SRF NIOBIUM THIN FILMS:

SUBSTRATES, NUCLEATION & GROWTH

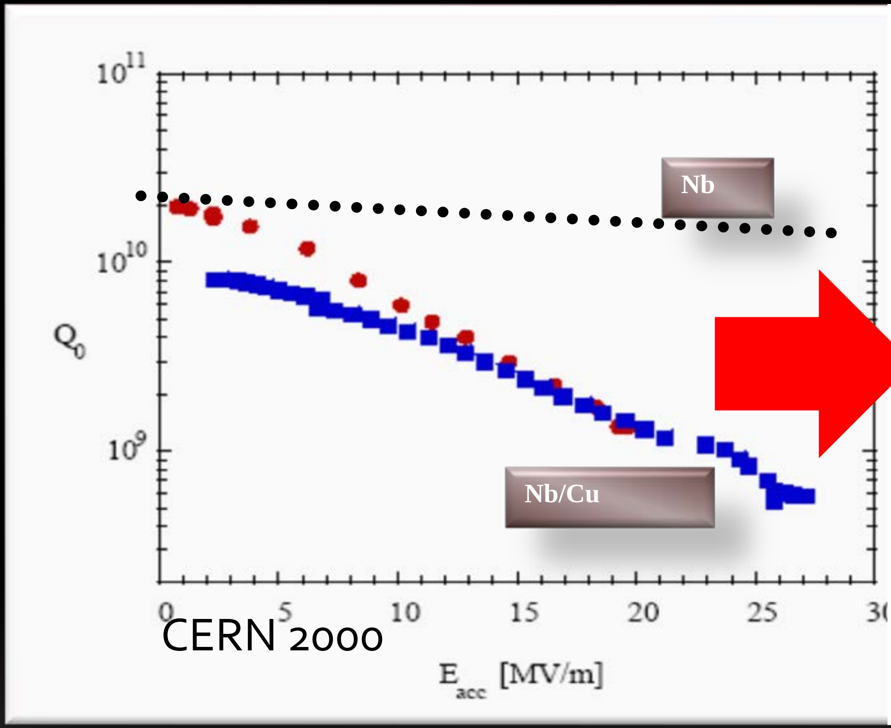
Anne-Marie VALENTE-FELICIANO

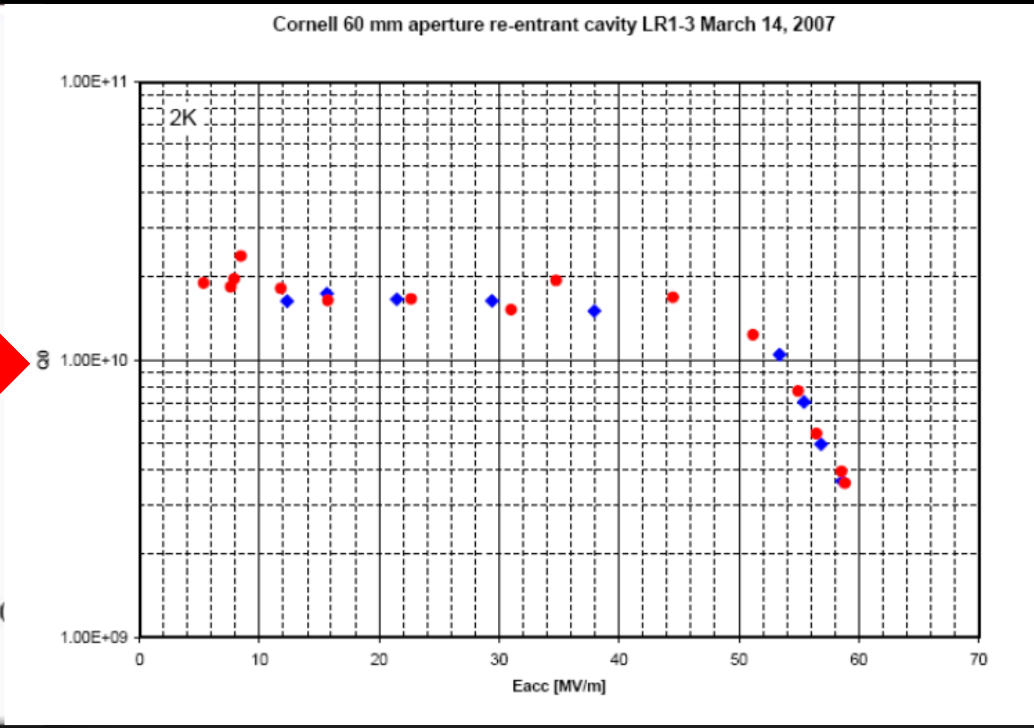
OUTLINE

- Approach/Motivation
- Substrates
- Nb nucleation
- Nb crystal growth
- Concluding Remarks

Thin Films: niobium –state of the art

1.5 GHz Nb/Cu cavities, sputtered w/ Kr at 1.7 K (Q_0=295/R_s)



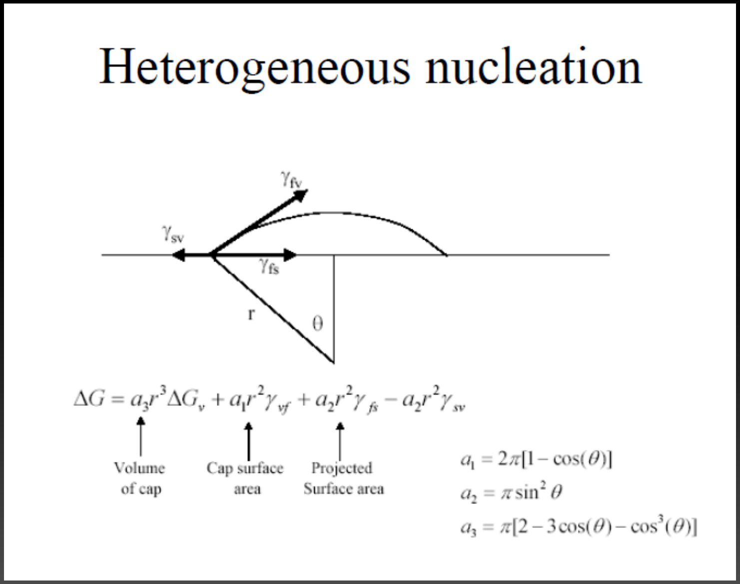


Bulk-like Performance Nb film ➡

- ❑major system simplifications.
- ❑highest level of quality assurance and reliable performance.
- ❑Use of substrates with higher thermal conductivity

Substrate, nucleation and crystal growth : Why do we care?

