#### **Part 2: "Practical topics" relating to** Chemical Vapor Deposition (CVD) systems

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# We will discuss:

- □ Related topics in thin films
- □ Low pressure CVD
- □ Thermal oxidation
- Plasma-enhanced CVD
- □ Atomic layer deposition (ALD)
- Metalorganic chemical vapor deposition (MOCVD)

# **1. Related topics in thin films**

#### Home-built thin film deposition systems in our laboratory



#### Roll-to-roll Process for Amorphous Silicon Thin Film Solar Cells (Tran et al.)



#### Cluster-tool System (www.appliedmaterials.com)



#### Terra G on-line Sputtering (www.appliedfilms.com)



#### **Evaporated Magnetic Tape (Sony)**

 T.Ito, J. Applied Physics, vol.9, no.7, April 2002

• Schematic of SAIT tape



#### **Our Sputtered Metal Films**





Thin film vs Thick film Practical definition

# **THIN FILM:THICKNESS** < 1μm</th>**THICK FILM:THICKNESS** > 1μm

#### **How to Make Thin Films?**



### **Thin Film Deposition System**



## **Properties that are required in Thin Films?**

- Good electrical and optical properties
- Excellent adhesion
- Low residual stress
- Low pin hole density
- Good mechanical strength
- Good chemical resistance
- Many others

## **Substrate**

- Provides the *template* for deposition and growth of films.
- Has effect on *interfacial structural*, mechanical and physical properties of films.
- Clean surface
- The first few atomic layers are involved.

#### **Surface Structure of Some Materials**



#### **Four Stages of Film Growth**



(M.Ohring, Materials Science of Thin Films, Academic Press, 2002)

#### **Structure Zones**

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- Zone 1 (T<sub>S</sub>/ T<sub>M</sub> <0.3) : columnar, consisting of inverted conelike units capped by domes separated by voided boundaries several nanometers wide. Limited adatom motion, "cauliflower-type).
- Zone 2 (0.3<T<sub>S</sub>/T<sub>M</sub><0.45) : columnar but tighter grain boundaries about 0.5 nm wide.
- Zone 3 (T<sub>S</sub>/ T<sub>M</sub> >0.5) : grains that grow in size by bulk diffusion.



#### Dependence of Grain Size on Temperature as a Deposition Parameter



2012, р. 314)

(c) 600 C and (d) 800 C. Jun-Ho Cha et al. J. Korean Physical Society, vol. 50., no. 3, (2011), 2280-2285.

#### Quick measurement of Resistance of Thin Films



#### **Problem 1**

An aluminium film of a thickness of 500 nm was coated on a glass substrate. The film has a sheet resistance of 15 Ω/square. Calculate resistivity of aluminium film.

$$R_{n} = \frac{P}{t} \Rightarrow P = R_{n}t = 15 \times 5 \times 10^{5}$$
$$P = 7.5 \times 10^{-4} \Omega - cm$$

## Do thin films have stress?

- The stress may be compressive (expanding in the direction parallel to the substrate) or tensile (contracting)
- The total stress ρ can be expressed in terms of external stress, intrinsic stress and thermal stress.

$$\sigma_{total} = \sigma_{external} + \sigma_{thermal} + \sigma_{intrinsic}$$

#### Do thin films have stress?

- Thermal stress p<sub>thermal</sub> is caused by the difference in coefficient of thermal expansion (CTE) of the film and the substrate.
- if the coefficient of thermal expansion (CTE) of thin film is greater than that of the substrate, we will have a compressive stress. On the other hand , a tensile stress will be obtained when CTE of thin film is smaller than that of the substrate.
- Compressive stress is released by buckling; whereas tensile stress is released by cracking.

Al film (1 μm thick), silicon (500 μm thick) CTE of Al : 23 x10-6 C<sup>-1</sup> CTE of silicon : 2 x10-6 C<sup>-1</sup>



## Problem 2

The coefficient of thermal expansion (CTE) of silicon at 50 C is 2.3x10<sup>-6</sup>/C. How much would a 10 mm chip increase in length if heated to 300 C?.

The increase in length if the 10 mm chip is heated to 300 C would be :  $\Delta L = (300 - 50)C \times 2.3 \times 10^{-6} C^{-1} \times 10mm$   $= 5.7 \times 10^{-3} mm$ 

# Step coverage

Conformal vs non-conformal



- Non-conformal (poor) step coverage is good for lift-off.
- ✓ Conformal (good) step coverage is good for electrical conduction.



#### Thin film filling issues:

(a) shows good metal filling of a via or contact hole in a dielectric layer

(b) silicon dioxide dielectric filling the space between metal lines, with poor filling leading to void formation

(c) poor filling of the bottom of a via hole with barrier or metal



SEM photo showing typical coverage and filling problems

## **Simple Unit Cells**



(a) Simple cubic



(b) Pedantically correct simple cubic









#### **Diamond Lattice Unit Cell**

Example 6-7-23 Calculate the density of bcc iron where a = 2.866 Angstroms.

From example 6-7-7, it is known that one unit cell of iron (Fe) has 2 atoms. Weight of each Fe atom is:  $\frac{55.85g/mol}{6.023 \times 10^{23} atoms/mol} = 0.9275 \times 10^{-22}g$ Weight of one unit cell of Fe is:  $0.9275 \times 10^{-22} \times 2 = 1.855 \times 10^{-22}g$ Volume of one unit cell of Fe is:  $a^{3} = (2.866 \times 10^{-8} cm)^{3} = 23.54 \times 10^{-24} cm^{3}$ And the density of Fe =  $\frac{1.855 \times 10^{-22}g}{23.54 \times 10^{-24} cm^{3}} = 7.88g/cm^{3}$ 

#### **Problem 3**

Calculate the density of bcc iron where a = 2.866 Angstroms .

it is known that one unit cell of iron (Fe) has 2 atoms .

Weight of each Fe atom is:  $\frac{55.85g/mol}{6.023 \times 10^{23} atoms/mol} = 0.9275 \times 10^{-22}g$ Weight of one unit cell of Fe is:  $0.9275 \times 10^{-22} \times 2 = 1.855 \times 10^{-22}g$ Volume of one unit cell of Fe is:  $a^{3} = (2.866 \times 10^{-8} cm)^{3} = 23.54 \times 10^{-24} cm^{3}$ And the density of Fe =  $\frac{1.855 \times 10^{-22}g}{23.54 \times 10^{-24} cm^{3}} = 7.88g/cm^{3}$ 



(c) bcc

Let's assume that atoms are rigid spheres having radii equal to <sup>1</sup>/<sub>2</sub> the distance between nearest neighbors. Calculate ratio of the volume occupied by the atoms to the total available volume of a simple cubic lattice.



Occupied volume = 
$$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left(\frac{a}{2}\right)^3 = \pi \frac{a^3}{6}$$
  
Total cell volume =  $a^3$   
Ratio =  $\frac{\pi a^3}{6a^3} = \frac{\pi}{6}$ 

$$a = 2r$$

Using the same conditions in example 1. Calculate ratio of the volume occupied by the atoms to the total available volume of body-centered cubic lattice







Use the conditions in example 1. Calculate ratio of the volume occupied by the atoms to the total available volume of a diamond structure.



Calculate ratio of the volume occupied by

the atoms to the total available volume of a face centered cubic lattice.

 $Diagonal 4r = \sqrt{2a} \Longrightarrow r = \frac{\sqrt{2a}}{4}$ Occupied volume =  $4\left(\frac{4}{3}\pi r^3\right) = \frac{\sqrt{2}}{6}\pi a^3$ Total volume =  $a^3$ Ratio =  $\frac{\sqrt{2}}{6}\pi$  $d_1 = r = \frac{\sqrt{2}a}{4}$ 

## What is Epitaxy?

Greek root: *epi* means "above" and *taxis* means "ordered"

Deposition of a layer on a substrate which matches the crystalline order of the substrate



- Epitaxy: Deposition and growth of monocrystalline structures/layers.
- Epitaxy types:
  - Homoepitaxy: Substrate & material are of same kind. (Si-Si)
  - Heteroepitaxy: Substrate & material are of different kinds. (Ga-As)







# The importance of lattice matching: lattice constant of the grown layer has to match with that of the substrate. Otherwise dislocations will occur. (Alan Doolittle)



- Trying to grow a layer of a different material on top of a substrate leads to unmatched lattice parameters.
- This will cause strained or relaxed growth and can lead to interfacial defects.
- Such deviations from normal would lead to changes in the electronic, optic, thermal and mechanical properties of the films.





Figure 2.8 A TEM comparable to the schematic of Figure 2.7 that shows the (111) planes of aluminum epitaxially overgrown on silicon and the (111) planes of the silicon substrate.

#### The importance of lattice matching: lattice constant of the grown layer has to match with that of the substrate. Otherwise dislocations will occur. (Alan Doolittle)

2.5



dislocations.

6.1

Their thermal expansion coefficients are also comparable.
# **Thin Film Deposition System**



# Why do we need vacuum in the thin film deposition systems?





#### **Mean Free Path**

In air at ambient temperature  $\lambda = \frac{6.6}{P(Pa)} = \frac{0.05}{P(Torr)} (mm)$ 



#### Problem 8

#### Calculate the mean speed of argon at 27 C.

 $k = Boltzmann \ cons \tan t = 1.38 \times 10^{-23} J / K$ 

m (mass of the arg on molecule) = 39.94



m= mass of the molecule

k = <u>Boltzmann's</u> constant = 1.38 x10-16 ergs/K T = temperature (K)



 $<sup>\</sup>overline{c} = \left[\frac{8 \text{ kT}}{\pi m}\right]^{1/2}$  T = 27 c = 300 k  $k = 1.38 \times 10^{-23} \text{ J/k} \text{ ; } \text{ m} = 39.94 \times \frac{1}{6.022 \times 10^{23} \times 10^{3}} \text{ (kg)}$   $\overline{c} = \left(\frac{8 \times 1.38 \times 10^{-23} \times 300}{\pi \times 39.94 \times 1.66 \times 10^{-27}}\right] \frac{(\text{J/kg})^{1/2}}{(\text{J/kg})^{1/2}}$   $\overline{c} = 3.98 \times 10^{2} \text{ (m/sec)} = 3.98 \times 10^{9} \text{ cm/sec}$ 

= 1,432.8 km/hr

JET 747 : 570 mph (920 km/hr)

### What a residual gas analyzer (RGA) can do?

- ✓ Base pressure finger prints
- ✓ Leak detection
- ✓ Virtual leaks/desorption
- ✓ Outgasing/ bakeout cycles
- ✓ Pumping performance
- ✓ Chamber contaminants

### Residual Gas Analyzer (RGA)



- A heated filament (iridium wire with a thorium oxide or yttrium oxide coating) emits electrons, which bombard the incoming gases, giving them an electrical charge.
- Electric field is used to manipulate the charged (or ionized) molecules.
- The ions formed on the anode are pulled away by the potential on the focus lens and formed into a beam (the focus lens is biased negatively with respect to the anode).
- Part of the beam is injected into the mass filter; the remaining portion strikes the exit lens and is neutralized, resulting in a current flow.



- · Measures the partial pressures of gases in a mixture.
- Consists of three parts : the ion source, the <u>quadrupole</u> mass filter and the ion detector.
- Gases are analyzed by ionizing some of the gas molecules in the ion source, separating the ions by mass (in the mass filter), and measuring the quantity of ions at each mass (in the detector)
- The sensor works only in a high-vacuum environment because the ions, once created must not collide with other gas molecules.
- The mass filter differentiates and rejects all ions except those of a specific mass-to-charge ratio for detection.



