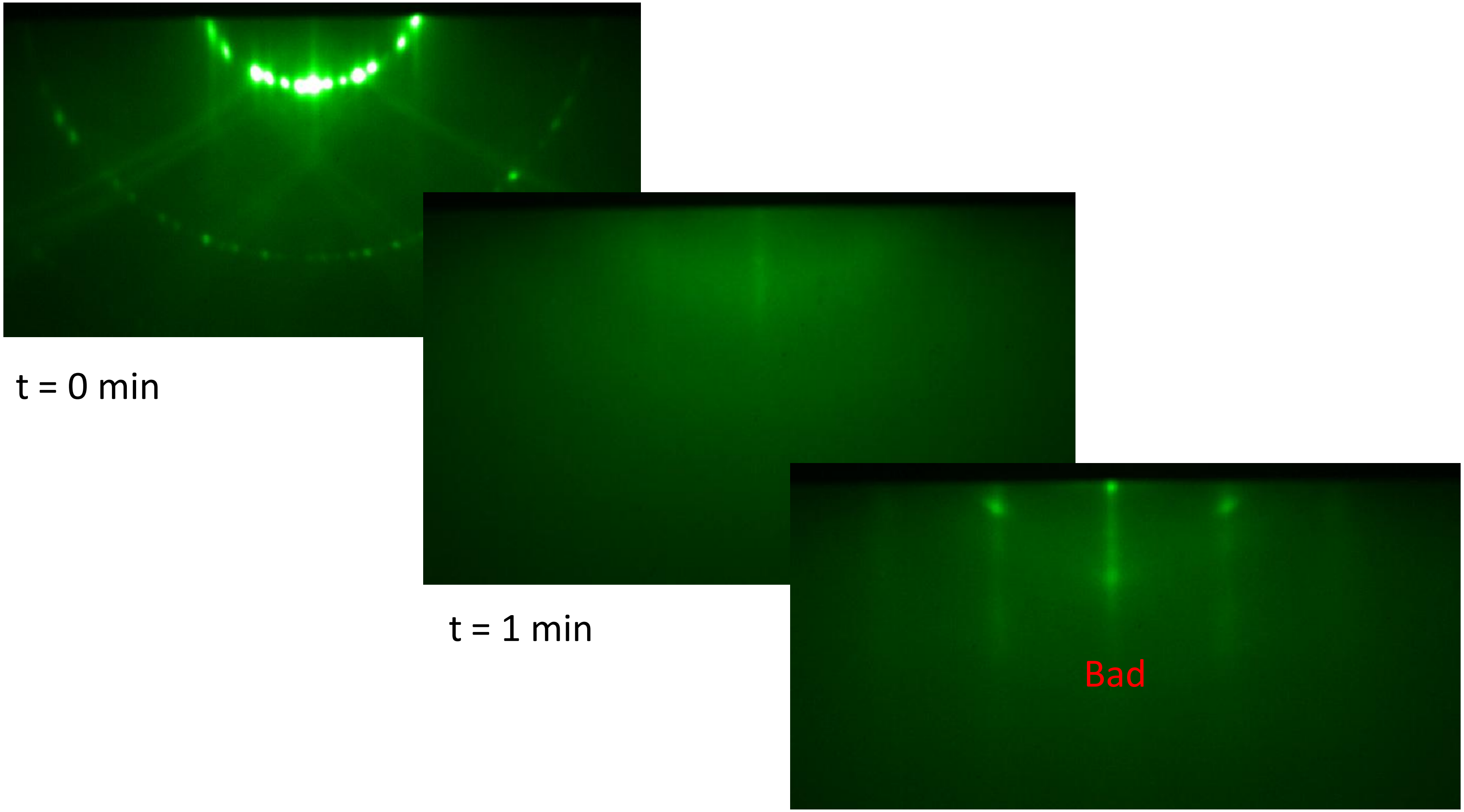


No extra spot

UV Ozone cleaned for 5 min

Bi_2Se_3 Growth on Si (111)