The thickness of interest for SRF applications corresponds to the RF penetration depth, i.e. the very top 40 nm of the Nb film. However the final surface is dictated from its origin, i.e. the substrate, the interface, and deposition technique (ion energy, substrate temperature…)



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.

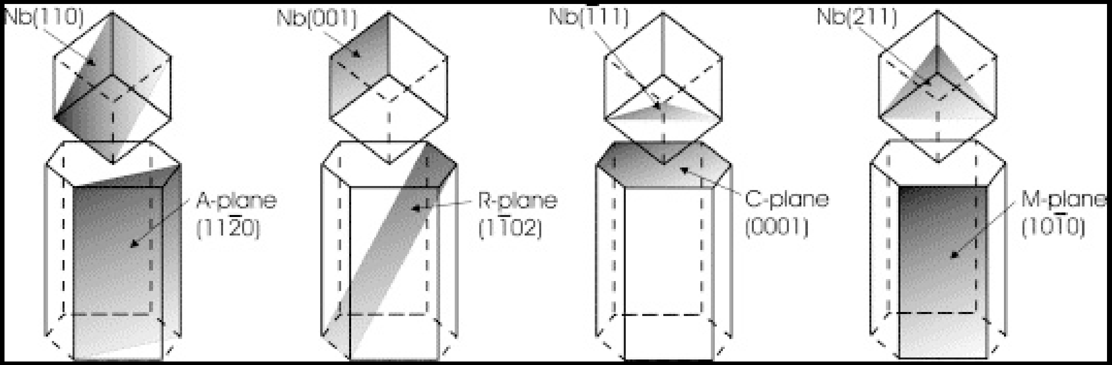
Substrate nature & substrate/film interface

Two common structures:

1. Hetero-epitaxy (film growth driven by orientation of underlying crystalline substrate)
2. Fiber structure (film grows on amorphous surface)

Hetero-epitaxial growth:

The growth of a crystal of a certain material on the crystal face of another material. The thin-film will be a single crystal if the substrate happens to be a single crystal.



