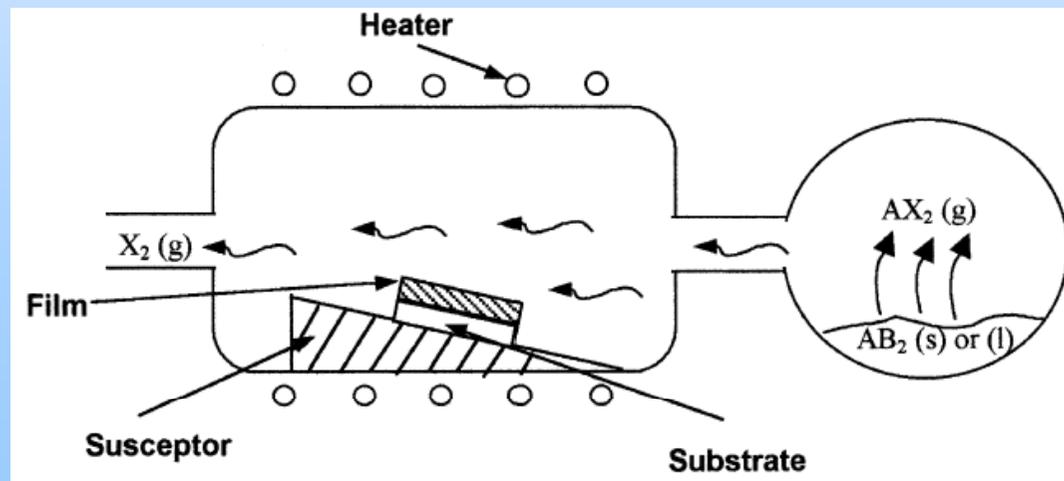


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Definition

- Chemical Vapour Deposition (CVD) involves the dissociation and/or chemical reactions of gaseous reactants in a activated (heat, light, plasma) environment, followed by the formation of a stable solid product.
- The deposition involves homogeneous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions which occur on/near the vicinity of a heated surface leading to the formation of powders or films, respectively.
- Though CVD has been used to produce ultrafine powders, this lecture is mainly concerned with the CVD of films and coatings.



Conventional CVD Processes (Ordinary CVD)

- Reactions driven by thermal energy supplied solely.
- Reactants are in ground states.
- Reactions progress under nearly thermodynamic equilibrium.

Plasma (Photon) Enhanced (PE) CVD

- Film formation resulting from the reactivity of excited species.
- Substrate temperature does not cross over activation energy.
- Substrate temperatures much lower than those used in thermal CVD.
- Cold plasma is generated at low pressure (0.1 – 10 Torr).
- MFP is short as several micrometers.
- Most electron energies are within a range of 0.5 – 10 eV.
- Plasma density is not high.

CVD named by parameter applications

1. atmospheric-pressure CVD
2. Low-pressure CVD
3. High-temperature CVD
4. Low-temperature CVD
5. plasma-assisted CVD
6. Photon-enhanced CVD

Conventional CVD Processes

1. Decomposition reactions:



2. Reduction and oxidation reactions:

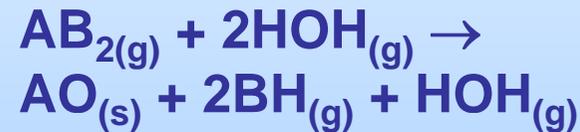


C = hydrogen or metal

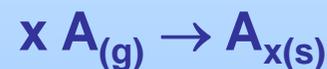


D = oxygen or nitrogen

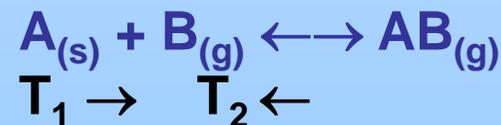
3. Hydrolysis reactions:



4. Polymerisation reactions:

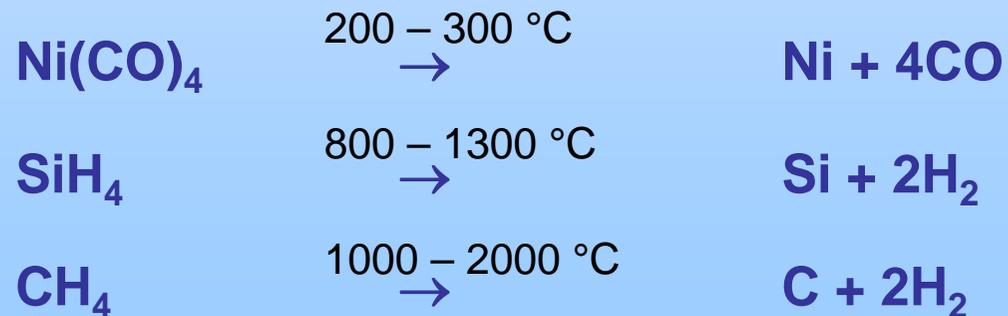
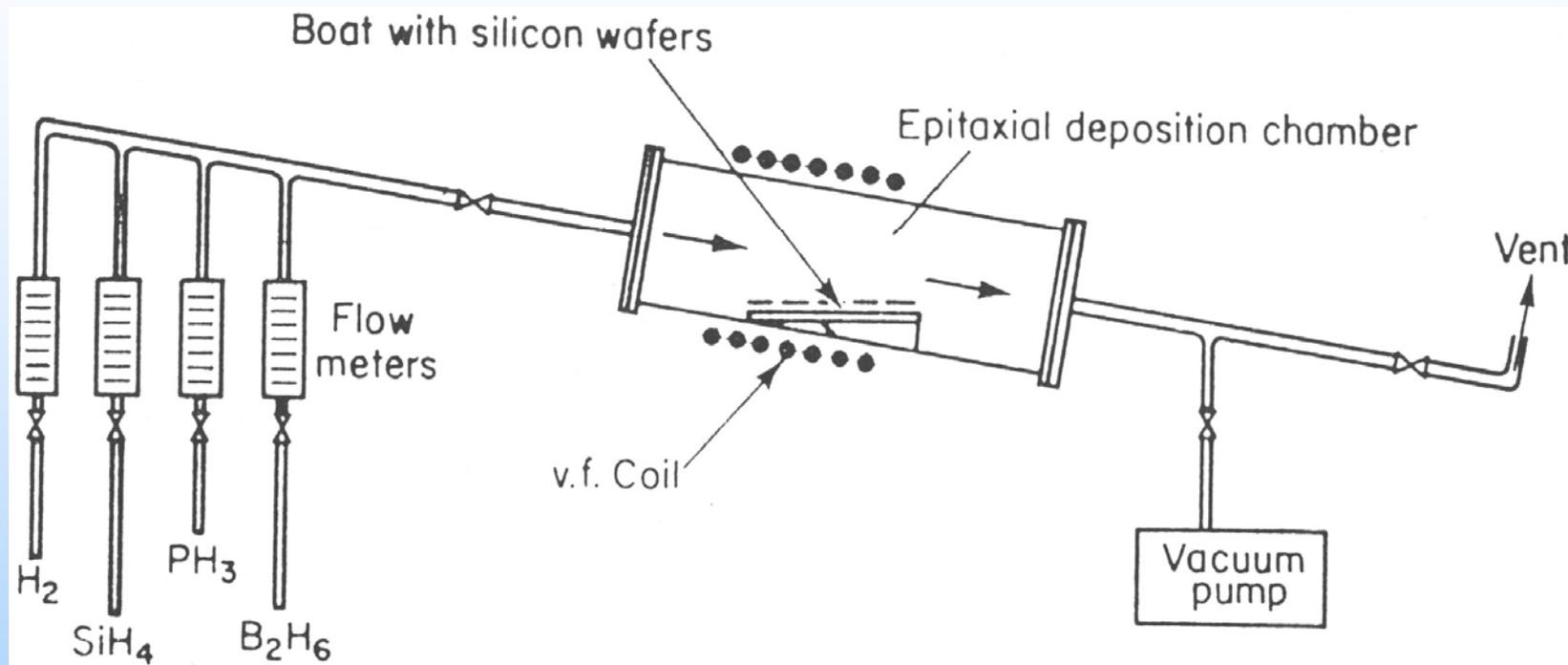


