

## Thin Film Deposition

**Physical Vapor Deposition (PVD)**

- Evaporation
- Sputtering
- “Molecular Beam” Epitaxy

**Chemical Vapor Deposition**

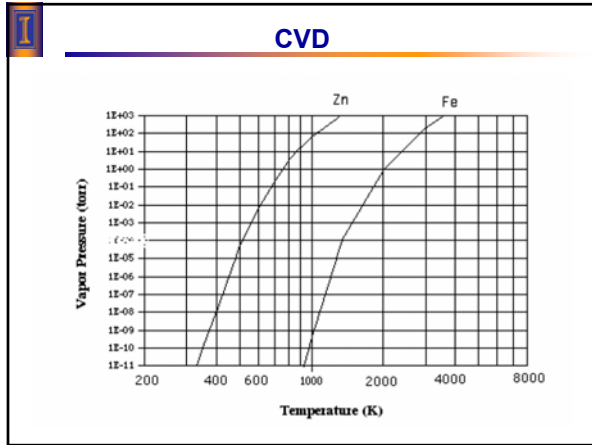
- CVD from salts
- MOCVD
- OMCVD

**Wet Chemical Methods**

- Electrodeposition
- Sol-gel Deposition & Spin Coating

## Evaporation

- Evaporation
  - Mostly for metals
  - High vacuum
  - Poor step coverage
    - heating/rotation
  - Crucible heating
    - Resistive
    - Inductive
    - Electron-beam



## Gas Transport

**Gas Transport**

- Viscous flow (moment transfer)
- Diffusion (particle transfer)
- Convection
- Thermal conductivity (energy transfer)

Issues:

- film thickness uniformity
- growth rates
- efficient utilization of process gases
- computer modeling of CVD reactor

## What's in a Vacuum?

Composition of gas in vacuum chamber is very different from atmosphere

pumps remove certain gasses preferentially (depends on pump type: e.g. Turbomolecular)

Component	Volume % in dry air	Volume % in ion pumped chamber at $2 \times 10^{-9}$ torr
N <sub>2</sub>	78 %	trace
O <sub>2</sub>	21 %	trace
Ar	0.93 %	trace
CO <sub>2</sub>	0.03 %	3 %
CH <sub>4</sub>	trace	3 %
H <sub>2</sub> O	trace	5 %
CO	trace	6 %
H <sub>2</sub>	trace	78 %

## Gas Phase Mass Transport

**Mass transport in gas**

mass transport depends on

fundamental parameters	experimental parameters
reactant concentration	pressure
diffusivity	gas velocity
boundary layer thickness	temperature distribution
	reactor geometry
	gas properties (viscosity ...)

goals

- deliver gas uniformly to substrate (uniform films)
- optimize flow for maximum deposition rate

**Two flow regimes**

- Molecular flow
  - diffusion in gas
    - $D \sim T^{3/2} / P$  from Kinetic Theory of Gases
    - reduce Pressure for higher D and higher deposition rate
- Viscous flow
  - low flow rates produces laminar flow (desired)
  - high flow rates produces turbulent flow (avoid)

**laminar flow: simple case: flow past a plate**

near plate velocity = 0 => stagnant layer

- diffuse gas through stagnant layer to surface

**ICBST:**

$$\delta(x) = \sqrt{\frac{4Dx}{v_0}} = \sqrt{\frac{4D}{v_0} x}$$

gas viscosity, chamber dimension, Reynolds number, gas density, gas velocity

## Reynolds Number

**Reynolds number:**  $Re = \frac{\text{ratio of inertia to viscosity forces}}{(\text{density}) \cdot (\text{velocity}) \cdot (\text{distance}) / \text{viscosity}}$

$Re < \sim 2000$  for laminar flow  
 $Re > \sim 3000$  for turbulent flow

**Typical values of Reynolds number**

- Spermatozoa  $\sim 1 \times 10^{-2}$
- Blood flow in brain  $\sim 1 \times 10^2$
- Blood flow in aorta  $\sim 1 \times 10^3$
- Onset of turbulent flow  $\sim 2.3 \times 10^3$
- Person swimming  $\sim 4 \times 10^6$
- Aircraft  $\sim 1 \times 10^7$
- Blue Whale  $\sim 3 \times 10^8$
- A large ship (RMS Queen Elizabeth 2)  $\sim 5 \times 10^9$

## Physical methods to produce thin layers

**Sputtering:** originally a method to clean surfaces,  $Ar^+$ -ions are accelerated in an electrical field and hit the target that has to be cleaned; as a consequence surface atoms or molecules are removed from the surface

**Epitaxy:** Thin **oriented** layers (thickness of some  $\mu m$ ) are deposited on a **substrate** with similar crystal structure (e.g. InAs:  $a=603.6$  pm on GaAs:  $a=565.4$  pm, both sphalerite structure).

**Molecular Beam Epitaxy (MBE):** Evaporation at very low deposition rates under ultrahigh vacuum but at relatively low substrate temperatures

**Gas phase epitaxy (CVD = Chemical Vapour Deposition):** Decomposition of molecules in the gas phase (e.g. by radiation or electron beam/Laser) and deposition on a suitable substrate; (e.g. fabrication of LEDs with GaP und  $GaAs_{1-x}P_x$ , epitaxial layers are produced by thermal decomposition of compounds like  $AsH_3$ ,  $AsCl_3$ ,  $PH_3$ ,  $PCl_3$ , ...)