(1) Bi_2Se_3 growth @ 350 °C



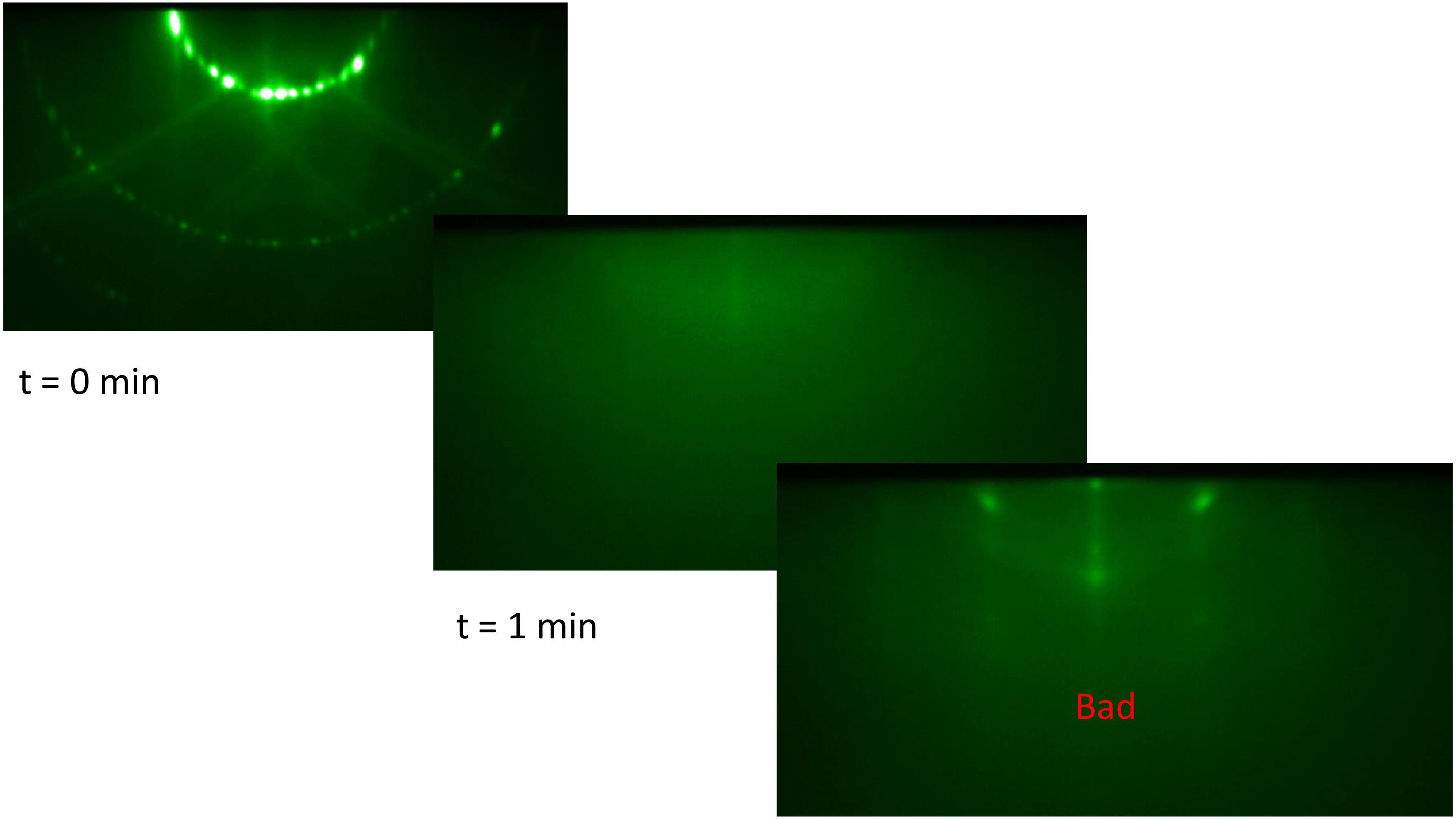
t = 0 min

t = 1 min

Bad

t = 3 min

(2) Bi_2Se_3 growth @ 250 °C

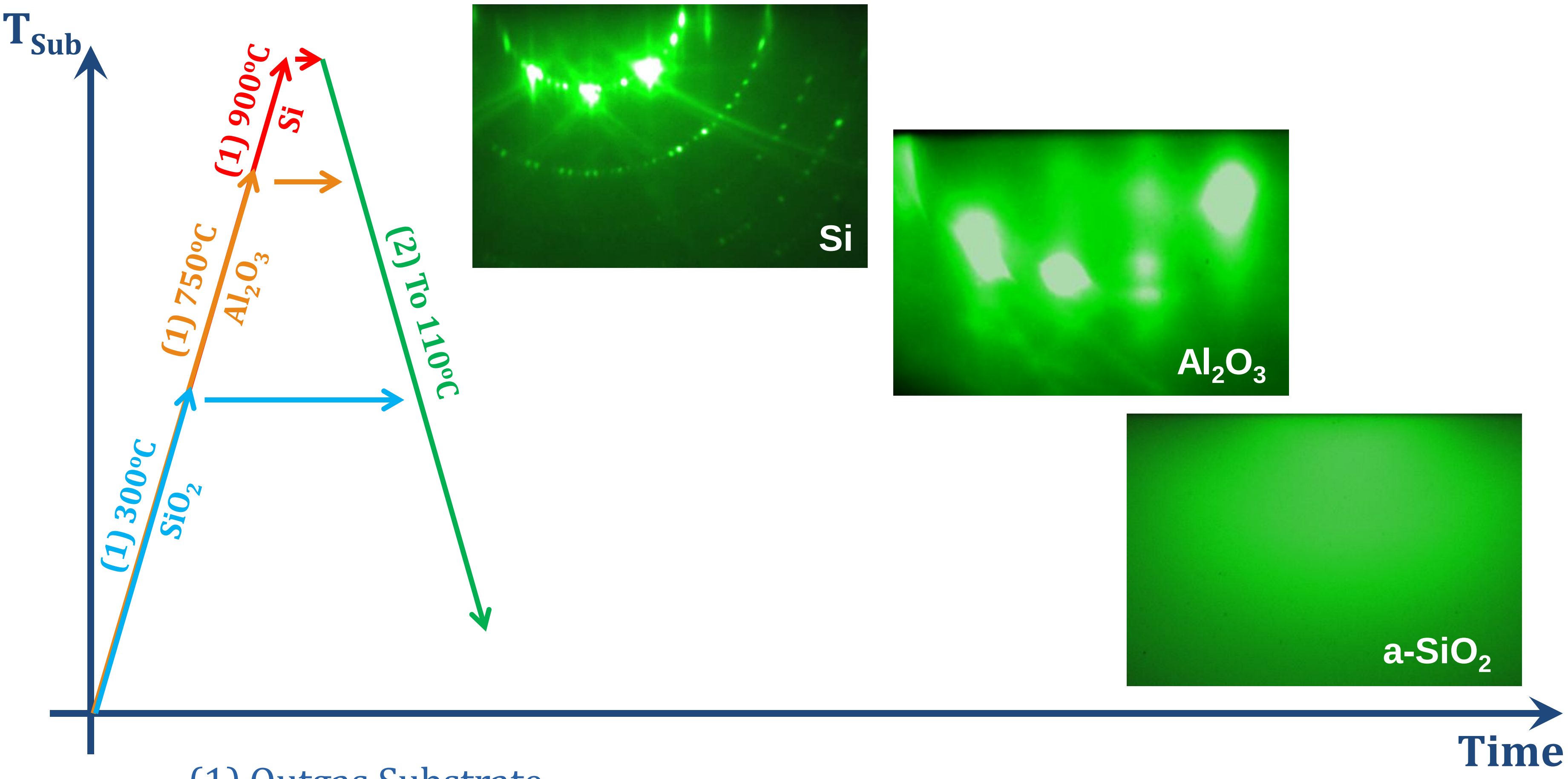


t = 0 min

t = 1 min

t = 3 min

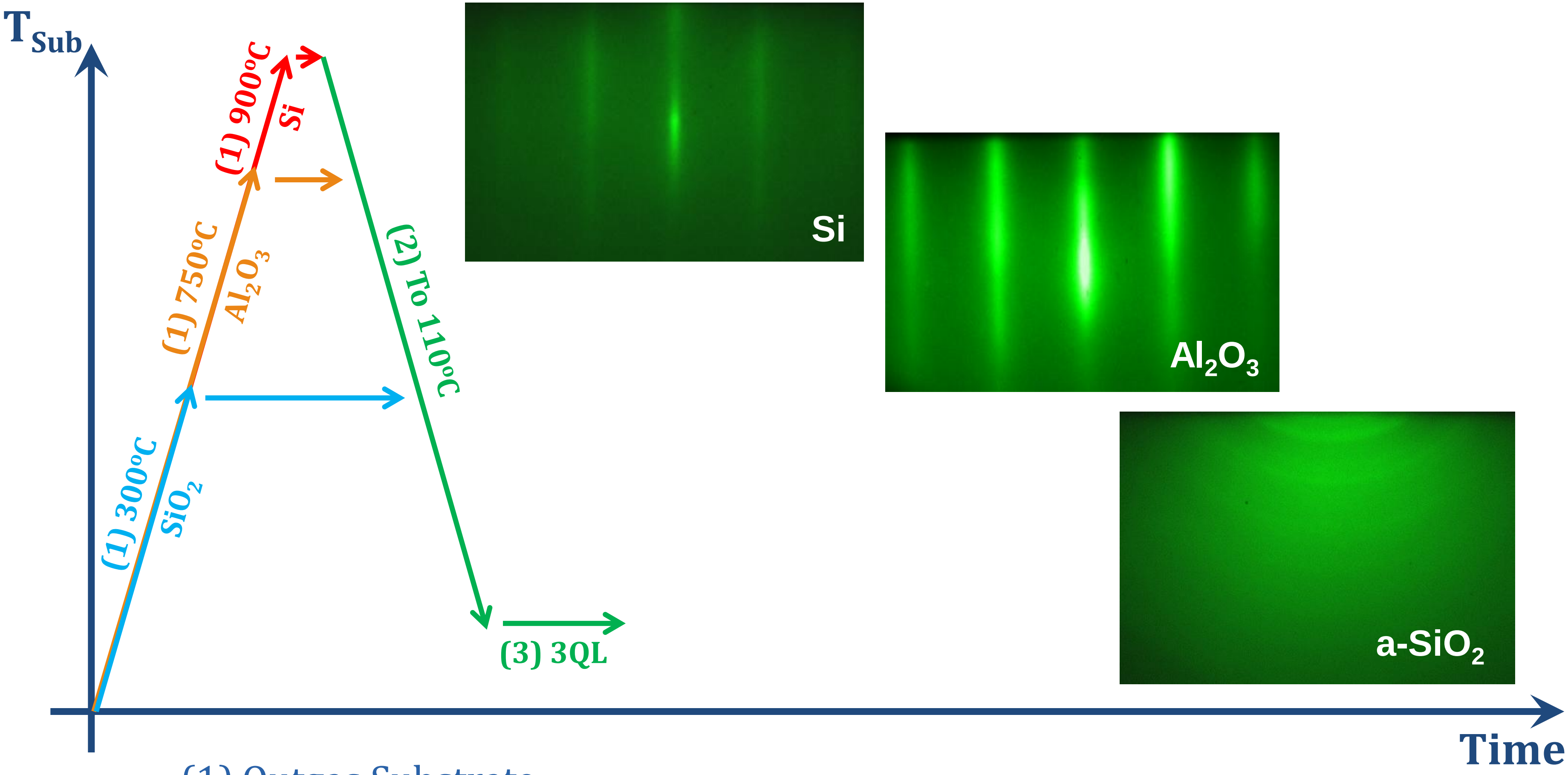
