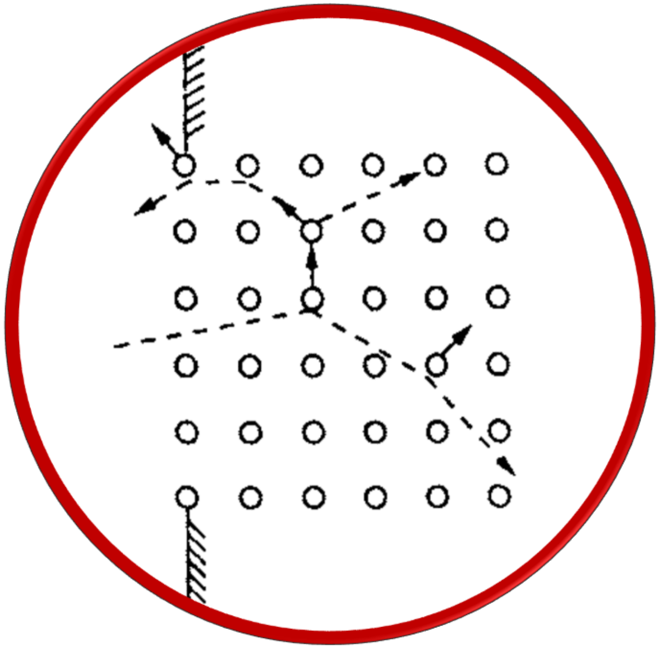
plasma and ion beam processing of thin films



contents

targets

At present, targets of virtually **all important materials are commercially available** including all of the important classes of solids, e.g., metals, semiconductors, oxides, fluorides, borides, carbides, nitrides, silicides, and sulfides.

Targets come in a **variety of shapes** (e.g., rectangular, triangular, and circular plates, conical disks, toroids) and in assorted sizes. For example, targets range in size from ~ 10cm dimensions for laboratory purposes to several meters for coating architectural glass.

In general, the **metal and alloy targets are fabricated by melting** either in vacuum or under protective atmospheres, followed by thermomechanical processing involving some combination of forging, extrusion, rolling, and annealing, and ending with machining to final dimensions.

Refractory alloy targets, e.g., Ti-W, are hot-pressed via the **powder-metallurgy route**. Similarly, **ceramic and oxide targets** are generally prepared by **hot pressing of powders**. The elemental and metal targets generally have purities of 99.99% or better, whereas those for the nonmetals have typical upper purity limits of 99.9%.

For **microelectronic purposes purities an order of magnitude higher** are demanded together with stringent stoichiometries. While the metal targets usually attain theoretical densities, lower densities are achieved during powder processing. These are prone to greater arcing rates, emission of particulates, release of trapped gases, nonuniform target erosion.

Prior to use, **targets must be bonded to a cooled backing plate** to avoid thermal cracking during sputtering. Metal-filled epoxy cements of high thermal conductivity are employed for this purpose.

Ohring 2002

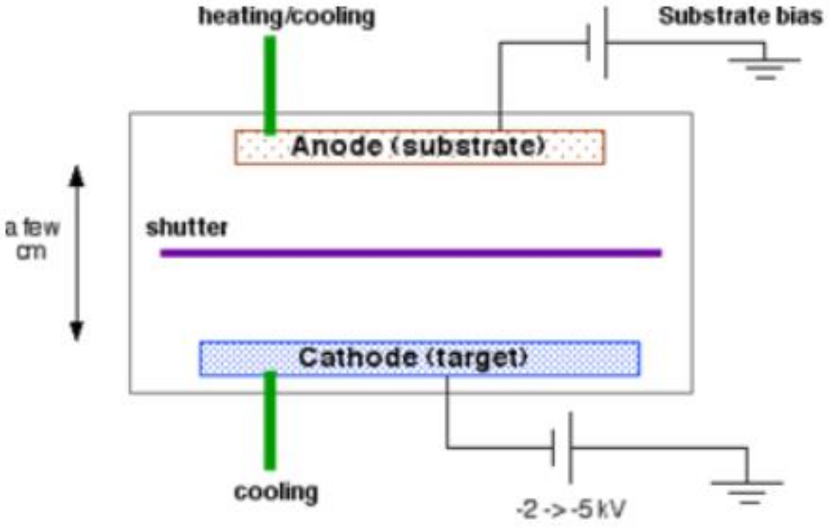
DC sputtering

DC sputtering

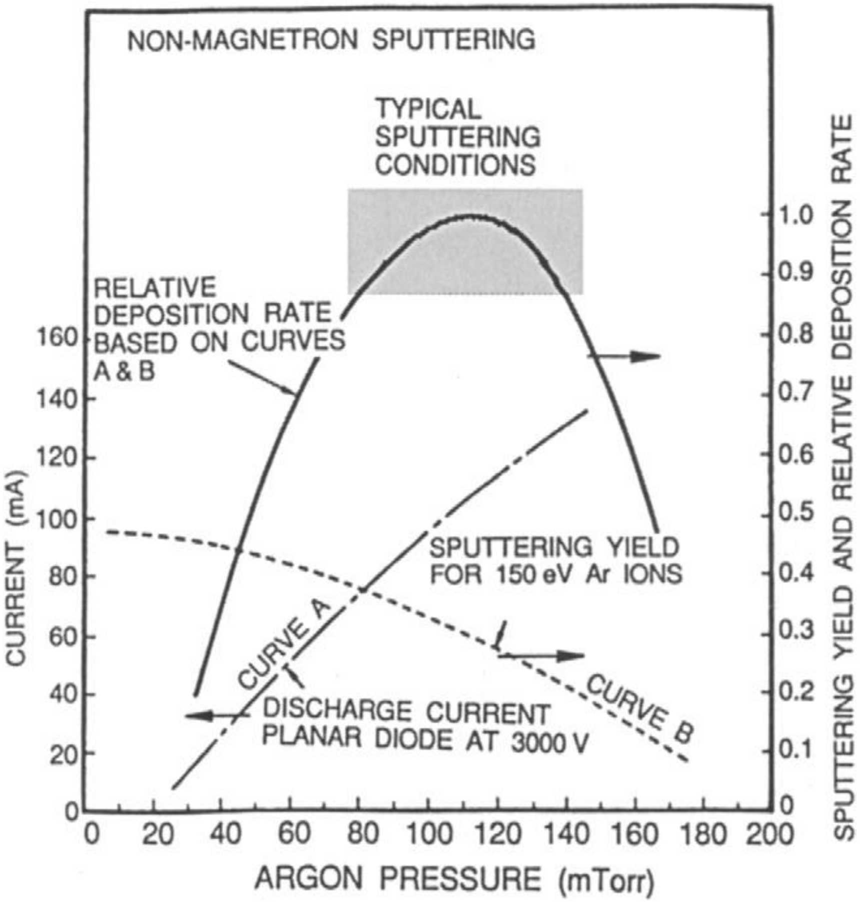
- Initially pump system down to 10^{-6}–10^{-7}Torr for purity.
- Then let in controlled amount of the gas to be ionized (generally Argon).
- Eventually the chamber pressure will be around 1 –100 mTorr. This number is determined by the pressure required to have a sustainable plasma given the chamber dimensions.
- The main control is the energy of the ions.–They need to be in the right range for sputtering.

Some Limitations of DC Sputtering

- The high pressures required to achieve a plasma can degrade film quality.
- Only a small fraction of the gas is converted to ions.
- All of this results in deposition rates that are low (~ 100 Å/ min).



DC sputtering



The relative film **deposition-rate depends on sputtering pressure and current**.

At **low pressures**, the cathode sheath is wide, ions are produced far from the target, and their chances of being lost to the walls is great. The mean free electron path between collisions is large, and electrons collected by the anode are not replenished by ion-impact-induced secondary-electron emission at the cathode. Therefore, ionization efficiencies are low and selfsustained discharges cannot be maintained below about 10 mtorr (~10^{-2}mbar).

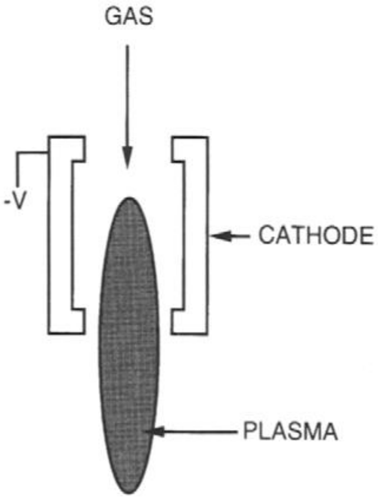
As the **pressure is increased** at a fixed voltage, the electron mean free path is decreased, more ions are generated, and larger currents flow **(curve A).**

But if the **pressure is too high**, the sputtered atoms undergo increased collisional scattering and are not efficiently deposited **(curve B).**

A **trade-off** in these opposing is shaded in and include the relatively high operating pressure of ~ **100 mtorr** (~10^{-1}mbar).