#### **Residual Gas Analysis**

- Interpretation and Cracking Patterns (continued):
- Using Cracking Patterns it is possible to identify all species
- NOTE: The cracking pattern is directly related to the energy of the electrons used i.e.



is characteristic of a species



#### RGA cracking patterns (from Hiden) N<sub>2</sub> vs CO

Cracking Patterns:

Cracking arises during ionisation when the high energy electrons used not only ionise species but fragment them. For CO:  ${}^{12}C^{16}O + e^{-} \rightarrow ({}^{12}C^{16}O)^{+}$  lonisation to give a peak at m/e= 28  ${}^{12}C^{16}O + e^{-} \rightarrow {}^{12}C + {}^{16}O^{+}$  Cracking to give a peak at m/e = 16  ${}^{12}C^{16}O + e^{-} \rightarrow {}^{12}C^{+} + {}^{16}O$  Cracking to give a peak at m/e= 12

This fragmentation can be used to differentiate isobaric species:

 $^{12}C^{16}O$  from  $^{14}N_2$  for example

 $^{14}\mathrm{N}_2$  has peaks at m/e 28 ( $^{14}\mathrm{N}_2^+$ ) and m/e 14 ( $^{14}\mathrm{N}^+$ ) from:

$^{14}$ N <sub>2</sub> + e <sup>-</sup> $\rightarrow$ ( <sup>14</sup> N <sub>2</sub> ) +	<b>Ionisation</b> to give a peak at m/e= 28
$^{14}\text{N}_2$ + e <sup>-</sup> $\rightarrow$ $^{14}$ N + $^{14}$ N +	Cracking to give a peak at m/e =14
$({}^{14}N_2)$ + + e <sup>-</sup> $\rightarrow$ ( ${}^{14}N_2$ )++	<b>Ionisation</b> to give a peak at m/e= 14

Disctinction between these two gases N<sub>2</sub> and CO is possible by analyzing their cracking patterns.



#### **Residual Gas Analysis**

- Interpretation (continued):
- Isotopic Abundance.

#### Many species exist as several naturally occurring isotopes:

Atom	Isotopes and relative abundances	
Carbon	$^{12}C - 100$ , $^{13}C - 1.1$	
Nitrogen	$^{14}N - 100$ , $^{15}N - 0.4$	
Oxygen	<sup>16</sup> O - 100, <sup>18</sup> O - 0.2	
Fluorine	Monoisotopic	
Chlorine	$^{35}Cl - 100, ^{37}Cl - 32.5$	
Bromine	$^{79}Br - 100, ^{81}Br - 98$	
Iodine	Monoisotopic	
Phosphorous	Monoisotopic	
Sulfur	$^{32}S - 100, ^{34}S - 4.4$	
Silicon	$^{28}$ Si - 100, $^{29}$ Si - 5.1, $^{30}$ Si - 3.4	

#### Isotope

✓ One of two or more atoms that have the same atomic number (the same number of protons) but a different number of neutrons. Carbon 12, the most common form of carbon, has six protons and six neutrons, whereas carbon 14 has six protons and eight neutrons.

✓ The nucleon number (protons + neutrons) is customarily written as a superscript preceding the chemical symbol for the element. For example, <sup>16</sup> O represents oxygen-16, which has 8 protons and 8 neutrons, while <sup>12</sup> C represents carbon-12, with 6 protons and 6 neutrons.

#### **Mass Flow Controller**



- Consisting of a mass flow meter, a controller and a valve.
- Located between the gas source and chamber.
- In sccm (standard cubic centimeter per minute) which is defined as a flux of one cm<sup>3</sup> of gas per minute at 0C (273K) and 1 atmosphere.



**Problem** 

Convert sccm (standard cubic centimeter per unit) to molecules/minute

#### Problem 9

# Convert sccm (standard cubic centimeter per unit) to molecules/minute

 $I \operatorname{sccm} = \frac{1}{22.4 \times 10^{3}} \frac{\operatorname{moles}}{\operatorname{minute}} = \frac{6.023 \times 10^{25}}{22.4 \times 10^{3}} \operatorname{molecules/minute}$   $= 0.267 \times 10^{20} \operatorname{molecules/minute}$ Another way of calculation :  $V = hRT \Rightarrow n = \frac{PV}{RT}$   $n = \frac{(1atm)(0.001L)}{(0.0824 \frac{Latm}{mol \cdot K})(273K)(1min)}$   $Isccm = n \times (6.023 \times 10^{23} \operatorname{molecules})$   $= 2.69 \times 10^{19} \operatorname{molecules/min}.$ 

A gram molecule of any material contains an Avogadro number of molecules

#### 6.02 x10<sup>23</sup> is Avogadro's number

# **Contamination Control**

# **Contamination Control**

- **80-90 cleaning steps** (256-Mb 0.25 μm DRAM process).
- There are 3 main categories of contamination: (1) Particles; (2) Films ; (3) Metallic (such as Fe, Cu) and Ionic (such as sodium , Na); and Other sources.
- > 50% of the yield losses are due to micro-contamination.
- As a rule of thumb, a particle that exceeds 20-50% of the minimum feature size could cause a fatal effect.



Source of contamination in IC fabrication

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(a)SEM of a particle on a wafer (uncovered); (b) SEM of the same particle covered by an overlying film. (from Stanley Wolf)



SEM photograph of a human hair on an IC surface, with metal lines having a minimum feature size of about 5  $\mu$ m (from Stanley Wolf).



SEM photographs of examples of particle types found on IC wafers: (a) extra material; (b) embedded particle; (c) missing pattern; (d) poly flake; (e) surface particle; (f) missing pattern (from Stanley Wolf)

### **Factors Contributing to Quality Products**



## The manufacturing environment is critical for product quality

#### Facility Parameters That Need To Be Controlled



> Temperature







>Air Cleanliness

Room Pressure



>Air movement

>Lighting







#### The environment comprises aspects such as:

- 1. Light
- Temperature 2.
- Humidity 3.
- Air movement 4.
- Microbial contamination 5.
- Particulate contamination 6.

#### Uncontrolled environments can lead to:

- Product degradation & contamination
- Loss of Product & Profit A



Factors Contributing to Quality Products

### **Sources of contamination**



 A typical smoker is expelling 10,000 to 20,000 0.03 µM particles 10 minutes after stopping. A non smoker generates less than 1,000.



#### Particle emission from human activity

(without cleanroom gowning isolation. Source: American Air Filter Res. Labs)

PEOPLE ACTIVITY	PARTICLES/MINUTE (0.3 microns and larger)
Motionless (Standing or Seated)	100,000
Walking about 2 mph	5,000,000
Walking about 3.5 mph	7,000,000
Walking about 5 mph	10,000,000
Horseplay	100,000,000



# **Clean Room Dos And Don'ts**

### Dos:

- Change gloves whenever they get dirty or torn
- Use a fresh pair of gloves whenever handling wafers
- Wipe down wafer handling areas with isopropanol
- Use clean room paper and dust-free ball point pens

### Don'ts:

- Touch your face or skin with gloves
- Touch building hardware, oily machinery, or wafer loading areas
- Lean on equipment
- Wear cosmetics, powders, or colognes
- Wear anything on fingers no rings and bracelets
- Use paper, pencils or markers that leave dust or lint

# **Modular Cleanrooms**

- Reducing design, engineering, construction time, therefore reducing costs.
- Can be expanded by adding other modules.
- Can be taken down and moved to other facilities.
- Air handling and filtration equipment are built with the modular room ceiling.
- ✓ Hookups for electrical and plumbing are part of the design.
- ✓ Circulating and non-recirculating type.



# We will discuss:

- □ Related topics in thin films
- Low pressure CVD
- □ Thermal oxidation
- Plasma-enhanced CVD
- □ Atomic layer deposition (ALD)
- Metalorganic chemical vapor deposition (MOCVD)

## **Chemical Vapor Depositions**







# **Gases in Semiconductors**

- Gas is one of the four states of matter : solid, liquid, plasma and gas.
- There are two types : bulk gases (oxygen, hydrogen,helium, argon..) and specialty gases (also known as process gases).
- High purity : 99.99999% for bulk gases and 99.99% for specialty gases.
- Many process gases are toxic (e.g. arsine, phosphine), corrosive (e.g. hydrogen chloride, chlorine), reactive (e.g. tungsten hexafluoride) and pyrophoric (e.g. silane).

Gases play a vital role in many of the thin film processes. In this module we shall look into the properties of gases some of which can be applied in the later modules.

### **Masses and Numbers of Atoms**

Let us pick up hydrogen as an example Mass = 1.66x 10<sup>-24</sup> g

There are  $6.02 \times 10^{23}$  atoms in 1 g of atomic hydrogen (1 gram molecule)

A gram molecule is a quantity of material corresponding to the molecular weight in g. The molecular weight of an element is the ratio of the mass of one atom of that element to that of a hydrogen atom .

6.02 x10<sup>23</sup> is Avogadro's number

A gram molecule of any material contains an Avogadro number of molecules

### **Mean Speed**

#### Calculate the mean speed of argon at 27 C.

 $k = Boltzmann \ cons \tan t = 1.38 \times 10^{-23} J / K$ 

m (mass of the arg on molecule) = 39.94



m= mass of the molecule

k = <u>Boltzmann's</u> constant = 1.38 x10-16 ergs/K T = temperature (K)



JET 747 : 570 mph (920 km/hr)

$$\overline{c} = \left[\frac{8kT}{Tm}\right]^{\frac{1}{2}}$$

$$T = \frac{27C}{300k} = \frac{300k}{1.38 \times 10^{-23} J/k} ; m = \frac{39.94 \times 1}{6.022 \times 10^{23} \times 10^{3}} (kg)$$

$$\Rightarrow \overline{c} = \left(\frac{8 \times 1.38 \times 10^{-23} \times 300}{\pi \times 39.94 \times 1.66 \times 10^{-27}}\right) \left(\frac{J/kg}{2}\right)^{\frac{1}{2}}$$

$$\overline{c} = 3.98 \times 10^{2} (m/sec) = 3.98 \times 10^{9} cm/sec$$

0

= 1,432.8 km/hr

# Type of Gas Flow

#### 107 10<sup>6</sup> SYSTEM DIMENSIONS (cm) 105 VISCOUS 10<sup>4</sup> 10<sup>3</sup> 10<sup>2</sup> TRANSTION 10 1 101 102 MOLECULAR 103 104 105 $10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 10 10^{-2} 10^{-3}$

PRESSURE (Torr)

#### Types of air flow through cylinder tube having a diameter of 50 cm at RT

$\lambda/d$ (d=50cm)	Pressure (Torr.)	λ(cm)	Gas flow
10	10-5	500	molecular
0.1	$10^{-3}$ (0.01< $\lambda$ <d)< td=""><td>5</td><td>transition</td></d)<>	5	transition
0.01	10 <sup>-2</sup>	0.5	transition
0.001	$10^{-1}$ ( $\lambda < 0.01d$ )	0.05	viscous
0.0001	1	0.005	viscous

# **Type of Gas Flow**





© Molecular flow

# **Pressure Units**

Low vacuum : 10<sup>5</sup> Pa (750 torr) – 3x10<sup>3</sup> Pa (25) torr) Medium vacuum : 25 torr- 7.5x10<sup>-4</sup> torr High vacuum :  $7x10^{-4}$  torr – 7.5x10<sup>-7</sup> torr Very high vacuum : 7.5x10<sup>-7</sup> torr - 7.5x10<sup>-10</sup> torr Ultra high vacuum : 7.5x10<sup>-10</sup> torr – 7.5x10<sup>-13</sup> torr

# **Pressure Units**

1 pascal (Pa) =  $7.5 \times 10^{-3}$  torr = 7.5 mtorr Hg 1 torr = 133.3 Pa 1 bar =  $1 \times 10^5$  Pa = 750 torr 1 atm = 1.013 bar = 760 torr 1 atm = 14.7 psi

One atmosphere (at sea level, 0C) is a pressure to be able to balance a column of mercury (Hg) of 760 mm in height.

