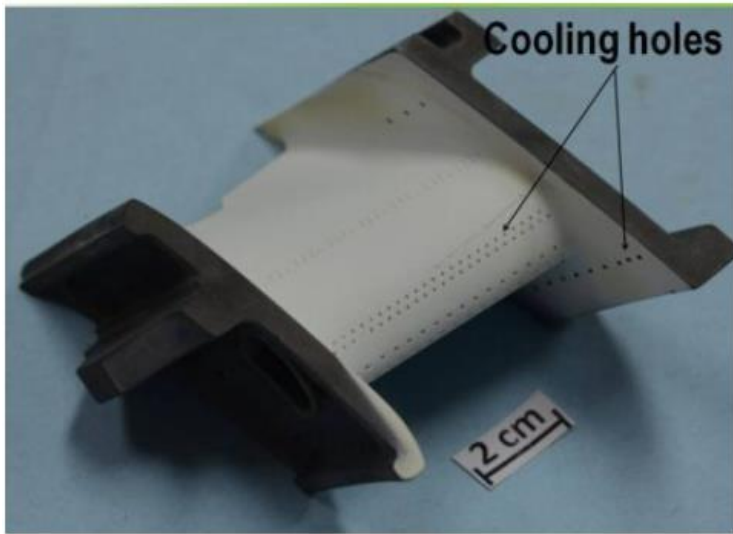


# Surface coatings and Treatments

# Surface Coatings

- Surface properties of an engineering component often influences its performance apart from material and manufacturing process.
- Coatings are generally used for
  - Improved wear and corrosion resistance
  - Reduce friction
  - Improved oxidation or hot corrosion resistance
  - Better fatigue resistance
  - For rebuilding surfaces on worn tools , dies etc.
  - Modify surface texture
  - Reduce bacterial attack or growth (anti-bacterial coatings)
  - Aesthetic applications

# Examples



Ceramic coatings on turbine blades



Ni-SiC composite coatings



Carbon based composite coatings



Near Net Shape Production  
([www.globalspec.com](http://www.globalspec.com))



Parts Repair Technology  
([www.cntrline.com](http://www.cntrline.com))



Food processing



# Coatings classification

- Based on thickness
  - Thin film coatings (Coating thickness  $< 10$  microns)
  - Thick coatings (Coating thickness  $> 10$  microns)
- Thin film coating techniques
  - PVD – physical Vapour Deposition
  - CVD – Chemical Vapour Deposition
  - ALD – Atomic Layer deposition
- Thick coatings deposition techniques
  - Thermal spray coating - Plasma spray, HVOF, Cold Spray
  - Electroplating
  - Electroless plating
  - Cladding
  - Micro arc oxidation (MAO)

# Thin-Films and Applications

<b>Thin-film Properties</b>	<b>Applications</b>
<b>Optical</b>	<b>Reflective/antireflective coatings</b> <b>Decoration (colour, luster)</b> <b>Memory discs (CDs)</b> <b>Waveguides</b>
<b>Electrical</b>	<b>Insulation, conduction</b> <b>Semiconductor devices</b>
<b>Magnetic</b>	<b>Memory discs/devices</b>
<b>Chemical</b>	<b>Barriers to diffusion or alloying</b> <b>Protecting against corrosion or oxidation</b> <b>Gas/liquid sensors</b>

# Thin-Films and Applications

<b>Thin-film Properties</b>	<b>Applications</b>
<b>Mechanical</b>	<b>Tribological coatings (wear resistant)</b> <b>Erosion resistance coatings</b>
<b>Thermal</b>	<b>Barrier layers</b>

# Thin Films

☆ **"Thin Film"** coatings having a thickness of less than ten microns

☆ **"Grown Film"**

Convert Original Substrate Material ( $\text{SiO}_2$  Formed by Oxidation of Si)

☆ **Deposited Film**

❖ **Chemical Vapor Deposition**

❖ **Physical Vapor Deposition**

❖ **Electrodeposition**

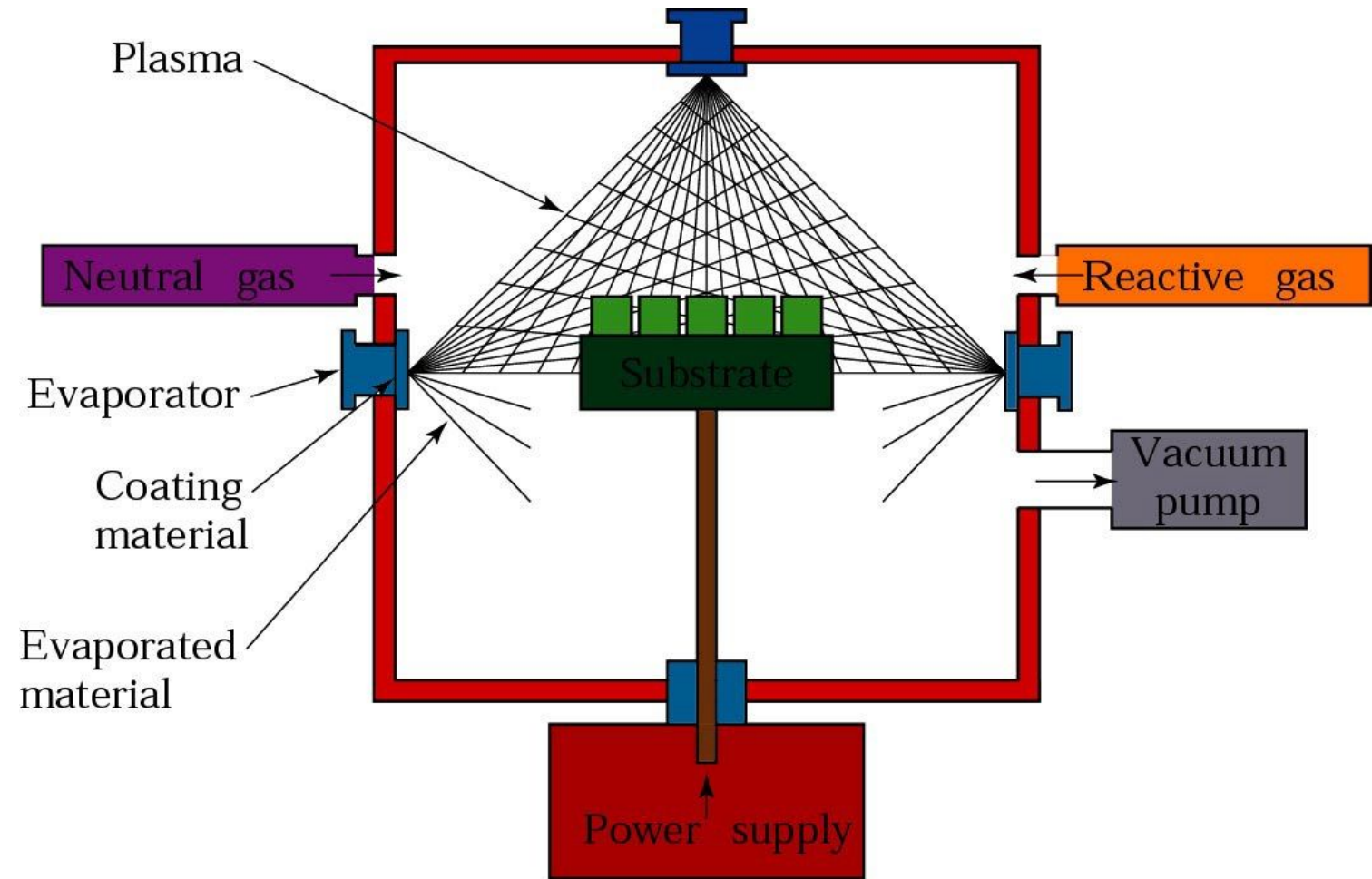
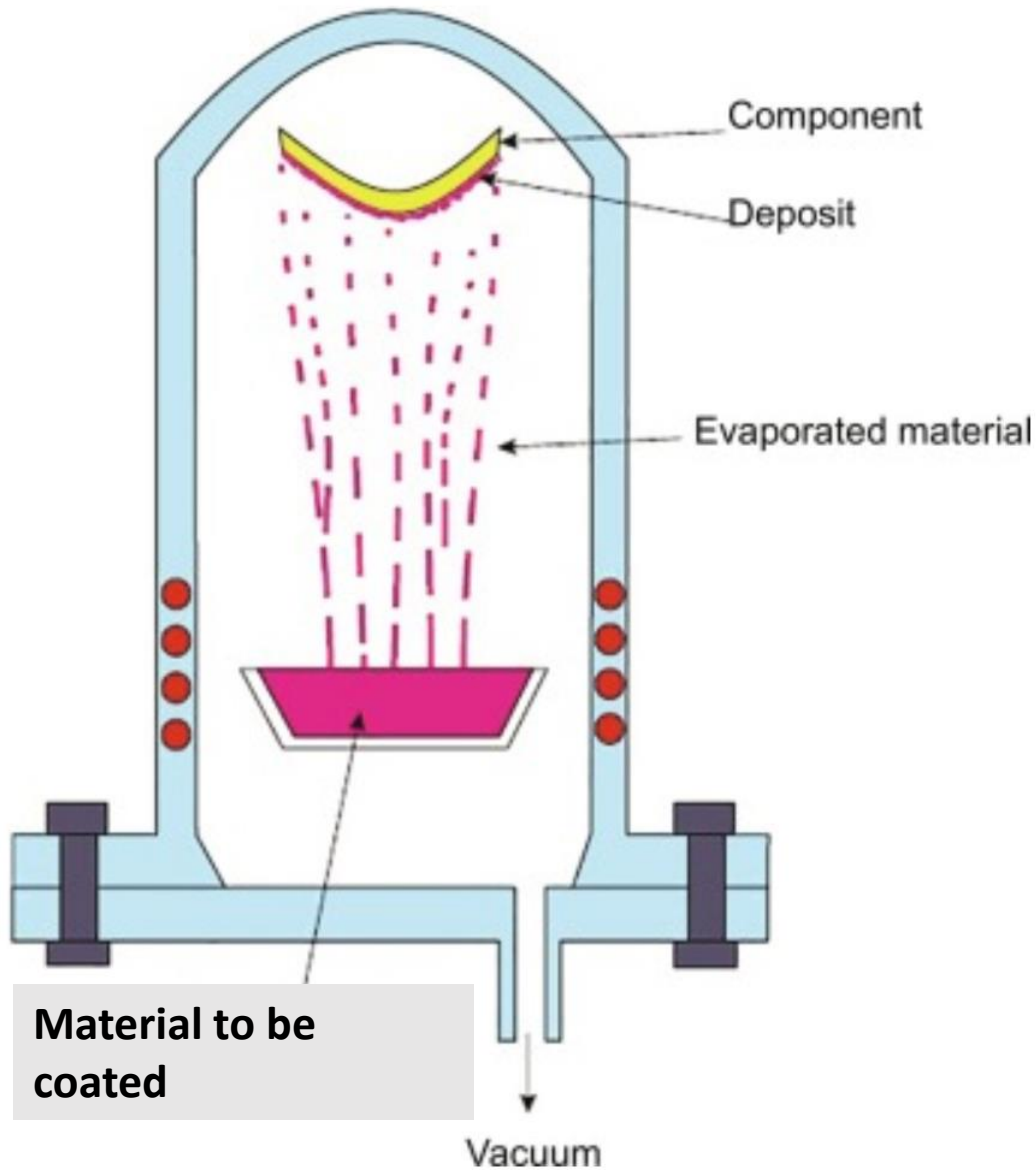
❖ **Molecular Beam Epitaxy**