## Sputtering

- Physical process
  - Chemically inert atoms (Ar) ionized in plasma
  - Ions accelerated into a target by the E-field
  - Atoms from the **target** knocked out (sputtering)
  - These atoms reach the **substrate**

## Sputtering

**Atoms into gas state**

at target:

- target atoms ejected
- target ions ejected (1 - 2 %)
- electrons emitted
  - helps keep plasma going
- $Ar^+$  ions reflected as Ar neutrals
- Ar buried in target
- photons emitted

We are most interested in the first of these: target atoms going into the gas phase

## Sputtering

Comparison of evaporation and sputtering

EVAPORATION	SPUTTERING
low energy atoms	higher energy atoms
high vacuum path	low vacuum, plasma path
<ul style="list-style-type: none"> <li>• few collisions</li> <li>• line of sight deposition</li> <li>• little gas in film</li> </ul>	<ul style="list-style-type: none"> <li>• many collisions</li> <li>• less line of sight deposition</li> <li>• gas in film</li> </ul>
larger grain size	smaller grain size
fewer grain orientations	many grain orientations
poorer adhesion	better adhesion
	wider range of materials
	better step coverage (but not as good as CVD)

## Sputtering

- momentum transfer process
  - involves top 10 Å
  - model as hard sphere collisions
    - good for energies  $< 50$  keV
- 95 % of incident energy goes into target
  - => COOL the target
- 5 % of incident energy is carried off by target atoms
  - typical energies of 5-100 eV
- target atoms come off with a non-uniform distribution
  - more atoms normal to the surface
  - cosine distribution (like surface source)

## Sputtering

Why sputtering? What's wrong with evaporation?

- some materials are difficult to evaporate.
- low melting point substrates.
- evaporating thick layers quickly may burn photoresist or heat up target.
- Adhesion of sputtered films is often better.
- Deposition is different from evaporation- which is from a point source.
- - changes in composition easy to do.

## Sputtering

### Sputtering alloy targets

composition of alloy in film is approximately the same as alloy in target (unlike evaporation)

Why ?

- rapid mixing in liquids (evaporation)
- slow diffusion mixing in solids (sputtering)
  - target reaches steady state
  - surface composition balances sputter yield

### Transport to substrate

- Target atoms pass through Ar gas and plasma environment
  - one Ar<sup>+</sup> ion for every 10,000 Ar neutrals
  - electrons in plasma collide with Ar neutrals to form ions and more electrons
- Target atoms collide with Ar atoms, Ar<sup>+</sup> ions and electrons
  - treat as random walk "diffusion" through gas
  - target atoms lose energy (down to 1-10 eV)
  - chemical reactions may occur in gas
  - not a line of sight process (unless pressure reduced)
    - can coat around corners

## Sputtering

### Deposit on substrate

- target atoms and ions impinge
- electrons impinge
- Ar atoms impinge
  - Ar pressure about 0.1 torr
  - Ar may be incorporated into film
- energetic particles may modify growth
- substrates heat up
  - 100 - 200 C is common

## Sputtering Yield

S = number ejected / number incident

S depends on

- target material
  - binding energy
  - mass of atoms
- sputtering gas
  - mass of atoms (S increases for heavier gasses)
  - incident energy (S increases for higher energies)
- geometry
  - most efficient 20-30 degrees from glancing
  - depends on momentum and energy transferred
    - these depend on relative masses and collision angle
    - maximum energy transferred to target atom in hard sphere collision

S  
perpendicular  
60-70°  
glancing  
angle of incidence

$$E_{max} = \frac{4 M_{12} M_{21} \alpha}{(M_{12} + M_{21})^2} E_{12}$$

- depends on binding energy of target atom
- number of layers involved in process
  - mean free path of ion in target
    - typically about 2 layers
- surface density of target atoms
- collision cross section of ion with target atom

## Sputtering

### DC sputtering

simplest - basically what we have talked about so far

## DC Sputtering

### Parameters:

- **Argon Pressure**
  - optimum deposition rate around 100 mTorr
  - compromise between
    - increasing number of Ar ions
    - increasing scattering of Ar ions with neutral Ar atoms
  - if you can increase the number of ions without increasing the number of neutrals, can operate at lower pressures
- **Sputter voltage**
  - maximize sputter yield (S)
  - typically -2 to -5 kV
- **Substrate Bias Voltage**
  - substrate is being bombarded by electrons and ions from target and plasma
    - sputtering film while you deposit
    - neutral atoms deposit independently
    - put negative bias on the substrate to control this
    - can significantly change film properties
- **Substrate temperature**
  - control with substrate heater
  - heating from deposited material
    - increases with increasing sputter voltage
    - decreases with increasing substrate bias
- **Deposition rate**
  - changes with Ar pressure
  - increases with sputter yield
    - usually increases with high voltage
- **Particle Energy**
  - increases with increasing sputter voltage
  - decreases with increasing substrate bias
  - decreases with increasing Ar pressure

## MBE

### Molecular Beam Epitaxy

- evaporation at very low deposition rates
- typically in ultra-high vacuum
- very well controlled
- grow films with good crystal structure
- expensive
- often use multiple sources to grow alloy films
- deposition rate is so low that substrate temperature does not need to be as high

Half of the lasers that are used in CD players are grown by MBE, as well as those in pen-sized laser pointers.