# **Example 10**

Therefore 
$$\frac{1 Torr = \frac{1}{750} bar = 1.33 \times 10^{-3} bar}{Or \ 1 Torr = 1.33 \ mbar}$$

What is the corresponding units of 1 Torr in (a) Pa, (b) in bar $?_{\sim}$ 

# **Mean Free Path**

- The mean free path is the average distance traveled by a gas atom between collision with other gas atoms.
- Mean free path decreases at higher pressures.
- A large number of gas particles in a gas at a given pressure causes a large number of collisions.
- Procedure to calculate the mean free path : the gas particles are treated as hard spheres and the collision occurs whenever the two gas molecules are within a distance from each other.



Collision frequency 
$$= \frac{c}{\lambda}$$
  
In air at ambient temperatur  $e$   
 $\lambda = \frac{6.6}{P(Pa)} = \frac{0.05}{P(Torr)} (mm)$ 

# **Example 11**

Gas atom has a diameter of 3A. The collision will take place if the gas atom lies within 3A from the center of the next gas atom. In other words, the collision area has a radius of 3 A.



Therefore, the collision area is :  $Area = \pi \times 3^2 = 3.14 \times 9A = 28.26 \times (10^{-8})^2 \ cm^2$   $= 28.26 \times 10^{-16} \ cm^2 = 2.83 \times 10^{-15} \ cm^2$ Since 760 Torr has  $6.02 \times 10^{23}$  molecules at 22.4 liters,  $1 \ Torr = \frac{6.02 \times 10^{23}}{760} = 7.92 \times 10^{20} \ molecules \ at 22.4 \ liters$  $1 \ milliTorr = 7.92 \times 10^{17} \ molecules / 22.4 \ liters$ 

(Hint: a gram of molecule of gas at standard 0C and standard pressure (1 atmosphere) contains 6.02x  $10^{23}$  molecules (Avogadro constant) and occupies a volume of 22.4 liters. The gas particles are treated as hard spheres and the collision occurs whenever the two gas molecules are within a distance from each other where d is the particle diameter. The cross section  $\sigma=\pi d2$ ; the mean free path  $\lambda = 1/n\sigma$ .)

An ideal atom has a diameter of 3A. What is the mean free path at 1 milliTorr and at 0 C?.



 $1milliTorr = 7.92 \times 10^{17} molecules / 22.4 liters$ 

Number of molecules/1 mL is  $\frac{7.92 \times 10^{17}}{22.4 \times 10^{3}} = 3.54 \times 10^{13} \text{ molecules}$ Therefore , 1 molecule will occupy a volume of  $\frac{1}{3.54 \times 10^{13}} = 2.857 \times 10^{-14} \text{ cm}^{3}$ The mean free path is volume/area, which is  $= \frac{2.857 \times 10^{-14}}{2.83 \times 10^{-15}} = 10 \text{ cm}$ The mean free path of the atom at 1 milliTorr, 0 C is 10 cm.

The other approach of calculating the mean free path can be described as follows:

$$\lambda = \frac{1}{n\sigma}$$
  
The mean free path =  $\frac{1}{3.54 \times 10^{13} \text{ molecules / } \text{cm}^3 \times (2.83 \times 10^{-15}) \text{cm}^2}$   
= 10 cm

# **The Ideal Gas Law**

#### pV=nRT

#### pV=NkT

Where p=pressure

V=Volume

n=the amount of substance of the gas , mol. or <u>kmol</u>. N=Number of particles under consideration

T=Temperature

k=Boltzmann's constant

R=Gas constant

#### A mixture of several gases

If  $n_A$  of a gas A is injected into a volume V, then  $p_A = n_A \left(\frac{RT}{V}\right)$ If  $n_B$  of a gas B is injected into a volume V, then  $p_B = n_B \left(\frac{RT}{V}\right)$ 

The total pressure p (according to Dalton's law) is  $p = p_A + p_B$ 

# Example 12

A 22.4 liters vessel contains 2 mol. H<sub>2</sub> and 1 mol N<sub>2</sub> at 273K. What are the partial pressure of the components in the vessel?

$$P_{H_2} = n_{H_2} \frac{RT}{V} = \frac{2 \text{ mole} \times 83.14 \text{ mbarLmol}^{-1} \text{K}^{-1} \times 273 \text{K}}{22.4 \text{L}}$$

$$P_{H_2} = 2026 \ mbar$$
  
 $P_{N_2} = n_{N_2} \frac{RT}{V} = 1013 \ mbar$   
Total P= P\_{H2} + P\_{N2} = 3039 \ mbar.

### **Problem 13**

150 g of  $CO_2$  occupies a volume of 60 L at a pressure of 1 atm.

(a) What is the temperature of the gas?; (b) If the volume is increased to 100 L, what will be the pressure?.
(Hint: the ideal gas law pV=nRT, where R is the gas constant)

a) 
$$PV = nRT \Rightarrow T = \frac{PV}{nR}$$
  

$$= \frac{1atm \times 60L}{3.4 \text{ mol} \times 0.0821 \text{ L} \cdot atm.\text{mol}^{-1} \text{ K}^{-1}} \approx 215 \text{ K}$$
Where  $n = \# \text{ Mole of } CO_2 \text{ GAS}$   

$$= \frac{150g}{44g} = 3.4 \text{ mol}$$
 $R = 0.0821 \text{ L} \cdot afm \cdot \text{mol}^{-1} \text{ K}^{-1}$   

$$= 83.14 \text{ mbar L mol}^{-1} \text{ K}^{-1}$$
b)  $P_2 = \frac{P_1V_1}{V_2} = \frac{1atm \times 60L}{100 \text{ L}} = 0.6 \text{ atm}$ 

# **Gases Safety**


## Cylinder Components (Air Products & Chemicals)



# Cylinder Identification And Markings



- Specification number consists of three sections.
- DOT- signifies that the cylinder conforms to Department of Transportation (DOT) specification.
- · 3AA specifies type and material of cylinder construction.
- 2265 indicates service pressure for which the cylinder is designed at 70°F.



Cylinder serial number (Matheson Tri-Gas number)

Original inspector's insignia



Date of initial hydrostatic testing

# **M2-10: Gas Detection and Monitoring**

Safety hazards of some commonly used gases (TLV-TWA :threshold limit values ,long term exposure; TLV-STEL: short term exposure; IDLH: immediately dangerous to life)

#### Threshold Limit Values (TLV's)

- <u>Time Weighted Average</u> (TWA)
  - Average 8 hour exposure, 5 days a week
- <u>Short Term Exposure Limit</u> (STEL)
  15 minutes, 4 times a day
- Immediately Dangerous to Life and Health
  (IDLH)

Chemical name	Chemical symbol	Combustible/ Explosive	Health hazard class	TLV- TWA (ppm)	TLV- STEL (ppm)	IDHL (ppm)
Argon	Ar		0			
Diborane	B <sub>2</sub> H <sub>6</sub>		3	0.1	0.3	40
Dichlorosilane	SiH <sub>2</sub> Cl <sub>2</sub>		3	5		100
Helium	He		0			
Hydrogen	H <sub>2</sub>	X	0			
Nitrogen	N <sub>2</sub>		0			
Nitrogen trifluoride	NF <sub>3</sub>		3	10	15	2000
Nitrous oxide	N <sub>2</sub> O	X	2	50		
Oxygen	O <sub>2</sub>	X	0	none	none	none
Phosphine	PH <sub>3</sub>	X	4	0.3	1	200
Silane	SiH <sub>4</sub>	X	4	5		
Tungsten hexafluoride	WF <sub>6</sub>		3	3	6	
Tetraoetho- Silicate (TEOS)	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> SiO <sub>4</sub>	X	2	10		1000

## **Compressed Gas Cylinders**

Compressed Gas Any material or mixture with an in-container pressure exceeding 40 psia at 70°F, or a pressure exceeding 104 psia at 130°F, or any liquid flammable material having a vapor pressure exceeding 40 psia at 100°F [sec. 173.300(a)].

- Come in many shapes and sizes
- Commonly constructed of Carbon Steel or Aluminum
- Standard size 1A cylinder pressurized to 2200 psig holds approx. 225 ft<sup>3</sup> of gas in an internal volume of 1 <sup>1</sup>/<sub>2</sub> ft<sup>3</sup>!



## **Cylinder storage**





- Double restrain cylinders with non-combustible material (i.e., chain)
- Label <u>Full</u> versus <u>Empty</u>
- Signs for hazardous gases
- Keep away from traffic areas
- Store in fire resistant, well ventilated, dry areas



- Keep away from flames or sparks
- Keep caps on when not in use
- Store in areas <125°F
- Keep oxidizers 20 ft. from flammables
- Corrosives should be stored less than
  6 months



### **Single Stage Regulator**



#### **Regulator Operation**

- Always ensure the P/A knob is backed off counterclockwise to ensure there is no load on the regulator load spring – prior to opening the cyl valve!
- Never open a cylinder valve all the way. 1 ½ to 2 turns is usually sufficient
- Always stand with the cylinder valve between you and the regulator when opening the cylinder valve and/or adjusting pressure on the regulator
- Do not use the temporary shut-off valve to turn off gas flow if the shut-off duration will be longer than 20 min.
- Use cross or T-purge assemblies if regulators are to be used for toxic or corrosive gases!



Reduces the inlet supply pressure in "one step", from the inlet supply pressure to the final outlet pressure



### **Two-stage Regulator**





Reduces the pressure in "*two steps*" from a high pressure inlet source, to the final outlet working pressure  Delivery "set pressure" remains constant as the inlet supply pressure decays

 Recommended for continuous use applications, such as carrier gas supply to GC's or other analytical instruments, where it is critical that a constant delivery set pressure be maintained

### **Regulator Operation**

- Always ensure the P/A knob is backed off counterclockwise to ensure there is no load on the regulator load spring – prior to opening the cyl valve!
- Never open a cylinder valve all the way. 1 ½ to 2 turns is usually sufficient
- Always stand with the cylinder valve between you and the regulator when opening the cylinder valve and/or adjusting pressure on the regulator
- Do not use the temporary shut-off valve to turn off gas flow if the shut-off duration will be longer than 20 min.
- Use cross or T-purge assemblies if regulators are to be used for toxic or corrosive gases!





# **Installing a regulator**

- **\*** Make sure the cylinder is properly secured and you have the correct regulator.
- **\*** Remove the cylinder valve cap. Place it somewhere nearby.
- **Check to see if Teflon or washer is required.**
- **Regulator outlet A is shut. Screw clockwise. Not overtight.**
- **\*** The regulator control valve B is shut. Screw is counterclockwise.
- Screw the regulator by hand until it is almost finger tight.
- **\*** Further tighting with a wrench.





# Installing a regulator (cont'd)

- In case of corrosive or reactive gases, purge the regulator (Monel, SS) with an inert dry gas.
- ✤ In case of acetylene, alloys containing copper or silver can cause explosion.
- Open the tank valve slowly (counterclockwise). Watch the tank pressure on the regulator C
- Slowly turn the regulator valve B until the regulator pressure D is at the desired level.
- Open the regulator outlet valve A.
- Check the system for leaks using Snoop (preferred, no residue) or some soapy water.





### **Disconnecting a regulator**

- Shut the tank valve on the gas cylinder.
- Slowly open the outlet valve A
- **\*** Watch the pressure gauges C and D drop to zero.
- **\*** Open the regulator control valve B (clockwise) to ensure all pressure has been released.
- ✤ In case of a corrosive gas, purge the system with a dry inert gas.
- **Solution** Disconnect the regulator. Replace the protective cylinder cap.
- ✤ In case of a corrosive gas, purge it again with dry air or nitrogen
- If your cylinder is empty, it must be properly labeled "MT" and then returned to the distributor.