# PVD – Physical Vapour Deposition

- Vapour deposition – Substrate or work piece is subjected to chemical reactions by gases that contain chemical compounds of the elements that needs to be deposited.
- **Physical Vapour Deposition**
  - Process of depositing metallic or metal + ceramic thin films on different substrates.
  - Process is carried out in high vacuum and at temperatures between 200C and 500C.
  - Deposition occurs due to the thermal evaporation of the target.
  - Particles that needs to be deposited are carried are physically carried to the workpiece.
  - Material with high Vapour pressure are generally preferred for deposition using PVD.
  - Gold, Silver, Titanium films of thickness  $< 10$  microns can be deposited.



# PVD – Physical Vapour Deposition (Setup)



# PVD – Physical Vapour Deposition (Setup)

PVD process involves four steps: Evaporation, Transportation, Reaction, Deposition.

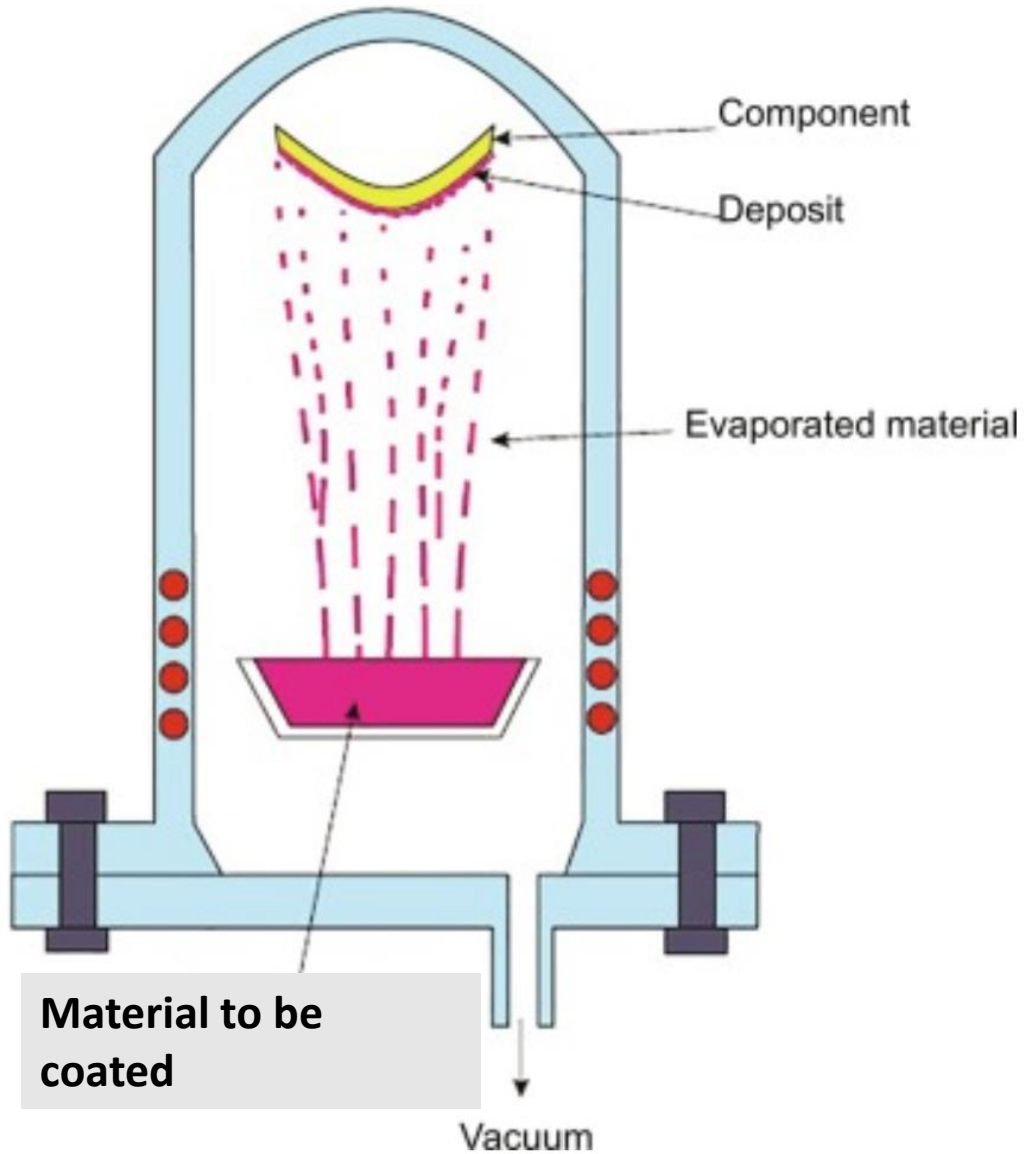
**Evaporation** – A target is bombarded by a high energy source such as a beam of electrons or ions. This dislodges atoms from the surface of the target, ‘vaporising’ them.

**Transport** – This is the movement of the vaporised atoms from the target to the substrate, or piece to be coated.

**Reaction** – In cases where metal is the target the PVD coatings will consist of metal oxides, nitrides, carbides and similar such materials. The atoms of metal will then react with the selected gas during the transport stage. The gases used in the above coatings may be nitrogen or oxygen or methane.