## Basic arrangement of the MBE process I

Target (can be cooled or heated)

GaAs

Production of a  $Ga_{1-x}Al_xAs$  on GaAs by the MBE process

Be

$Ga(CH_3)_3$

$AsH_3$

$Al(CH_3)_3$

Si

Effusion furnaces with a small pinhole

## MBE

### Epitaxy

epitaxy = growth of film with a crystallographic relationship between film and substrate

homoepitaxy (autoepitaxy, isoeptitaxy) = film and substrate are same material

heteroepitaxy = film and substrate are different materials

#### structures

- matched
  - common in homoepitaxy, sometimes in heteroepitaxy

film material			no strains or defects
substrate material			

- strained (pseudomorphy)
  - film grows with structure different from bulk

film material			strained film
substrate material			

## MBE Interfaces

Highly abrupt interfaces

Growing Epilayer

Misfit Dislocation

Pd/ZnO(000-1)

Pd

ZnO

## MBE Growth Mechanisms

Epi layer

Substrate

Growth direction

Homoepitaxy

Heteroepitaxy

same structure

different structure

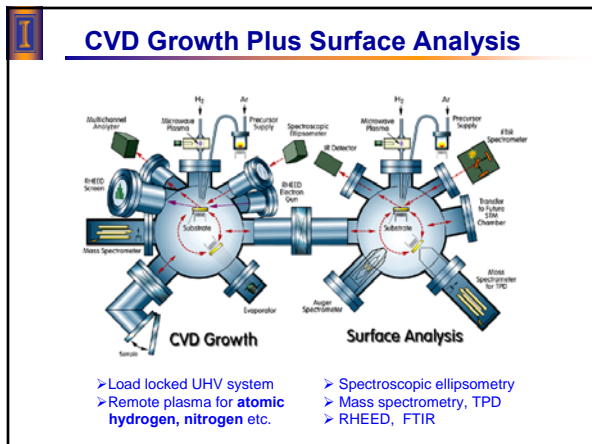
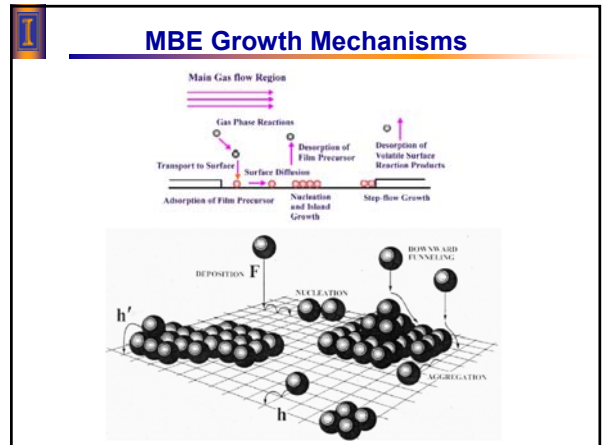
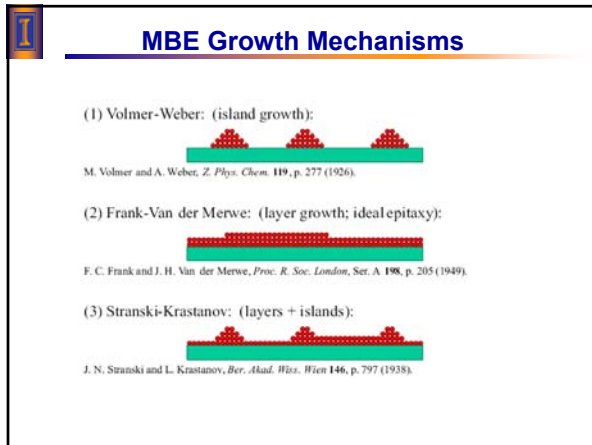
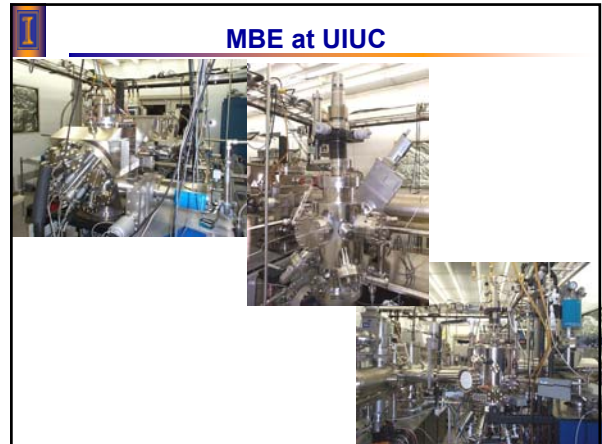
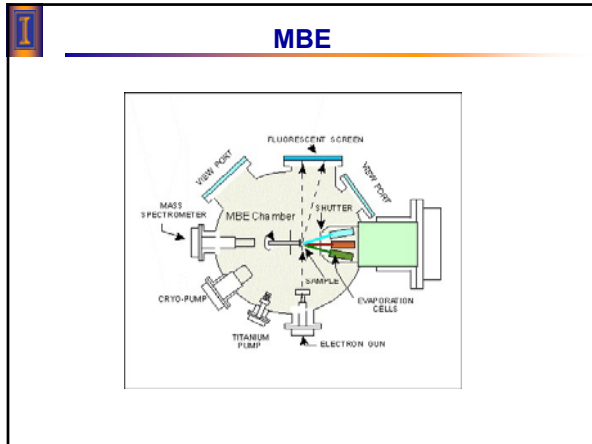
## MBE Growth Mismatches

