Building College-University Partnerships for Nanotechnology Workforce Development

Chemical Vapor Deposition
2 Modes, 1D, 2D

PennState

Outline

- Short overview: chemical vapor deposition
- Typical LPCVD systems/hardware
- Top down applications
  - 2D materials (thin films, VS growth, epitaxial systems)
- Bottom up applications
  - 1D materials (nanowires, VLS growth)

Introduction

- The term, Chemical Vapor Deposition (CVD) generally applies to a process which "converts" some precursor gas or gases, into a new material that is deposited on a substrate.
- The chemical reactions that cause the "conversion" into a new material are driven by energy supplied by;
  - Temperature (simply called CVD).
    - LIMITED USE -HEAT
  - Plasmas (called Plasma Enhanced Chemical Vapor Deposition, or PECVD).
- CVD process of these two modes are often done at low pressure, to obtain uniform deposition and better control of the chemical reaction.

LPCVD

- A widely used chemical vapor deposition tool that can be used for top down or bottom-up processing.
- Lower pressures are utilized to control reactions and film uniformity.
- Heat is used to initiate and increase reaction rates, i.e. processes are activated ($\alpha e^{-\Delta/kT}$).
- Probably 100's mT and higher, large chemistry C.

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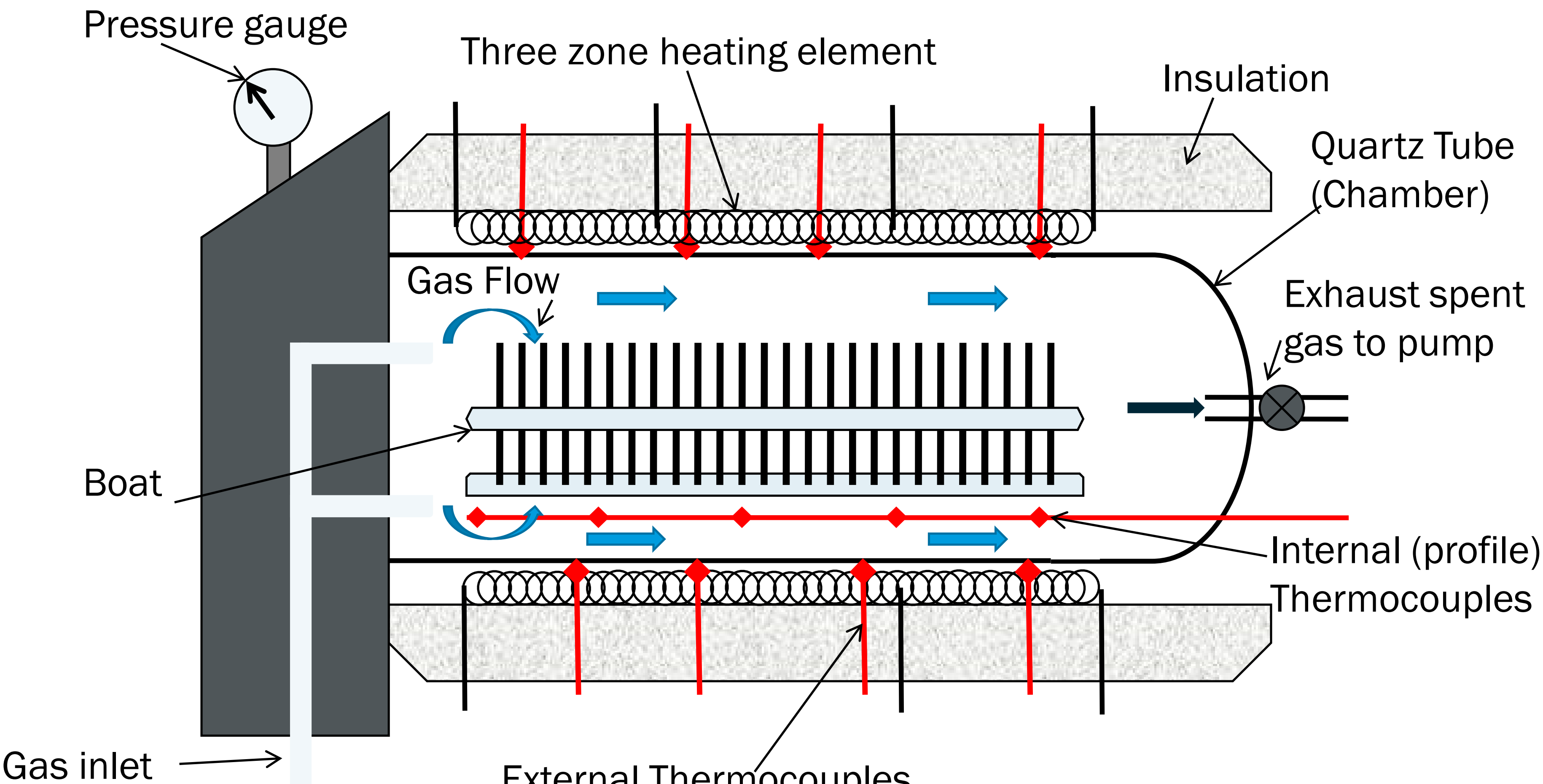
Form and Function

- LPCVD generally operates under medium vacuum (0.1 ~ few Torr).
- Medium vacuum increases the diffusivity of the reactant gas molecules.
- Since the reaction is not limited by the availability of gases at the substrate's surface, the chamber can be designed to optimize substrate capacity, and increase throughput.
- Typically, a recipe can take hours. This is not economically feasible for a single substrate, so batch processing occurs in most systems.

LPCVD Reactor

- Hot wall reactors are favored because they provide uniform temperature over a large operating length.
- Growth rate decreases further from the gas inlets. Increased temperature in the further regions of the tubes creates greater uniformity on the substrate.
- The chemistry and heat are balanced to provide uniformity across the substrate and the batch.

