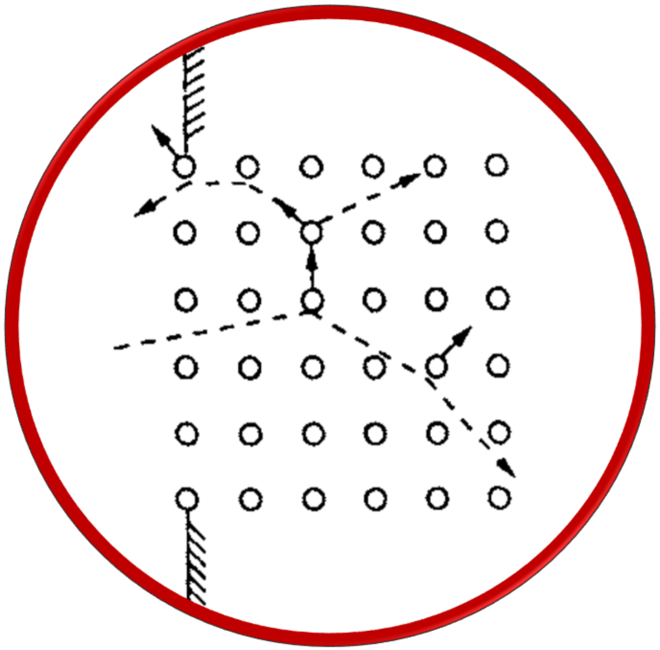
sputtering



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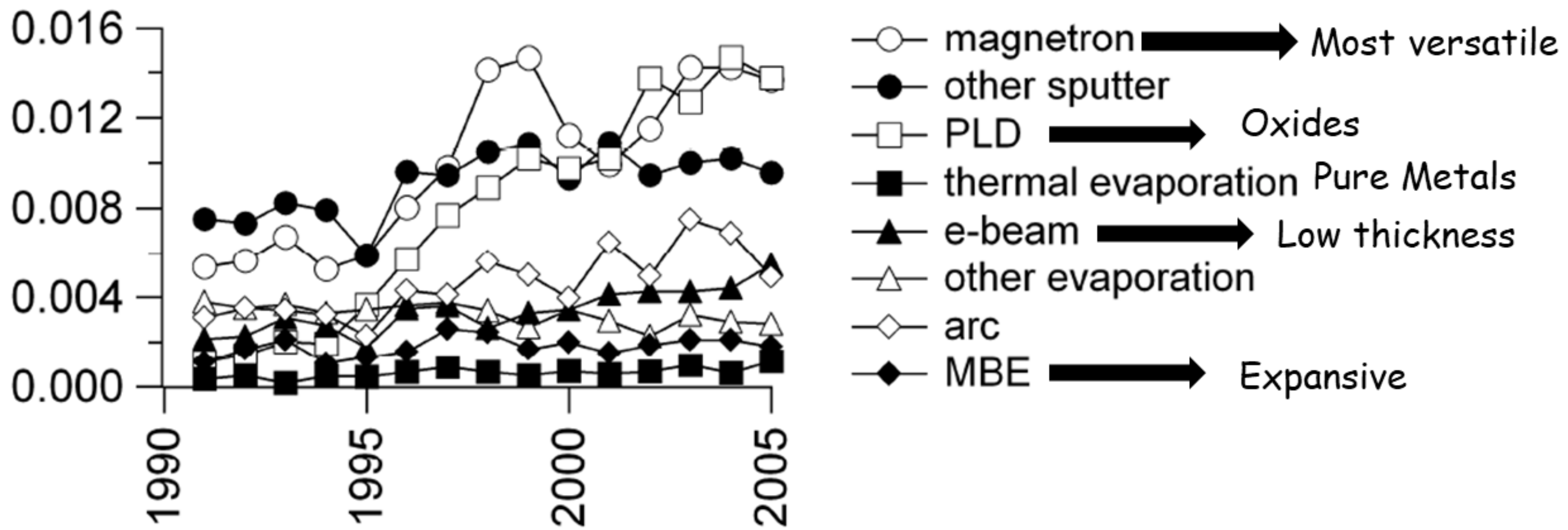
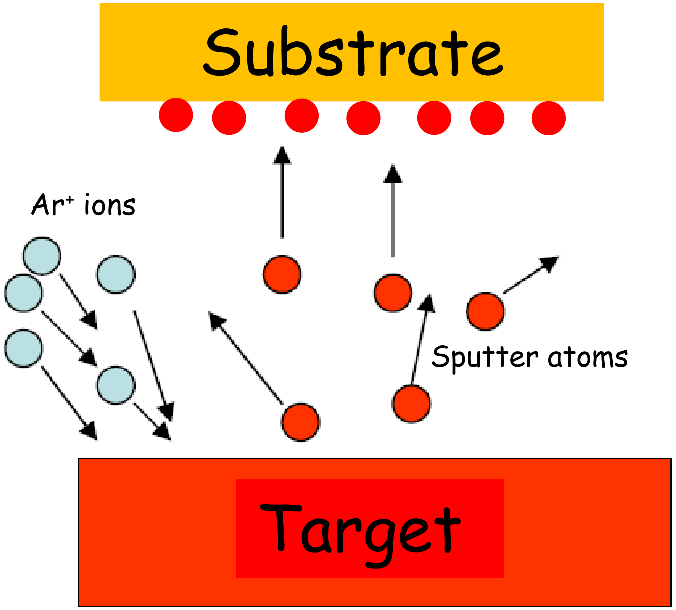


Normalized number of publications per year per deposition technique based upon data from the Web of Science

Sputtering

- **Instead of using heat** to eject material from a source, we can **bombard them with high speed particles**.
- The **momentum transfer** from the **particles to the surface** atoms can impart enough energy to allow the surface atoms to escape.
- Once ejected, these **atoms** (or molecules) **can travel to a substrate and deposit as a film**.
- There are several considerations here:
  - Creating, **controlling** and directing a **high speed particle stream**.
  - Interaction of these particles **with the source surface and emission yields**.
  - **Deposition** of the emitted atoms on the substrate and **film quality**.



Generating and Controlling the Plasma

- The process begins with a stray **electron near the cathode is accelerated towards the anode and collides with a neutral gas atom** converting it to a positively charged ion.

