Equipment and Process Design
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https://somphene.github.io/notes/

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1 **Lecture**

§1.1 Introduction

§1.2 Vacuum

The word vacuum comes from Latin- "vacua" meaning empty.

However no ideal vacuum. Vacuum is only partially empty space.

Pressure should be below atmosphere. Galileo succeeded in 1644 producing vacuum experimentally by submerging a glass tube filled with mercury and closed at one end.

Pascal also measured the altitude with Hg barometer.

Another discovery by Robert Boyle.

$$PV = nRT$$

What characterizes pressure?
Measure force per unit area of the vessel is called pressure. Compare to atmospheric pressure or by determining it in absolute units.

Power Conversion Table insert table(later)
Composition of atmosphere table (later)
Partial pressure of the gas is proportional to the vol% in atmosphere.

Boyle's Law, Charle's Lae and Gay-Lussac's Law.

1gm-mole of gas contains N_A atoms/molecules.

$$\frac{6.022 \times 10^{23}}{22.4 litres} = 2.69 \times 10^{22} particles/litre$$

Equation of State for ideal gas

$$pV = \frac{m}{M}RT$$

Vacuum Pump

Vacuum pump literally pulls (and pushes) gas molecules out of the vacuum chambers and does not let them go back into the system (one way track). Example: Rotary pump.

Pumping Speed

$$Q = \frac{d(PV)}{dt}$$

Units: Standard Liter per minute (SLM), SCCM

Mass is conserved. Mass flow rate balance.

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Check the manufacturer's table upto what pressure it is stable. We have only discussed single stage pump. It can give torque of upto.

For better performance, use two stage pumps can go upto 1 mbar. But adding more number of stages doesn't help.

Funcions of oil:

- providing a vacuum seal (primary role)

- lubricant

- cooling the pump

Insert diagram (later)

Rotary Vane, Oil sealed mechanical pump

In the compression stage, flap is not open and pressure of the gas goes up. Consequently, the partial pressure also goes up. If the partial pressure exceeds 32 mbar, then there is condensation. The condensed droplets will come down - water droplets mix with the oil so it degrades the performance. When oil is contaminated by moisture, ultimate pressure will be slightly higher than 1 mbar. This happens if the pump is kept idle for a long time, pump is accumulated with moisture. This moisture has some partial pressure. So get rid of the moisture.

Way out: Put on the pump and start the pumping action- water that is trapped turns to vapours. Get rid of vapours from this oil, dont want the vapours to come back to the oil. Prevent condensation. Dont want to increase pressure of water vapour more than 32 mbar (Torr). Put dry nitrogen or dry air. Adding nitrogen will not allow the partial pressure to exceed 32 mbar. This action is called air ballast. (**Ballasting**)

If the partial pressure of Silane goes above a particular cuttoff, it ignites. In the event of power failure or on switching off, rotor will go in the oppoisite direction and oil will contaminate the chamber. Solution **Inbuilt Solenoid wall**. It stays at 1 atm, so the reverse rotation doesn't happen.

Dry Mechanical Vacuum Pumps

In applications (semiconductors) where corrosive liquids are being used, oils can't be used. Use Dry pumps: No possibility of going back to chamber.

Disadvantages

- very expensive, create a lot of noise,

In lab, it takes few minutes to go to 10^{-3} Torr is easily reached. Efficiency of a pump depends on how much is the final pressure reached and how much time it takes for a fixed volume of chamber to get there.

Vapor Jet

Diffusion Pump

To go below 10^{-6} Torr, use **Diffusion pump**.

Diffusion pump construction. Cold trap containing liquid nitrogen. Heating of oil generates oil vapours. Heated to about $200^0C - 250^0C$. Get reflected from the metallic plate. Body is thoroughly water cooled. Condensed and cooled. When they are coming back they drag back the molecules in the air. Flow pattern is set up. Pumping air or argon doesnt have condensation temp near to this so that stays in vapour form. The molecules in flow pattern get dragged down to **ejector**.

Function of the rotary pump is to remove the molecules coming down.
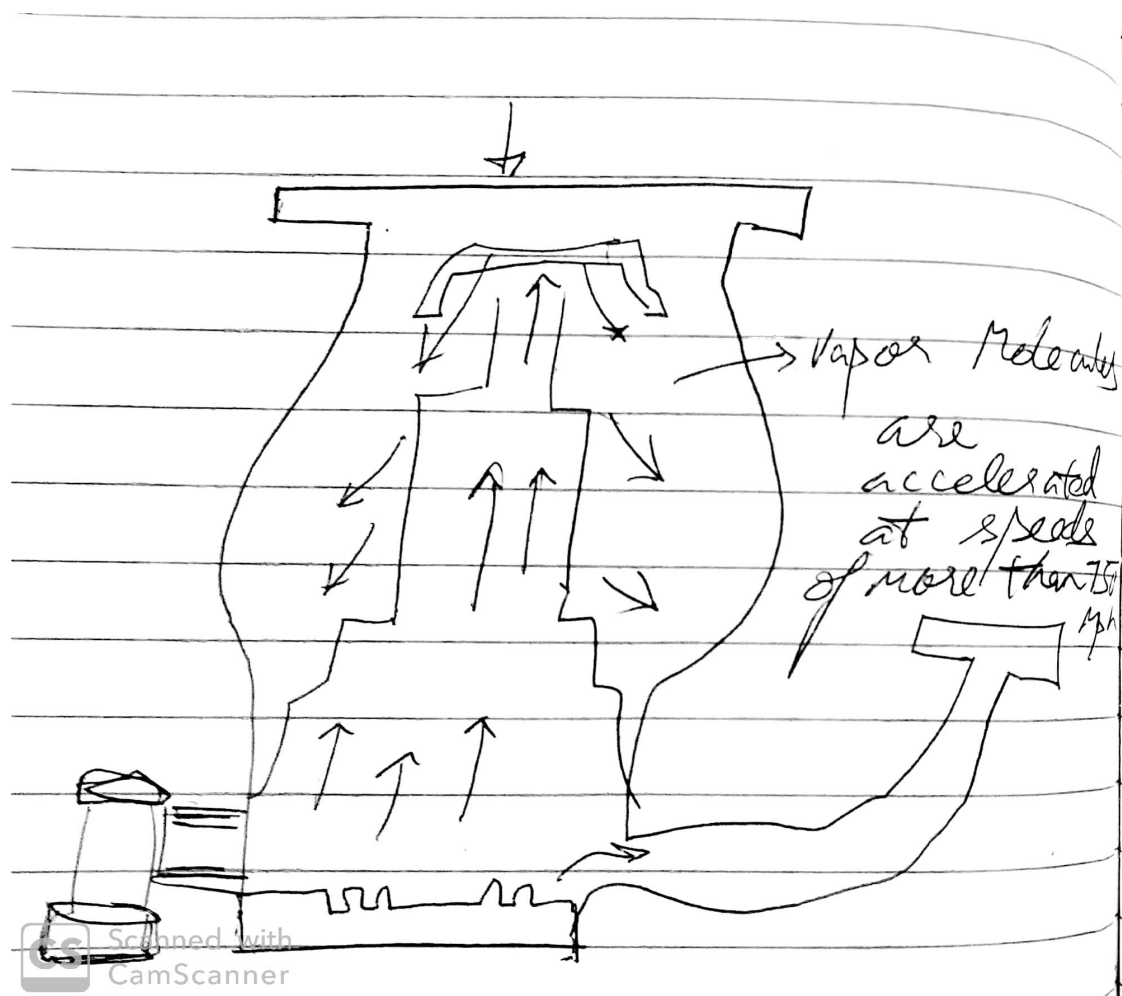
Figure 2.1: Pump diagram.