A. R. Wildes et al., Thin Solid Films, 401 7 (2001)

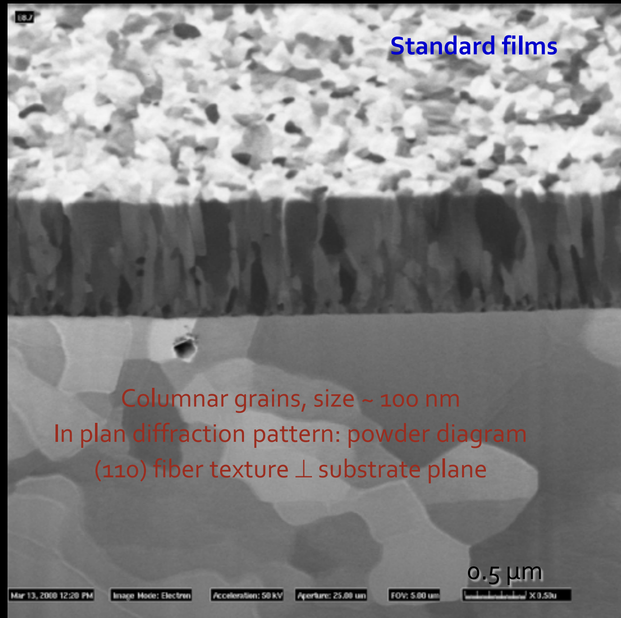
Nb[110] || Al2O3 [11-20], Nb[110] or Nb [111] || Al2O3 [0001]
Nb[110] || Cu [100], Nb[100] || Cu [110], Nb[110] || Cu [111]
Nb[110] || MgO [100], Nb[111] || MgO [110]

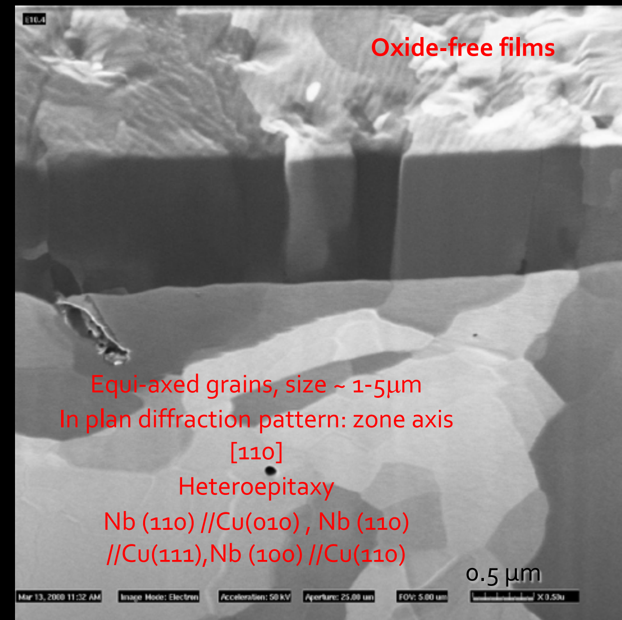
Lattice mismatch and difference in thermal expansion rate induce strain and stress during film growth.

