

# Basic Nanotechnology Processes

E SC 212

# **Unit 5**

## **Chemical Vapor Deposition**

### **Lecture 1**

#### **Typical LPCVD Systems/Hardware and Top Down Applications**

# Outline

## Part I

- Introduction
- Typical LPCVD systems/hardware
- Top down applications
  - 2D materials (thin films, VS growth)

## Part II

- 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).
  - Plasmas (called Plasma Enhanced Chemical Vapor Deposition, or PECVD).
  - Photons (usually called photo-chemical vapor deposition, or Photo-CVD).
- CVD process of all three types are often done at low pressure, to obtain uniform deposition and better control of the chemical reaction.

# LPCVD

- Low Pressure Chemical Deposition (LPCVD) is a term applied to thermally driven CVD done at low pressures.
- The combination of available chemistry, temperature, and substrate control the rate of deposition.

# 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 ( $\propto e^{-\Delta/kT}$ ).

# Outline

- Chemical Vapor Deposition
- Typical LPCVD systems/hardware
- Top down applications
  - 2D materials (thin films, VS growth)
- Bottom up applications
  - 1D materials (nanowires, VLS growth)

# Form and Function

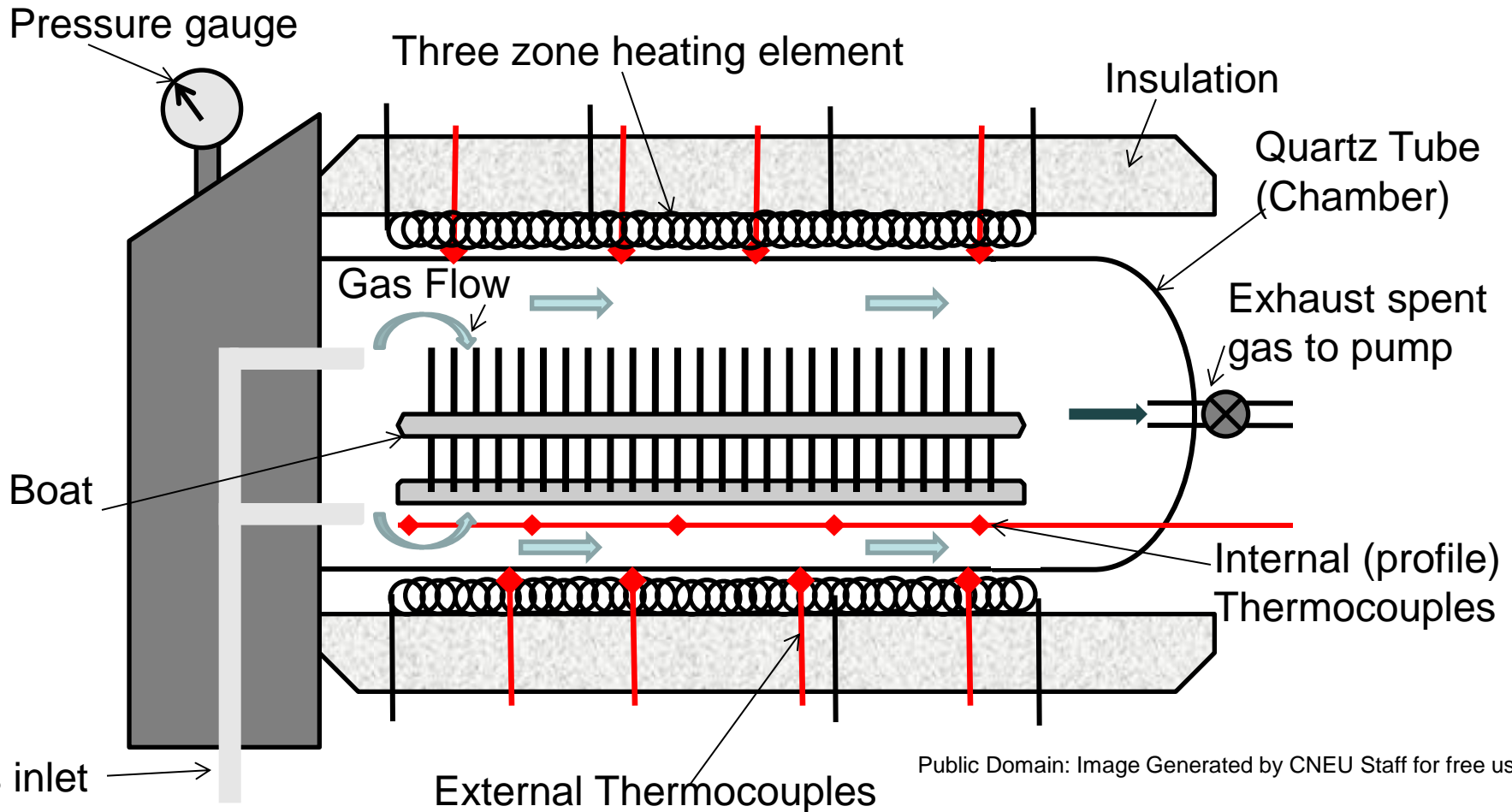
- LPCVD generally operates under medium vacuum (0.1 ~ few Torr).
- Medium vacuum increases the diffusivity of the reactant gas molecules.
- Since the reaction is not limited by the availability of gases at the substrate's surface, the chamber can be designed to optimize substrate capacity, and increase 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

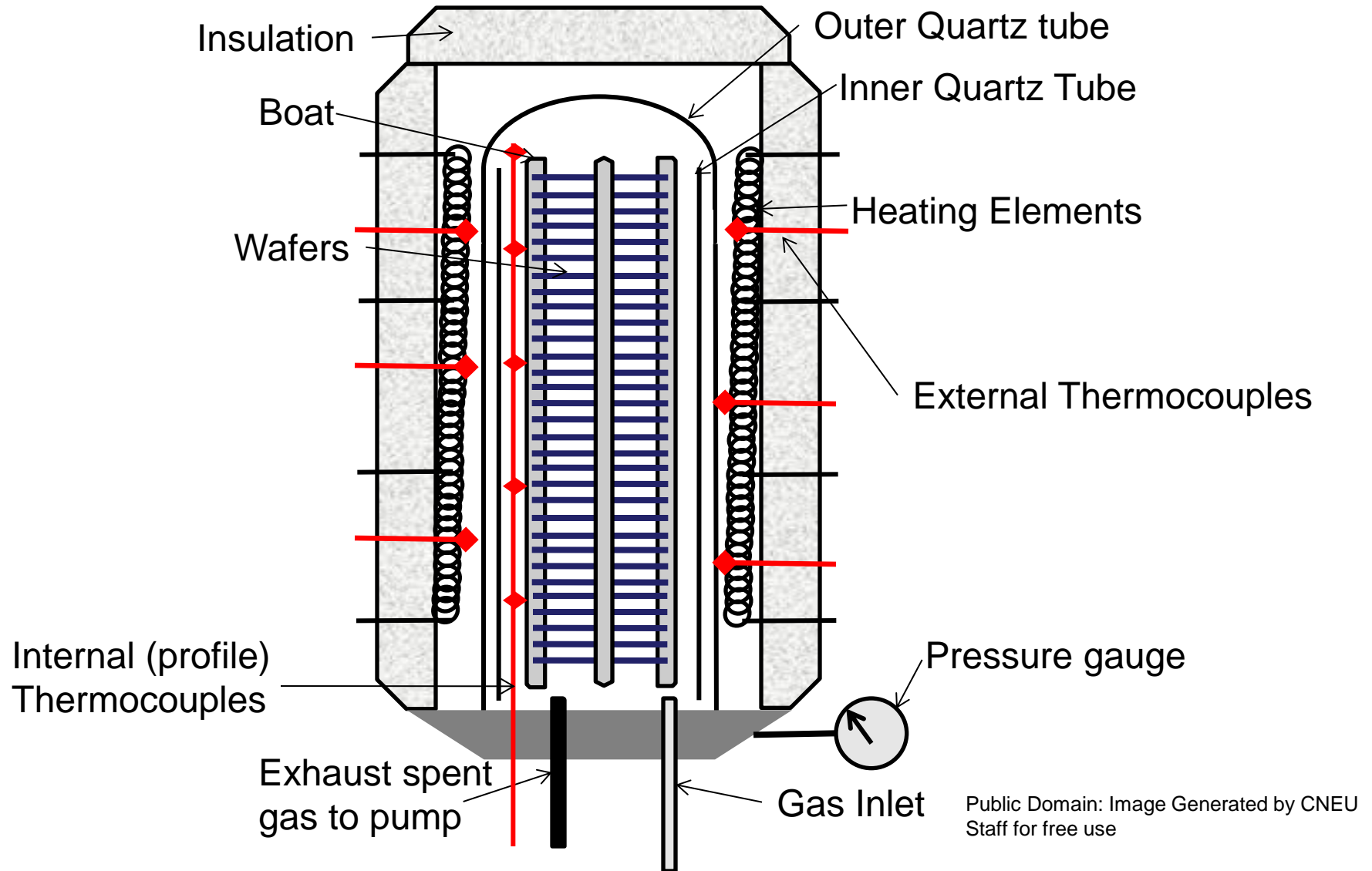
- Hot wall reactors are favored because they provide uniform temperature over a large operating length.
- Growth rate decreases further from the gas inlets. Increased temperature in the further regions of the tubes creates greater uniformity on the substrate.
- The chemistry and heat are balanced to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

# Batch LPCVD Horizontal Reactor



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# Batch LPCVD Vertical Reactor



# Horizontal versus Vertical reactors

- Vertical reactors tend to have less particulate problems.
- It is more difficult (\$) to control temperature in a vertical configuration.

# Typical LPCVD



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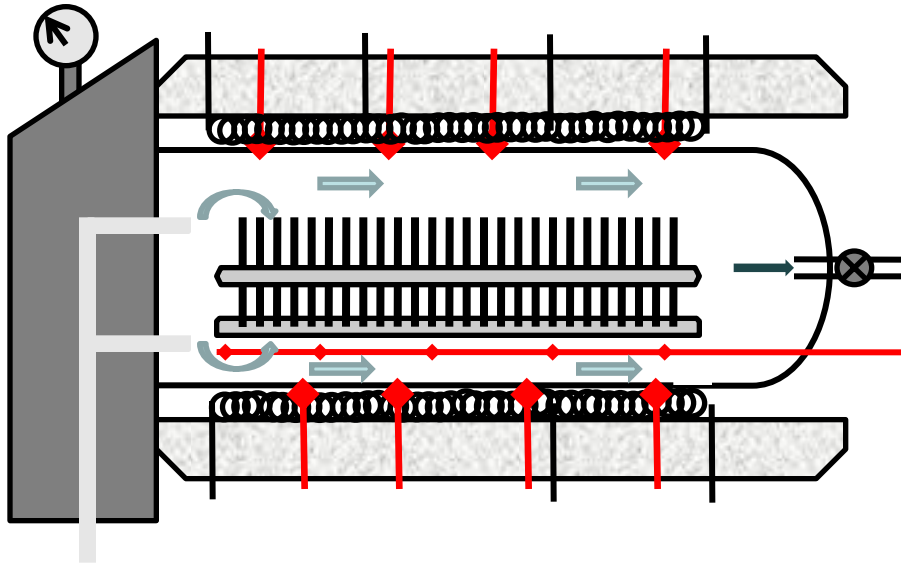
# LPCVD

- The system shown on the last slide is a typical horizontal hot wall batch processing furnace, with three temperature zones and quartz reactor tube.
- Substrates are closely packed vertically.
- Instead of diluted gases, low pressures are used to control gas phase nucleation.
  - 0.1 ~ few Torr.
  - Does not have an automatic loader (cost reducing).
- The design is very similar to the conventional process furnace. The furnace can be configured for atmospheric oxidation, and annealing with inert or reactive gas.