Ohring 2002

hollow cathode



The use of a hollow cathode is a way to **enhance ionization in a DC discharge.** Hollow-cathode sources are little more than a tube, or cylindrical hole in an electrode, through which ionized gas flows.

Operation of hollow cathodes is related to the "**pendel-electron" effect.** The discharge cavity consists of a negative glow region separated from opposite cathode surfaces by two dark spaces. In a pendulum-like motion, electrons emitted from the cavity surface are accelerated toward the negative glow, penetrate the opposite dark space, turn around, and enter the negative glow again.

This to-and-from electron motion leads to an enhanced gas-ionization rate and substantially increases the plasma density within the cavity.

Compared to glow discharges contained between parallel-plate electrodes, the **current densities in hollow cathodes are one to two orders of magnitude higher**. A highly ionized plasma is generated and issues as a jet into the main discharge region.

Ohring 2002

substrate bias

Energetic-particle bombardment prior to and during film formation and growth promotes numerous changes and processes at a microscopic level.

These include
- removal of contaminants,
- alteration of surface chemistry,
- enhancement of nucleation and renucleation
- higher surface mobility of adatoms,
- elevated film temperatures with attendant acceleration of atomic reaction and interdiffusion rates.

In summary, there are few ways to broadly influence such a wide variety of thin-film properties, in so simple and cheap a manner, than by application of substrate bias.

Ohring 2002

substrate bias

Negative DC or RF electric fields are often applied to bias the substrate in order to vary the flux and energy of depositing charged species.

With target voltages of -1000 to -3000 V, **bias voltages of - 50 to -300 V are typically used**. Because of charge-exchange processes in the anode dark space, **very few discharge ions strike the substrate** with full bias voltage.

Rather, a **broad low-energy distribution of ions and neutrals bombards the growing film**. The technique of applying bias has been utilized in all sputtering configurations, e.g., DC, magnetron, RF, reactive, and has been effective in modifying a broad range of properties in deposited films.

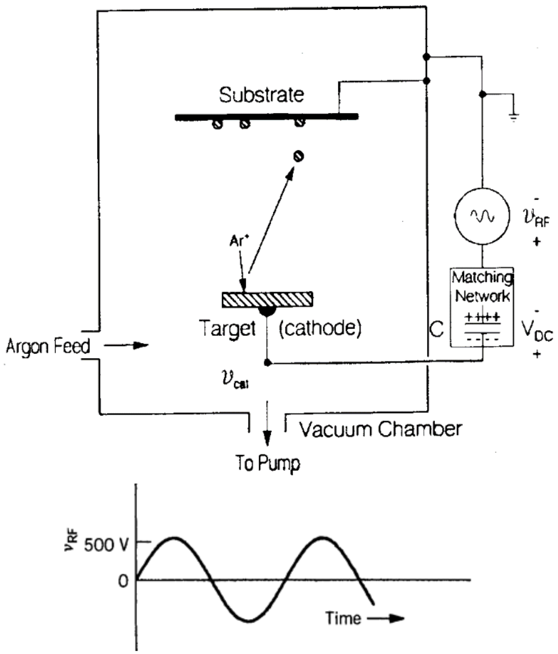
Examples include

improved film adhesion during initial stages of film formation;
substantial improvement in step coverage
increased film density (e.g., Cr);
significant reduction in resistivity of metal films (e.g.,Ta, W, Ni, Au, and Cr);
change in film hardness and residual stress (either increase or decrease);
enhanced optical reflectivity (e.g., W, Ni, and Fe films);
alteration of film morphology (e.g., columnar
microstructure of Cr replaced by a compacted, fine-grained structure).

Ohring 2002

RF (radio frequency) sputtering

- Instead of applying a DC voltage to the cathode, apply a voltage oscillating at radio frequency (RF), **typically around 13.56 MHz.**
- The RF peak to peak voltage is around 1000V, electron densities are around **10^9-10^{11}cm^{-3}**and the chamber pressure is 0.5 -10 mTorr
- On the **positive cycle, electrons are attracted to the cathode,** creating a negative bias on an insulating target (think of it as replenishing the negative charge on the target surface).
- On the **negative cycle ion bombardment continues**.
- By avoiding a constant negative voltage on the cathode, ion buildup is prevented for insulating targets.
- **Can operate at lower pressures** while still sustaining a plasma.
- **Normally both the target and substrate should sputter.** This can be overcome by making the target area small compared to the substrate.
- While any type of film can be RF sputtered, **deposition rates are still low.**
- Applying RF power is not so simple, power supplies are **expensive and additional circuitry is needed**



RF (AC) sputtering

Suppose we now **wish to deposit thin SiO_2 films by using a quartz disk of thickness d as the target in a conventional DC sputtering system**. DC sputtering will not work because q**uartz is an insulator**.

This impasse can be overcome, however, if we recall that **impedances of dielectric filled capacitors drop with increasing frequency**. Therefore, **high-frequency plasmas ought to pass current through dielectrics the way DC plasmas do through metal targets**.

The trick is to sustain the plasma while ensuring positive-ion bombardment of the cathode. It appears that **1 MHz is a very rough dividing line between low- and high-frequency plasma behavior**. In the former range of 60 Hz, audio, and low-frequency RF, ions are sufficiently mobile to establish a complete discharge at each electrode in each half cycle. **DC sputtering conditions essentially prevail at both electrodes.**

Above 1 MHz several important effects occur:

- First, **electrons oscillating** in the glow region **acquire enough energy** to cause **ionizing** collisions. We would not need secondary electrons from the cathode to maintain the plasma.
- Secondly, at radio frequencies, voltage can be coupled through any kind of impedance so that the **electrodes need not be conductors**. This makes it possible to sputter any material irrespective of its resistivity.
- A third important effect is the reduction of ion energy above 1 MHz. If for the same applied power, more is partitioned to electrons in raising their energies, less is available to ions.

Ohring 2002

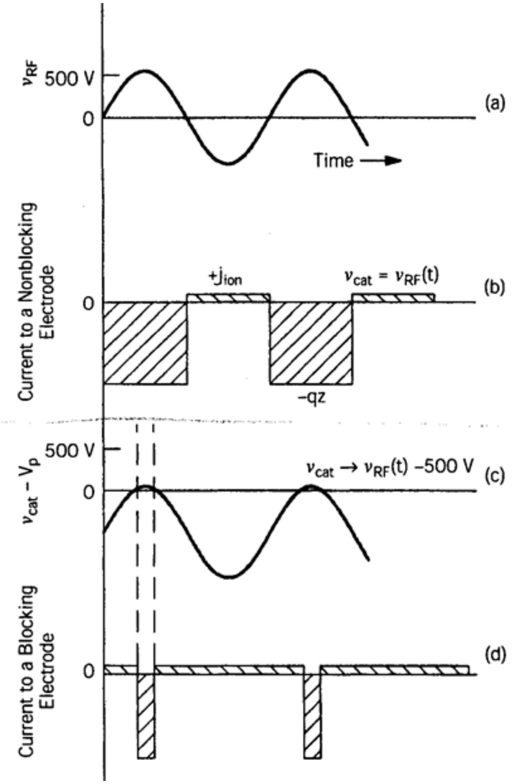
target self bias

Although we have established that RF discharges are sustainable, it is not clear how they can be used for sputtering.

RF sputtering essentially works **because the target self-biases to a negative potential for insulators**. Once this happens, it behaves like a DC target where positive ion-bombardment sputters away atoms for subsequent deposition.

Negative target bias is a consequence of the fact that electrons are considerably more mobile than ions and have little difficulty in following the periodic change in the electric field.

The disparity in electron and ion mobilities means that isolated positively charged electrodes draw more electron current than comparably isolated negatively charged electrodes draw positive ion current.



Ohring 2002

rf sputtering issues

Electrically, the target is usually the powered electrode and it must be insulated from the grounded substrate and the rest of the chamber. Because **the plasma discharge has capacitive as well as resistive characteristics**, efficient coupling of the RF power supply to the target is not trivial. What is required is **an impedance-matching network** consisting of **some combination of variable and fixed capacitors and inductors** to ensure maximum power delivery.

The frequency of **13.56 MHz** has been reserved for plasma processing and is most widely used.

In contrast to **DC discharges where the plasma is confined to the cathode, RF plasmas tend to fill the chamber volume**.

Since AC electricity is involved, **both electrodes should sputter**. This presents a potential problem because the resultant film may be **contaminated** as a consequence.

All kinds of insulating as well as conductive films have been RF sputtered over the years, but the **deposition rates are generally very low**. Film stoichiometries are problematical as metal-rich films tend to be deposited.