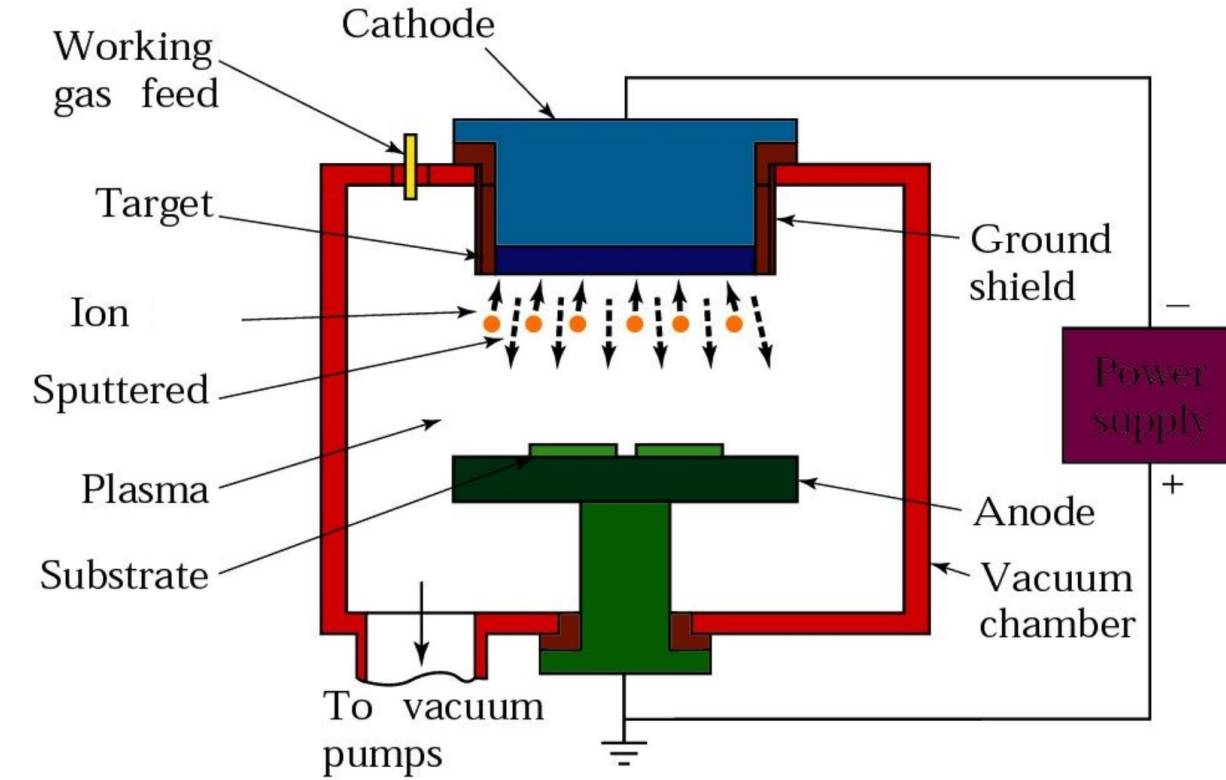
**Deposition** – This is when the coating builds up and bonds to the surface of the substrate. Sometimes penetrates the surface slightly, to give a lasting level of adhesion.

# PVD – Vacuum Evaporation



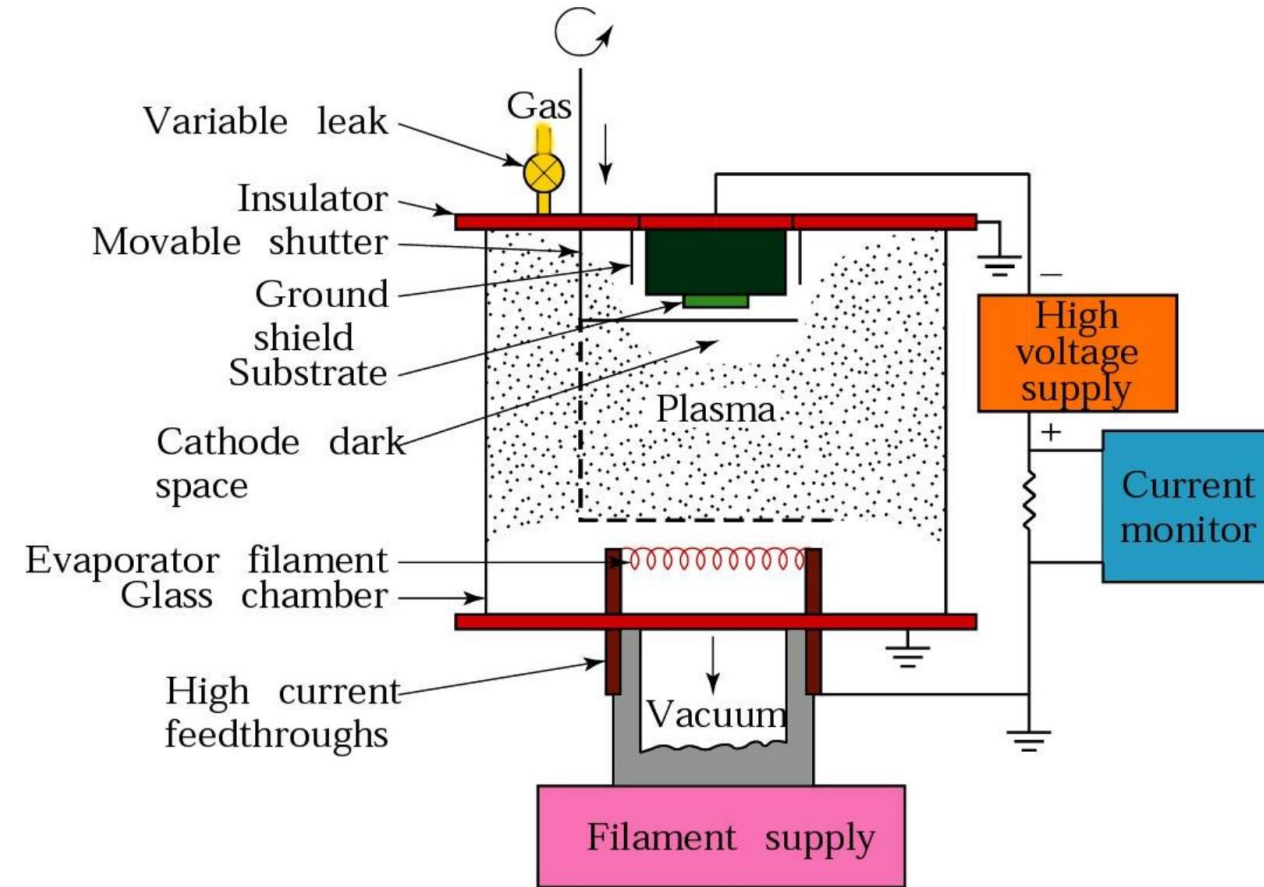
- Pure metals can be deposited onto a substrate by first transforming them from solid to vapor state in a vacuum and then letting them condense on the substrate surface.
- Material to be deposited is known as the source. Heating is accomplished in a vacuum
- Temperature required for vaporization is significantly below the corresponding temperature required at atmospheric pressure.
- Absence of air in the chamber prevents oxidation of the source material at the heating temperatures.
- Various methods can be used to heat and vaporize the material.

# PVD – Sputtering



- Surface of a solid is bombarded by atomic particles of sufficiently high energy.
- Individual atoms of the surface may acquire enough power due to the collision that they are ejected from the surface by transfer of momentum. This is the process known as sputtering.
- Most convenient form of high energy particle is an ionized gas, such as argon, energized means of an electric field to form a plasma.
- In principle, sputtering involves bombardment of the cathodic coating material with argon ions ( $\text{Ar}^+$ ), causing surface atoms to escape and then be deposited onto a substrate, forming a thin film on the substrate surface.

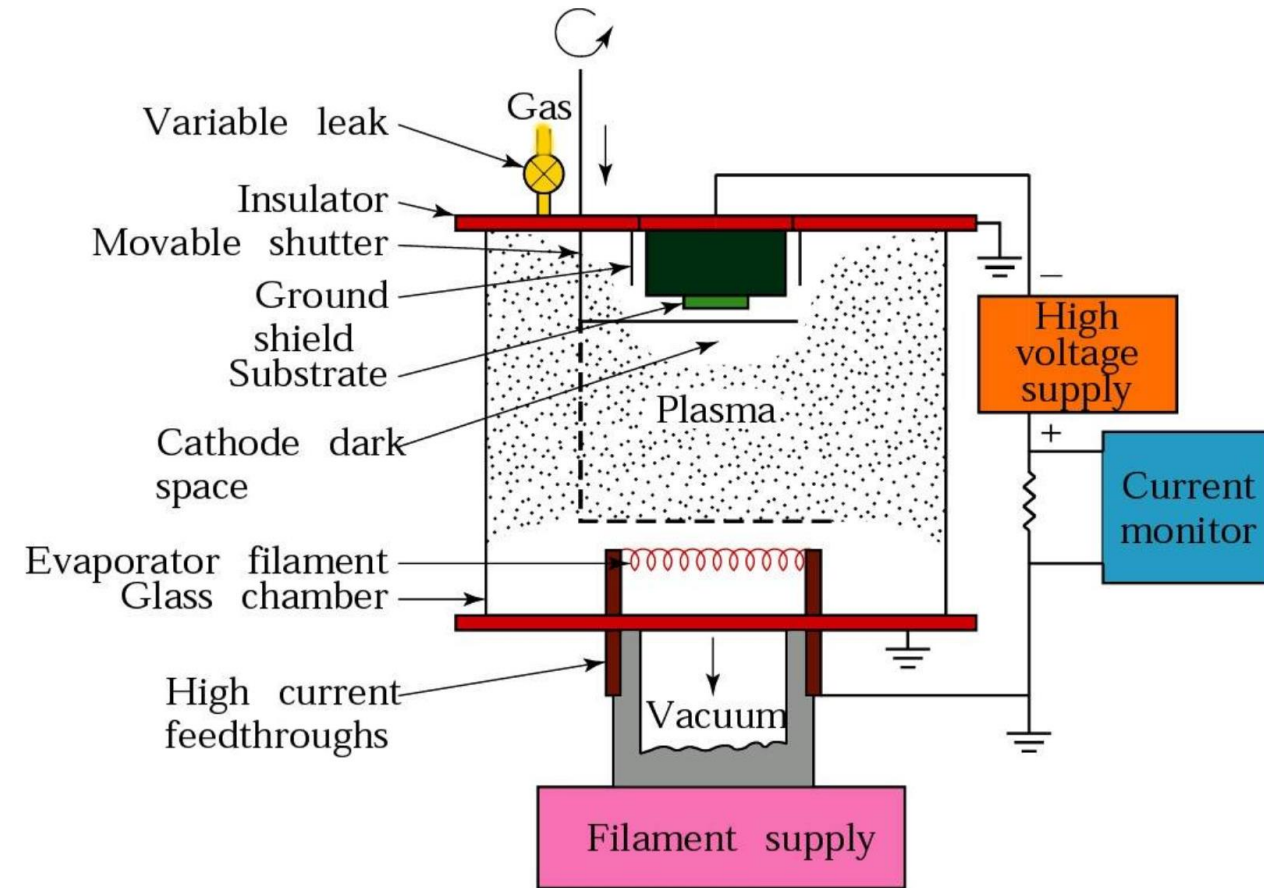
# PVD – Ion Plating



- Ion plating uses a combination of sputtering and vacuum evaporation to deposit a thin film onto a substrate.
- Substrate is set up to be the cathode in the upper part of the chamber and the source material is placed below it.
- Vacuum is then established in the chamber. Argon gas is admitted, and an electric field is applied to ionize the gas ( $\text{Ar}^+$ ) and build a plasma. This results in ion bombardment (sputtering) of the substrate so that its surface is scrubbed to a condition of atomic cleanliness.
- Source material is then heated to generate coating vapors.
- Heating methods used here are similar to those used in vacuum evaporation: resistance heating or electron beam bombardment.