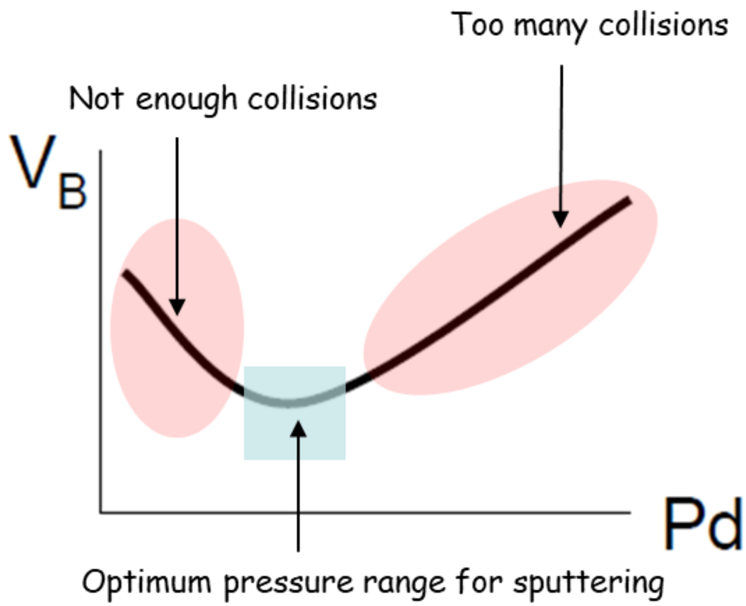
- **The process results in two electrons** which can then collide with other gas atoms and ionize them creating a cascading process until the gas breaks down.

- The breakdown voltage depends on the **pressure in the chamber (Paschen Curve) and the distance between the anode and the cathode.**

- **At too low pressures,** there aren't enough collisions between atoms and electrons to sustain a plasma.

- **At too high pressures,** there so many collisions that electrons do not have enough time to gather energy between collisions to be able to ionize the atoms.

$$e^- + A \rightarrow 2e^- + A^+$$



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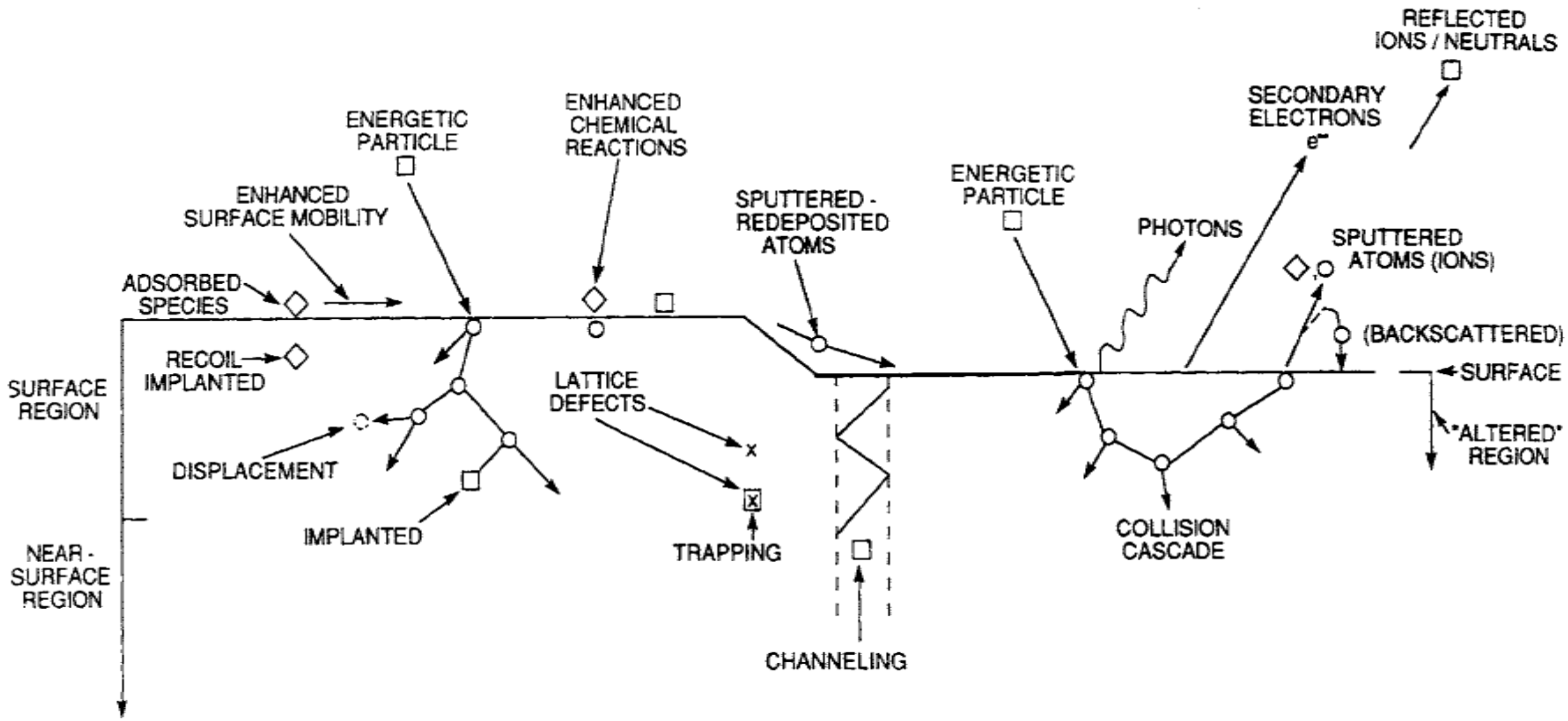
physics of sputtering



Upon bombarding a surface incoming ions may be reflected back, stick or adsorb, scatter, eject or sputter surface atoms, or get buried in subsurface layers (ion implantation).

Surface heating, chemical reactions, atom mixing, and alteration of surface topography are other manifestations of ion bombardment.