Al_2O_3:~1.9% (11-20)-12%(0001)
MgO:10.8%

Crystalline vs. Amorphous Substrate

CERN magnetron sputtered 1.5GHZ Nb/Cu films (coated with Ar)

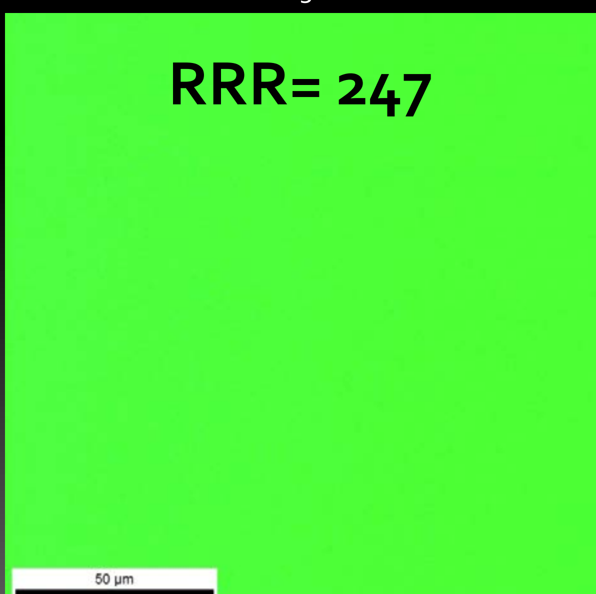


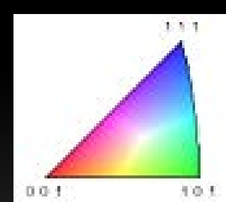


The presence of an oxide on the surface, common with metallic substrates , inhibits epitaxy. The film then grows along the close-packed plane direction where the system energy is minimum ([110] for Nb).

Courtesy of CERN/P. Jacob,FEI

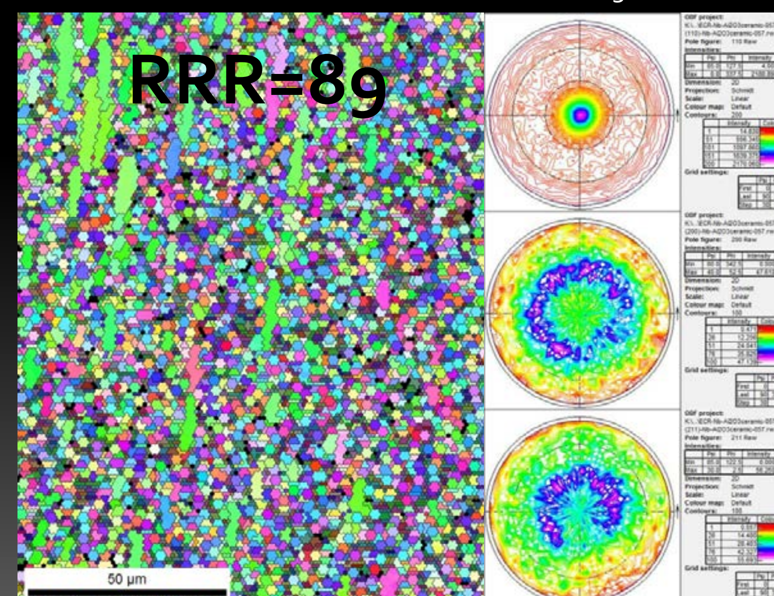
Crystalline Al_2O_3 (11-20)





