Jefferson Lab

Office of Science
U.S. DEPARTMENT OF ENERGY

ENERGETIC CONDENSATION

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OUTLINE

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- What is Energetic Condensation
- Energetic Condensation Processes
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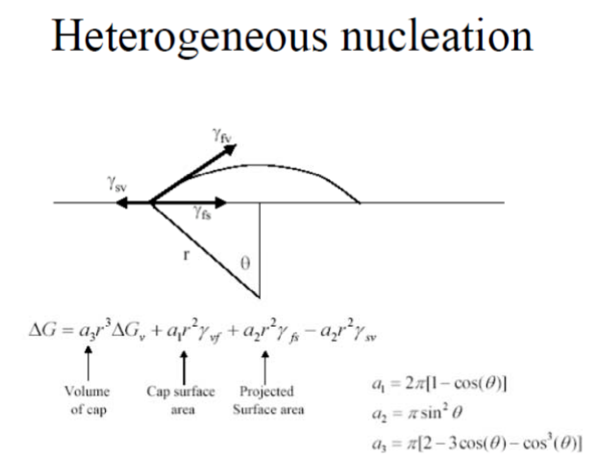
Film Nucleation & Growth

Heterogeneous nucleation.
Nucleation driven by nucleation centers such as defect, impurities on the substrate surface or the orientation of the underlying substrate in the case of hetero-epitaxy.



Heterogeneous nucleation

$$\Delta G = a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{vf} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv}$$

Volume of cap

Cap surface area

Projected Surface area

$$a_1 = 2\pi[1-\cos(\theta)]$$
$$a_2 = \pi \sin^2\theta$$
$$a_3 = \pi[2-3\cos(\theta)-\cos^3(\theta)]$$

Thin film growth from the gas phase=non-equilibrium process phenomenon governed by a competition between kinetics & thermodynamics.

- Production of ionic, molecular or atomic species in the gas phase.
- Transport of species to the substrate
- Condensation of species onto substrate directly or by chemical/electrochemical reaction.

Steps in Film Formation

1. Thermal accommodation
2. Binding
3. Surface diffusion
4. Nucleation
5. Island growth
6. Coalescence
7. Subsequent growth

Critical free energy (ΔG*) and critical radius (r*)

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

$$\frac{d\Delta G}{dr} = 0 = 4\pi r^2 \Delta G_V + 8\pi r \gamma$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_V)^2}$$

$$r^* = -\frac{2\gamma}{\Delta G_V}$$

Effective energy barrier for nucleation

Competing Processes in Nucleation

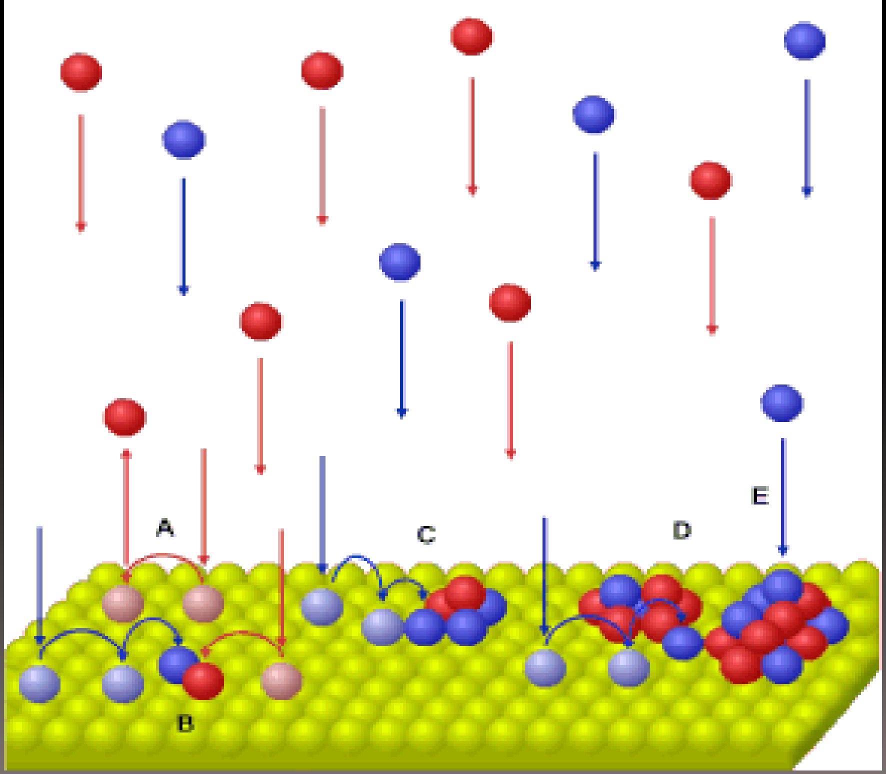
Condensation from the vapor involves incident atoms becoming bonded adatoms which diffuse over the film surface until trapped at low energy lattice sites.

The atoms are continuously depositing on the surface. Depending on their energy and the position at which they hit the surface:

- Re-evaporation from the surface
- Adsorption (**adatom**)
  - Covalent/ionic bond with a surface atom-**chemisorption**.
  - Van der Waal's bond with a surface atom -**physisorption**

sticking coefficient
=
mass deposited / mass impinging

Migration on the surface & interaction with each other or with the substrate atoms.



Surface diffusion
Bulk diffusion
Desorption
} quantified by the characteristic diffusion & sublimation activation energies

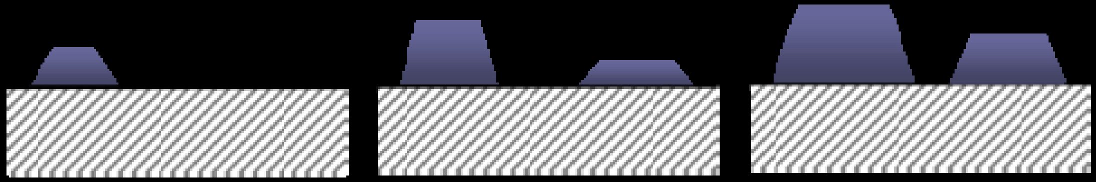
Shadowing — from the line of sight impingement of arriving atoms

The dominance of one or more of these interactions is manifested by different structural morphologies.

Thin Film Growth Modes

(i) 3-D or island growth mode, also known as **Volmer–Weber (VW) mode**

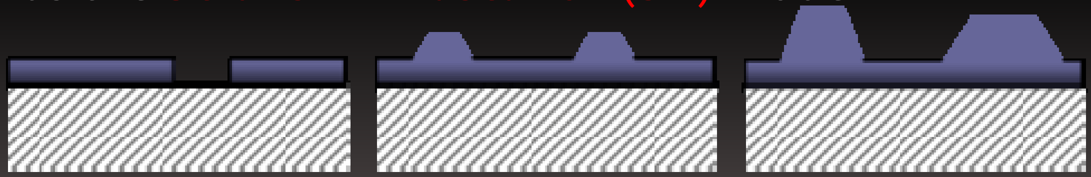
The adatoms have a strong affinity with each other and build 3-D islands that grow in all directions, including the direction normal to the surface. The growing islands eventually coalesce and form a contiguous and later continuous film.



(ii) 2-D or layer-by-layer growth, also known as **Frank–van der Merwe (FVDM)** mode

The condensing particles have a strong affinity for the substrate atoms: they bond to the substrate rather than to each other.

(i) a mixed mode that starts with 2-D growth that switches into island mode after one or more monolayers; this mode is also known as the **Stranski–Krastanov** (SK) mode.

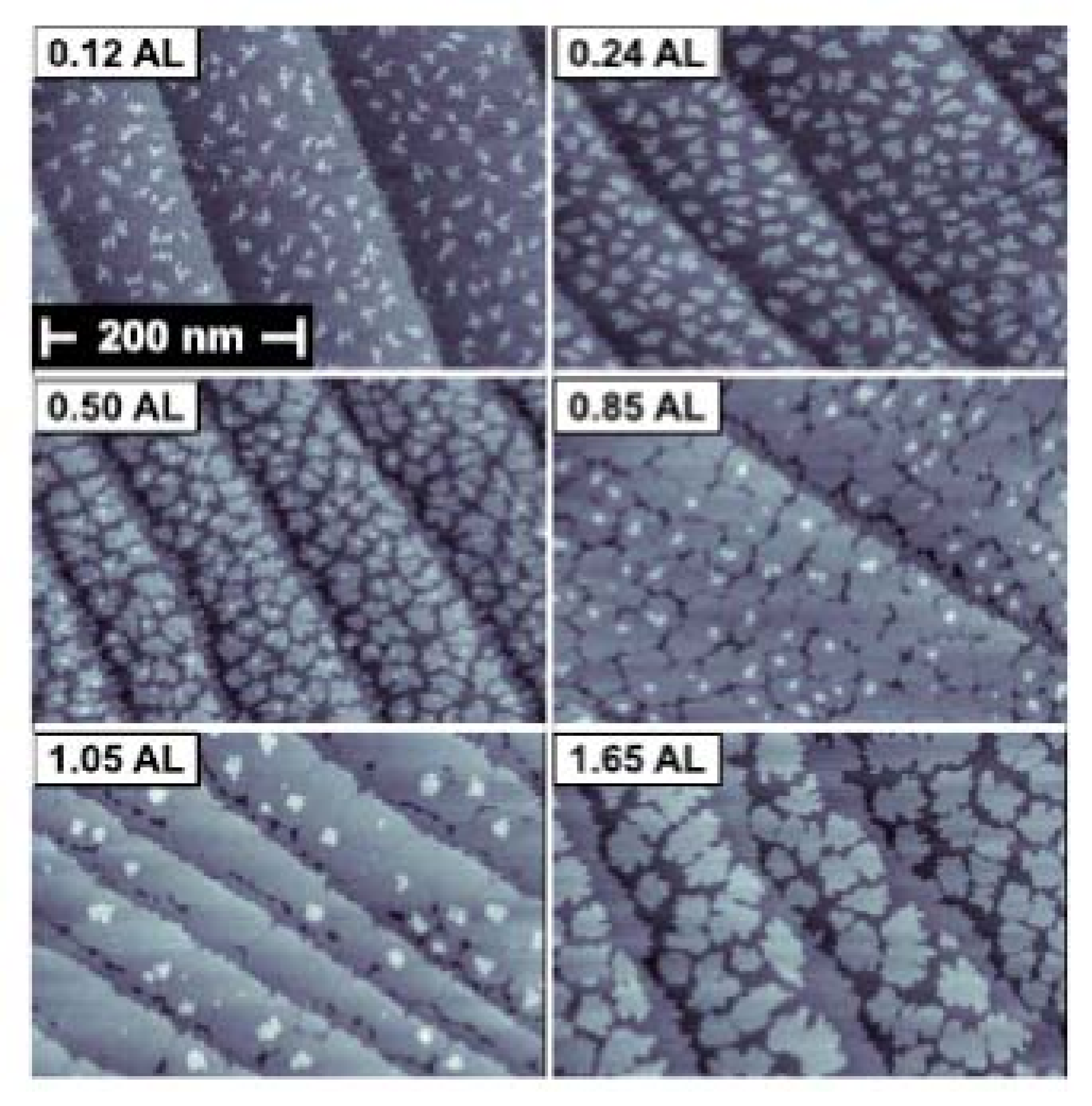


The film nucleation depends first and foremost on the nature of the material deposited (metal…)

Niobium as most metals grows often in the island mode, but of course it depends on the growth conditions.