## Things Not To Do!

- <u>Never</u> roll a cylinder to move it.
- <u>Never</u> carry a cylinder by the valve.
- <u>Never</u> leave a cylinder unsecured.
- <u>Never</u> force improper attachments on to the wrong cylinder.
- <u>Never</u> grease or oil the regulator, valve or fittings of an oxygen cylinder.
- <u>Never</u> refill a cylinder.
- <u>Never</u> attempt to mix gases in a cylinder.





#### **Emergency Plan**

- Every location where compressed gases are handled should have a written emergency plan covering steps to be taken in the event of an accidental release of gas
- This plan should consider the nature of the gases being handled, that is their chemical and physical properties

# At a minimum, the plan should specify the following :

- Alarm System & Evacuation Procedure
- Response Personnel
- Emergency Equipment
- Containment or disposal methods

## **Cylinder handling and transportation**

#### Wall Supported





Cylinder nesting (AIGA)

- Upon receipt, visually inspect the cylinders for obvious defects such as dents, large amounts of rust and missing or loose safety caps.
- Cylinders shouldn't be accepted unless identified with the appropriate labeling, and all them agree with one another!
- Use a cylinder cart and secure the cylinders with a chain when moving.
- Don't use the protective valve caps for moving or lifting the cylinders.





- Don't drop a cylinder, permit them to strike each other violently or be handled roughly. Unless cylinders are secured, regulators should be
- removed, valves closed and protective caps in place before cylinders are moved.
- Rolling cylinders in a vertical position on the bottom edge is to be avoided as much as possible. Gas cylinders must never be dragged or rolled in the horizontal position.



# Handling CVD Gases

Gases : toxic, flammable, orrosive explosive, carcinogenic or a combination of these. These gases can create harm operators, corrode equipment, decompose pump fluids and etch gas lines.

Storage : Keep gas cylinders <u>at a minimum number</u> with properly identified tags . The storage area should be <u>dry, cool, fire-proof and highly ventilated</u>. All metal in the enclosure would be grounded to avoid static arcing and sparking. Gas cylinders should be kept in a straight position and strapped tightly.

Disposal : Toxic gases should be trapped and neutralized before sending to the exhaust stack.

Some of the examples are : (i) **arsine** can be oxidized with sodium hypobromite solution ; (ii) **phosphine** is neutralized with sodium hypochlorite solution; (iii) **hydrogen sulfide** can be treated in ammonia solution and (iv) **diborane** can be hydrolysed by water.

### **Safety Procedures for Hazardous Gases**

- Conduct formal safety reviews and inspections/ implement safety training programs.
- **Double containment for gas lines**, where appropriate.
- Good ventilation for gas cylinders and gas lines
- Leak checking prior to use
- Use check valves
- Pressure and vacuum-cycle purge on process stations
- Automatic shutoff valves
- Backup power for fire protection and exhaust systems
- Install gas detection /alarm system
- Steel gas cabinets with locks and emergency shutoff valves.

# Hydrogen ambient

- > The reaction of hydrogen with air poses safety concerns.
- ➢ "Forming gas", a mixture of 5% hydrogen in nitrogen.
- Hydrogen is flammable when it is mixed with air in concentrations of 4-75% by volume.
- ➢ Pre-purging. Reduced oxygen level = (20%) x (0.5)<sup>N</sup>, where N= number of gas changes.
- > Post-purging.
- Safety interlocks to guard against an unexpected opening of the chamber.
- $\succ$  A "burn-box" near the gas exit

# Vacuum pumps



#### A base line pumpdown curve for a typical system



Rate Limiting Pumping Process (calibration curve)

(M. Ohring, Materials Science of Thin Films, 2<sup>nd</sup> edition, Academic Press, 2002)

# A pumpdown curve (black dashed line) for a hypothetical situation where the initial portion is different from the baseline



Since it happens at the portion where the bulk gas is removed , the causes could be : Type of the vent gas had been inadvertently changed; The rough vacuum gauge has a problem (may be an offset zero) -Roughing pump is loosing speed.

#### A pumpdown curve (black dashed line) for a hypothetical situation where the base pressure is elevated.





(deviation at elevated base pressure) Leak Increased permeation Excessive backstreaming from the pump.

#### **Vacuum Pumps**

#### **Pressure Ranges of Vacuum Pumps**



### **Mechanical Pump/ Two Stage Rotary Vane**

#### **Operation mechanism**



- Low ultimate pressure
- Second stage can be used to degas the oil that is admitted to the inlet stage.
- Gas load is less
- The compression ratio needs not to be too high as in a single stage.

### **Roots Pump**

#### **Operation mechanism**



- Has two counter –rotating 8 shaped –lobes mounted on parallel shafts that rotate in opposite directions.
- ✓ 3,000-5,000 rpm.
- Air enters from the inlet and trapped by the lower impeller.
- The volume is discharged in the third and fourth positions to the outlet
- Advantages : high capacity at low cost, reduction of oil contamination

### **Turbomolecular Pump**









- High rotational speed requires high reliability of the rotor bearings and the rotor integrity.
- Hydrogen does backstreaming.
- > Water cooling
- > High initial cost .
- One of the concerns with the turbomolecular pumps is that any particles getting into pump will damage the blades; therefore care must be taken during the maintenance of the pump.

### Cryopump





- First stage (surface at 65K, first pumping zone) : condensing water and other Type I gases (condensing at above 80K).
- Second stage (surface at 12K, cryocondensing

**ZONE):** entrapping nitrogen, oxygen, argon and other Type II gases (condensing at below 80K).

#### ✓ Third stage (cryosorbing)

**ZONE)**: immobilizing hydrogen, Helium, neon and Type III gases (non condensable gases).

*Cryocondensation* refers to the condensation of vapor on a cold surface; while *cryosorption* involves the absorption of a gas on a cold surface (hydrogen, helium, neon)

### **A Loadlock System**



## **Pump Down Calculation**

A chamber of 20 liters is pumped down using a double vane rotary pump having a pumping speed of 10 liters/sec. Calculate the time to reduce the chamber pressure from atmospheric pressure down to 0.2 millibar.

$$t = 2.3 \times \frac{V}{S} \times \log \frac{P_1}{P_2}$$
$$= 2.3 \times \left(\frac{20 L}{10 Ls^{-1}}\right) \times \log \left(\frac{760 Torr}{0.15 Torr}\right)$$
$$t = 17 \text{ sec}.$$

The pumping –down time t (in sec) is calculated, using the equation below, where V= volume (liters) , S= inlet pumping speed (liters/sec), P<sub>1</sub> = start pressure (millibar, Torr, Pasdcal) and P<sub>2</sub> = pumping down pressure (millibar, Torr, Pascal) 1 pascal (Pa) =  $7.5 \times 10^{-3}$  torr = 7.5 mtorr Hg 1 torr = 133.3 Pa 1 bar =  $1 \times 10^5$  Pa = 750 torr 1 atm = 1.013 bar = 760 torr 1 atm = 14.7 psi

One atmosphere (at sea level, 0C) is a pressure to be able to balance a column of mercury (Hg) of 760 mm in height.

# Low pressure Chemical Vapor Deposition (LPCVD)

# What is Thermal CVD?

- Thermal chemical vapor deposition (or CVD) has played an important in the semiconductor in providing high quality silicon oxide, silicon nitride, phosphosilicate, borophosphosilicate and polycrystalline silicon.
- Thermal Chemical Vapor Deposition (CVD) is the process of chemically reacting a volatile compound of a material by means of heat to be deposited with other gases to produce a solid film on a substrate.

# **Low Pressure CVD**

- Surface- reaction-rate- limited.
- Highly sensitive to temperature (Example : for LPCVD polysilicon, a deposition rate change of 2-2.5% for every degree change)
- As compared with APCVD, LPCVD has less gas phase reactions, resulting in less contamination.
- Is used to deposit polysilicon,  $Si_3N_4$ ,  $SiO_2$ , PSG, BSG, BPSG and tungsten.
- There are less concentrations of reactants at the outlet end than at the inlet end of the reactor (gas depletion effect).
- Horizontal tube LPCVD and vertical tube LPCVD, whereas the former is the most widely used in IC industry.
- The wafers are heated by resistive heating coils surrounding the reactor tube. The gases come in at one end and the reaction by-products are pumped out at the other end.

$$G = \frac{C_T k_s Y}{N_1} \quad \text{when } k_s \ll h_g$$

- $h_{\mbox{\tiny g}}$  : gas phase mass transfer coefficient
- k<sub>s</sub>: surface reaction rate constant
- N1 : number of atoms incorporated into a unit volume of the film.

Y: mole fraction of the reactant species when the reactant gas is diluted in an inert gas

C<sub>T</sub>: total number of molecules/cm<sup>3</sup>

#### **Fundamental transport steps in CVD process**

Main gas flow region





 $(CH_3)_3Ga + NH_3 \rightarrow GaN + 3CH4$ 

**Precursors** are intermediate reactions which form a gas species that does not contain the original gas components.

 $Si_2H_6$ ----- $\rightarrow$  2Si +3 H<sub>2</sub> (by product)

SiH<sub>4</sub>------ SiH<sub>2</sub> (silicon hydride, precursors)+ H<sub>2</sub>

(pyrolysis)

 $SiH_4 + SiH_2 - ---- \rightarrow Si_2H_6$  (intermediate reaction)

(final reaction)

- **Boundary layer** is a region where gas flow increases from the zero/ near zero gas flow velocity at the wafer surface to a gas flow farther from the surface.
- For a narrow boundary layer, the gas flow is virtually zero, giving a stagnant layer.

#### Hot- wall vs. Cold-wall Reactors

- T<sub>w</sub> = Wall temperature
- $T_s$  = Substrate temperature,

```
When T_w = T_s: Hot-wall CVD reactor
```

-Uniform reaction (advantage)

-Film forming reactions become pronounced on the chamber walls, causing flaking-off (disadvantage)

When  $T_w < T_s$ : Cold-wall CVD reactor

-Less deposition of materials on the wall (advantage)

-:Less uniform films (disadvantage)

#### Why most of the LPCVD use hot wall reactors?

#### Advantages:

- ✓ Uniform temperature distribution.
- Reduced convection effect.
- ✓ Operatedat 1-2 Torr; therefore poor thermal conduction.

#### Disadvantages:

- ✓ Particles can be deposited on the wall and flaked off during deposition.
- ✓ Materials previously deposited on the hot wall could deposit again on the wafer.

# **APCVD Reactors**

- The first CVD reactor to be used in the microelectronics industry.
- Mass transport limited rate.
- Simple design and high deposition rate.
- Continuous processing either on a moving plate or on the conveyor.



$$G = \frac{C_T h_g Y}{N_1} \quad \text{when } h_g << k_s$$

- $h_{\scriptscriptstyle \alpha}\,$  : gas phase mass transfer coefficient
- k. : surface reaction rate constant

N1 : number of atoms incorporated into a unit volume of the film.