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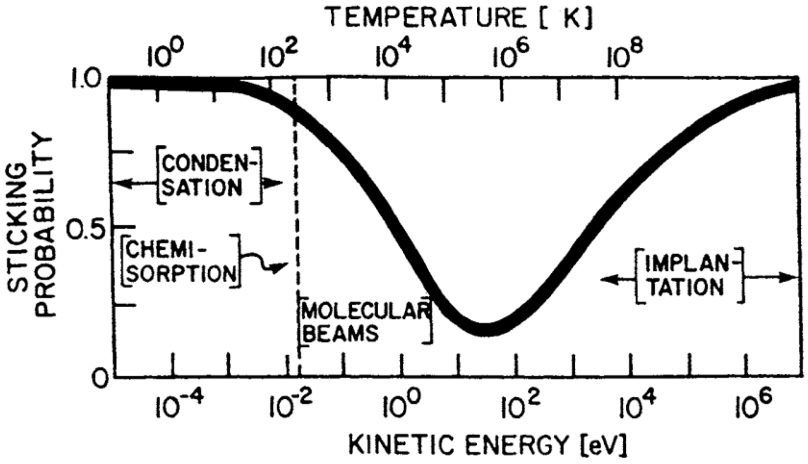
sticking probability

At kinetic **energies less than ~ 10^{-2} eV (the thermal energy kT** at room temperature), the sticking probability, defined as the ratio of the number of product or deposited atoms to the number of impinging ions, is **usually unity**; therefore, condensation as well as chemisorption occurs readily.

From **~ 10^{-2} eV to ~ 10^{4} eV** the ion sticking probability typically **drops, reaching a minimum of ~0.2 at 20 eV**, but thereafter it rises with increasing energy to about 0.6; important sputtering processes occur in this ion-energy range.

In the regime of ion implantation **from roughly 10^4 eV and above** (up to ~ 10^{6} eV), the sticking probability again rises to near **unity as ions are buried beneath the surface**. In this range of energies **the sputtering probability is small**. In addition to ion energy, other important variables include type of ion (mass, charge), the nature of surface as well underlying atoms, and the film or substrate crystallography and texture.



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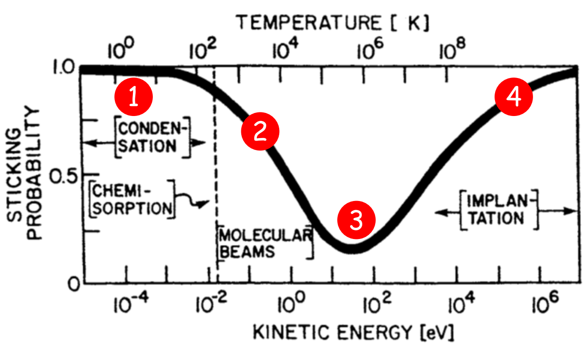
Ion-Surface Interactions

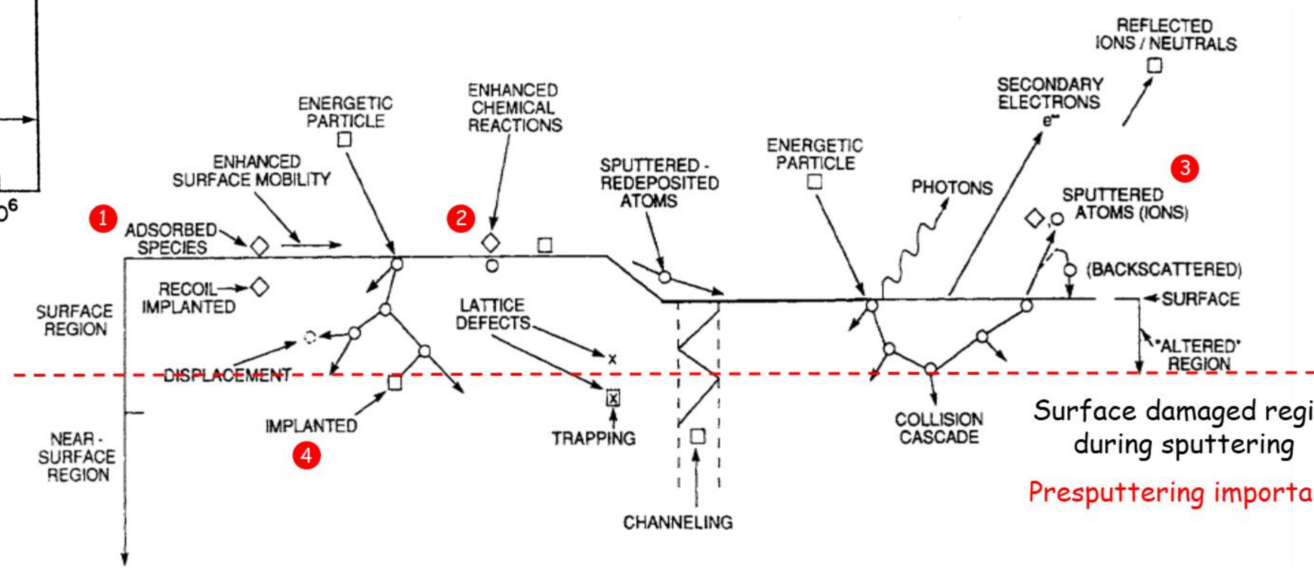
When ions bombard a surface, several things can happen:

- Reflection
- Sticking (adsorption)
- **Sputtering**
- **Ion implantation**
- Chemical reactions
- Electron and photon emission

The ion beam energy is the critical parameter

1. < 5 eV : Adsorption or reflection
2. 5 - 10 eV : Surface damage and migration
3. 10 - 3 keV : Sputtering
4. > 10 keV : Ion implantation





Surface damaged region during sputtering

Presputtering important

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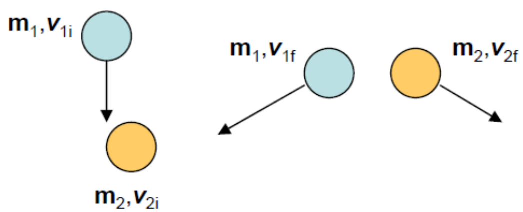
How Ions Sputter Atoms

When ions collide with surface atoms on the target, the energy transfer can knock some of these atoms off the surface.

- The key principle is energy and momentum conservation.
- In any collision, momentum is conserved.
- If the collision is elastic, kinetic energy is also conserved.
- The energies required for sputtering are much higher than lattice bonding or vibrational energies (which are the causes of inelastic interactions), therefore sputtering collisions can be considered **elastic**.