Batch LPCVD Horizontal Reactor



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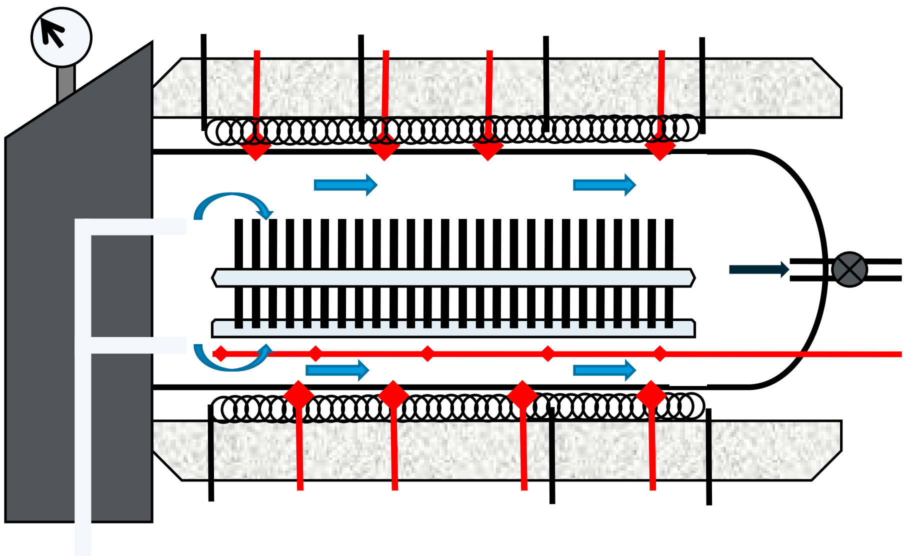
Automate Low Pressure Chemical Vapor Deposition



Automate Low Pressure CVD System

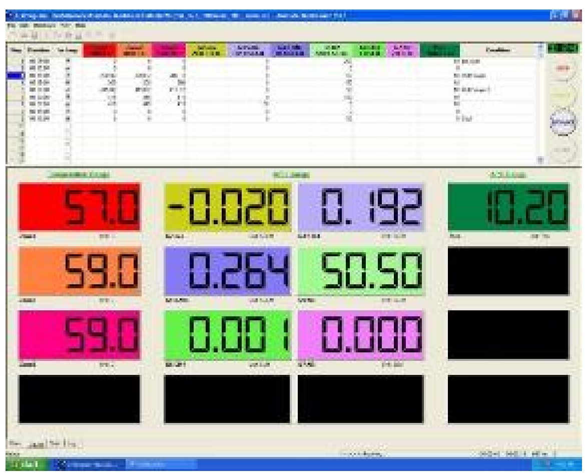
How It Works: A gas or vapor precursor is transformed into solids such as thin films, powders, or various structured materials inside a reactor. Temperature and pressure are controlled to tailor the deposition results.

Material / Applications: Chemical vapor deposition (CVD) is a versatile technique often used in the semiconductor industry for deposition of material on various substrates such as silicon nitride. It has also been used to produce carbon fibers, filaments, and tubular carbon materials for many years. Recently, CVD has been used to synthesize a variety of nanostructured materials, including carbon nanotubes and nanowires composed of various materials.

Hydride Gases	Diborane, Phosphine, Silane
Other Gases	Nitrogen, Hydrogen, Argon, Methane, Ethylene
Tube Dimensions	25mm diameter x 200mm single zone reaction chamber
Vacuum Base Pressure	20 mTorr
Pump Description	Rotary Vacuum Pump

~cost $120,000 tool only. A complete system price is approximately double this.

Automate LPCVD



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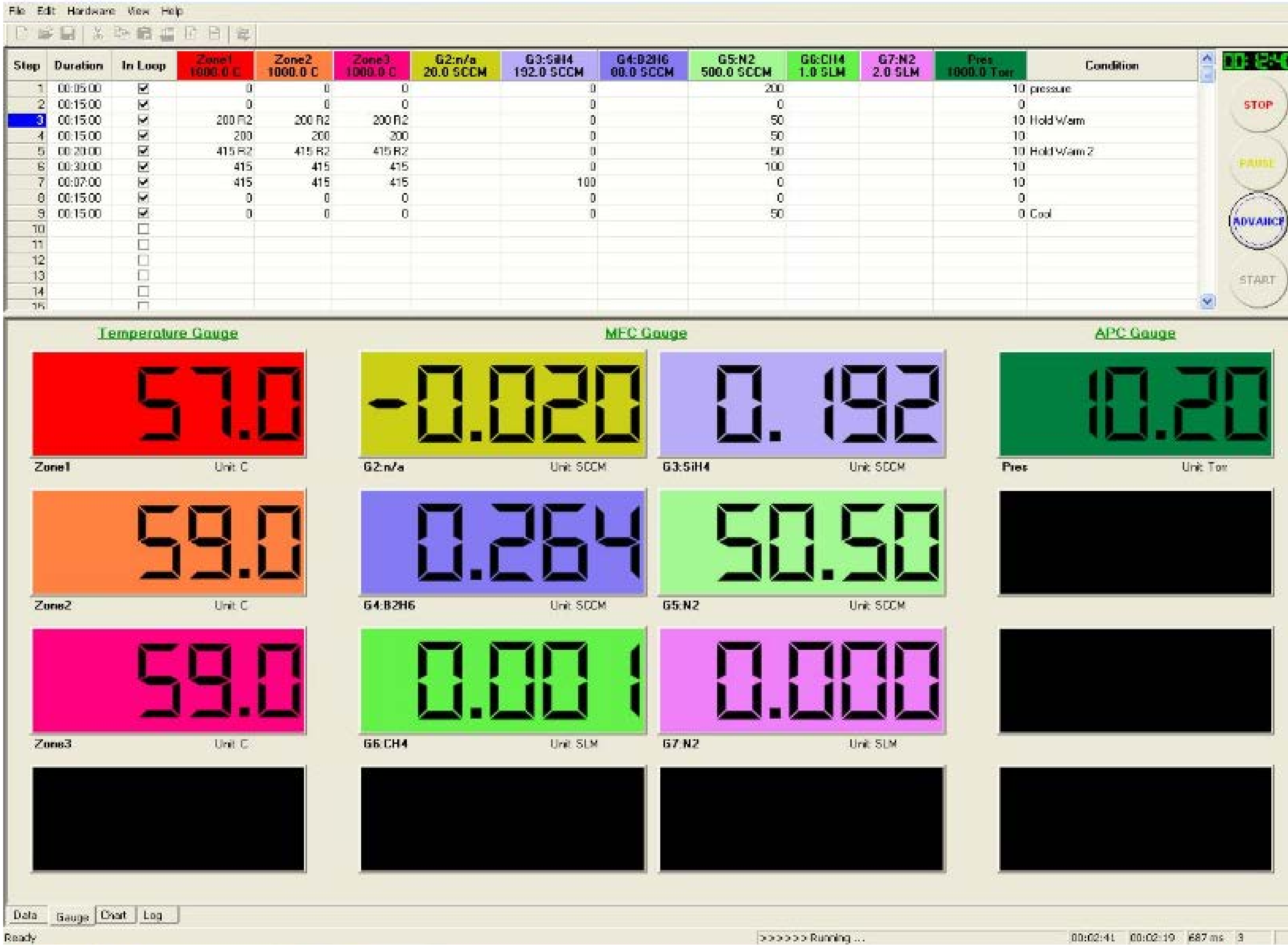
Screen Capture of the Automate LPCVD Control Screen