Film Coalescence

Coalescence: 3 common mechanisms
1. Oswald ripening: atoms leave small islands more readily than large islands. More convex curvature, higher activity, more atoms escape
2. Sintering: reduction of surface energy
3. Cluster migration:
Small clusters (<100Å across) move randomly
Some absorbed by larger clusters (increasing radius in height)



Topography STM maps of V islands deposited on Cr(001) substrates at 525 K with coverages from 0.12 to 1.65 AL. Layer-by-layer growth is observed. (*PRB 82, 085445, 2010*)

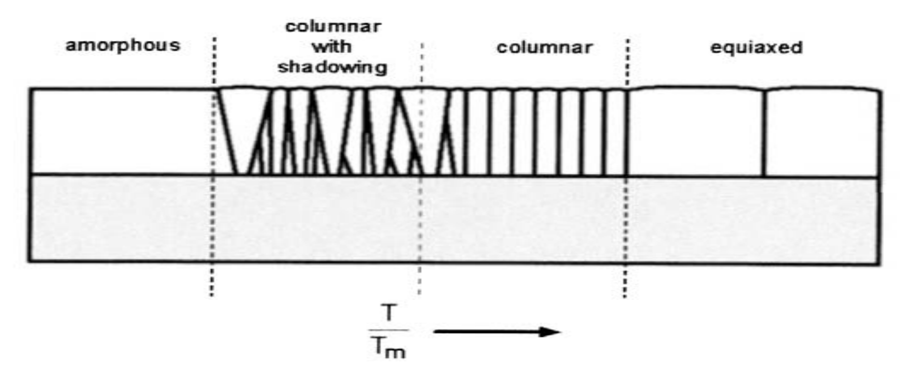
Once template has been formed, homo-epitaxy.

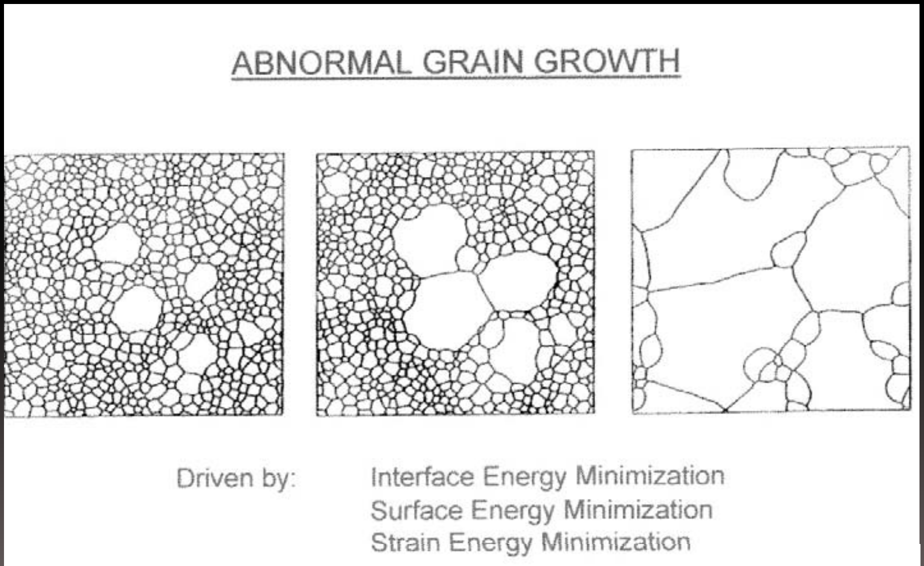
Similar studies for Nb growth on Cu are presently conducted by Prof. A Lukaszew's team (C. Clavero) Surface Science for Future Electronic Materials and Accelerator Applications", AVS, Nashville , Oct. 30 -Nov 4, 2011

Subsequent Film Growth

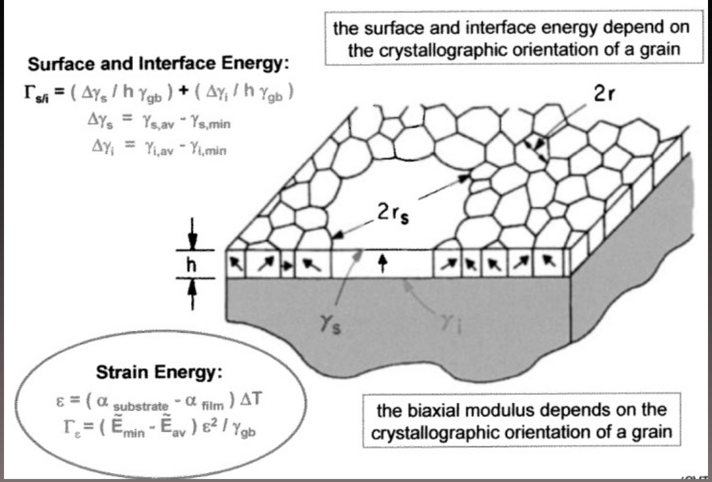
The grain size of a polycrystalline film is affected by:

- Substrate temperature during deposition (high for large grains)
- Adatom diffusivity (high)
- Annealing temperatures (high)
- Deposition flux (low)
- Impurity content (low)
- Film thickness (high)
- Energy of the deposited atom (high)
- Energy of bombarding ions/atoms (high)
- T_m of Material (low)
- The materials class (metals)





H.J. Frost, C.V. Thompson, and D.T. Walton, Acta Metall. **40**, p. 779, 1992.
R. Carel, C.V. Thompson, H.J. Frost, Acta Metall. Mater. **44**, 2479 1996.



the surface and interface energy depend on the crystallographic orientation of a grain

Surface and Interface Energy:

$$\Gamma_{s/i} = (\Delta\gamma_s / h\,\gamma_{gb}) + (\Delta\gamma_i / h\,\gamma_{gb})$$
$$\Delta\gamma_s = \gamma_{s,av} - \gamma_{s,min}$$
$$\Delta\gamma_i = \gamma_{i,av} - \gamma_{i,min}$$

Strain Energy:

$$\varepsilon = (\alpha_{substrate} - \alpha_{film})\,\Delta T$$
$$\Gamma_\varepsilon = (\tilde{E}_{min} - \tilde{E}_{av})\,\varepsilon^2 / \gamma_{gb}$$

the biaxial modulus depends on the crystallographic orientation of a grain

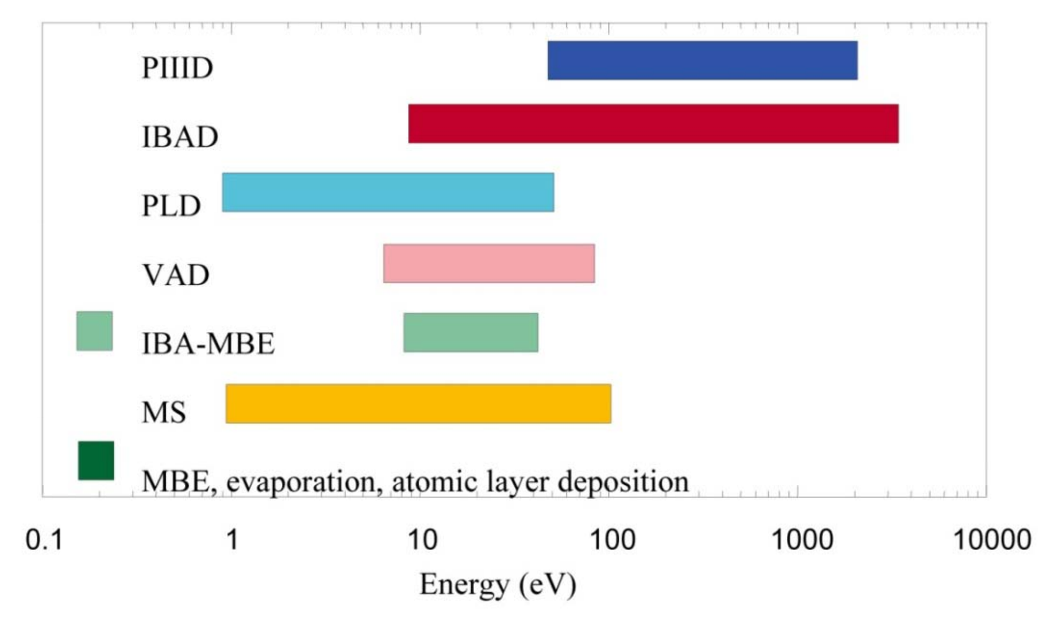
Deposition Techniques

Control over the deposition process is exercised by only

3 first-order vapor parameters & 1 first-order substrate parameter.

Vapor parameters	**Absolute arrival rates of film atoms** **Partial pressures of background gases in the chamber** **Energies of the deposition fluxes.**
Substrate parameter	Substrate **temperature T**.

Without energetic atoms, only the substrate temperature influences the processes of physi- and chemisorption, thermal desorption, nucleation, nuclei dissociation, surface diffusion, and formation of specific nucleation sites.



Typical energy ranges for different PVD processes.

PIIID = plasma immersion ion implantation and deposition

IBAD = ion beam assisted deposition

PLD = pulsed laser deposition

VAD = vacuum arc deposition

IBA-MBE = ion beam assisted molecular beam epitaxy

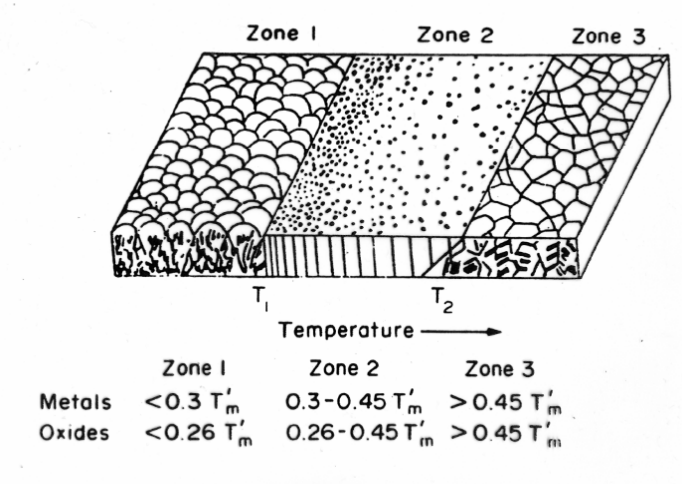
MS = magnetron sputtering

MBE = molecular beam epitaxy.

However practical substrates for SRF cavities (Al, Cu) may not allow heating to high temperature!