Two-Step Growth Process



(1) Outgas Substrate

(2) Cool to 110°C

Two-Step Growth Process

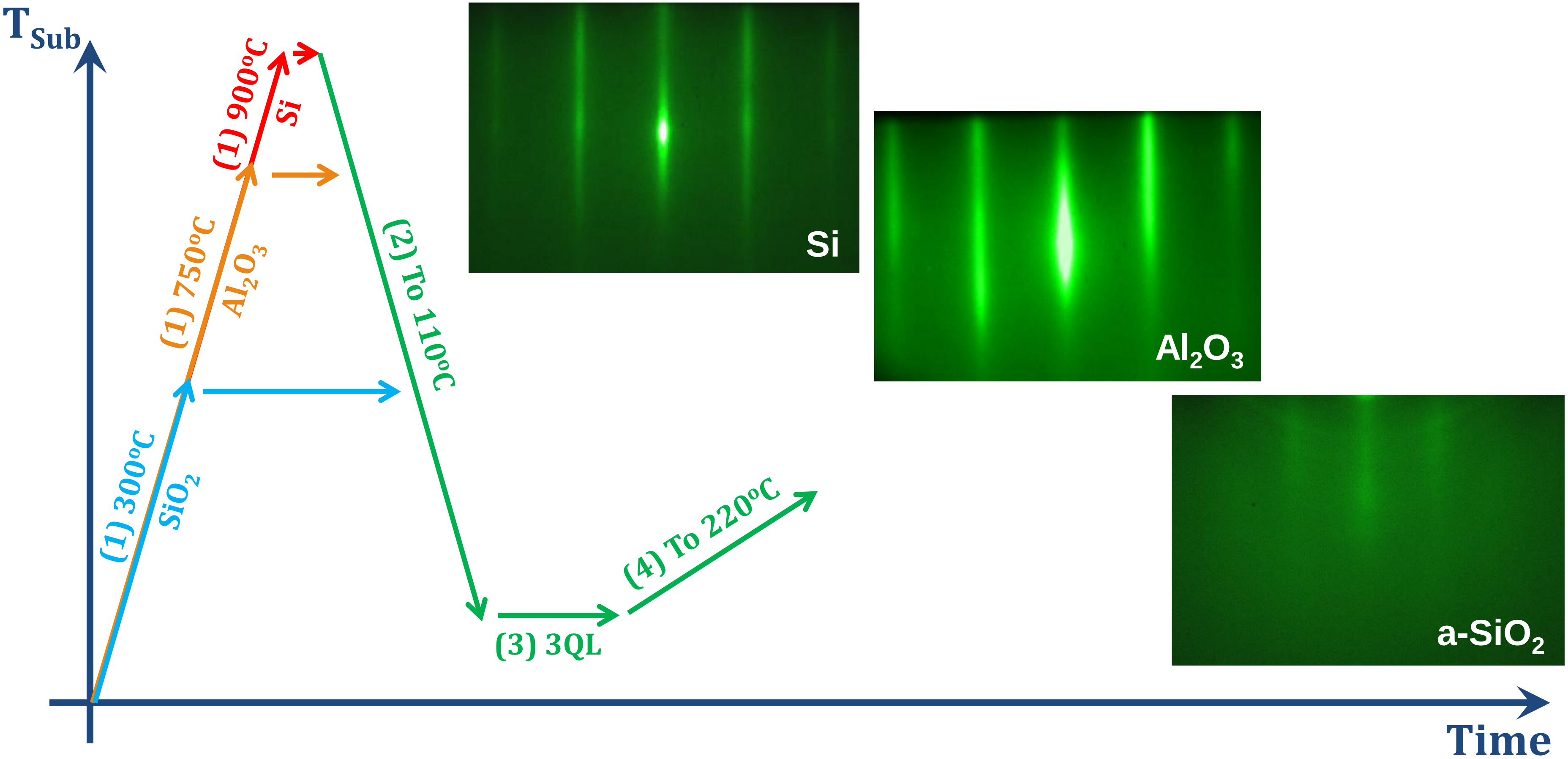


(1) Outgas Substrate

(2) Cool to 110°C

(3) Deposit 3QL at 110°C

Two-Step Growth Process



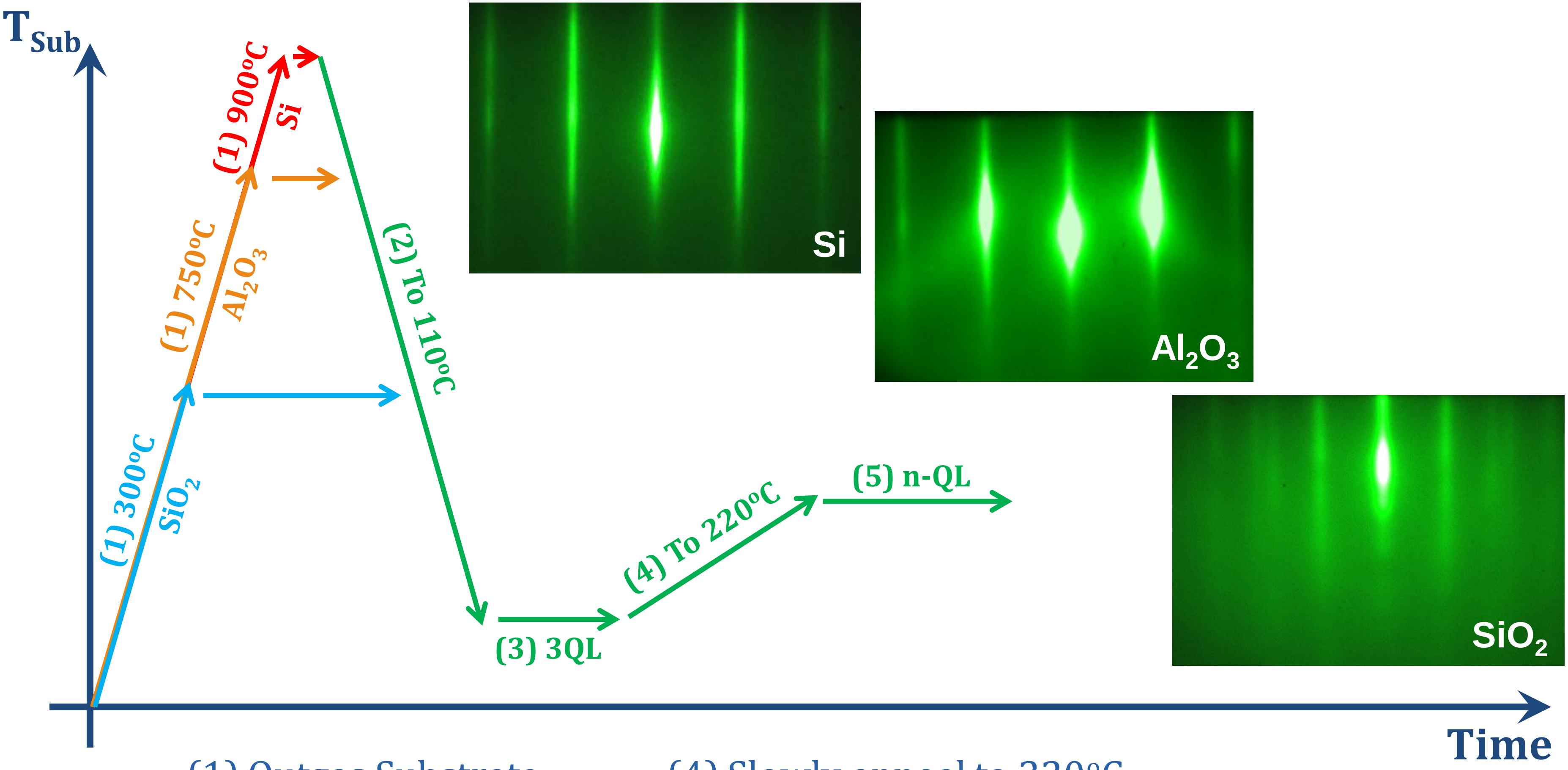