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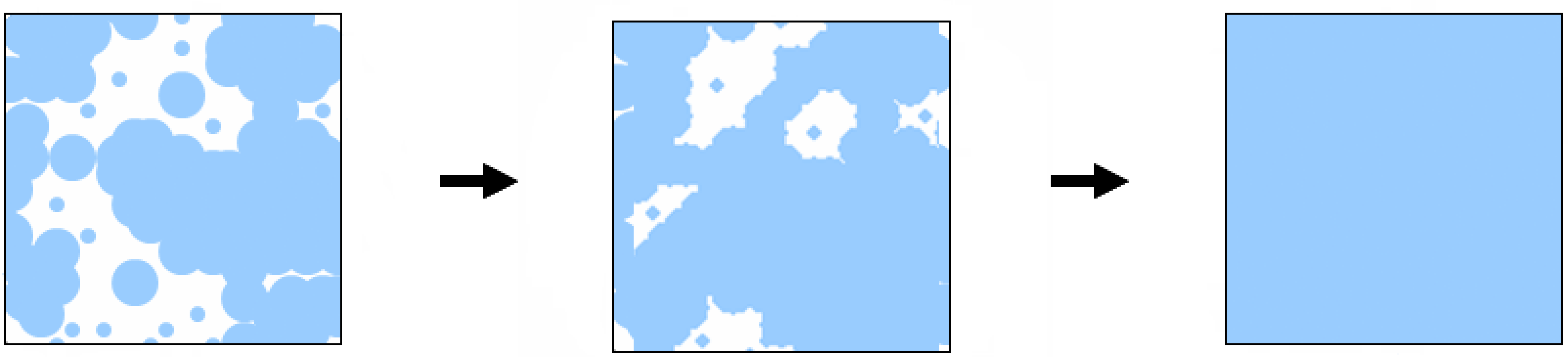
Vapor Solid (VS) Growth

- The Vapor Solid mode is used to describe thin film growth on a substrate.
- The length of time it takes for a CVD reaction to occur is limited by the slowest step.
- Mass-transport limited, refers to the limitation of the speed of CVD by the availability of process gases.
- Reaction rate (or kinetics) limited, refers to the limitation of the speed of CVD by the chemical reaction on the surface of the substrate.

Thin Film Growth Sequence

- Thin film growth occurs when island clusters coalesce, or combine, eventually forming a continuous film.



What happens on the deposition surface?

Adatom: An atom intended to be adsorbed and incorporated on the surface.

Vapor deposition consists of the following basic atomic processes in sequence:

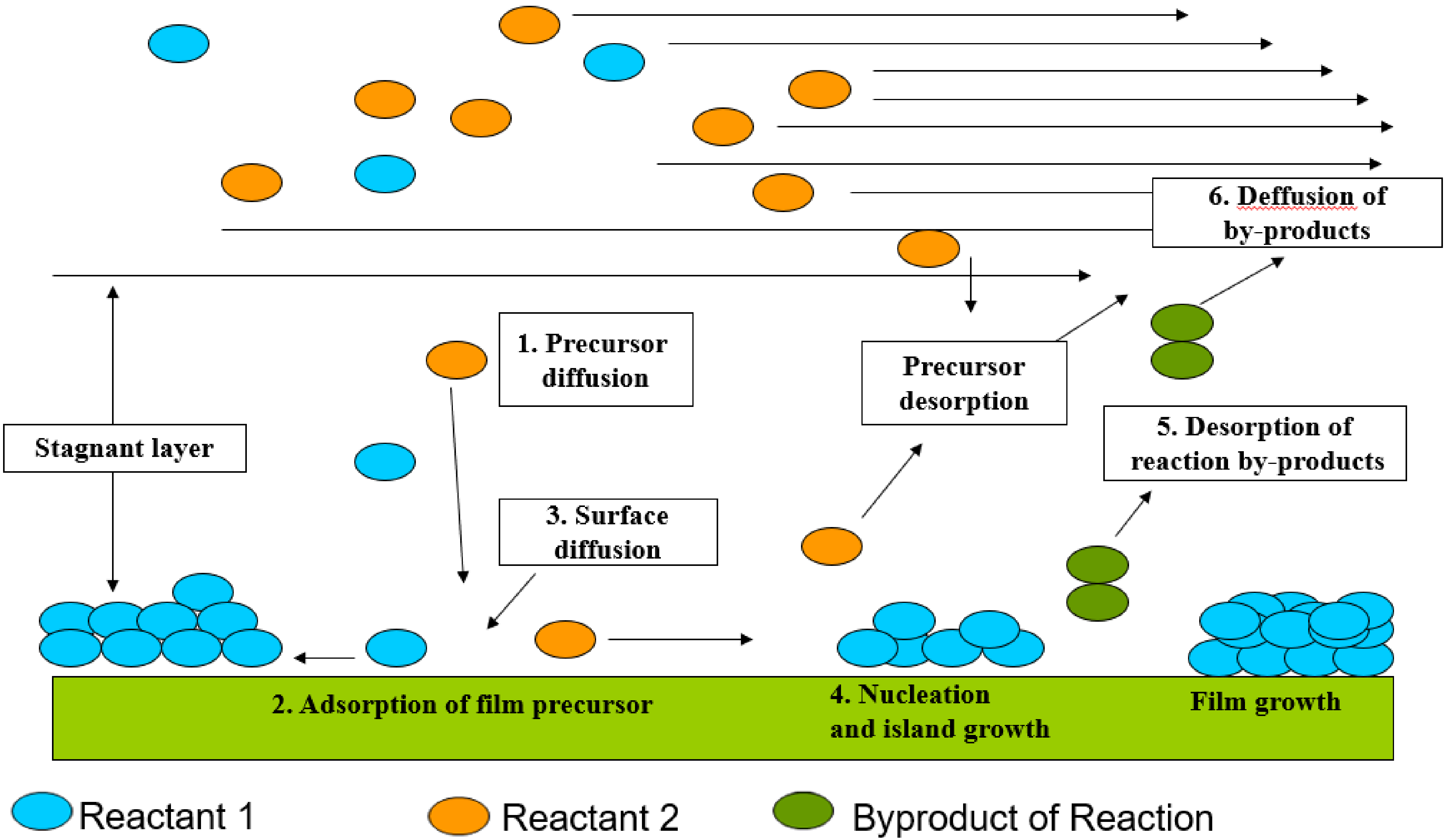
1. **Physisorption:** Adsorption of the arriving atoms (molecules) on the deposition surface via weak forces (van der Waals attraction).
2. **Surface diffusion:** Diffusion of the physisorbed species on the surface before they get incorporated into the film.
3. **Chemisorption:** Reaction of the physisorbed species with each other and the deposition surface to form the bonds of the film material (incorporation) $\rightarrow$ nucleation and growth.