Momentum

$$\mathbf{p} = m\mathbf{v}$$

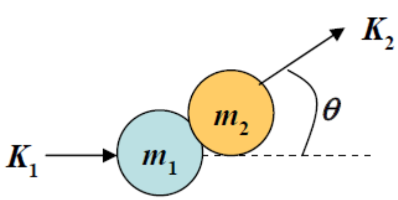
Kinetic Energy

$$K = \frac{1}{2}mv^2$$

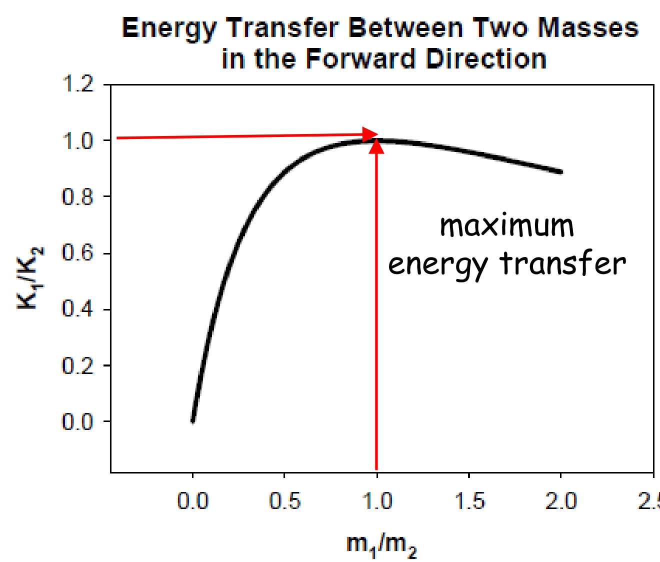
$$\mathbf{p}_i = m_1\mathbf{v}_{1i} + m_2\mathbf{v}_{2i} \quad = \quad \mathbf{p}_f = m_1\mathbf{v}_{1f} + m_2\mathbf{v}_{2f}$$

$$K_i = \frac{1}{2}\left(m_1 v_{1i}^{\,2} + m_2 v_{2i}^{\,2}\right) \quad = \quad K_f = \frac{1}{2}\left(m_1 v_{1f}^{\,2} + m_2 v_{2f}^{\,2}\right)$$

Maximum energy transfer in such a collision occurs when the masses are equal.



$$\frac{K_2}{K_1} \propto \frac{4m_1m_2}{(m_1+m_2)^2}\cos^2\theta$$



Sputter yield

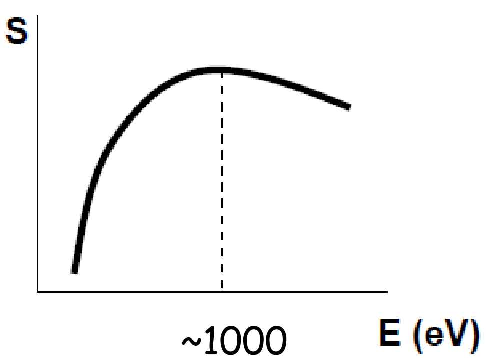
When the ion impact establishes a train of collision events in the target, leading to the ejection of a matrix atom, we speak of sputtering. Since sputtering is the result of momentum transfer it has been aptly likened to "atomic pool" where the ion (cue ball) breaks up the close-packed rack of atoms (billiard balls), scattering some backward (toward the player). The sputter yield S is defined as

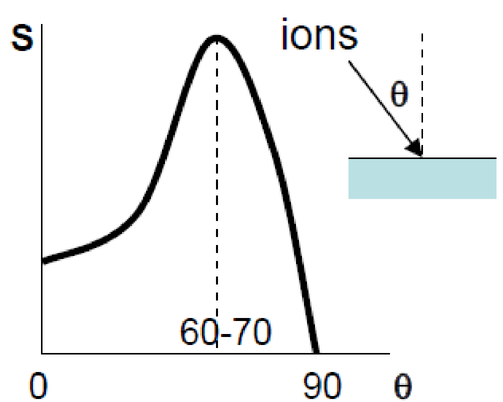
$$s = \frac{\textit{Number of sputtered atoms}}{\textit{Incident particles}} = \frac{3}{4\pi^2}\alpha\frac{4M_1M_2}{(M_1+M_2)^2}\frac{E}{U_s}$$

E the energy of the projectile and M1 and M2 the masses of the projectile and the target atom (in amu). Us is the surface binding energy.

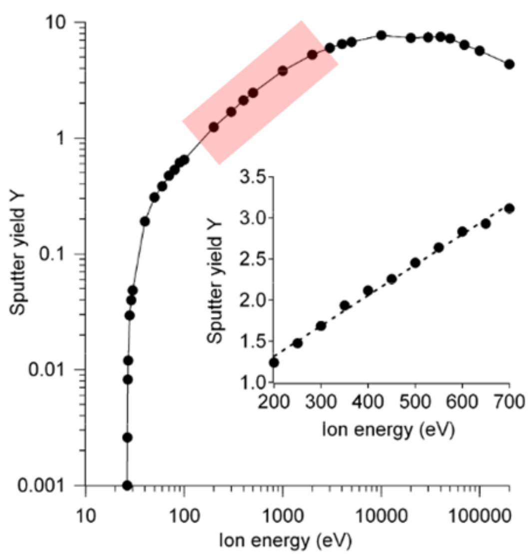
- S depends on type of target atom
  - binding energy of target atoms
  - relative mass of ions and atoms
  - incident ion energy
  - angle of incidence of ions

- S can range from **0.1 to 10**





Ex. Sputter yield with energy for Copper



Sputter yield: Single knock-on

Table 4-2

Sputtering Yield Data for Metals (Atoms/Ion) and Semiconductors (Molecules/Ion)