# Typical Gas Scrubber

- Delatech 857 Controlled Decomposition / Oxidation System (Gas Burner) Scrubber
  - Known as a CDO (Controlled Decomposition/Oxidation Unit).
  - Uses a two stage process in which the exhaust is first oxidized at high temperatures (around 850°C).
  - Scrubbed with water to remove particulates and mineral acids. This type of system requires a waste water stream of about two gallons per minute.

# Automate Low Pressure Chemical Vapor Deposition



**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.

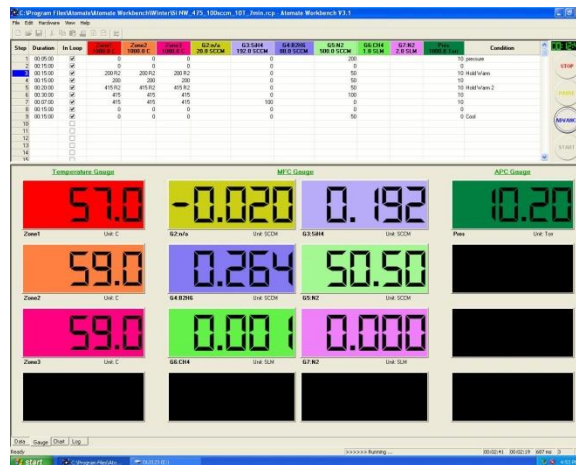


Automate Low Pressure CVD System

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

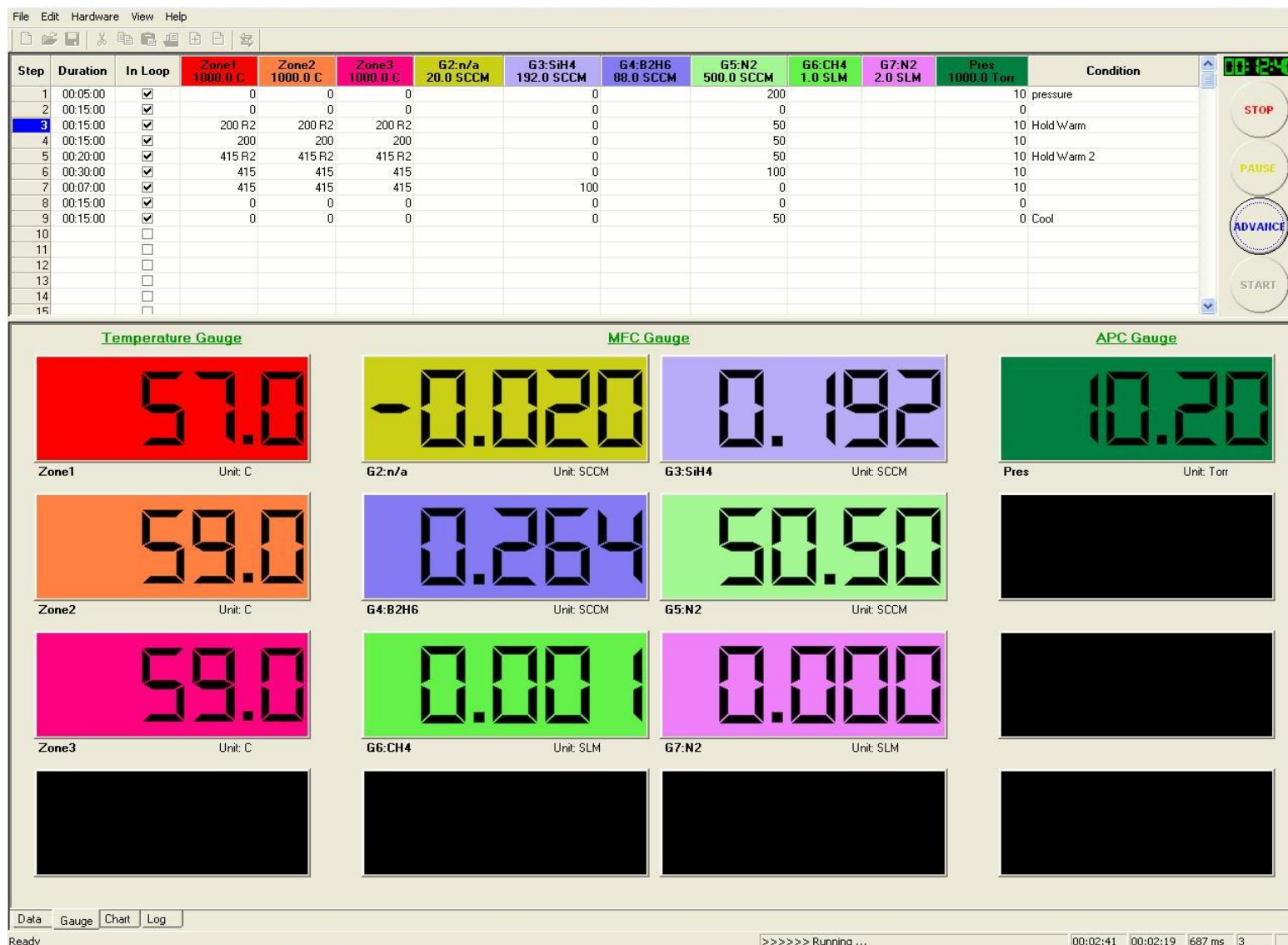


# Automate LPCVD



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# Screen Capture of the Automate LPCVD Control Screen



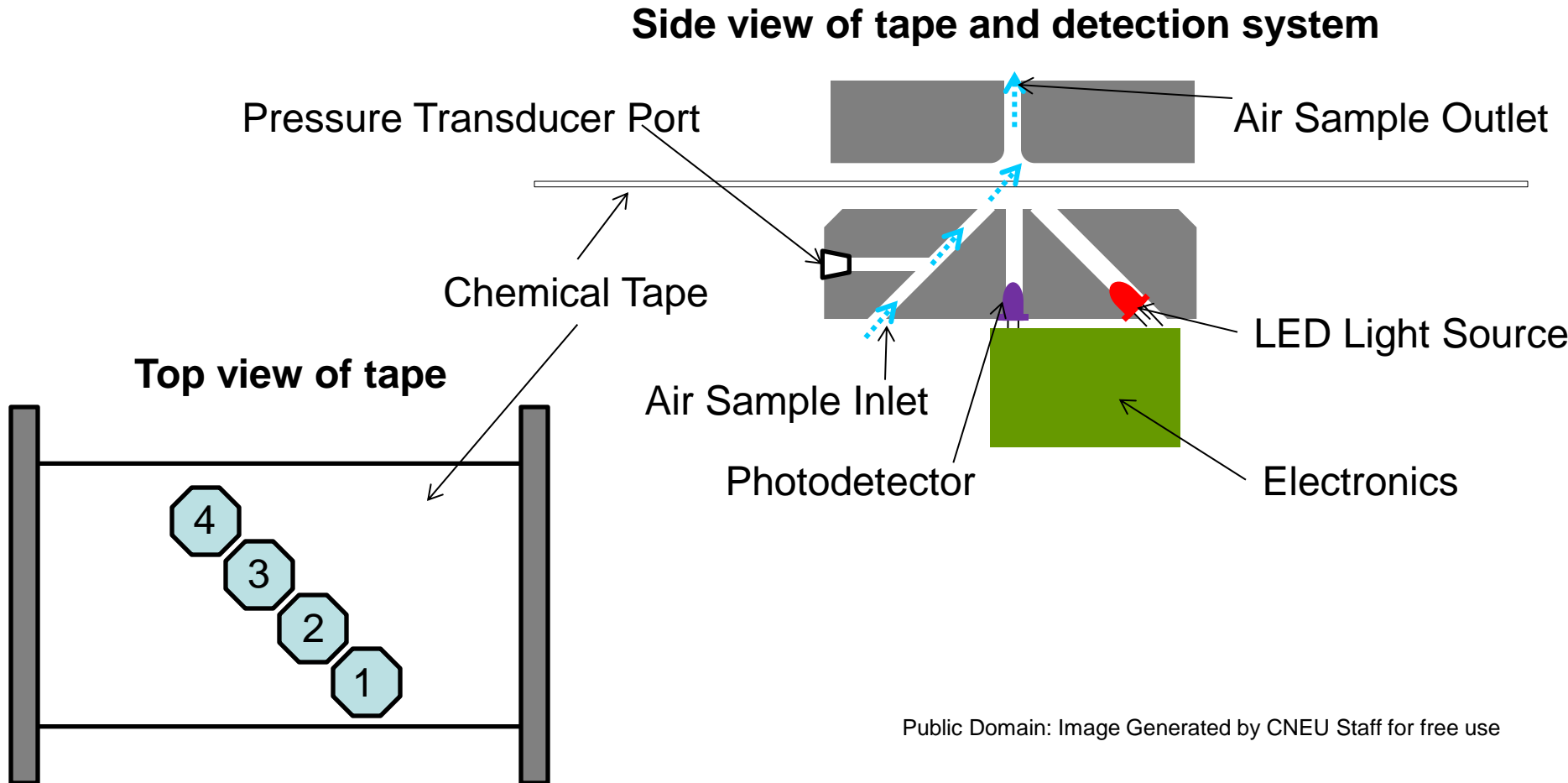
# Gas Detection LPCVD

- Air samplers
- Hydride reactive tape
- Audible and visual alarms
- Readings continuously taken/stored.



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# Gas Detection for a Typical LPCVD



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# Gas Detection for LPCVD

- There are six air samplers connected to the monitoring tape placed throughout the gas delivery system, the tool, and the room.
- When a hydride gas comes in contact with the monitoring tape, a chemical reaction takes place changing the optical properties of the tape in the position corresponding to the air sampler where the leak is occurring.
- A sensor recognizes the change in the optical properties of the tape and triggers the audible and visible alarms.
- The system saves the concentration and type of gas, as well as its position on the tape, in memory until it is cleared.
- Currently the system is set up to recognize a concentration of 1ppb of hydride gas.
- Each Unit is ~\$15,000 with an annual maintenance contract of \$5,000/year (2008).
- Each tape cassette is replaced every 3 months at a cost of ~\$1,600/year (4 test points).

# Gas Scrubber for Small Volume LPCVD

The scrubber is intended for the conversion of hydride materials from the incoming gas stream into non-hazardous materials. Scrubbers can be designed for any other specific chemistry.