Six Steps in VS Growth

1. Rapid diffusion of growth species (such as vapor or liquid phase) to the growing surface.
2. Adsorption and desorption of growth species onto and from the growing surface. This step may be rate limiting if the concentration of growth species is low. (mass transport).
3. During surface diffusion, an absorbed specie may either be incorporated into the growth site, and become part of the crystal, or escape from the surface.
4. The absorbed growth species are irreversibly incorporated into the crystal structure when supersaturation of the growth species occurs. This step is always rate liming and determines the growth rate. (kinetics).
5. By-products of the growth reaction will desorb from the surface, allowing more growth species to adsorb to the surface, continuing growth.
6. By-products diffuse away from the surface and are evacuated from the growth chamber.

C. Guozhong. *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*. Imperial College Press. London 2007

Six Steps in VS Growth



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Rate-Limiting Steps in VS Growth

- When adsorption of the growth species to the growth surface is rate-limiting, the condensation rate, *J* (atoms/cm^2sec), is directly proportional to the vapor pressure *P*, of the growth species in the vapor. The condensation rate, *J* is dependent on the number of growth species absorbed onto the growth surface.

C. Guozhong. *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*. Imperial College Press. London 2007

Rate-Limiting Steps in VS Growth

- Accommodation Coefficient (α): the fraction of impinging growth species that becomes accommodated on the growing surface. This is a surface specific property e.g.;
  - Material morphology, chemical affinity, orientation, planarity, etc.
- A surface with a high α will have a high growth rate as compared with a low α.

C. Guozhong. *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*. Imperial College Press. London 2007

Defects in VS Growth

- A high vapor pressure (or high concentration) of growth species in the vapor phase will increase the deposition rate and probability of defect formation, such as impurity inclusion and stack faults.
- A high vapor pressure may cause secondary nucleation or homogeneous nucleation on the growth surface, which can effectively terminate homogeneous single crystal growth.

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Surface Reactions

- The time a growth species takes to absorb to the growth surface and either react with the surface, or diffuse away from the surface without reacting is called the residence time (τ_s).
- This can be thought of as a race between physisorption, desorption, and chemisorption. Typically this is ~10^{-12} sec.
- Residence time can be calculated by:

$$\tau_s = \frac{1}{v} \exp\left(\frac{E_{des}}{kT}\right)$$

- Where:
  - *v = Vibrational frequency of the adatom*
  - *E_{des} = desorption energy required for the growth species escaping back to vapor.*
  - *k = Boltzmann constant*
  - *T = Temperature*

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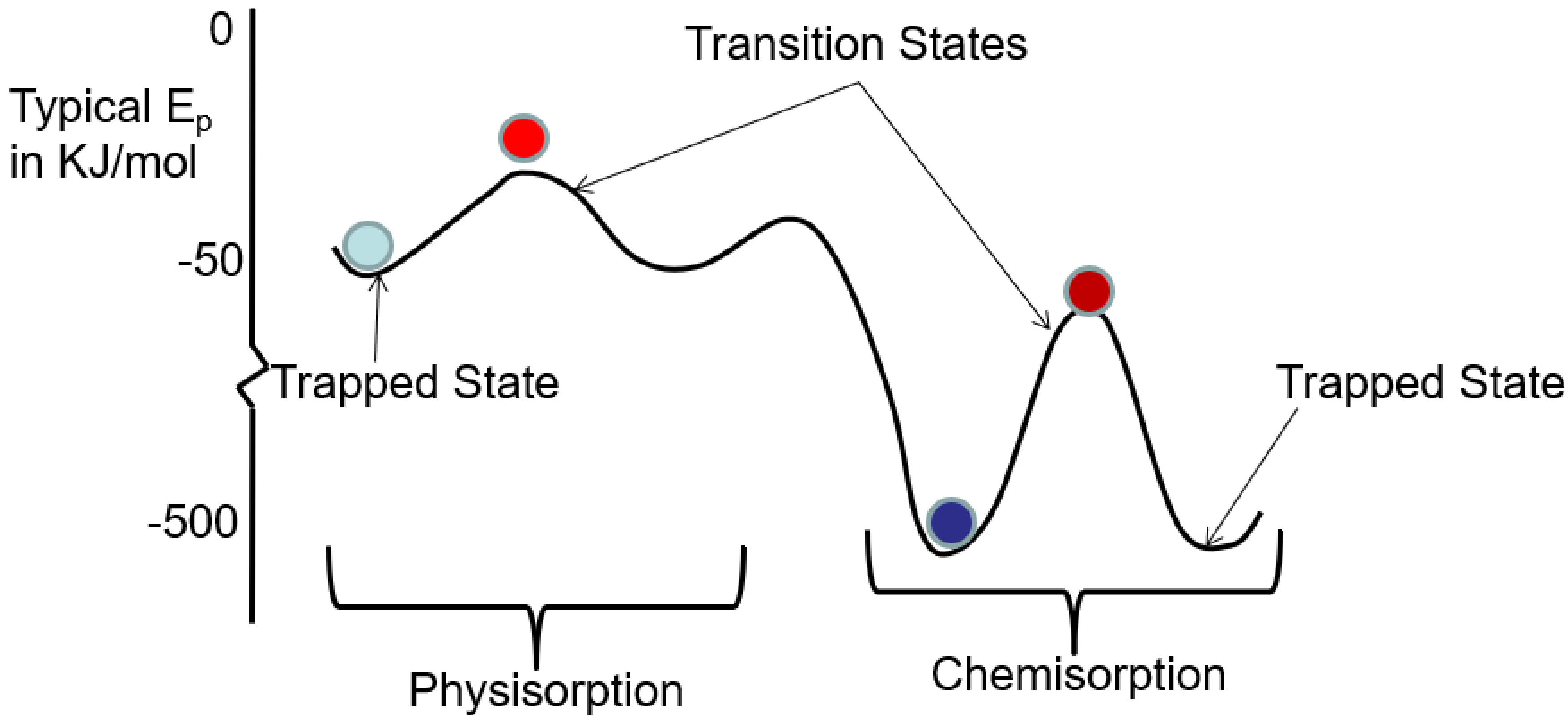
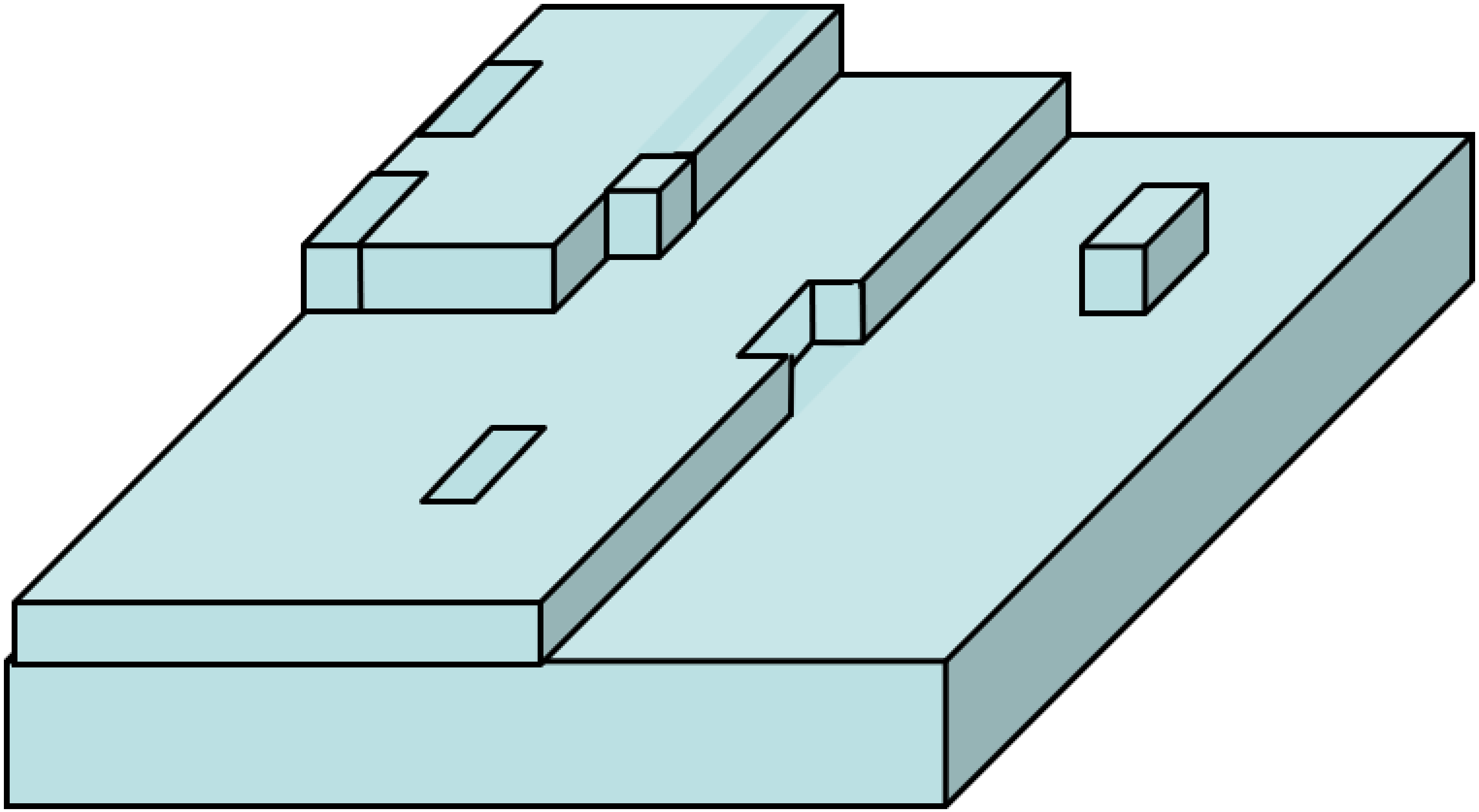
Surface Reactions