Pumping speed: In the range $10^{-3} - 10^{-7}$ Torr stays constant. Insert diagram (slides)(later)

> **Example 2.0.1** (Detection applications)
>
> BC (Boron Carbide) was to be deposited. Boron interacted with moisture to form Boric Oxide and film was degraded. Even at 10^{-2} Torr, there is enough moisture sitting on the walls. This is why 10^{-6} Torr is needed.

> **Question 2.0.2.** Why is the pumping speed decreasing after 10^{-3} Torr.

Answer: If proper flow pattern is not setup, then pumping action is not set up.

Maximum tolerable force line Rather than directed, they go ballistic. Inspite of all, some molecules will try to go but if there is a liq. N_2 cooled so that there is a surface of cooled temp between the chamber and pump. So they will get condensed.
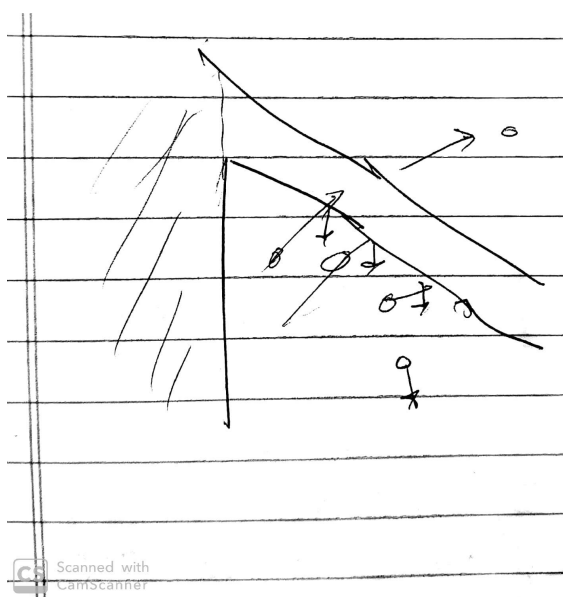
Figure 2.2: Flow diagram

Control of pumping speed

Traps reduce the conductance of tubes (based on dia).

> **Question 2.0.3.** What if we want low pumping speed?

Answer Introduce an orifice that can be opened in a controlled manner. Reduce the effective pumping speed.

> **Example 2.0.4** (control of pumping speed)
>
> Insert 1inch diameter opening. What is the conductance in series/ parallel?

Gas Load

Outgasing: Surface has adsorbed (by VanderWaal forces) gases. On reducing pressure, they start to release. The baking also gives activation energy to desolve. In addition

to actual gases being added, there will be additional **outgassing, backstreaming, diffusion, permeation, leaks**.

System Pressure- Volume gas

The pressure evolution in a vacuum system of volume V and effective pumping speed S is given by

$$-V\frac{dP}{dt} = S \cdot P$$

The term on the left represents the rate.

$$t = \frac{V}{S}ln\left(\frac{P_i}{P_f}\right)$$

Final pressure will have additional leaking as described in the previous subsection.

$$P_\infty = \frac{Q_\infty}{S}$$

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Previously we said that there is no ideal vacuum, there are leaks. Hence extra load.

§3.1 Total Gas Load

§3.1.i System Pressure

Definition 3.1.1 (Outgassing). **Outgassing rate**(q):

$$Q_{outgas} = q_{outgas} \times A$$

Tables are given for average outgassing rates.

§3.1.ii Gas Composition

Level of vacuum	Values
$Rough$	$Value1$
$High$	$value2$
$Ultra-HighVacuum$	$value3$

Insert diagram (schematic of vacuum system) (later)

Higher pressure on other side so open the gate valve slowly. Otherwise it will disturb the trajectories of the vapours, spoiled the vacuum system- oil is ecerywhere- in vacuum chamber, will require cleaning the vacuum chamber with acetone.

10^{-5} to 10^{-6} will take 40 minutes more because moisture, outgassing, slow evolution of the adsorbed gas.

Plasma generation won't happen. Moment the pump starts, input liquid nitrogen in trap. The whole region in the trap will be at low temp and backspilling of oil is prevented.

§3.2 How the Gauge works

Question 3.2.1. How to quantify the vacuum?

The simplest one is the thermocouple gauge. Resistance heating (of filament in the vacuum chamber) causes temperature change. Low pressure: Heat removal from the filament will be less if no. of particles is less.

§3.2.i Priani Guage

Principle similar to the thermocouple gauge. Here better accuracy because using Wheatstone bridge. Another filament, say Tungsten is included, rest are outside- to detect the null. Feed some current into the filament for resistance heating. $R = R_0(1 + \alpha \Delta T)$. Loss of heat from this filament ($I^2 R$) depends on the number density of the gas in the vicinity of the filament. We can change the resistance to get back the null $\implies$ gives us the

change in resistance required.