Sputtering gas energy (keV) →	He 0.5	Ne 0.5	Ar 0.5	Kr 0.5	Xe 0.5	Ar 1.0	Ar threshold voltage (eV)
Ag	0.20	1.77	3.12	3.27	3.32	3.8	15
Al	0.16	0.73	1.05	0.96	0.82	1.0	13
Au	0.07	1.08	2.40	3.06	3.01	3.6	20
C	0.07	—	0.12	0.13	0.17		
Co	0.13	0.90	1.22	1.08	1.08		25
Cu	0.24	1.80	2.35	2.35	2.05	2.85	17
Fe	0.15	0.88	1.10	1.07	1.0	1.3	20
Ge	0.08	0.68	1.1	1.12	1.04		25
Mo	0.03	0.48	0.80	0.87	0.87	1.13	24
Ni	0.16	1.10	1.45	1.30	1.22	2.2	21
Pt	0.03	0.63	1.40	1.82	1.93		25
Si	0.13	0.48	0.50	0.50	0.42	0.6	
Ta	0.01	0.28	0.57	0.87	0.88		26
Ti	0.07	0.43	0.51	0.48	0.43		20
W	0.01	0.28	0.57	0.91	1.01		33
GaAs		0.10	0.83			1.52	20–25
InP			1.00			1.4	25
GaP			0.87				36
SiC		0.13	0.40				17
InSb			0.50				

High sputtering yield

Low sputtering yield

In this case ion-surface collisions set target atoms in motion and may simply give rise to separate knock-on events. If enough energy is transferred to target atoms, they overcome forces that bind them and sputter.

The threshold energy, E_{th} , is the minimum energy required to do this. Typical values for E_{th} range from 5 to 40eV and depend on the nature of the incident ion, and on the mass and atomic number of the target atoms. Most important, however, is the binding energy of atoms to the surface (U_s).

Typically, U_s may be assumed to be the heat of sublimation or vaporization and ranges between 2 and 5 eV. A simple approximations states $E_{th} = 4U_s$, for $0.08 < M_1/M_2 < 1$. Experimentally measured values for E_{th} are shown in the table for a number of metals and semiconductors.

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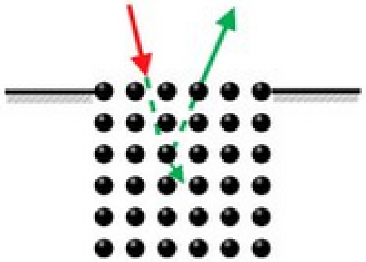
Sputter regimes

- **Single Knock-On**

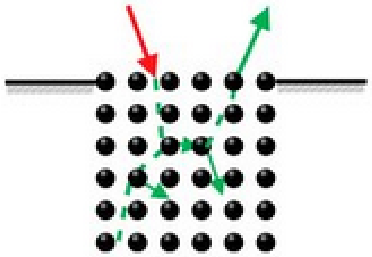
The initial ion-surface collision sets target atoms in motion. If enough energy is transferred, binding forces can be overcome. Typical threshold energies are in the 10 - 30 eV range.



(a) single knock-on (low energy)

- **Linear Collision Cascade**

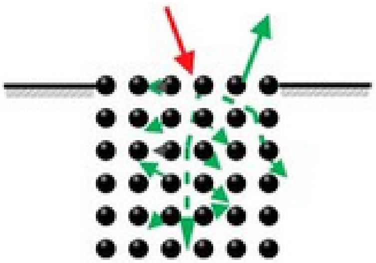
At higher ion energies (100 eV - 10 keV) recoil is minimal and a cascading effect produces sputtering.



(b) linear cascade

- **Spike (High energy)**

In the spike regime the density of recoil atoms is so high that the majority of atoms with in the spike volume are in motion and the region of collisions become so dense that multiple collisions occur simultaneously.



(c) spike (high energy).

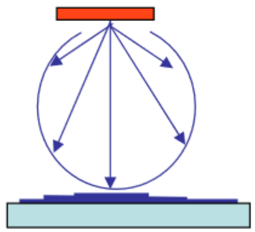
Angular and Energy Distribution of Ejected Atoms

- Sputtered atoms have relatively small energies, typically between 2 - 7 eV (in thermal evaporation, these values are even smaller, around 0.1 eV).
- The number distribution as a function of energy is Boltzmann like.
- The angular distribution is cosine-like and depends on ion energy, the target's type and crystallography.

Isotropic flux

(Cos θ) Dependence

Better step coverage

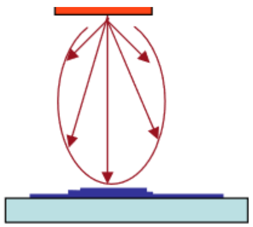


Higher P

Anisotropic flux

(Cos^n θ) Dependence

Poor step coverage

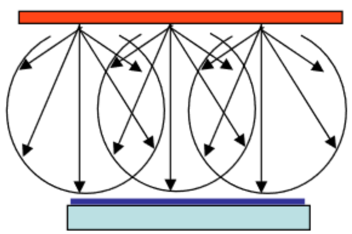


Lower P

Large target, small substrate

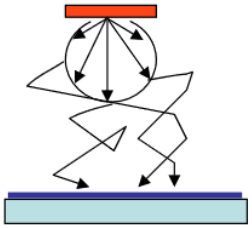
Moving substrates

=> Good step coverage, more uniform thickness



Higher pressure => shorter λ, better step coverage …but more trapped gas

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P}$$



p	λ (cm)
10 mT	2
1 mT	20

sputtering of alloy targets

In contrast to the fractionation of alloy melts during evaporation, with subsequent loss of deposit stoichiometry, sputtering allows for the deposition of films having the same composition as the target source.

This is a primary reason for the widespread use of sputtering to deposit metal alloy films.

We note, however, that each alloy component evaporates with a different vapor pressure and sputters with a different yield.

Why, then, is film stoichiometry maintained during sputtering and not during evaporation?

One reason is the generally much greater disparity in vapor pressures compared to the difference in sputter yields under comparable deposition conditions. Secondly, and more significantly, melts homogenize readily because of rapid atomic diffusion and convection effects in the liquid phase; during sputtering, however, minimal solid-state diffusion enables the maintenance of the required altered target surface composition.