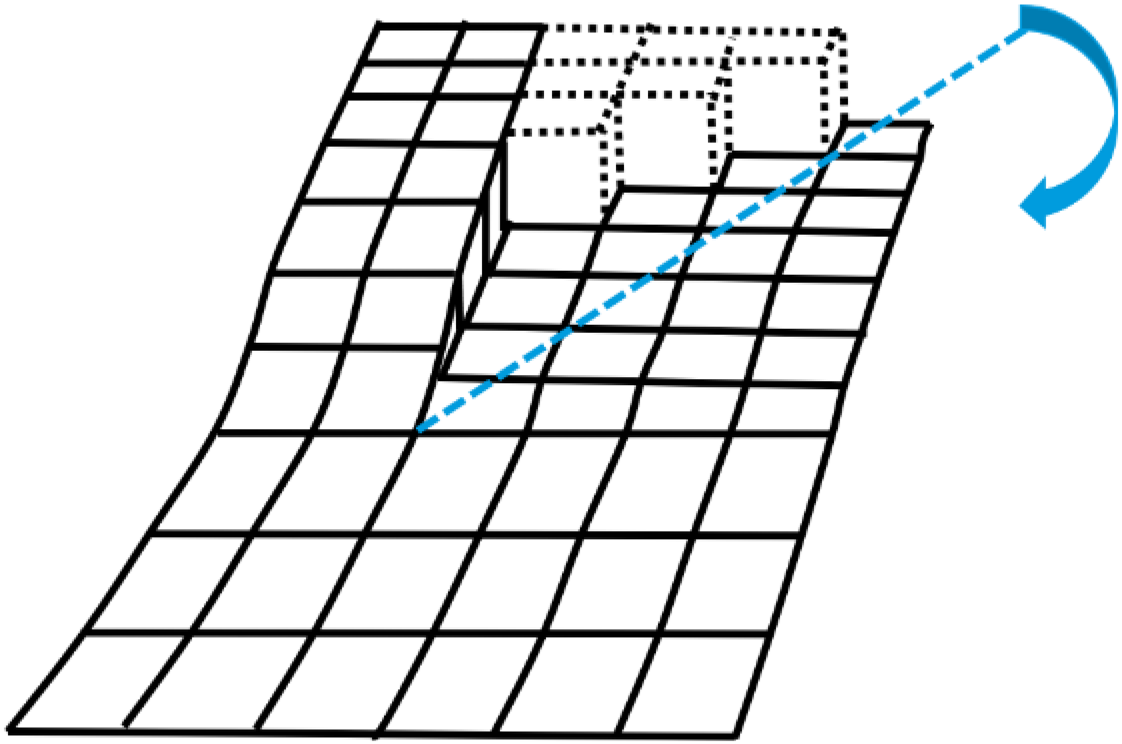
Surface diffusion takes place by the hopping of an atom (molecule) from a physisorption state into an adjacent one. The atom (molecule) is weakly trapped in each physisorption state by a potential well due to the dipole interaction. Hopping requires thermal energy to overcome this potential barrier and so it is thermally activated. The end result is a reduction in energy of the adatom and material growth.

VS Growth



Note, that the reaction is related to Gibbs free energy, and the available surface energy.

VS Growth



The step morphology (screw dislocation) provides energetically favorable sites for a reduction in the Gibbs free energy of an adatom.

VS LPCVD Thin Films Advantages

- Advantages:
  - Excellent uniformity.
  - Conformal step coverage.
  - Large substrate capacity / high deposition rate.
  - Variety of materials.
  - Good control over the process, doping versatility.
  - Stoichiometry is the same in a “wider window” of operation, as compared to the PECVD.

VS LPCVD Thin Films Disadvantages

- Disadvantages:
  - High temperature
  - Low deposition rate
    - Batch processing may negate the rate issue.
  - More maintenance (particle deposition on walls means more down time for cleaning).
  - Requires vacuum system.
  - Contamination
  - Requires additional gas dispersion tubes, as well as more expensive and complicated cage boats.