5. Transport reactions:



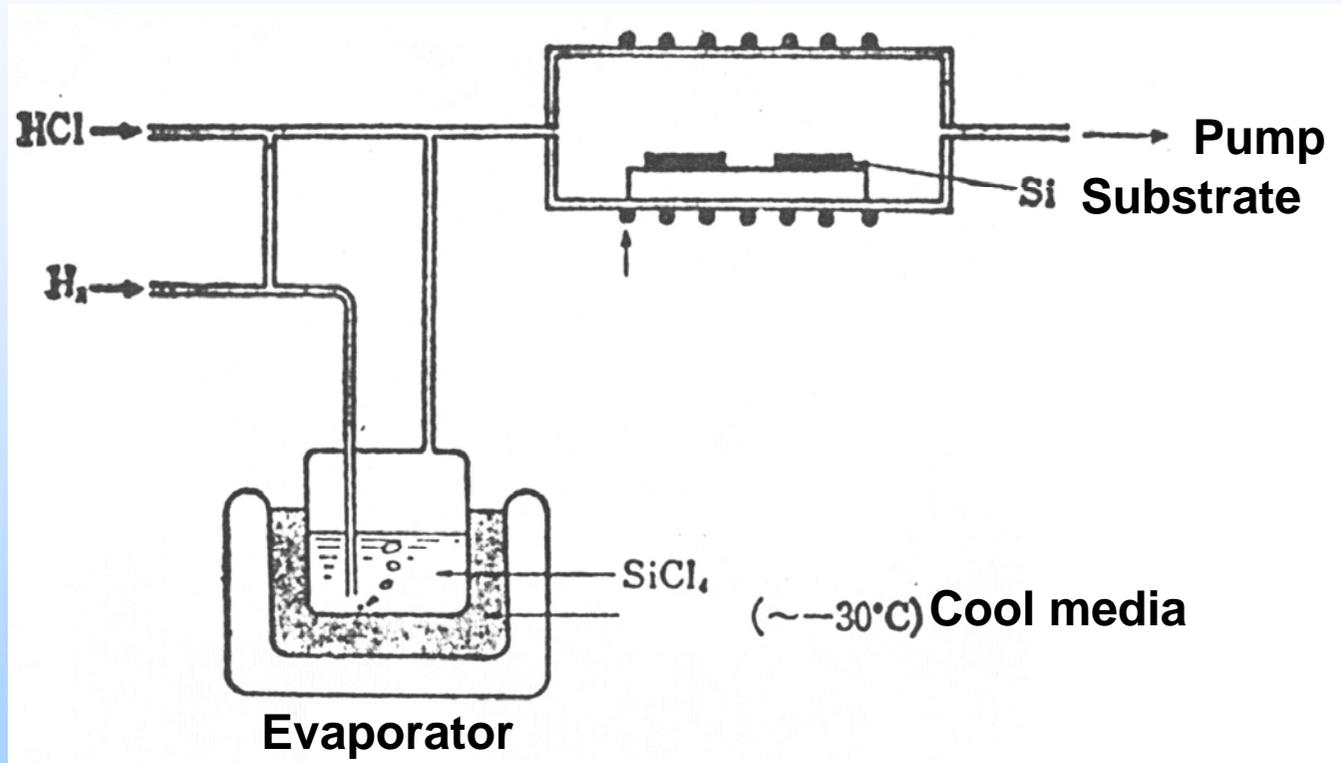
Decomposition reactions

Gas dilution hydride system



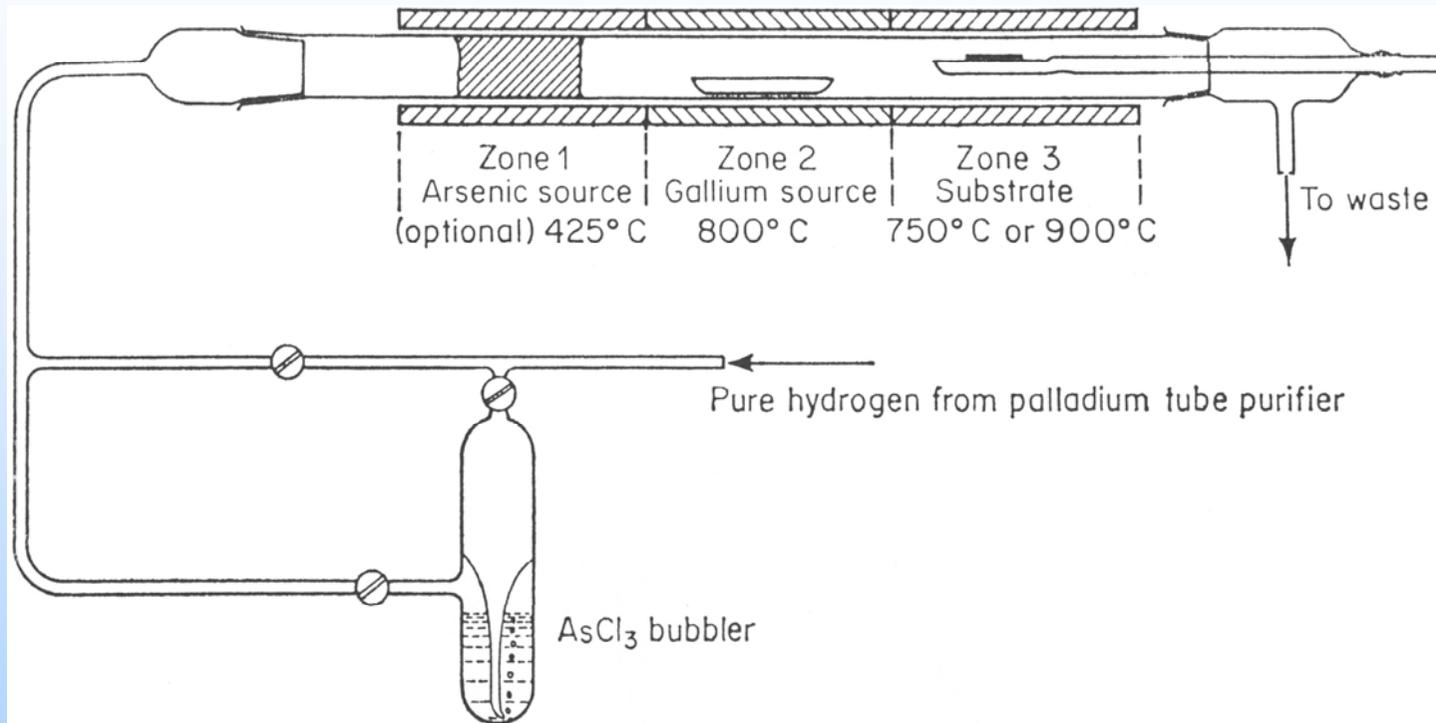
Reduction reaction

To prepare Si single crystalline layer

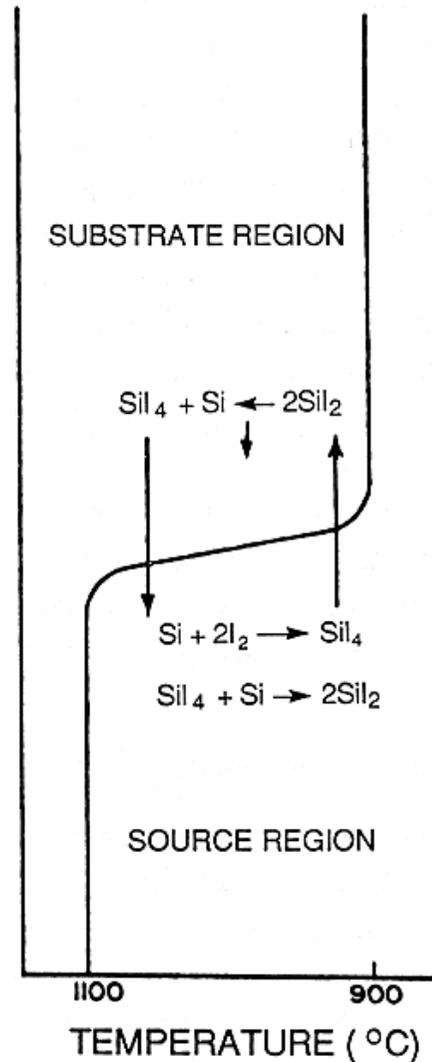
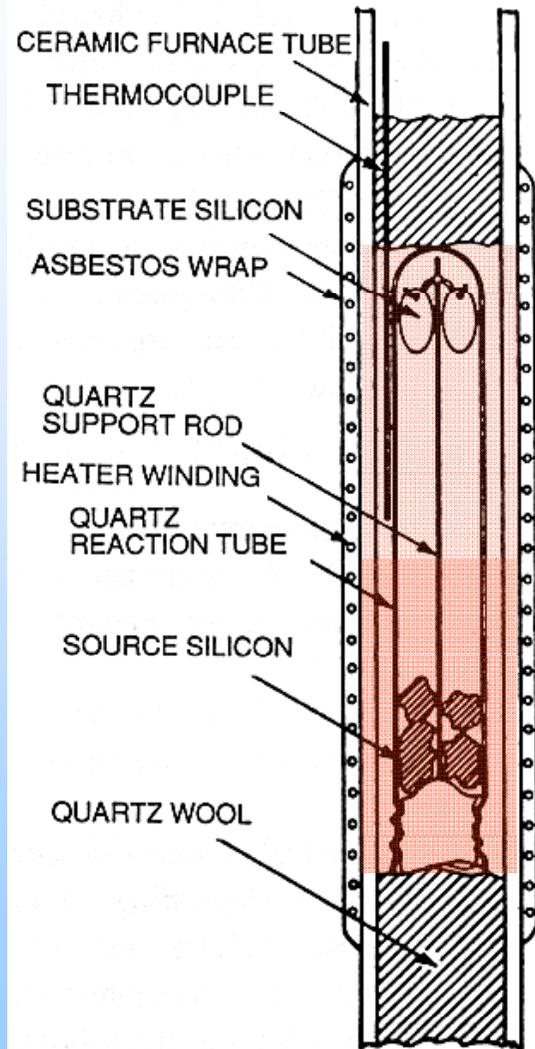


Transport reactions

System for the preparation of GaAs layers using AsCl_3 and Ga



Disproportionation – system based on the Si-I₂ equilibrium



Limitation of
conventional CVD =
high temperature
→ **PECVD**

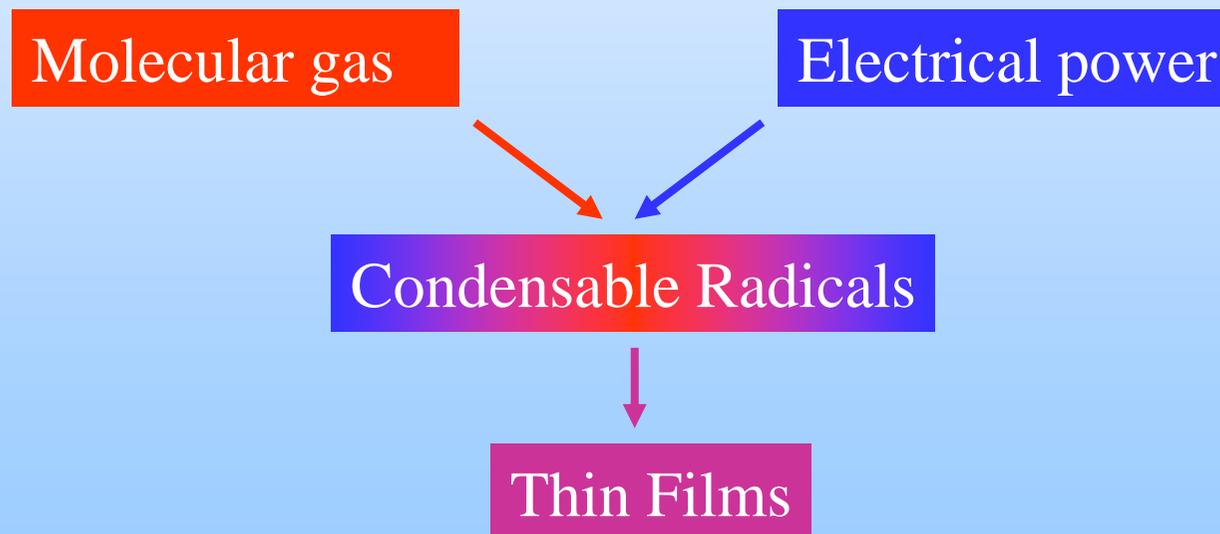
Plasma Enhanced Chemical Vapor Deposition

Different Names – the Same Process

- Plasma Deposition
- Glow Discharge Deposition
- Plasma Enhanced (Chemical Vapor) Deposition (PECVD)
- Plasma Assisted (Chemical Vapor) Deposition (PACVD)
- Electron Assisted (Chemical Vapor) Deposition (EACVD)
- Plasma Polymerization
- Glow Discharge Polymerization

Plasma Enhanced Chemical Vapor Deposition

PECVD: A thin film deposition techniques in which molecular gases are decomposed into condensable radicals by supplying electrical power via electron impact dissociation

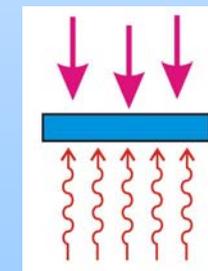
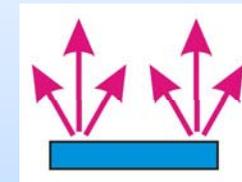
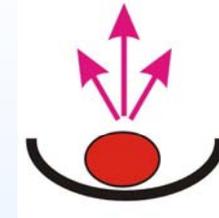


Why PECVD?