# PVD – Ion Plating



- Vapor molecules pass through the plasma and coat the substrate.
- **Application** : TiN coating of high-speed steel cutting tools (e.g., drill bits).
- **Advantages**: Coating uniformity and good adherence, high deposition rates, high film densities, and the capability to coat the inside walls of holes.

PVD process	Advantages/limitations	Materials that can be coated
Vacuum evaporation	Equipment is relatively low-cost and simple; deposition of compounds is difficult; coating adhesion not as good as other PVD processes.	Ag, Al, Au, Cr, Cu, Mo, W
Sputtering	Better throwing power and coating adhesion than vacuum evaporation. Can coat compounds. Slower deposition rates, and more difficult process control than vacuum evaporation.	Al <sub>2</sub> O <sub>3</sub> , Au, Cr, Mo, SiO <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> , TiC, TiN
Ion Plating	Good and uniform coverage. Excellent coating adhesion. Most complex process control, higher deposition rates than sputtering.	Ag, Au, Cr, Mo, Si <sub>3</sub> N <sub>4</sub> , TiC, TiN

# Advantages and Limitations

- **Advantages**

- Very versatile process.
- Can deposit any material that can be vaporized
- Almost no scope for chemical reaction of the in-flight deposit
- Minimal damage to the substrate

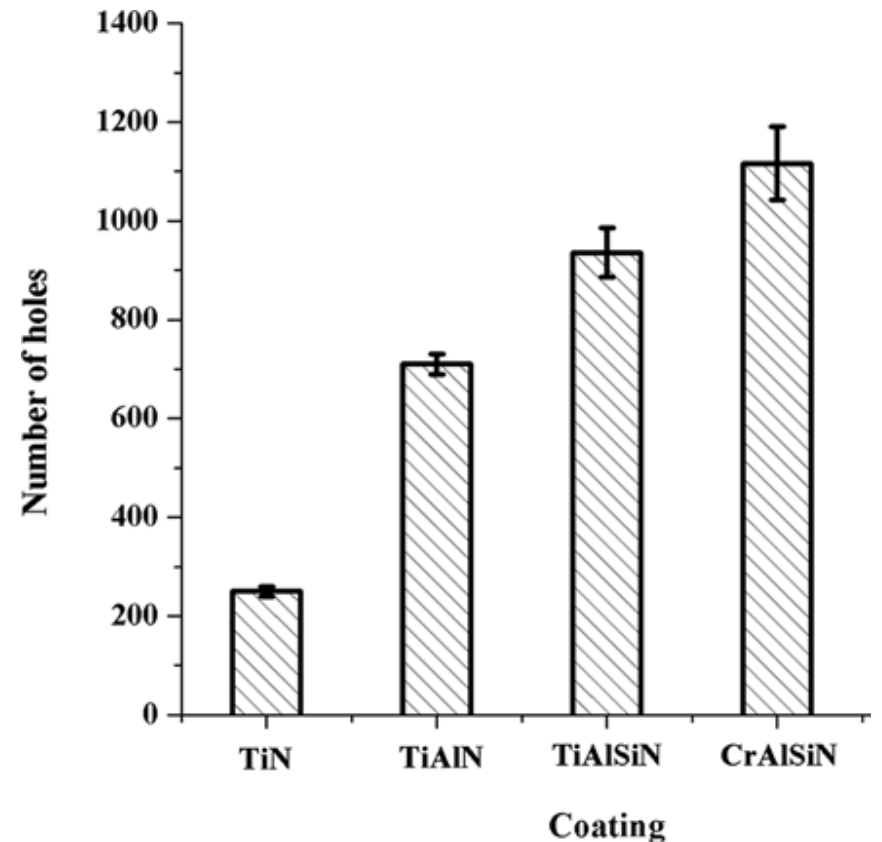
- **Limitations**

- Line-of sight processes – Shadowing effects
- Sometimes non-uniform thickness is reported
- Difficult to coat materials with low Vapour pressure
- Slow deposition rates (sputter PVD)
- Sputter PVD – Gas traces are sometimes found in the coated films, and the entrapped gases sometimes affect mechanical properties adversely.

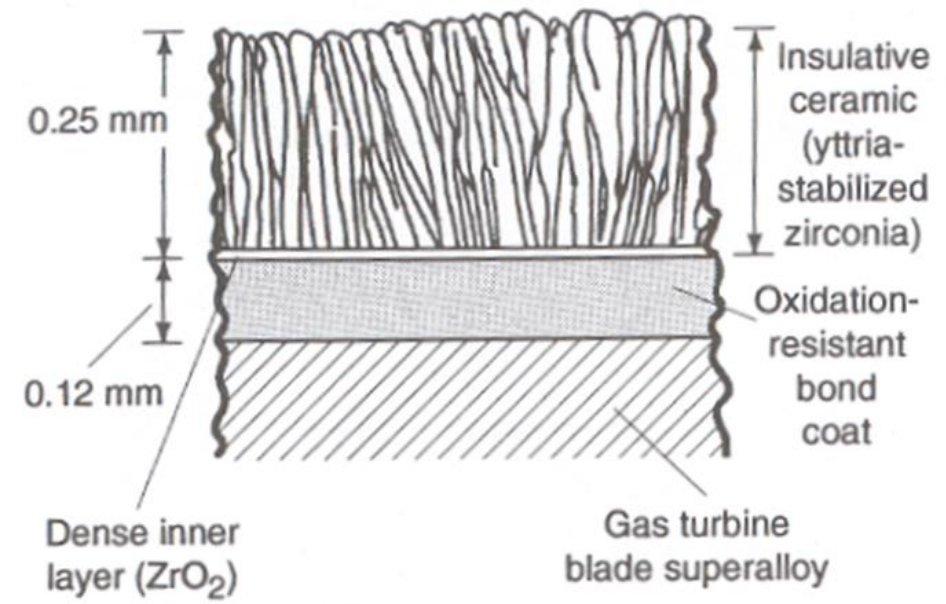
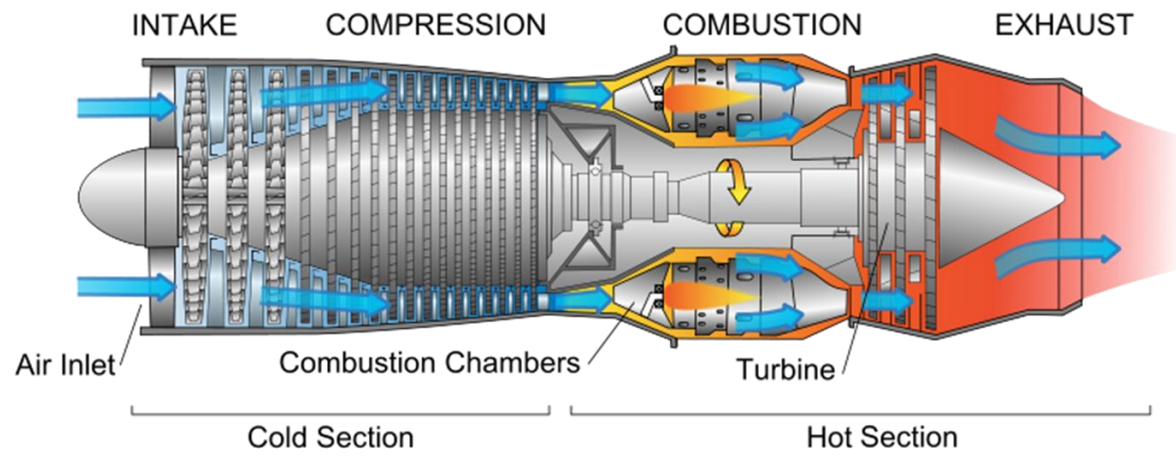


