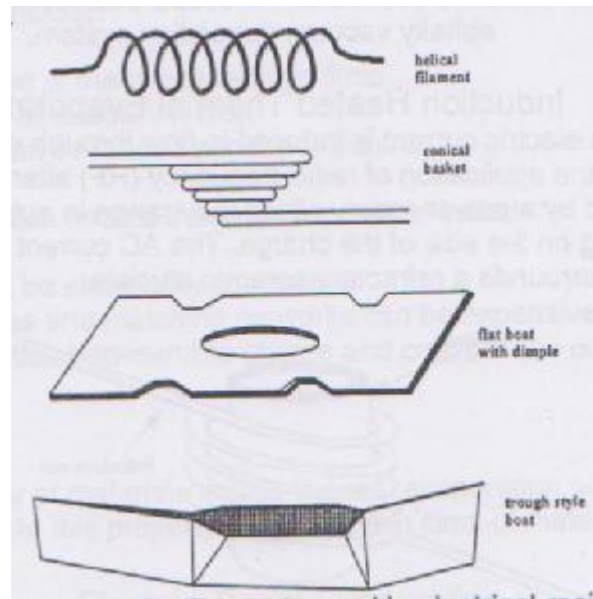


There exists a great variety of filament configurations ranging from straight and coiled wires to "boats" and boxes:



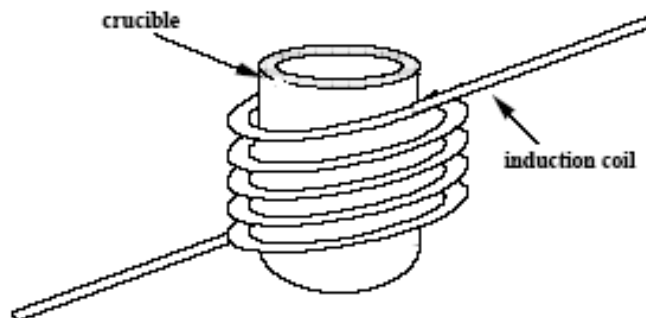
Configurations for filaments used in electrical resistance heated thermal evaporation

Each type of filament is designed for a unique application. Coil filaments made of refractory metal strands are loaded with the charge by hanging small sections of wire made of the charge material on the coil. Upon heating, the charge melts, and wets the coil. Further heating causes the evaporation of the charge from the coil filament. Very rapid heating of a filament with hanging charge material may cause the charge to melt locally and fall off the filament. Some skill is required to attain thin film deposits from run to run which have consistent thicknesses. One technique that helps is to carefully weigh the charge for each run, keeping the weight the same, and operating the filament so as to completely evaporate the charge each run. There are some inherent disadvantages of resistance heated thermal evaporation that should be kept in mind when selecting a deposition technique:

- 1) The source may generate impurities which may co-deposit in the condensing thin film.
- 2) Accurate control of the deposition rate is difficult.
- 3) The composition of alloy thin films deposited may differ from that of the charge material (especially if the elements in the alloy have markedly different vapor pressures).
- 4) The amount of material which may be evaporated per run is limited.
- 5) The substrate will experience heating due to radiant energy from the source.

Induction Heated Thermal Evaporation

In this technique an electric current is induced to flow through an electrically conductive charge material by the application of radio-frequency (RF) alternating current. The RF current is generated by a power supply which may range in output from 1 to 50 kilowatts, depending on the size of the charge. The AC current is flowed through the copper coil which surrounds a refractory ceramic crucible



A crucible and coil used for induction heating for thermal evaporation

Maximum operating temperatures for refractory oxide crucibles

Metal to be evaporated	ThO ₂	BeO	ZrO ₂	Al ₂ O ₃	MgO
Nickel	stable	stable	stable	stable	stable
Titanium	<1800 °C	<1800 °C	<1800 °C	<1800 °C	<1800 °C
Silicon	<1600 °C	<1600 °C	<1600 °C	<1400 °C	<1400 °C
Zirconium	<1800 °C	<1600 °C	<1800 °C	<1600 °C	no data
Tantalum	<1900 °C	<1600 °C	<1600 °C	<1900 °C	<1900 °C
Molybdenum	<2300 °C	<1900 °C	<2300 °C	<1900 °C	<1900 °C
Tungsten	<2200 °C	<1800 °C	<2000 °C	<1900 °C	<1900 °C

Advantages of induction-heated thermal evaporation as compared to electrical resistance evaporation include:

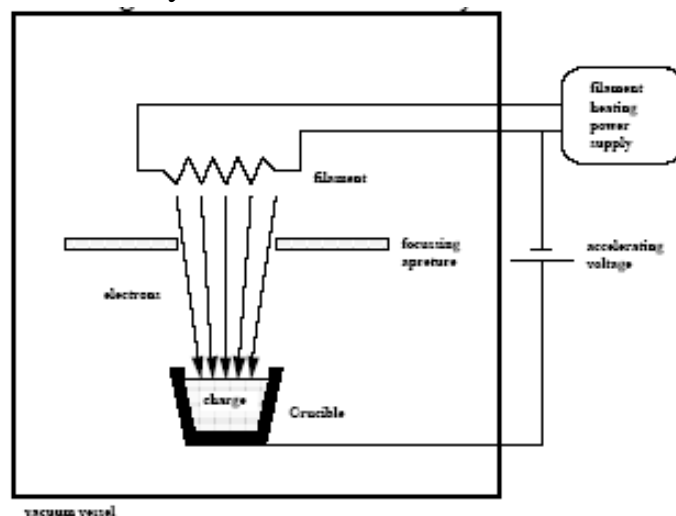
- 1) Low contamination of the deposited thin films .
- 2) Improved control of deposition rate.
- 3) Larger charges can be loaded per deposition run.