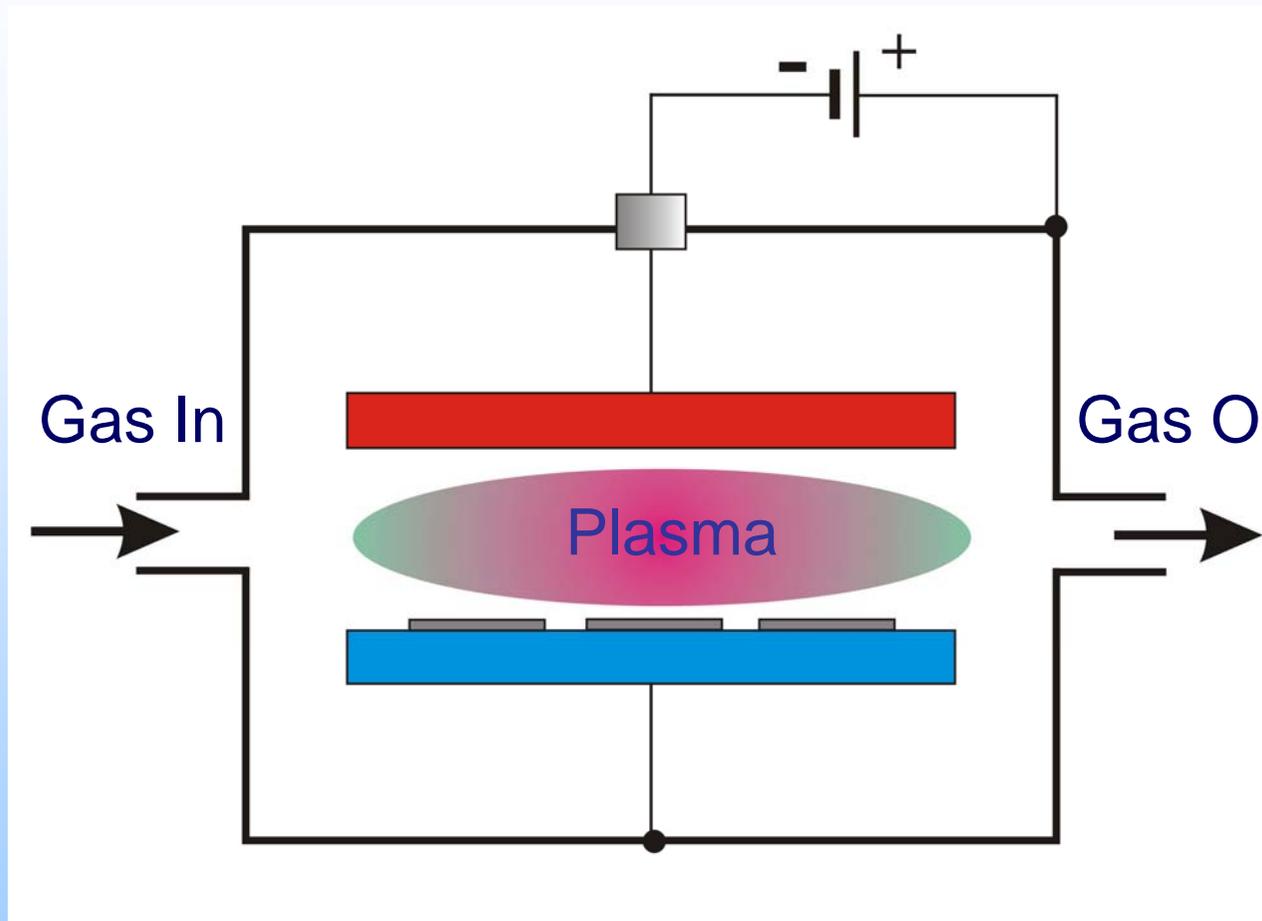
- **Evaporation:** Alloys fractionate; Crucible interactions; line of sight
- **PECVD:** no fractionation, no crucible, not line of sight

- **Sputtering:** Limited composition control; line of sight
- **PECVD:** Excellent composition control, not line of sight

- **CVD:** High temperatures, small areas
- **PECVD:** Much lower temperatures and inherently large areas