ECR Nb films Coated simultaneously

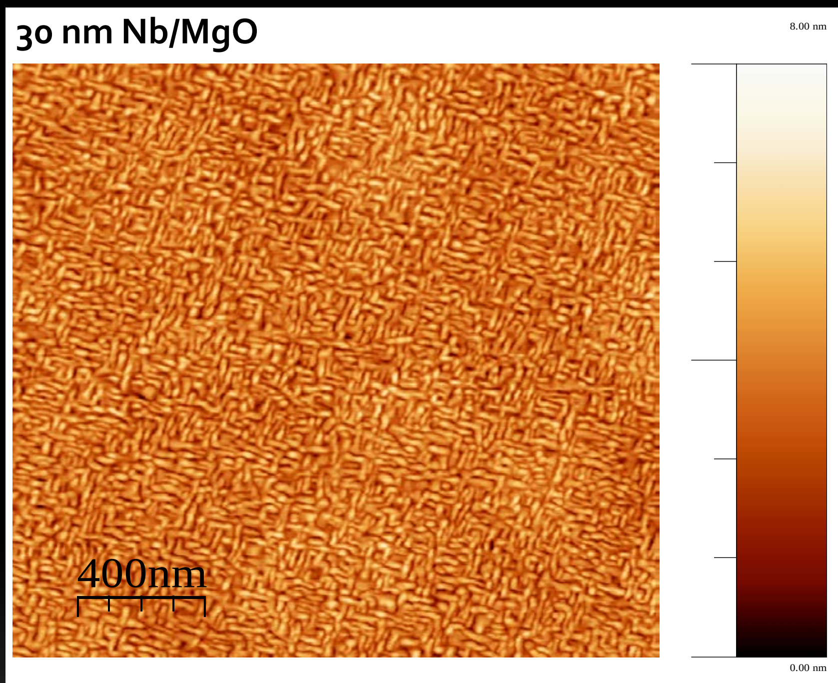
"Amorphous" Al_2O_3 ceramic

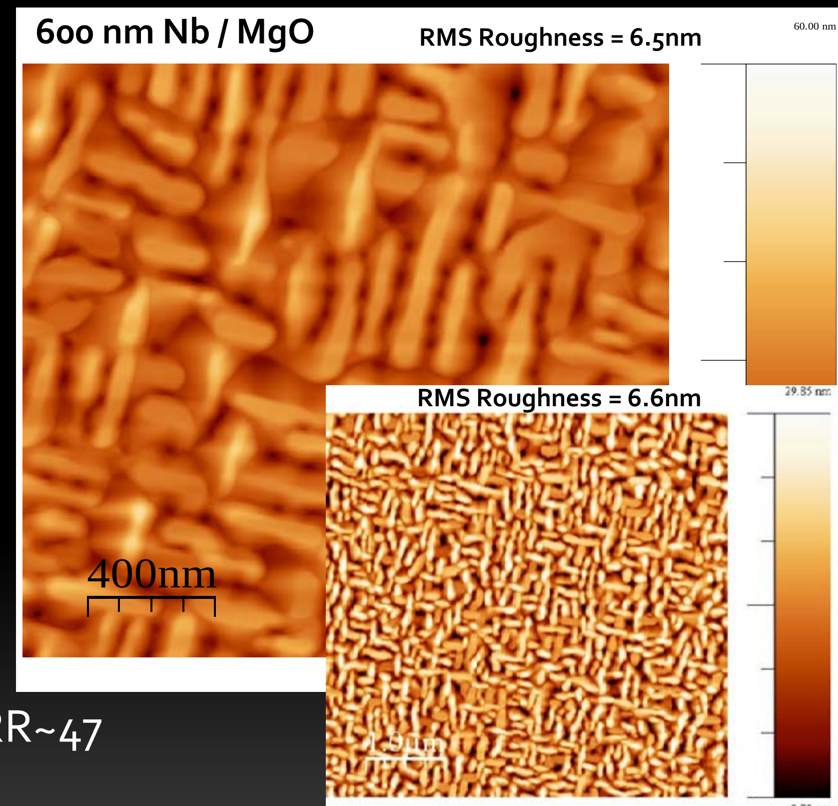


Growth domains due to substrate

Growth domains due to 2 possible equivalent
orthogonal orientations
are possible for the (011) Nb film on the MgO (100)

Morphology of Nb grown on MgO (100) A. Lukaszew et al., College William & Mary





Magnetron sputtering 600nm , 600°C, 7h, RRR~47
ECR 620nm , 360°C, 30', RRR~50

Similar growth variations for Al_2O_3, Cu…(different angles)