In addition, **it is difficult to make high-purity, dense compound (e.g., oxide, nitride) targets**. Since ceramic and oxide insulators are simultaneously mechanically brittle and poor thermal conductors, they are **susceptible to thermal-stress cracking** when subjected to ion bombardment at high power levels.

Ohring 2002

magnetron sputtering

Magnetron sputtering is the **most widely used variant of DC sputtering**.

One to **two orders of magnitude more current** is typically drawn in magnetron than simple DC discharges for the same applied voltage.

Important implications of this **are higher deposition rates** (e.g., ~ 1 μm per minute for Al metallization alloys)

Another important advantage is **reduced operating pressures**. At **typical magnetron-sputtering pressures of a few millitorr, sputtered atoms fly off in ballistic fashion** to impinge on substrates. Avoided are the gas phase collisions and scattering at high pressures which randomize the directional character of the sputtered-atom flux and lower the deposition rate.

A fundamental reason for these beneficial effects in magnetrons is **the displacement of the Paschen curve to lower Pd values** relative to simple discharges.

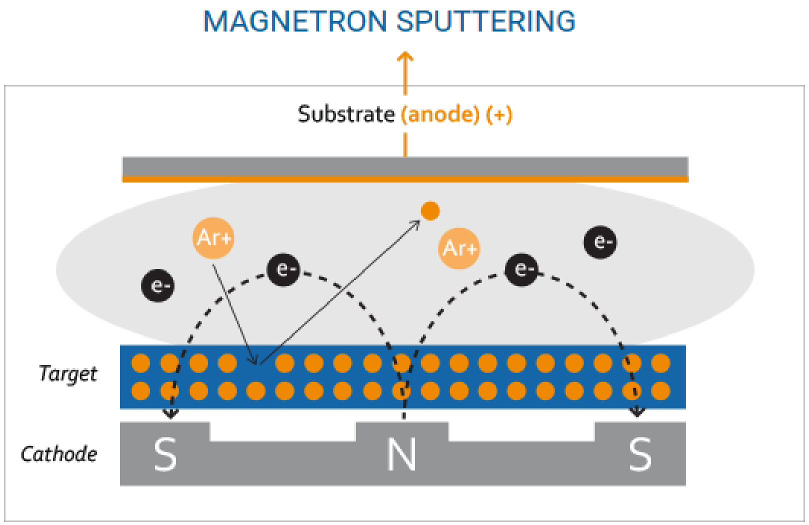
Therefore, **for the same electrode spacing and minimum target voltage a stable discharge can be maintained at lower pressures**. These attributes of magnetron sputtering should be borne in mind as we now proceed to discuss three popular target geometries employed in magnetron sputtering.

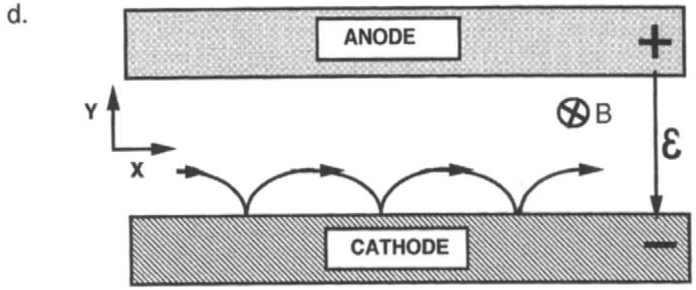
Ohring 2002

magnetron sputtering

- Magnetron sputtering is a **highly versatile thin film deposition technique** for coating films with excellent adhesion and high density. Magnetron sputtering is a plasma-based coating process where a **magnetically confined plasma is created near the surface** of a target material. Positively charged energetic ions from the plasma collide with the negatively charged target material, and atoms from the target are ejected or “sputtered”, which then deposit on a substrate.

- Magnetron sputtering uses a **closed magnetic field to trap electrons**, increasing the **efficiency of the initial ionization process and creating the plasma at lower pressures**, **reducing both background gas incorporation in the growing film and energy losses in the sputtered atom through gas collisions**. Magnetron sputtering is often chosen for the deposition of metallic and insulating coatings that have specific optical or electrical properties.





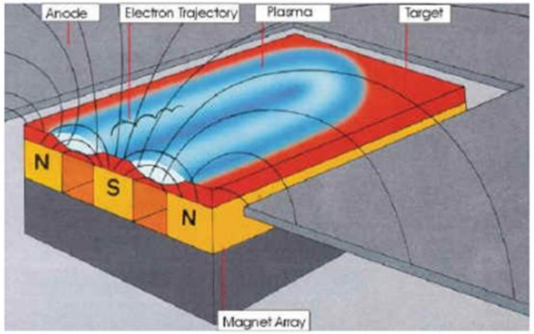
Ohring 2002

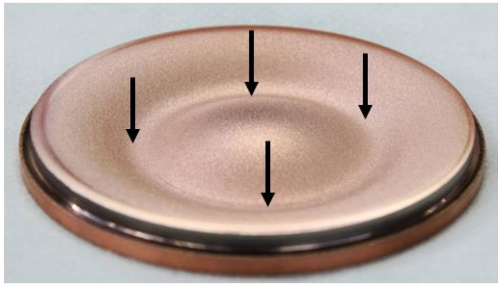
magnetron sputtering

- Advantages of Magnetron Sputtering
  - High deposition rate
  - Reducing electron bombardment of substrate
  - Extending the operating vacuum range –ability to operate at lower pressures

- Parameters for Magnetron Sputtering
  - Deposition pressure : 0.1 to 1 Pa (10^{-4} to 10^{-2} mbar)
  - Deposition rate : 0.2 ~ 2-6 μm/min (10 times higher than conventional sputtering)

- Disadvantages for Magnetron Sputtering
  - An erosion track in the target –This leads to poor efficiency of sputtering yield versus target volume compared to non-magnetron sputtering
  - Non-uniform removal of particles from target result in non-uniform films on substrate



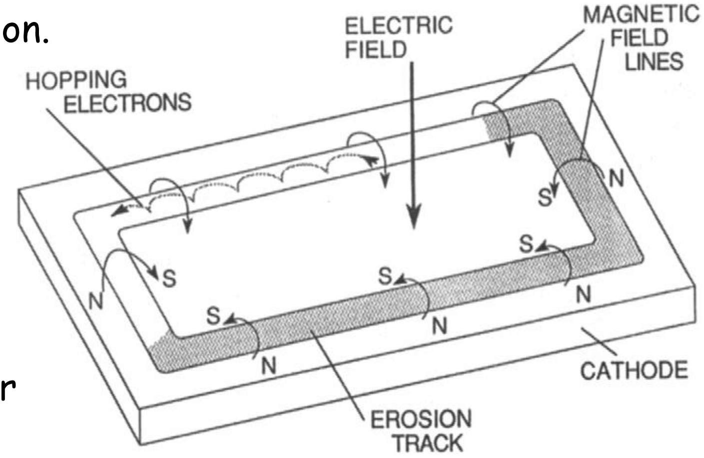


planar magnetron

Of the three magnetron configurations, the planar one with **parallel target and anode** electrode surfaces is most common.

A typical DC electric field of E ~ 100 V/cm is impressed between the target (cathode metal to be sputtered) and anode (substrate) plates.

Small permanent magnets are arranged on the back of the target in either ellipse-like or circular rings depending on whether the targets are rectangular or circular



To conceptually understand magnetron operation, consider the simple case of a single bar magnet, whose north and south poles are spaced far apart, mounted parallel to the back plane of the target.

Roughly half of the total magnetic field (B) distribution emerges from the north pole roughly perpendicular to the front target face into the interelectrode space.

Then the field lines arch over with a portion parallel to the target surface, i.e., the magnetron component. Finally B returns roughly normal to the target surface into the south pole, completing the closure of field lines.

If we now imagine a linear array of such bar magnets, a **B field tunnel** is created on the front surface of the target. Electrons launched slightly off the target normal will initially spiral along the B field lines emanating normal to the target. In the region where E and B fields are perpendicular to one another, electrons are forced to drift in a cycloidal hopping motion along the tunnel track length

Ohring 2002

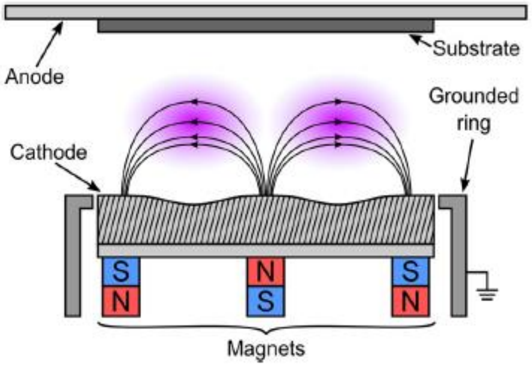
planar magnetron

The center portion of the magnet is of one polarity, and the outer periphery is of the other polarity. So the **assembly consists of an outer annular magnet and an inner magnet of opposite polarity**, and the magnetic field lines go out from the center of the cathode and go back into the cathode at the annular.