# Applications

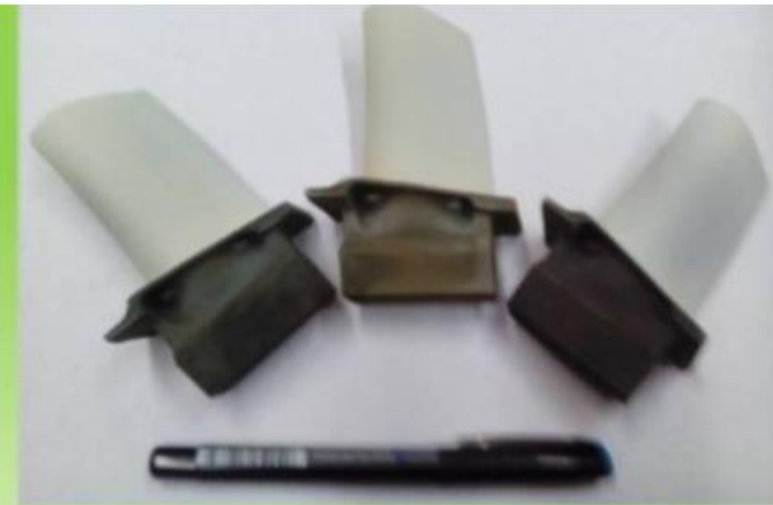
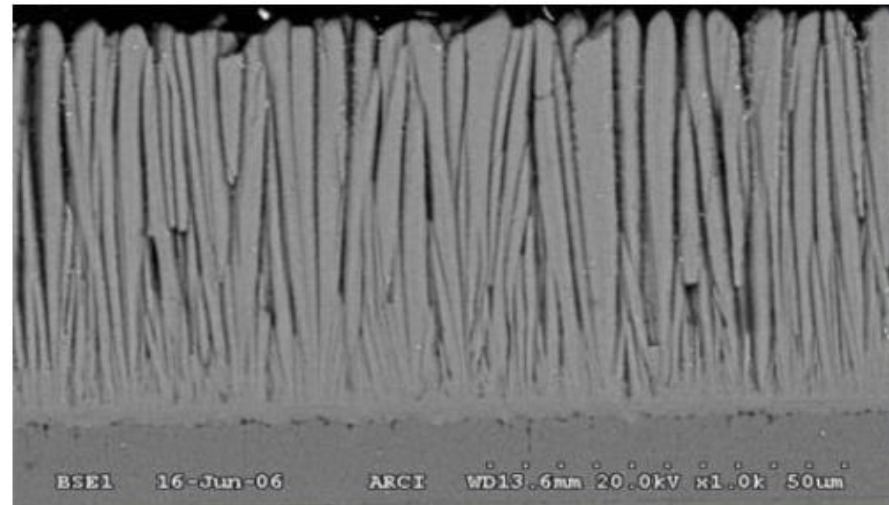
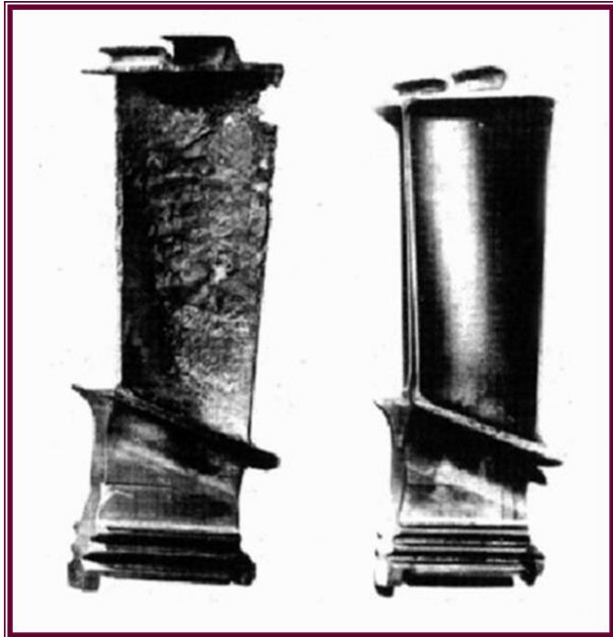
- Thin decorative coatings on metal parts such as trophies, toys, watch cases etc.
- Anti-reflection coatings of magnesium fluoride ( $\text{MgF}_2$ ) onto optical lenses.
- PVD is applied in the fabrication of electronic devices, principally for depositing metal to form electrical connections in integrated circuits.
- Finally, PVD is widely used to coat titanium nitride (TiN) onto cutting tools and plastic injection molds for wear resistance.



Uncoated drill bit : 70 holes



Cross section illustrating the strain-tolerant columnar  $\text{ZrO}_2$  microstructure of EB-PVD zirconia thermal barrier coatings.



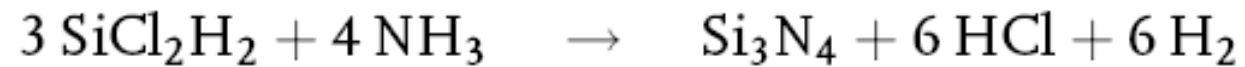
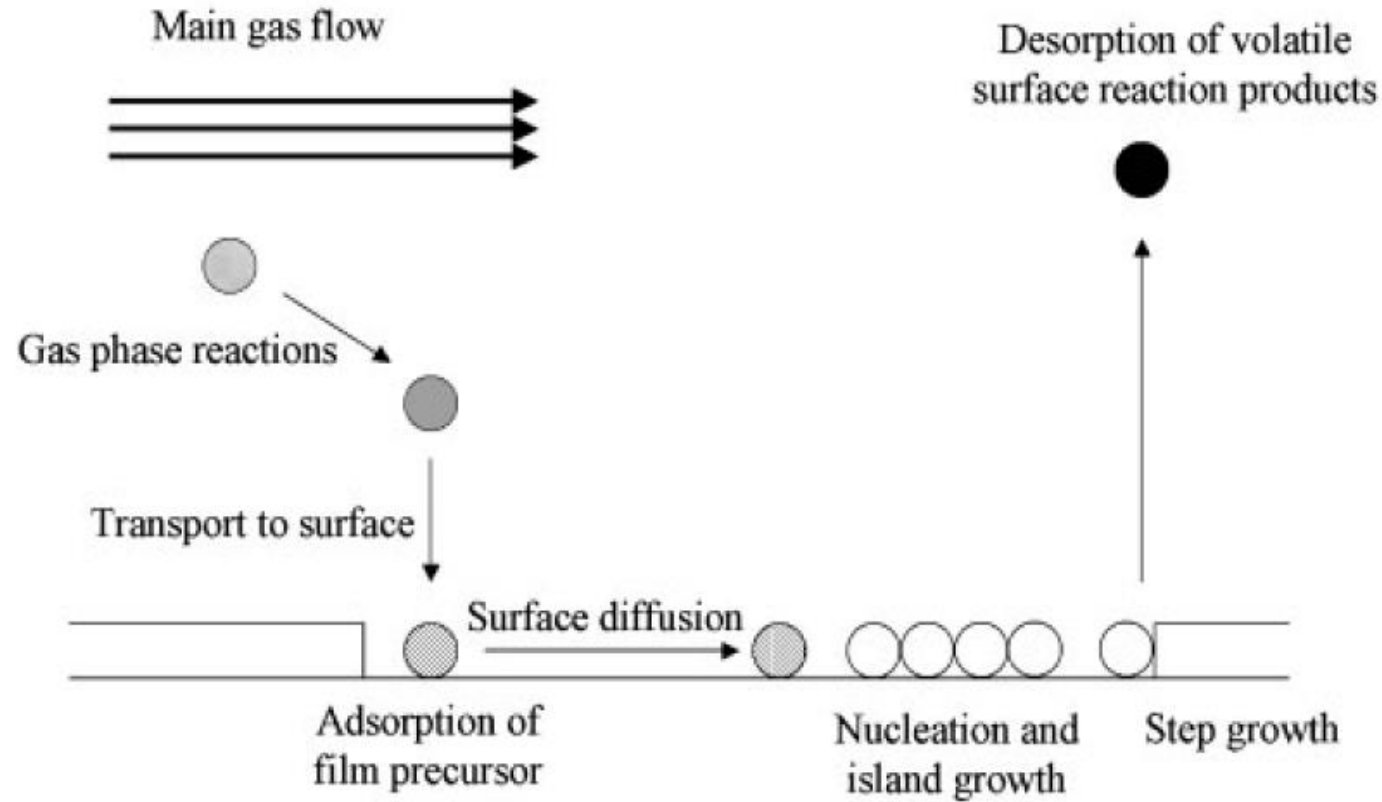
# Chemical Vapour Deposition (CVD)

# Chemical Vapour Deposition (CVD)

- CVD has been defined as “a material synthesis process whereby constituents of the vapor phase react chemically near or on a hot substrate surface to form a solid product.”
- The CVD deposition results from a set of phenomena occurring in the gas phase and/or at the surface of the substrate.
- Resistance heat, radio frequency, plasma and laser can induce the chemical reaction.
- The selection of process parameters can be done based on the coating structure or properties.