Pirani gauge is ok for 10^{-3} Torr but for lower pressures, need other methods.

§3.2.ii Penning Gauge

Electron ion pairs attracted towards opposite electrodes, while moving collisions leading to secondary ionization, current build up. Hence degree of ionization is used for measuring the vacuum level. Can always increase the probability of collisions by increasing the magnetic field $\implies$ Current multiplication. The electrons are directed along field lines and probability of collisions increases hence current magnitude increases.These are small gauges but Magnetic field can be high. Radius of gyration can be low so as to confine the electrons within the area of the plates. This is called **Penning Gauge**.

§3.2.iii Capacitance Manometer for up to 10^{-5} Torr

Accuracy of Pirani Gauge is low in low pressure such as in, Diamond thin films, solar cell deposition etc. Pressure causes buckling- displacement of diaphragm changes and hence capacitance changes.

§3.2.iv Hot Filament Ion Gauge for up to 10^{-5} Torr

Read at home. Also ***Assignment will be given***.

§3.3 Helium Leak Detection

When it comes to identifying leaks in pressure lower than 10^{-6} Torr, use a **Hellium Spectrometer**. When using a large device, connect the Helium system to the vacuum chamber. Objective is to get to 10^{-8} Torr. Helium can permeate through very narrow channels. Extract gas, ionize the gas (how? later in the lecture). Helium ions are unique. They have a signature of $\frac{e}{m}$ ratio. That will give us what region has Helium.

References: David Garton, Walter Umrath, A Roth. Calculate the conductance. In sputtering, what are the pressures at various locations?... Assignment will be mailed.

§3.4 Design Aspects of Sputtering System and Deposition of Thin Films by Physical Vapour Deposition

PVD part is for lab purposes only.

> **Question 3.4.1.** What are thin films? Why do we need them?

Thin films: Microscopically thin layer of a material deposited on a metal. Optical systems can be few nanometers, some other applications could be in micrometers.

> **Question 3.4.2.** Why Hard coatings?

From BARC experience: Tribological applications, cutting, milling, drilling, high speed drilling for a hard surface. Stainless steel has hardness of 2 GPa will last for 2 weeks. In the

workshop, TiN has 10-15 times more hardness than stainless steel. Necessity in industry. Tremendous scope for development in this area- Huge startup market.

> **Example 3.4.3** (Hard coatings)
>
> Various tribological coatings are: Nitrdes of Ti, Ti-Al, Cr, Diamond (2 GPa), Carbon, alloys. Cannot cut steel by diamond because of steel's affinity for carbon.

§3.4.i Deposition Techniques

We shall discuss sputtering (classified as PVD). Skip to Thin film Deposition Processes.

> **Question 3.4.4.** Hat is PVD?

- Produce condensable vapor by physical means and its deposition on a substrate as a thin film.

- Deposition species are atoms or molecules or a combination.

> **Question 3.4.5.** How to physically produce a vapour?

Near the cathode, there is localized heating- high temp generated to melt. We can expose to laser beam, electron beam, etc. Momentum of the electrons in electron beam is stopped hence energy generated and temp rises.
Sputtering by plasma: dc. Radio frequency for dielectric sputtering and magnetron for higher sputtering rate.

§3.4.ii Thermal Evaporation

- Material heated to attain gaseous state, caried out under high vacuum conditions (10^{-7}). Insert diagram of bell jar vacuum system for deposition of thin films by electrical resistance thermal evaporation (later). Copper will melt easily, without Tantalum impurity. Water is adsorbed onto the surface. Shutter is kept to act as protective covering. When sure of no contaminants, expose to the material that is being evaporated. Must get 10^{-6}, at least 10^{-5}. Initially adsorbed gas, now gone. Can keep quartz crystal monitors based on piezoelectric effect. The mass changes and hence natural frequency of vibrations changes. Another way is to go to angstrom level, strain is produced and we can get the deposition rate. Thicknesses are predtermined for applications.

- Pump down to $1\mu torr$

- Place wafers upside down to reduce particles.

§3.4.iii Resistance heated evaporation sources

Diagram (later). Indirectly heated by charge.

§3.4.iv Electron Beam Heated Evaporation

In thermal evaporation I^2R heating melts the material and it gets deposited. Here by Richardson Law, on heating Tungsten filament, stable current coming out of it, to a narrow orifice which is grounded. When the electrons are emitted from the surface, they are accelerated by the electric field (gradient of potential diff is large). Having generated the electron beam, material to be evaporated is kept (diagram (later)), impress a magnetic field. Bend the beam by Lorentz force to get it to the centre of the crucible. Vacuum in the two are different. We have also used this for Uranium (235, 238) evaporation, laser to separate. Huge power used. Electron guns that operate t $1200kW$ also exist in other countries. Kinetic energy of electrons generates heat. Melts and evaporates. Vapor generated come up and deposit uniformly. In some application, suppose we need 20 multilayers (glasses that we wear have graded refractive index). We can rotate to get multilayer coatings.

> **Question 3.4.6.** Why is there a graphite lining in the hearth?

Near its melting point, each material has its own partial pressure. Copper can melt at 1000^0C but carbon has $T_m = 3000^0C$ so its partial pressure is negligible. Some other materials have lower melting points.

> **Question 3.4.7.** What are the drawbacks?

- At $> 10kV$ incident electrons may produce X-rays. For commercial systems this is infeasible.

- Re-deposition of metal droplets blown of the source by vapor.

§3.4.v Electron beam heated evaporation

- More complex, but extremely versatile.

- 270^0 is most preferred.

§3.4.vi Evaporation Support Materials

- Refractory metals:
    - Tungsten (W) : MP $= 3380^0, P^* = 10^{-2} torr$ at 3230^0C
    - Tantalum (Ta): MP $= 3000^0, P^* = 10^{-2} torr$ at 3060^0C

not go through the transparancies, CVD just for sake of completeness.

§3.5 Chemical Vapour deposition

Chemical Vapour Deposition: of a solid on a heated surface by chemical methods. Advantages are:

- High throwing power for ease of filling.