(1) Outgas Substrate

(2) Cool to 110°C

(3) Deposit 3QL at 110°C

(4) Slowly anneal to 220°C

Two-Step Growth Process



(1) Outgas Substrate

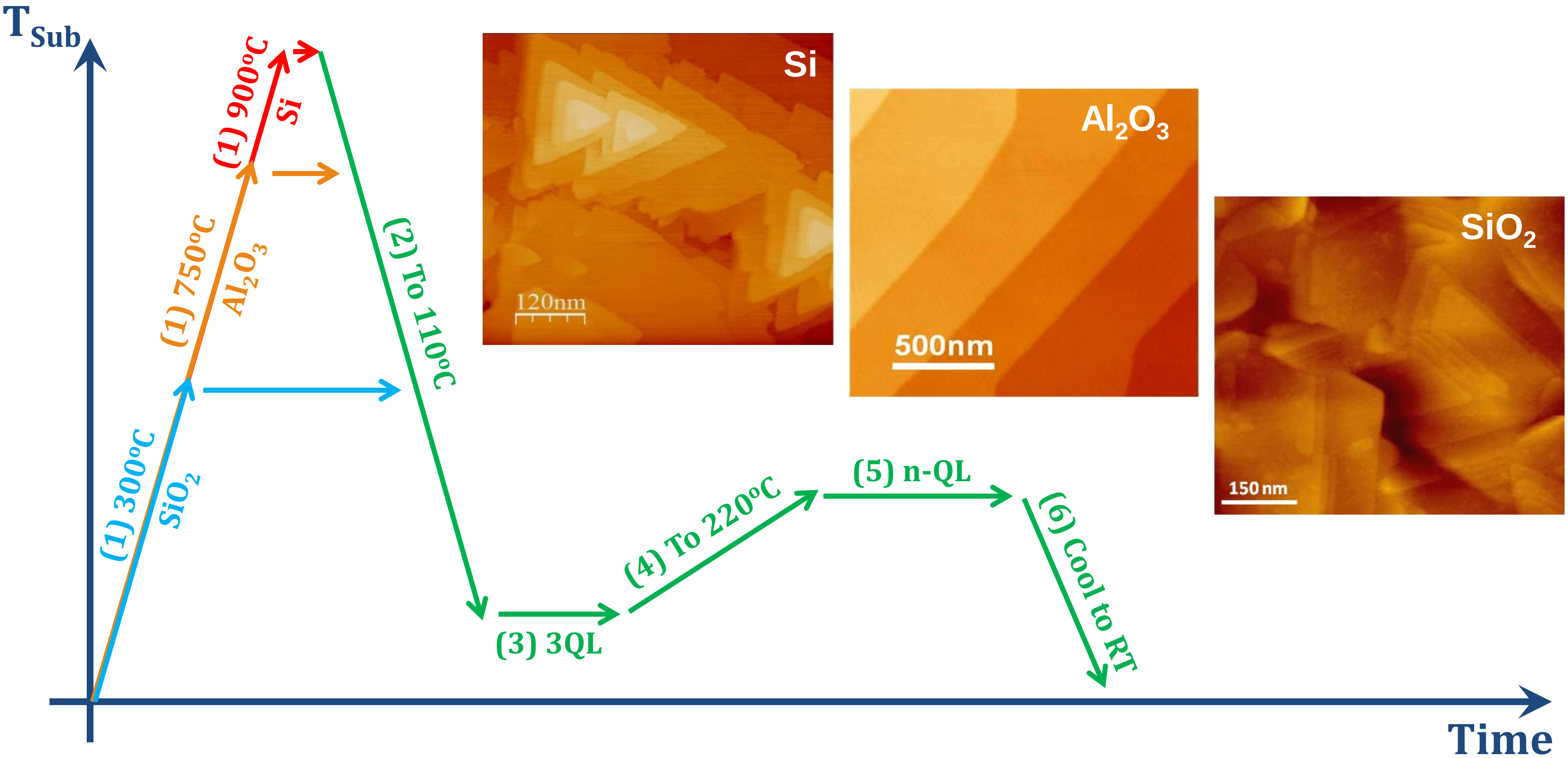
(2) Cool to 110°C

(3) Deposit 3QL at 110°C

(4) Slowly anneal to 220°C