# Chemical Vapor Deposition

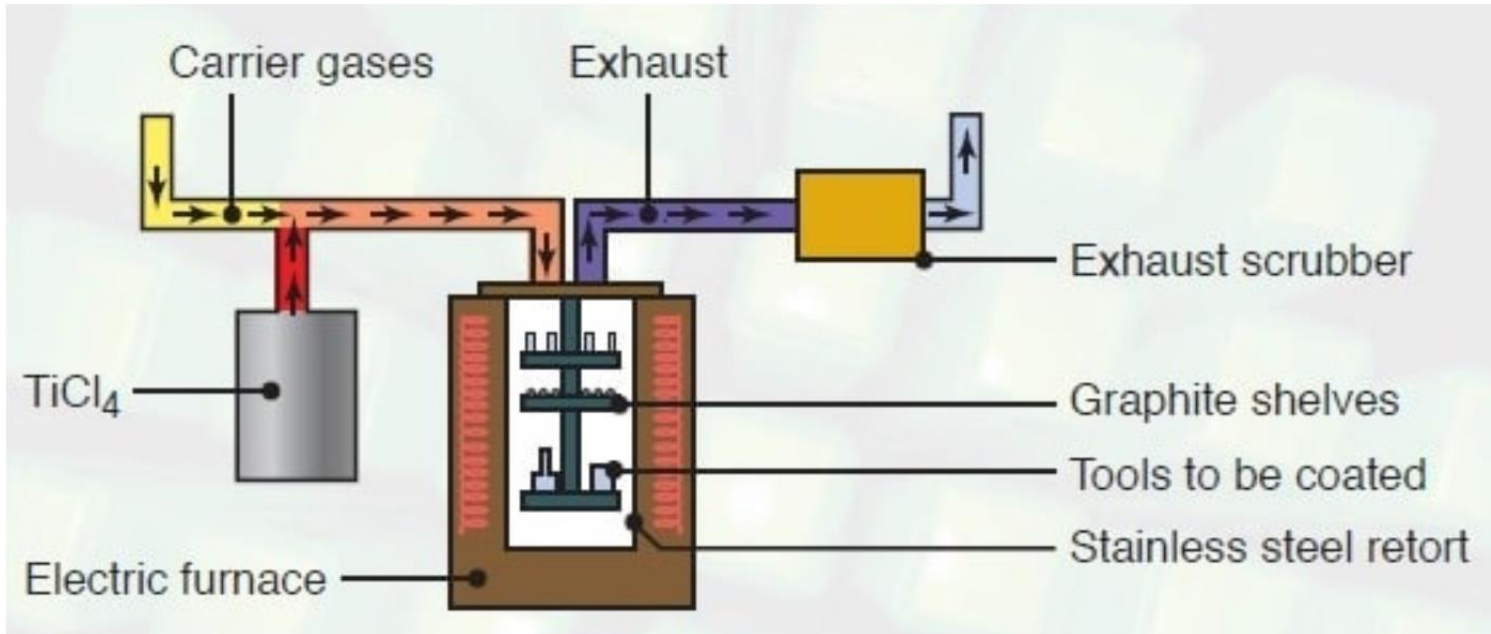
SiN



Dichlorosilane



# Chemical Vapor Deposition



- Titanium tetrachloride gas combines with hydrogen and nitrogen and form Titanium nitride.
- Titanium nitride is coated on the tools.
- Tools placed on graphite shelves and is heated to  $950^{\circ}\text{C}$ .
- HCl is formed as by product and is let off from exhaust.

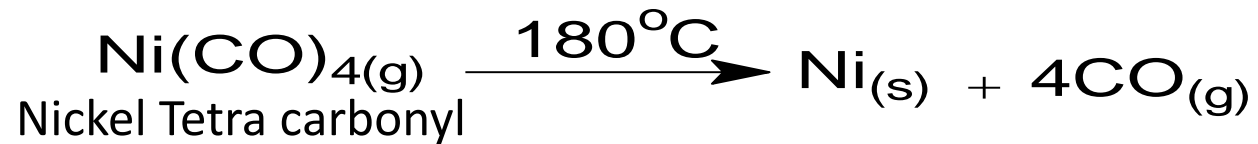
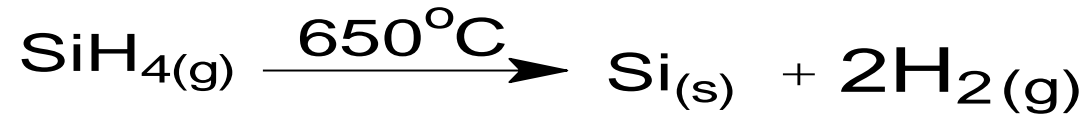
# Steps involved in CVD process

- Transport of the precursor to the deposition site/substrate;
- Gas-phase reactions;
- Adsorption of the precursor on the substrate surface;
- Surface processes : Diffusion of the precursor to the growth site
- Incorporation of the metal into the growing film;
- Easy desorption of by-products;
- Mass transport of the byproducts from the CVD reactor.



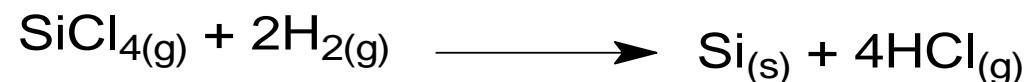
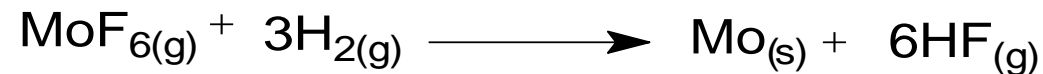
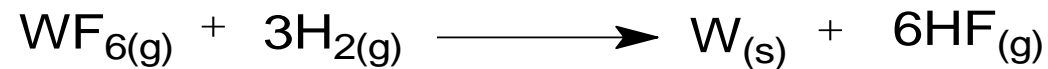
# Different types of chemical reactions used in CVD

Pyrolysis - hydrides, carbonyls, and organic compounds on hot substrates. E.g.,



## Reduction

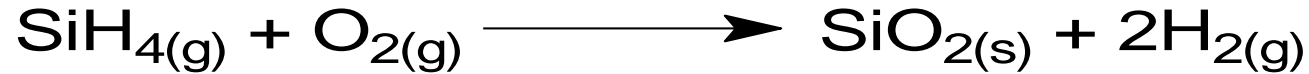
Hydrogen gas for the reduction of gaseous species such as halides, oxyhalides, or oxy-containing compounds





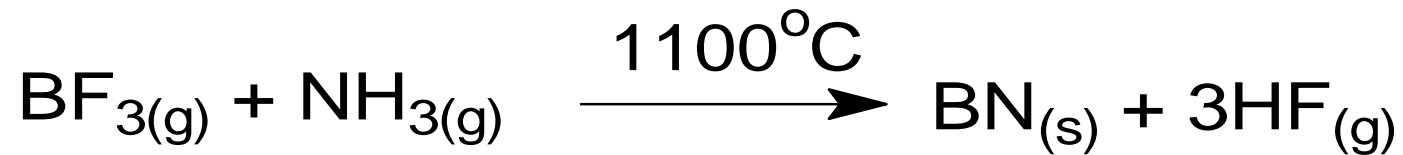
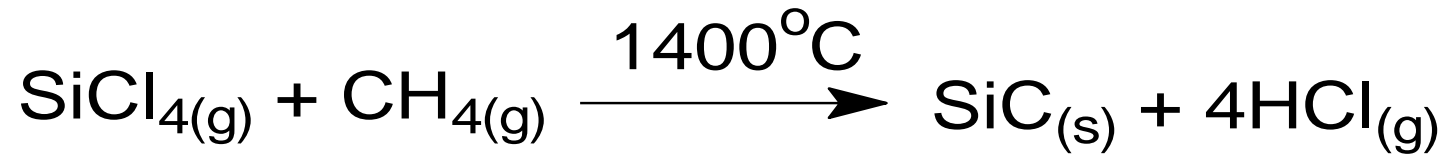
## Oxidation

Oxidation is an important constituent of CVD reactions. Common sources of oxygen are the element itself and CO<sub>2</sub>. Ozone also has been used for the deposition of SiO<sub>2</sub>.



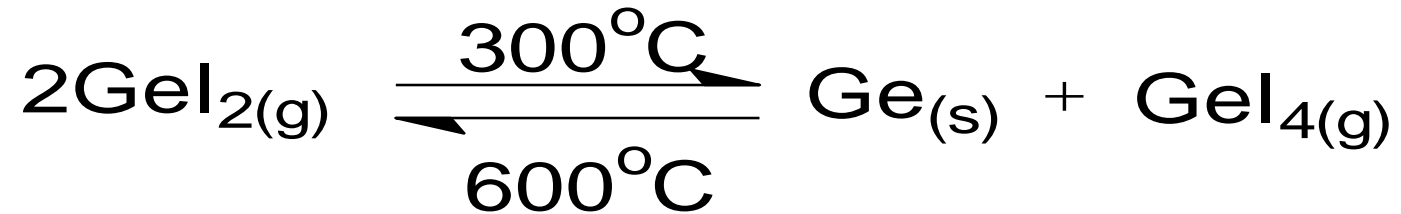
## Compound formation

A variety of carbide, nitride films, and coatings can be readily produced by CVD techniques. The deposition of carbides is usually obtained by reacting a halide with a hydrocarbon, such as methane. The deposition of nitrides is generally based on ammonia, which is preferred to nitrogen.