Y: mole fraction of the reactant species when the reactant gas is diluted in an inert gas

C<sub>T</sub>: total number of molecules/cm<sup>3</sup>

# **APCVD Reactors**

- Poor step coverage
- Problems with material deposits on the nozzles.
- Reactor geometry design and gas flow pattern are critical.
- Gases are injected from cooled, nitrogen shrouded nozzles and pass through narrow slots of an injector head. The gas mixing takes place millimeters above the wafer (substrate) surface.
- The exhausted gases are vented to a scrubber by high nitrogen flow to avoid recirculation and gas phase reactions (nitrogen curtains)



# Schematic of a LPCVD System

Molecular Physics Lab., Institut Ruder Boskovic


## **Silicon dioxide**

 SiH<sub>4</sub> + O<sub>2</sub> Reactions (silane oxidation): temperatures = 240-550 C, 5-30 nm/minute.

$$SiH_{4} + O_{2} \rightarrow SiO_{2} + 2H_{2}$$

$$Or \qquad SiH_{4} + 2O_{2} \rightarrow SiO_{2} + 2H_{2}O$$

- SiH<sub>4</sub> + N<sub>2</sub>O Reactions : temperatures = 800-860 C, 5 nm/minute.  $SiH_4 + 2N_2O \rightarrow SiQ_2 + 2H_2 + 2N_2$
- SiH<sub>2</sub>Cl<sub>2</sub>+ N<sub>2</sub> Reactions (oxidation of chlorosilanes): temperatures= 900-915 C, 0.9 nm/min.
- Si<sub>2</sub>Cl<sub>6</sub> + N<sub>2</sub>O Reactions : temperatures = 550-850C, higher deposition rate than with SiH<sub>4</sub> gas.
- Reactions based on Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> Temperature range = 675-695 C, 30 nm/min.

# Nitrides and Oxynitrides

- Final passivation layer or a protection layer
- Mask for the selective oxidation of silicon
- Dielectric materials in the stacked of oxide-nitride-oxide in DRAM capacitors
- Sidewall spacer
- CMP stop layer in shallow trench isolation processes and
- An etch stop layer  $3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$

# About BSG, PSG and BPSG

- Wide applications in silicon devices
- BSG and PSG can be prepared by either hydride or TEOS based chemistry using APCVD or LPCVD.
- The phosphorous content (2-8 wt.%) in PSG decreases with increasing temperature while boron content (2-7 wt%) increases with increasing temperature.
- Borophosphosilicate (BPSG) is excellent insulator and allows smoothing of the device topography.
- Content of B and P in BPSG is 3-5 wt.% each in the ternary compound.
- BPSG can be prepared from the hydrides using APCVD or from organometallics using LPCVD.



- Polysilicon film is composed of small crystal regions with a sheet resistance of 10-35  $\Omega$ -cm.
- Polysilicon can be formed by thermally decomposing silane in the temperature range of 550-650 V (LPCVD system)

 $SiH_4$  (gas) --> Si (solid) +  $2H_2$  (gas)

n-type and p-type polysilicon can be made by doping the material with for example phosphine (PH<sub>3</sub>) and arsine (AsH<sub>3</sub>), respectively. Implantation/annealing can also be used for doping.

# **CVD in Making Tungsten (W)**

- Applications in the interconnections, contact hole and via plug filling in IC technologies, along with other refractory metals such as Ti, Mo, Ta.
- High thermal stability
- Excellent conformal step coverage
- Having a coefficient of thermal expansion (CTE) being close to that of silicon, i.e. 2 x10<sup>-6</sup>/degree C.
- Less electromigration (as compared with aluminium).
- High corrosion resistance.
- Poor adhesion to oxides and nitrides (disadvantage)
- High resistivity (disadvantage)



Can be deposited either from WF<sub>6</sub> or WCl<sub>6</sub> (WF<sub>6</sub> is preferable, at a higher cost!). →
 WF<sub>6</sub> (gas) + 3 Si -----→ 2W (solid) + 3SiF<sub>4</sub> (gas)

(Oiling a reduction relation)

(Silicon-reduction reaction)

 $WF_6$  (gas) + 3 H<sub>2</sub>-----  $\rightarrow$  W (solid) + 6HF (gas) (Hydrogen- reduction reaction)

 $2WF_6(gas) + 3 SiH_4(gas) ----- \rightarrow 2W(solid) + 3SiF_4(gas) + 6H_2$ (Silane-reduction reaction)

## What is TEOS?

### Molecular structure



- The practical temperature range for silicon dioxide films is 675- 695 C, which limits their uses in depositing oxide films on AI. (PECVD with TEOS is more adequate and will be discussed in Module 7 on PECVD).
- The chemical reaction is:

Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (liquid) -- $\rightarrow$  SiO<sub>2</sub> (solid) + 4C<sub>2</sub>H<sub>4</sub> (gas) + 2 H<sub>2</sub>O (gas)

• Oxygen rich TEOS/O<sub>2</sub> is needed for good quality oxide films .

- Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEtraethyl OrthoSilicate, TEOS)
- Less hazard than silane.
- Relatively inert, a liquid form at room temperature.
- Providing more conformal films than silane.
- Can be supplied to the chamber using either a bubbler with nitrogen as a carrier gas or a direct liquid injection.

## **Schematic of a LPCVD System**



University of Wisconsin-Madison







## Why most of the LPCVD use hot wall reactors?

#### Advantages:

- ✓ Uniform temperature distribution.
- ✓ Reduced convection effect.
- ✓ Operated at 1-2 Torr; therefore poor thermal conduction.

#### **Disadvantages:**

- Particles can be deposited on the wall and flaked off during deposition.
- Materials previously deposited on the hot wall could deposit again on the wafer.

## Deposition Rate vs. Substrate Temperature (For example SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4)</sub>



Total pressure : 0.7 Torr;  $N_2O/Si_2Cl_6$  and  $NH_3/Si_2Cl_6$  were used for  $SiO_2$  and  $Si_3N_4$ (J.L. Vossen, Thin Film Processes, Academic Press, 1991). The rate R is related to the temperature by the Arrhenius equation :

 $R(T) = R_0 e^{-EA/kT}$ Or  $R(T) = R_0 exp(-E_A/kT)$   $E_A = activation energy$   $R_0 = temperature independent$ frequency factor T = temperature (in Kelvin)

#### Problem

Silicon dioxide films of different deposition conditions were coated on a silicon wafer, using LPCVD. Two deposition rates were obtained at two different substrate temperatures : 1  $\mu$ m/min. at 700 C and 1.5  $\mu$ m/min. at 850 C. Calculate the activation energy of the coating.

### **Example 14**

Silicon dioxide films of different deposition conditions were coated on a silicon wafer, using LPCVD. Two deposition rates were obtained at two different substrate temperatures : 1 µm/min. at 700 C and 1.5 µm/min. at 850 C. Calculate the activation energy of the coating.

Let's set the deposition rates be  $R_1$  and  $R_2$  and the activation energy  $E_A$ .

$$R_{1} = R_{0}e^{-\left(\frac{E_{A}}{kT_{1}}\right)}; R_{2} = R_{0}e^{-\left(\frac{E_{A}}{kT_{2}}\right)}$$

$$\frac{R_{1}}{R_{2}} = \frac{R_{0}e^{-\left(\frac{E_{A}}{kT_{1}}\right)}}{e^{-\left(\frac{E_{A}}{kT_{2}}\right)}} = e^{\left(\frac{E_{A}}{kT_{2}} - \frac{E_{A}}{kT_{1}}\right)} = e^{\frac{E_{A}}{k}(\frac{1}{T_{2}} - \frac{1}{T_{1}})}$$

$$\ln \frac{R_{1}}{R_{2}} = \frac{E_{A}}{k}(\frac{1}{T_{2}} - \frac{1}{T_{1}}) \rightarrow E_{A} = \frac{k\ln(\frac{R_{1}}{R_{2}})}{\frac{1}{T_{2}} - \frac{1}{T_{1}}}$$

$$= \frac{8.617 \times 10^{-5} \times \ln\left(\frac{1}{1.5}\right)}{\left(\frac{1}{1123} - \frac{1}{973}\right)}$$
  
E<sub>A</sub> = .255 eV

# We will discuss:

- □ Related topics in thin films
- □ Low pressure CVD
- □ Thermal oxidation
- Plasma-enhanced CVD
- □ Atomic layer deposition (ALD)
- Metalorganic chemical vapor deposition (MOCVD)

# **Atmospheric Pressure CVD**

# **APCVD Reactors**

- The first CVD reactor to be used in the microelectronics industry.
- Mass transport limited rate.
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# We will discuss:

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- □ Low pressure CVD
- □ Thermal oxidation
- Plasma-enhanced CVD
- □ Atomic layer deposition (ALD)
- Metalorganic chemical vapor deposition (MOCVD)

## **Thermal oxidation process**

- One of the two main advantages of Si
- Dry oxidation : Si +  $O_2 \rightarrow SiO_2$
- Wet oxidation :  $Si + 2H_2O \rightarrow SiO_2 + 2H_2$
- Oxygen must diffuse through the oxide to react at the Si/SiO2 interface, so rate depends on the thickness of the oxide and reduces as the oxidation progresses.
- Temperatures between 800 and 1200°C
- Dry (molecular oxygen) : better oxide but slow (gate oxide)
- Wet (steam water vapor) : fast but porous (isolation)





# **Properties of thermal SiO<sub>2</sub> film**



**Thermal SiO<sub>2</sub> is amorphous.** Weight Density =  $2.2 \text{ gm/cm}^3$ Molecular Density = 2.3E22 molecules / cm<sup>3</sup>

- (1) Excellent Electrical Insulator Resistivity > 1E20 ohm-cm Energy Gap ~ 9 eV
- (2) High Breakdown Electric Field
  - > 10MV/cm
- (3) Stable and Reproducible Si/SiO<sub>2</sub> Interface





Professor Nathan Cheung, U.C. Berkeley

## **Properties of thermal SiO<sub>2</sub> film**

(5) SiO<sub>2</sub> is a good diffusion mask for common dopants

$$D_{sio_2} \ll D_{si}$$
 e.g. B, P, As, Sb.



\*exceptions are Ga (a p-type dopant) and some metals, e.g. Cu, Au

(6) Very good etching selectivity between Si and SiO<sub>2</sub>.



Professor Nathan Cheung, U.C. Berkeley



5. Diffusion Source6. Dielectric Materials for Capacitor in DRAM

- 1. Mask against implant or diffusion of dopant into Si
- 2. Electrical isolation for device isolation
- 3. Gate oxide in MOS structures
- 4. Surface passivation (corrosion, impurity, stress etc.)



## Kinetics of thermal SiO<sub>2</sub> film growth



Professor Nathan Cheung, U.C. Berkeley

#### Thickness of silicon consumed during oxidation



#### **Problem**

For XSi = 0.5 µm, calculate the thickness of the oxide layer.

## **Problem 15**

For XSi = 0.5 µm, calculate the thickness of the oxide layer.



Professor Nathan Cheung, U.C. Berkeley

### Problem 16

A <100> silicon wafer has a 2000-Å oxide on its surface (a) How long did it take to grow this oxide at 1100°C in dry oxygen?





(b)The wafer is put back in the furnace in wet oxygen at 1000° C. How long will it take to grow an additional 3000 Å of oxide?



(b) The total oxide thickness at the end of the oxidation would be  $0.5 \,\mu\text{m}$ which would require  $1.5 \,\text{hr}$  to grow if there was no oxide on the surface to begin with. However, the wafer "thinks" it has already been in the furnace 0.4 hr. Thus the additional time needed to grow the 0.3  $\mu\text{m}$ oxide is 1.5-0.4 =  $1.1 \,\text{hr}$ .

#### Problem 17

(a) How long does it take to grow 0.1 µm of dry oxide at 1000 °C?

(b) After step (a), how long will it take to grow an additional 0.2μm of oxide at 900 °C in a wet ambient ?



(a) From the "1000°C dry" curve in Slide 3-3, it takes 2.5 hr to grow 0.1 µm of oxide.

(b) Use the "900°C wet" curve only. It would have taken 0.7hr to grow the 0.1 μm oxide and 2.4hr to grow 0.3 μm oxide from bare silicon. The answer is 2.4hr–0.7hr = 1.7hr.