Each scrubber canister is ~\$8,500/year to maintain

[NovaSafe webpage](#)

[NovaSafe Product Info](#)

# Outline

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



# 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.



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# 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:

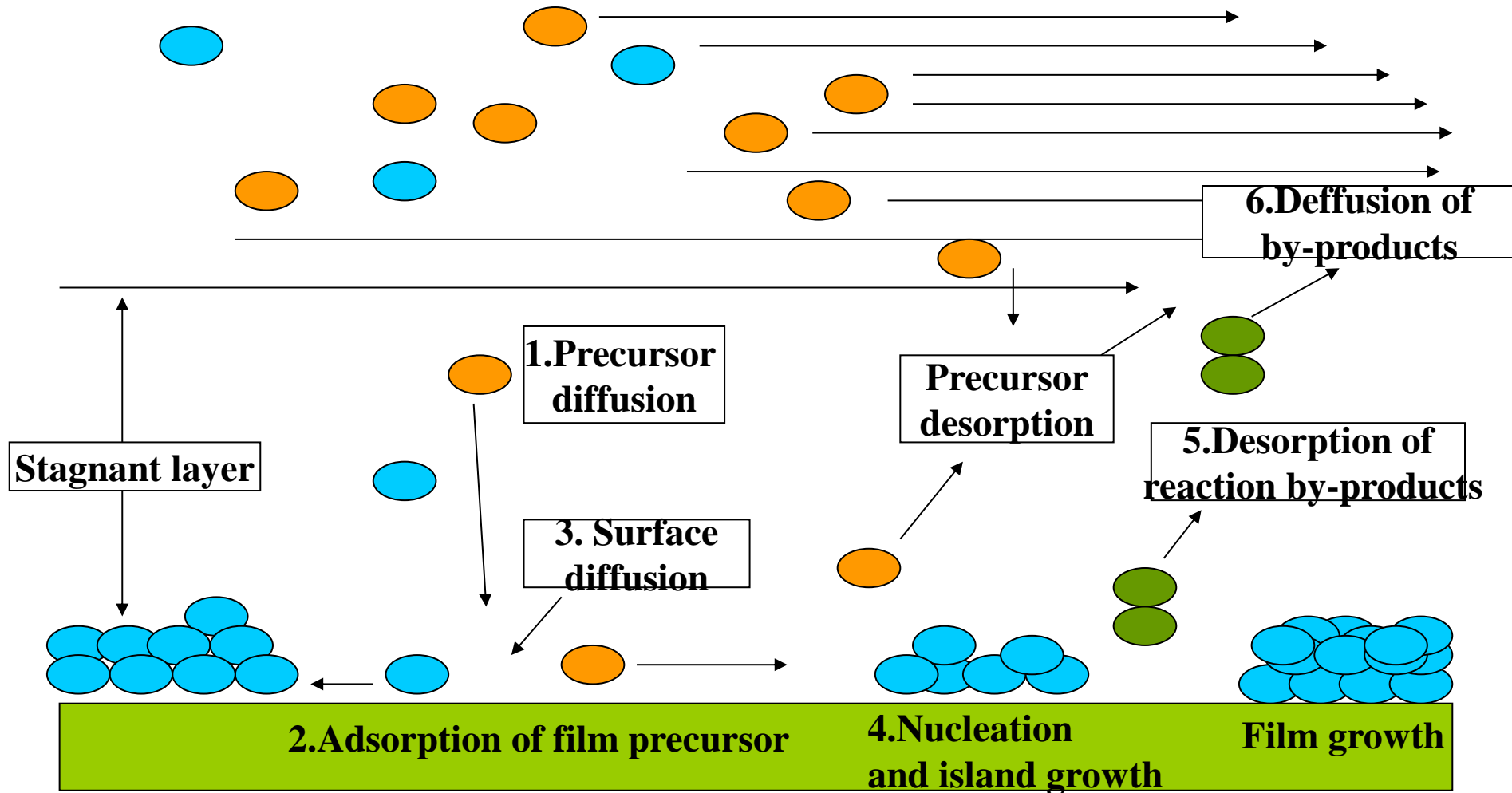
- 1. Physisorption:** Adsorption of the arriving atoms (molecules) on the deposition surface via weak forces (van der Waals attraction).
- 2. Surface diffusion:** Diffusion of the physisorbed species on the surface before they get incorporated into the film.
- 3. Chemisorption:** Reaction of the physisorbed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



Reactant 1



Reactant 2



Byproduct of Reaction

# 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<sup>2</sup>sec), 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.

# Rate-Limiting Steps in VS Growth

- Accommodation Coefficient ( $\alpha$ ): 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  $\alpha$  will have a high growth rate as compared with a low  $\alpha$ .

# Rate-Limiting Steps in VS Growth

- The Condensation rate can be calculated by:

$$J = \frac{\alpha \sigma P_0}{\sqrt{2\pi m k T}}$$

- Where:

- $\alpha$  = accommodation coefficient
- $\sigma$  = the supersaturation of the growth species in vapor  $(P - P_0)/P_0$
- $P_0$  = the equilibrium vapor pressure of the crystal
- $m$  = atomic weight of the growth species
- $k$  = Boltzmann constant
- $T$  = temperature

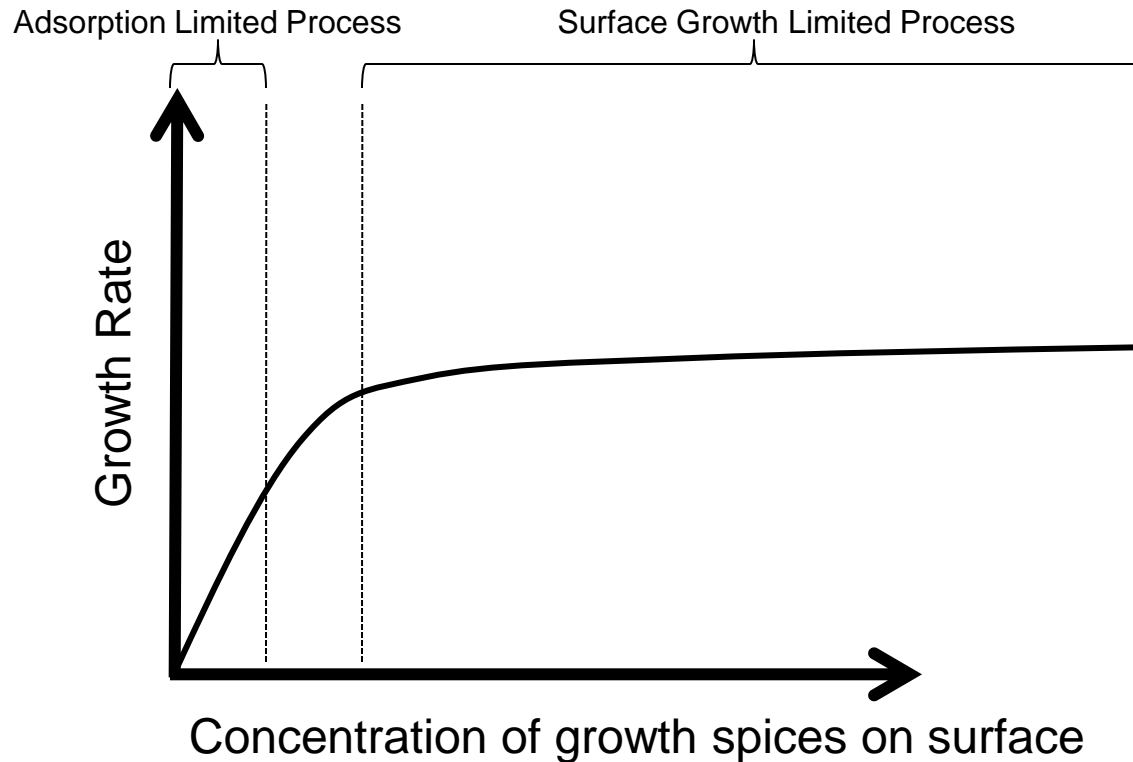
C. Guozhong. *Nanostructures & Nanomaterials: Synthesis, Properties & Applications*.  
Imperial College Press. London 2007

# 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.



# Defects in VS Growth



Growth curve depicting the growth rate and reactant growth spices concentration on the surface relationship between.

When concentration of the growth spices are low the growth rate is primarily adsorption limited, and so the growth rate is linear. However, when concentration of the growth spices is high the growth rate becomes independent of the reactant growth spices concentration and surface reaction becomes the limiting step.

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# Surface Reactions

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

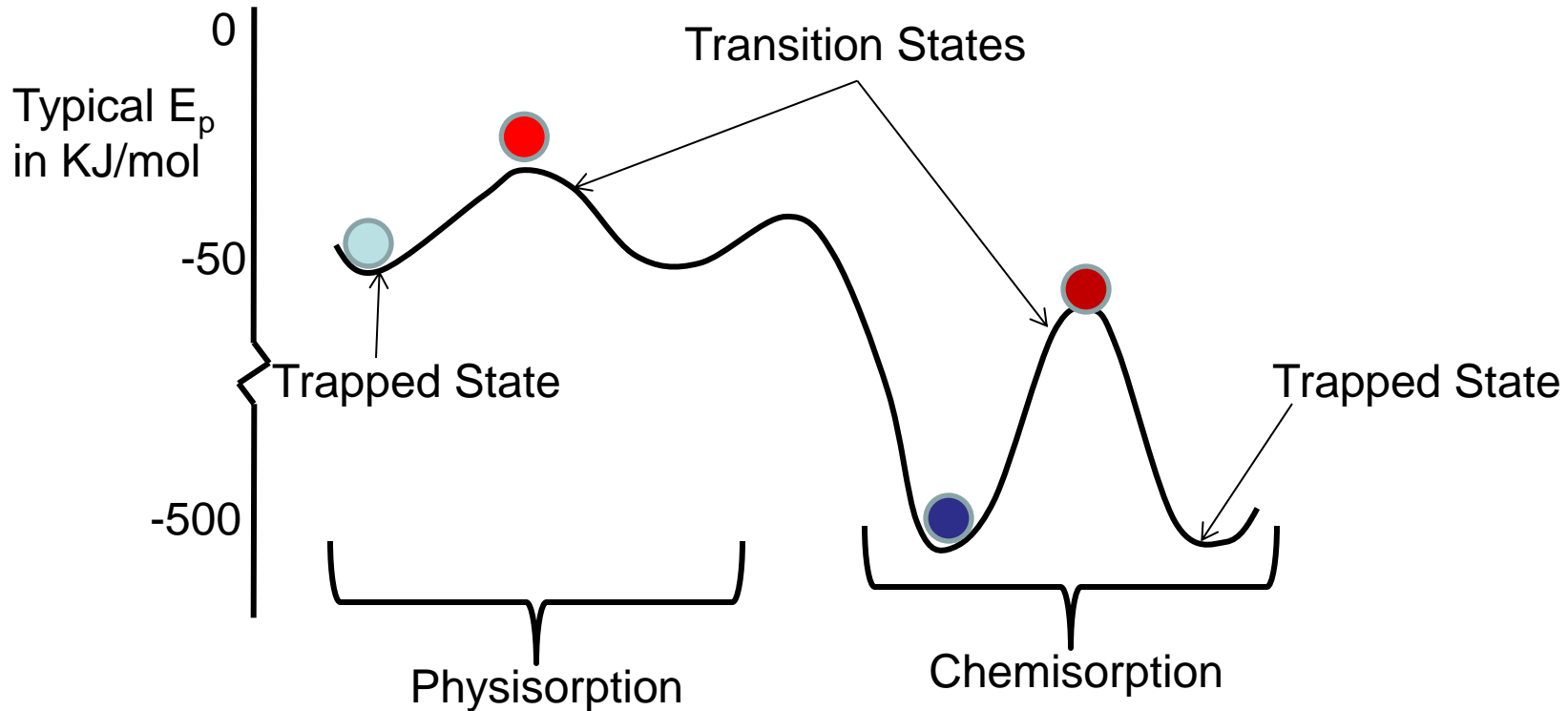
$$\tau_s = \frac{1}{\nu} \exp\left(\frac{E_{des}}{kT}\right)$$

- Where:

- $\nu$  = Vibrational frequency of the adatom
- $E_{des}$  = desorption energy required for the growth species escaping back to vapor.
- $k$  = Boltzmann constant
- $T$  = Temperature