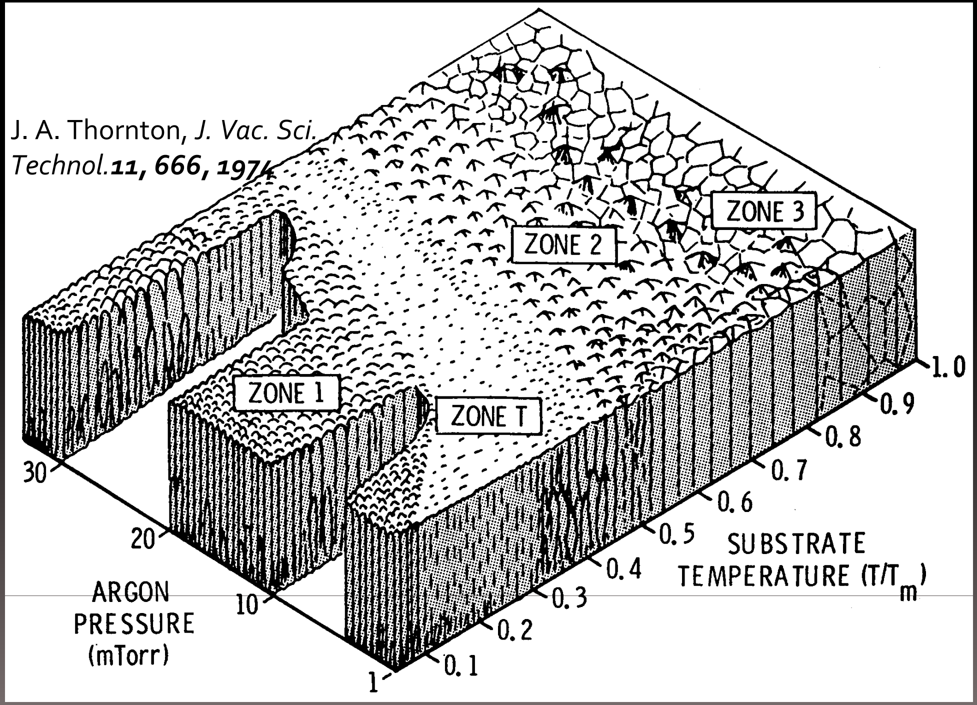
Energetic Condensation

- Zone Structure Model--



	Zone 1	Zone 2	Zone 3
Metals	$<0.3\ T'_m$	$0.3-0.45\ T'_m$	$>0.45\ T'_m$
Oxides	$<0.26\ T'_m$	$0.26-0.45\ T'_m$	$>0.45\ T'_m$

Figure 1. Structure-Zone model of Movchan and Demchishin.[2]



J. A. Thornton, *J. Vac. Sci. Technol.* ***11*****, *666*, 1974**

- Zone 1
  - -lack of surface mobility
  - -random direction of incoming vapor atoms
  - -shadowing

  → loose fibrous structure, voids, porosity

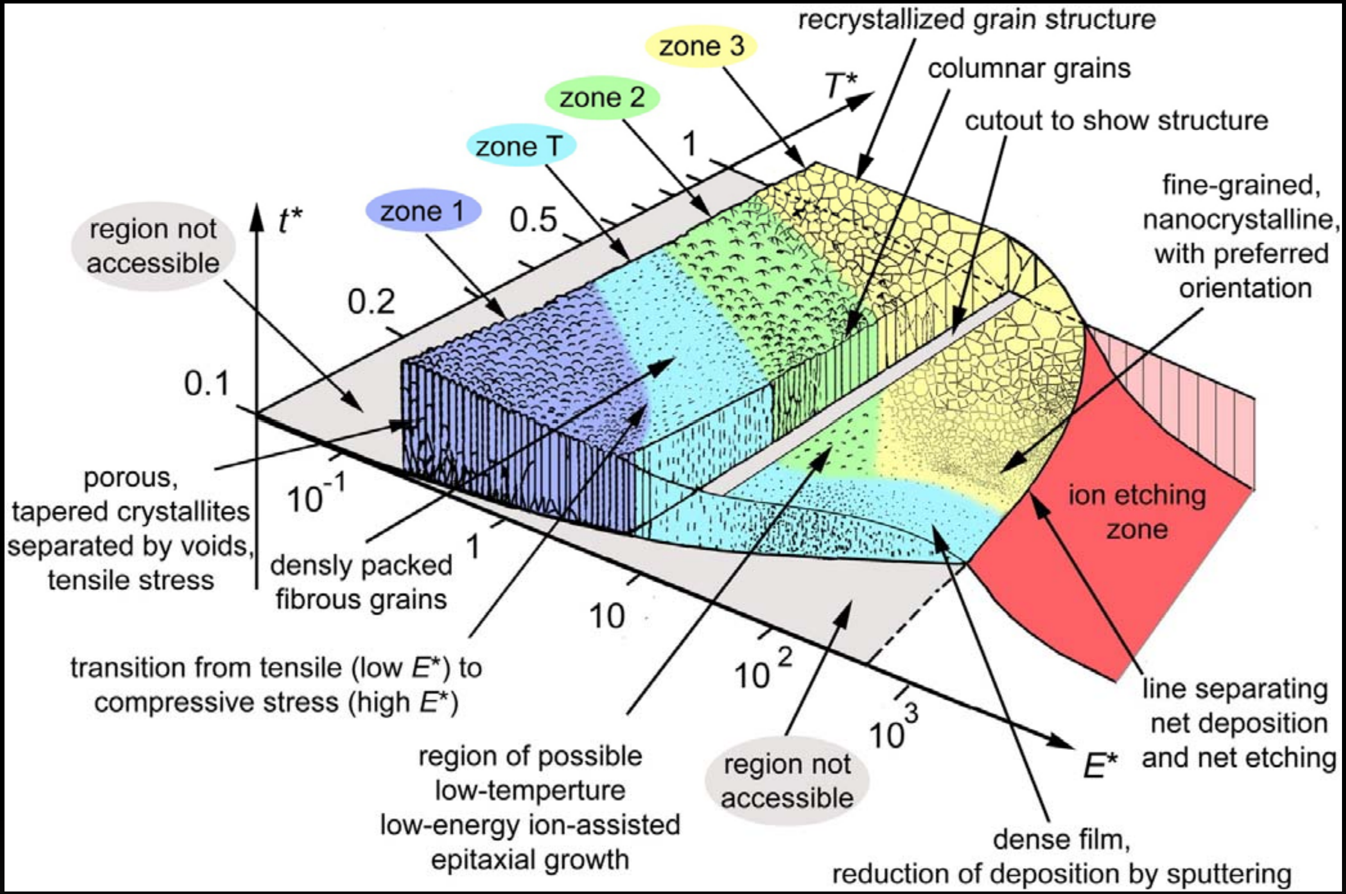
- Zone T - transition between Zones 1 and 2 (Thornton)

  - more tightly packed fibrous grain structure but not fully dense

- Zone 2 - Ts ~ < 0.3 Tm - fully dense columnar grain structure with long columns extending from substrate to film surface

- Zone 3 - Ts ~ > 0.45 Tm – no longer columnar –recrystallized with random orientation

Generalized Structure Zone Diagram



Generalized Structure Zone Diagram

A. Anders, Thin Solid Films
518(2010) 4087

ENERGETIC CONDENSATION: HiPIMS, CED (Vacuum Arc Dep.), ECR…

Deposition process where a significant fraction of the condensing (film-forming) species have hyper-thermal & low energies (10 eV and greater).

Energetic condensation is characterized by a **number of surface and sub-surface processes that are activated or enabled by the energy of the particles arriving at the surface such as desorption of adsorbed molecules, enhanced mobility of surface atoms, and the stopping of arriving ions under the surface.**

Energetic Condensation

Energetic condensation can be defined as a deposition process where a significant fraction of the condensing (film-forming) species have hyper-thermal energies, which, in most cases, imply energies of about 10 eV and greater.

Energetic condensation is characterized by a number of surface and subsurface processes that are activated or enabled by the energy of the particles arriving at the surface such as desorption of adsorbed molecules, enhanced mobility of surface atoms, and the stopping of arriving ions under the surface.

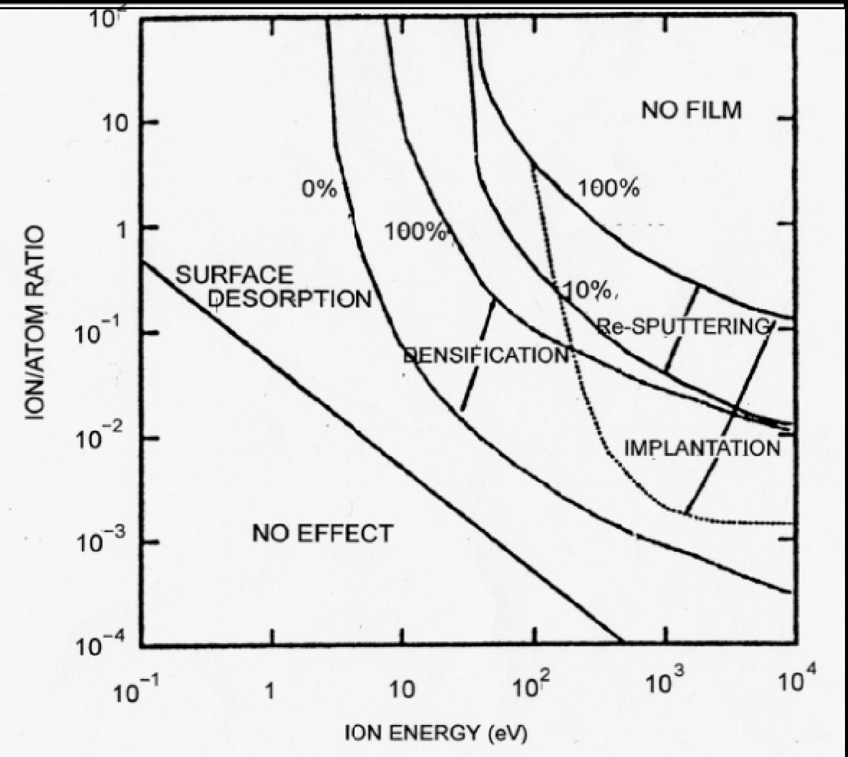
- **Crystalline defects, grains connectivity and grain size may be improved with an higher substrate temperature which provides higher surface mobility (important parameter is the "homologous temperature" $T_{substrate}/T_{melting\_of\_film}$)**
- **However the used substrate may not allow heating**
- **The missing energy may be supplied by ion bombardment**
    - In bias sputter deposition a third electron accelerates the noble gas ions, removing the most loosely bound atoms from the coating, while providing additional energy for higher surface mobility
- The purpose of using energetic condensation is to improve film structure on low temperature substrates by adding energy to the film during condensation to compensate for the lack of thermally induced growth processes.
- One process, **ion beam assisted deposition (IBAD)**,

uses a secondary source of ions to co-bombard the film from conventional sources during growth.

- A second process, **direct ion deposition**, uses vacuum plasmas formed from the material being deposited to produce a film grown from metal ions.

Effect of ion energy and substrate temperature

- Energetic particle bombardment (kinetic & potential energy) promotes competing processes of defect generation and annihilation.



Regions of dominance for various ion-bombardment processes as a function of ion/atom ratio & ion energy.