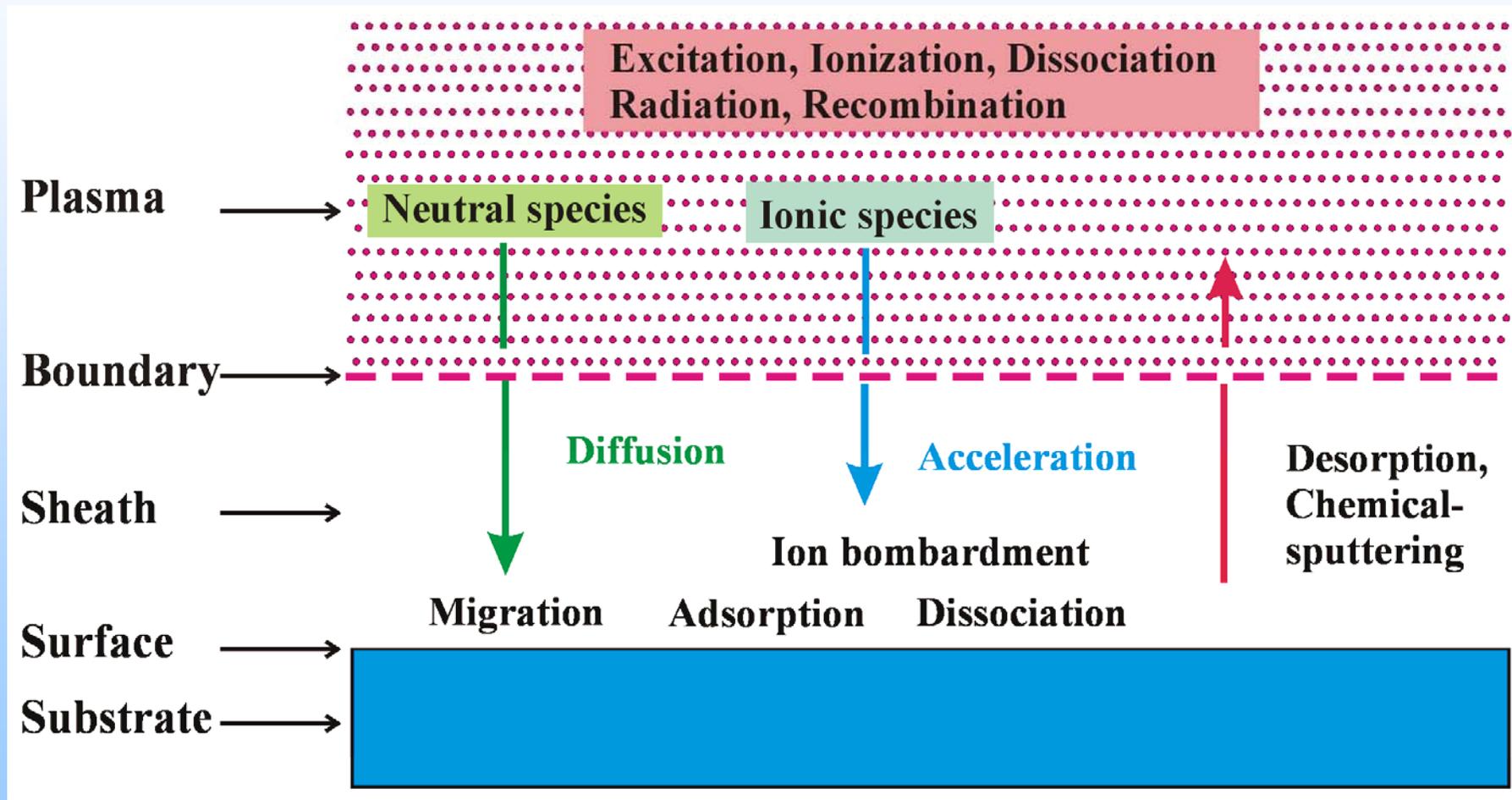


PECVD: Effective Deposition Technique



A few hundreds volts and a few hundreds mTorr
Glow Discharge Plasma

Schematic representation of plasma enhanced CVD reaction process



Plasma Enhanced CVD

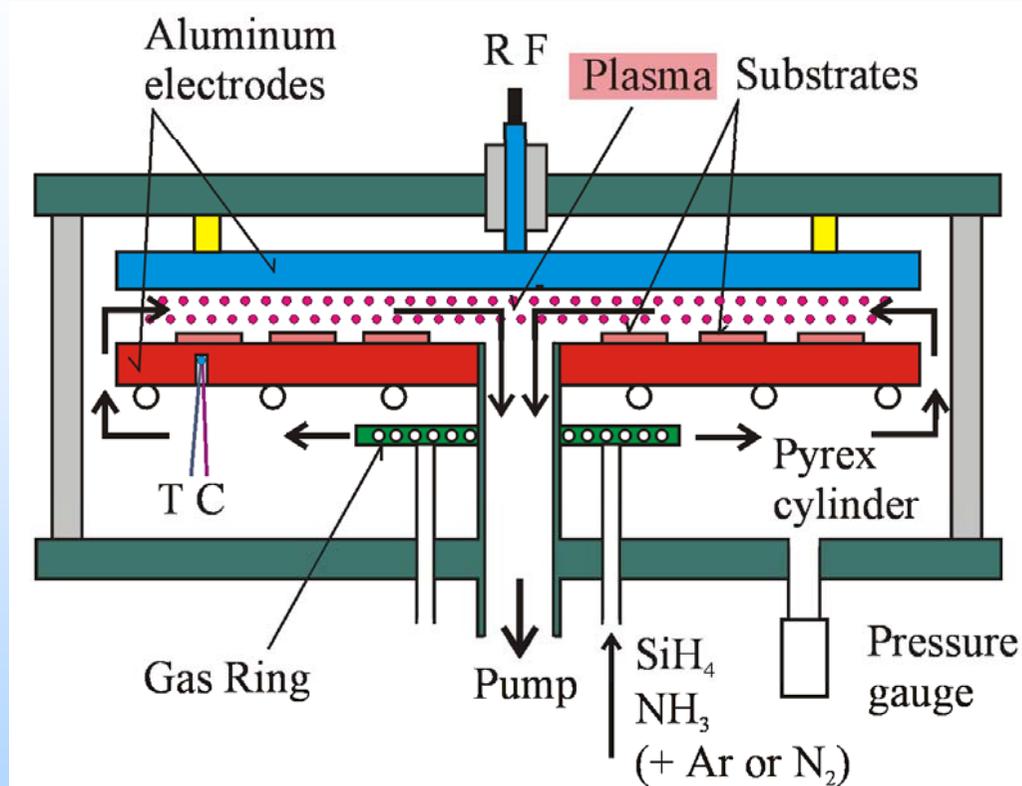
In Plasma:

- Excitation, dissociation and ionization by electron impact.
- Excited molecules, atoms, radicals, molecular and/or atomic ions diffuse to the substrate.
- Reactants and the configuration of electrodes and substrate holder cause a spatial distribution in particle density.
- Adsorbed particles migrate in searching for adsorption sites.
- Atoms react with each other, form clusters, thermodynamically stable clusters (nuclei) which then expand to films.
- Dissociation of molecules during adsorption may also occur.
- Bombardments of ions accelerated in the sheath affect surface reactions.

Reaction Mechanisms

- Complex reaction mechanisms in PE CVD:
- Cold plasma is not in the thermal equilibrium
- Gases are polyatomic molecules
- Lack of basic data (e.g. reaction cross sections)
- Both processes in the plasma volume and on the substrate contribute to the film formation