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

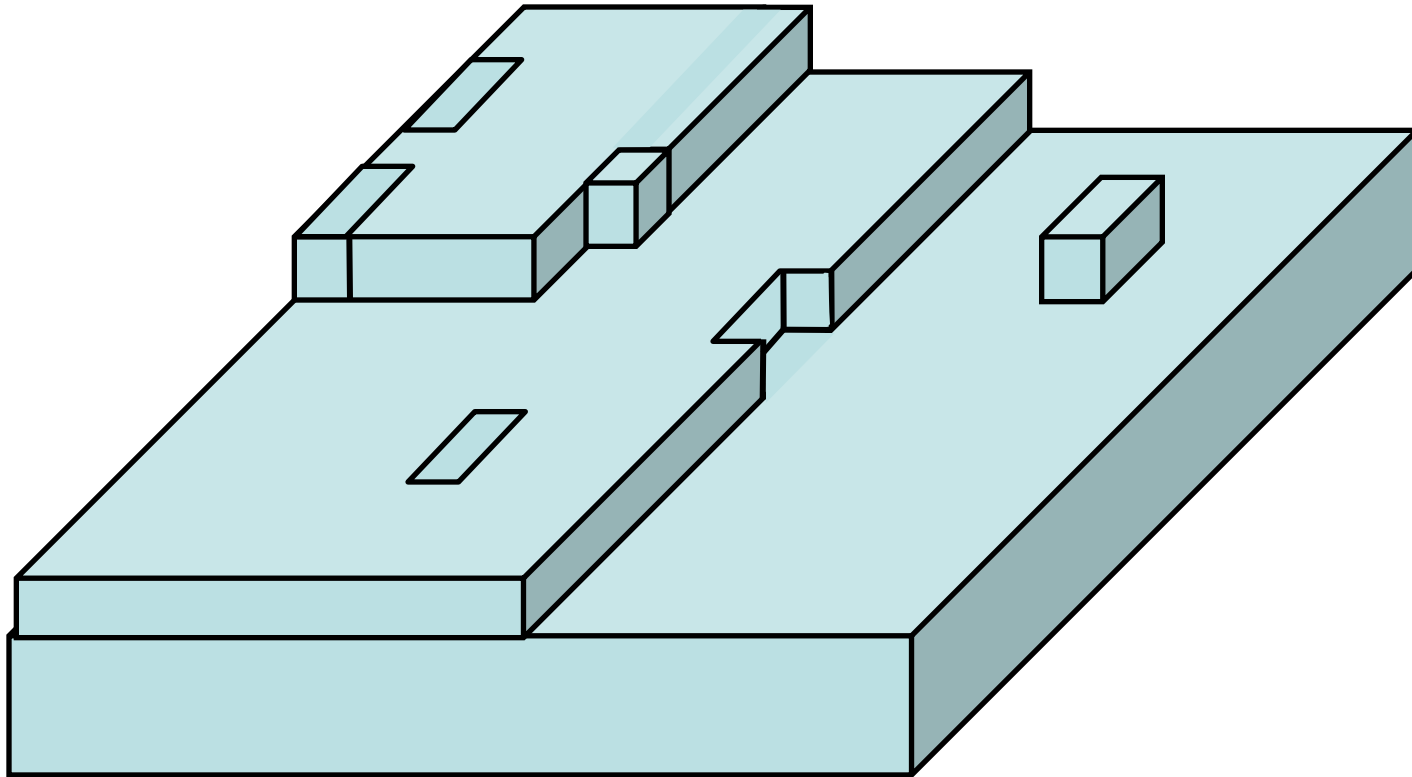
# Surface Reactions



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.

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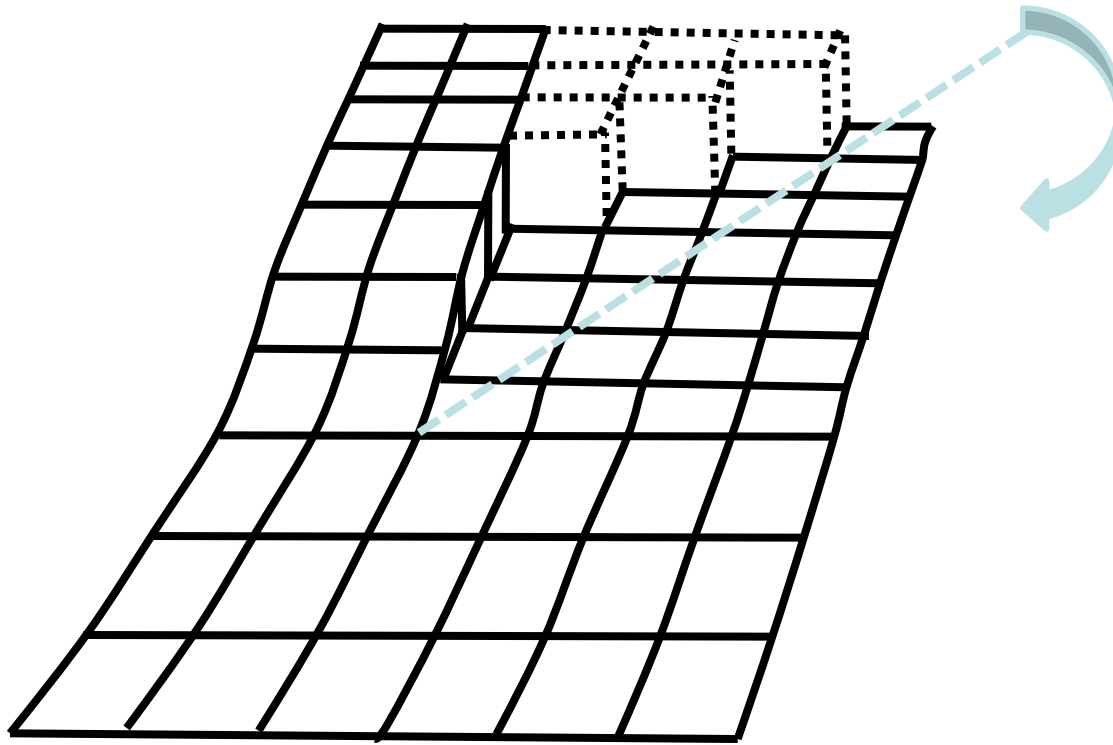
# VS Growth



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

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# VS Growth



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

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# VS Silicon Dioxide 2D Materials

- LPCVD oxides are used for:
  - Biological applications.
  - Optics
  - In ULSI multilevel metallization.
  - As an interlayer dielectric.
  - For shallow trench isolation oxide fill.

# VS Silicon Dioxide 2D Materials

- $\text{SiO}_2$  with silane
  - 425 - 435°C creates a film with poor step coverage
  - Gases - silane,  $\text{O}_2$ ,  $\text{PH}_3$  (for doping)
  - Pressure - 300 – 400 mTorr
  - Deposition rate -150 Å/min
- $\text{SiO}_2$  can also be created using TEOS
  - Tetraethylorthosilicate,  $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$

# VS Silicon Nitride 2D Materials

- Often used as a final passivation layer, because it offers good protection from the diffusion of moisture and impurities.
- Excellent step coverage and high conformal coverage.
- Also used as a mask material.



# VS Silicon Nitride 2D Materials

- $3\text{SiCl}_2\text{H}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{HCl} + 6\text{H}_2$ 
  - 780 to 850°C
  - Gases -  $\text{NH}_3$ ,  $\text{SiH}_2\text{Cl}_2$
  - Pressure - 300 mTorr
  - Deposition rate - 40 Å/min

# VS Polysilicon 2D Materials

- Used as a flexible material in MEMs applications.
- Ability to be doped to a specific resistivity.
- Ability to change mechanical properties.
- Excellent interface characteristics with  $\text{SiO}_2$ .
- Compatibility with subsequent high-temperature processing.
- Higher reliability than possible metal electrodes.
- Ability to be deposited conformally over steep topography.

# VS Polysilicon 2D Materials

- $\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$ 
  - Deposited between 575 and 650°C.
  - Gases -  $\text{SiH}_4$  and  $\text{PH}_3$
  - Pressure - 300 mTorr
  - Deposition rate - 100Å/min

# Thermal CVD Films and Coatings

Deposited material	Substrate	Input reactants	Deposition temperature (°C)	Crystallinity
Si	Single-crystal Si	SiCl <sub>2</sub> H <sub>2</sub> , SiCl <sub>3</sub> H, or SiCl <sub>4</sub> + H <sub>2</sub>	1050–1200	E
Si		SiH <sub>4</sub> + H <sub>2</sub>	600–700	P
Ge	Single-crystal Ge	GeCl <sub>4</sub> or GeH <sub>4</sub> + H <sub>2</sub>	600–900	E
GaAs	Single-crystal GaAs	(CH <sub>3</sub> ) <sub>3</sub> Ga + AsH <sub>3</sub>	650–750	E
InP	Single-crystal InP	(CH <sub>3</sub> ) <sub>3</sub> In + PH <sub>3</sub>	725	E
SiC	Single-crystal Si	SiCl <sub>4</sub> , toluene, H <sub>2</sub>	1100	P
AlN	Sapphire	AlCl <sub>3</sub> , NH <sub>3</sub> , H <sub>2</sub>	1000	E
In <sub>2</sub> O <sub>3</sub> :Sn	Glass	In-chelate, (C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(OOCH <sub>3</sub> ) <sub>2</sub> , H <sub>2</sub> O, O <sub>2</sub> , H <sub>2</sub>	500	A
ZnS	GaAs, GaP	Zn, H <sub>2</sub> S, H <sub>2</sub>	825	E
CdS	GaAs, sapphire	Cd, H <sub>2</sub> S, H <sub>2</sub>	690	E
Al <sub>2</sub> O <sub>3</sub>	Si, cemented carbide	Al(CH <sub>3</sub> ) <sub>3</sub> + O <sub>2</sub> , AlCl <sub>3</sub> , CO <sub>2</sub> , H <sub>2</sub>	275–475 850–1100	A A
SiO <sub>2</sub>	Si	SiH <sub>4</sub> + O <sub>2</sub> , SiCl <sub>2</sub> H <sub>2</sub> + N <sub>2</sub> O	450	A
Si <sub>3</sub> N <sub>4</sub>	SiO <sub>2</sub>	SiCl <sub>2</sub> H <sub>2</sub> + NH <sub>3</sub>	750	A
TiO <sub>2</sub>	Quartz	Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> + O <sub>2</sub>	450	A
TiC	Steel	TiCl <sub>4</sub> , CH <sub>4</sub> , H <sub>2</sub>	1000	P
TiN	Steel	TiCl <sub>4</sub> , N <sub>2</sub> , H <sub>2</sub>	1000	P
BN	Steel	BCl <sub>3</sub> , NH <sub>3</sub> , H <sub>2</sub>	1000	P
TiB <sub>2</sub>	Steel	TiCl <sub>4</sub> , BCl <sub>3</sub> , H <sub>2</sub>	> 800	P

Note: E = epitaxial; P = polycrystalline; A = amorphous.