# We will discuss:

- □ Related topics in thin films
- □ Low pressure CVD
- □ Thermal oxidation
- Plasma-enhanced CVD
- □ Atomic layer deposition (ALD)
- Metalorganic chemical vapor deposition (MOCVD)

# What is plasma?

A sea of neutral atoms where: Number of positively charged particles (*ions*) = number of negatively charged particles (*electrons*) per unit volume

#### **Glow Discharge**

A state, overall must always remain neutral, although portion of it may be charged negatively or positively

Most thin film processes utilize glow discharges, but "plasmas" and "glow discharges" are often used interchangeably



# What is plasma?

A sea of neutral atoms where: Number of positively charged particles (*ions*) = number of negatively charged particles (*electrons*) per unit volume

<u>Glow discharge</u> - globally neutral, but contains regions of net positive and negative charge

Most thin film processes utilize glow discharges, but "plasmas" and "glow discharges" are often used interchangeably



lick to add notes

### The plasma state is the fourth state of matter



### **Colors in a discharge tube with different inert gases**





### **Different plasma colors in a sputtering chamber**



For the sputtering of ITO : with 97% argon + 3% oxygen (left) and with argon only (right)



CuZnSnS4 with argon (left) and TiN with a mixture of argon and nitrogen (right)

# **DC Glow Discharge**

- When a large voltage is applied, say 100 V/cm, any free electrons are rapidly accelerated toward the anode.
- They quickly attain high velocity (*kinetic energy*) because THEY HAVE SUCH A LOW MASS.
- Since kinetic energy is related to temperature, the electrons are "HOT" in an environment of heavy, slow-moving "COLD" gas molecules.

- Before application of the potential, gas molecules are electrically neutral with a few (if any) charged particles.
- Occasionally, a free electron may be released from a molecule by the interaction of (for example, a cosmic ray, a photon etc.)



- The average energy is expressed in electron volts (eV).
   kT= 1/40eV at 290 K.
- Average electron energy = 2eV
   = 23200 K !

(electron has a very small heat capacity)

• Temperature of ion = 500 K.



#### DC Glow Discharge (cont'd)

- Electrons begin to collide with gas molecules, and the collisions can be either elastic or inelastic
- Elastic collisions deplete very little of the electron's energy and do not significantly influence the molecules because of the great mass difference between electrons and molecules.
- $\checkmark$  Mass of electron = 9.11 e-31 Kg; mass of Argon= 6.64 e-23 g.
- ✓ Inelastic collisions excite the molecules of gas or ionize them by completely removing an electron.





# **Paschen Curve**



$$V_{B} = \frac{APd}{\ln(Pd) + B}$$

## **DC Glow Discharge**

Positive ions are accelerated toward the negative electrode (cathode). Collision with the cathode causes the emission of **secondary electrons** which are emitted from the cathode into the plasma.



Free electrons from secondary emission and from ionization are accelerated in the field to continue the above processes, and a steady state self-sustaining discharge is obtained.



Electrons are lost by: (a) Drift and diffusion to the chamber walls, (b) recombination with positive ions, (c) attachment to neutral molecules to form negative ions.



- 1 -- Cathode Dark Space (Crooke's Dark Space)
- 2 -- Negative Glow
- 3 -- Faraday Dark Space
- 4 -- Positive Column



Cathode

Anode



## **DC Glow Discharge**



http://www.exo.net/~pauld/origins/glowdisharge.html





Aston dark space: with low energy electrons and high energy ions moving in opposite direction.

Cathode dark space (space charge sheath): most of the discharge voltage is dropped; with large electric field and an insufficient # of electrons.

Negative glow region: equal # of electrons and ions (10^9-10^13 cm^-3)- glow discharge operation region. Faraday dark region: Electrons have lost most of their energy through either ionizing collisions or elastic collisions; left over energy is too low to excite the gas atoms.

Positive column: electrons are accelerated by local electric fields; the losses are mainly through diffusion to the walls.

Anode dark space: deficient of electrons

# (B. Chapman, Glow Discharge Processes, John Wiley & Sons, 1980)


### **Electron and ion current density**

Neutrals	$m = 6.6 \ 10^{-2}  {}^{3}g$	$en_{e}\bar{c}_{e} = 1.6 \times 10^{-19} \times 10^{10} \times 9.5 \times 10^{7} coulomb.cm$
	$T = 20^{\circ}C = 293K \equiv 1/40eV$ $\overline{c} = 4.0  10^{4} \text{ cm/sec}$	$j_e = \frac{e}{4} = \frac{1}{4} = \frac{1}{4} + \frac{1}{2} $
lons	$m_i = 6.6 \ 10^{-2.3} g$	$j_e = 38 \frac{mA}{cm^2}$
	$\overline{c_i} = 5.2 \ 10^4 \text{ cm/sec}$	$j_{i} = \frac{1.6 \times 10^{-19} \times 10^{10} \times 5.2 \times 10^{4}  coulomb.cm}{2}$
Electrons	$m_e = 9.1  10^{-2.8} g$ $T_e = 23.200 K \equiv 2eV$	4 cm <sup>2</sup> .sec
	$\overline{c}_{e} = 9.5  10^{7} \text{ cm/sec}$ $\overline{c} = \left(\frac{8 \text{kT}}{\pi \text{m}}\right)^{\frac{1}{2}}$	$J_i = 21 \frac{1}{cm^2}$

### Calculating Vp-Vf near the sheath

Using the values in Table 3-1and equation (3.6), calculate  $(\bigvee_{t} \bigvee_{t})$  near the sheath assuming that the electron density and ion density being the same in the plasma.

$$\frac{n_e \bar{C}_e}{4} = \frac{n_i \bar{C}_i}{4}$$
$$\frac{n'_e}{n_e} = \exp{-\frac{e(V_p - V_f)}{kT_e}}$$

From the first equation and by the assumption that electron density being equal to the ion density, one can write the following equations:



### **About Plasma-enhanced CVD**

Plasma –Enhanced Chemical Vapor Deposition (PECVD) has been established itself as an important process for making a wide range of materials in the electronic industry. Some of them are silicon oxide, silicon nitride , polycrystalline silicon, amorphous silicon and diamond like carbon.

- Glow- discharge plasma is sustained within chamber where vapor –phase chemical reactions and film deposition occur simultaneously.
- A glow discharge is a self-sustaining, weakly ionized plasma that emits light and contains equal volume concentrations of positively and negatively charged species.
- The gas is subjected to an electric field. The electric field initially reacts mostly with the free electrons in the gas.
- Higher deposition rates at lower temperatures (major advantage), allowing for example deposition of silicon dioxide or silicon nitride on aluminium).
- \* Good adhesion, low pin holes, good step coverage.
- RF frequency being in the range from a few KHz to GHz range ; 5 milliTorr to 5 Torr, electron and ion density of 10<sup>9</sup> – 10<sup>11</sup>/ cm<sup>3</sup>; average energies being 1- 10 eV.

# **Basic Steps of Film Growth**

- The basic elements of a PECVD process : (a) creation of reactive species in the gas phase by electron impact; (b) transport of the reactive species to the film surface and (c) bonding to the film surface.
- The electrons gain sufficient energy from the electric field so that they can collide with the reactant gas molecules; The molecules decompose into for example radicals, ion species, atoms and molecules in excited states, resulting chemical reactions at lower temperatures.
- The energetic species are then absorbed on the film surface.
- The absorption and migration create film conformality in deposited films.

> Less stoichiometric.



### **Precision 5000 System**

- Commercially available in 1987. The first "cluster tool" to gain widespread industry acceptance.
- Four individual process chambers with a central loadlock/wafer handling.
- Both CVD coating and etching can be done sequentially.
- Plasma cleaning is automatically after each run.
- 200 mm wafer, 1-3 % uniformity





Cluster-tool System (www.appliedmaterials.com)

## Schematic of a PECVD System



# PECVD amorphous silicon and polysilicon are industrial materials



### A-Si:H Modules (United Solar)



## **Applied Materials' Systems**



#### APCVD, LPCVD, and PECVD Comparison

CVD Process	Advantages	Disadvantages	Applications
APCVD	Simple, Fast Deposition, Low Temperature	Poor Step Coverage, Contamination	Low-temperature Oxides
LPCVD	Excellent Purity, Excellent Uniformity, Good Step Coverage, Large Wafer Capacity	High Temperature, Slow Deposition	High-temperature Oxides, Silicon Nitride, Poly-Si, W, WSi <sub>2</sub>
PECVD	Low Temperature, Good Step Coverage	Chemical and Particle Contamination	Low-temperature Insulators over Metals, Nitride Passivation

# We will discuss:

- □ Related topics in thin films
- □ Low pressure CVD
- □ Thermal oxidation
- □ Plasma-enhanced CVD
- □ Atomic layer deposition (ALD)
- Metalorganic chemical vapor deposition (MOCVD)

# What is ALD?

- ALD (Atomic layer deposition) previously known by the name ALE (Atomic layer Epitaxy) was originated by T.Suntola in Finland.
- Deposition method by which precursor gases or vapors are alternately pulsed on to the substrate surface.
- Precursor gases introduced on to the substrate surface will chemisorb or surface reaction takes place at the surface.

Atomic Layer Deposition Is a type of Chemical Vapor Deposition that uses a multitude of chemical precursors that are periodically injected into the deposition system and the precursors are not present at the same time in the system.

## Atomic Layer Deposition General Features

- Self-limiting film growth (gas surface reactions occur till surface is saturated).
- Accurate film thickness control (thickness can be as low as 1 nm)
- Sharp interfaces
- Films are very uniform, smooth and stoichiometric.
- Good reproducibility
- Good conformality
- Excellent step coverage even at high aspec ratios.
- Multilayer processing capability
- High film qualities at relatively low temperatures (as low as 180 C).
- Disadvantages: (1) Slow growth rate (0.1 nm/sec @ 300 C for HfO2); (2) Limitation of precursor selection and (3) Low precursor utilization efficiency.

### Deposition mechanism of ALD ALD Cycle

(i) exposure of the first precursor

(ii) purge by gas flow, or evacuation of the reaction chamber

(iii) exposure of the second precursor

(iv) purge or evacuation.

- Steps:
  - Self-terminating reaction of the first reactant (Reactant A)
  - Purge or evacuation to remove non-reacted reactant and by products
  - Self-terminating reaction of the second reactant (Reactant B)
  - Purge

This is considered as one reaction cycle



#### ALD: Fundamental aspect of film growth (G.R. Gong , 2004)



Simplified deposition cycle: ZnCl<sub>2</sub>+H<sub>2</sub>S => ZnS+2HCl

- 1) Pulse of ZnCl, precursor.
- Purge to flush extra ZnCl<sub>2</sub> away, leaving surface saturated with self limited monolayer of ZnCl<sub>2</sub>.
- Pulse of H<sub>2</sub>S reacts with ZnCl<sub>2</sub> to ZnS. Byproduct is HCl.
- Purge to flush unreacted H<sub>2</sub>S and HCl away. Leaving monolayer ZnS on the surface.



### **Atomic Layer Deposition**

$$\begin{aligned} Substrate - AH + ML_x &\rightarrow Substrate - AML_y \\ - OH + Al(CH_3)_3 &\rightarrow -O - Al(CH_3)_2 + CH_4 \\ 2 \times \left[ -O - Al(CH_3)_2 \right] + 4H_2O \rightarrow -O - Al(OH) - O - (OH)Al - O - 4CH_4 + H_2O \end{aligned}$$

The molecular precursors  $ML_x$  are introduced in the chamber separately, one precursor at a time. M= AI, W, Ta, Si, etc... and L= atomic or molecular ligands.