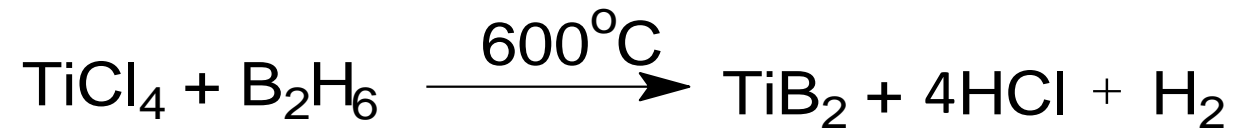
# Disproportionation

These reactions are possible when a non-volatile metal can form volatile compounds having different degrees of stability depending on the temperature. This manifests itself in compounds, typically with halides, where the metal exists in two valent states e.g.,  $\text{GeI}_4$  and  $\text{GeI}_2$ , such that the lower valent state is more stable at higher temperatures.



## Synthesis

Synthesis implies the reaction between two or more volatile compounds to form several compounds, one of which will precipitate as a deposit on the substrate and the other, being in the gaseous state will be flushed out of the system.



# Requirements of an ideal precursor

CVD allows the fundamental properties of an ideal precursor to be defined depending on the constraints of the process, the general criteria for the selection of precursors may be modified by more specific requirements

## An ideal precursor should have

- Volatility
- Thermal stability during its evaporation and transport in the gas phase
- Should decompose cleanly on pyrolysis without contamination of the growing film (e.g., by carbon).

Moreover, it should have a high purity

- Should be non-toxic
- Stable in its container over a long period since its rate of consumption is usually rather low and
- Readily available in consistent quality and quantity at low cost

# Complexity of CVD

- Thermodynamics
  - Vapor pressures
  - Reaction takes place at specific P and T (stable phases)
- Kinetics
  - Various steps need to take place, each with a barrier
  - Different regimes can affect rate of deposition, quality of product and even change the product phase
- Gas flow
  - A very important processing variable

# Types of CVD

1. Thermally activated CVD that uses thermal energy to activate the chemical reactions;
2. Photo-assisted CVD that uses light to activate chemical reactions
3. Metallo-organic CVD that uses metallo-organic sources and
4. PA-CVD that uses plasma to activate chemical reactions.

# CVD: Advantages

- ❖ Versatile process
- ❖ Higher thickness compared to PVD
- ❖ Good uniformity
- ❖ Handle large wafers
- ❖ Low deposition temperature
- ❖ Low power source
- ❖ High growth rates possible (by controlling flow rates of gases, time and temperature)
- ❖ good reproducibility

# CVD - Coating Applications

- *Friction-reducing* coatings for use in sliding and rolling contacts, for example.
- *Corrosion-resistant* coatings (Ta, Nb, Cr, etc.).
- *Erosion-resistant* coatings (TiC, Cr<sub>3</sub>C<sub>2</sub>, B<sub>4</sub>C, etc.).
- *Heat-resistant* coatings (Al<sub>2</sub>O<sub>3</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>, etc.).
- *High temperature superconductors* for use in medical, power grid, high-energy physics applications. Examples are YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (YBCO).
- *Fibers* for use in fiber-reinforced materials (fibers of boron, silicon carbide, boron carbide, etc.).
- *Structural shapes* (tubes, crucibles, heating elements, etc.) of, for example, tungsten and silicon carbide.
- *Decorative* coatings of, for example, TiN (gold color) on watches.
- *Conductive coatings* for integrated circuit interconnects, display applications, solar cells