# 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.

# Outline

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

# Vapor-Liquid-Solid (VLS) Growth

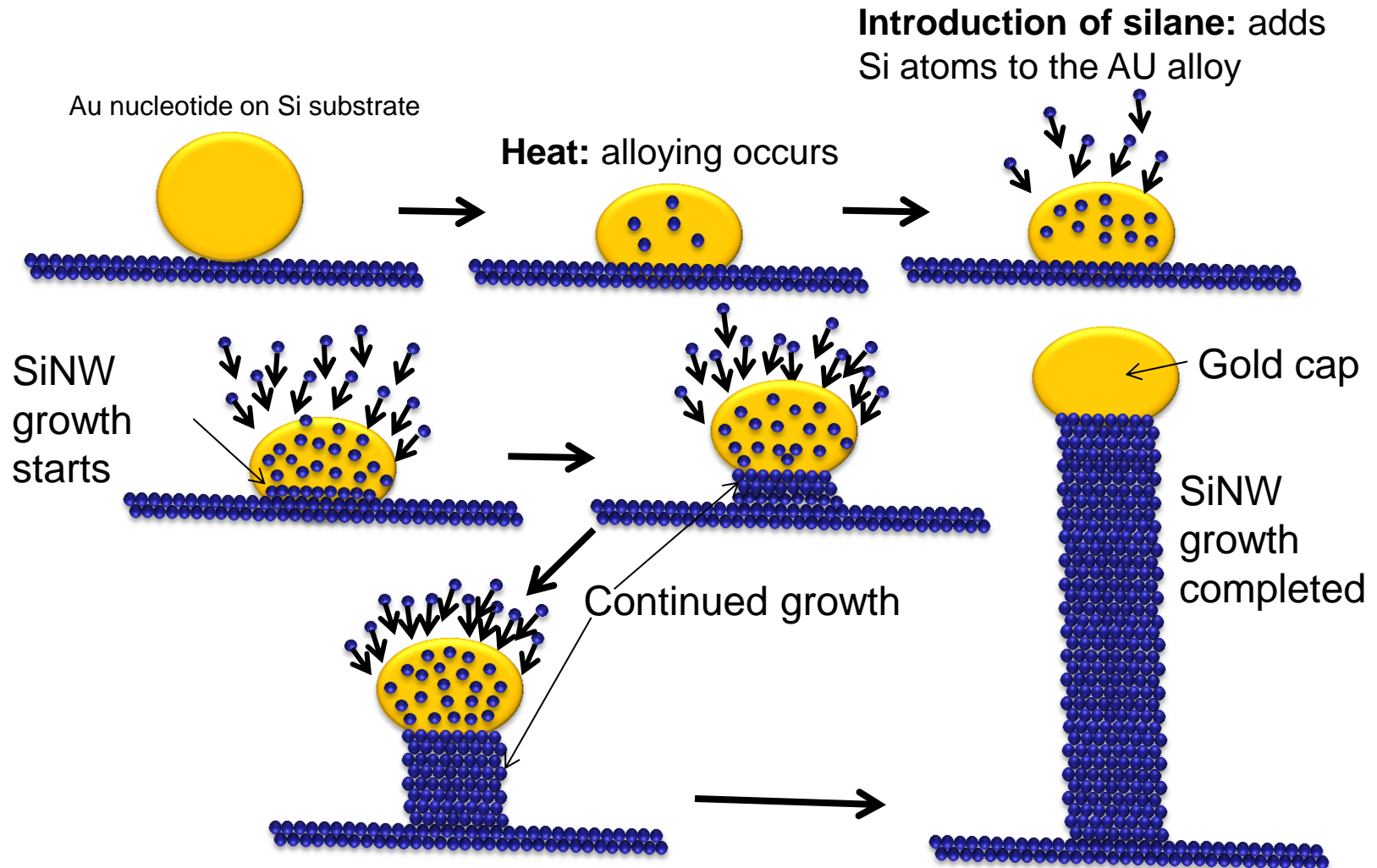
- In VLS growth, a catalyst is introduced to direct the growth to a specific orientation in a confined area.
- The catalyst forms a liquid droplet that acts as a nucleation site for the growth species, resulting in a one dimensional growth.
- There are seven requirements for VLS growth.



# Requirements for VLS Growth on a Crystalline Substrate

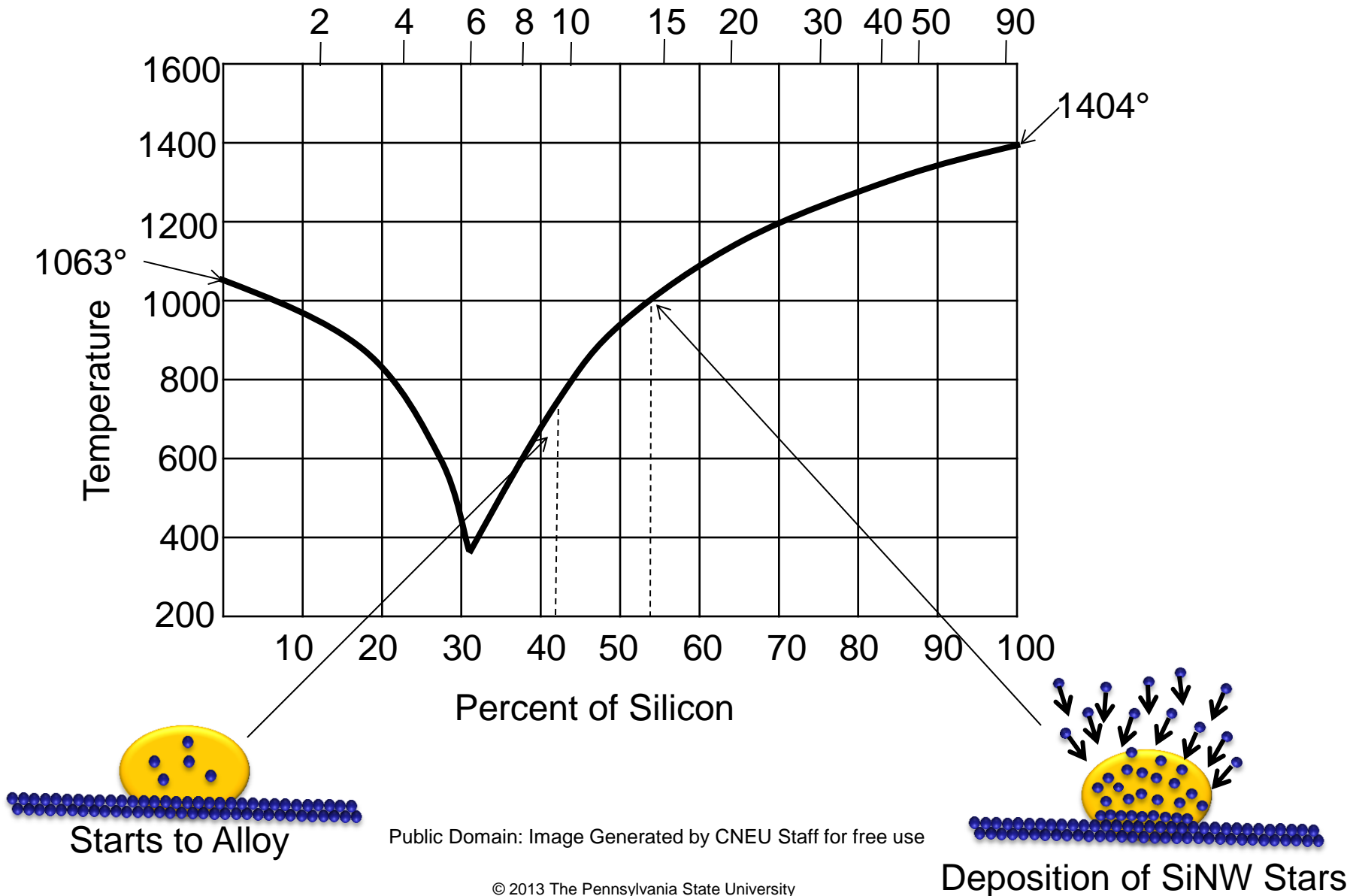
1. The catalyst is heated to a liquid on the crystalline material.
2. The catalyst's distribution coefficient must be less than unity at the deposition temperature.
3. The catalyst's equilibrium vapor pressure over the droplet must be small. The increased temperature causes the catalyst to start to evaporate, 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.

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



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# VLS Growth



# Relative Supersaturation Levels

- Anisotropic growth requires a low supersaturation.
- Bulk crystal growth is favored when a medium supersaturation is achieved.
- Polycrystalline and powdered materials occur from homogeneous nucleation and result from high supersaturation.

# VLS Growth

- The Kelvin equation shows equilibrium vapor pressure solubility is dependent on the surface energy and a radius of the catalyst.

$$\ln \left( \frac{P}{P_0} \right) = - \frac{2\gamma\Omega}{kTr}$$

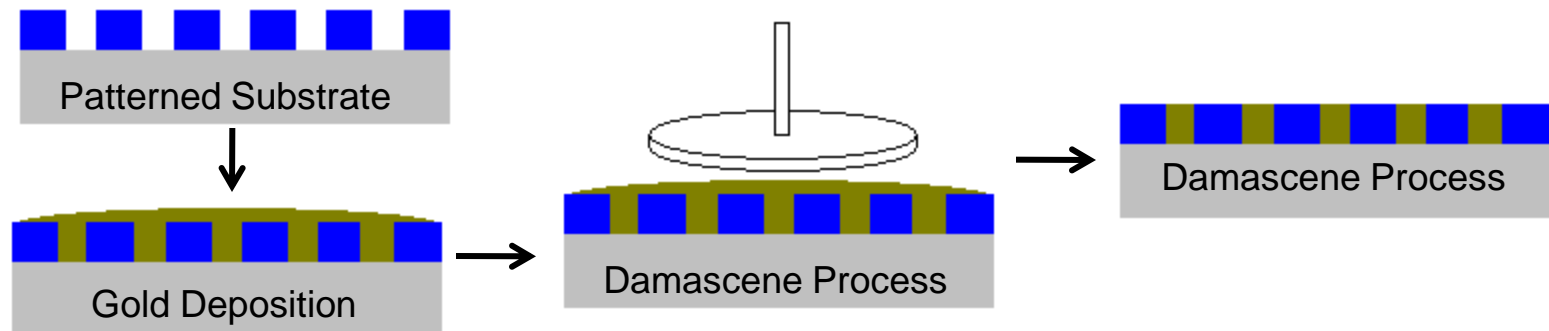
- Where:
  - $P$  = vapor pressure of a curved surface
  - $P_0$  = *vapor pressure of a flat surface*
  - $\Omega$  = *atomic volume of catalyst*
  - $r$  = surface radius
  - $\gamma$  = surface energy interface between the nanowire and the catalyst

# VLS Growth Rate

- The VLS mechanism utilizes the same six steps as VS growth, but these steps are localized at the catalyst site.
- Growth rate is determined by the diameter of the catalyst.
- The catalyst radius is determined by the wetting angle or the catalyst/substrate interaction.