Disadvantages of induction heated thermal evaporation include:

- 1) The charge must be electrically conductive.
- 2) RF power supplies and matching networks can be expensive and quite large.
- 3) Chemical interaction between the charge and crucible can occur.

Electron Beam Evaporation

In this thermal evaporation process, a beam of energetic electrons generated from a heated filament supplies the thermal energy to evaporate of the charge. There are several variants of the electron beam evaporation process. All electron beam thermal evaporation systems have an anode (biased positively) and a cathode (either grounded, or biased negatively with respect to the anode). The two divisions we will cover are self accelerated and work-accelerated electron beam evaporators. In the work-accelerated scheme, electrons emitted from a heated tungsten filament are attracted to the charge material by an applied high voltage bias (10- 40 kV DC). A focusing aperture aids in minimizing spurious heating of the vessel interior by off-axis electrons.



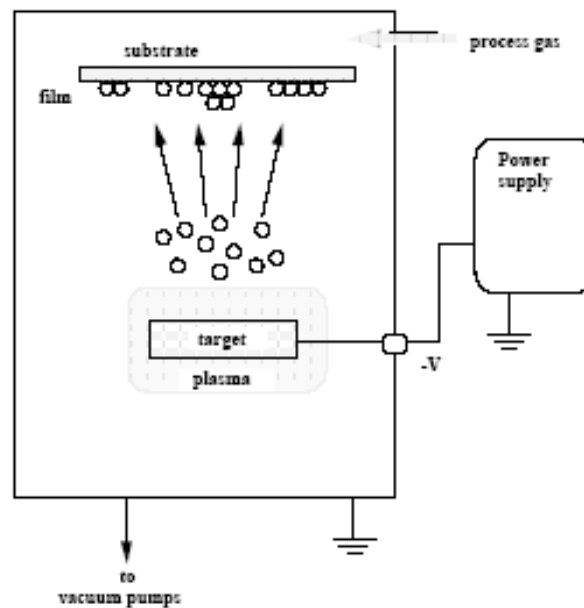
A work-accelerated electron beam evaporator

Sputter Deposition of Thin Films

Unlike thermal evaporation, in which a material is heated to increase its equilibrium vapor pressure, in sputter deposition, material is made to go into the vapor phase by the physical interaction of particles impacting the source material (often referred to as the "target"). There is a wide variety of sputtering techniques that are currently used to deposit thin films for use in magnetic storage media (cassette tapes, computer discs), optical thin films and microcircuits. The forms of sputtering which will be described are: diode sputtering, magnetron sputtering, RF sputtering, and ion beam sputtering.

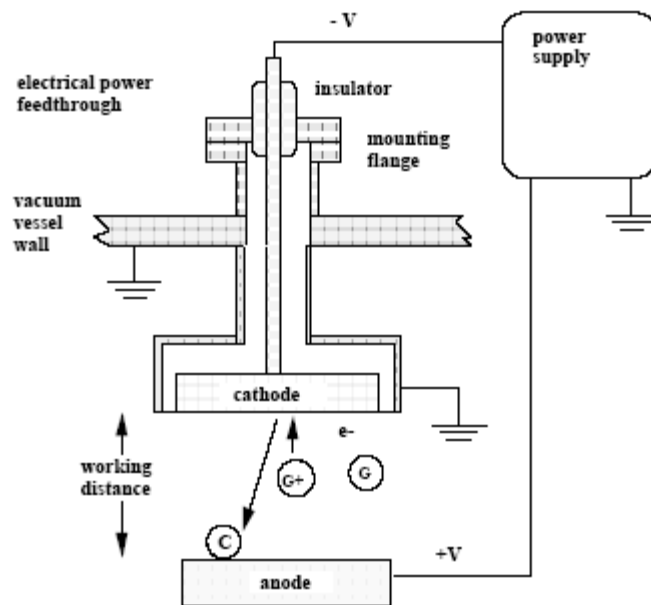
Diode Sputtering

A simple diode sputtering process system is presented in figure Following evacuation of the vessel to its base pressure to reduce contamination of the film by atmospheric gases or water vapor, a process gas (most often Argon) is admitted into the vessel. The pressure of this process gas is maintained at a user-selectable pressure between 1-100 mTorr using a set of upstream mass flow controllers to regulate the process gas mix, as well as a downstream throttling gate valve. Such a valve, situated right at the turbo pump, is equipped with a controller that can perform fast, real-time pressure control using a capacitance manometer as a sensor element. An electric bias of from 500 to 5000 V DC is applied to the target. Electrons emitted by the target strike process gas molecules in the vicinity of the target, and may cause the gas to become ionized. The positive ions thus created are accelerated towards the cathode by the applied negative bias. When the positive ions collide with the cathode, the kinetic energy transferred is sufficient to eject atoms of the cathode material. Secondary electrons, ions, and light (IR, visible, UV and X-rays) are also emitted during this collision.



Simplified representation of a diode sputter deposition process.