J.M.E Harper et al., Ion Bombardment Modification of Surfaces: Fundamentals and Applications, eds. O. Auciello and R. Kelley, Elsevier, Amsterdam, 1984

- **Promotion of surface diffusion of atoms**
- **Surface displacement** (epitaxial growth)
- **Bulk displacement** cascades :defects followed by re-nucleation
- Post-ballistic thermal spike → **atomic scale heating , annihilation of defects** followed by **re-nucleation** (transient liquid, **large amplitude thermal vibrations** facilitating diffusion, migration of interstitials inside grains & adatoms on the surface).
- E_{pot}/E_{kin} per incident particle as well as the absolute value of the kinetic energy will shift the balance and affect the **formation of preferred orientation and intrinsic stress** (Minimization of volume free energy and surface free energy density).
- **Sub-implantation** - insertion of atoms under the surface yet still very little annealing .
- Sputtering yield is increased & **net deposition rate is reduced (re-sputtering).**
- **Film growth ceases** as the average yield ~1 (400-1400eV)
- **Surface etching** as energy further increased is further increased

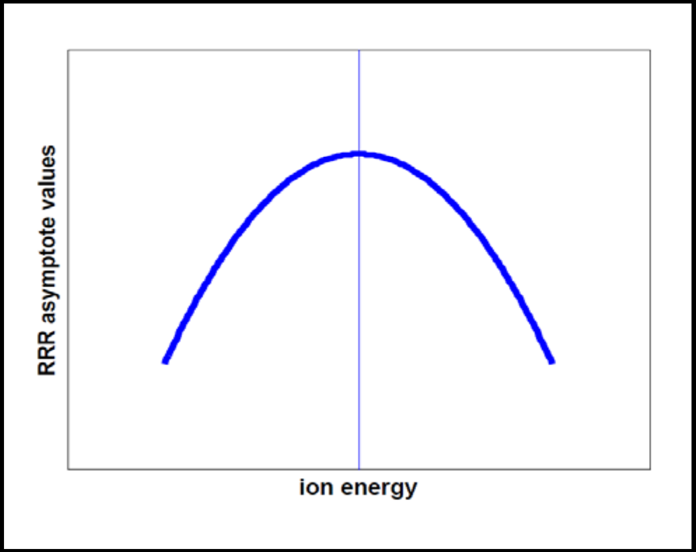
- At higher temperature (higher homologous temperature or temperature increase due to the process itself) the grains are enlarged because the increase of adatom mobility dominates over the increased ion-bombardment-induced defects and re-nucleation rates.

All energy forms brought by particles to the surface will ultimately contribute to broad, non-local heating of the film and shift the working point of process conditions to higher homologous temperature.

Effects of energetic condensation

The additional energy provided by fast particles arriving at a surface can induce the following changes to the film growth process:

- residual gases are desorbed from the substrate surface
- chemical bonds may be broken and defects created thus affecting nucleation processes and film adhesion
- film morphology changes
- microstructure is altered
- stress in the film alters

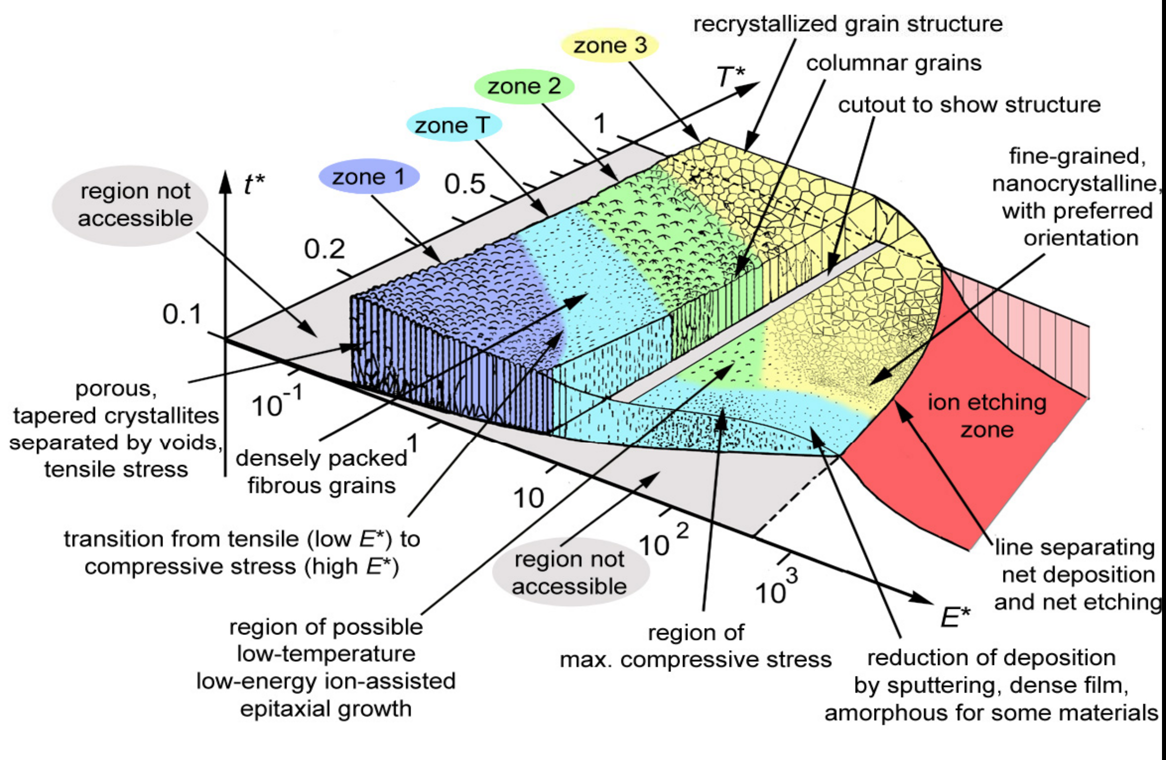


As a result of these fundamental changes, energetic condensation allows the possibility of controlling the following film properties:

- the density of the film may be modified to produce improved optical and corrosion-resistant coatings
- the film composition can be changed to produce a range of hard coatings and low friction surfaces
- crystal orientation may be controlled to give the possibility of low-temperature epitaxy.

Morphology

Generalized Structure zone Diagram (2010), derived from Thornton's diagram for sputtering (1974)

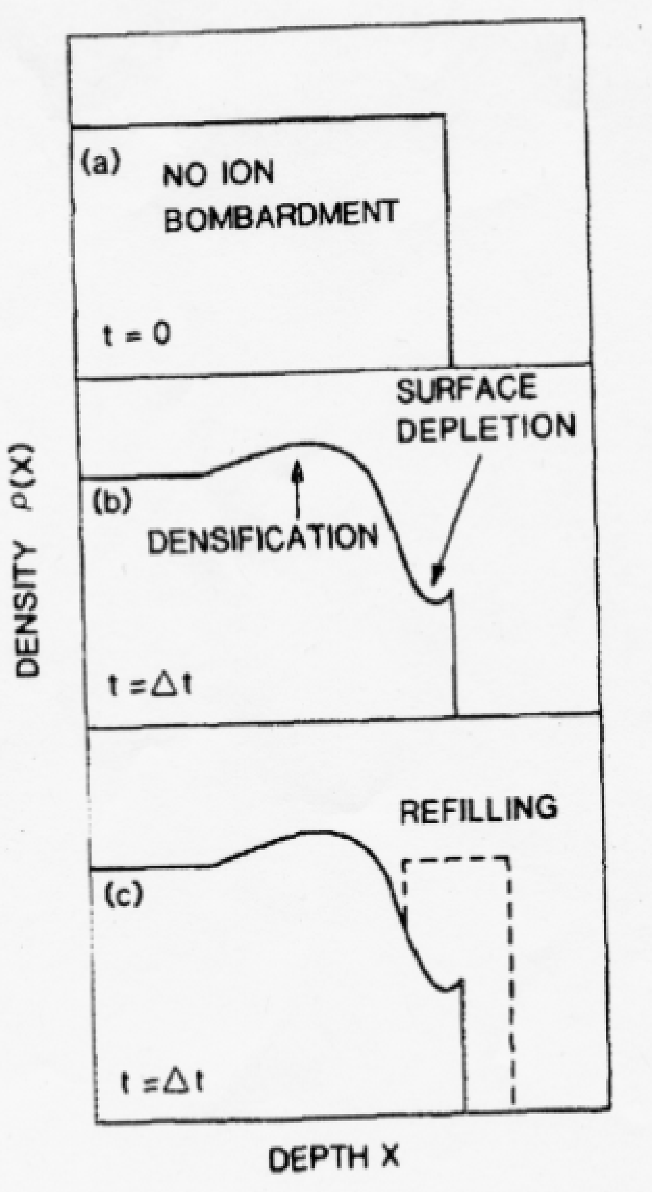


Cross-sectional microscopy studies of films show that additional energy provided by ion bombardment can reduce and even eliminate columnar-type growth as shown by Petrov et al. This group varied the bias step by step during deposition in a dc planar magnetron system when sputtering TiN. A substrate bias greater than 120 V was sufficient to produce fully dense films for substrate temperatures of 300 °C but a bias exceeding 240–280 V was required and substrate temperature of 900 °C before columnar growth was interrupted.

It thus appears that it is a **combination of substrate temperature and added energy, both leading to increased surface mobility of atoms, which will influence the film nucleation and subsequent morphology**.

Effects of energetic condensation

-Sub-implantation & creation of defects-



With the typical energies involved (10eV-10keV), displacement of surface and subsurface atoms is possible. The incoming ions are inserted in the subsurface region, just a few atoms below the surface. If the substrate is biased, the sub-implantation depth may be many monolayers deep, and at higher bias (many kV) may reach a depth that qualifies the process as ion implantation.

Insertion of ions causes densification of the region where the ion comes to rest.

- -at low ion energies densification is enhanced through increased surface mobility
- - at a few hundred eV an ion will penetrate the surface a few nm and also lose energy through collisions with subsurface atoms (sub-implantation) in a collision cascade aiding densification (Karl-Heinz Mueller, J. Appl. Phys. 59, 1986, 2803)

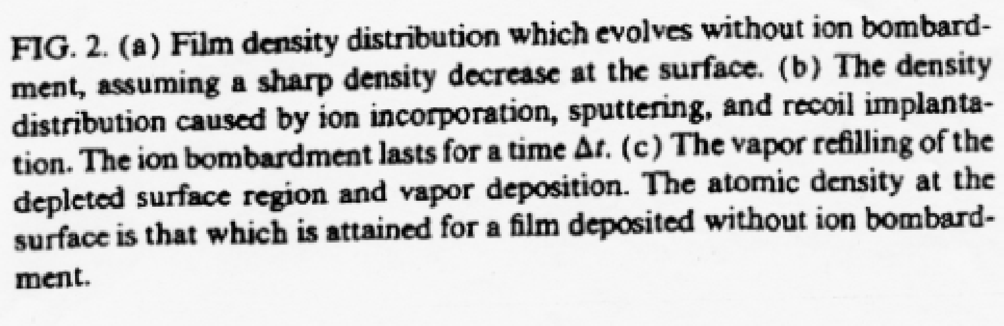
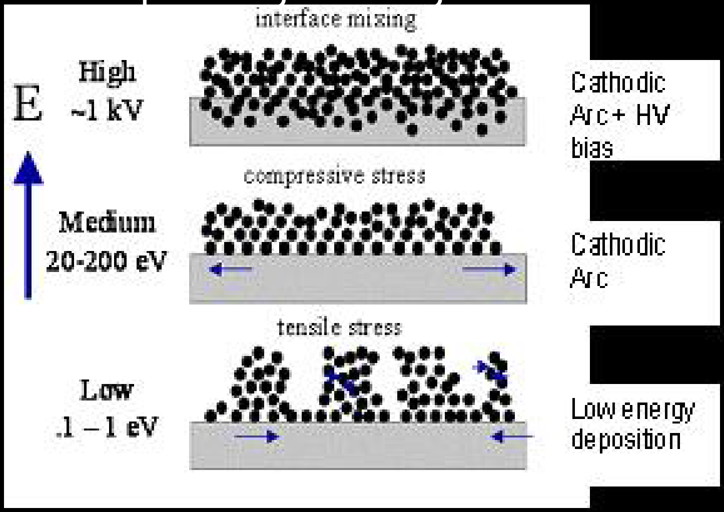