Since the electrons spend more time where the electric field is perpendicular to the magnetic field, the **ideal geometry would be to have the magnetic field parallel to the cathode surface**.

However, in reality the magnetic field produced by the magnet and its associated pole pieces comprise **field lines, which extend from the sputter surface and return thereto** to form an arch over what is referred to as the erosion region.

Within this **arch, ionizing electrons and ionized gas are confined forming a dense glow discharge and consequently a high level of sputter activity**. We refer to this region as the ionization region. If the cathode plate is circular (can also be rectangular) the magnetic confinement leads to a luminous torus shaped plasma that hovers next to the target.



Lundin 2018

pulsed power magnetron sputtering

It is not uncommon for **metal targets to be poisoned** or **acquire a different surface composition from that of the bulk**.

Reactive gases are usually responsible and often result in the **formation of dielectrics, e.g., oxides, which tend to readily charge up**.

If the surface potential is negative, ion impingement may initially cause sputtering but since the secondary electron emission coefficient is less than unity, **a positive surface charge develops. Ion bombardment is discouraged and then ceases**, which prevents sputtering.

However, given sufficient charge buildup, local dielectric breakdown of the insulating films causes arcing over the target surface (unipolar arcs) as well as to neighboring hardware (bipolar arcs). As a result, the target erodes by cratering with the ejection of liquid droplets that create defects when incorporated into growing films.

In addition to particle splatters, arcing prevents the stable operation of DC power supplies, particularly during the reactive sputtering of dielectric films. Eliminating this serious problem is simple in principle; **discharge the positive surface charge!**

Pulsed-power sputtering technology was developed to do this. Typically, square or sinusoidal **voltage pulses are applied to the target at frequencies of several tens of kilohertz, where pulse magnitude, polarity, width, and off-time can all be varied.**

Ohring 2002

pulsed power magnetron sputtering

In the case of **bipolar pulses**, for example, **asymmetric positive and negative voltage polarities are applied,** e.g., a -400 V pulse for 80-90% of the voltage cycle followed by a + 100 V pulse for 20-10% of the remaining time.

During the **positive portion of the cycle, electrons are drawn to the target in order to neutralize the positive charge buildup** that leads to arcs. After discharging, **the target is again negatively powered and sputtered** until it is time to discharge it again, etc.

Commercial pulsed-power supplies incorporate arc suppression electronics which sense the initiation of arc currents and either rapidly reduce the power or apply a positive voltage in response.

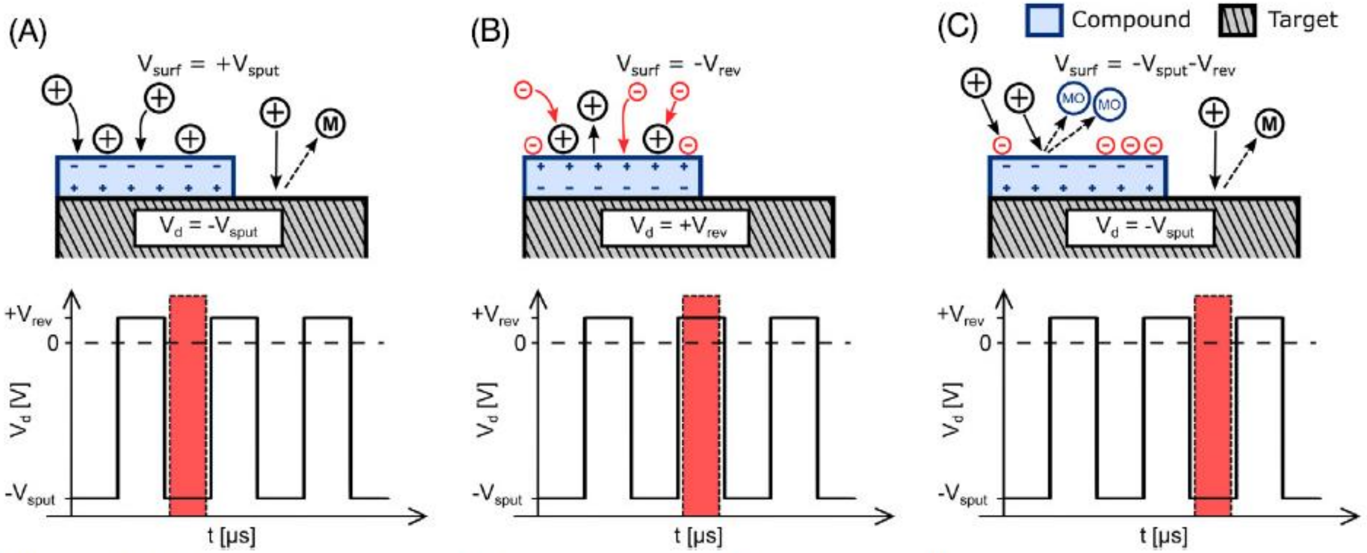


Figure 1.11 Preferential sputtering by asymmetric bipolar sputtering. Three points in time are displayed: (A) normal sputter mode, (B) reversal mode, and (C) return to sputter mode. After Sellers (1998).

Ohring 2002
Lundin 2016

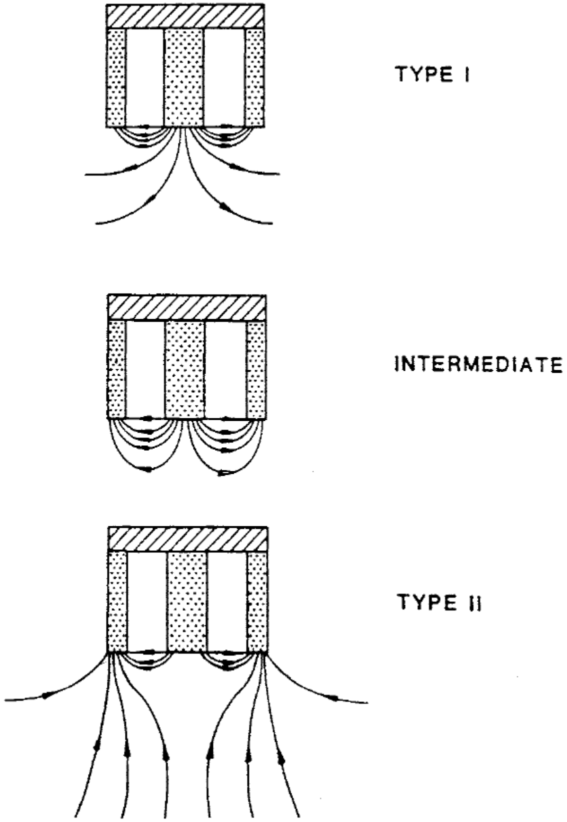
unbalanced magnetron sputtering

We have already noted the benefits of electron and plasma confinement.

But **too much confinement at the cathode surface may be undesirable** if not enough plasma is available at the anode to activate reactive gases or promote ion bombardment for the desired modification of growing films.

The problem can be overcome through **selective strengthening of the magnetic field at the target ends** so that more of the secondary electrons can escape their confinement as shown in the so-called "type-II" unbalanced magnetron configuration.

Magnetrons can also be unbalanced through placement of stronger magnets in the middle relative to the outer end of the target ("type I").



Planar magnetron configurations.
Type-I (unbalanced)
Intermediate (balanced).
Type-II (unbalanced).

Ohring 2002

magnetron sputtering problems

- Target Integrity

In planar magnetron sputtering, **targets erode preferentially** in the racetrack region where the plasma is most intense. This leaves a kind of racetrack ditch or depression that progressively deepens, surrounded by a much larger target area that suffers less loss of metal. Such target erosion a) leads to **low process efficiency**, b) **inhomogeneous metal loss during reactive sputtering** such that the racetrack remains metallic while the surrounding target area becomes covered with insulator films, **enhancing the probability of arcing** and c) The **uniformity of deposited films is affected**.

- **Particulate Contamination**

Conventional wisdom assumes that the primary sources of microcontamination are **arcing**, **gas-phase nucleation of particles**, and **reactor wall and substrate films that have flaked** off due to stress buildup. In addition special processes happen at the target where the highly nonuniform plasma density, typical of magnetron sputtering, results in simultaneous material removal and **redeposition** in adjacent target regions.

- **Film Uniformity:**

As in the case in evaporation, the sputter deposition of uniformly thick blanket films on flat substrates is generally achieved without difficulty. It is when substrates contain **steps** and **trenches that uniform film coverage of these features is considerably more challenging**. When the aspect ratio of the hole is high, early coverage of the corner and upper sidewalls physically **shadows the lower regions** from subsequent deposition.