The ejected (sputtered) material travels towards surfaces in the vacuum vessel where it condenses to form films. Since the process gas pressure is in the range of from 1 to 100 mTorr, a significant amount of scattering of the sputtered material by the process gas occurs. In this scattering, sputtered material loses its directional identity, may become neutral, if it was ionized, and also loses kinetic energy. The visible glow that surrounds the cathode during sputtering is called the "glow discharge" or plasma. Visible light of the plasma has a color which is characteristic of the process gas and the material being sputtered. This visible light may be used to monitor the chemical composition of the plasma using a visible light spectrometer (details of this and other deposition monitoring techniques will be covered later in this unit). One requirement of the diode sputtering technique is that the cathode be electrically conductive. Elements and compounds which are insulators can be sputtered by other techniques.



Detail of the operation of a diode sputter deposition process.

Typical operating parameters for DC diode sputtering are:

Current density at the cathode: 1 mA/cm²

Process gas pressure (Argon): 30 to 80 mTorr

Cathode bias: -3000 VDC

Working distance 2 to 8 cm

Depending on the composition of the cathode, this set of parameters should yield a deposition rate of from 60 to 400 Å/minute. It should be noted that the rate of erosion of the cathode is expected to be greater than the rate of deposition at the substrate.

Sputtering Yield

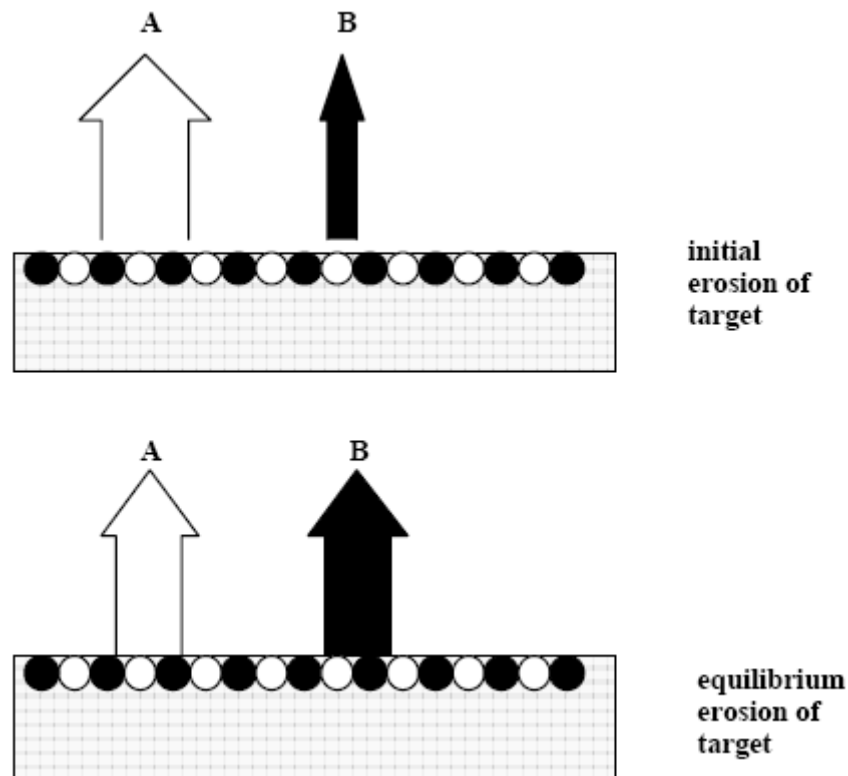
The number of target atoms which are ejected from the cathode for every incident ion is called the "Sputtering yield". The magnitude of the sputtering yield is a function of the composition of the process gas and target material, the energy of the incident ions, and the angle of incidence of the ions on the target. In general, the sputter yield is greatest for the following set of conditions:

- 1) High atomic weight process gas.
- 2) Low atomic weight cathode material.
- 3) Low concentration of reactive gas species in the vessel.

The noble gas Argon is the most commonly employed process gas for sputter deposition processes, as it has a high sputter yield for most metals, is chemically inert and non-toxic, and is relatively inexpensive (compared with the other noble gases (Krypton and Xenon)).

Sputtering Alloys and Compounds

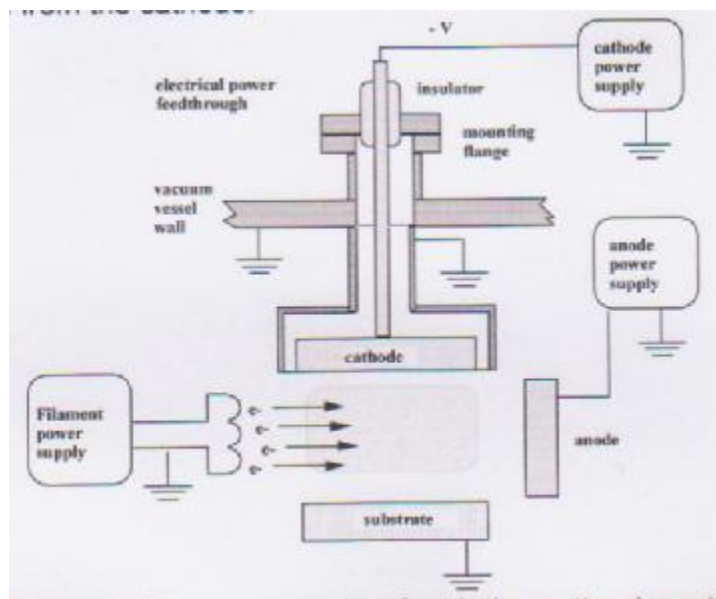
The deposition of thin films of metallic alloys and some chemical compounds may be accomplished by sputtering. In general, the composition of thin films deposited by sputtering will have the same overall chemical composition as the source (target) after an initial equilibration period. In figure 14.18 is presented a simplified representation of a two component alloy target, made of "A" and "B". Assume that the sputtering yields for material "A" is higher than for material "B". Initially, as material is sputtered from this compound cathode the vapor stream will be higher in concentration of "A" due to its larger sputter yield. After some time, the surface of the cathode will become depleted in "A" and more concentrated in "B". When this occurs, the thin films being deposited will have approximately the same composition as the target.