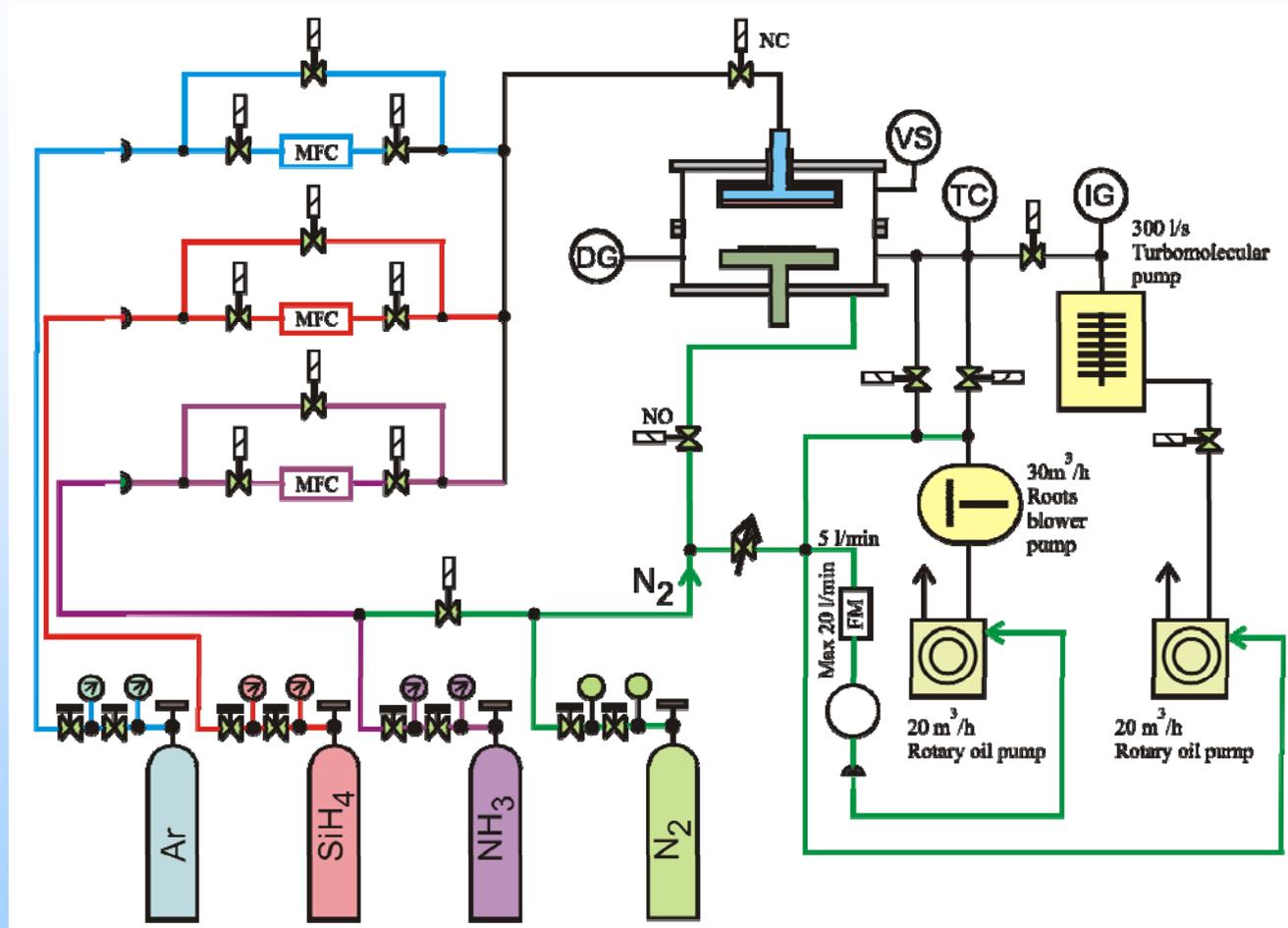
System Design for Plasma Enhanced CVD



A parallel plate reactor in which reaction gas flow radially

- Plasma enhanced CVD differs from sputter deposition and ion plating.
- Thin film is produced by reactions among gaseous species themselves in the plasma.
- Therefore, supplying the reactants into the reaction zone needs special consideration.

Diagram of a PE CVD System



MFC - mass flow controller, NC - normally closed, NO - normally opened, FM - Rotor meter, VS - vacuum switch, TC - thermocouple, DG - Diaphragm gauge, Ig - Ionization gauge

Examples of PE CVD Deposited Materials

Semiconductors

- $\text{SiH}_4, \text{Si}_2\text{H}_6$ amorphous Si
- $\text{SiF}_4 + \text{H}_2, \text{SiH}_4$ amorphous Si
- $\text{SiH}_4 + \text{GeH}_4$ Si-Ge alloys
- $\text{CH}_4, \text{C}_2\text{H}_n$ amorphous C
- SiH_4 & ($\text{B}_2\text{H}_6, \text{PH}_3$) p and n dopants

Conductors

- $\text{WF}_6 + \text{H}_2$ tungsten
- $\text{MoF}_6 + \text{H}_2$ molybdenum
- $\text{TiCl}_4 + \text{SiH}_4$ titanium silicide
- $\text{SiH}_4 + \text{PH}_3$ n⁺ amorphous Si

Insulators

- $\text{SiH}_4 + (\text{NH}_3, \text{N}_2)$ nitride
- $\text{SiH}_4 + (\text{N}_2, \text{CO}_2, \text{O}_2)$ oxide
- $\text{SiH}_4 + (\text{CH}_4, \text{C}_2\text{H}_n)$ Si-C alloys
- $\text{CH}_4 + \text{H}_2$ Diamond
- $\text{B}_2\text{H}_6 + \text{NH}_3$ Boron nitride
- $\text{BF}_3 + \text{N}_2 + \text{H}_2 + \text{He} + \text{Ar}$ Boron nitride
- $\text{TiCl}_4 + \text{O}_2$ Titanium oxide

Applications of Plasma Enhanced CVD

ICs

- Encapsulation for scratch and particle protection of Integrated Circuits (IC).
- Interlevel dielectrics for multilevel metallization structures.
- Capacitor dielectrics, diffusion masks, or photolithographic mask coatings.

Optics

- Optical antireflection coatings.
- Fabrication of optical waveguide fibers and films.
- Production of amorphous silicon and other semiconductor films for cheap solar cells.

Electronic and Protective Materials

- Important materials: Amorphous silicon, silicon nitride, **amorphous carbon, DLC; diamond**

Surface Modification by Cold Plasma

- Carbides and nitrides of transition metals have unique properties
- Chemical and thermal stability, hard, often good electrical and thermal conductors but brittle and difficult to machine
- To give metals heat resistance, anticorrosion properties or wear resistance – modification after machining
- Cold plasma – for nitrided or carburized materials at lower temperatures

Cold plasma have widely been applied to

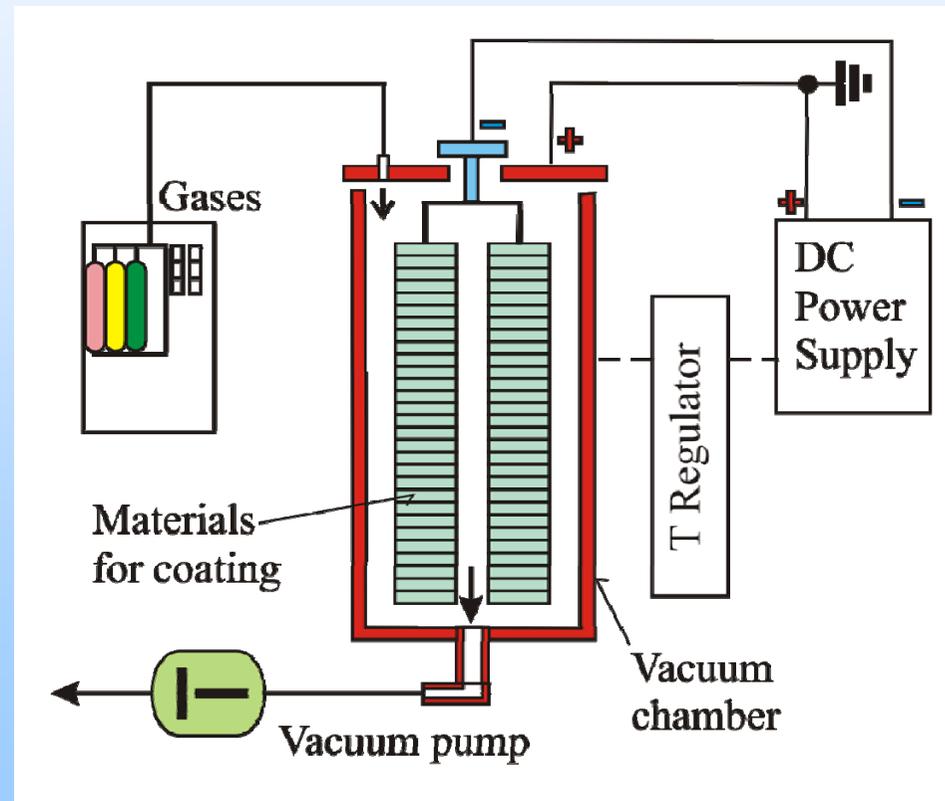
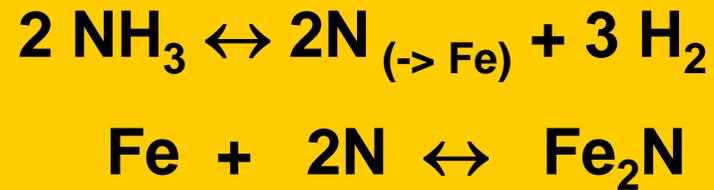
- Surface hardening, making protective or tribological coatings.
- Semiconductors: Nitriding and oxidation - important for the formation of electrically insulating films
- Polymers - treating surfaces at low temperature to improve wettability or adhesion strength