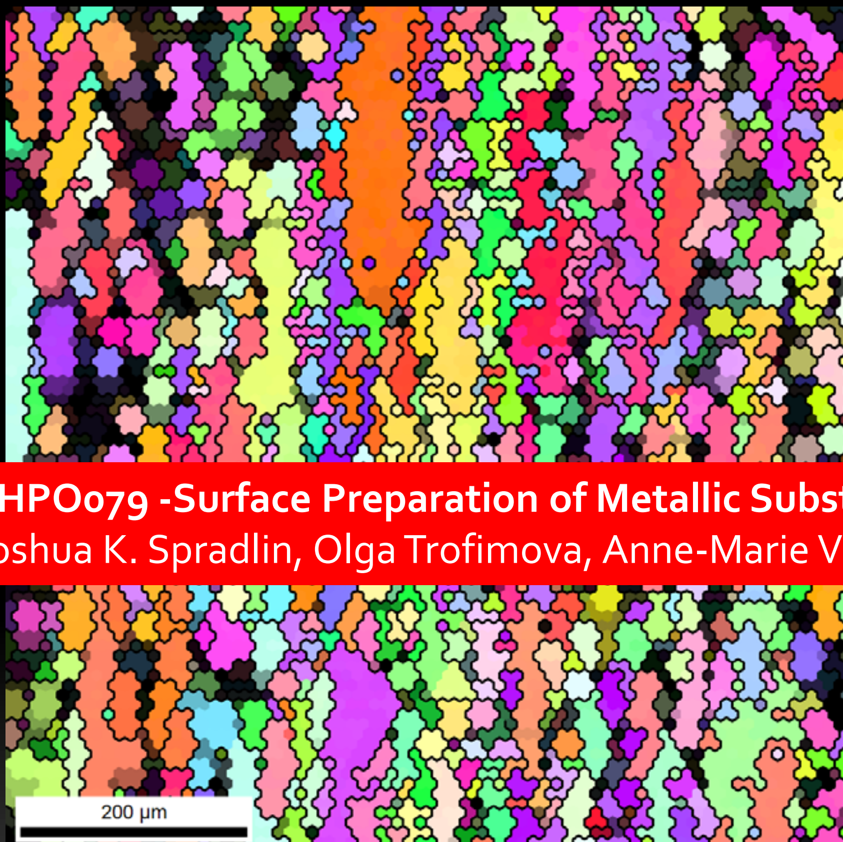
Substrate quality

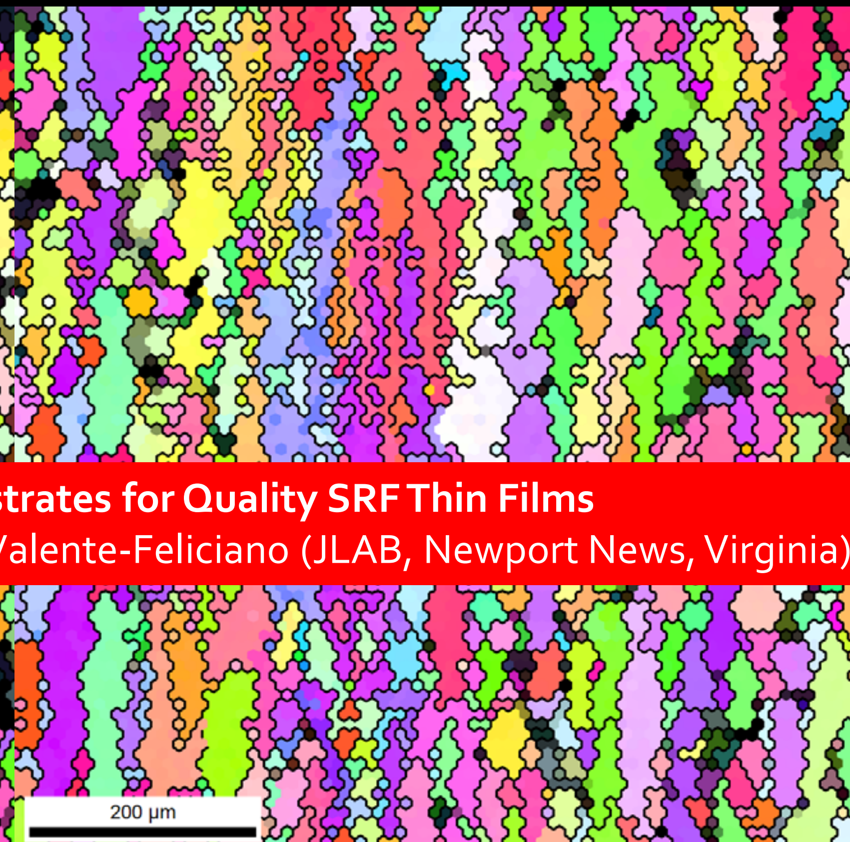
Crystallinity or crystal quality

Nb/Cu, fine grain – effect of temperature pre-treatment

750µm x 750µm, 10µm

100x





THPO079 -Surface Preparation of Metallic Substrates for Quality SRF Thin Films
Joshua K. Spradlin, Olga Trofimova, Anne-Marie Valente-Feliciano (JLAB, Newport News, Virginia)