Ohring 2002

reactive sputtering

In reactive sputtering, thin films of compounds are deposited on substrates by sputtering from metallic (not nonmetallic) targets in the **presence of a reactive gas** usually **mixed with an inert working gas (invariably Ar)**.

The most common compounds reactively sputtered and the reactive gases employed are:

Oxides (oxygen) - - Al_2O_3, In_2O_3, SnO_2, SiO_2, Ta_2O_5.
Nitrides (nitrogen, ammonia) - - TaN, TiN, AlN, Si_3N_4, CN_x.
Carbides (methane, acetylene, propane) - - TiC, WC, SiC.
Sulfides (HzS)--CdS , CuS, ZnS.
Oxycarbides and oxynitrides of Ti, Y, Al, and Si.

Irrespective of which of the above materials is being considered, during reactive sputtering the resulting film will usually be a **solid solution alloy of the target metal doped/alloyed with the reactive element, a compound, or some mixture of the two.**

Ohring 2002

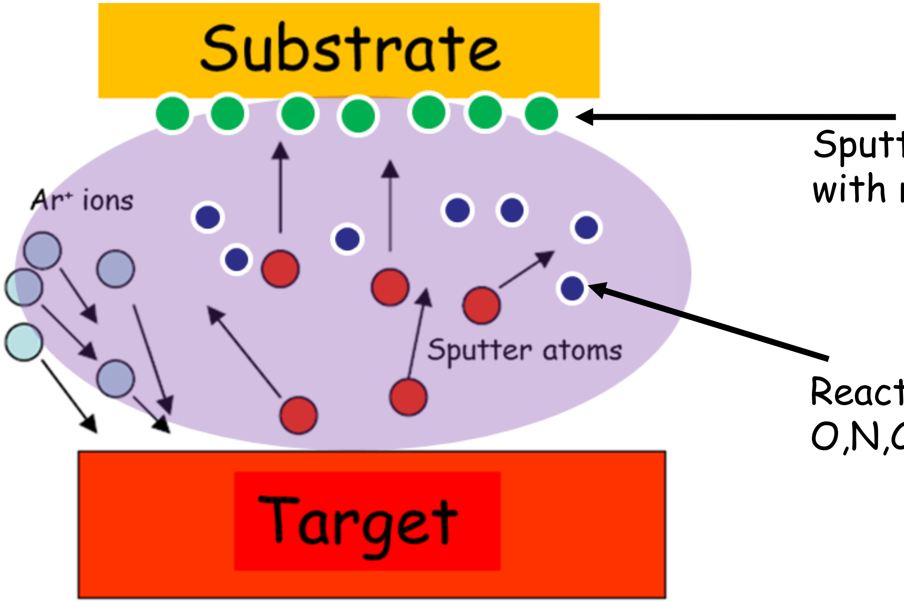
reactive sputtering

Sputtering metallic target in the presence of a reactive gas mixed with inert gas (Ar)

A mixture of inert +reactive gases used for sputtering
Oxides – Al_2O_3, SiO_2, Ta_2O_5 (O2)
Nitrides – TaN, TiN, Si_3N_4 (N_2, NH_3)

- Chemical reaction takes place on substrate and target
- Can poison target if chemical reactions are faster than sputter rate
- Adjust reactive gas flow to get good stoichiometry without incorporating excess gas into filmcarbides – TiC, WC, SiC (CH_4, C_2H_4, C_3H_8)

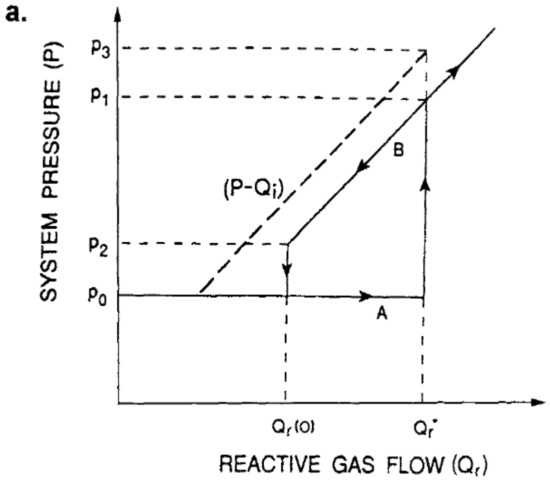
- stoichiometric ratio depend on **Ar/Gas ratio**
- Excess gas leads to **corrosion of target** and effect the sputtering rates and composiion.



Sputter atoms reacts with reactive gas atoms

Reactive gas atoms
O,N,C

reactive sputtering



First, consider the dotted line representing the variation of P with flow rate of an inert sputtering as (Q_i).

As Q_i increases, P increases because of the constant pumping speed.

When reactive N_2 gas is introduced into the system Q_r increases from $Q_r(0)$, the system pressure essentially remains at the initial value, P_o, because N_2 reacts with Ta and is removed from the gas phase.

But beyond a critical flow rate, Q*, the system pressure jumps to the new value P_1.

Once the equilibrium value of P is established, subsequent changes in Q_r cause P to increase or decrease linearly as shown.

As Q_r decreases sufficiently, P again reaches the initial pressure.

The hysteresis behavior represents two stable states of the system with a rapid transition between them. In state A there is little change in pressure, whereas for state B the pressure varies linearly with Q_r.

Ohring 2002

reactive sputtering

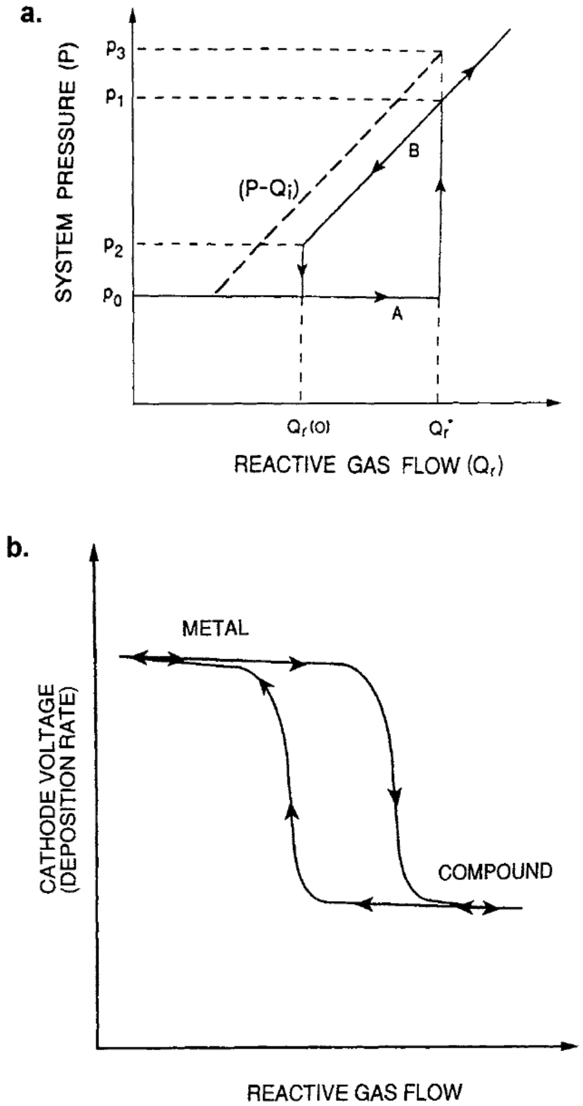
All of the reactive gas is incorporated into the deposited film in state A the doped metal, and the atomic ratio of reactive gas dopant to sputtered metal increases with Q_r.

The transition from state A to state B is triggered by compound formation on the metal target.

Since ion-induced secondary-electron emission is usually much higher for compounds than for metals, Ohm's law suggests that the plasma impedance is effectively lower in state B than in state A.

This effect is reflected in the hysteresis of the target voltage with reactive gas flow rate as schematically depicted.

By substituting deposition rate for cathode voltage, this same hysteresis behavior also describes the reactive sputtering rate for metals and compounds as a function of Q_r



Ohring 2002

reactive sputtering

In practice, **sputter rates of metals drop dramatically** when compounds form on the targets. Corresponding decreases in deposition rate occur because of the lower sputter yield of compounds relative to metals.

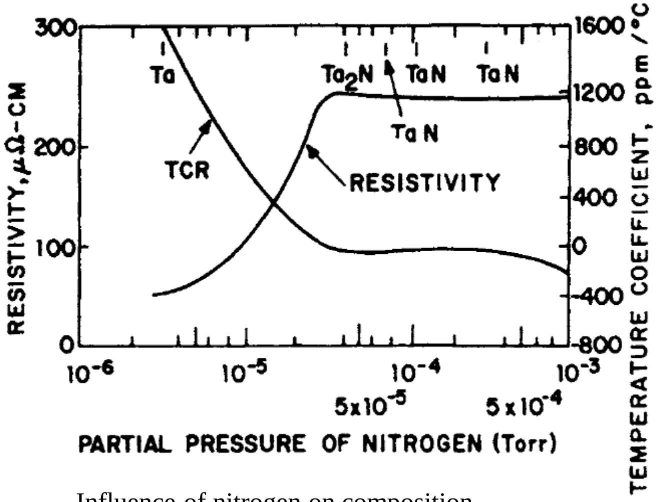
The effect is very much **dependent on reactive gas pressure**

Conditioning of the target in pure Ar is essential to restore the pure-metal surface and desired deposition rates.