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Vapor-Liquid-Solid (VLS) Growth

- In VLS growth, a catalyst is introduced to direct the growth to a specific orientation in a confined area.
- The catalyst forms a liquid droplet that acts as a nucleation site for the growth species, resulting in a one dimensional growth.
- There are seven requirements for VLS growth.

C. Guozhong. *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*. Imperial College Press. London 2007

Requirements for VLS Growth on a Crystalline Substrate

1. The catalyst is heated to a liquid on the crystalline material.
2. The catalyst's distribution coefficient must be less than unity at the deposition temperature.
3. The catalyst's equilibrium vapor pressure over the droplet must be small. The increased temperature causes the catalyst to start to evaporate, decreasing the volume of the catalyst. This will reduce the diameter of the nanowire and when the catalyst evaporates completely, growth of the nanowire stops.
4. The catalyst must be chemically inert, so it does not interact with the growth species or the by-product species.
5. The interfacial energy between the catalyst and the growth surface plays an important role in growth. A small wetting angle will result in a large growth area and a large diameter nanowire.
6. To grow a nanowire from a complex compound, one of the constituents of the compound can be used as a catalyst.
7. Well defined crystallography at the solid-liquid interface is required for controlled unidirectional growth. Using a single crystal substrate is the easiest way to achieve a desired crystal orientation.

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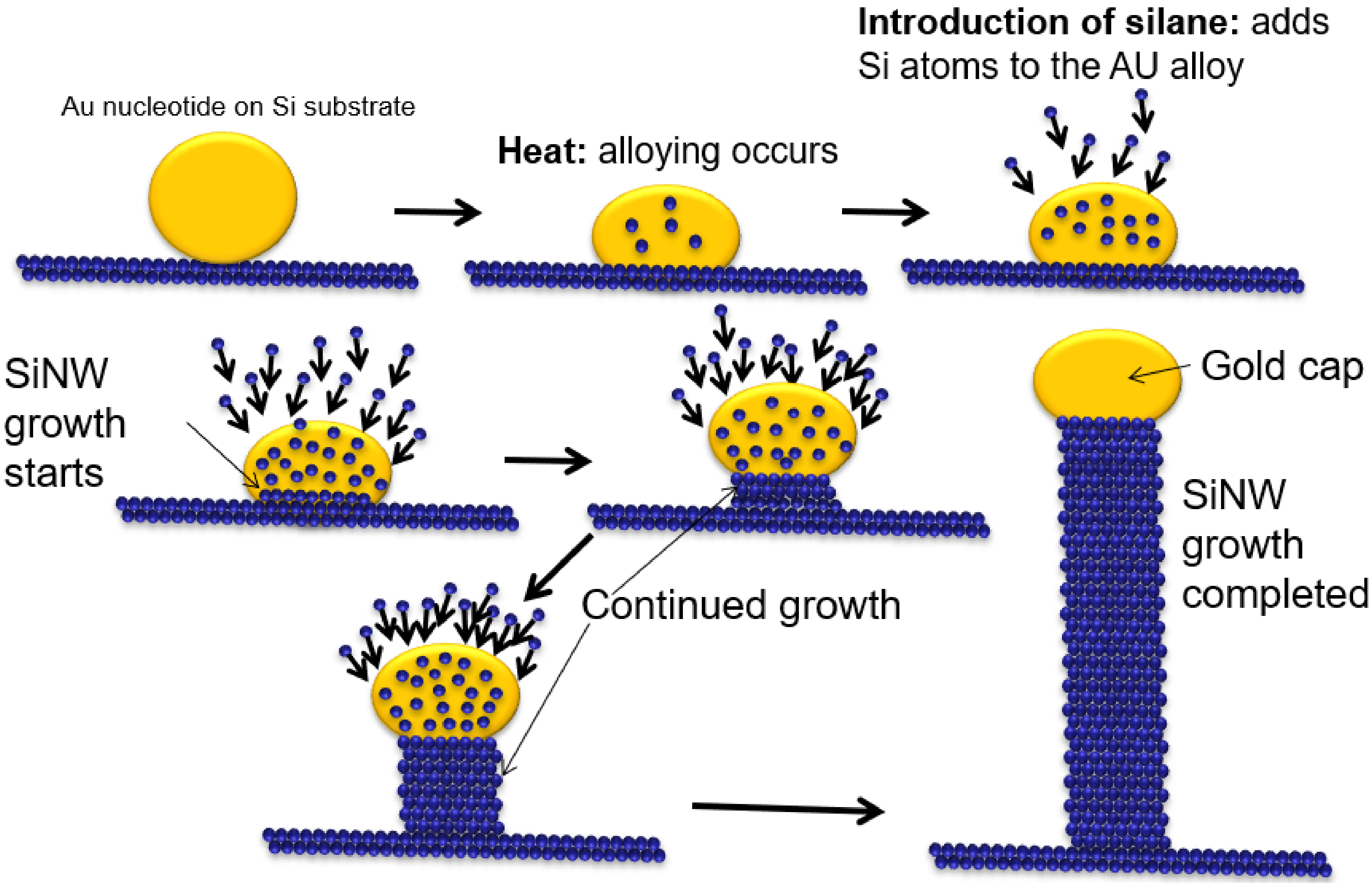
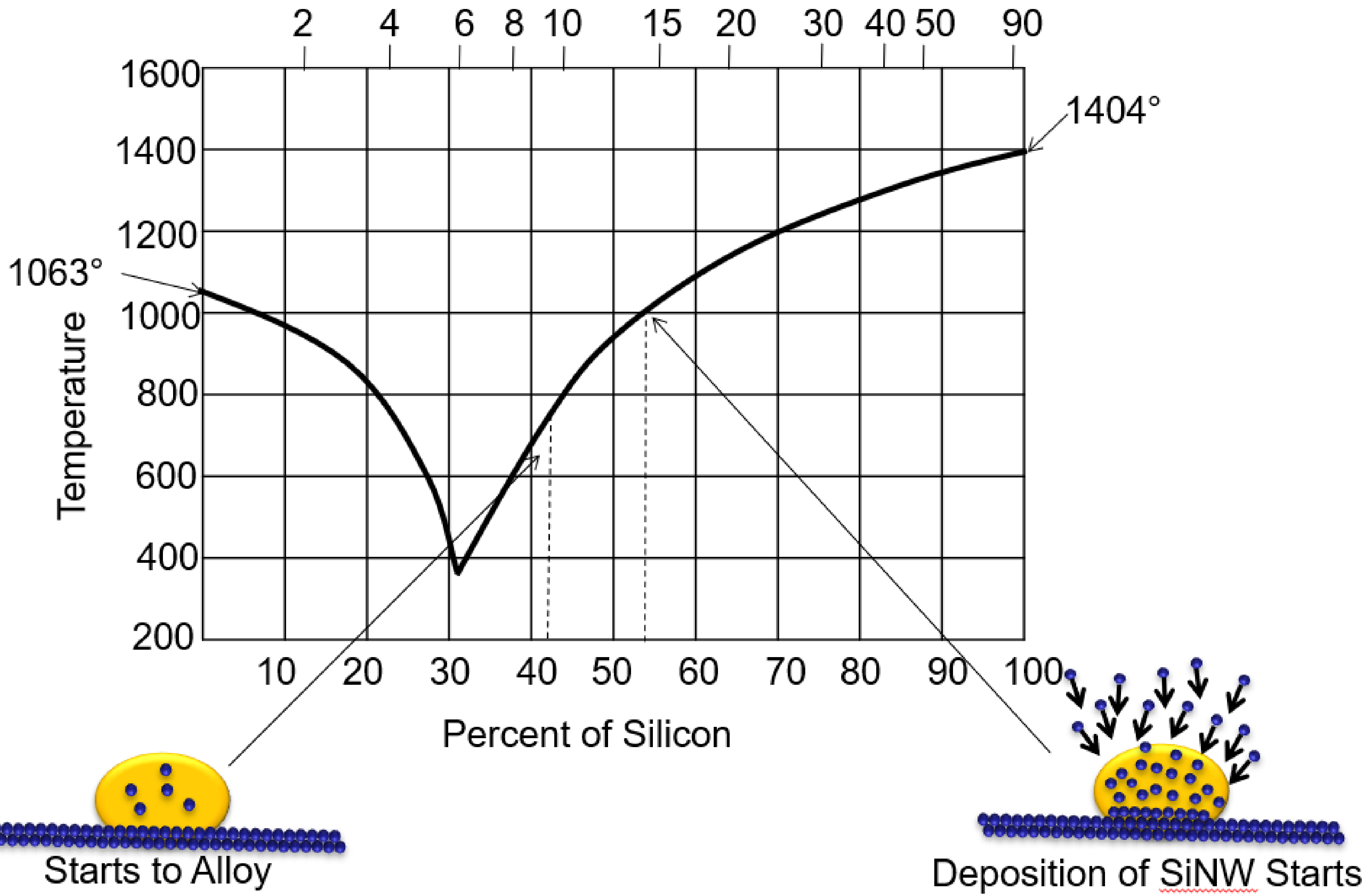
An Example: Silicon Nanowires Produced by Chemical Vapor Growth Using the Vapor-Liquid-Solid (VLS) Mechanism