Sputtering alloy target made of "A" and "B".

Triode Sputtering

In this process, an auxiliary set of electrodes are employed to enhance the electron emission and increase the ionization of the process gas to generate a higher flux of material sputtered from the cathode.



Detail of the components of a triode sputter deposition system.

Three separate power supplies are used: one to resistively heat a filament to emit electrons, one to accelerate the electrons into the anode, and a high voltage power supply to accelerate positive ions towards the cathode. High deposition rates ($>1000 \text{ \AA/minute}$) may be achieved using this configuration.

Typical ranges for the operating parameters are:

Current density at the cathode: $10\text{-}100 \text{ mA/cm}^2$

Process gas pressure (Argon): $0.5 \text{ to } 30 \text{ mTorr}$

Cathode bias: $-50 \text{ to } -500 \text{ VDC}$

Filament current: $0.05 \text{ to } 1 \text{ amp}$

Anode bias: $+50 \text{ to } 100 \text{ VDC}$

Working distance: $2 \text{ to } 20 \text{ cm}$

Due to the high currents and the intense plasma generated, active water cooling of the sputter target and electron accelerating anode is required. The power supplies should be interlocked with cooling water flow monitors to interrupt power in the event of cooling water loss. Triode sputtering systems have successfully been operated for deposition of a wide range of materials, but the complexity of the process, and the difficulty in scaling the process hardware up in physical size has limited its commercial application.

Arc Deposition

High current, low voltage electric arcs, if constrained, may be used to create evaporant for thin film coatings. There are several techniques used to control the arc, including use of electrically insulating hearths, electrostatic, and magnetic constraints. Arc deposition has been demonstrated to produce thin films having high densities and excellent adherence to the substrate. Normally the arc process is conducted in a UHV environment, but partial pressures of reactive process gases, such as oxygen and nitrogen have been used to deposit metal oxide and nitride thin films. High deposition rates, in the range of from $50 \text{ to } 500 \text{ \AA/second}$ have been reported for the arc deposition process. One current drawback to this technique is the creation of macro-particles along with the atomic and ionic evaporant. These macro-particles have diameters ranging from

0.5 to 50 μm , and are co-deposited in the film, degrading the film's appearance and physical properties. Significant effort has been expended to eliminate the macro-particles without reducing the deposition rate. Once this is accomplished, arc deposition may provide a viable alternative to electroplating.

Laser Ablation

High energy density pulsed laser beams have been used to deposit thin films of a variety of elements, alloys and compounds. In this process, a laser source, external to the vacuum vessel generates a beam which is focused, passed through a viewport and impinges on a target within the vacuum vessel. Sufficient energy is generated to blast (ablate) material from the surface of the target. This ablated material consists of neutral atoms, ions, clusters of atoms and macro particles. The amount of material deposited per laser pulse is very consistent, allowing one to accurately deposit films of a specified thickness. The deposition rate is low compared to other techniques (electron beam evaporation and sputtering, for example). The range of commonly used operating parameters is given below:

laser power: 100 to 500 mJ

spot size at target 0.1 to 0.25 cm^2

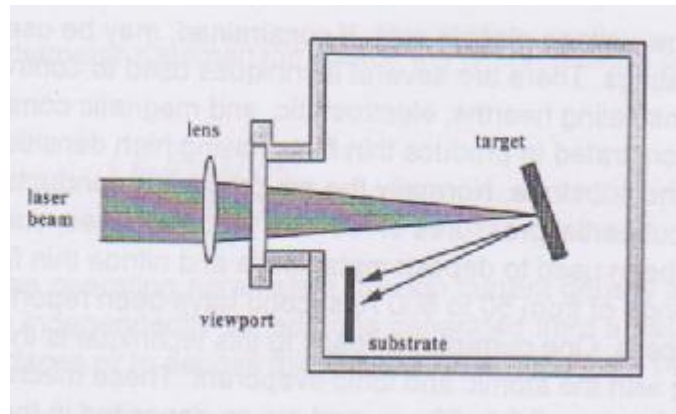
power density at target: 400 to 5000 mJ/cm^2

pulse duration: 5 to 50 ns

wavelength: 250 to 308 nm

pulse frequency: 1 to 20 Hz

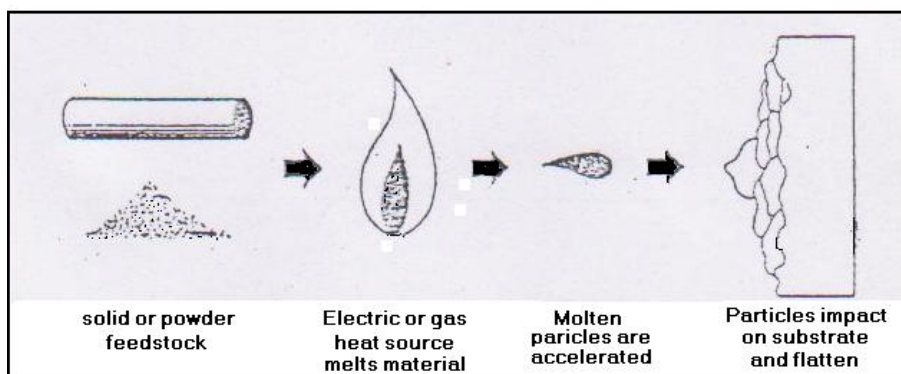
Laser ablation, as a deposition technique is currently limited to research and development laboratories due to the low deposition rate, the additional safety issues involved with the use of UV lasers and the expense of the equipment. Some of the thin films that have been deposited using laser ablation include super conducting thin films, ceramic coatings, and amorphous metallic layers.