Considerable variation in the composition and properties of reactively sputtered films is possible depending on operating conditions.

The case of tantalum nitride is worth considering in this regard. One of the first electronic applications of reactive sputtering involved deposition of TaN resistors employing DC power at voltages of 3 to 5 kV, and pressures of 30mtorr.

The dependence of the resistivity of "tantalum nitride" films is shown, where Ta, Ta_2N, TaN or combinations of these form as a function of N_2 partial pressure.



Influence of nitrogen on composition, electrical resistivity, and temperature coefficient of resistivity of reactively sputtered Ta films.

Ohring 2002

ion plating

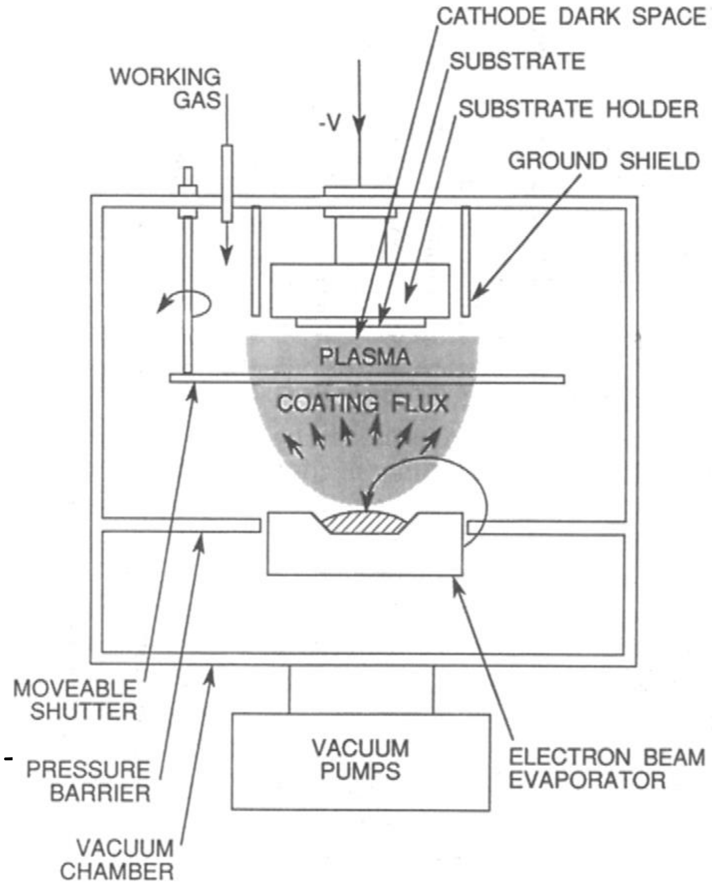
Ion plating refers to **evaporated film deposition** processes in which the **substrate is exposed to a flux of high energy ions** capable of causing appreciable sputtering before and during film formation.

Prior to deposition, the substrate, negatively biased from 2 to 5 kV, is **subjected to inert-gas ion bombardment** at a pressure in the millitorr range for a time sufficient to sputter clean the surface and remove contaminants. **Then the system pressure is reduced and source evaporation** begun **without interrupting the sputtering**.

Clearly, the **sputtering rate must be less than the deposition rate**. Once **the interface between film and substrate has formed, ion bombardment may or may not be continued**.

Film **deposition rates by ion plating (0.1-25 μm/min)** fall between those for sputtering (0.01-2 μm/min) and evaporation (0.1-75 μm/min).

The chief advantage of ion plating is the **ability to promote excellent film adhesion.** In contrast to the relatively sharp film-substrate interfaces for evaporation and sputtering, **ion plating results in graded and diffuse interfaces**.



Ohring 2002

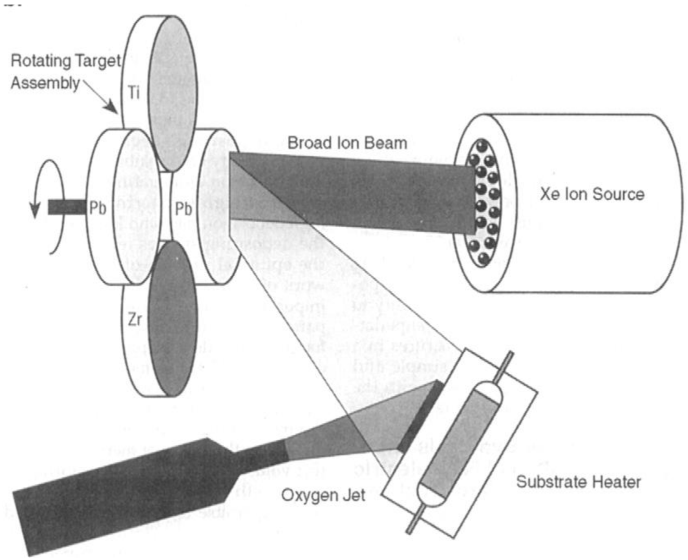
ion beam assisted deposition

Ion bombardment of films during sputter deposition is particularly effective in modifying film properties. However, **process control in plasmas is somewhat haphazard** because the direction, energy, and flux of the ions incident on the growing film cannot be easily regulated.

Ion-beam-assisted processes were invented to provide **independent control of the deposition parameters and the characteristics of the ions bombarding the substrate**.

Ion sources are generally employed in **two distinct modes**:
1) The first uses an **inert-gas ion beam to controllably sputter atoms from a target**; here the function of the beam is to promote the supply of target atoms for deposition.
2) In the second mode **the beam, composed of either inert- (e.g., Ar^+) or reactive-gas ions (e.g., O_2^+), is directly aimed at the substrate**; here the purpose of the beam is to **modify the properties of the growing film** by some combination of bombardment, reaction, or burial within it.

It is common, however, to incorporate **both ion-beam functions in a single vacuum chamber**. This necessitates at least two ion sources. For example, in a simple dual ion-beam system, one ion source is used for sputtering while the second supplies ions to modify the depositing film.



Ohring 2002

ion cluster beam deposition

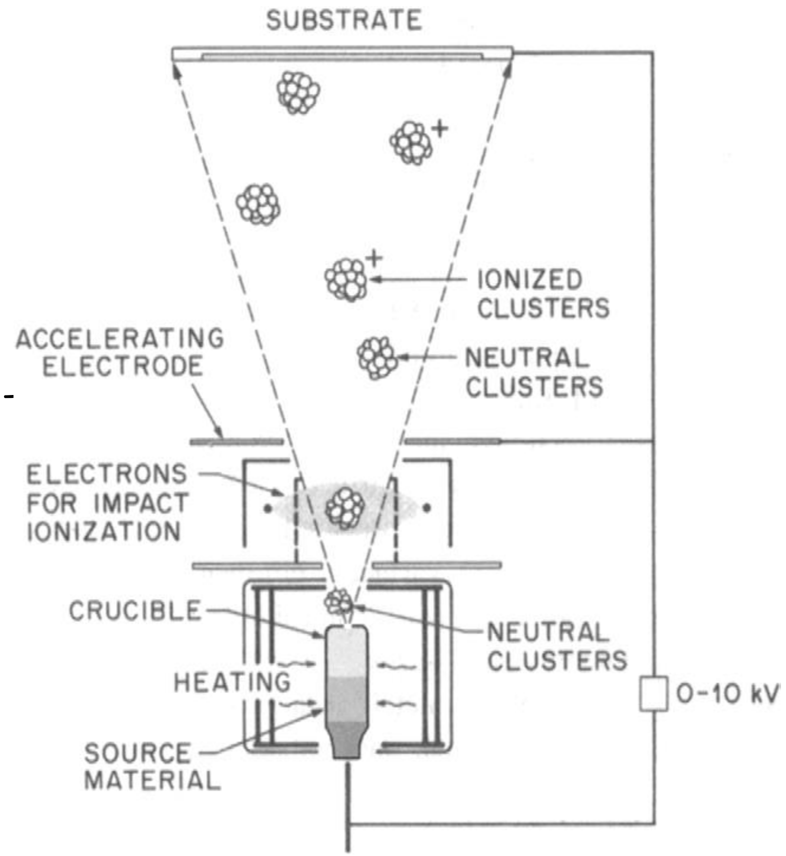
Vapor phase aggregates or clusters, thought to contain a few hundred to a few thousand atoms, are created, ionized, and accelerated toward the substrate.