Separate layers

thickness of epilayer < critical thickness

thickness of epilayer > critical thickness

Misfit dislocation

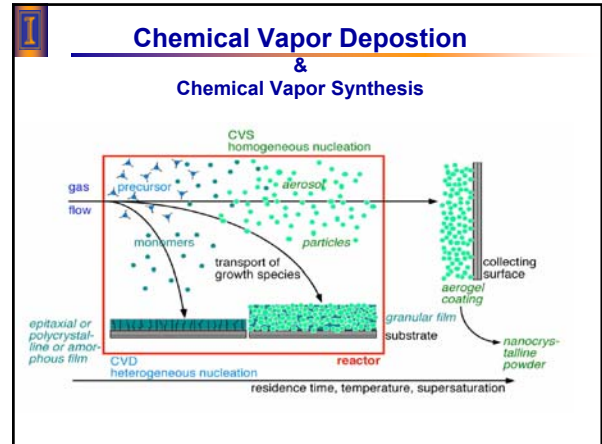




## CVD Sources

**CVD Sources**

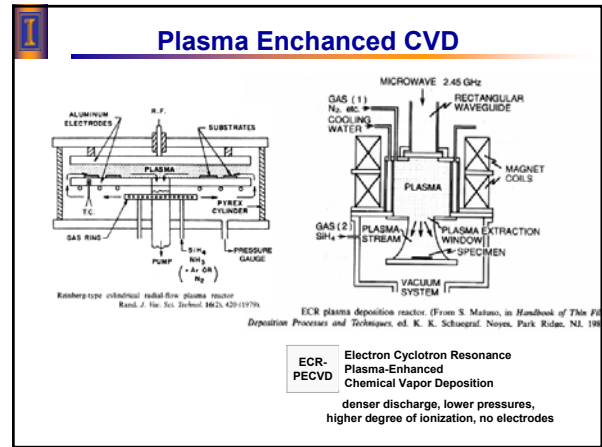
- types of sources
  - gasses (easiest)
  - volatile liquids
  - sublimable solids
  - combination
- materials should be
  - stable at room temperature
  - sufficiently volatile
    - high enough partial pressure to get good growth rates
  - reaction temperature < melting point of substrate
  - produce desired element on substrate with easily removable by-products
  - low toxicity



## Thermal CVD Films & Coatings

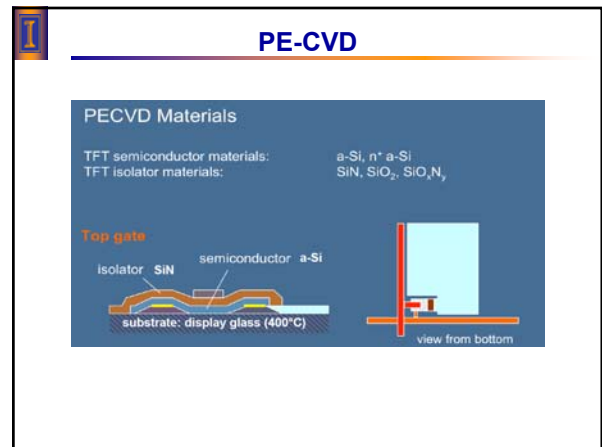
Deposited material	Substrate	Input reactants	Deposition temperature (°C)	Crystallinity
Si	Single-crystal Si	SiCl <sub>4</sub> , H <sub>2</sub> , SiCl <sub>4</sub> , H <sub>2</sub> , or SiCl <sub>4</sub> + H <sub>2</sub>	1050-1200	E
Si		SiH <sub>4</sub> + H <sub>2</sub>	600-700	P
Ge	Single-crystal Ge	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-ohate, (C <sub>2</sub> H <sub>5</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>	300	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	A
SiO <sub>2</sub>	Si	SiH <sub>4</sub> + O <sub>2</sub> , SiCl <sub>4</sub> , H <sub>2</sub> + N <sub>2</sub> O	850-1100	A
Si <sub>3</sub> N <sub>4</sub>	SiO <sub>2</sub>	SiCl <sub>4</sub> , H <sub>2</sub> + NH <sub>3</sub>	750	A
TiO <sub>2</sub>	Quartz	Ti(O <sub>2</sub> C <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.



## PECVD

Film	Source gases	Deposition temperature (°C)
<b>Elemental</b>		
Al	AlCl <sub>3</sub> -H <sub>2</sub>	100-250
a-B	BCl <sub>3</sub> -H <sub>2</sub>	400
a-C	C <sub>2</sub> H <sub>4</sub> -H <sub>2</sub> /Ar	25-250
a-Si	SiH <sub>4</sub> -H <sub>2</sub>	300
e-Si	SiH <sub>4</sub> -H <sub>2</sub>	400
<b>Oxides</b>		
Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub> -O <sub>2</sub>	100-400
SiO <sub>2</sub>	SiCl <sub>4</sub> -O <sub>2</sub>	100-400
TiO <sub>2</sub>	TiCl <sub>4</sub> -O <sub>2</sub>	100-500
<b>Nitrides</b>		
AlN	AlCl <sub>3</sub> -N <sub>2</sub>	<1000
BN	B <sub>2</sub> H <sub>6</sub> -NH <sub>3</sub>	300-700
	BCl <sub>3</sub> -NH <sub>3</sub> /Ar	300-700
Si <sub>3</sub> N <sub>4</sub>	SiH <sub>4</sub> -NH <sub>3</sub> -N <sub>2</sub>	25-500
TiN	TiCl <sub>4</sub> -N <sub>2</sub> -H <sub>2</sub>	100-300
<b>Carbides</b>		
B <sub>4</sub> C	B <sub>2</sub> H <sub>6</sub> -CH <sub>4</sub>	400
BCN	B <sub>2</sub> H <sub>6</sub> -CH <sub>4</sub> -N <sub>2</sub>	~25
	C <sub>2</sub> H <sub>4</sub> -BN	250
SiC	SiH <sub>4</sub> -C <sub>2</sub> H <sub>4</sub>	140-600
TiC	TiCl <sub>4</sub> -CH <sub>4</sub> -H <sub>2</sub>	400-900
<b>Borides</b>		
TiB <sub>2</sub>	TiCl <sub>4</sub> -BCl <sub>3</sub> -H <sub>2</sub>	480-650