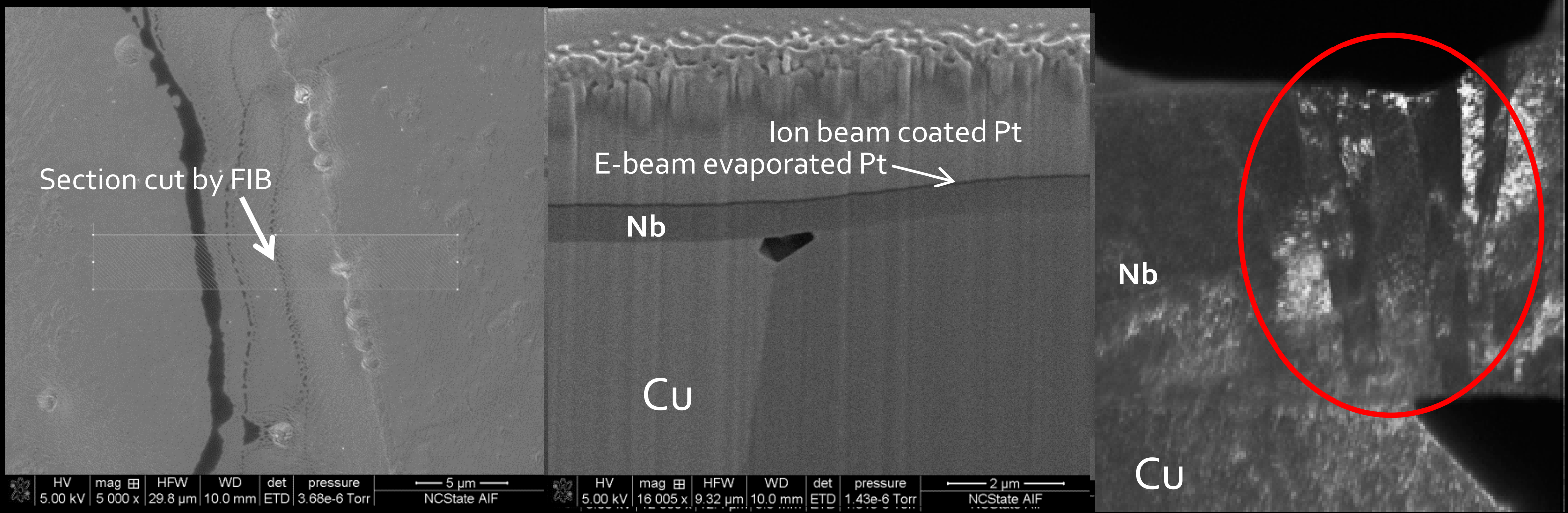
-120V, bake@360°C
CI =0.09
Oxide dissolution in the bulk

-120V, bake@700°C
CI =0.29
Oxide dissolution in the bulk
Annealing of substrate defects

Substrate roughness and defects

Whatever the inherent nature of the film, the roughness of the substrate will dictate the minimum roughness of the film (the final roughness depends as well on the coating technique and other refinements).

Any defect (scratch, pin-hole) is duplicated and enhanced in the film as it grows.



Substrate cleanliness

Impurity on the substrate surface will drift into the film (blemishes on the film surface even if one cannot see them before sample coating).

ECR films grown on MgO side by side: **RRR from 348 to 156** – SIMS data revealed on **H signal 2 orders higher for the lower RRR**.

Impurities also act as nucleation centers and can alter the nucleation and subsequent crystal growth of the film.