Disadvantages:

- Toxic precursor handling becomes a problem.

- Even in deopisition of solar cells, toxic byproducts. Best solar cells from Panasonic also produced by CVD.

No more discussion on CVD.

§3.5.i Difference between PVD, CVD

- (later)

> **Question 3.5.1.** Need of Vacuum in PVD?

Protect purity, collision with residual gas during transport. No need to worry about inflation and growth.

§3.5.ii Sputtering process

We have a solid surface. Rare gas doesnt interact with solid. Energy low then adsorbed on the surface. If the energy of ions are in $10keV$, momentum excahange, atoms displaced or implanted (if energy is high). Finally energu is dissipated. For low energy, bounced back. When around $10keV$, collision cascade onto the surface. Some atoms come out of the surface due to instability. Incident atoms setup collision cascade and become unstable. Some of the atoms come out of the surface. Atom which is sputtered out of the surface is deposited to form the coating.

Sputtering Impact of the atom or ion on the surface produce sputterin from the surface resulting from momentum transfer leading to collision cascade.

We need energetic ions. How to deposit $4m \times 4m$ mirror, cant do ion beam. Need a huge source of ions: uniform incidence of ions onto the substrate surface. Film likely to be amorphous. Mobility of ions on the surface hence doesnt crystallize.

Basic feautres of sputtering:

- Target surface doesnt melt.

§3.5.iii Sputter yield

Number of target atoms emitted per something(later)

- Helium is not used since we need high atomic weight process gas (momentum shouldnt change easily).

- Low atomic weight cathode material.

> **Question 3.5.2.** Why is sputtering preferred?

High chemical purity. Good adhesion between thin film and the substrate. Deposition of very thin layers and multiple layers of different materials. No need for high temerature.

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§4.1 Sputter deposition

The transfer of momentum from incident energetic particles to a solid resulting in the ejection of surface atoms.

Sputtering Yield is different for different particles. For depositing a given stoichiometry, need to optimize the paramters apriori. Maximum yield for the following conditions:

- High Atomic weight process

- Different packing density in different plane directions (1,1,1) different arrangement of atoms than (1,0,0).

- low atomic wieght cathode material

- low concentration of reactive gases in the environment.

§4.2 Parameters that can be controlled during sputtering

§4.3 Why Sputtering is preferred?

Last time CVD was introduced briefly. Chemical deposition results in thin film by splitting the chemical precursors. These are toxic. Lot of Carbon content in reactions. Exhaust also toxic. In sputtering, no toxic.

- High Purity- no gases, no carbon contamination.

- good adhesion

- Deposition of very thin films: Lenses have 20-30 layers of varying refractive index thin films.

§4.4 Why Argon is used as Inert Gas?

§4.5 Plasma

Definition 4.5.1. Plasma: An assemblage of free positively and negatively charged particles ans neutrals, where the negative and positive charges nearly balance each other at the microscopic level ($n_e = n_i$). Also called fourth state of matter.

Example 4.5.2

Plasma is present in Gas discharges in laboratory, Fusion reactors, nuclear fusion: high energy needed to overcome repulsion at very small scales to end up with 14.2 MeV.

> **Example 4.5.3**
>
> Water going to hydrogen and oxygen ions if too much energy is dumped into it.

Degree of ionization:

$$\frac{n_i n_e}{n_a} = \left(\frac{2\pi m_e KT}{h^2}\right)^{\frac{3}{2}} \left(\frac{2G_i}{G_a}\right)$$

Net charge density is zero. Lets put a positive test charge as a perturbation. Charge neutrality deviated, leads to electric field.

Debye Layer: Because of perturbation, shielding of test charge. Fall of field falls very fast. Charge deviation from the neutrality existing up to Debye layer.
Collective Behaviour: Electron cloud tries to come towards the ion cloud. Oscillations get set up.

Summary: Plasma has

$$n_e = n_i \tag{4.1}$$

$$\lambda << L \tag{4.2}$$

$$\omega_p >> \omega_c \tag{4.3}$$

$$N_D >> 1 \tag{4.4}$$

$$N_D = n\frac{4}{3}\pi\lambda_D^3 \tag{4.5}$$

$$\lambda_D = \left(\frac{\epsilon_0 k_B T_e}{e^2 n_e}\right)^{\frac{1}{2}} \tag{4.6}$$

By calculation, the field needed to separate the electrons from the ions required is $\sim 5 \times 10^9$ V/cm. But actually energy needed is lower. The large # of collisions help in getting the energy lower by exchange of particles.
Suppose we have a gas. Some fixed ionization potential. If photon of energy higher than ionization energy is incident, it is absorbed and the gas ionizes. The calculations give = 1239.8nm which indicates Ultraviolet radiations.

$$\frac{1}{2}mv_e^2 = |eV|$$
$$\frac{1}{2}Mv_i^2 = |eV|$$
$$\text{For} V = 10V$$
$$v_e \sim 1.8 \times 10^8 cm/sec$$

For $n_e \sim n_i$, it is evident that most of the discharge current(later).
Ion and neutral have almost the same mass so complete transfer of momentum and energy. When electrons collide with the neutrals and ions, energy momentum transfer is very small fraction of the total available.

§4.6 How is the plasma generated

Cathode and Anode in a discharge tube. Strength of the electric field (V/d), will generate electron-ion pairs. In a normal room, the collisions make these pairs recombine and

neutralize continuously. However, in a Discharge Tube, electric field will direct the electrons towards the anode with a high velocity, and ions towards the cathode with low velocity. Electric field acting on the particles will accelerate them in opposite directions, gain more energetic and collide with other particles and transfer the energy. Say Argon transfers the energy to neutral atom which gets excited and then keeps exciting to higher and higher states. The lifetime of excited states is greater than the rate of collisions so that the excited states don't de-excite by the time next collision happens.

§4.7 Electric Discharge regimes

Dark discharge, glow discharge and arc discharge. Voltage vs current graph. On raising the voltage, current rises, then Saturates. Once breakdown voltage is reached, normal glow: column has become conducting and voltage drops down. There is a glow which increases with increase in current to an abnormal glow. Non-uniformity (presence of sharp objects) causes corona discharge as these pointy objects have large Electric field concentrators. This is why there is hysteresis. Heavy energy ions bombardment at the cathode: Secondary electron generation at the cathode are vital to creating the plasma. The supply of secondary electrons is possible because of this. The enegy of electrons cycles with higher energy.