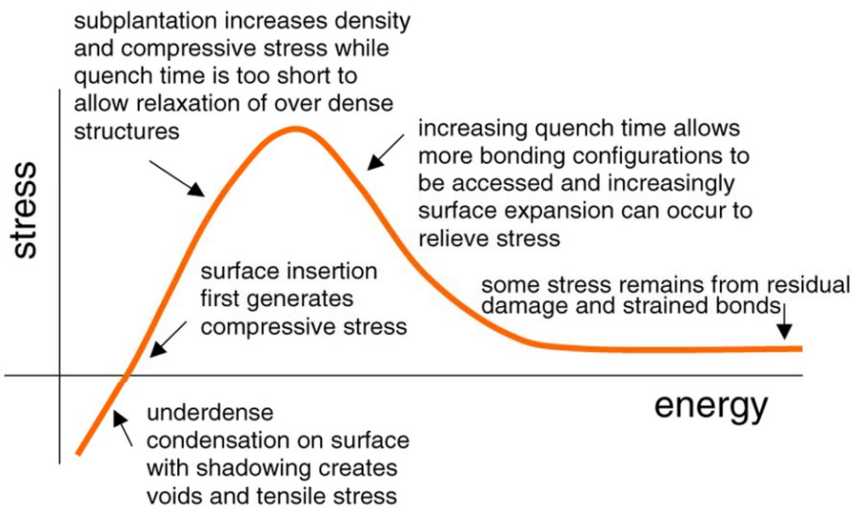
FIG. 2. (a) Film density distribution which evolves without ion bombardment, assuming a sharp density decrease at the surface. (b) The density distribution caused by ion incorporation, sputtering, and recoil implantation. The ion bombardment lasts for a time Δt. (c) The vapor refilling of the depleted surface region and vapor deposition. The atomic density at the surface is that which is attained for a film deposited without ion bombardment.

Effects of energetic condensation

-Control of Stress-

Comparison of stress build-up in low energy deposition, energetic condensation, and energetic condensation plus high voltage bias





[M. M. Bilek, D. R. McKenzie "A comprehensive model of stress generation and relief processes in thin films deposited with energetic ions" Surf. And Coat. Techno. 200 (2006) 4345-4354]

-Crystal Growth & Preferred Orientation-

Control of crystal growth is possible due to the potential control in nucleation, growth, and atom mobility provided by the additional energy available in ion assisted/direct ion deposition processes.
For example, it has been shown that the defect level in TiN grown epitaxially on MgO (100) decreases as the ion energy increases in the region of 100-200eV .

Ion bombardment brings energy and momentum to the growing film, thereby affecting its microstructure. The surface temperature is higher than the substrate temperature. Therefore, energetic condensation has a direct influence on the grain size – apart from the often-quoted substrate (bulk) temperature.

Films made by energetic condensation tend to grow with a preferred orientation, the specifics depending on the ion bombardment parameters. The growing film tends to prefer an orientation that is thermodynamically stable at low levels of biaxial stress.
There is a direct link between microstructure and ion-generated stress, and ultimately the thermodynamic driving forces of minimizing the system's energy affects both stress and preferred orientation.

Effects of energetic condensation

- Interface Mixing & Improvement in Adhesion-

- Effective surface cleaning at ~25 eV/ion and above.
- Atomic mixing across the substrate-film interface (ion stitching) due to the energy loss during the stopping of incident ions inducing atomic relocation of the substrate material or surface sputtering, where the energy and momentum transferred to substrate atoms is sufficient for the secondary particle to be removed from the surface .
- For metal ion deposition in vacuum this process is highly effective by using high ion energies at the beginning of the deposition followed by the energy desired for film growth for the rest of the film.
- But can induce lattice damage

There are numerous examples of improved adhesion resulting from energetic ion irradiation of films. There is no clear evidence if the prime cause for this improvement is a result of atomic mixing across the interface, or, enhanced surface mobility leading to better bonding.

-Surface Roughness-

G. Keppel, et al, "Comparison Between the Morphology of Superconducting Niobium Films by Magnetron Sputtering and Cathodic Vacuum Arc"

-roughness versus deposition angle for 100 V bias

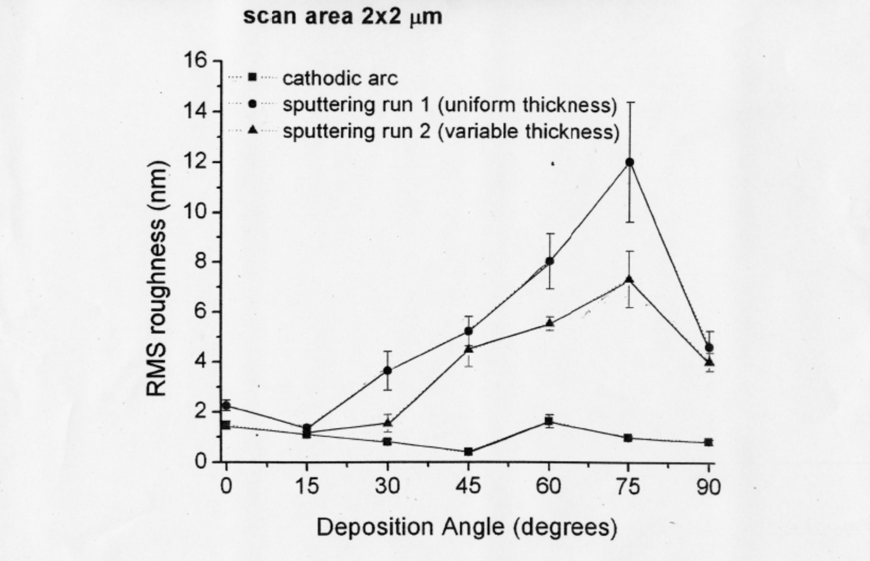
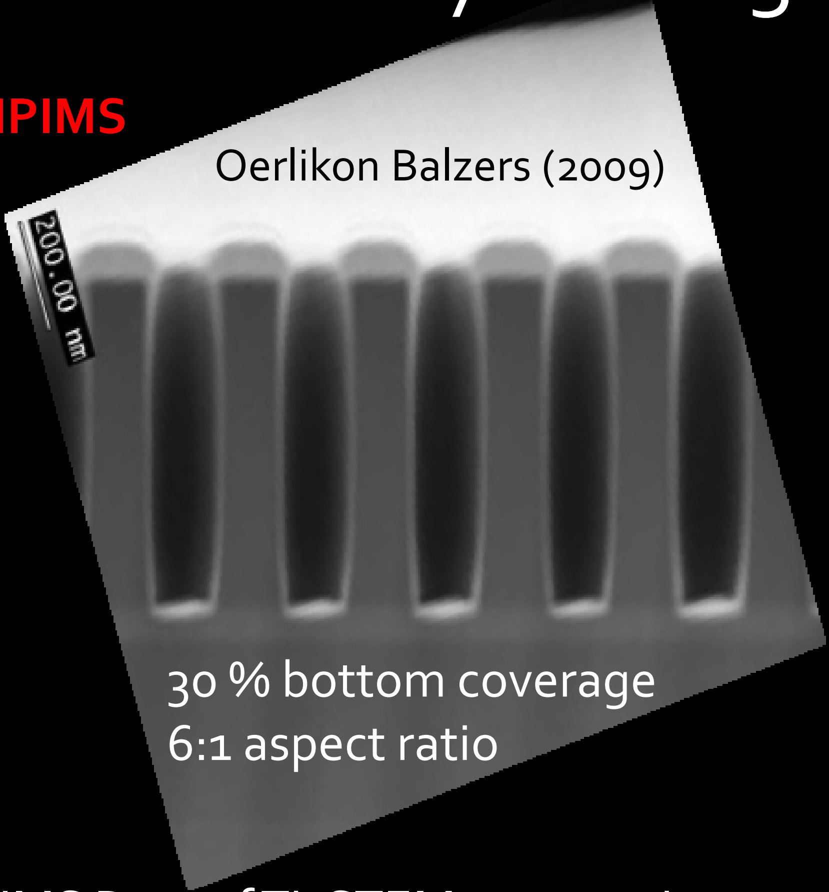


FIG. 6 Comparison of measured roughness for sputtered and arc deposited samples

Conformality of Energetic Condensation Processes

A. Anders, SRFTF Workshop 2010

HIPIMS

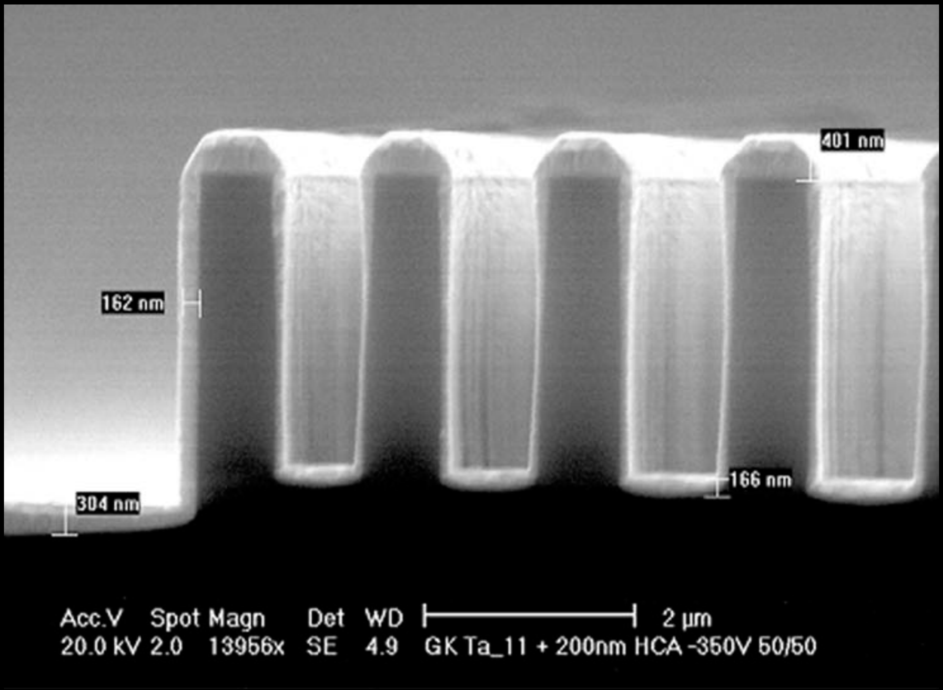


Oerlikon Balzers (2009)