## CVD Reaction Types

**CVD**

CVD is used to grow a thin layer of advanced materials on the surface of a substrate

Applications:

- integrated circuits, optoelectronic devices and sensors
- catalysts
- micromachines, and fine metal and ceramic powders protective coatings

- Pyrolysis
- Reduction
- Oxidation
- Compound formation
- Disproportionation
- Reversible transfer

## CVD Types

- APCVD: Atmospheric Pressure CVD
- LPCVD: Low Pressure CVD
- MOCVD: MetalOrganic CVD
- OMCVD: OrganoMetallic CVD
- PECVD: Plasma Enhanced CVD
- HDPCVD: High Density Plasma CVD
- LACVD: Laser-Assisted CVD
- IICVD: Ion-Induced CVD

## CVD Reaction Types

**Types of CVD reactions**

**Pyrolysis - thermal decomposition**

$$AB(g) \rightarrow A(s) + B(g)$$

ex: Si deposition from Silane at 650 C

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$

use to deposit: Al, Ti, Pb, Mo, Fe, Ni, B, Zr, C, Si, Ge, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, BN, Si<sub>3</sub>N<sub>4</sub>, GaN, Si<sub>1-x</sub>Ge<sub>x</sub>, ...

**Reduction**

SiH<sub>4(g)</sub> → Si<sub>(s)</sub> + 2H<sub>2(g)</sub> (650° C)  
SiH<sub>4</sub> silane, Si<sub>(s)</sub> amorphous

Ni(CO)<sub>4(g)</sub> → Ni<sub>(s)</sub> + 4CO<sub>(g)</sub> (180° C)  
Ni(CO)<sub>4</sub> Ni carbonyl

## OM CVD Precursors

Compound	p at 298 K (torr)	A	B	Melt point (°C)	
TMAI	Al(CH <sub>3</sub> ) <sub>3</sub> I <sub>2</sub>	14.2	2780	10.48	15
TEAl	Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	0.041	3625	10.78	-52.5
TMGa	Ga(CH <sub>3</sub> ) <sub>3</sub>	238	1825	8.5	-15.8
TEGa	Ga(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	4.79	2530	9.19	-82.5
TMIn	In(CH <sub>3</sub> ) <sub>3</sub>	1.75	2830	9.74	88
TEIn	In(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	0.31	2815	8.94	-32
DEZn	Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	8.53	2190	8.28	-28
CpZMg	Mg(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.05	3556	10.56	175

Approximation for vapor pressure p at temperature T

$$\log(p) = B - A/T$$

## CVD Reaction Types

**Reduction**

often using H<sub>2</sub>

$$AX(g) + H_2(g) \rightleftharpoons A(s) + HX(g)$$

often lower temperature than pyrolysis

reversible => can use for cleaning too

ex: W deposition at 300 C

$$WF_6(g) + 3H_2(g) \rightleftharpoons W(s) + 6HF(g)$$

use to deposit: Al, Ti, Sn, Ta, Nb, Cr, Mo, Fe, B, Si, Ge, TaB, TiB<sub>2</sub>, SiO<sub>2</sub>, BP, Nb<sub>2</sub>Ge, Si<sub>1-x</sub>Ge<sub>x</sub>, ...

SiCl<sub>4(g)</sub> + 2H<sub>2(g)</sub> → Si<sub>(s)</sub> + 4HCl<sub>(g)</sub> (1200° C)  
SiCl<sub>4</sub> silicon tetrachloride, Si<sub>(s)</sub> epitaxial

WF<sub>6(g)</sub> + 3H<sub>2(g)</sub> → W<sub>(s)</sub> + 6HF<sub>(g)</sub> (300° C)

MoF<sub>6(g)</sub> + 3H<sub>2(g)</sub> → Mo<sub>(s)</sub> + 6HF<sub>(g)</sub> (300° C)

## CVD Reaction Types

**Oxidation**

often using O<sub>2</sub>

$$AX(g) + O_2(g) \rightarrow AO(s) + [O]X(g)$$

ex: SiO<sub>2</sub> deposition from silane and oxygen at 450 C (lower temp than thermal oxidation)

$$SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2H_2(g)$$

use to deposit: Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, ZnO, ...

SiH<sub>4(g)</sub> + O<sub>2(g)</sub> → SiO<sub>2(s)</sub> + 2H<sub>2(g)</sub> (450° C)  
SiH<sub>4</sub> silane

SiH<sub>4(g)</sub> + 2H<sub>2(g)</sub> + O<sub>2(g)</sub> → SiO<sub>2(s)</sub> + 4HCl<sub>(g)</sub> (1500° C)

2AlCl<sub>3(g)</sub> + 3H<sub>2(g)</sub> + 3CO<sub>2(g)</sub> → Al<sub>2</sub>O<sub>3(s)</sub> + 3CO<sub>(g)</sub> + 6HCl<sub>(g)</sub> (1000° C)

## CVD Reaction Types

**Compound formation**

often using ammonia or water vapor

$$\text{AX(g)} + \text{NH}_3\text{(g)} \rightarrow \text{AN(s)} + \text{HX(g)}$$

$$\text{AX(g)} + \text{H}_2\text{O(g)} \rightarrow \text{AO(s)} + \text{HX(g)}$$

ex: deposit wear resistant film (BN) at 1100 C

$$\text{BF}_3\text{(g)} + \text{NH}_3\text{(g)} \rightarrow \text{BN(s)} + 3\text{HF(g)}$$

use to deposit: TiN, TaN, AlN, SiC, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, SiO<sub>2</sub>, ...