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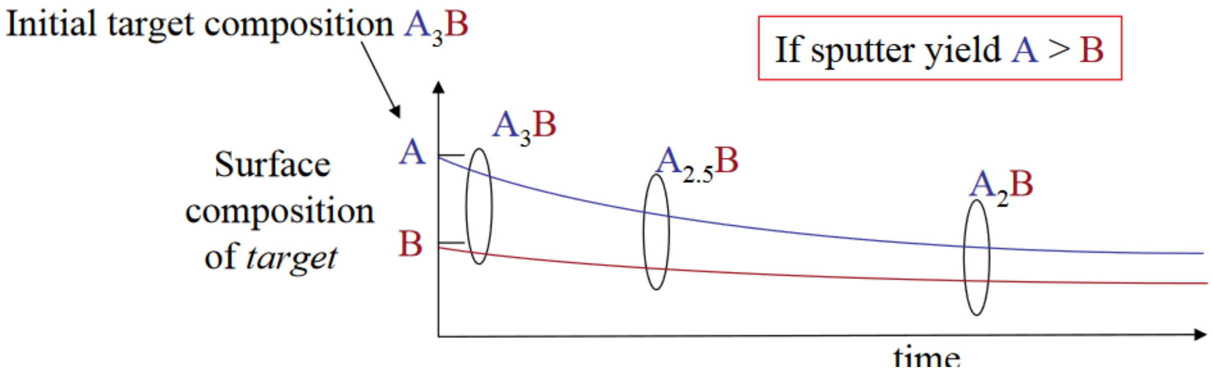
sputtering of alloy targets

Composition of alloy in film is approximately the same as alloy in target (**unlike evaporation**)

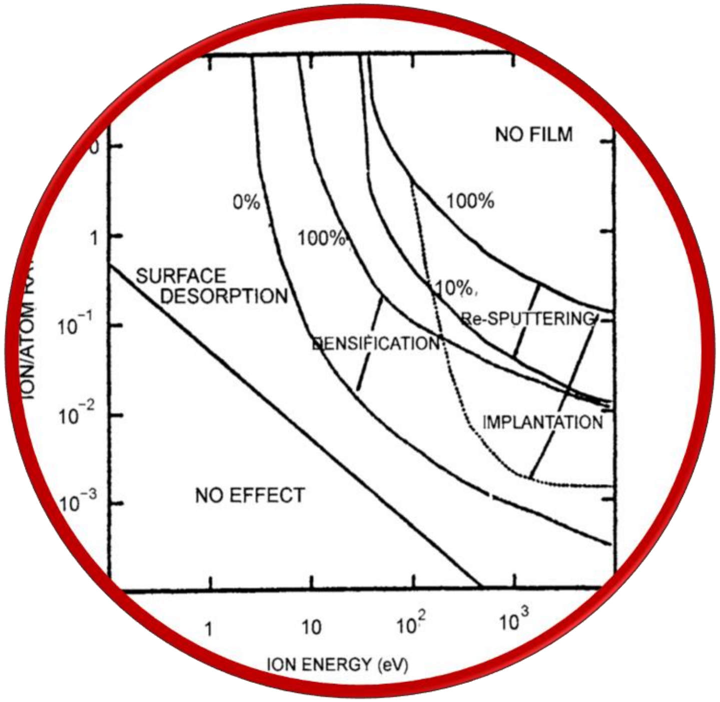
Target composition vs. film composition

Sputtering removes outer layer of target; can lead to problem with multi-component system, but only initially

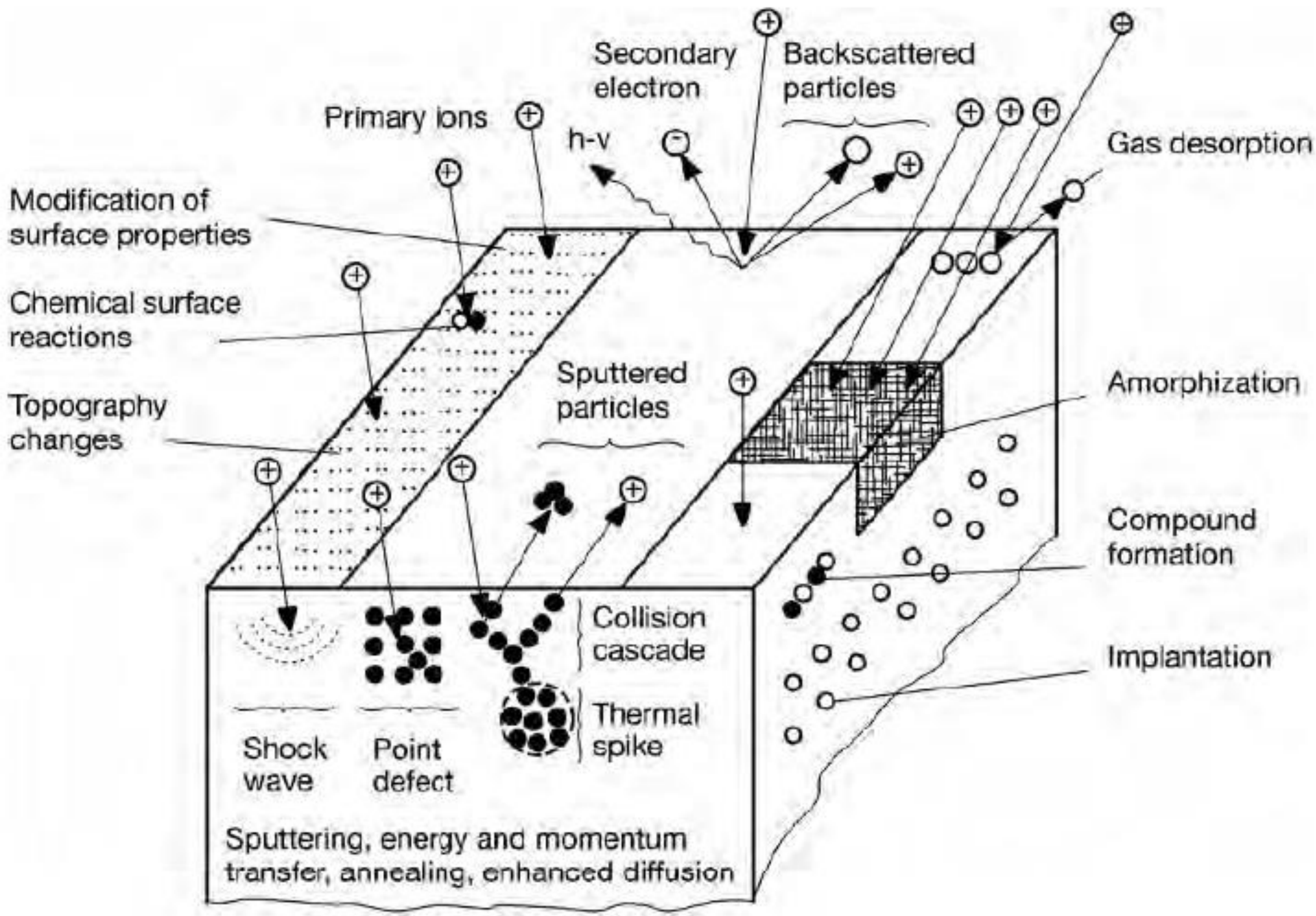


- Alloy sputtering is a self-regulating process.
- If the sputter yield of one species (A) is larger than the other (B), then the surface will initially be depleted of A.
- Now, since the surface has more of B, more of it will sputter off.
- An equilibrium will be reached around the stoichiometric ratio.