As a result of impact with the substrate, the cluster breaks apart, releasing atoms to spread across the surface.

Cluster production is, of course, the critical step and begins with evaporation from a crucible containing a small aperture or nozzle. The evaporant vapor pressure is much higher (10^{-2} - 10 torr) than in conventional vacuum evaporation. For cluster formation the nozzle diameter must exceed the mean free path of vapor atoms in the crucible.

Viscous flow of atoms escaping the nozzle then results in an adiabatic supersonic expansion and the formation of stable cluster nuclei.

Optimum expansion further requires that the ratio of the vapor pressure in the crucible to that in the vacuum chamber exceed 10^4 to 10^5.



Ohring 2002

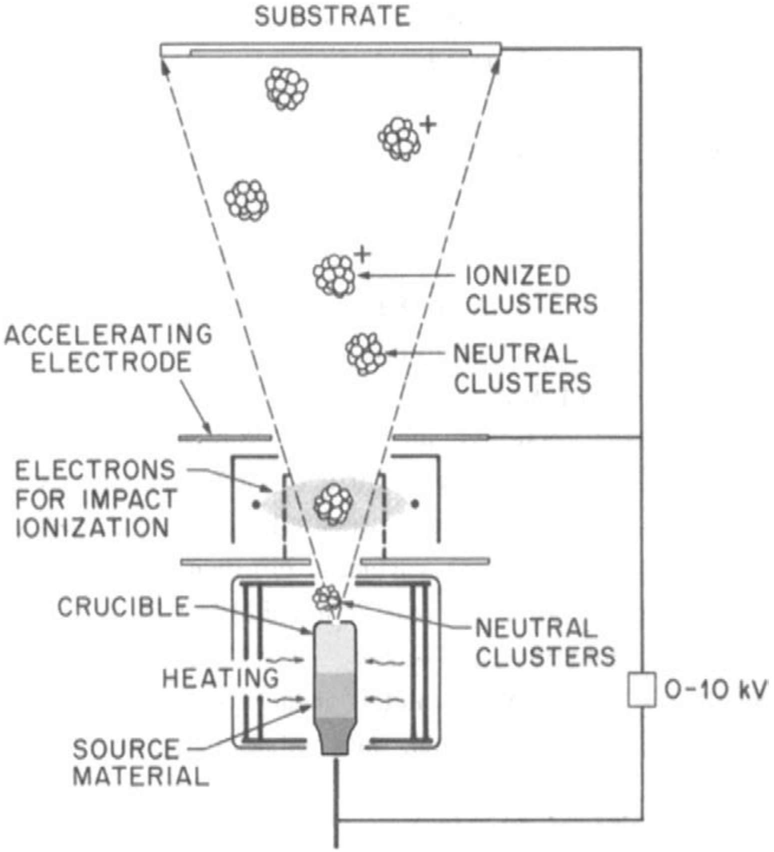
ion cluster beam deposition II

The arrival of ionized clusters with the kinetic energy of the acceleration voltage (0-10 kV), and neutral clusters with the kinetic energy of the nozzle ejection velocity, modifies film nucleation and growth processes in many of the ways

As a result, strong adhesion to the substrate, elimination of the columnar-grain morphology, and epitaxial growth can be achieved at low temperatures.

Moreover, the magnitude of these effects can be modified by altering the accelerating voltage and extent of electron impact ionization. Virtually all classes of film materials have been deposited.

Among additional ICB deposition effects that have been observed are high-yield lateral sputtering, shallow ion implantation, reactive formation of thin films, and smoothing or planarization of surfaces.



Ohring 2002

nanoparticle deposition

The gas aggregation technique is based on homogeneous nucleation

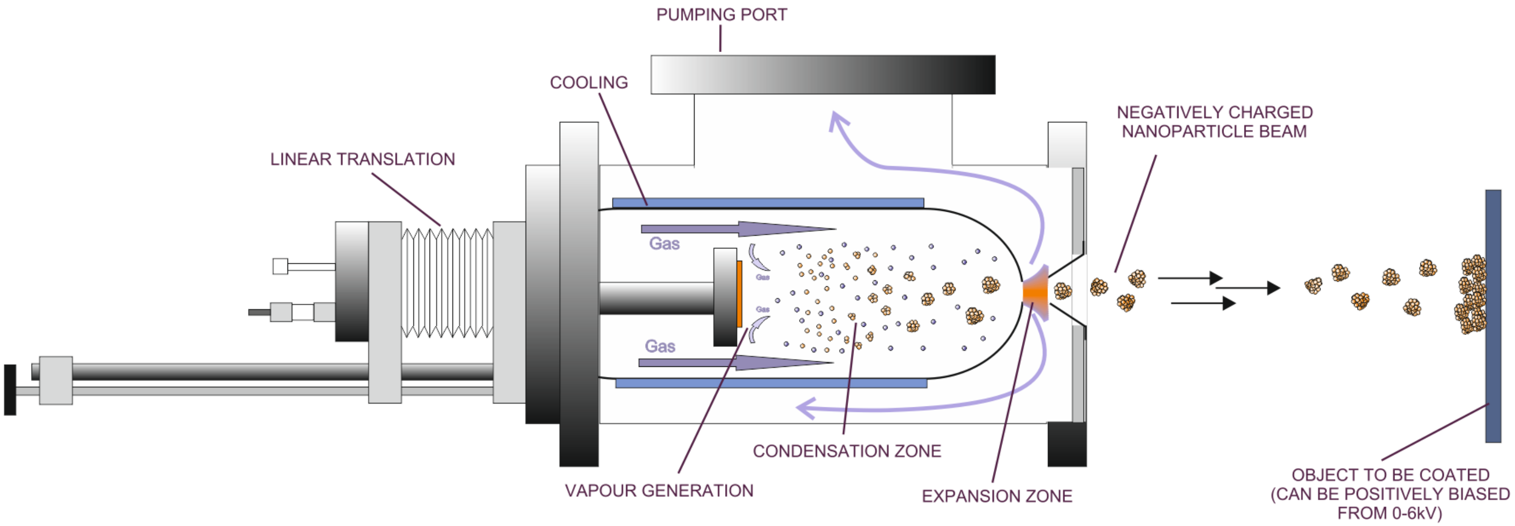
Process steps:
1: starting in the gas phase (solid or liquid targets are vaporized using different techniques: laser, sputtering, heating, etc.)
2: homogeneous nucleation in the gas phase
3: further condensation leading to the formation of nanoparticles considered as <u>stable</u>
4: coagulation (i.e. coalescence) leading to the formation of <u>aggregates</u>
5: deposition onto substrate.