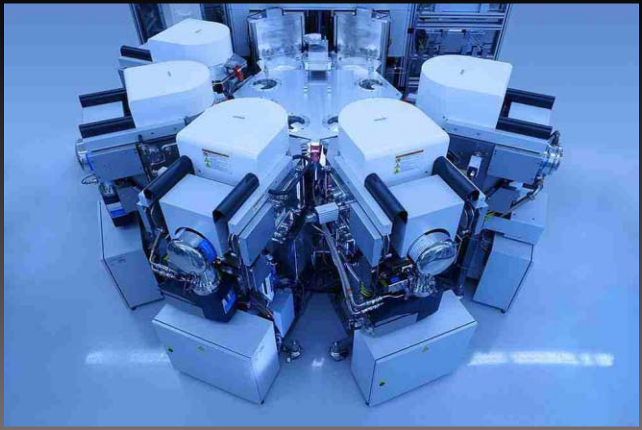
30 % bottom coverage
6:1 aspect ratio

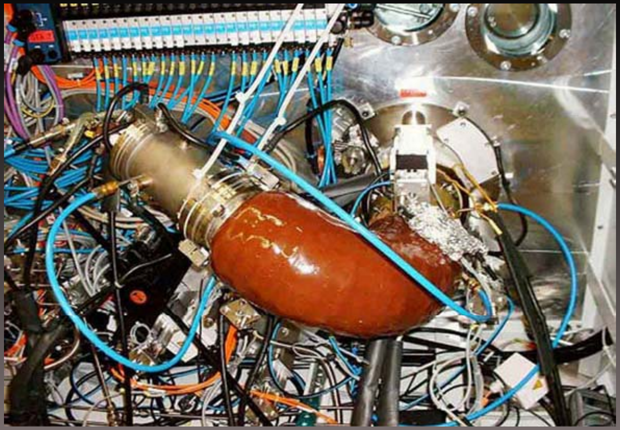
HIPIMS Dep. of Ti, STEM 250 nm vias

Pulsed Arc



P. Siemroth, et al., Thin Solid Films **308, 455 (1997),** and Surf. Coat. Technol. **133-134, 106 (2000).**





METHODS OF ENERGETIC CONDENSATION

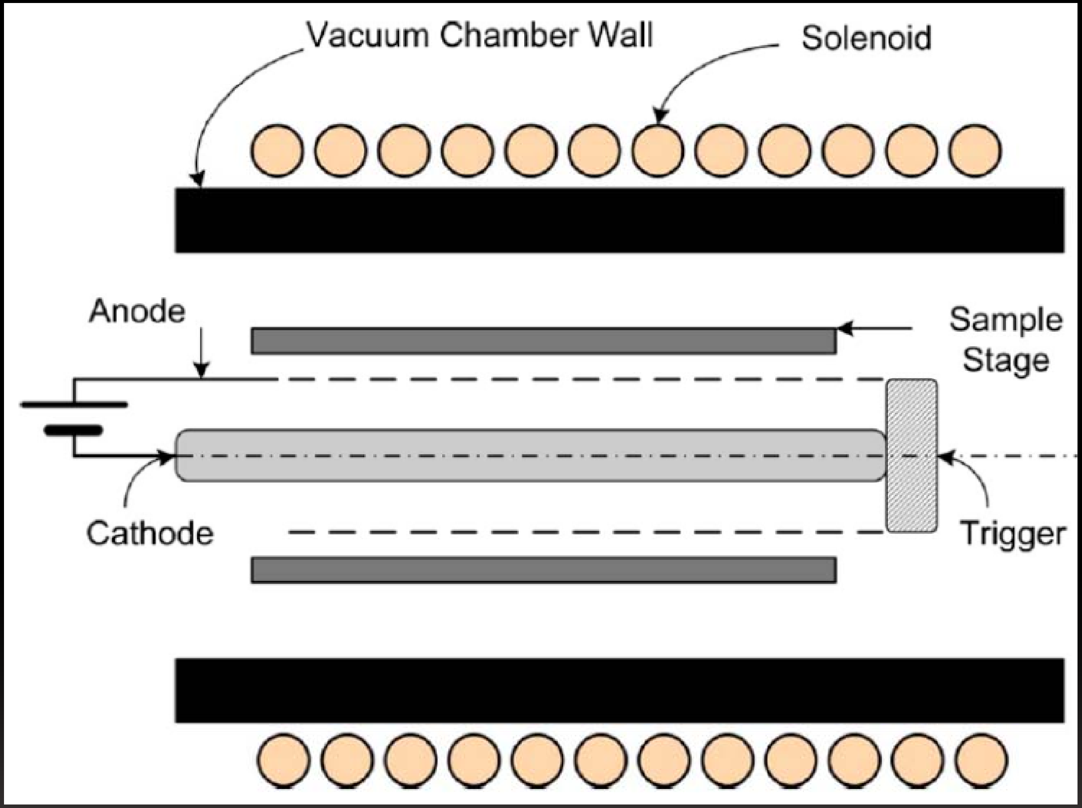
All methods have the common factor that they deliver to a substrate, in a controlled vacuum or reactive gas environment, a supply of film material and, at the same time, energetic bombardment .

- Ion beam assisted deposition
  - Independent metal vapor and ion source
  - Electron beam ionization of metal vapor source
  - High Power pulsed magnetron
  - Unbalanced magnetron
  - Biased magnetron

- **Direct ion deposition**
  - **Vacuum arc deposition**
  - **High Power Impulse magnetron sputtering (HiPIMS/ HPPMS)**
  - **ECR vacuum plasma**
  - Metallic Plasma Pulsed Ion Immersion Implantation Deposition (MPIIID)

Vacuum Arc Plasma

A cathodic vacuum arc is characterized by plasma production at micrometer-size cathode spots which are rapidly moving across the cathode.



X. Zhao, et al., J. Vacuum Sci. Technol. A 27 (2009) 620.

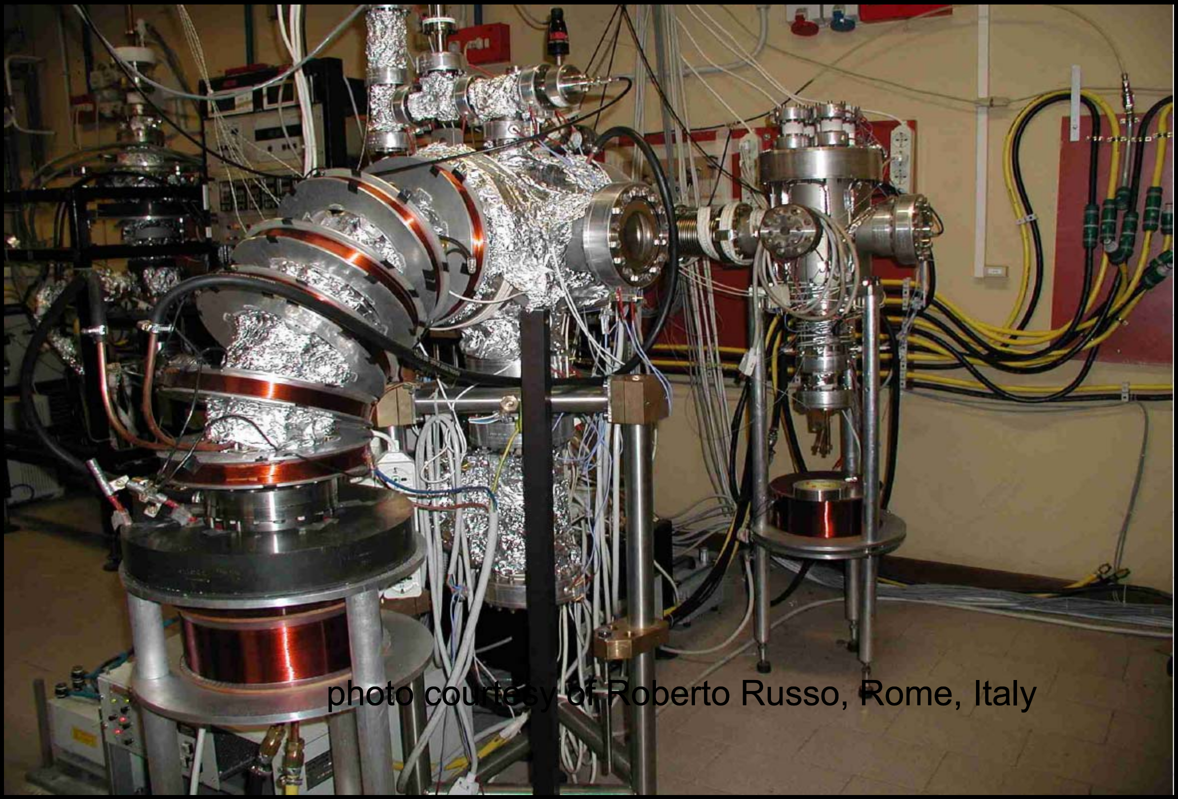
Ionization ratio can be close to 100% is achieved in vacuum arc deposition.

The arc evaporation process begins with the striking of a high current, low voltage arc on the surface of a cathode (known as the target) that gives rise to a small (usually a few μms wide), highly energetic emitting area known as a cathode spot. The localized temperature at the cathode spot is extremely high (around 15000 °C), which results in a high velocity (10 km/s) jet of vaporized cathode material, leaving a crater behind on the cathode surface. The cathode spot is only active for a short period of time, then it self-extinguishes and re-ignites in a new area close to the previous crater. This behavior causes the apparent motion of the arc.

As the arc is basically a current carrying conductor it can be influenced by the application of an electromagnetic field, which in practice is used to rapidly move the arc over the entire surface of the target, so that the total surface is eroded over time.

The arc has an extremely high power density resulting in a high level of ionization (30-100%), multiple charged ions, neutral particles, clusters and macro-particles (droplets).

Vacuum Arc plasma characteristics



- ☐ The plasma ball exerts a considerable pressure on the partially molten surface, reaching up to 40–50 bar and ejecting molten droplets, leading to macro-particles within the plasma stream .

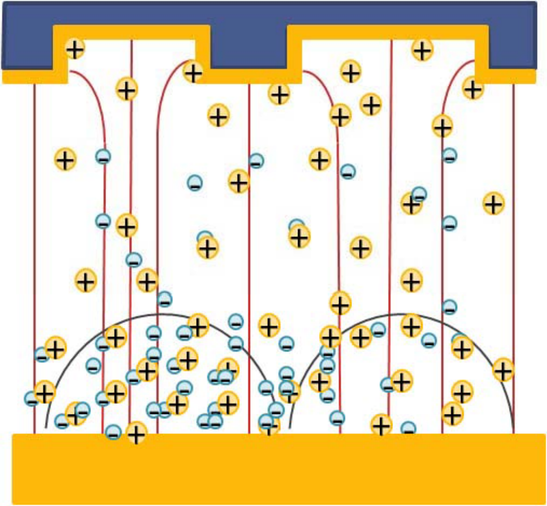
The presence of these macro-particles in deposited films is a major obstacle for the broad application of cathodic arc deposition for high quality defect-free functional coatings. V Various configuration of Filtered Cathodic arc have been developed to overcome this drawback.