ion bombardment during film growth

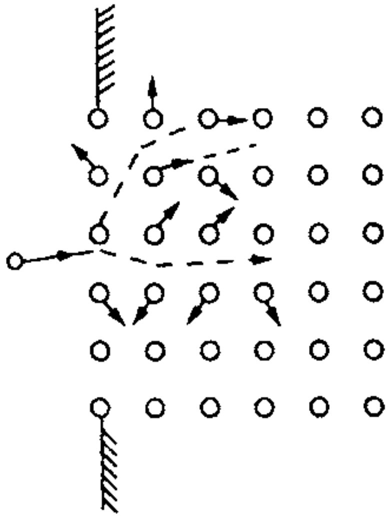


Ion bombardment- overview over mechanisms



Holmberg 2008

temperature spike



During plasma-deposition processes, it is common for atoms that will eventually comprise the film **to deposit together with a flux of energetic, bombarding inert or reactive gas ions**.

As long as **more incident atoms deposit than are sputtered** away, the film **thickens**.

simultaneous impingement of (neutral) evaporated metal and residual gas atoms affects the resultant **film purity**,

Even at the thermal energies ($k_B T$) involved in the condensation of atoms from the vapor phase, **the release of latent heat induces a temperature spike** in the film at the point of impingement.

The **maximum thermal-diffusion distance** (r) for such a depositing adatom has been estimated as

$r = 0.4 a_r (E/E_s)^{1/3}$,

where E is the energy transferred, E_s is the activation energy for surface diffusion, and a_r is the atomic radius.

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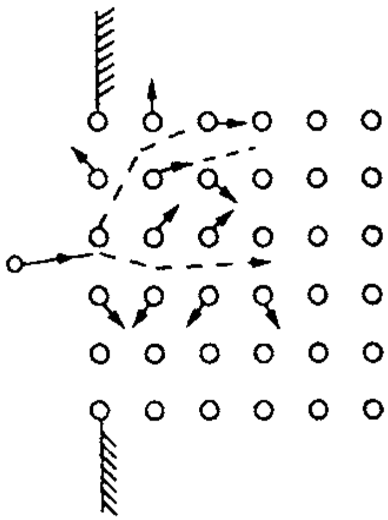
temperature spike



For ion energies **at the sputtering threshold** where $E/E_s \sim 30$, r is calculated to be only **1.2a$_r$**.

Thus, **adatoms do not move much more than an atomic distance away** from where they impinge.

At much **higher energies**, however, **a spike regime** is entered **where all of the atoms are simultaneously in motion** within a local volume of the bulk.

Atoms within the spike **resemble a high-temperature, pressurized gas bubble**.

Ejection of atoms in such a thermal spike can be expected as a result of **vaporization rather than a collisional mechanism**.

From the examples given it is clear that in the energy window of **a few to a few tens of electron volts, surface diffusion occurs**; but at higher energies **subsurface atom motion becomes** more important.

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structural modification

Provided an **elastic collision approximates** what happens between an incident ion and the surface of a depositing film, considerable **sub- and near-surface atomic shuffling** may occur.

Because of upward momentum transfer, this eventually leads to rearrangement of surface atoms. Thus we may expect modification of **both film structure and film composition.**

Ion bombardment of growing films modifies at least four measurable characteristics of its structure:

surface topography and roughness,
crystallography and texture,
grain structure, including grain size and morphology,
defects and stress.

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vacuum/evaporation vs plasma/sputtering

Vacuum/evaporation and **plasma/sputtering** are both **low-pressure environments**, but introduction of cathode and anode electrodes and a means of coupling electromagnetic energy to the system partially ionizes the discharge gas.

Electrons travel faster and are more energetic than ions. Furthermore, **electron collisions with reactive gases create metastable species** that promote **plasma-assisted chemical reactions**.

Central to thin-film deposition processes is the **ion bombardment of cathodes**. Upon impact, a **train of events** is initiated resulting in **the ejection or sputtering of atoms from them**. Critical in this regard is the sputter yield, the property that determines how efficient the process is.

Once ejected, these atoms fly through the intervening plasma where they deposit sequentially at the substrate (anode). Here again ion bombardment plays a beneficial role, this time to modify the structure and composition of the growing films.

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vacuum/evaporation vs plasma/sputtering

	Vacuum/evaporation	Plasma/sputtering
A. Source attributes		
1. Phase	Melt or solid	Solid target
2. Mechanism of atom removal	Thermal evaporation (hot source)	Ion bombardment and collisional momentum transfer (cool target)
3. Energy supplied to source	Thermal energy ~0.1 to 0.2 eV/atom + ΔH_v	> 20 eV/atom
4. Atom removal rate	$\sim 1.3 \times 10^{17}$ atoms/cm^2-s for $M = 50$, $T = 1500$ K, $P_e = 10^{-3}$ torr (Eq. 3-2)	$\sim 10^{16}$ atoms/cm^2-s at 1 mA/cm^2 and $S = 2$
5. Atom emission geometry	$\cos\phi$ and $\cos^n\phi$	$\cos\phi$ as well as directional according to crystallography
6. Applicability, availability	All materials, generally high purity	Targets of all materials, variable purity
B. Gas phase attributes		
1. Composition	Evaporant atoms, associated and dissociated compound fragments, residual gases	Sputtered atoms, assorted metastable ionized and excited species, sputtering gas, ions, electrons, residual gases
2. Pressure	High to ultrahigh ($\sim 10^{-5}$ to 10^{-10} torr)	~1–100 mtorr discharge
3. Species energy	~0.1–0.2 eV for evaporants	3–10 eV for sputtered atoms 2–5 eV for electrons
4. Atomic mean free path	Larger than evaporant–substrate spacing. No gas collisions in vacuum	Less than target–substrate spacing. Many gas collisions in the discharge
C. Condensed film attributes		
1. Energy of condensing atoms	Low (0.1 to 0.2 eV)	High (~a few eV); higher with substrate bias
2. Gas incorporation	None	Some
3. Adhesion to substrate	—	Generally good
4. Film stoichiometry	Generally different from multicomponent alloy and compound sources	Same as the target composition

Sputtering with "cold" target surface!