Generally a hydrogen containing material AH is used to react with the metal precursor and to form the exchange reaction by-product

- an –OH terminated surface is exposed to a flux of AI(CH<sub>3</sub>)<sub>3</sub> to form AI(CH<sub>3</sub>)<sub>2</sub> and a volatile CH<sub>4</sub> by attaching AI(CH<sub>3</sub>)<sub>3</sub> to each –OH site.
- The reaction self-limited (or self-saturated) when all the \_OH sites are reacted.
- The surface is then exposed to H<sub>2</sub>O which reacts with the –CH<sub>3</sub> sites to produce a volatile CH4 and attaches –OH per each - CH<sub>3</sub> site. The reaction self-saturated when all the - CH3 sites are reacted.
- In the same time, adjacent -AI(OH)<sub>2</sub> cross-link by reacting one of the –OH species to produce H<sub>2</sub>O to form –AI-O-AI network. The cycle is complete.

#### ALD cycle of aluminum oxide deposition (Cambridge Nanotech)



In air  $H_2O$  vapor is adsorbed on most surfaces, forming a hydroxyl group. With silicon this forms: Si-O-H (s)

After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.



Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

 $AI(CH_3)_{3(q)} + : Si-O-H_{(s)} \longrightarrow : Si-O-AI(CH_3)_{2(s)} + CH_4$ 

 $\begin{aligned} Substrate-AH + ML_x &\rightarrow Substrate-AML_y \\ -OH + Al(CH_3)_3 &\rightarrow -O - Al(CH_3)_2 + CH_4 \\ 2 \times \left[ -O - Al(CH_3)_2 \right] + 4H_2O \rightarrow -O - Al(OH) - O - (OH)Al - O - 4CH_4 + H_2O \end{aligned}$ 



In air H<sub>2</sub>O vapor is adsorbed on most surfaces, forming a hydroxyl group. With silicon this forms: Si-O-H (5)

After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.



Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

Al(CH<sub>3</sub>)<sub>3 (g)</sub> + : Si-O-H (s) ---- :Si-O-Al(CH<sub>3</sub>)<sub>2 (s)</sub> + CH<sub>4</sub>

Excess TMA Methane reaction product CH, Methane reaction p

Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.



 $\begin{aligned} Substrate-AH + ML_{x} &\rightarrow Substrate-AML_{y} \\ -OH + Al(CH_{3})_{3} &\rightarrow -O - Al(CH_{3})_{2} + CH_{4} \\ 2 \times \left[ -O - Al(CH_{3})_{2} \right] + 4H_{2}O \rightarrow -O - Al(OH) - O - (OH)Al - O + 4CH_{4} + H_{2}O \end{aligned}$ 

After the TMA and methane reaction product is pumped away, water vapor  $(H_2O)$  is pulsed into the reaction chamber.



Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.



H<sub>2</sub>O reacts with the dangling methyl groups on the new surface forming aluminumoxygen (AI-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again metane is the reaction product.



After the TMA and methane reaction product is pumped away, water vapor  $(H_2O)$  is pulsed into the reaction chamber.



The reaction product methane is pumped away. Excess  $H_2O$  vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.

$$\begin{aligned} Substrate-AH + ML_x &\rightarrow Substrate-AML_y \\ -OH + Al(CH_3)_3 &\rightarrow -O - Al(CH_3)_2 + CH_4 \\ 2 \times \left[ -O - Al(CH_3)_2 \right] + 4H_2O &\rightarrow -O - Al(OH) - O - (OH)Al - O - 4CH_4 + H_2O \end{aligned}$$



The reaction product methane is pumped away. Excess  $H_2O$  vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.



One TMA and one  $H_2O$  vapor pulse form one cycle. Here three cycles are shown, with approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes e.g. 3 sec.

Two reaction steps in each cycle:

 $\begin{array}{l} \mathsf{AI(CH_3)_3}_{(g)} + : \mathsf{AI-O-H}_{(s)} \longrightarrow : \mathsf{AI-O-AI(CH_3)_2}_{(s)} + \mathsf{CH_4} \\ \\ \mathsf{2} \mathsf{H_2O}_{(g)} + : \mathsf{O-AI(CH_3)_2}_{(s)} \longrightarrow : \mathsf{AI-O-AI(OH)_2}_{(s)} + 2 \mathsf{CH_4} \end{array}$ 

### **ALD: Applications**





Hausmann et al. Thin Solid films 2003.

High aspect ratio ALD of Ta2O5 in vias of 170 nm dia, 7 microns deep







MEMS microengine consisting of a gear turning on a hub. (Appl. Phys. Lett. 82 (2003) 2883).

MEMS devices contain 3D structures where ALD could be

(maybe is) used for:

- wear-resistant
- lubricating
- anti-stiction
- insulating
- charge dissipation coatings



Figure 8. MEMS cantilever coated with 60 nm thick, protective alumina using ALD (from [30]).



ALD coated (Al<sub>2</sub>O<sub>3</sub>/ZnO) rf MEMS capacitive switch (Sens. Actuat. A 135 (2007) 262).



# We will discuss:

- □ Related topics in thin films
- □ Low pressure CVD
- □ Thermal oxidation
- Plasma-enhanced CVD
- □ Atomic layer deposition (ALD)
- Metalorganic chemical vapor deposition (MOCVD)

## **MOCVD : General features**

- Various combinations of organometallic compounds and hydrides
- Can be used to grow a large variety of materials on larger substrates (2", 4", 6", 8").
- Becoming the epitaxial growth technique for many commercial products.
- Films can be grown at high temperatures.
- Less accurate in thickness measurements at nano levels
- Less sharp transition between two layers.
- Sources are generally toxic and/or pyrophoric, chemically active.

# ARCO Solar Built the first largest 6.5 MW Solar PV Plant in San Luis Obispo County, California in September 1987



# The story of ZnO doped with III elements and hydrogen (ZnO-III)

>Indium – free Lower cost , highly abundant >Nontoxic > Doping (III elements, Fluorine). Nanostructure. > Highly transparent, high conductivity, high figure of merit > surface morphology (deposition parameters, etching, textured surface, high haze than FTO, self- texturing with LPCVD or B doing) Stable against chemical attack, thermal, and plasma environments than FTO. Resulting element Sn can cause optical loss, unwanted diffusion- $\rightarrow$ reduction in efficiency. ► Low process temperature (LPCVD, < 200 C) ≻ High deposition rate (20 A/sec) Iarge area production-oriented (Microelectronic technology such as sputtering, CVD such as LPCVD, APCVD, and MOCVD)

#### Electrical and optical characteristics of sputtered ZnO-III –Hydrogen (ARCO Solar 1984)



n=2.6 (AZO), n= 2 (ZO) Sputtering target :ZnO+ 2 wt.% Al<sub>2</sub>O<sub>3</sub> T<sub>S</sub>-= RT- 300 C, T<sub>a</sub>=300-400 C 0.3-1.0 W/cm<sup>2</sup>



Diethylzinc (DEZ), H<sub>2</sub>O and TMA (LPCVD)

4.9 x10<sup>-4</sup> - 6.4 x10<sup>-4</sup> Ω-cm (34 cm<sup>2</sup>/V-sec (mobility) , 2.8x10<sup>20</sup> /cm<sup>3</sup>

N.T.Tran et al. US patents 4,623,601, 4,940,495, 5,135,581, 5,397,920

### Performance of Historic ZnO/CdS/CuInSe<sub>2</sub> Solar Cells (1984)



### Performance of Historic ZnO/ Polysilicon Solar Cell (1984)



### ZnO-III in CIGS Solar cells (ARCO Solar, 1984)



AREA		1.90 cm2
Jsc		35.296 ma/cm2
Voc		0.438 volts
Jpm		30.176 ma/cm2
Vpm		0.319 volts
Pdm		9.625 mw/cm2
FF		62.3 %
Eff	0	9.62 %
dV/dJ QVoc Cor.C		2.21 ohn-cn2 0.000
dJ/dV evneg Cor.C		0.64 mS/cm2 0.000

Diethylzinc (DEZ), water vapor as the zinc and oxygen precursor As for the dopants, trimethylaluminum and diborane diluted in hydrogen or helium or argon were used for Al and B dopant in the ZnO matrix, respectively.



### ZnO-III in a-Si solar cells (ARCO Solar, 1984)







### ZO-III has a higher figure of merit [J.Meier et al, Orkelin]

#### Asahi U



LPCVD ZnO



- Schott glass AF45 (BZO, LPCVD)
- Sharp, large pyramids, deep altitude (BZO).
- BZO (2.5-2.7 μm, 4 Ω/square) and FTO (0.8-0.9 μm, 12 Ω/square) show higher transmittance at 500 nm or beyond.
- FTO has higher band gap therefore higher transmittance than BZO at below 400nm.
- BZO has higher diffused transmission at around 400 nm.



Surface morphology of ZnO-III depends on the substrate temperature and on the deposition methods (i.e APCVD vs LPCVD)



(a) top view of FZO (APCVD), (b) top view of BZO )LPCVD)
(c) cross sectional view of FZO (APCVD) and

(d) cross sectional view of BZO (LPCVD)

[Source: First Nano]

### A-Si PV module



# IC Energy's processing steps in making a- Si:H double junction tandem module (Tran et al.)



# A-Si :H double junction tandem module (L 1245 mm x W 635 mm x D 7.5 mm, IC Energy)





### Growth of III-V semiconductors

### Group III MO Precursors

Precursor TMGa	Svmbol (CH₃)₃Ga	Advantages liquid, high vapor pressure	Disadvantages
TEGa	(C₂H₅)₃Ga	liquid, low carbon contamination, decomposes by β-hydride elimination reaction, used in LP MOVPE systems	low vapor pressure, less stable than TMGa, strong parasitic reactions
TMin	(CH₃)₃In	solid, good vapor pressure for MOVPE, also exists as solution TMIn	low vapor pressure
TEIn	(C2H5)3In		very unstable
TMAI	(CH3)3Al	liquid, good vapor pressure, good long term stability	oxygen contamination
TEAI	(C2Hs)3AI	liquid, low carbon contamination	low long term stability

TM = Trimethyl, TE = Triethyl (Ga = Gallium, In = Indium, Al = Aluminum)





(R.D. Dupuis, J. Crystal Growth, 178(1997) 56
### Growth of III-V semiconductors (cont'd)

Precursor	Symbol	Advantages	Disadvantages
Arsine	AsH₃	good pressure control for MOVPE, inexpensive	very toxic, high pyrolysis temperature (T <sub>1/2</sub> = 600°C)
Phosphine	PH₃	good pressure control for MOVPE, inexpensive	very toxic, high pyrolysis temperature (T <sub>1/2</sub> = 850°C)
ТВА	(C <sub>4</sub> H <sub>9</sub> )AsH <sub>2</sub>	liquid, good vapor pressure for MOVPE, very low carbon contamin., good stability, low pyrolysis temperature ( $T_{1/2} = 380^{\circ}C$ )	expensive for many applications
ТМА	(CH₃)₃As	liquid, used to grow C doped GaAs	
TBP	(C <sub>4</sub> H <sub>9</sub> )PH <sub>2</sub>	liquid, good vapor pressure for MOVPE, good stability, low pyrolysis temperature $(T_{1/2} = 450^{\circ}C)$	expensive for many applications
Ammonia (for nitrides)	NH <sub>3</sub>	good stability, only practically available nitrogen precursor	high pyrolysis temperature

TM = Trimethyl, TB = Tertiarybutyl (A = arsine, P = phospine)