Huttel 2017

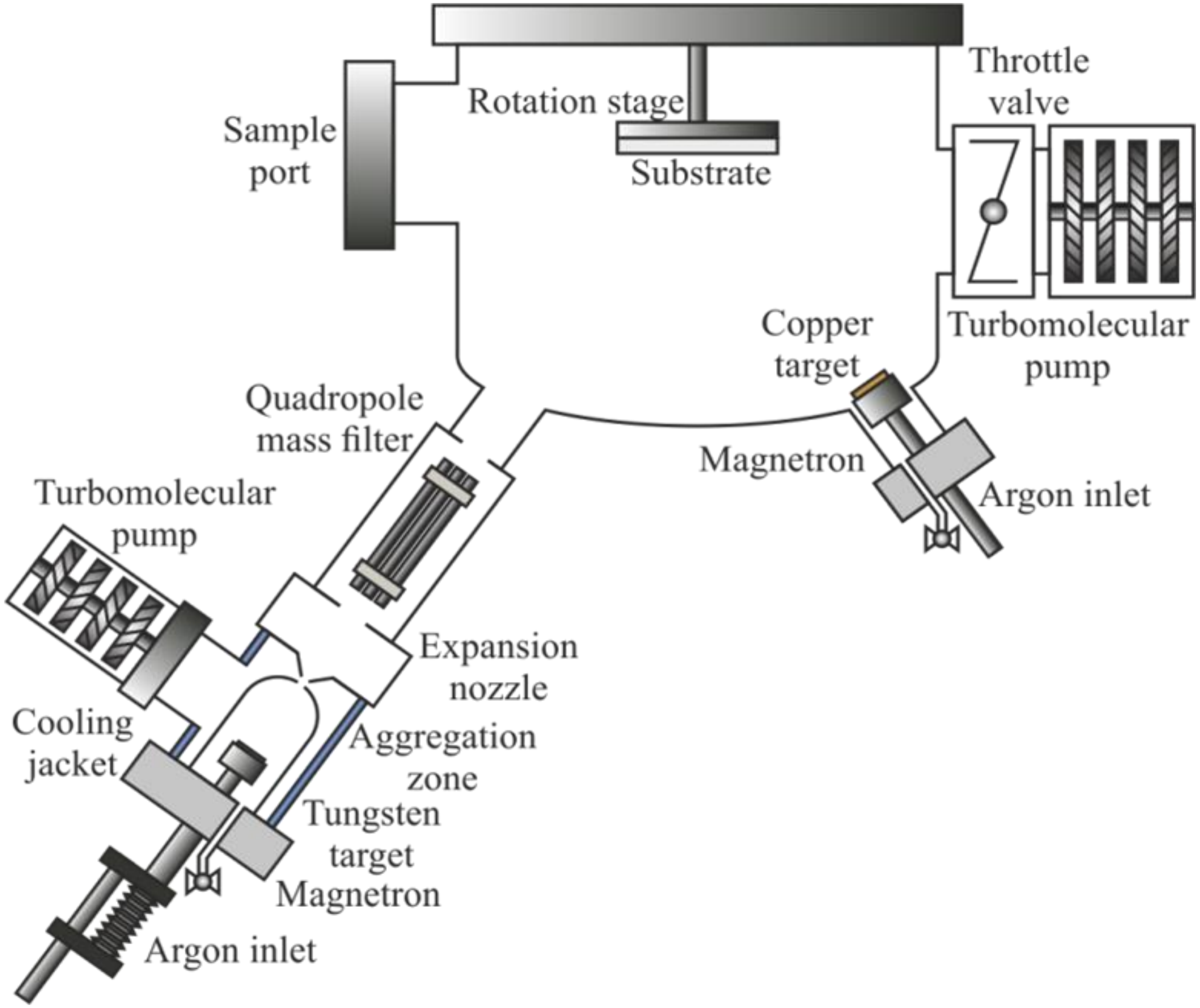
nanoparticle deposition

"terminated gas condensation" source

The vapor becomes supersaturated due to collisions with the surrounding inert gas atoms which are cooled by the cold walls of the aggregation zone, condenses into nanoclusters, and is carried out of the condensation chamber by a continuous flow of gas.



nanoparticle codeposition



Ohring 2002

applications of sputtering

- Single and multilayer metal conductor films for microelectronics and semiconductor devices, e.g. Al, Mo, Mo/Au, Ta, Ta/Au, Ti, Ti/Au, Ti/Pd/Au, Ti/Pd/Cu/Au, Cr, Cr/Au, Cr/Pd/Au, Ni–Cr, W, W–Ti/Au, W/Au.
- Compound conductor films for semiconductor electrodes, e.g. WSi_2, $TaSi_2$, $MoSi_2$, PtSi.
- Barrier layers for semiconductor metallization, e.g. TiN, WTi (70at.%W–30at%Ti) or (90wt%W – 10wt%Ti)
- Magnetic films for recording, e.g. Fe–Al–Si, Co–Nb–Zr, Co–Cr, Fe–Ni–Mo, Fe–Si, Co–Ni–Cr, Co–Ni–Si.
- Optical coatings – metallic (reflective, partially reflective), e.g. Cr, Al, Ag.
- Optical coatings – dielectric (AR and selective reflective), e.g. MgO, TiO_2, ZrO_2.
- Transparent electrical conductors, e.g. InO_2, SnO_2, In–Sn–O (ITO), ZnO : Al.
- Electrically conductive compounds, e.g. Cr_2O_3, RuO_2.
- Transparent gas/vapor permeation barriers, e.g. SiO_2□x, Al_2O_3.
- Diffraction gratings, e.g. C/W.
- Photomasks, e.g. Cr, Mo, W.
- Wear- and erosion-resistant applications (tool coatings), e.g. TiN, (Ti–Al)N, Ti(C–N), CrN, Al_2O_3, TiB_2.
- Decorative applications, e.g. Cr, Cr alloys, copper-based alloys (gold-colored).
- Decorative and wear-resistant applications, e.g. TiC, TiN, ZrN, Ti(C–N), (Ti–Al)N, Cr, Ni–Cr, CrN, HfN, nanolayers, nanocomposites.
- Dry lubricant films – electrically non-conductive, e.g. MoS_2.
- Dry lubricant films – electrically conductive, e.g. WSe_2, $MoSe_2$.
- Freestanding wire, foils, and structures.

Mattox 2010

conclusion

- **All** important classes of **materials are available as target** in a variety of shapes
- the **basic configuration of two electrically powered electrodes** separated by a plasma is common to a number of film deposition and etching processes. Problems: **high pressures** and related **low film quality**, **low ionization degrees**, **low deposition rates** irrespective of DC, AC, or RF powering, or whether reactive gases are present or not.
- A **hollow cathode** exhibits enhanced ionization degree and higher discharge currents compared to a planar diode configuration.
- **Substrate bias** of -50V to -300V lead to a broad energy distribution (collisions prior arrival) of ions bombarding the growing film that lead to improved adhesion, better step coverage, increased density and alternation of film morphology related to removal of contaminants, enhanced nucleation and renucleation and huigher surface adatom mobility.
- **RF sputtering** at 13.56 MHz: electron bombard during negative and ions during positive cycle the target and therefore charge built-up for insulating targets is prevented. At RF frequencies essentially the electrons move. Sputtering occurs because a self-bias at the target establishes which leads to dc-like sputtering. Deposition rates are comparable low and non-conducting targets are susceptible to thermal stress.
- **Magnetron sputtering** processes relying on magnetic confinement of the plasma are now universally employed because they yield films of all materials at relatively high deposition rates, at lower pressures.
- **Typical magnet arrangements** are an outer annular magnet and an inner magnet of opposite polarity at the backside of the cathode target.

Ohring 2002

conclusion

- **Pulsed power magnetron sputtering** exploit discharge pulses to the target at frequencies of several tens of kilohertz, where pulse magnitude, polarity, width, and off-time can all be varied. This prevents arcing and the formation of dielectrics such as oxides at the target surface.
- **Unbalanced magnetron sputtering** exhibit less confined plasmas that allows for extension of the plasma to the anode to promote ion bombardment at the substrate.
- **Typical problems** with magnetron sputtering are **inhomogeneous target erosion**, **particulate contamination**, and **film uniformity**.
- Sputter deposition of **nonmetallic films, e.g., oxides or nitrides**, can be done either employing cathodes of these materials as in **RF sputtering**, or more commonly now by **reactive sputtering** using metal targets. A **mixture of inert and reactive gases** used for sputtering leads to chemical reactions during film growth. **Target poisoning** and related compound formation can be prevented using pulsed plasmas.
- **Ion plating** combines **evaporation with high energy ion bombardment/sputtering** of the substrate (2-5KV). Deposition rates are between evaporation and sputtering.
- **Ion beam assisted deposition** aim at independent control of ions and energies of the ions. Inert gas ion beams are used for cleaning and target sputtering. In the second mode ions are directed at the substrate to modify film properties.
- **Ion cluster beam** exploit vapor cluster agglomeration and acceleration of clusters to the substrate
- **Virtually any material can be deposited with Magnetron sputtering** and is therefore used widely in industry
- **Hybrid film-deposition systems** combining two or more of the following features, i.e., evaporation, sputtering, low voltage-high current arcs, inertgas plasmas, chemically reactive plasmas, and ion beams, have been widely used. They include ion plating, cathodic arc, and ion-beam-assisted deposition processes.

Ohring 2002

exercises

- Which target materials are available for sputtering
- Describe the basic components of a DC sputter system
- Why is the optimal pressure around 0.1 mbar so high in a DC sputtering system
- Define "sputter yield"
- Why is a substrate bias used?
- Explain how a hollow cathode target works
- Explain the operation and effects of magnetron sputtering
- How is step coverage controlled in sputter deposition systems?
- Sputtering: Why is the target negatively biased? How is the break down voltage related to system pressure and inter electrode distance in DC discharge.?
- Magnetron Sputtering: State the limitation of planar diode sputtering. What is meant by ExB drift motion of a charged particle? Show the drift motion near the surface of rectangular planar magnetron. Why the trajectory of the electron near the surface of cylindrical magnetron is that of a cycloid? How is the performance of a magnetron evaluated?
- State the limitation of balanced magnetron and specific advantage of unbalanced magnetron?
- Radio Frequency and Pulsed DC Sputtering
  Why RF sputtering can be done at lower target voltage and process pressure than that required in DC sputtering? How does a negative bias develop on a non-conducting target? Can a conducting target be connected to RF power? How may the pulse-ON and OFF time be selected during pulse DC sputtering? Is there any advantage of providing pulse DC supply even to a conducting substrate?
- Sputter Deposition of Nitride Coating: State the advantage of reactive sputtering over direct sputtering of TiN. How may the partial pressure of N_2 affect Ti:N ratio in the coating
- Polymers are among the few materials that are not made by sputtering. Why? Start the discussion with atomistic processes at the sputter target.

Ohring 2002