hard surface coatings

$$\text{SiCl}_4\text{(g)} + \text{CH}_4\text{(g)} \rightarrow \text{SiC(s)} + 4\text{HCl(g)} \quad (1400^\circ\text{C})$$

$$\text{TiCl}_4\text{(g)} + \text{CH}_4\text{(g)} \rightarrow \text{TiC(s)} + 4\text{HCl(g)} \quad (1000^\circ\text{C})$$

$$\text{BF}_3\text{(g)} + \text{NH}_3\text{(g)} \rightarrow \text{BN(s)} + 3\text{HF(g)} \quad (1100^\circ\text{C})$$

MOCVD:

$$(\text{CH}_3)_3\text{Ga(g)} + \text{AsH}_3\text{(g)} \rightarrow \text{GaAs(s)} + 3\text{CH}_4\text{(g)} \quad (650-750^\circ\text{C})$$

## CVD Reaction Types

**Disproportionation**

compounds involving elements with multiple valence states

$$2\text{AB(g)} \rightleftharpoons \text{A(s)} + \text{AB}_2\text{(g)}$$

ex:  $\text{Ge}_4\text{(g)} \rightarrow \text{Ge}_2\text{(g)} + \text{Ge film}$

use to deposit: Al, C, Ge, Si, III-V compounds, ...

**Reversible Transfer**

$$\text{As}_{2\text{(g)}} + \text{As}_{2\text{(g)}} + 6\text{GaCl}_{3\text{(g)}} + 3\text{H}_{2\text{(g)}} \rightleftharpoons 6\text{GaAs}_{\text{(s)}} + 6\text{HCl}_{\text{(g)}} \quad \text{Entropically driven}$$

As<sub>2</sub> + 3H<sub>2</sub> → 2AsH<sub>3</sub> + 3HCl + 3As

750 C →

← 850 C

use to deposit: GaInAs, AlGaAs, InP, FeSi<sub>2</sub>, ...

## CVD of Si

**CVD**

- *amorphous* silicon (low T, high w)
  - solar cells
  - thin film transistors (flat panel displays, X-ray detectors)
  - electrophotography (copy, FAX, scanner)
- *polycrystalline* silicon (intermediate T and w)
  - gate electrode in MOS devices (metal oxide semiconductor)
  - high resistance resistors contacts
- *epitaxial* silicon (high T, low w)
  - true substrate for microprocessor chips

## PE-CVD of Si

DISPLAYS **unaxis**

Displays Core Competencies

### PECVD Coating System

- High quality glass coating of Si-based materials by using the Plasma Box™ concept.
- Highly uniform and reliable parallel coating process (50 pcs per hour).
- Low particle contamination of coatings.
- Very low cost of ownership CoO (up-time: > 93%).

## CVD of Carbon

**'carbon' from the gas phase:**

- soot
- fullerenes
- nanotubes
- diamond
- polymers

[Homann, Angew. Chem. 110 (1998), 2572]

## CVD of Carbon

benzene / oxygen flame

- **fullerenes**  
unimolecular 'zipper' reaction at *high temperature* and *low concentrations*
- **polycyclic aromatic hydrocarbons (PAH)**  
growth by C<sub>2</sub>H<sub>2</sub> addition in *oxidative part of flame*
- **soot** (30-60 nm particles)  
bimolecular reaction at *low temperature* and *high concentrations*

[Homann, Angew. Chem. 110 (1998), 2572]

## Carbon Black

Furnace Process

- heating with natural gas
- evaporation of heavy oil
- pyrolysis of evaporated oil => hydrogen and carbon black

adjustment of

- porosity by quenching
- particle size by temperature
- particle aggregation by potassium salts

**degussa.** [courtesy H. Mühlenweg]

## Carbon Black

= 4 kg carbon black / tire

Degussa production reactor for carbon black

## CVD of Diamond

method:

- suppress graphite formation
- selective etching of generated graphite:

$$C_xR_y(\text{gas}) \Leftrightarrow xC_{\text{solid}} \downarrow + yR_{\text{gas}}$$

$$nC_{\text{graphite}} + mE \xrightarrow{k_{\text{graphite}}} C_nE_m(\text{gas})$$

$$nC_{\text{diamond}} + mE \xrightarrow{k_{\text{diamond}}} C_nE_m(\text{gas}) \uparrow$$

$\frac{k_{\text{graphite}}}{k_{\text{diamond}}} \approx 100$  for  $E = H$

**CVD:** diamond formation in the metastable region of the phase diagram by pyrolysis of organic compounds

[P. K. Bachmann, Adv. Mater. 2 (1990), 195, R. F. Davis (ed.), Diamond Films and Coatings, 1993]

## Diamond CVD

includes:

- thermal CVD
- hot filament CVD
- MW plasma CVD
- DC jet data
- RF torch CVD
- ECR-MW-plasma CVD
- DC glow discharge data
- flames

[Bachmann, Ber. Bunsenges. 95 (191), 1390]

## Diamond CVD

**hydrogen rich plasmas:**

- substrate is H-terminated
- H<sup>+</sup> stabilizes sp<sup>3</sup> bonded carbon
- H<sup>+</sup> etches selectively sp<sup>2</sup>
- H<sup>+</sup> suppresses PAH formation

**growth species:**

- CH<sub>3</sub><sup>•</sup> radical on (100) surfaces
- C<sub>2</sub>H<sub>2</sub> on (111) surfaces