(R.D. Dupuis, J. Crystal Growth, 178(1997) 56

## Growth of III-V semiconductors (cont'd)

#### **Dopant Precursors**

Precursor	Symbol	Advantages	Disadvantages	
DMZn (p-dopant)	(CH <sub>3</sub> ) <sub>2</sub> Zn	liquid, high vapor pressure, very common Zn precursor	Zn often has very high diffusion coefficient in solid, diffuses via interstitials	
Carbontetrachloride (p-dopant in GaAs)	CCl4	liquid, C is shallow acceptor in GaAs, C has low diffusion coeff., used for sharp interfaces, e.g., for high p-type doping in HBTs	usage might be subject to legal regulation due to ozone depleting character of chemical	
Carbontetrabromide (p-dopant )	CBr <sub>4</sub>	used in similar applications as CCl <sub>4</sub>	same as for CCl <sub>4</sub>	
Silane (n-dopant)	SiH <sub>4</sub>	used as n-dopant for electronic devices	gaseous, flammable, high pyrolysis temperature	
Disilane (n-dopant)	Si <sub>2</sub> H <sub>6</sub>	used in similar applications as SiH <sub>4</sub> , but lower pyrolysis temp., better doping uniformity than SiH <sub>4</sub>	gaseous, flammable	
DETe (n-dopant)	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Te	liquid, used in LED production		





(R.D. Dupuis, J. Crystal Growth, 178(1997) 56

### **Metalorganic compounds**

- Optimal thermal decomposition temperature between 300 and 500°C
  ⇒ availability of transported reactant at the substrate surface.
- The vapor pressure of the MO source is an important consideration in MOCVD, since it determines the concentration of source material in the reactor and the deposition rate. Too low a vapor pressure makes it difficult to transport the source into the deposition zone and to achieve reasonable growth rates. Too high a vapor pressure may raise safety concerns if the compound is toxic.
- Vapor pressures of Metalorganic compounds are calculated in terms of the expression

Compound		P at 298 K	А	В	Melt point
		(torr)			(°C)
(Al(CH <sub>3</sub> ) <sub>3</sub> ) <sub>2</sub>	TMAI	14.2	2780	10.48	15
$Al(C_2H_5)_3$	TEAl	0.041	3625	10.78	-52.5
Ga(CH <sub>3</sub> ) <sub>3</sub>	TMGa	238	1825	8.50	-15.8
$Ga(C_2H_5)_3$	TEGa	4.79	2530	9.19	-82.5
In(CH3) <sub>3</sub>	TMIn	1.75	2830	9.74	88
$In(C_2H_5)_3$	TEIn	0.31	2815	8.94	-32
Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	DEZn	8.53	2190	8.28	-28
Mg(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	Cp2Mg	0.05	3556	10.56	175

#### Vapor pressure of most common MO compounds

#### Log(p)=B-A/T

Vapor pressure vs temperature of some metalorganic sources (B,A= constant; p: vapor pressure , T : temperature)

### **Gas reaction**

- **P**<u>vrolvsis</u> temperature & stability is proportional with bond strength.
- Bond strength is inversely proportional to number of C

horizontal gas flow gas phase CH, boundary layer mass transport CH, -radical to the surface by diffusion CH. precursor decomposition CH.-H + H = Hadsorption wafer surface incorporation atomic step surface diffusion and reaction and growth

#### $(CH_3)_3Ga + NH_3 \rightarrow GaN + 3CH4$

TEM image of InGaN MQW LD wafer



Examples:

**Pyrolysis temperature increases by the following order:** TEAs  $\rightarrow$  TMAs  $\rightarrow$  AsH3 or TEGa  $\rightarrow$  TMGa

Decomposition degree increases by the following order: TMGa-→ Ga

- Homogeneous reaction: gas phase, boundary layer
- Heterogeneous reaction: reactor, substrate surface
- Reaction temp. of heterogeneous reaction is lower ٠

#### $R_nA + DH_n - \rightarrow AD + nRH$

Where: R: containing organic radicals such as methyl (CH<sub>3</sub>) and ethyl ( $C_2H_5$ ); A: group III; D : group V

n-GaN/sapphire interface

#### **MOCVD systems: Main components**



### Reactors



Horizontal Tube Reactor AIX 200RF

 Vertical reactors: gases enter from top, sample mounted horizontally on a fast-rotating (~500-1000RPM) susceptor plate.

 Horizontal reactors: gases inserted laterally with respect to sample standing horizontally on a slowlyrotating (~60RPM) susceptor plate.

**Planetary reactors** 





H. M. Manasevit, "Single-crystal gallium arsenide on insulating substrates," Appl. Phys. Lett., vol. 12, no. 4, pp. 156–159, Feb.

http://www.ledmarketresearch.com/blog/Aixtron\_Regains\_Q4\_LED\_Le ad



Aixtron's latest design uses either a 12 x4 inch configuration to deliver growth on substrates with a combined area of 150 inch2.



Aixtron's fully loaded 49x2inch planetary reactor can produce epiwafers with uniformity suitable for LED manufacturing

#### Planetary Reactor AIX 2600 G3 -Susceptor (horizontal type)



4" wafer on rotating satellite main susceptor disk

collector ring



. Automated loading and unloading of an Aixtron G5 HT MOCVD reactor. The transfer system picks up the entire wafer platform satellite disk pre-loaded with wafers. The reactor shown here is opened for demonstration purposes only.

Reactor for 8 x 4 " wafers (Aixtron)

http://www.electroig.com/articles/sst/2012/01/aixtron-sells-multiplemocvd-reactors-to-hb-led-maker.html



# **Additional materials**

### **MOCVD for MEMS**



Fig.2. SEM picture of suspended GaN microstructures: a microdisk array, microcantilever arrays (linear and circular), a microbeam and beam arrays.

Zhenchuan Yang et al. 211<sup>th</sup> ECS Meeting, Abstract #799 The Electrochemical Society



# Thin films

#### Example



**THIN FILM:THICKNESS** < 1μm</th>**THICK FILM:THICKNESS** > 1μm

 > 1 micon or less
 > Not fully dense
 > Under stress
 > Quasi 2-D (because too thin)
 > Strongly influenced by surface &

interface effects

### **Example 3**

What is the corresponding units of 1 Torr in (a) Pa, (b) in bar?...

(a) 1 Torr= 133.3 Pa (b) since 1 bar = 750 Torr

Therefore  $\begin{array}{l} 1\mathit{Torr} = \frac{1}{750}\mathit{bar} = 1.33 \times 10^{-3} \mathit{\ bar} \\ \mathit{Or} \; 1\mathit{\ Torr} = 1.33 \mathit{\ mbar} \end{array}$ 

# **Mean Free Path**

- The mean free path is the average distance traveled by a gas atom between collision with other gas atoms.
- Mean free path decreases at higher pressures.
- A large number of gas particles in a gas at a given pressure causes a large number of collisions.
- Procedure to calculate the mean free path : the gas particles are treated as hard spheres and the collision occurs whenever the two gas molecules are within a distance from each other.



Collision frequency=
$$\frac{c}{\lambda}$$

In air at ambient temperature

$$\lambda = \frac{6.6}{P(Pa)} = \frac{0.05}{P(Torr)} (mm)$$

#### Structure Zone Diagram (J.A.Thornton, Ann. Rev. Mater. Sci.7, 239, 1977)

#### Sputtered films



- Zone 1 (T<sub>s</sub>/ T<sub>M</sub> < 0.3): columnar, "cauliflower-like".
- Zone T : Fibrous, poorly defined structure.
- Zone 2 (0.3< T<sub>s</sub>/ T<sub>M</sub> < 0.45): Columnar, tighter grain boundaries of 0.5 nm wide.
- Zone 3 ( $T_s/T_M > 0.5$ ) : Grains grow by diffusion.

# Columnar Structure of Ni- Cr



Zone 1 (TS/ TM <0.3) : columnar, consisting of inverted conelike units capped by domes separated by voided boundaries several nanometers wide. Limited adatom motion, "cauliflower-type). Zone 2 (0.3<TS/ TM <0.45) : columnar

but tighter grain boundaries about 0.5 nm wide.

Zone 3 (TS/ TM >0.5) : grains that grow in size by bulk diffusion.

### **CVD** system





# How do we create bandgap engineered structures (Allan Doolittle)



## ALD Reactors (B. H. Choi)



# **Atomic Layer Deposition**

- The molecular precursors ML<sub>x</sub> are introduced in the chamber separately, one precursor at a time.
- M= AI, W, Ta, Si, etc...and L= atomic or molecular ligands.
- Reaction of the metal precursor is generally followed by a step to purge with an inert gas to get rid of this precursor from the chamber before another precursor is introduced.
- Generally a hydrogen containing material AH is used to react with the metal precursor and to form the exchange reaction by-product

### ALD Reactors (B. H. Choi)



- <u>Reactant is supplied in the main inert gas flow for the sequencing.</u>
- Flow speed, pressure and the timing of the inert gas flow are important to keep the sequences separated and to ensure the necessary purging between the reaction sequences.

# ALD of Al<sub>2</sub>O<sub>3</sub> on Si



# **Atomic Layer Deposition : Growing ZnS**



ALD uses typically two chemicals to create alternate, saturated, chemical reactions on the surface, resulting unique <u>self-limiting growth</u> with excellent features like conformality, uniformity, repeatability and accurate thickness control.

Typical growth rate is less than one molecule layer / deposition cycle, although some precursors can provide several layers in a cycle. By supplying enough precursor guarantees uniform film thickness / deposition cycle. Self-limiting reaction provides repeatable amount of film, resulting very repeatable growth rate for each process condition.

## Atomic Layer Deposition : A Tool for Nanotechnology



Simplified deposition cycle: ZnCl<sub>2</sub>+H<sub>2</sub>S => ZnS+2HCl

- 1) Pulse of ZnCl<sub>2</sub> precursor.
- Purge to flush extra ZnCl<sub>2</sub> away, leaving surface saturated with self limited monolayer of ZnCl<sub>2</sub>.
- Pulse of H<sub>2</sub>S reacts with ZnCl<sub>2</sub> to ZnS. Byproduct is HCl.
- Purge to flush unreacted H<sub>2</sub>S and HCl away. Leaving monolayer ZnS on the surface.

# Reactors with different wafer sizes (Aixtron)



AIX 2800G4-R including Automated Satellite Handler:



# Bandgap engineering

**Bandgap engineering:** the ability to tailor the electronic and chemical properties of semiconductor materials by varying the composition and impurity concentrations through out the body of a semiconductor device.



Bulk Well Wire Dot

Quantum well: The conduction electrons are confined in a narrow dimension.

Quantum wire: a structure such as a copper wire that is long in one dimension, but has a nanometer size as its diameter. The electrons move freely along the wire.

Quantum dot: may have the shape of a tiny cube, a short cylinder or a sphere of nanometer dimensions.



# **Bandgap engineering**

Compound Semiconductors allow us to perform "Bandgap Engineering" by changing the energy bandgap as a function of position. This allows the electrons to see "engineered potentials" that "guide" electrons/holes in specific directions or even "trap" them in specific regions of devices designed by the electrical engineer.

Example: Consider the simplified band diagram of a GaN/  $Ga_{0.75}In_{0.25}N/GaN$ LED structure. Electrons and holes can be "localized" (trapped) in a very small region – enhancing the chance they will interact (recombine). This is great for light emitters!









#### **Problem 8**

- (a) How long does it take to grow 0.1 µm of dry oxide at 1000 °C?
- (b) After step (a), how long will it take to grow an additional 0.2μm of oxide at 900 °C in a wet ambient ?



(a) From the "1000°C dry" curve in Slide 3-3, it takes 2.5 hr to grow 0.1µm of oxide.

(b) Use the "900°C wet" curve only. It would have taken 0.7hr to grow the 0.1 μm oxide and 2.4hr to grow 0.3 μm oxide from bare silicon. The answer is 2.4hr–0.7hr = 1.7hr.

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