VLS Growth



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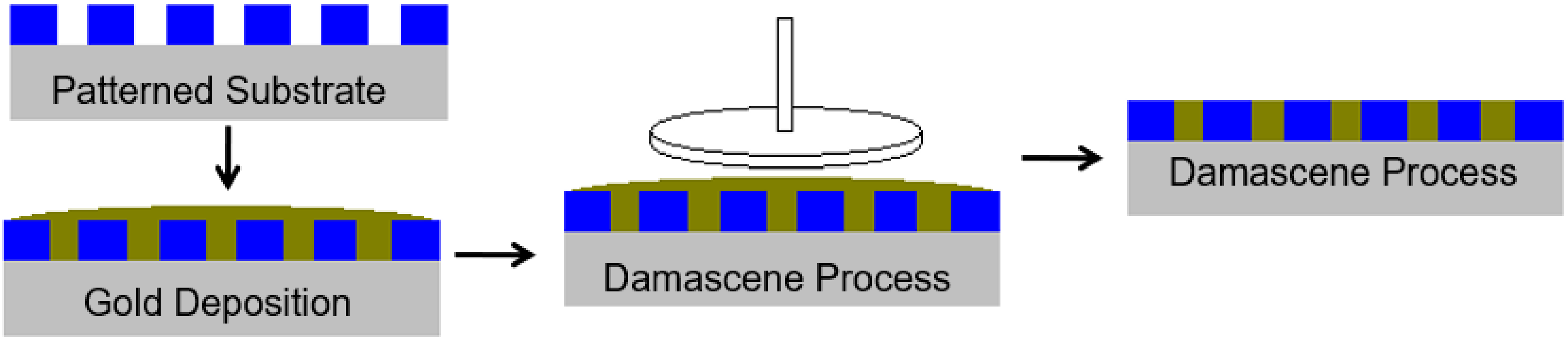
1404°
1063°
Temperature
10
20
30
40
50
60
70
80
90
100
Percent of Silicon
Starts to Alloy
Deposition of SiNW Starts

Deposition methods for catalysts

- Sputtering / evaporation / nucleation.
- Nanoparticles in solution / colloidial seeding.
- E-beam lithography
- Damascene filled pockets on a substrate.



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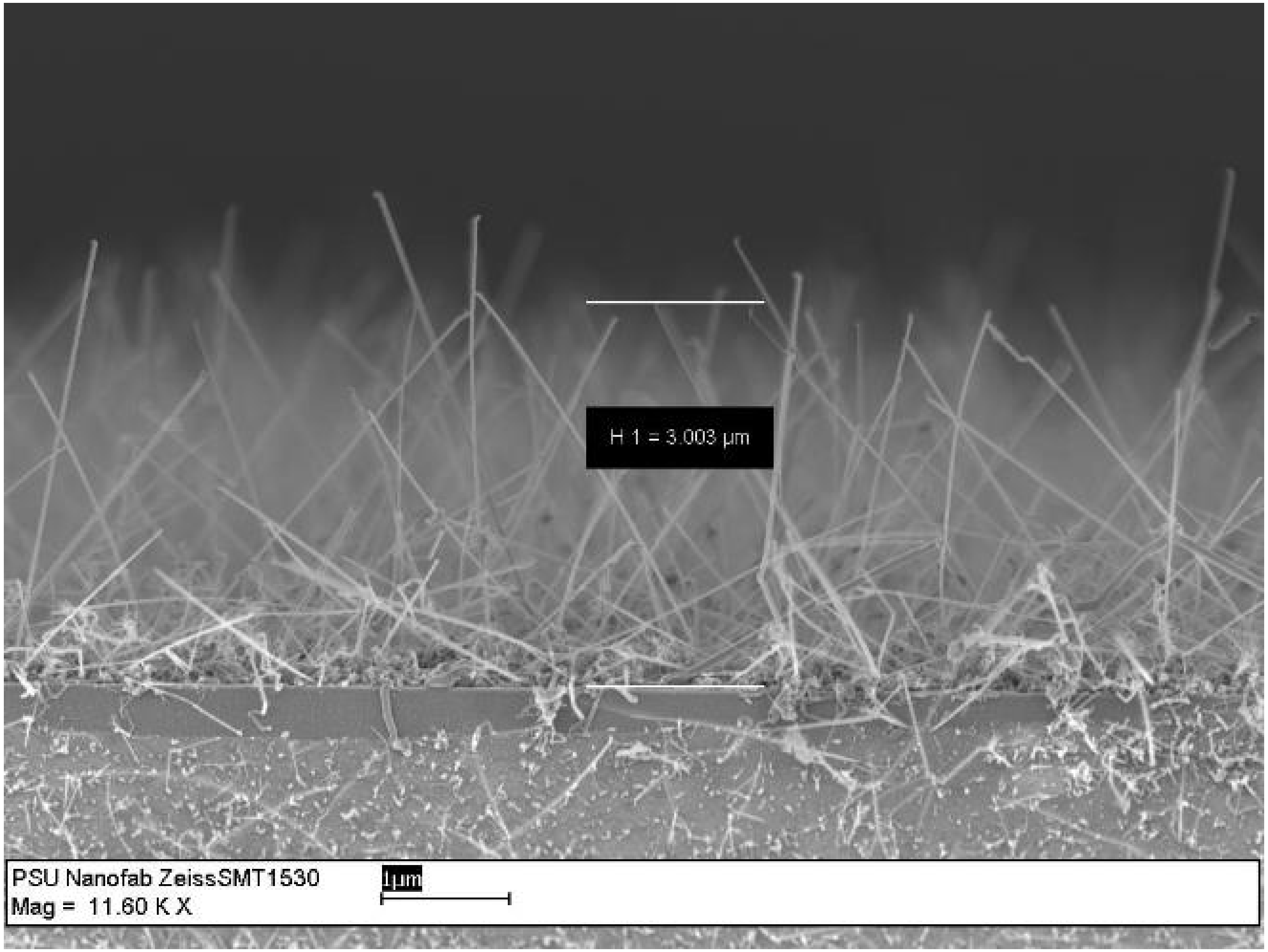
How Do You Choose a Catalyst for VLS Growth?