+ high T<sub>gas</sub> (up to 3000°C) (growth species)  
 + 900°C < T<sub>substrate</sub> < 1200°C (crystallinity, graphitization)

[R. Davis (ed.), Diamond Films and Coatings, Noyes 1993, L. Ley, PHILIZ 32/5 (2001), 212]

## Diamond CVD (Ar plasma)

[D. Gruen et al. ANL]

## Diamond CVD

C<sub>60</sub> fragments into carbon dimers  
x 15+ fragments

Reconstructed diamond (100)

Carbon dimer insertion - Step 1

Carbon dimer insertion - Step 2

**hydrogen depleted plasmas:**

- C<sub>60</sub> or methane in Ar
- growth species: C<sub>2</sub>-molecules

[D. Gruen, Annu. Rev. Mater. Sci. 29 (1999), 211]

## Diamond CVD

microwave plasma:  
free standing, transparent diamond membranes

[Fraunhofer-IAF, Freiburg, courtesy of P. Koidl]

## C Nanotube CVD

selective growth on SiO<sub>2</sub> from xylene / ferrocene (10 μm/min)

[Wei, et al., Nature 416 (2002), 495]

## Carbon Nanotube CVD

in situ HRTEM images + DFT-calculations

=>

step edges on Ni particle are growth sites

[Helveg, et al., Nature 427 (2004), 426]

## Rational Precursor Selection

**Precursor Criteria**

- Thermally decompose to highly-reactive carbon species; *i.e.*, C, CH, CCl, C<sub>2</sub>
- Volatile, stable leaving groups upon decomposition; *i.e.*, HCl, H<sub>2</sub>O, CO<sub>2</sub>
- Water-soluble

**Example:**  
Sodium Dichloroacetate

Remnant carbon only!

**Design Criteria Summary**

M<sub>m</sub>X<sub>m</sub>C<sub>n</sub>(CO<sub>2</sub> or SO<sub>3</sub>)<sub>a</sub>H<sub>b</sub>X<sub>c</sub> where M = alkali metal ion, X = halide or OH

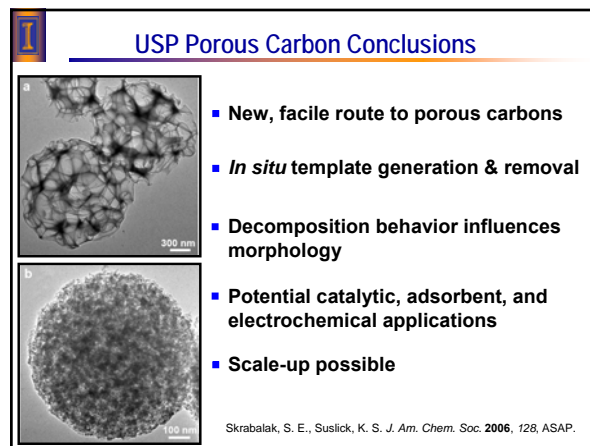
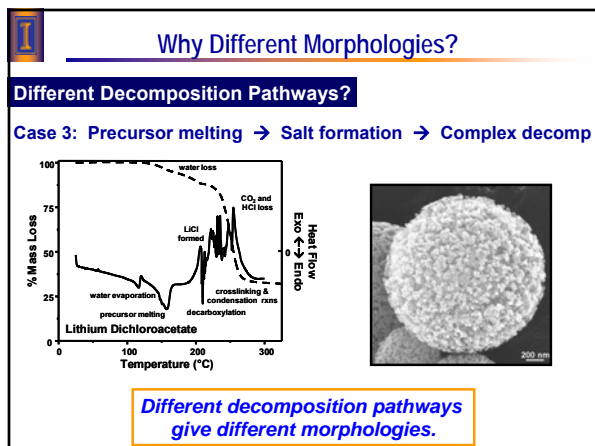
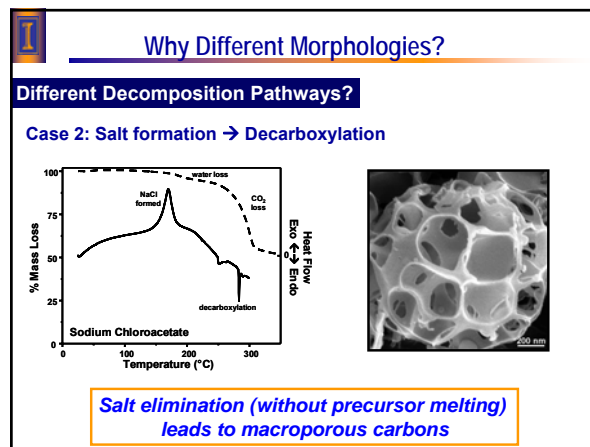
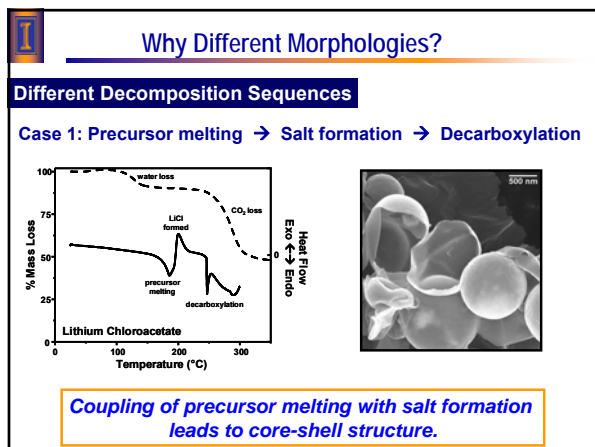
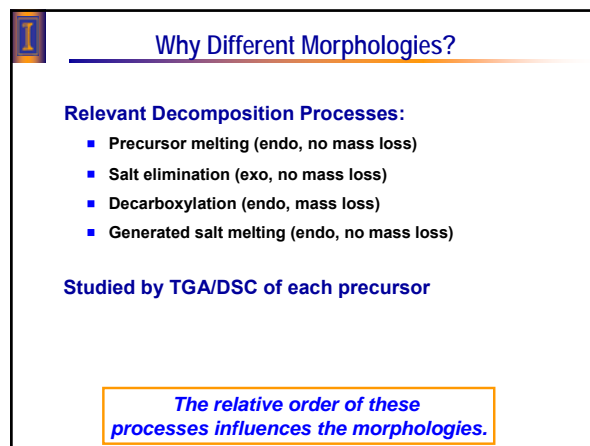
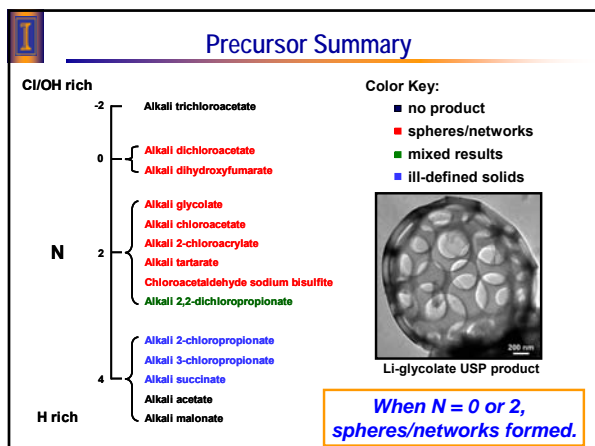
N = b - c where N = excess of H atoms