(5) Deposit required QLs at 220°C

Two-Step Growth Process



(1) Outgas Substrate

(2) Cool to 110°C

(3) Deposit 3QL at 110°C

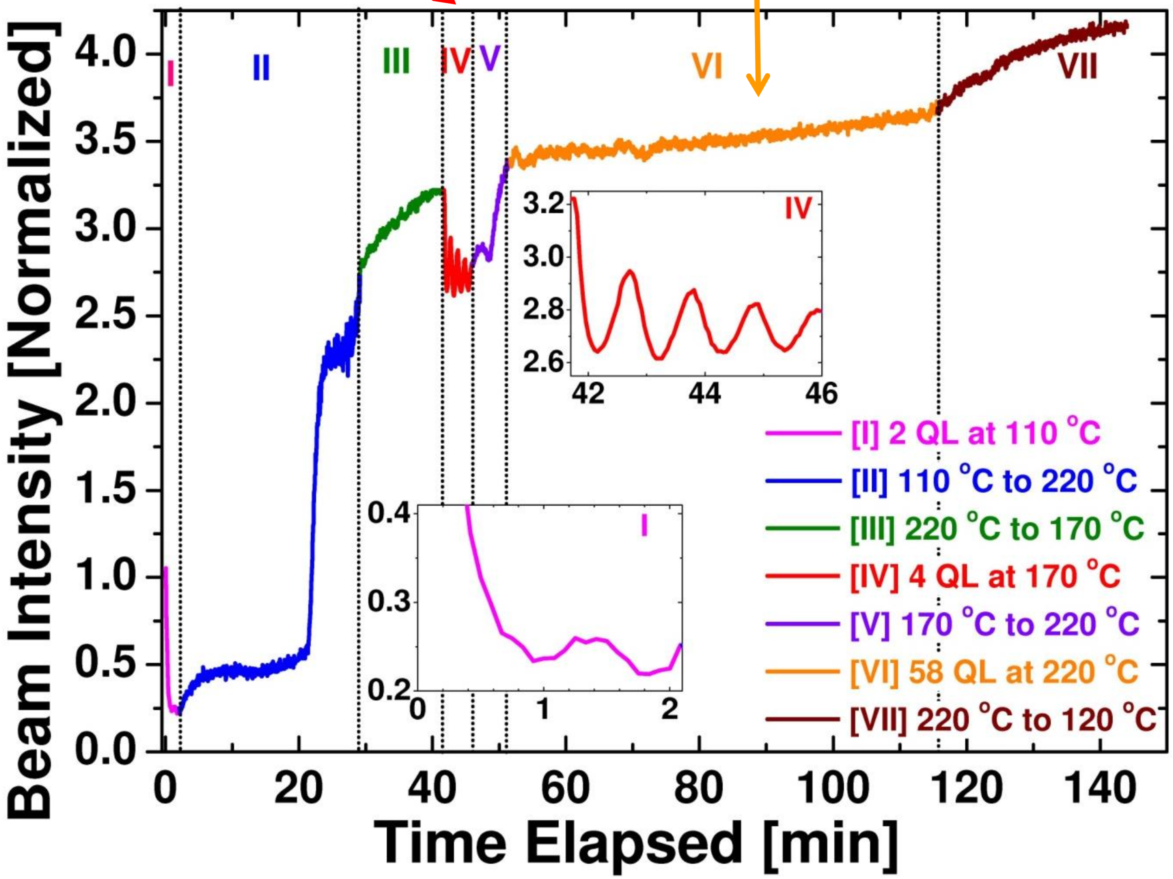
(4) Slowly anneal to 220°C

(5) Deposit required QLs at 220°C

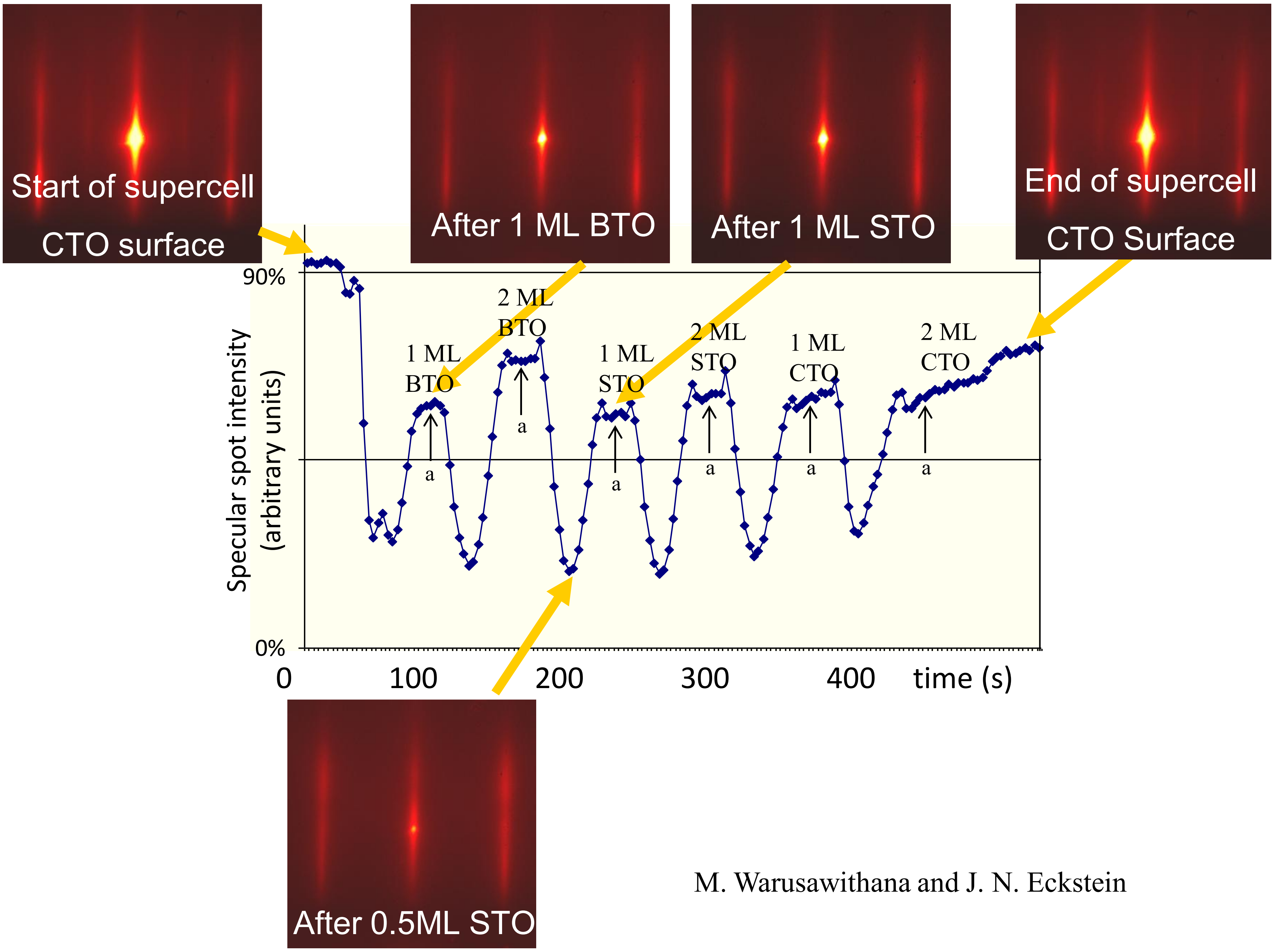