Deposition of a thin film by laser ablation.

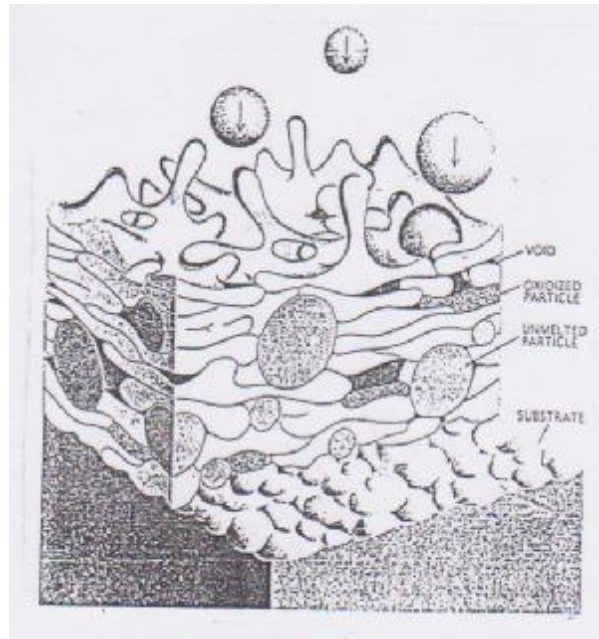
Plasma – Sprayed coating

The hot, high-speed flame of a plasma gun can melt a powder of almost any ceramic and spray it to form a coating for protection against corrosion, wear or high temperature.



PLASMA GUN ionizes a stream of gas and injects powdered coating material into the resulting flame. An inert gas mostly argon, flows through the space between a conical cathode and a ring – shaped anode. There the gas is ionized by an arc, sustained by a powerful direct current. The resulting plasma jets out through the nozzle and sweeps up powdered spray material fed by a carrier gas. Cooling water circulates through the gun to prevent it from melting.

BUILDUP of a plasma – sprayed coating is a chaotic process. Molten particles spread out and splatter as they strike the target, at first locking onto the irregularities of the roughened surface and then interlocking with one another. Voids result as the growing deposit traps air. In some cases particles overheat in the flam and become oxidized, other particles may not melt and simply get embedded in the deposit.



APPLICATIONS:

- 1- Turbine blades.
- 2- Jet Engine.
- 3- High Temperature Reactor.

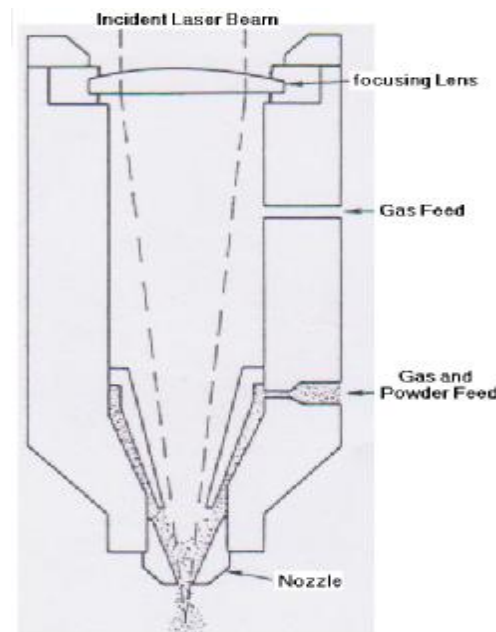
LASER – PARTICLE COATING

Processes based on the fusion of applied powder particles to metal base-plates using a continuous CO_2 laser beam, (50 Kw).

A mixed – particle laser – clad overlays for wear resistance in critical components of coal slurry pipelines. Varying mixtures of hard particles (WC, TiC or MoSi_2) and cobalt – base alloy powders were employed. Surface coating processes involving hard – phase composite structures have shown excellent wear resistance.

Laser Cladding Experiments:

A coaxial laser – powder feed process shown schematically in figure:



Laser – Processed composite metal cladding

The module consisted of a cylindrical chamber with two internal section, a ZnSe focusing lens and an exit nozzle at the bottom of the chamber.

An inert gas stream containing the powder cladding particles was introduced into the conical chamber section which surrounded the upper section. A second inert gas feed was introduced into the upper chamber section to prevent back streaming of the particles and to protect the lens.

The converging laser – gas and powder – gas streams were merged in the conical nozzle and projected out of the exit orifice to ward the substrate surface. The premixing of powder and laser beam to the substrate via direct particle heating. However, some laser radiation still reached the substrate surface directly.

Co₂ laser source produced the beam 4cm in diameter used in these experiments. The cladding process was found to perform best with about half the maximum power output of the laser. The cladding powder was fed into a gas stream from a vibratory reservoir by an auger feed screw. The powder flow was controlled by variation in the carrier gas pressure, the vibration amplitude and

screw rotation speed. The powder feed rate most often employed in these experiment was about 25 min^{-1} ($50 \text{ mm}^3 \text{ S}^{-1}$). Surface overlays were produced by translating the sample coupons under the process module at a distance of about 3 mm below the nozzle exit hole.