When choosing a catalyst for VLS growth of nanowires, the metal and the materials of the nanowire must be stable in the liquid phase but must not form compounds more stable than the desired nanowire.

Catalyst	Nanowire Material	Reference
Fe, Ni, Au Fe	Si Ge	*Science*. Vol 279 (1998)
Sn	SnO_2	*Chemical Physics Letters. Vol* 369 (2003)
Au Cu	GaAs, ZnSe, CdSe GaAs	*Adv. Mater.* No 4 (2000)
Sn	ZnO	*J. Phys. Chem B*. Vol, 108 (2004)
Ni, Au, Fe, Co	GaN	*Inst. Phys. Journal. Issue 10 (2005)*

LPCVD Grown SiNWs



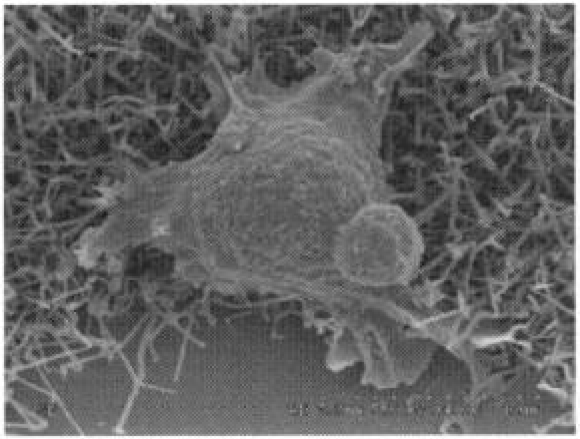
Edge view FESEM image of 4 minute deposition sample showing average nanowire height/length (Average height = 3.003 µm). Magnification 11.60Kx

Silicon Nanowire as Bio-scaffolding

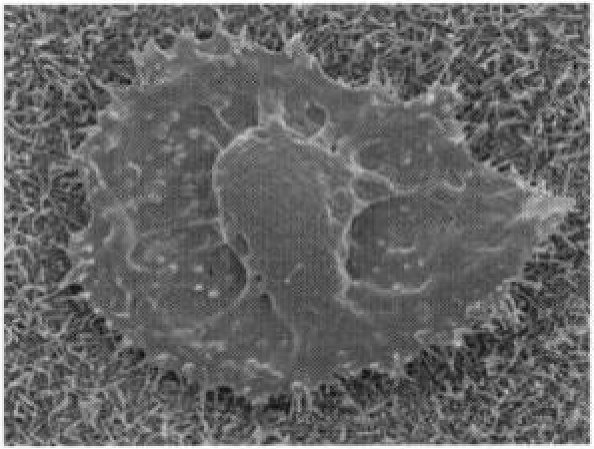
- Cytoplasmic prolongation is essential for tissue formation, development, cellular location, and communication.
- Fibroblast cells showed increased activity on gold modified SiNW surfaces, indicating an increase in biocompatibility.
- H.S. Wen *et al* attribute the increase in cellular prolongation to the remarkable biocompatibility of gold.

H. S. Wen *et* al Microprocesses and Nanotechnology, 2007 digest of Papers. 42-43 Nov. 2007

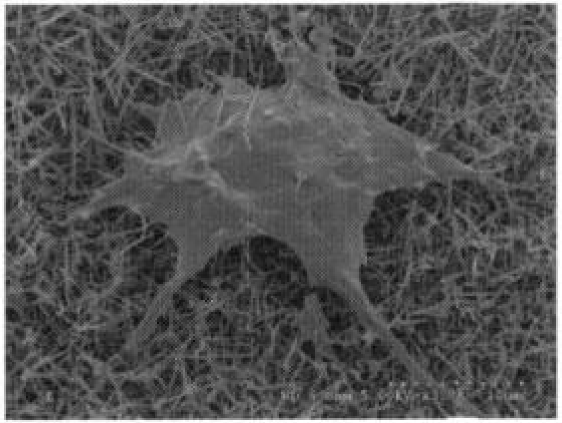
Silicon Nanowire as Bio-scaffolding



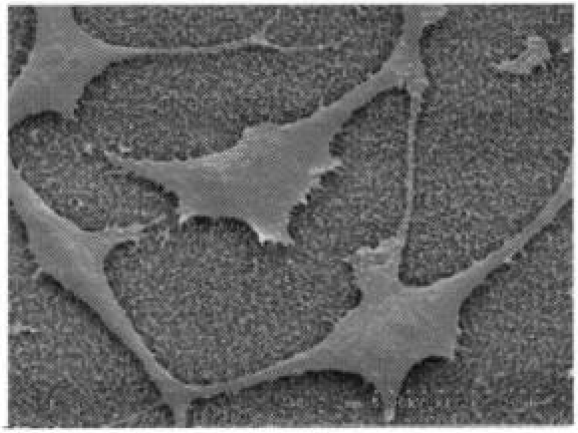
The SEM micrograph of fibroblasts on SiNWs substrate with 1 hr culture.



The SEM micrograph of fibroblasts on Au-coated SiNWs substrate with 1 hr culture



The SEM micrograph of fibroblasts on SiNWs substrate with 3 hr culture.



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Any Questions?

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