Ion Nitriding and Ion Carburizing

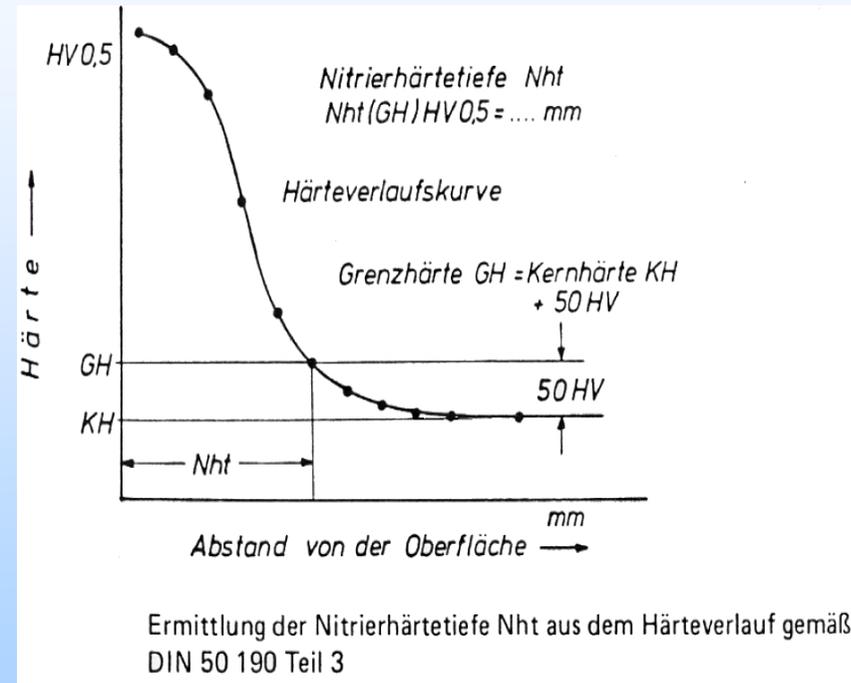
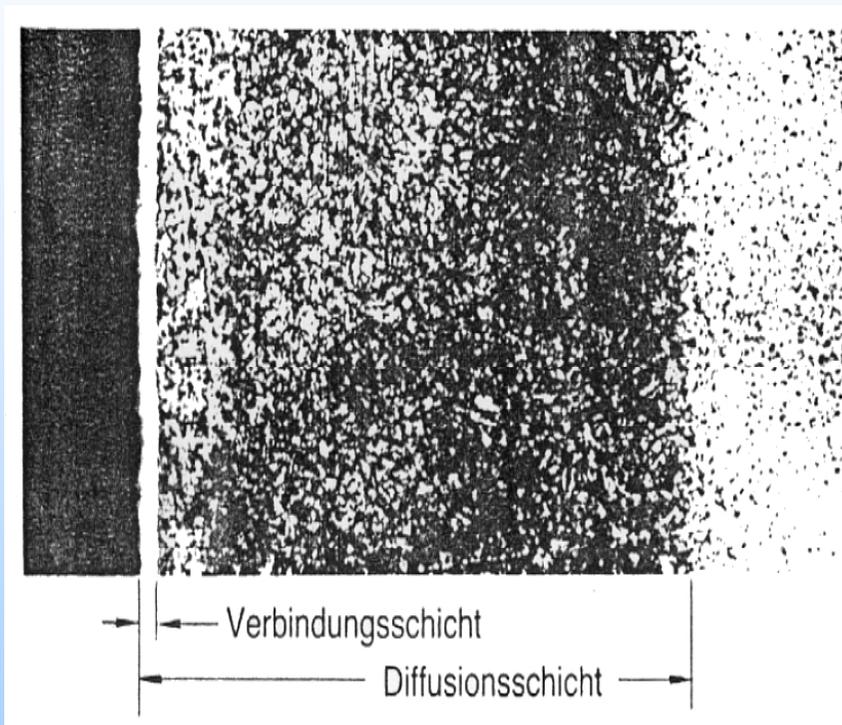
- Iron nitrides: γ' -Fe₄N, ϵ -Fe₂₋₃N, and ξ -Fe₂N are thermodynamically unstable.
- Nitriding of the Fe in ambient N₂ gas at atmospheric pressure does not take place.
- Hard Fe₄N layer can be formed by heating iron to ~ 500 °C in NH₃.
- Salt bath nitriding is an additional technique for surface hardening of iron and steel.
- Cold plasma is advanced nitriding technique for iron and steel used in industry.

Ion Nitriding

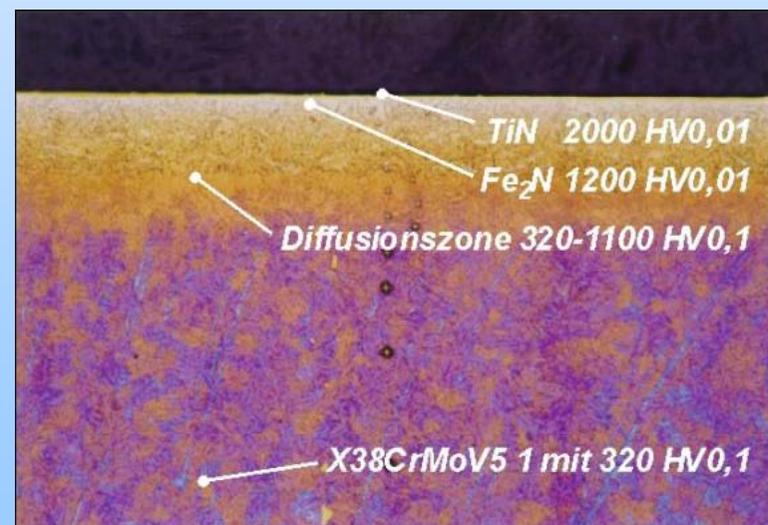
- Pure N₂ or N₂-H₂ mixed gas at 0.5 – 10 Torr.
- Abnormal DC glow discharge at 300 – 1200 V.
- Workpieces - cathode; chamber – grounded anode.
- Temperature ordinarily between 400 – 600 °C for steel.
- Iron nitrides are formed on the surface of steel substrate.
- Nitrogen diffusion layer exists in the bulk, below the compound layer.