Chemical methods of film formation:

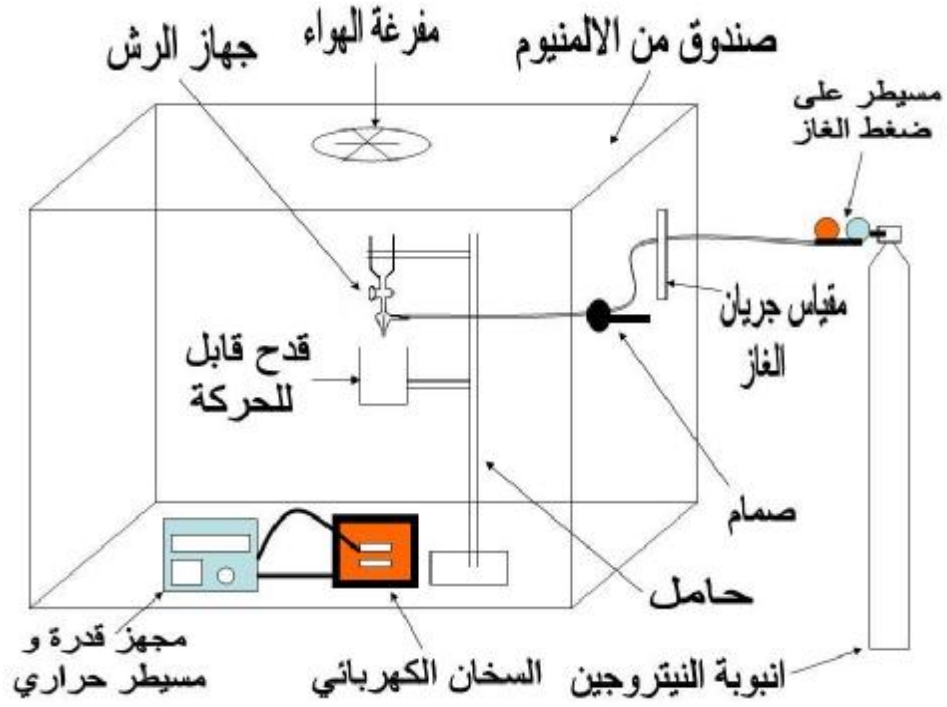
Chemical methods are fast, simple equipment are used and there for is more economical than other methods are either:

- 1- Electroplating.
- 2- Spray deposition (pyrolysis).
- 3- Chemical Vapour Deposition (CVD).
- 4- Chemical Bath Deposition (CBD).

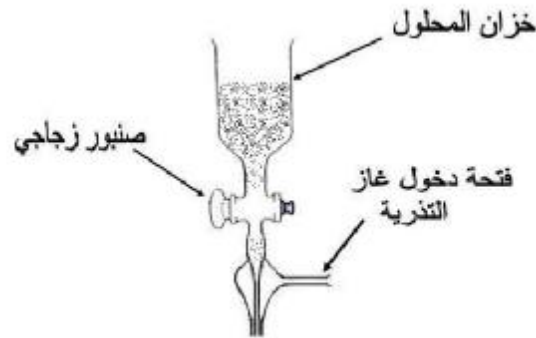
Spray deposition(pyrolysis):

تتألف منظومة الرش الكيميائي الحراري (Pyrolysis) من الأجزاء الآتية و كما موضح في الشكل:

- جهاز الرش (Sprayer system) يتألف من (خزان ، صمام ، أنبوب شعري ، غرفة هوائية) .
- حامل جهاز الرش (Holder of sprayer nozzle) .
- الضخان الكهربائي (Electric heater) .
- مضخة الهواء (Compress air) أو أنبوبة غاز النيتروجين و قد تم استخدام غاز النيتروجين بدل الهواء الاعتيادي .
- مسيطر حراري (Temperature indicator controller) .
- مزدوج حراري (Thermo couple) .
- عداد زمني (Timer) .
- مقياس جريان (Flow meter) .

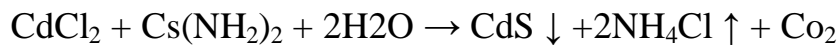


منظومة الرش الكيميائي الحراري

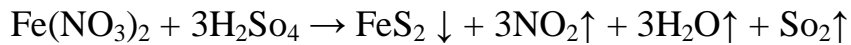


جهاز الرش

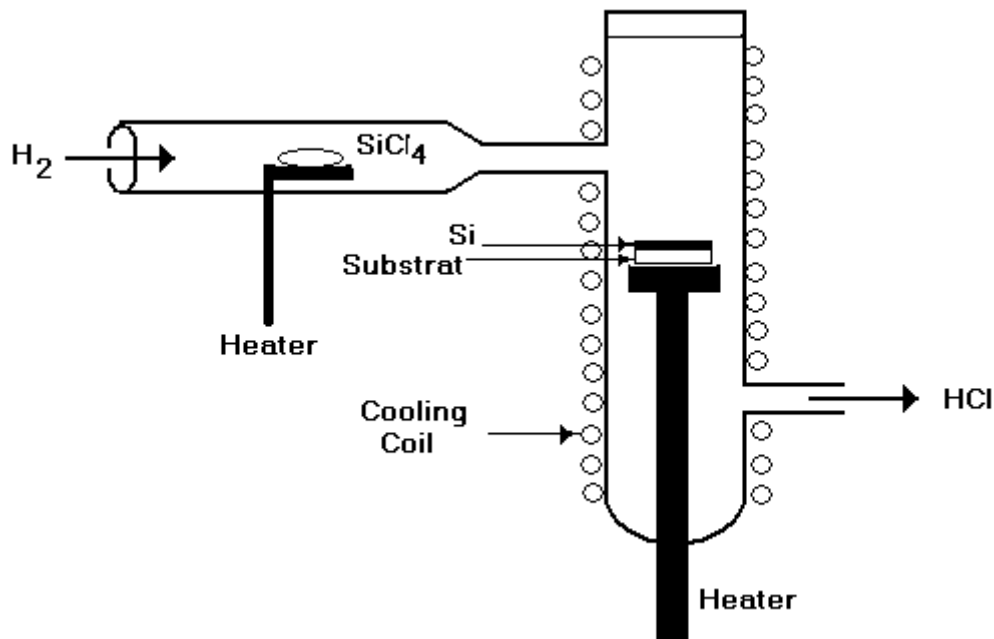
CdS thin film:



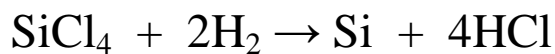
FeS₂ thin film:



Chemical Vapour Deposition (CVD):



(CVD)



Chemical Bath Deposition (CBD):

What is Chemical Bath Deposition?

Chemical deposition refers to the deposition of films on a solid substrate from a reaction occurring in a solution (almost always aqueous). Chemical bath deposition (CBD) is also known as solution growth is a controlled precipitation. It is an analogue, in the liquid phase, of the well known chemical vapors deposition in the gaseous phase. The reaction takes place between the dissolved precursors generally in aqueous solution at low temperature (30-80°C).

Which Materials Can Be Deposited by CBD?

In principle, CBD can be used to deposit any compound that satisfies four basic requirements :

1-The compound can be made by simple precipitation.

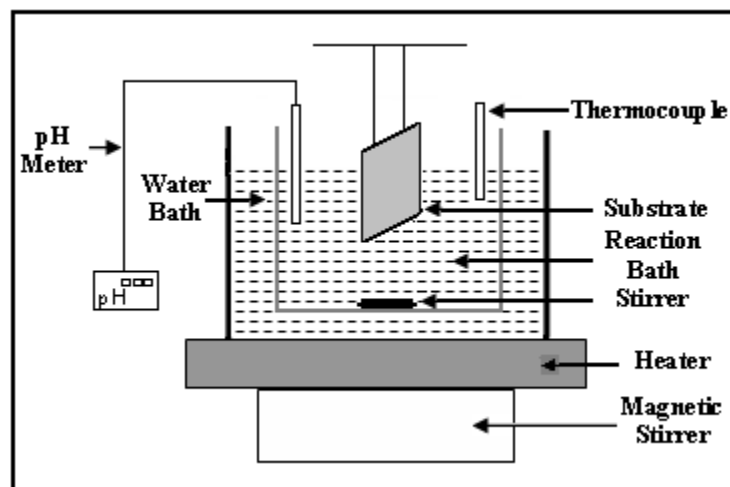
- 2- The compound should be relatively and preferably highly soluble in the solution used except in a very few cases, this has been water.
- 3- The compound should be chemically stable in the solution.
- 4- If the reaction proceeds via the free anion, then this anion should be relatively slowly generated to prevent sudden precipitation.

Advantages of the (CBD) Process:

1. It is a very simple and inexpensive technique suitable for a large area, and gives good adherent deposition with uniformity.
2. It is a low temperature less than 90°C deposition method.
3. Film can be deposited on all kinds of substrates glass, ceramic, polymer, while a limited number of substrate materials can withstand high temperature and chemical corrosion in spray pyrolysis.
4. In CBD the deposition forms ions in aqueous solution, which slowly being generated. The solubility product helps to maintain the stoichiometric constant for any ratio of cations and anions.
5. CBD gives the best photoconductivity and morphological properties such as roughness and pinhole density when compared to films processed by other techniques.

Limitation of (CBD):

- The CBD method has a limitation regarding the temperature of deposition. The temperature is normally restricted to about 100 °C.
- The generation and disposal of large quantities of hazardous waste.



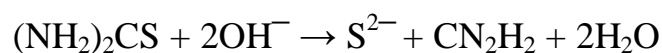
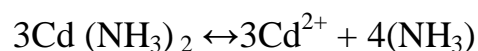
Experimental set up of chemical bath deposition

Mechanisms of Chemical Bath Deposition (CBD):

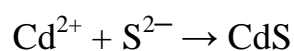
The Simple Ion – by – Ion Mechanism:

The simplest mechanism, often assumed to be the operative one in general, is commonly called ion – by – ion mechanism, since it occurs by sequential ionic reaction. Initially diffusion of the ions to the substrate, and then nucleation of the ions are facilitated by the substrate to form compound nuclei, and growth of the compound crystals. Finally compound crystals which are in continued growth, adhere to each other through Van der Waals forces. The conceptually simplest mechanisms are:

(dissociation of complex to free Cd^{2+})

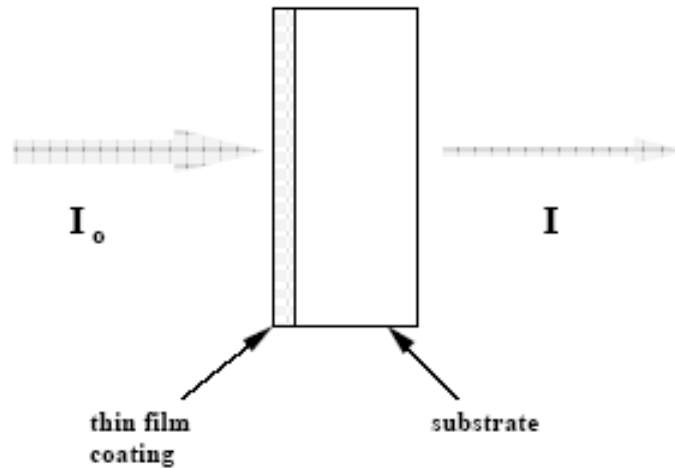


(CdS formation by ionic reaction)



Optical:

Optical transmission data may also be used to monitor the thickness of a film during deposition, and can yield quantitative data if an independent thickness calibration is performed.