(6) Cool to Room Temperature

RHEED oscillation in the intermediate growth condition: Layer-by-layer growth

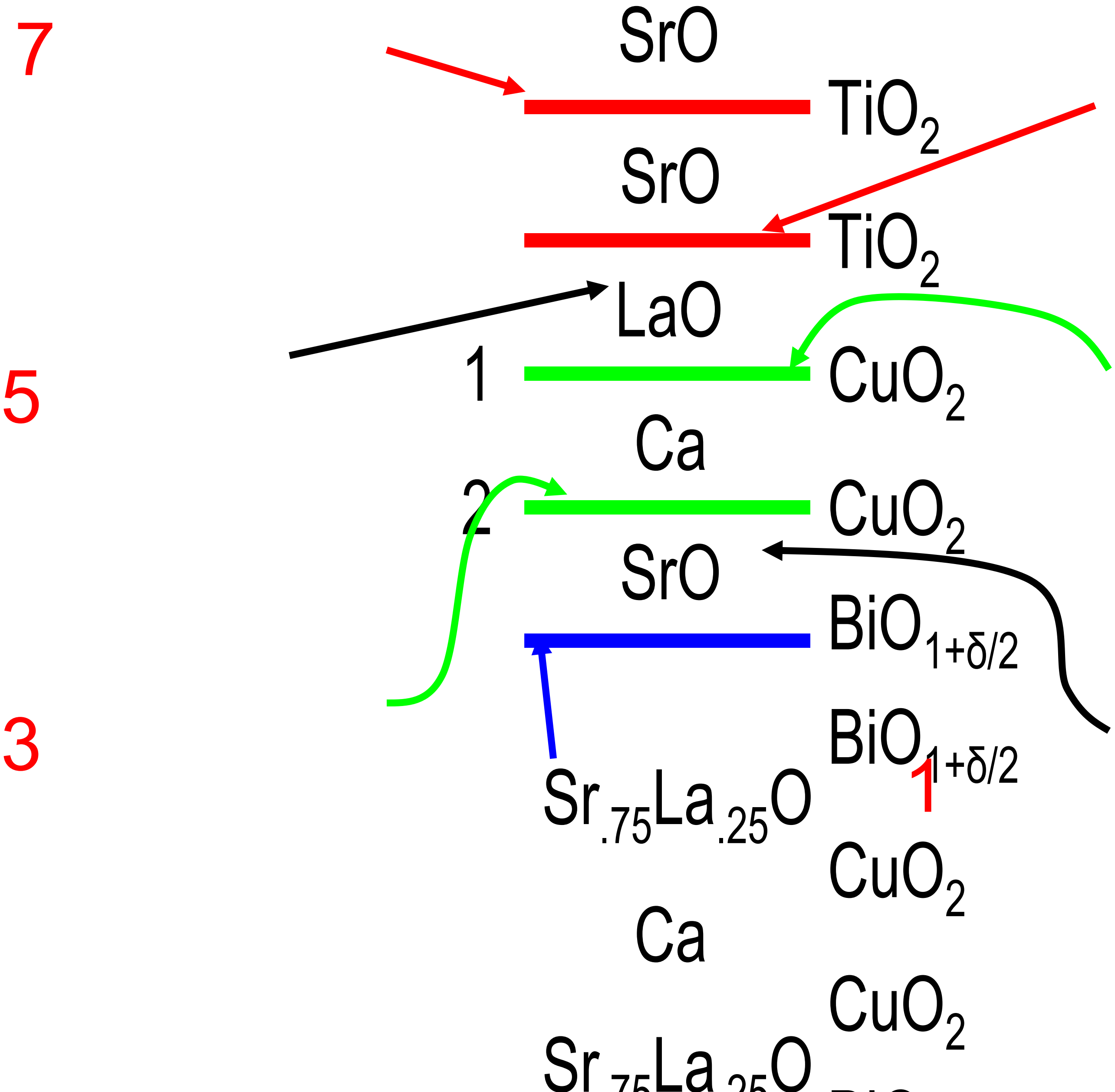
Best growth condition: Step-flow growth ➔ no RHEED oscillation



Growth of other systems