Filtered cathodic (UHV) arc deposition of Niobium

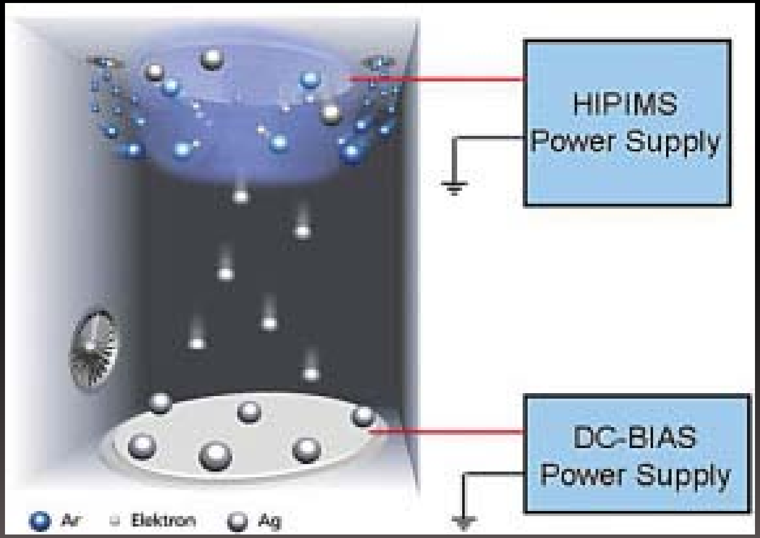
- ☐ Elevated temperatures of at least 200–300 °C are usually employed to improve adhesion properties while additionally influencing the morphology and properties of the coatings themselves.
- ☐ A huge variety of applications is currently used in industry, foremost coatings for tools and decorative purposes, using planetary gear drives and multiple cathodes or a combination of magnetrons and arcs for homogeneity as well as multi-component coatings or direct multilayers

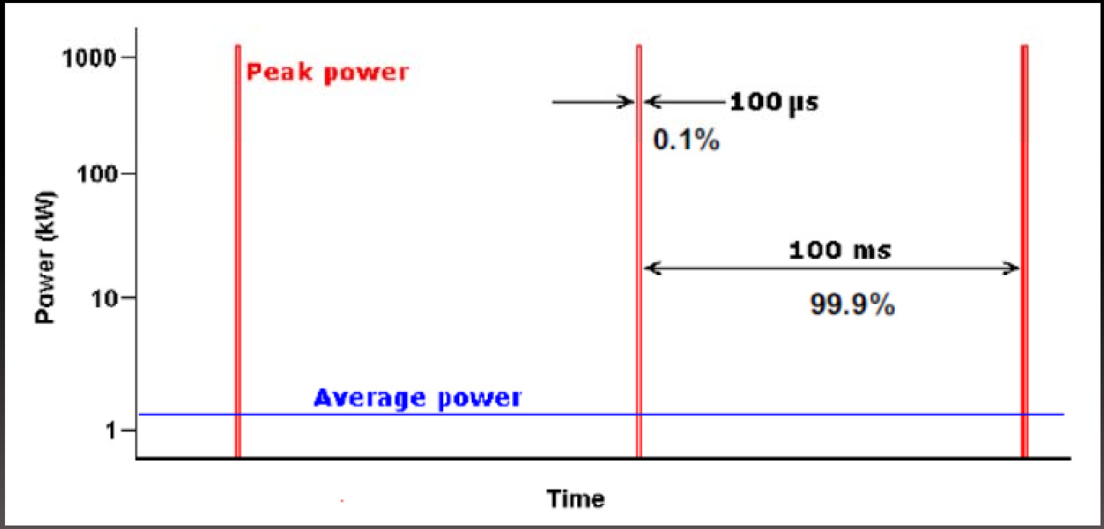
High Power Impulse Magnetron Sputtering (HiPIMS/HPPMS)

A. Anders, Surf. Coat. Technol. **205** (2011) S1.



As a first step, decreasing the duty cycle allows a corresponding increase in power during the on-time. HIPIMS is observed when a power density about two orders of magnitude higher than for conventional sputtering is maintained. Typical pulse lengths of 10–400 μs are used with pulse frequencies in the range of 50–500 Hz, yield a duty cycle around 0.5–5% at instantaneous power densities larger than 1 kW/cm2. At these greatly enhanced power densities, ionization of sputtered atoms occurs much more frequently than in conventional magnetron sputtering, thus increasing the fraction of ionized sputter material and reducing the necessary amount of sputter gas.





HiPIMS film properties

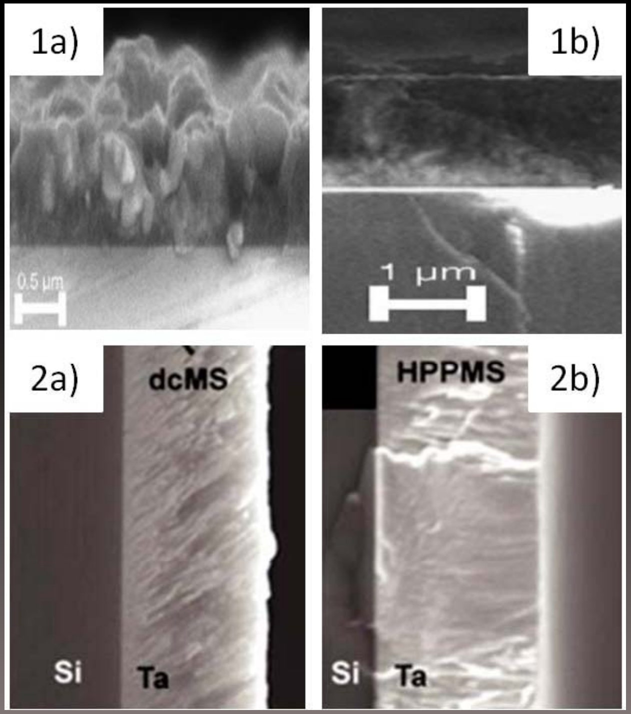
Use of High Power Impulse Magnetron Sputtering (HiPIMS) produces films with enhanced properties

The target material is partly ionized such that the ions will reach the substrate with a higher energy and, in case of an applied bias voltage to the substrate, always normal to the surface.

The intense pulse plasma density provides a large concentration of ions producing high-quality homogeneous films.

The high ionization fraction allows fine control of the sputtered species during deposition

- very high purity
- Excellent adhesion
- better (normal) conductivity,
- Large crystal grains, low defect density
- Suppression of columnar structure
- Superior density
- Decreased roughness
- Homogeneous coating even on complex-shaped surfaces
- Phase composition tailoring
- Interface engineering

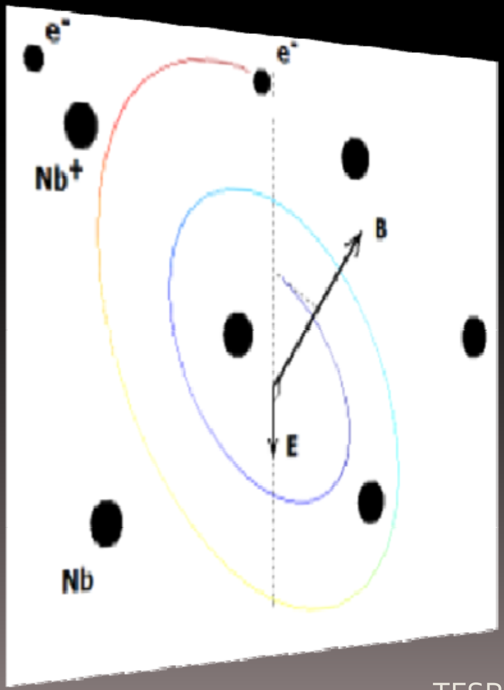


ELECTRON CYCLOTRON RESONANCE

An electron in a static and uniform magnetic field will move in a circle due to the Lorentz force. The circular motion may be superimposed with a uniform axial motion, resulting in a helix, or with a uniform motion perpendicular to the field, e.g., in the presence of an electrical or gravitational field, resulting in a cycloid. The angular frequency (ω = 2πf) of this cyclotron motion for a given magnetic field strength B is given by

$$\omega = \frac{eB}{m}$$

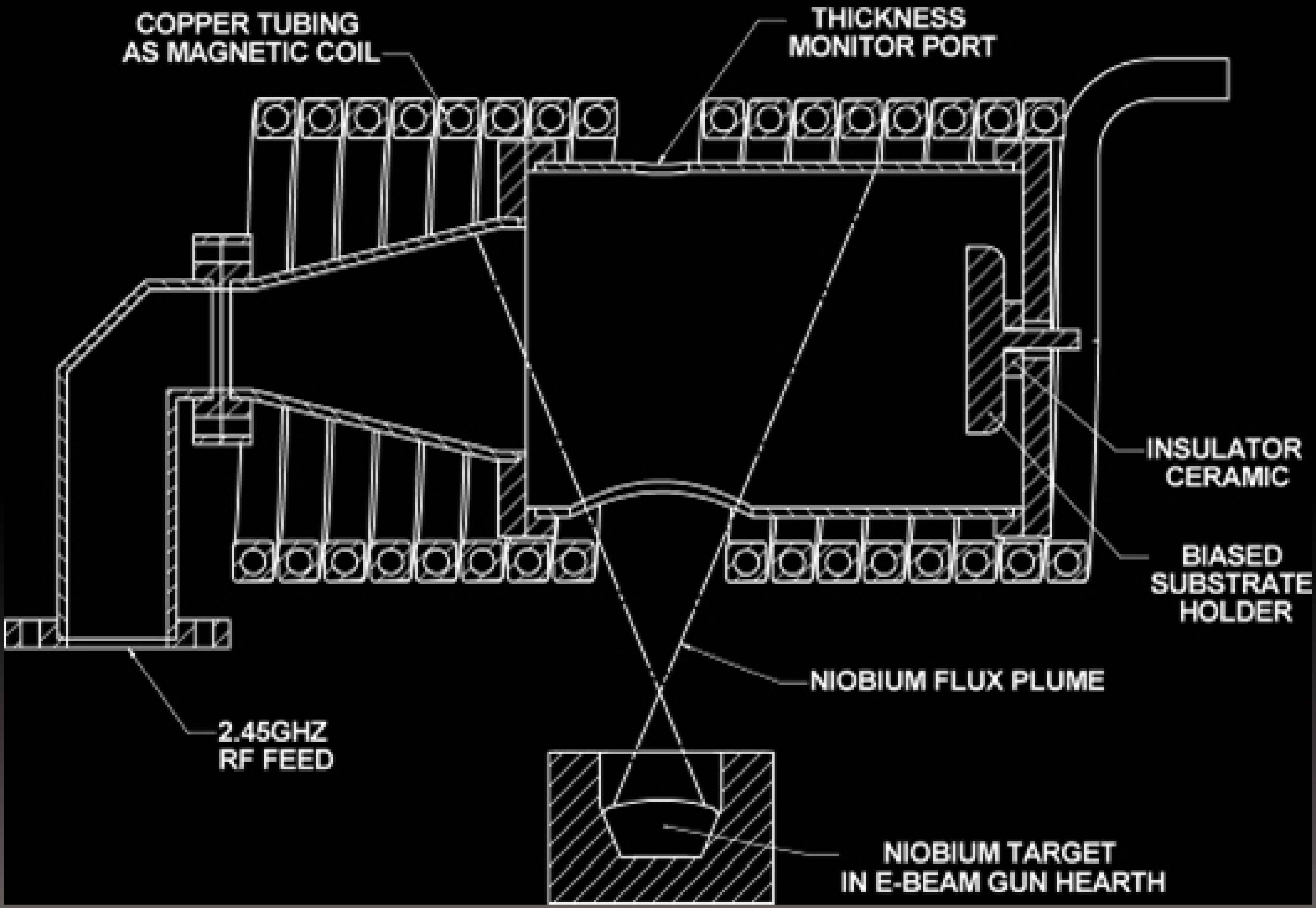
where e is the elementary charge and m is the mass of the electron.



For the commonly used microwave frequency 2.45 GHz and the bare electron charge and mass, the resonance condition is met when B = 875 G .

Energetic Condensation via ECR

Niobium vapour produced by an e-beam gun is ionized by an ECR process. The Nb ions can be accelerated to the substrate by an appropriate bias. Energies in excess of 100 eV can be obtained.