§4.8 Plasmas- DC Glow Discharge

Around the Cathode dark, then negative glow, Faraday dark space, positive column with stiations -which is the plasma.

§4.8.i Paschen Curve

pd Product needs to be optimized. Need to throttle pumping speed to get to the optimal point of the **Paschen Curve**: V vs *pd*. Minimum sparking voltages table.

§4.8.ii The Glow Discharge

The drift velocities of ions and electrons are very different. Ions around cathode form a positive space charge. Whatever the voltage that is applied, the space charge and negative cathode gives a strong potential gradient. Maximum of the voltage drop is across cathode and space charge around it. Length of positive column has very weak voltage gradient. If across the cathode strong electric field, Argon ions hit it with very high speed and cause sputtering. This is how **DC Sputtering takes place**. Number density vs length plots. Potential drop plot.
For resistance, strong space charge is generated and causes **Arcing**.

> **Example 4.8.1** (DC Sputter Deposition)
> Put target on cathode. Argon ions sputter the cathode by collision. Deopist coating.

Conventional D.C. sputtering

- Arcing : to be avoided to prevent non-homogeneity.

§4.9 R.F. Sputtering

- Consider a quartz disk to be used as a sputter. Target in conventional DC sputtering system for depositing a SiO_2. Use AC field. Impedance of dielectric falls at high frequency.

- Frequencies less than 50 kHz: electrons and ions in plasma are mobile- both following swtiching of anode and cathode. Basically d.c. sputtering of both the surfaces.

- Frequencies more than 50 kHz:
    - Ions (heavy) can no longer follow the switching.
    - electrons can neutralize positive charge build up.

§4.9.i R.F. Sputter Deposition

Blocking capacitor used to prevent current flow from the Ac source. The gas is under low pressure. Plasma is formed. Electron and ions in the volume formed. Negative space charge accumulated on the capacitor. On the reverse, ions should come and neutralize but mobility is lower than that of electrons, hence overall # of electrons are more than ions. Negative charge accumulation will give negative charge on the plate in steady state. That is steady state negative voltage - Biasing. The electrons in the vicinity are pushed away and create a sheath. Some positive potential develops on plasma- Plasma Potential. In the process hits the target. Most RF generators have R.F. impedance of 50 ohms. Plasma generated may not have impedance equal to 50 ohms. The power is not optimal. Spoils the R.F. generator easily. Make sure that there's no reflected power. Need to Match Impedance. Do by Matching network. It tunes the resistance and capacitance to get the required impedance.

$$\frac{V_1}{V_2} = \left(\frac{A_2}{A_1}\right)^m$$

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§5.1 RF Sputter Deposition

Diffusion of electrons leads to plasma potential too be positive. Need a negative charge on the blocking capacitor. Oscillating frequency source. electrons get attracted to the positive plate, negative space charge gets built. Due to difference in mobilities of ions and electrons, per cycle negative charge accumulated is not compensated by the ions. Thus negative voltage is developed - called **Negative charge "self bias"**. More # of electrons, less ions, dark band which is called shield. Electric field is set up and the positive ions bombard the powered electrode, thus leading to the sputtering of the target. The substrate. Developed negative DC potential, can't pass through the capacitor because of infinite impedance. It will decay over time, but continuously supplying RF. All power standards work at 50 ohms. If the full RF power is not dumped, reflected power comes with reverse loading. This could damage the expensive equipment. Hence impedance matching to make the load 50 ohm. By adjusting the capacitor, can tune the reflected power to zero. How to measure RF voltage, and DC voltage that is induced. For RF, $j\omega L$, for DC, can put a simple voltmeter.

§5.2 RF Plasma

Small target being sputtered. If there is a situation of not being able to ground the state,

$$\frac{V_1}{V_2} = \left(\frac{A_2}{A_1}\right)^m$$

We have to floor.

§5.3 Disadvantages

- Low deposition rate

- RF power supplies are complex to design, relatively expensive

- Scale up of RF system needs huge power supplies that are difficult to build.

§5.4 Reactive Sputtering

- Deposit films of insulating materials from a metallic target forming insulator through chemical reaction with a background.

§5.5 Magnetron Sputtering

Higher rate of sputtering. Put a magnetic field so that Electrons with velocity get acted on by Lorentz force $qv \times B$. The orbital motion increases probability that they collide with neutral species and create ions.

§5.5.i Impact of magnetic field on Ions

Hopping radius $r \sim \frac{1}{B}\sqrt{\frac{2m}{e}V_d}$
where V_d = voltage drop across dark space/sheath, nearly 100V.
As a result:

- current density

- (later)

§5.6 Ionized sputter deposition

Depositing atoms that are themselves ionized. In some of the systems, additional means available. For cutting tools.

Question 5.6.1. What is the advantage of magnetron sputtering?

Increased ionization efficiency in the magnetron mode. Some of the applications are mentioned. We stop discussion on this module here.

6 Design aspects of Plasma Nitriding Processes

Nitriding must have been discussed during Heat Treatment. Scope for technology in India.

> **Question 6.0.1.** What is Nitriding?

Nitriding, Nitro-carburising are temperature treatments that produce thin, hard layers on the steel surface to improve its wear. Moment hardness increase, loss of ductility. Stainless Steel has many elements. Hardness is around $2GPa$. In the workshop, if double the hardness, they last for 12 weeks. In Steel, Chromium nitride, other nitrides, all hard ceramics. Intrinsic hardness goes up. Composite hardness goes up. Even though particles are discrete, form Si nitride, vanadium nitride, volume is more, local expansion, leads to zonal compression. Hardness enhancement is because of two reasons. Leads to enhancement of hardness. We can make the component hard but at the cost of fracture toughness.

Nitrogen has to diffuse, needs heat. Thermochemical Treatment.