Sputtering with more energy/atom!

Evaporation with higher rate!

Evaporation sources often more pure!

Evaporation lower pressure!

Sputtered species higher energy!

Evaporation cleaner fims!

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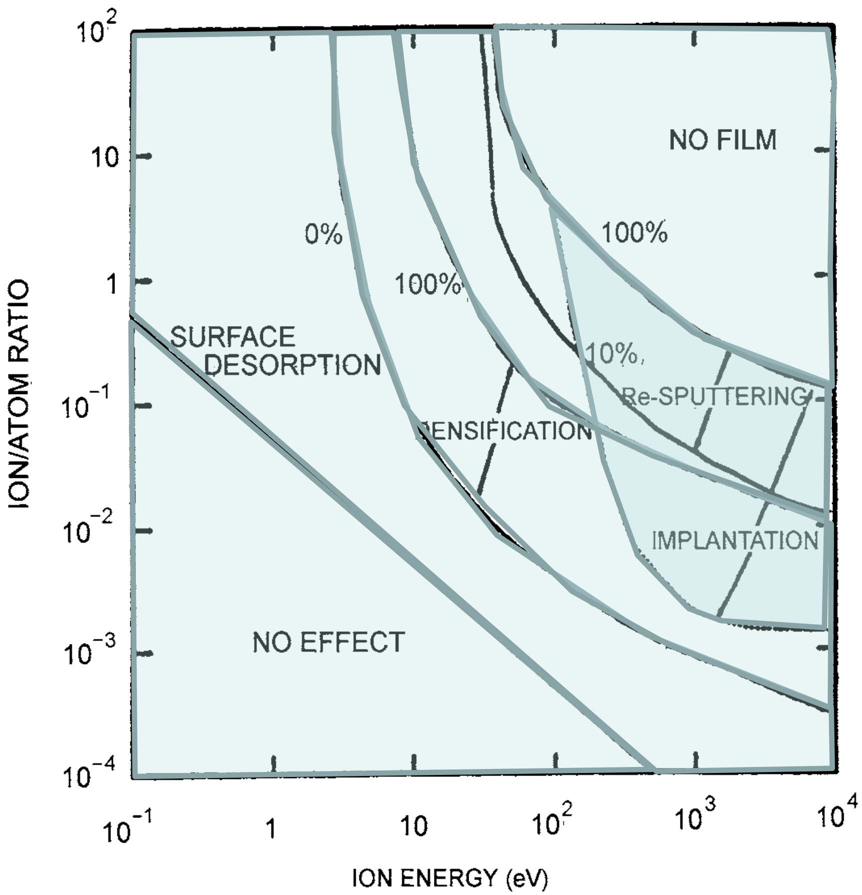
regions of dominance for various ion-bombardment processes



When the ion/atom ratio and ion energy values are both below threshold levels defined by the line with slope equal to - 1 , ion bombardment simply does **not modify film properties.**

Irrespective of ion energy, **desorption of surface impurities** occurs at the lowest ion fluxes.

However, as the ion/atom, flux ratio increases, **film densification** and **ion implantation** become more probable; in general densification proceeds at lower ion energies than those required for implantation.

Resputtering effects dominate at the highest flux levels and ion energies.

No film forms if the atom flux is simply too low; in such a case all that happens is ion implantation and sputtering or etching of the substrate.

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summary

- Sputtering: high energy particles eject target atoms through momentum transfer. These atoms travel to the substrate and form the film.
- Optimum pressure to sustain the plasma (too low then not enough collisions, too high not enough time to gain enough energy)
- Upon bombardment incoming ions may be reflected back, stick or adsorb, scatter, eject or sputter surface atoms, or get buried in subsurface layers (ion implantation). Surface heating, chemical reactions, atom mixing, and alteration of surface topography also happens.
- The ion beam energy is the critical parameter with < 5 eV : Adsorption or reflection; 5 - 10 eV : Surface damage and migration; 10eV - 3 keV : Sputtering; >10 keV : Ion implantation
- The sticking probability is lowest in the range 0.2eV and 20eV
- Ions sputter like billard balls: maximum energy/momentum transfer at mass ratio=1
- Sputter yield varies 0.1-10
- The energy threshold energy is typically 4x heat of sublimation
- There are three different sputter regimes: single knock-on, linear collision cascade and spike regime
- Angular distribution of sputtered atoms follows a cosine law and number distribution the Boltzmann distribution
- Alloy targets are widely used as compared to evaporation as surface composition stays stable due to minimum surface diffusion in the solid.
- During ion bombardment of the growing film similar processes as at the target surface happen. Film topography, microstructure, density etc. is affected.
- Compared to evaporation the target surface stays cold, atoms exhibit higher energy. Evaporation yields higher deposition rates, operates at lower pressures and films are cleaner.

exercises

- Explain why there is an optimum pressure to maintain the plasma.
- Name the processes that happen when the surface is hit with energetic particles from the plasma
- Give ion beam energy ranges for Adsorption, surface damage/migration, Sputtering and ion implantation to happen
- For which mass ratio maximum energy transfer happens during sputtering
- Define the term "sputter yield". What are typical numbers (range). Give a range of typical threshold energies for sputtering.
- Explain the sputter regimes as a function incident ion energy. Which laws follow angular and energy distribution?
- Why is the composition of the deposited film closer to the target in sputtering than in evaporation.
- How far do adatoms move when they arrive with thermal energies (KT)? Explain the term temperature spike at higher arrival energies.
- How does ion bombardment affect the film microstructure?
- Compare plasma sputtering to evaporation. Point out at least 4 differences.
-