# Deposition methods for catalysts

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



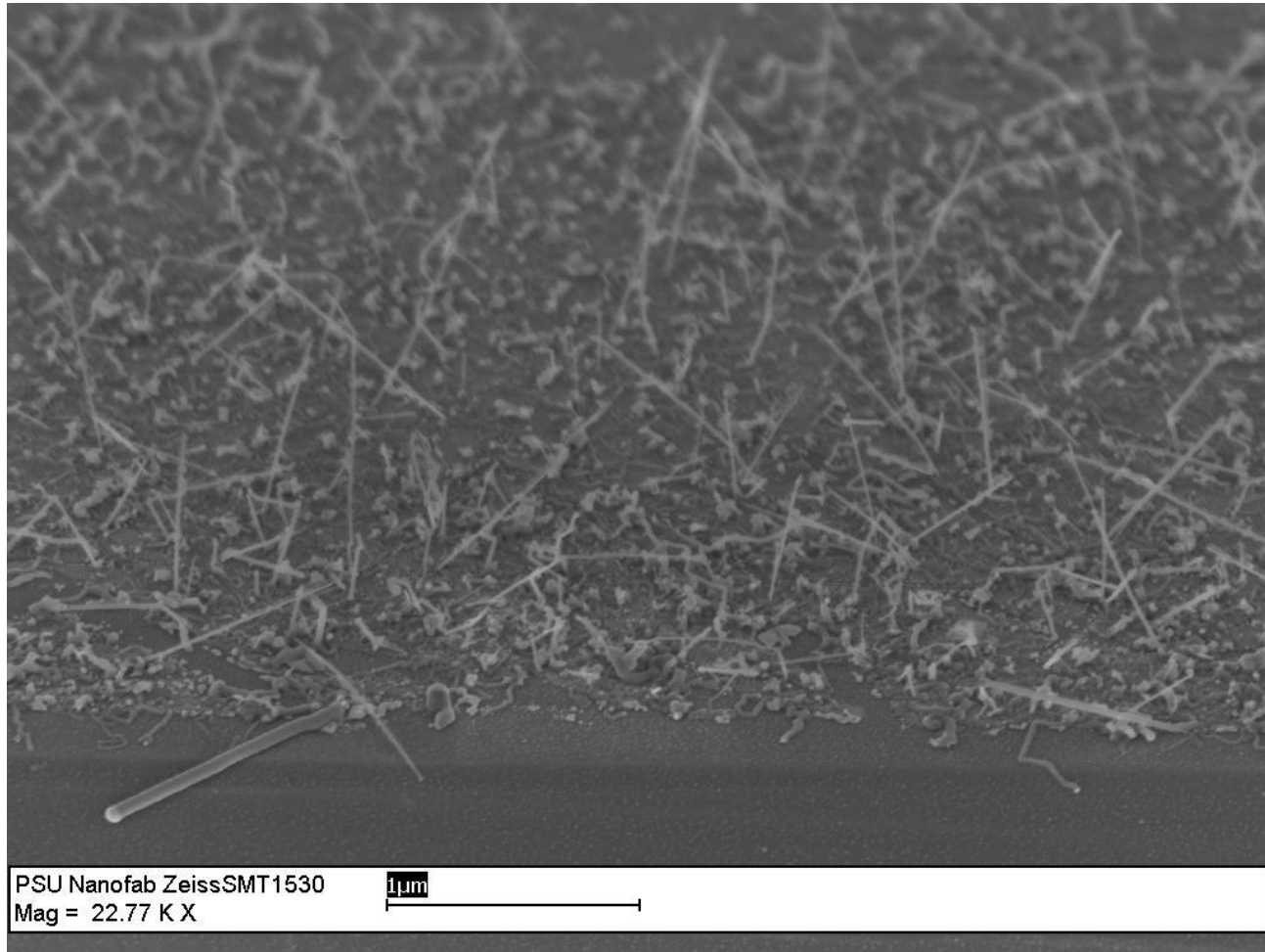
# How Do You Choose a Catalyst for VLS Growth?

\*\*\*\*\* 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	<i>Science</i> . Vol 279 (1998)
Sn	SnO <sub>2</sub>	<i>Chemical Physics Letters</i> . Vol 369 (2003)
Au Cu	GaAs, ZnSe, CdSe GaAs	<i>Adv. Mater.</i> No 4 (2000)
Sn	ZnO	<i>J. Phys. Chem B</i> . Vol, 108 (2004)
Ni, Au, Fe, Co	GaN	<i>Inst. Phys. Journal</i> . Issue 10 (2005)

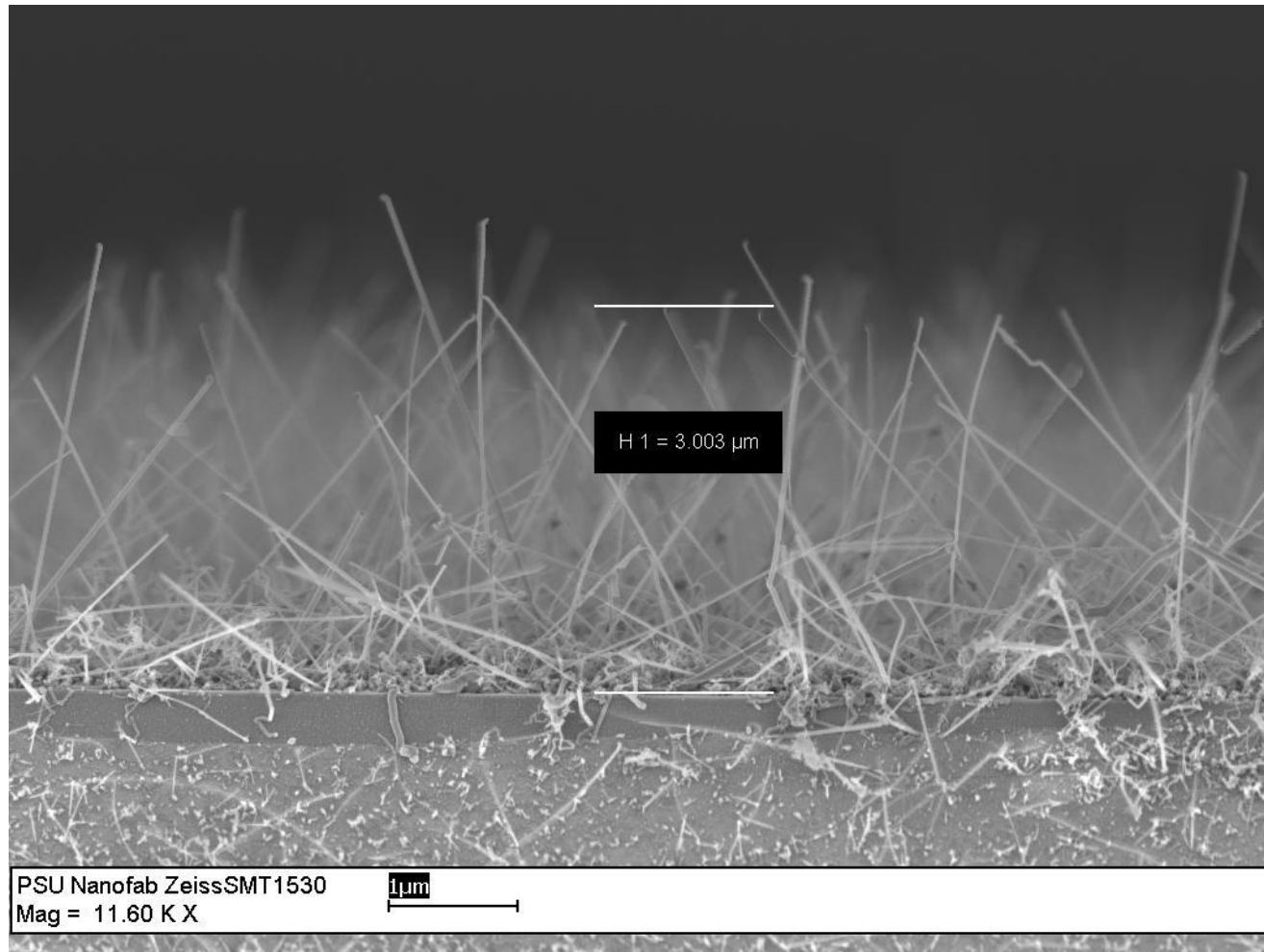


# LPCVD Grown SiNWs



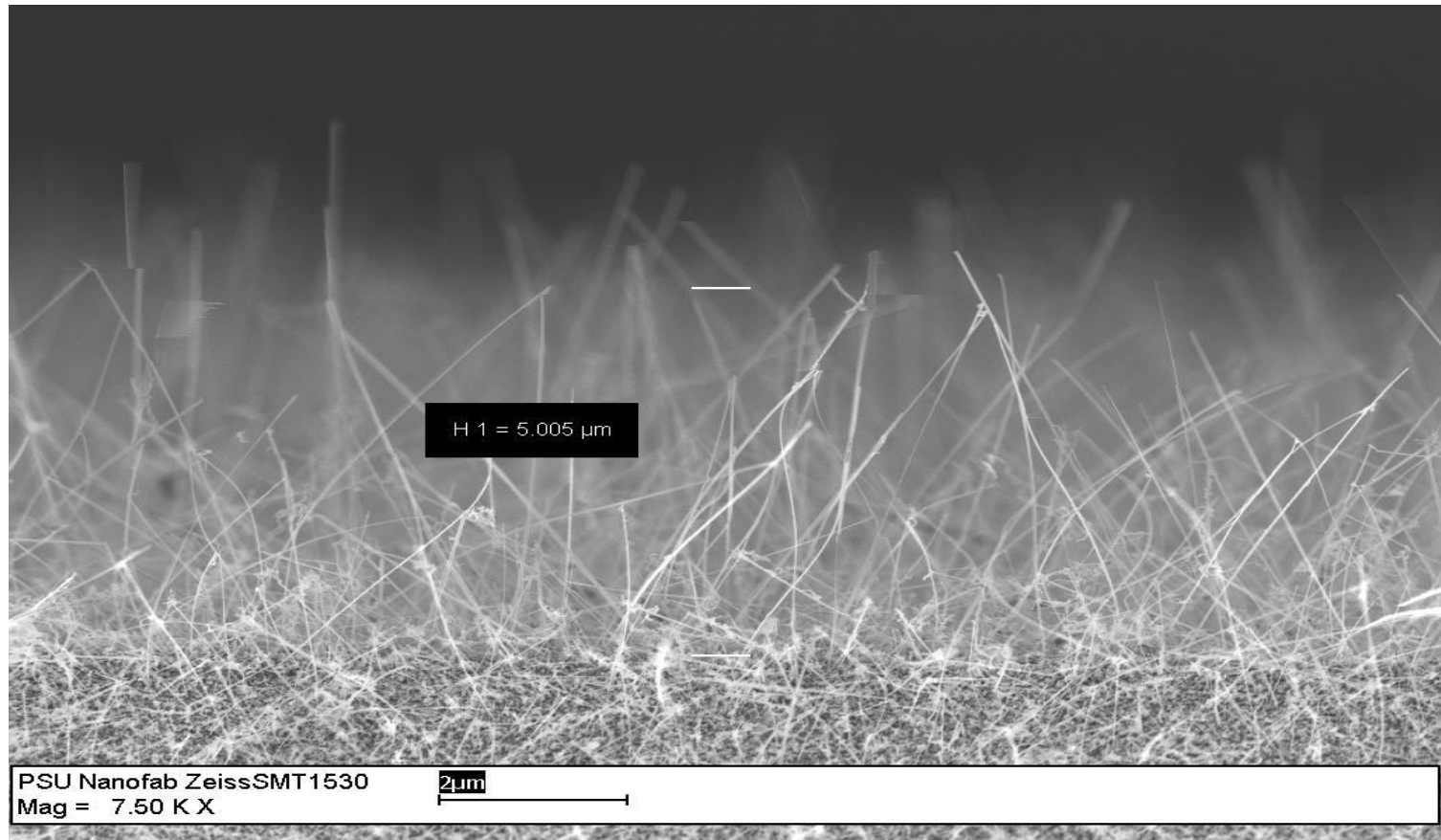
Angle view FESEM image of 2 minute deposition sample showing a side on view of nanowires. Lengths were less than 1  $\mu$ m. Magnification 22.77Kx

# LPCVD Grown SiNWs



Edge view FESEM image of 4 minute deposition sample showing average nanowire height/length (Average height = 3.003  $\mu\text{m}$ ). Magnification 11.60Kx

# LPCVD Grown SiNWs



Edge view FESEM image of 6 minute deposition sample showing average height/length of nanowires (Average height = 5.005  $\mu\text{m}$ ). Magnification 7.50Kx