§6.1 Nitriding Process

Need supply of nitrogen activity. When the nitrogen diffuses from the surface into the core, it is firs dissolved interstitially. If the conc, exceeds 2.5% solubility limit, then a single or multi-phase nitride is formed. Intrinsic hardness of composite goes up. Preferably carry treatment at $400^0 - 600^0$. Ammonia in contact with heated steel surface, catalytically decomposed into nitrogen, diffuses into the steel.

If at the same time carbon diffuses to the surface zone, process is called **nitrocarburizing**. Fe-C phase diagram, on crossing 4. something, starts forming Fe_4N upto 6.7%. Beyond γ phase, $\epsilon + \gamma$, both provide corrosion resistance and hardness. Hardness of around 14-15 GPa on the surface. Hard case formed on the top. Soft ductile matrix below. Phases are crystallographically different. These two phases expand at different rates. If the case os thick, there will be microcracking. Top layer comes out. Objective to get a single phase. Ductile loss. Better of with single phase nitride on top. Mixture of phases is trouble.

§6.2 Carburizing

Invlolves changing carbon content of the surface followed by quenching to convert surface layers to martensite. Carbon can diffuse in but on cooling, it will tend to come out. On diffusing in, suddenly quench it so that carbon diffused in stays there. Strong martensite structure formed.

§6.3 Nitrocarburizing

§6.4 Porosity

Got a situation with diffused nitrogen (Nitriding). We need nascent Nitrogen not molecules. If the nascent nitrogen is not reacting, they can form nitrogen molecules that tries to come out and forms pores. Gas nitriding process creates porosity or blisters on the surface. To get precision machine tools, can't afford to have blisters. Removing of 14-15GPa hardness layer will be lost if tried to polish.

§6.5 Layer structure in nitrided zone

γ compound layer.

§6.6 Nitriding process

Substrate, γ phase, below that is the diffusion layer.

- Ammonia creates nascent nitrogen which diffuses in.

- Use molten salt which provides nitrogen.

- low energy nitrogen plasma

Sketch of gas nitriding chamber and equipment. Job kept on the platform with motor and fan. Ammonia tank fills in through flow meter. Small fraction of Ammonia goes outside, to bubble it through water. Huge units. Needs to burn continuously for 60-70 hours. $2N \longleftrightarrow N_2$, in addition, atomic hydrogen also $2H \longleftrightarrow N_2$. Ammonia conc. in air 25% is flammable environment, can lead to fires. Hence components of gas nitriding chamber must be periodically examined for any signs of fatigue or corrosion and if discovered, must be replaced.

Treatment cycle is long. Safety issues because of leak. Here ammonia concentration is not dilute, can be fatal for aquatic species even in minute quantities which constitutes an environmental hazard. Ammonia handling, safety aspects without too much of control. Some of the nitrogen can come out and create blisters.
In any industrial coating, get rid of oxide phase.

§6.7 Salt Bath Nitriding/Liquid Nitriding

A mixture of molten potassium. Salt bath is heated. Disposing of poisonous components is not easy.. Secondary waste components. Contaminating surface, cleaning is not easy. It is an old technology with a negative impact on environment. Salt bath nitriding will not give pure nitriding but carbon nitriding.

§6.8 DC Plasma

Cathode has samples to be treated. Cathode is negative. Argon gas in the system. Depending on voltage and pd product, there is a breakdown if gas and plasma formation.

Positive ions, go towards the cathode. Impact the ions with energy. Initially, if there was a steel with oxide on surface. Removed by sputtering. This is called **Sputter cleaning**. Hydrogen generated will remove. Nitrogen plasma is formed. Cathode is at negative. Around it there will be a plasma. Forms sheath around the cathode. Previous technique, Provided nitrogen activity and diffused in nitrogen. Here we have provided nitrogen concentration. Heat dissipation is automatic. Dont need heaters. Efficient. Chamber with power supply. Leak is visible very easily. Plasma generated in the chamber. Operate at high current density. Abnormal glow region in voltage characteristics diagram (later). Gas consumption: from 20 l/h to 500 l/h, treatment time.

§6.9 Technical Advantage-Plasma Nitriding

Gear cutter, Through the sheath, uniform nitrogen. Batch processing during plasma treatment. Abnormal glow discharge- current density is high. At voltage of $1 keV$, the power supply required is huge, so impossible to nitride 25 cm in one go.

§6.10 Properties of Plasma Nitrated surfaces

- Improvement in surface hardening

- greater wear resistance

- Longer fatigue life

- Corrosion resistance

- Process can be applied to wide variety of metals
    - Cast iron
    - Stainless Steel
    - Tantalum

Biggest advantage that lapping is not needed. Read upto

§6.11 Plasma Carburizing

Work piece is heated.

§6.12 Active Screen Plasma Nitriding

In recent years, an innovative Active Screen (Through Cage) Plasma Nitriding. Pendulum motion of two walls can create arc. In this situation, no active potential, immersed in plasma, hence results are good. Components being immersed in plasma. Whether nitrogen ions or nascent nitrogen is still debated on. Oxide layer, White layer and diffusion zone. Generte some Fe_3O_4 layer, acts as corrosion response.

§6.12.i Ecological Advantage: Emissions comparison for gas and plasma nitrides

The gas consumption in plasma nitrides is ten times lesser.

Huge gas consumption	Less consumption
	cleaning not a problem
	Health safety issues

§6.13 Automobile gear manufacturing

Global gear production
China
South Asia
Eastern Europe
Huge scope, at present the plasma nitriding. Industries want.

7 Lecture Jan 30

§7.1 Logistics by Gauri Shankar

Starting monday, 2-5pm. Prof. Patil uses motion energy. Prof. Gaurishankar will teach generation of energy. From different types of waste, we can generate waste. Throughout Feb and March. Timing sharp at 2pm.

§7.2 Design of Microvawe Sintering Furnace

In powder metallurgy we have seen the process of sintering. Densification of powder compact. Conventionally heating is generated by resistance heating $I^2 R$ will be the heat generated. In case of microwave sintering, needs high temperatures. Suppose high melting point ceramics like alumina are used. **Microwaves** are electromagnetic waves with wavelengths ranging from 1m to 1mm which corresponds to frequencies b/w 0.3 to 300 GHz. For microwave heating, the two most commonly used frequencies are 0.915 and 2.45 GHz.