Coating structure nitrided machine part

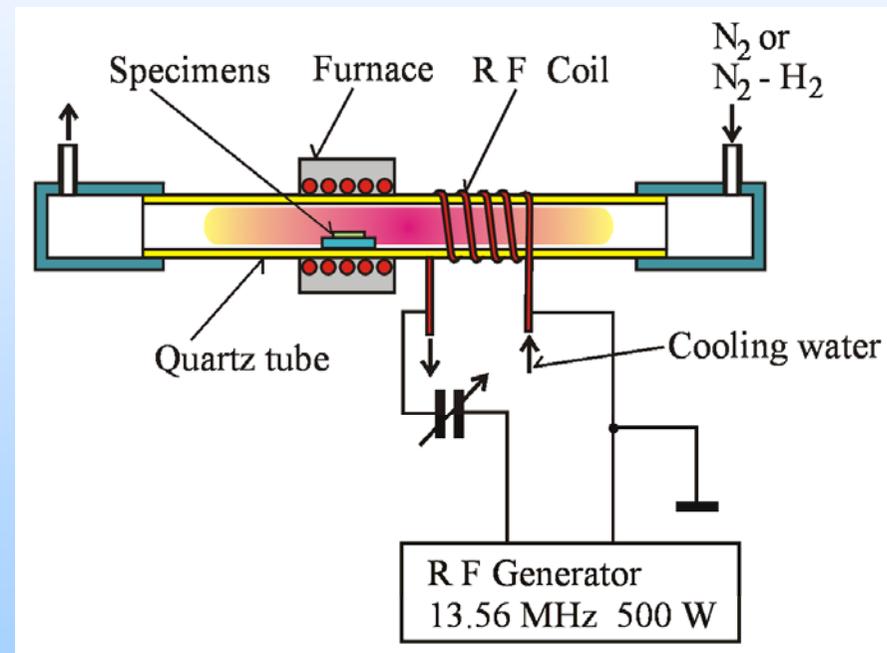


- Compound layer thickness increases with increasing nitriding time.
- Nitriding rates are 2 – 2.5 - times larger than in ammonia gas nitriding at the same temperature.
- At temperatures higher than 500 °C, the thickness of the hardened layer increases but the surface hardness decreases.
- Chemical composition of the nitride layer (only a diffusion layer without a compound layer or a single phase compound layer of Fe_4N) can be controlled by changing the ratio of N_2 and H_2 .
- Ion nitriding is effective not only for steel, but also for stainless steel.



Plasma Nitriding

- Workpieces of metals at floating potential - nitrided in a RF plasma.
- N_2 or N_2 - H_2 mixed gas employed as the nitriding agent.
- RF discharge between 5 and 20 Torr
- RF power between 200 and 300 W.
- Nitriding of Ti, Zr at 900 °C;
Nitriding steel at 550 °C.
- Modified layer as large as 50 μm .

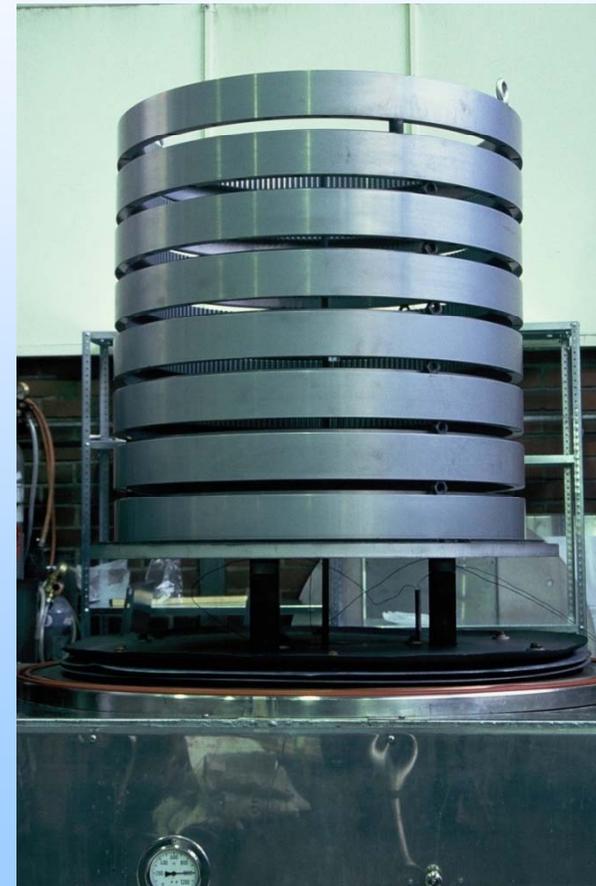


PLATEG

PulsPlasma[®]-Nitrieranlage PP 300 ø 2000 x 3200

PulsPlasma[®] nitriert - mit Verbindungsschichtbildung

Zahnkranz, 42 CrMo 4



Plasma Oxidation and Plasma Anodization

- Surface oxidation of materials at a floating potential in a cold plasma is called **plasma oxidation**
- Plasma oxidation for materials at positively bias potential is called **plasma anodization**
- Plasma anodization is employed for obtaining a thick oxide layer
- Both techniques provide dense oxide films on solid material surfaces at $< 300\text{ }^{\circ}\text{C}$
- High oxidation rate can be achieved by plasma anodization
- Oxide film thickness and oxidation rate can be controlled by bias voltage and /or current

- These techniques have been applied for the formation of electrically insulating films on either metals and semiconductors surfaces (Al, Si, Nb, GaAs, InP).
- Disadvantages of conventional high temperature oxidation: (for Si): oxidation-induced **sticking faults**, **excessive diffusion** of dopants, evaporation of elements (from InP, GaAs) such as As, and P during oxidation.
- Low temperature plasma processing is an alternative.
- Good insulating **pinhole free** films with **high breakdown voltages**, can be formed at low temperatures on semiconductors.
- In high temperature superconducting oxides, plasma oxidation techniques are applied to improve the oxygen incorporation.

Hydrogen Neutralization in Semiconductors

- Interest in the effect of hydrogen plasma exposure on properties of semiconductors.
- Hydrogen passivates deep level defects in semiconductors and improves the performance of electronic devices.
- Numerous types of plasma systems (RF, microwave discharges) have been used for hydrogen plasma exposure.
- Sample which is normally placed at floating potential: directly immersed in the plasma or immersed in the downstream afterglow.
- The depth of passivation shows characteristic diffusion limited $t^{1/2}$ dependence - sample temperatures: 100 – 350 °C to permit diffusion of hydrogen.
- Pure hydrogen plasma
- Small amounts of (0.1 – 0.3 %) of H₂O or O₂ can be added into an hydrogen plasma.

- **Oxygen** addition drastically increases the steady-state H atom concentration and oxygen does not diffuse into Si under conditions of shallow impurity passivation.
- Hydrogenation of InP shows very significant surface degradation due to P loss and subsequent In droplet formation.
- It is necessary to provide a simultaneous P overpressure, or to protect the InP surface with a thin H permeable cap layer.