Wu, G., et al.
J. Vac. Sci. Technol. A Vol. 21, No. 4, (2003)

Generation of plasma

3 essential components:

Neutral Nb vapor

RF power (@ 2.45GHz)

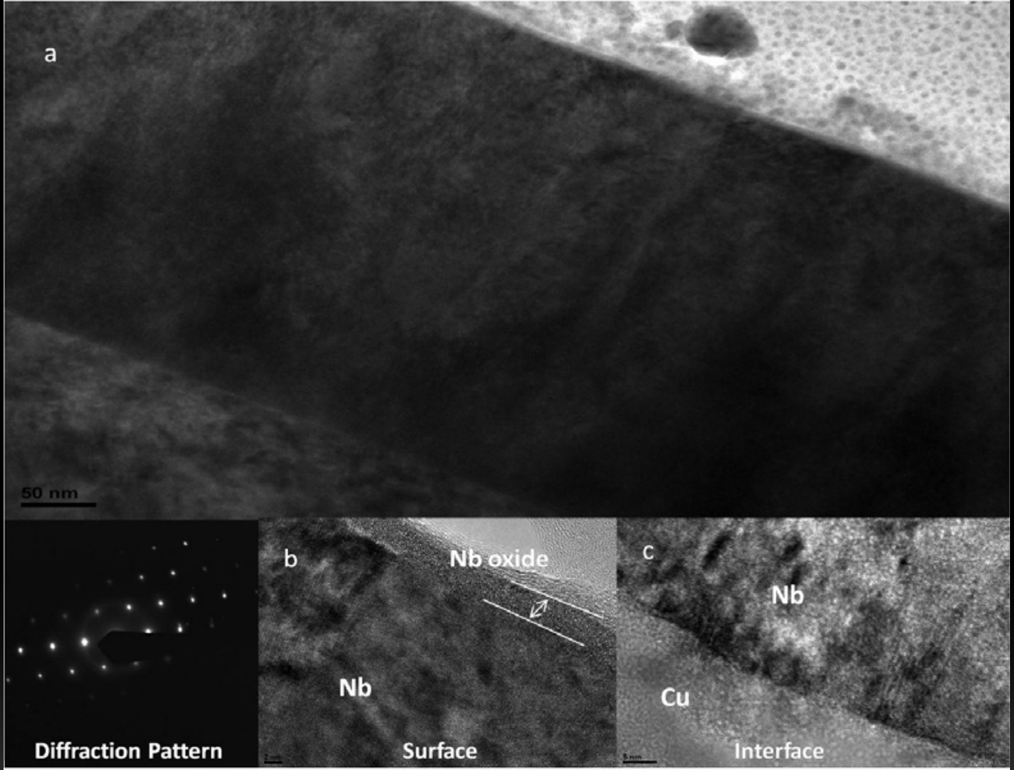
Static B ⊥ E_{RF} with ECR condition

Nb ion energy : 64eV

ECR plasma characteristics

ECR ion sources are able to produce singly charged ions with high intensities
ECR plasma source has some excellent features such as low pressure plasma generation, the capability of ion energy control and high ionization efficiency

- No working gas
- High vacuum ie. reduced impurities
- Singly or "quasi-singly charged" ions
- Controllable deposition energy
- 90° deposition flux
- Excellent bonding
- No macro particles



ECR also used to assist other deposition techniques such as

ECR-CVD
ECR-MS

APPLICATIONS of ENERGETIC CONDENSATION

☐ Hard coatings

Cathodic arc deposition is actively used to synthesize extremely hard film to protect the surface of cutting tools and extend their life significantly.

☐ Phase composition tailoring.

Numerous studies have demonstrated that energetic ions can be used for this purpose, since they can trigger surface and bulk diffusion processes, induce changes in the film structure, and cause generation of internal stresses. The high fluxes of ionized material available in HPPMS for example have been found to allow for control of the phase formation in both elemental and compound films.

☐ High quality dense coatings

Dense highly reflective coatings for advanced laser applications, including micro mirrors in laser scanners or endoscopes, on very thin substrates of less than 50 μm thickness.

☐ Multilayers for optical, magnetic applications

☐ Application to Superconducting RF materials

Higher density, reduced defects, better structure compared to commonly used magnetron sputtering

Residual Resistivity Ratio (300K/10K) is >300 for pure bulk Nb; low values are indicative for contamination and defect density (

RRR for sputtered films ~ 10-40

RRR for arc deposited and ECR deposited films ~ 20...400

Summary

- With increasing deposited energy per particle, a higher (transient) mobility of the atoms impinging on the surface is obtained, thus increasing the apparent surface temperature.
- At identical deposition rates, the larger mobility will lead to a higher diffusivity, thus allowing a further transport from the original arrival site and earlier coalescence . Changes in the surface morphology and texture are observed with higher energies leading to films with larger grains and less defects while the momentum of the incoming particles can lead to alignment or orientation of the growing crystallites
- The ion bombardment can be tailored to enhance the surface mobility during growth without leading to defect generation in the bulk below the surface: the transferred energy has to be between the surface threshold and the bulk threshold for displacements.
- Non-thermal energy can be used to reduce the substrate temperature during film growth due to the supplementary surface mobility.
- High degree of ionization is envisaged to permit a more direct control of particle momentum, direction, and magnitude
- By avoiding the presence of a background gas at low and very low pressures, both incorporation of impurities and scattering processes of particles are avoided, or at least minimized.

- Control of crystal growth possible due to the potential control in nucleation, growth, and atom mobility provided by the additional energy available in ion assisted/direct ion deposition processes
- Film properties

  Control of energetic ion bombardment leads to improved adhesion, reduced substrate temperatures, control of intrinsic stress within the films as well as adjustment of surface texture, film density, phase formation and nano-topography.

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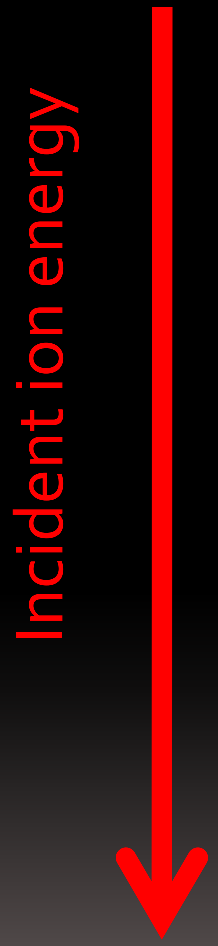
Effect of ion energy on film growth

A. Anders / Thin Solid Films 518 (2010) 4087–4090

kinetic energy of arriving positive ions {
- an initial component from the plasma, E_0
- a change due to acceleration in the sheath,

$E_{kin}=E_0+QeV_{sheath}$

where Q =ion charge state number, e =elementary charge, and V_{sheath} is the voltage drop between plasma and substrate surface.



Non-penetrating ions (or atoms) in the film bulk

- Promotion of **surface diffusion of atoms**.
- **Between the surface displacement energy and bulk displacement energy: epitaxial growth** is promoted because no defects are created in the film bulk .
- **Atomic displacement cascades** if $E_{kin} > E_{bulk\ displacement}$, (12–40 eV)

Penetrating particles :

- very short (~100 fs) **ballistic phase with displacement cascades** followed by a **thermal spike phase** (~1 ps) (mobility of atoms in the spike volume very high) ~ **transient liquid large amplitude thermal vibrations** still facilitate diffusion (migration of interstitials inside grains & adatoms on the surface).

The driving force is the gradient of the chemical potential, leading to minimization of volume free energy and surface free energy density with contributions of interface and elastic strain energies and often resulting in a film where grains have a preferred orientation.

- As E_{kin} increase, e.g. by biasing, the sputtering yield is increased and **the net deposition rate is reduced**. **Film growth ceases** as the average yield approaches unity, for most elements between 400 eV and 1400 eV
- **Surface etching** as E_{kin} is further increased.

Effect of ion energy and substrate temperature

- Energetic particle bombardment promotes competing processes of defect generation and annihilation.
  - Kinetic energy → displacement and defects followed by re-nucleation
  - Release of potential energy & post-ballistic thermal spike → atomic scale heating, annihilation of defects.
    - E_{pot}/E_{kin} per incident particle as well as the absolute value of the kinetic energy will shift the balance and affect the formation of preferred orientation and intrinsic stress .

      Maximum of intrinsic stress for E_{kin} ~100 eV; the actual value depends on the material and other factors. insertion of atoms under the surface yet still very little annealing .

- At higher temperature (higher homologous temperature or temperature increase due to the process itself) the grains are enlarged because the increase of adatom mobility dominates over the increased ion-bombardment-induced defects and re-nucleation rates.

All energy forms brought by particles to the surface will ultimately contribute to broad, non-local heating of the film and shift the working point of process conditions to higher homologous temperature.

Energetic Condensation Processes

-Atomic Scale Heating-

Each ion delivers significant kinetic and potential energy, and both contribute to what may be called atomic scale heating (ASH). Both are usually greater than the binding energy, surface binding energy, and activation energy for surface diffusion, and therefore both can be expected to have a significant effect on film evolution and resulting film properties.

The total energy that an ion of charge state Q brings to the substrate can be calculated by adding kinetic and potential energies, reduced by the energy required to capture Q electrons from the substrate:

When the majority of condensing species are ions, each of the atoms in the growing film is subject to ASH several times, namely, once when it arrived and again when neighboring atoms arrived. ASH could replace conventional heating and so produce dense films via enhanced surface mobility at generally low bulk temperature.

ASH eventually gives rise to temperature elevation of the substrate and the growing film as a whole. If the substrate is attached to a heat sink, its bulk may stay close to the original temperature, for instance close to room temperature for water-cooled holders.

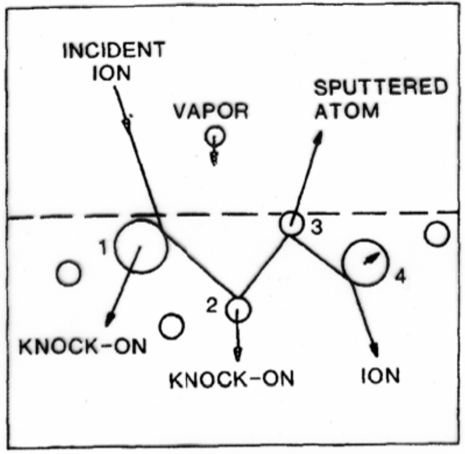


FIG. 1. Processes occurring at the surface of an ion-assisted film. While vapor condenses at the surface, incident ions strike the target atoms (1,2) at or near the surface and drive them into the target. Some knock-on atoms (3) might leave the surface as sputtered atoms. For others (4), the energy transfer may be too small to leave their sites.

-Sub-implantation-

- Energy transfer to knock-on atoms ~10E^{-13} sec.
- Collisional cascade, thermalization ~10E^{-11} sec.
- Fills sub-surface voids
- At high energies the rate of defect creation can exceed defect annealing

Energetic Condensation Processes

-Secondary Electron Emission-

Emitted secondary electrons are in the same electric field of the sheath that accelerated the (positive) ions, but now it accelerates the (negative) electrons in the opposite direction. The electrons may interact with the arc plasma, especially with the colder plasma electrons, as well as with the background.

-self-sputtering & sticking coefficient-

Not all ions are incorporated on/into the substrate, rather, depending on the energy and incident angle of the arriving ion and the kind of substrate material, some ions may "bounce" back as neutralized atoms and therefore contribute to the density of neutral atoms rather than to film growth. Sticking probability for incoming energetic ions.

When an arriving atom becomes incorporated into the substrate, the collision cascade under the surface can lead to the expulsion of one (or more) surface atoms(sputtering). If the arriving ion and the sputtered atom are of the same material, one speaks of self-sputtering. This reduces the effective film deposition rate, and in case the yield exceeds unity, no film is grown.