§7.3 Microwave-materials interaction

Microwave interaction is used to generate heating. Interaction of electromagnetic waves at molecular level and the dielectric properties ultimately determine the effect of the electromagnetic field on the material. Incident wave has E and H fields, the dipoles in materials is deflected by the fields and leads to resistance which causes heating. Electromagnetic waves should be able to penetrate the materials.

§7.4 Dielectric Properties

It is the **dipole polarization** that is the most important one for energy transfer at the molecular level. Dipole changes its orientation and results in polarization that in turn creates a time lag called **relaxation time**. This time lag is due to dissipation of energy as heat within the material. Microwave heating is a result of this energy loss. To transmit electromagnetic waves, need materials that are low loss- insulators, hence called Transparent. Opaque: electrons excited by incoming radiation so that oscillations are set up which radiate their own energy. Hence don't use metals inside the microwave. Reverse output leads to arcing on the metal. Even ceramic plates with ceramic lining shouldn't be used. **Absorber** (lossy vs mixed) has penetration from partial to total. Matrix composites: dielectric properties of each constituent is different. Penetration depth for metals is few microns. Electric field doesn't go beyond that. Scientifically, the microwave heats the material. Penetration depth is defined as distance in direction of penetration at which incident power is reduced to half

$$D_p = \frac{3}{8.66\pi \tan \delta (\epsilon')^{\frac{1}{2}}}$$

where ϵ' is capacitive part of the complex permittivity. In metals, the propagation is described in terms of skin depth. Higher conductivity, lower the skin depth. Skin depth

is given by

$$\delta = \frac{1}{\nu\pi\mu\sigma}$$

Materials with low dielectric loss factors have a very high penetration depth.
Most effective transfer of microwave energy is in the middle of the conductivity range.
The dielectric properties are dependent on the mobility of the dipoles within the structure,
and therefore the dielectric properties are functions of temperature and frequency. Thus
the ability of the material to absorb energy changes during processing.

Example 7.4.1 (SiC)

SiC Ceramic has a loss factor of 1.71.at 2.45 GHz, but at higher frequency, it changes
(later)

Heating patterns in conventional and microwave furnaces. Sample surface gets heated
up. On going to 1800^0C, it will heat up the sample surface. Driving force for sintering is
minimization of surface energy. Hence, on surface first, slowly moving inwards. When we
start with the green compact of a powder, 40% volume is inside. Grain growth causes
porosity to be trapped. Gases inside cant comes out if the outside surface is sintered first.
Porosity causes stress concentration. Sample fails. Let us assume that they are uniformly
penetrated into the material. Power dissipation by a dielectric in a microwave is:

$$P = 2\pi f\epsilon(E^2/2)\tan\delta \tag{7.1}$$

where P= Power dissipated in the material
ϵ- Dielectric Permittivity
(later).
Dipole interacts with electric field, resistance, heat generation. Loss of heat energy from
surface is more than that from the core. In the core, heat will be more. $tan\delta$ which
tells you about how the power is dissipated, higher the mobility, higher the $\tan\delta$. $\tan\delta$
Higher at centre than at the surface. More heat generation at the centre. Temperature
more at centre. $\tan\delta$ is more for higher temperature as it is the dipole response to
electric field and higher temp means high mobility $\implies$ higher $\tan\delta$. This leads to
Temperature gradient b/w centre and surface. Sintering proceeds from centre to surface.
Heat gradients are from inside to outside. Outside surface being porous, this leads to
uniform sintering. In microwave sintering, temp goes up to 1600^0C quickly because
system inertia is very poor. Volumetric heating from inside leads to low system inertia.
Gives fine microstructure.

§7.5 Conventional Processing

We have discussed

- High temperature

- too ling duration

- Surface heated first

- Large grain growth

- Selective evaporation

- Huge power supply.

Materials with loss dielectric factors (or conductivity). Cermaics are good candidates if in appropriate range (later).
The loss tangent, $\tan \delta$, varies at room temperature.

§7.6 Temperature dependence

Temperature dependence of loss ($\tan \delta$) of cermaics: Very small at temperatures up to $400^0 C$ and then rise exponentially Thermal alloy, melts quickly due to exponential
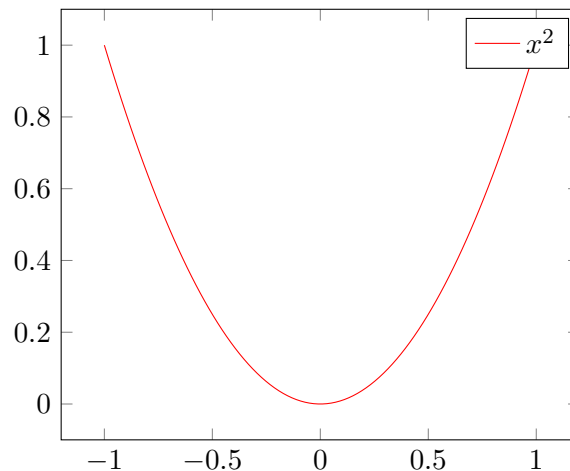

Figure 7.1: Temperature dependence

dependence of the loss function on temperature.

§7.7 Nano Materials

Optical, mechanical properties. Need to avoid grain growth. Pass the sintering temperature quickly. Waveguides propagate microwave energy. Rectangular duct used to propagate energy through it. Antenna, cavity: electrons subjected to both electric and magnetic fields, they get accelerated and generate radiation. Applicator, three port circulator provides protection as it allows flow in one direction, reflects the one coming back to another direction. Three stub tuner. Power properly matched so that there's no reflected power. Dummy load, applicator, generator, circulator, power monitor, tuner, short circuit termination.

§7.8 Components

- Microwave source

- Transmission line

- Applicator

The ability to focus E field into sample by solving Maxwell's Equations in cavity boundary conditions and get regions of high concentration.

TM Mode resonant mode for cylindrical sample: Field interacts maximum if kept centrally, aligned with the axis.
Temperature profile within the sample in conventional heating, microwave heating ans microwave hybrid heating.