N = 0 when ideal precursor decomposition occurs

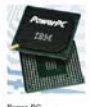
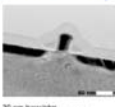
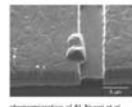
## Alkali-Metal Dichloroacetate (N=0)

- 1.5 M aq. solutions  
furnace temp: 700 °C  
flow: Ar(g) 2.0 ft<sup>3</sup>/hr
- Carbon/alkali-chloride composites formed
- XRD evidence for salt formation, otherwise amorphous

*Collection dissolves generated salt, leaving porous carbon.*

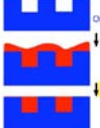


## Cu CVD

=> new materials and processes

	$T_m$ [°C]	$\rho$ [g/cm <sup>3</sup> ]	electro- migration	corrosion in air	CVD etching
Al	660	2.65	-	-	+
W	3400	5.7	++	-	+
Cu	1083	8.97	+	-	+
Ag	961	1.57	-	-	+
Au	1064	2.35	++	++	-



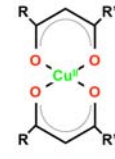
Oxide

Cu-CVD


CMP (nanoparticle slurries)

MRS Bulletin 8/1994

## Cu CVD



= CuX<sub>2</sub>



= CuXL

X = hfac  
 copper-di-(1,1,1,5,5,5-hexafluoro)-2,4 pentandionate  
 L = VTMS  
 copper-di-(1,1,1,5,5,5-hexafluoro)-2,4 pentandionate, vinyl-trimethylsilane

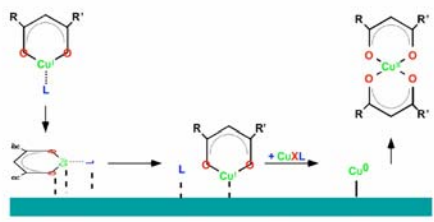
[Kodas & Hampden-Smith, The Chemistry of Metal CVD, VCH 1994; MRS Bulletin 8/1994]

## Cu CVD

CuX <sub>2</sub>	CuXL
<ul style="list-style-type: none"> <li>• solid =&gt; difficult delivery</li> <li>• low vapor pressure (10 Torr / 200°C)</li> <li>• low deposition temperature (400°C)</li> <li>• growth rates up to 200Å / min</li> <li>• impurities               <ul style="list-style-type: none"> <li>• reaction with water (oxide)</li> <li>• ligand decomposition (carbon)</li> </ul> </li> <li>• reduction source required</li> </ul>	<ul style="list-style-type: none"> <li>• liquid =&gt; simple, controllable delivery</li> <li>• high vapor pressure (0.3 Torr / 40°C)</li> <li>• low deposition temperature (150 - 200°C)</li> <li>• growth rates up to 1µm / min</li> <li>• high purity film with low specific resistance</li> <li>• thermally induced disproportionation</li> </ul>

[Kodas & Hampden-Smith, The Chemistry of Metal CVD, VCH 1994; MRS Bulletin 8/1994]

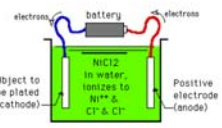
## Cu CVD



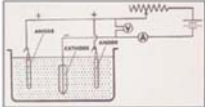
[Kodas & Hampden-Smith, The Chemistry of Metal CVD, VCH 1994; MRS Bulletin 8/1994]

## Electrodeposition (a.k.a. Electroplating)

- Metal ions (+) in solution deposited
- Au, Cu, Cr, Ni, permalloy (magnetic iron-nickel alloy)
- Plating uniformity depends on uniform current density over the plate
- Rough surfaces



## Electroplating



http://www.ganekin.com/books/chem/chem/electroplating-and-electroplating.htm

Typically to make thick layers of metal (>~1µm) on top of evaporated and patterned metals.