M. Warusawithana and J. N. Eckstein



7

SrO

TiO_2

SrO

TiO_2

LaO

5

1 CuO_2

Ca

2 CuO_2

SrO

$BiO_{1+\delta/2}$

3

$BiO_{1+\delta/2}$

1

$Sr_{.75}La_{.25}O$

CuO_2

Ca

CuO_2

$Sr_{.75}La_{.25}O$

6

4

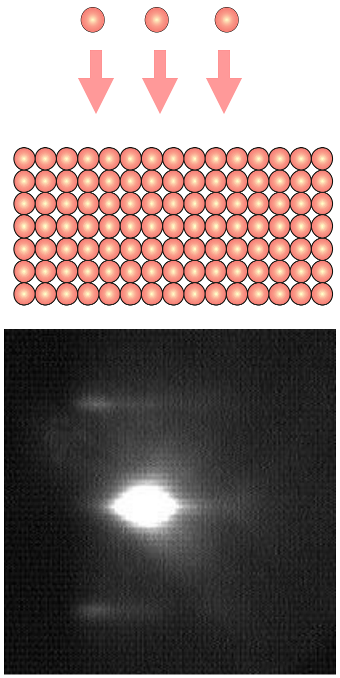
2

Growth of Epi-Re/Epi-Al_2O_3/Poly-Al

Epitaxial Re/Al2O3

@ 850 °C

Re

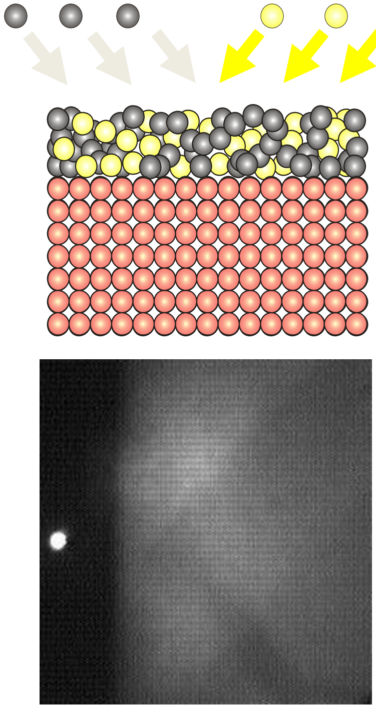


Amorphous AlOx

@ RT

Al

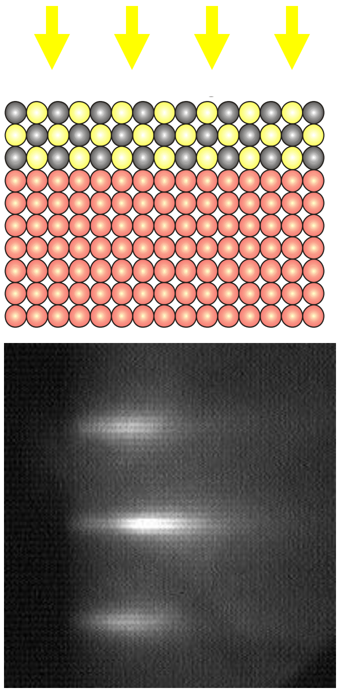
10^{-6} Torr O2



Epitaxial Al2O3

@ 800 °C

4×10^{-6} Torr O2,



Polycrystalline Al

@ RT

Al