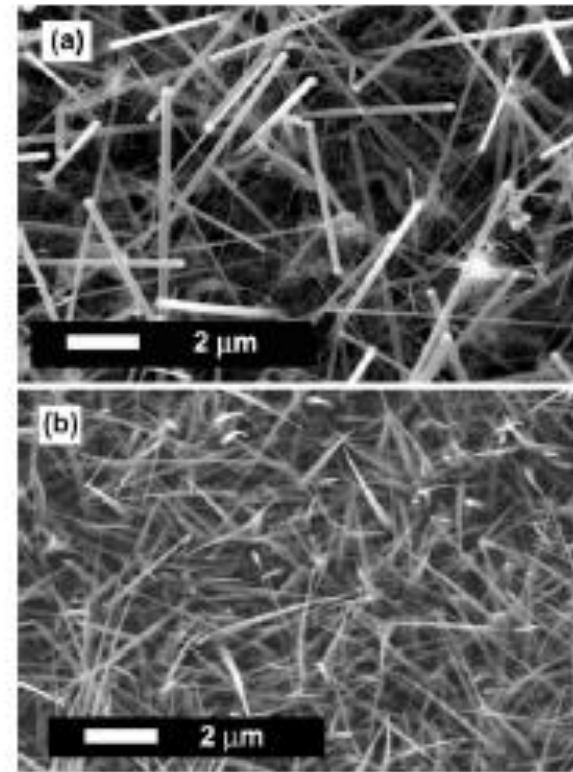
# Typical LPCVD Recipe for SiNWs

- Vent the vacuum chamber.
- Load the samples.
- Pump system to 10-20mTorr (base pressure limited by Fomblin prepped mechanical pump).
- Purge the system with N<sub>2</sub> for 5 min to ensure no oxygen is in the system.
- Heat LPCVD to 200°C at 10°C/min, flowing N<sub>2</sub> to maintain a pressure of 10T.
- Hold at 200°C for 10min to stabilize system temp.
- Heat to target temperature 415°C and hold for 30min to stabilize system temp.
- Run process: 100 SCCM SiH<sub>4</sub> for 2, 4, and 6min.
- Ambient N<sub>2</sub> system cooling to room temp (~2hrs)

Sample	Average Wire Diameter	Average Wire Length	Nanowire Growth Rate
Two Minute	26.21 nm	~1.0 µm	~0.5 µm/min
Four Minute	32.61 nm	3.00 µm	0.75 µm/min
Six Minute	24.38 nm	5.00 µm	0.83 µm/min

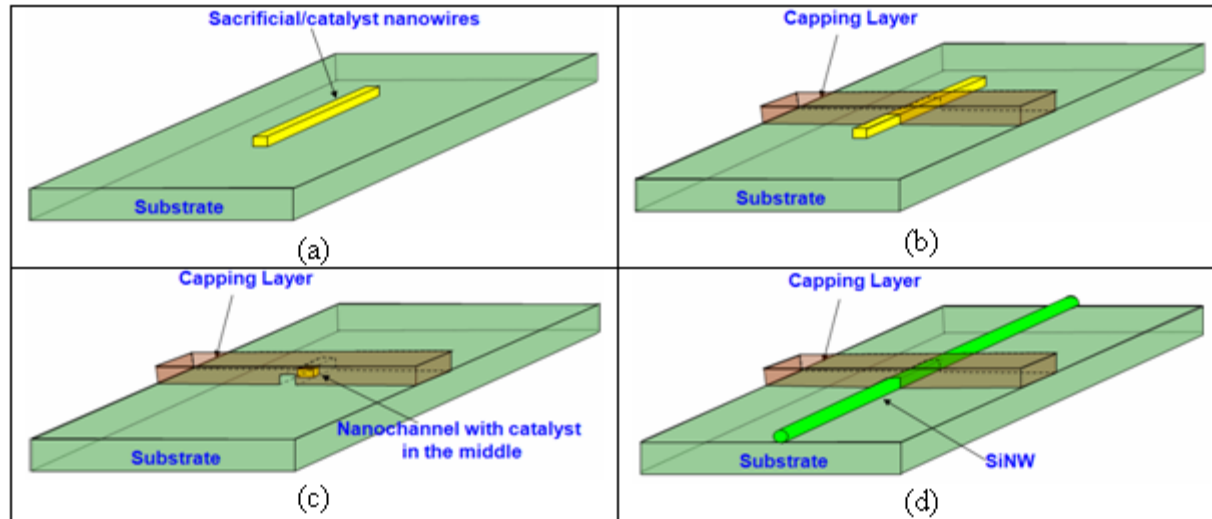
# An example: Silicon/Germanium Nanowires Produced by Chemical Vapor Growth Using the Vapor-Liquid-Solid (VLS) Mechanism

Silicon/germanium (SiGe) alloy nanowires



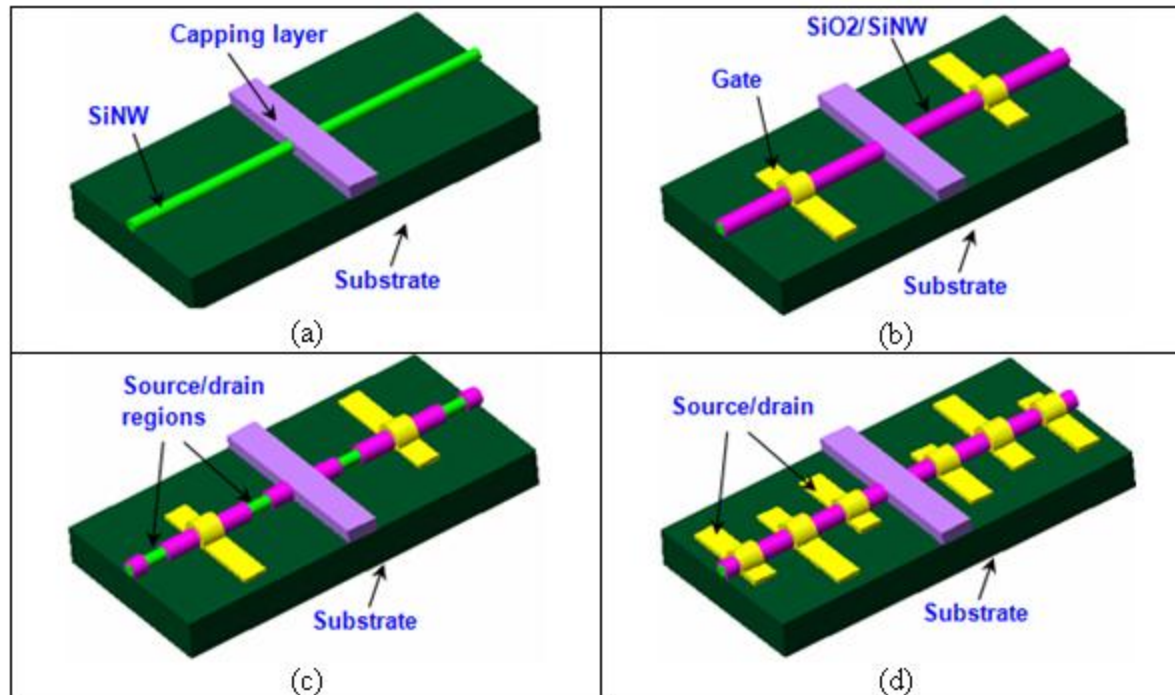
Lew et al., Adv. Mater. Vol.15(24), pp. 2073

# Self Assembling Si Nanowires



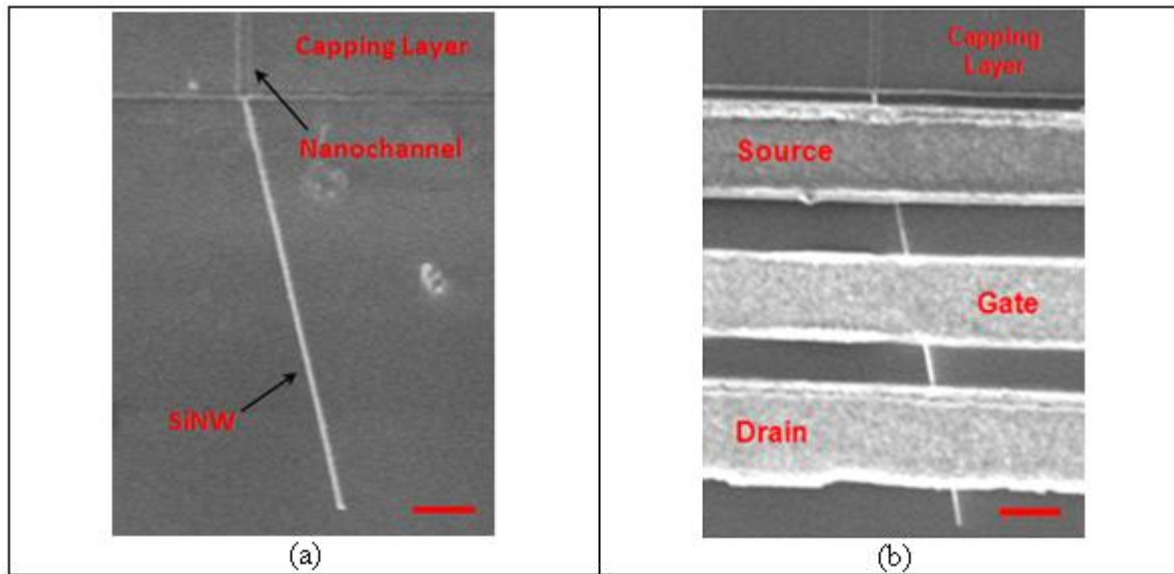
Process flow for the fabrication of “grow-in-place” Si nanowire using guiding nanochannel template. (a) Sacrificial/catalyst metal (Au) line defined by e-beam lithography and lift-off. (b) Patterning and deposition of the capping layer. (c) Partial etching of the sacrificial metal to form empty nanochannels with catalyst in the middle. (d) Si nanowire growth and extrusion out of channel by the VLS mechanism.

# Self Assembling Si Nanowires



Schematic representations of the top-gate core-shell SiNW transistor fabrication process. (a) SiNW after Au etching and cleaning, (b) SiNW oxidation and gate contact patterning, (c) Source/drain region patterning and oxide removal, (d) Source and drain contact deposition. In this depiction, two transistors are fabricated using an extruded nanowire.

# Self Assembling Si Nanowires



SiNW AMOSFET transistor (a) grow-in-place SiNW before transistor fabrication. (b) the corresponding SiNW transistor after gate and source/drain patterning.



# Silicon Nanowire as Bio-scaffolding

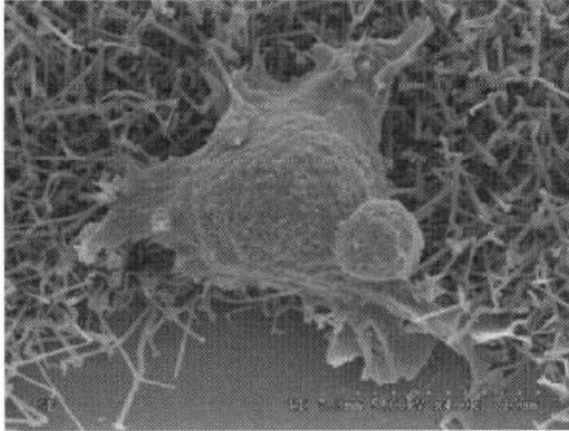
- H.S. Wen *et al* grew SiNWs using the VLS method described earlier, to investigate biocompatibility of SiNWs with fibroblast cells.
- Fibroblast cells were cultured with both raw SiNWs and gold surface modified SiNWs for 30min, 1 hr, and 3hrs, then imaged with an SEM.

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

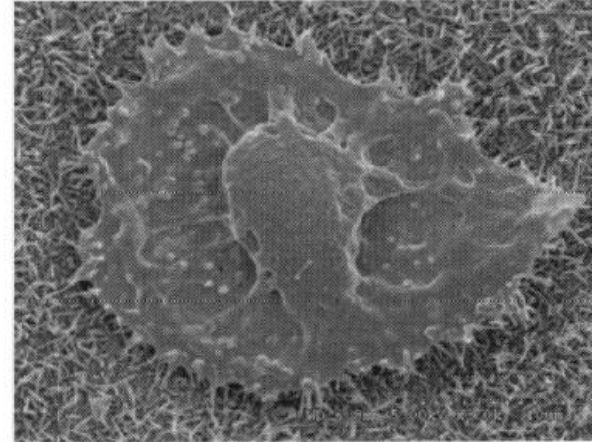
# Silicon Nanowire as Bio-scaffolding

- 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.