# **Electroplating**



# Background

## Electroplating for tribological applications



Automotive industry



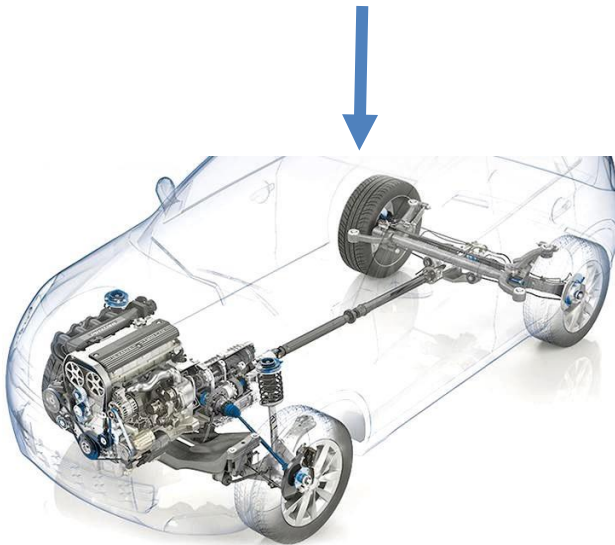
Marine industry



Aerospace industry



Household appliances



bushing



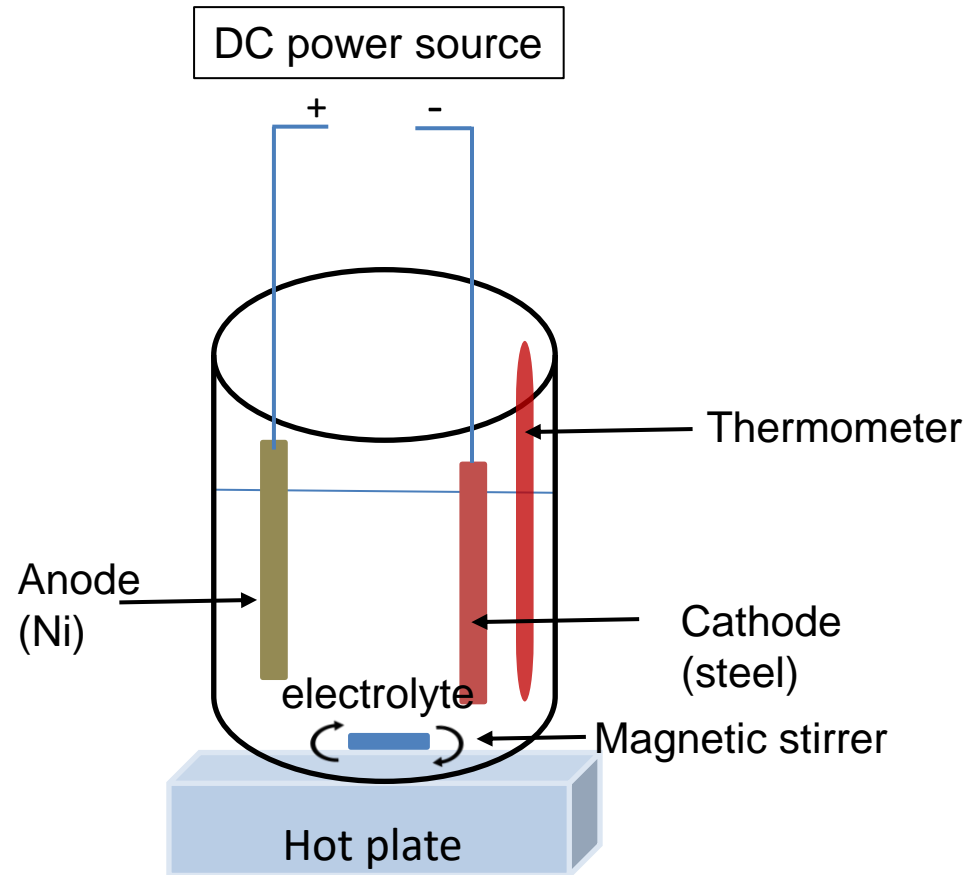
bearing

**Reducing expenses  
Reduce energy losses  
Extend bearing life**



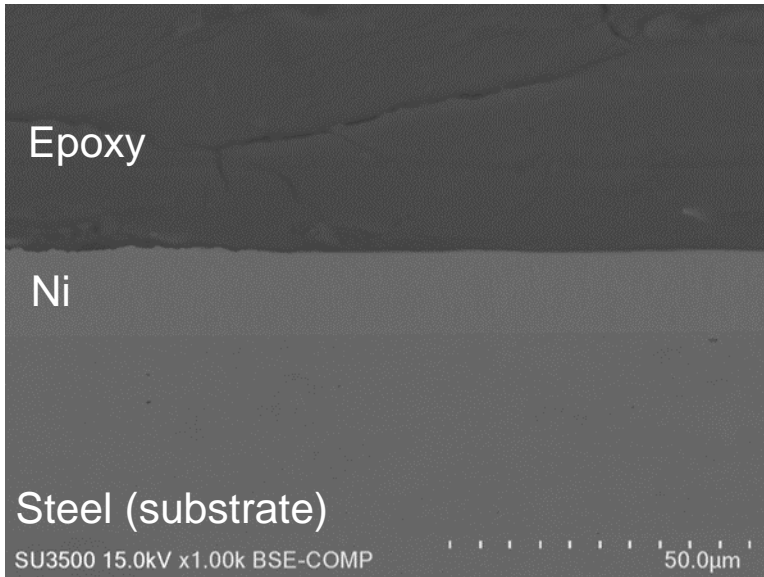
**Reducing friction and wear**

# Electrodeposition

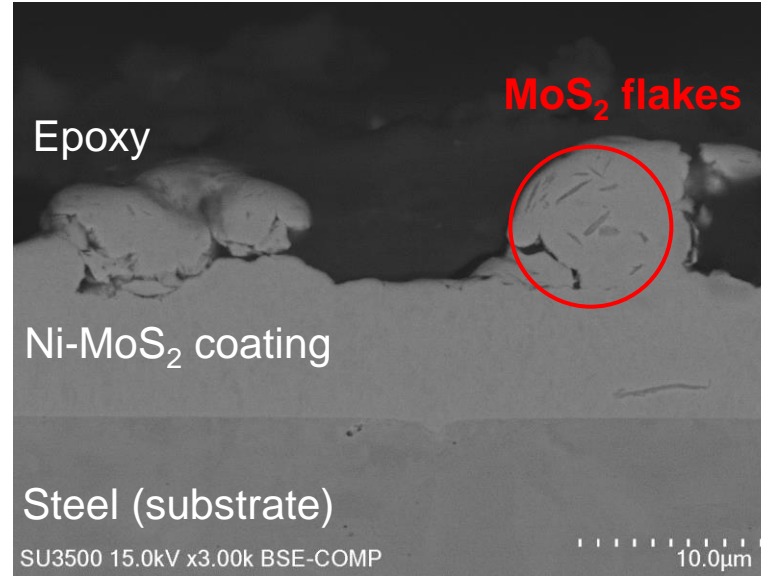


# Cross section of coatings

Pure Ni



Ni-MoS<sub>2</sub>-30°C



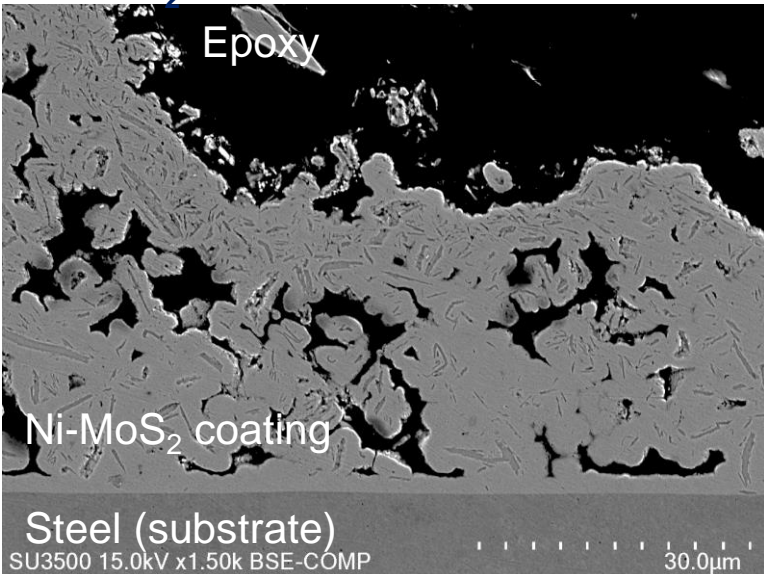
Pure Ni coating  
Thickness :  $13.5 \pm 1.5 \mu\text{m}$

MoS<sub>2</sub> content in initial bath 15g/L

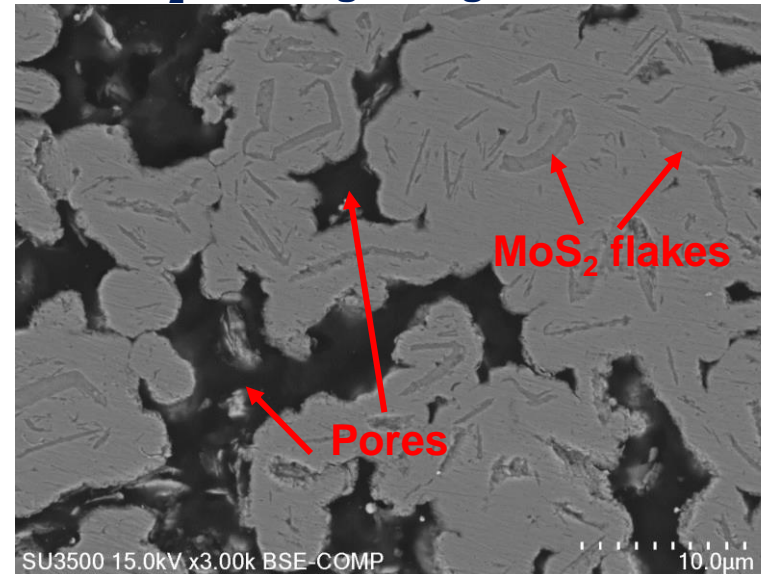
Ni-MoS<sub>2</sub>-30°C

MoS<sub>2</sub> volume fraction :  $2.1 \pm 0.6 \%$   
Thickness for flat area :  $11 \pm 2 \mu\text{m}$

Ni-MoS<sub>2</sub>-60°C



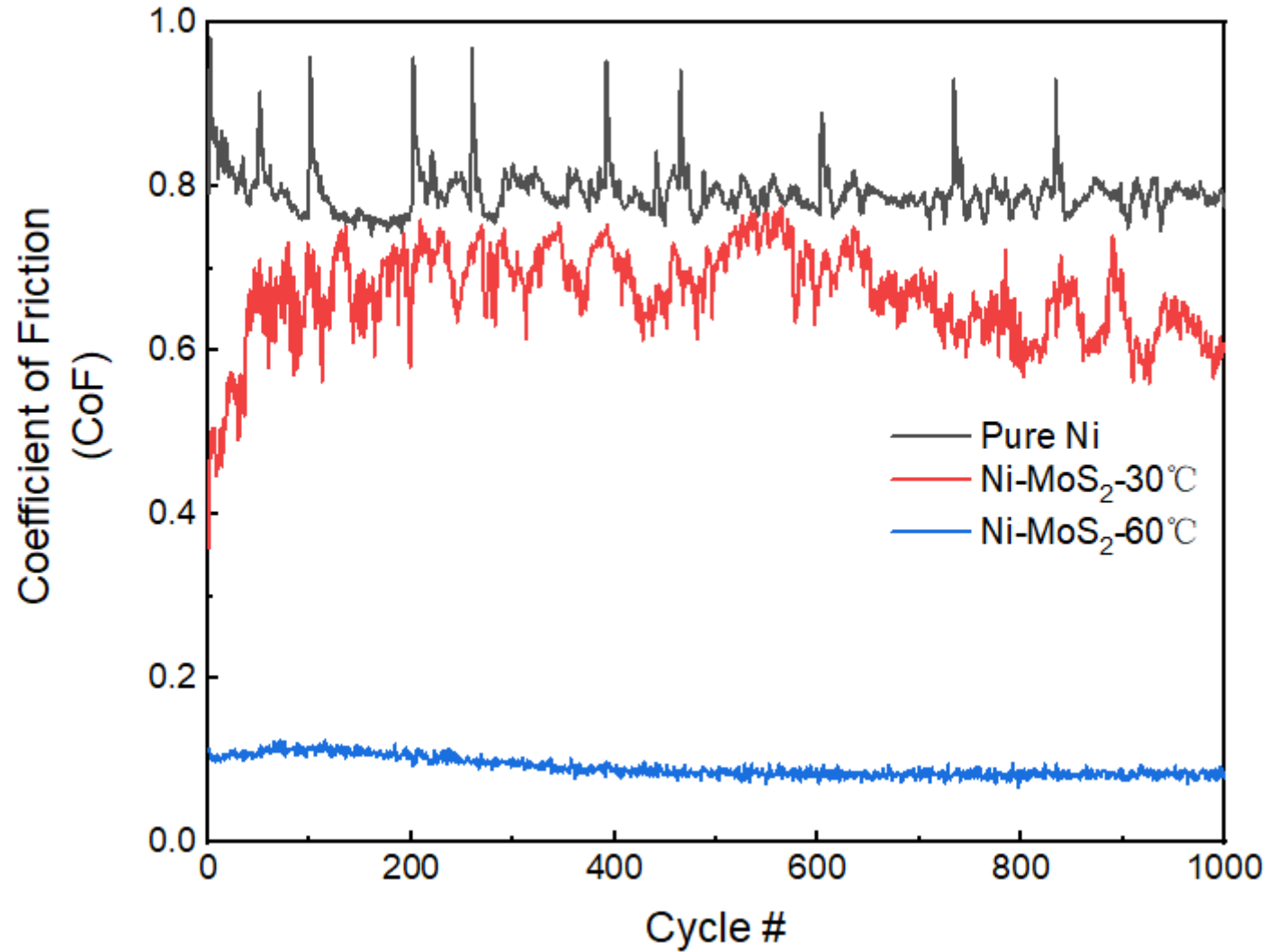
Ni-MoS<sub>2</sub>-60°C high magnification



Ni-MoS<sub>2</sub>-60°C

MoS<sub>2</sub> volume fraction :  $16 \pm 2.5 \%$   
Thickness :  $64 \pm 20 \mu\text{m}$

# Coefficient of friction



Coating	Average CoF
Pure Ni coating-1N	$0.79 \pm 0.03$
Ni-MoS <sub>2</sub> 30°C 1N	$0.67 \pm 0.05$
Ni-MoS <sub>2</sub> 60°C 1N	$0.09 \pm 0.01$

Thank you