Transmission of light through a thin film on a substrate.

$$\frac{I}{I_0} = e^{-ax}$$

where:

I_0 = intensity of the incident beam

I = intensity of the transmitted beam

a = absorption coefficient of the material
at the wavelength of interest

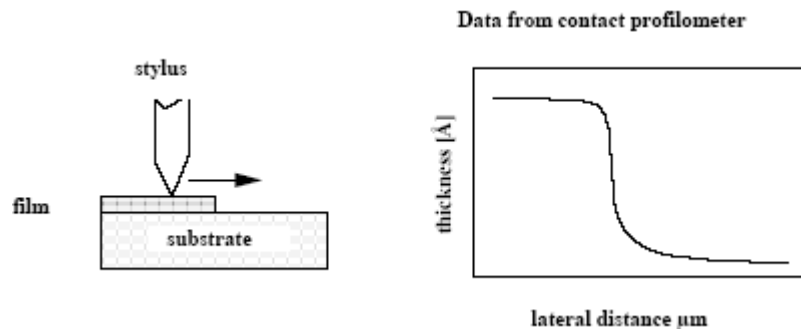
x = thickness of the material

The effect of absorption from the substrate must be taken into account in the thickness measurement by optical transmission. This can be accomplished by measuring the transmission of the uncoated substrate, and subtracting that value from the transmission measured during deposition.

Contact Profilometry:

In this ex-situ characterization technique, the sample is prepared by masking off a portion of a smooth substrate, such as floatglass, then depositing a thin film onto the sample. This creates coated and uncoated areas (a so-called "step slide") on the smooth substrate which can be used to determine film thickness.

After the part is removed from the deposition system, a ruby or diamond tipped miniature stylus is scrolled across the sample.



Stylus of contact profilometer on a "step slide" sample, and the resulting data.

Contact profilometry is frequently used to establish deposition rates, and as a means of calibration for in-situ rate monitoring techniques, such as the quartz crystal microbalance. Films having thicknesses of from 50 to 100,000Å have been accurately measured using contact profilometry.

Sheet Resistivity:

Some thin films are deposited with the goal of attaining a specified electrical characteristic, such as resistivity. These films may be characterized using a commercial instrument called a four-point resistivity probe. Current is passed between each of the points of the probe through the thin film, and is measured. The data is output as sheet resistivity expressed in ohms per square centimeter (Ω/cm^2).

Optical Transmission:

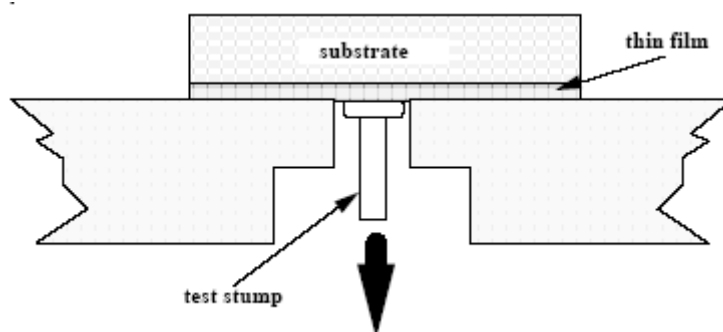
Optical transmission measurements often are more detailed and extensive than the optical monitoring described earlier for in-situ measurements. A single wavelength, or narrow band of wavelengths are often used, along with low resolution spectrometers for the in-situ optical measurements. Optics are often carefully inspected following deposition of a thin film coating to establish the transmission over a broad range of wavelengths.

Compositional analysis:

There are a variety of techniques used to determine the chemical composition of thin film coatings following a deposition run. These techniques may be grouped into two broad categories: destructive and non-destructive. Wet chemical analyses, in which the film is dissolved, the solution being analyzed using techniques such as atomic emission spectroscopy are obviously harmful to the coating. If destructive analytical techniques are to be used, it is possible to perform them on "dummy parts" that were coated along with the part of interest. Non-destructive analytical techniques include x-ray techniques (x-ray fluorescence, x-ray diffraction), electron spectroscopy for chemical analysis (ESCA) and other surface science techniques. Most of these non-destructive analytical methods are conducted under vacuum in relatively small chambers, which places size limitations on the parts to be analyzed.

Mechanical Testing:

Frequently the mechanical property of a thin film coating which is of most interest is its adhesion to a substrate. Simple tests of adhesion include the "scotch tape test" in which a piece of scotch tape is pressed firmly to the coated side of a part, then peeled away. Other more sophisticated tests of adhesion include the Sebastian pull test and the ring shear test. In the Sebastian test, a metal stump is glued to the thin film deposited onto a substrate. The force required to pull the stump away from the substrate is recorded, and plotted as a graph of stress (force per unit area) versus strain(deformation).



Sebastian pull test for adhesion of thin films.