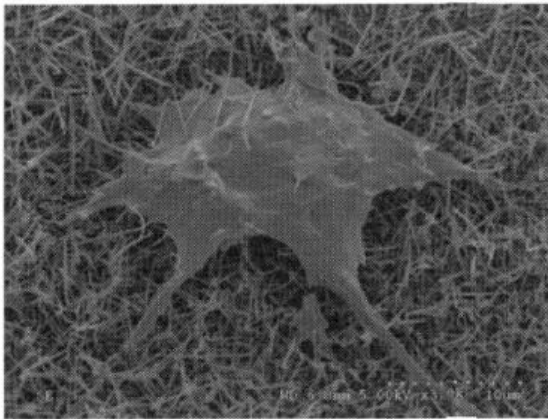
# Silicon Nanowire as Bio-scaffolding



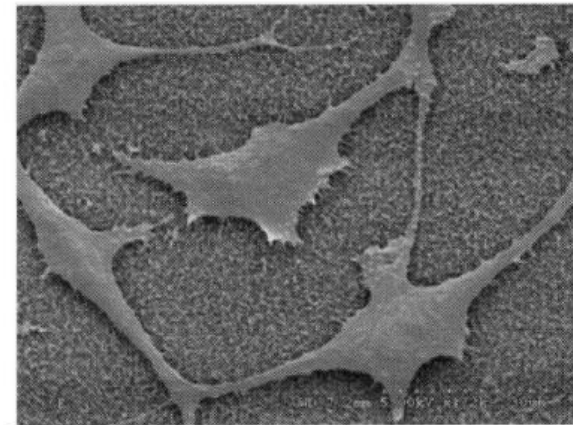
The SEM micrograph of fibroblasts on SiNWs substrate with 1 hr culture.



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.



The SEM micrograph of fibroblasts on Au-coated SiNWs substrate with 3 hr culture

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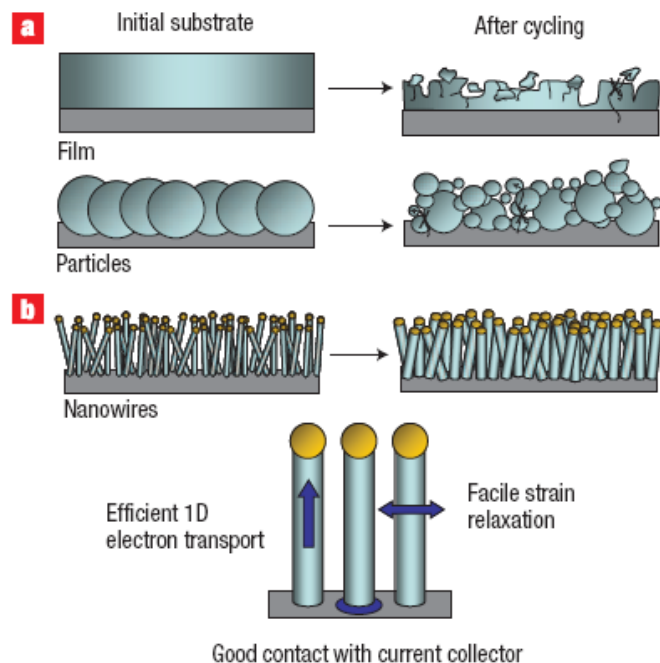
# SiNWs for Li Battery Anodes

- SiNWs have been investigated for use in rechargeable Li batteries, because they offer higher energy capacity and longer life between charges.
- Silicon has a charge capacity about ten times greater than traditional materials.
- However, silicon swells ~400% when charged, and traditional forms of silicon fail under this large strain.

# SiNWs for Li Battery Anodes

- SiNWs are grown directly on metallic current collecting substrates via Au catalytic VLS growth.
- SiNWs with average diameters of  $\sim 90\text{nm}$  allow for better accommodation of large volume changes without fracturing.
- Each SiNW growth from a metallic substrate contributes to the overall charge capacity, since each wire is electrically connected to the substrate.
- Since each SiNW is a 1 dimensional feature, there is an efficient pathway for electron transport.

# SiNWs for Li Battery Anodes



**Figure 1** Schematic of morphological changes that occur in Si during electrochemical cycling. **a**, The volume of silicon anodes changes by about 400% during cycling. As a result, Si films and particles tend to pulverize during cycling. Much of the material loses contact with the current collector, resulting in poor transport of electrons, as indicated by the arrow. **b**, NWs grown directly on the current collector do not pulverize or break into smaller particles after cycling. Rather, facile strain relaxation in the NWs allows them to increase in diameter and length without breaking. This NW anode design has each NW connecting with the current collector, allowing for efficient 1D electron transport down the length of every NW.

# LPCVD Growth of Carbon Nanotubes

- Mo:Fe:Al Alloy catalysts are deposited via Sol Gel, onto a porous substrate and heated in a tube furnace to anneal them to the substrate.
- Hydrocarbon gas is flowed over the pores in the substrate and nucleate at the catalyst.
- Nanotube growth occurs at the site of the catalysts.
  - Base growth and Tip Growth are possible.
- CVD can grow both MWNTs and SWNTs.
- SWNTs can be grown from hydrocarbon gas feeds at a temperature range of 800 – 1400°C.
- MWNTs can be grown from hydrocarbon gas feeds at a range of 600 – 800°C.

Ming Su, Bo Zheng, Jie Liu. A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity. Chemical Physics Letters 3222000.321–326

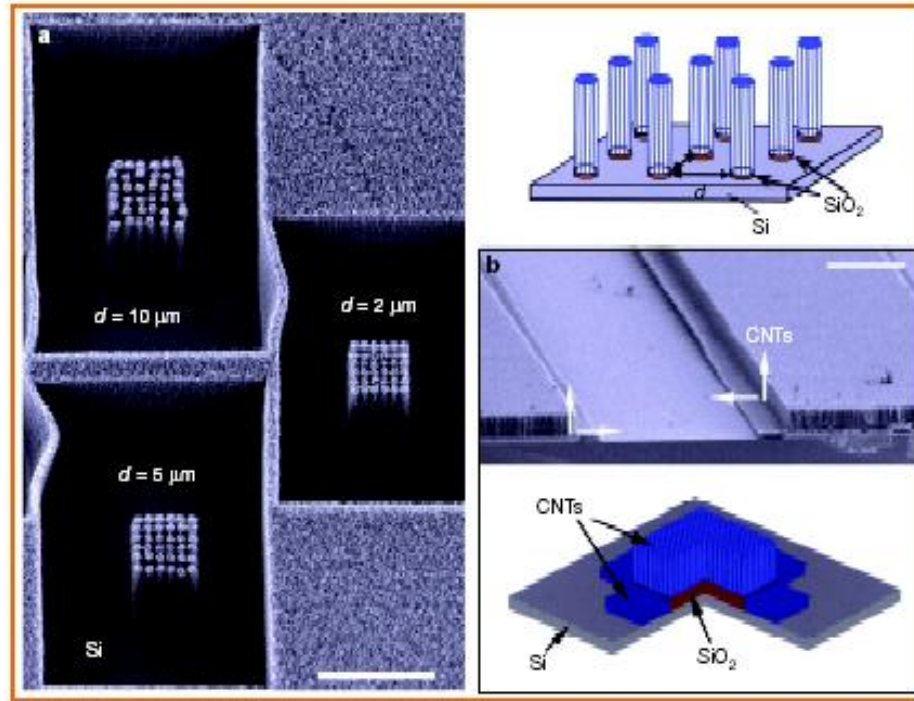
# LPCVD Growth of Carbon Nanotubes

- Synthesized SWNTs using the following CVD parameters:
  - 50mg Fe/Mo catalyst supported on  $\text{Al}_2\text{O}_3$  aerogel
    - The aerogel is a ultra-low density, highly porous material.
    - Fe/Mo has a proven track record of being a nucleation site for CNTs.
  - A furnace was heated to 100°C. From 850 – 1000°C, 100 sccm Ar was flown to purge the system.

Ming Su, Bo Zheng, Jie Liu. A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity. Chemical Physics Letters 3222000.321–326



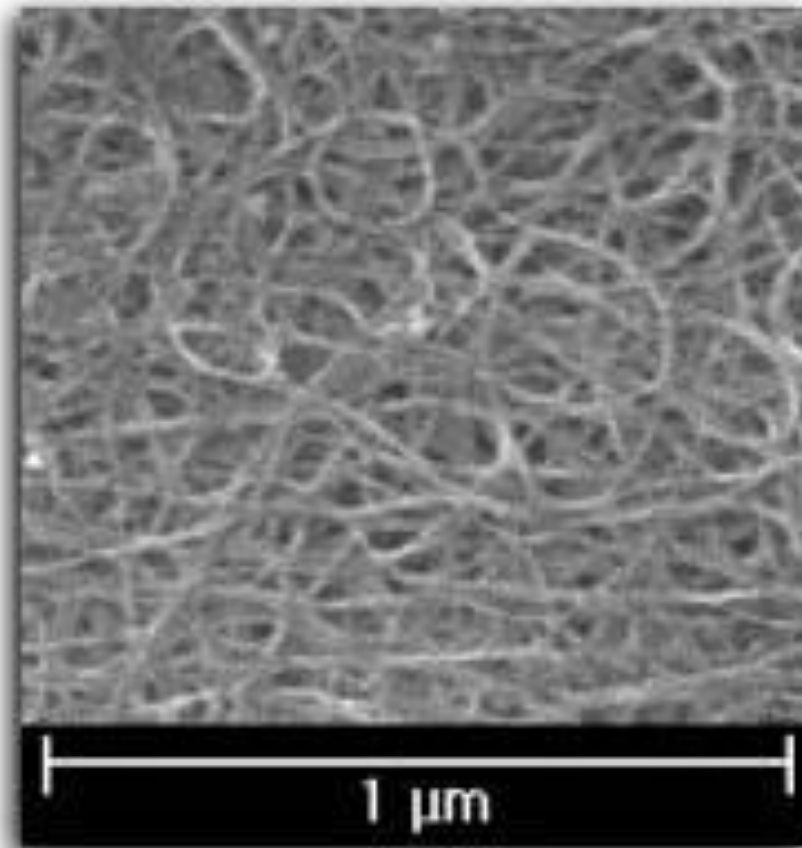
# LPCVD Growth of Carbon Nanotubes



Directed assembly of organized, multiwalled carbon-nanotube structures grown by chemical-vapour deposition. a, Image obtained by scanning electron microscopy of three blocks of cylindrical pillars (about  $10\mu\text{m}$  in diameter) of aligned carbon-nanotube arrays. Each pillar consists of several tens of nanotubes grown in vertical alignment and in a normal direction to SiO<sub>2</sub> patterns on the Si/SiO<sub>2</sub> template. No growth occurs on the Si parts of the template. The separation ( $d$  in diagram, top right) between pillars in the three blocks is indicated. B, Vertical and horizontal growth of aligned nanotubes (CNTs), viewed in a cross-section of a patterned Si/SiO<sub>2</sub> substrate. Scale bars,  $100\mu\text{m}$ .

B.Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath, P.M. Ajayan,  
Department of Materials Science and Engineering, Nature, Vol. 416, April 2002, page 495-496

# An example: Carbon Nanotubes (CNTs) Grown From Methane Gas Decomposition at Iron Nanoparticle Catalysts



[www.helixmaterial.com](http://www.helixmaterial.com)

# Applications of Carbon Nanotubes

- Hydrogen storage media
- Composites
- Flat panel displays
- Molecular manipulator and AFM tips