§7.9 Hybrid microwave

Metal will arc, hence put in a sealed ceramic tube. Sample has insulation because it will provide heat for the sample. Alumina or silica used. SiC susceptor ahs dielectric loss of 1. This will get heated up very easliy, hence convetnional heating of sample. Surface walls are metal to keep waves trapped inside.

$$Q_k = 2\pi Lk(T_f - T_s)\log\left(\frac{D_2}{D_1}\right)$$
$$Q_k = Q_C = IV$$

§7.10 Research

AKP30MG conventionally sintered vs Microwave sintered.

§7.11 Alumina- Zirconia Ceramics

Microwave sintering schedule for $Al_2O_3 : ZrO_2$ ceramics. Zirconia decides the size formation.
Appearance of highly transparent Al_2O-3, sample microwave sintered.

§7.12 Assignments

Assignments have been uploaded. Exam for 1hr in mid-February.

8 Lecture 3 Feb

§8.1 Personal Background

Roorkee background. Uncle's (who was a professor) advise to join Roorkee. Roorkee also famous as with IIT. Thompson college for civil engineers: diverted a canal starting for Bhardwal to Kanpur. The canal was so wide, covering many rivers. The engineers built many aquaducts where the river flows above the canal. There was another river going below the canal. Till date it is working. The inclination given to the bridges. It was one of the very best civil engineering colleges. He said that why to waste one year? So did Bachelors and passed out from Roorkee in 1971. Followed by Mtech at IITB. Did not sit for the placements.
Wanted to learn the subject. Went to Bokaro Plant for training. Dissapointed to find that there was no interest in training. Started with co-MTechs a magnetic storage product. Just copying the design was not satisfying so we built our own design in MIDC Kharagpur. Converted thei MTech research into industrial product. Replaced material for magnetic applications. Started a job in a world level plant- Oswal Fertilizers. HindCo bought them. Got assignment to revamp the use of sulphuric and nitric acid. Sulphur is imported from the middle east. Succeeded in bringing the technology from Loorgi Metallurgy. Not only worked with companies but also built myself. The Japanese put up regenerative Combustion systems.

> **Question 8.1.1.** What is regenerative combustion?

They could recover heat in the process of combustion. Based on Honeycomb (to come later).

§8.2 IITB Courses

Got an opportunity to teach at IITB. There's two courses out of which one is Equipment and Process Design. Two aspects: energy and environment. Japanese regenerative combustion system. Generate steam at 1600^0C.

§8.3 Purpose of Teaching

§8.3.i Superheated Steam Gasification

Plastic waste is a big problem. Cannot incinerate plastic. No pyrolysis either. Here, this technology does not burn, just decomposes. Saving of fuel. If we want to burn , mix air and start pressure to burn fuel oil. Dont think of quantity of air being put in. Refer to stoichiometry. Don't add excess air. Mixture of nitrogen and oxygen. From N_2, burning leads to NO_x. These are harmful. Hence the technology. Will teach both technology's energy and environmental aspects. Controlling air to fuel ratio. Two things at the same time to cut down the fuel and cost; pollution control: such as chlorine, sulphur dioxide. Plastic is a big menace. Gasification of plastics. Mercury is very dangerous. Emissions contain mercury, carbon monoxide. How to process these. Can see several flares in plants. In cement technology: neutralizing techniques. Convert to fertilizers. No

dumping. Capturing CO_2. Recover heat from the exhausts for Preheated combustion air. When air is burnt in ambient temperature that is at higher temperature, specific heat causes higher efficiency of combustion.

Plant diagram (later).

§8.4 Waste to Energy

§8.4.i Using High Temperature Steam Gasification

Gasification

- Biogas: Biological Gas. Water's heat is very high. Japanese collect all the leaves and they convert to air conditioning in all places. Hitachi using in thermochillers.

- Syngas: Synthesis gas could be water, butane, propane, butane. They synthesize together to form a product.

§8.5 Gasification

Gasification of biomass has been one of the prominent ways to produce fuel for various purposes. Biomass stsnds for bilogical mass. India is a large country with a huge landmass. This can provide sustainab;e quantity of fuel in terms of biomass. Biomass as trees, vegetables. Some of these trees have very high calorific values. Kashmiri trees have nearly 4 times the calorific value as that of methane. Methane has calorific value of 8000 kCal/kg. Depending on the cost of the tree, the calorific value changes. Also need to extract the thermal value in the right way. That is the main issue. We can not only do steam gasification, that decomposes into synthesis gas, which can ignite and generate heat, but there's another dimension to it. Three constraints: moisture. Loss of thermal value. Superheated Steam gasification needs adjuct processes to maintain the thermal value. In India, we have a lot of biomass at a very cheap price. If we can collect, the thermal value of biomass is ten times that of coal. Instead of importing coal and beneficiating it, use biomass. Municipal Solid Waste calorific value is 1000kCak/kg.

- This process converts waste such as biomass, municipal/residential, medical, plastics etc, into carbon monoxide and hydrogen a high temperatures with controlled amount of oxygen or steam.

- The resulting gas mixture is called Synthesis Gas or Syngas.

- Syngas as a fuel can be directly used for process heating, power generation and for allied application such as air heater, water heater, power engine.

The constraints in Biomass

- Moisture

- Ash

- Volatile

Need to maintain the thermal value. Moisture reduces the thermal value by forming steam and absorbing thermal energy by its latent heat. To remove moisture, need to

bring in an external source of heat. This costs more money. No external source if we can use a heat exchanger.

$$\text{Feed Rate} = 1000 \, \text{kg/hr} \times 540$$
$$\text{convert units} \implies = \frac{540000}{860}$$
$$= 627.90 \, \text{kWhr}$$

§8.6 High Temperature Steam Gasification

High Temperature Steam Gasification process converts the waste by direct decomposition at elevated temperature *without incineration*.

§8.6.i Advantages of Steam Gasification

Ordinary Steam Gasification. In Chemical Engineering, there is an Air gasification.

- *High Calorific Value* of the syngas is obtained compared to ordinary gasification process.

- The surplus steam is condensed to water in the downstream cooling process and it results no other gaseous component to dilute the gas.

- The tar produced during ordinary gasification process is completely reformed to gaseous components with super high temperature steam.

- System will be very compact and economical.

§8.7 Applications

- TBU