Can be improved by heating or using low energy ion beam to desorbed the impurities from the substrate surface

Substrate

- The substrate has a significant impact in the resulting performance of Nb films.
- The interface between substrate and film can be tailored to promote the desired film growth and properties.
- Oxides on metallic substrate can be removed to promote hetero-epitaxy: substrate heating, surface etching with Ar ions…
- The interface can also be amorphitized to grow independently of the substrate (anodization or modified otherwise).
- A **seed layer** can be coated at the interface to favor the growth of a particular structure, minimize the density of grain boundaries…

THPO062: Epitaxial Niobium Thin Films for Accelerator Cavities
William Roach, Douglas Barry Beringer, Cesar Clavero, Rosa A. Lukaszew (The College of William and Mary, Williamsburg), Charles E. Reece (JLAB, Newport News, Virginia)

Film Nucleation & Growth

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

Steps in Film Formation

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

- 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.

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

=– +4

=—— ( )

= -——

Effective energy barrier for nucleation

Competing Processes in Nucleation

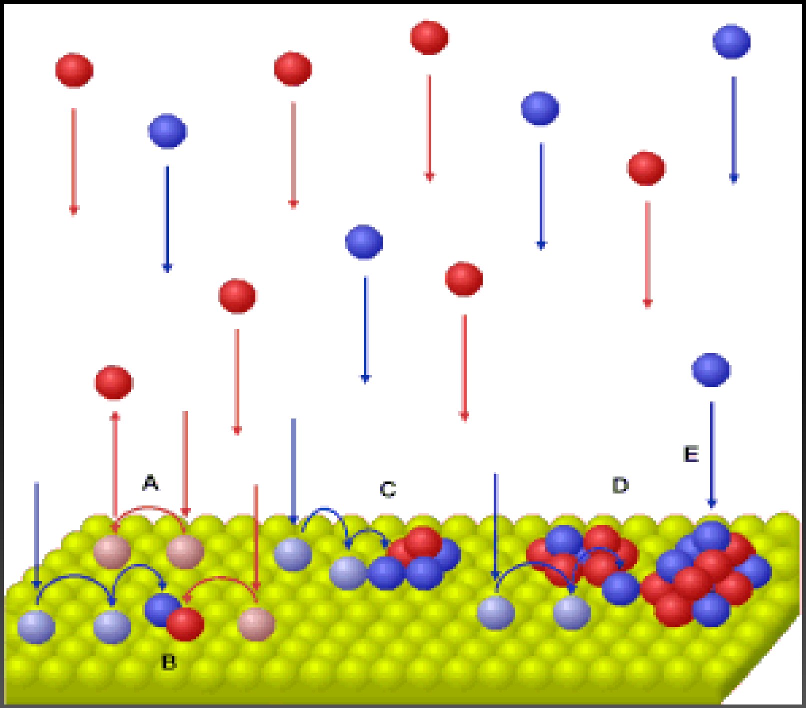
Condensation from the vapor involves incident atoms becoming bonded adatoms which diffuse over the film surface until trapped at low energy lattice sites.

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

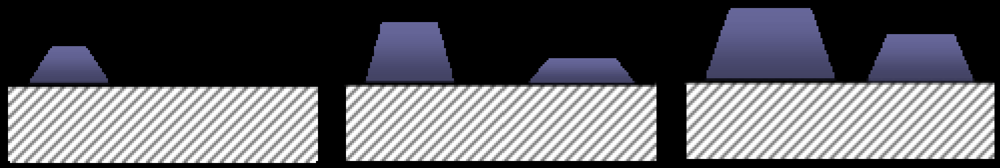
Shadowing — from the line of sight impingement of arriving atoms

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

Thin Film Growth Modes

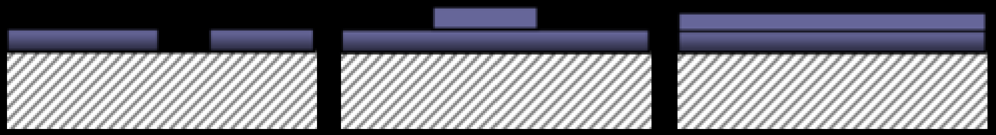
(i) 3-D or island growth mode, also known as **Volmer–Weber (VW) mode**

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.

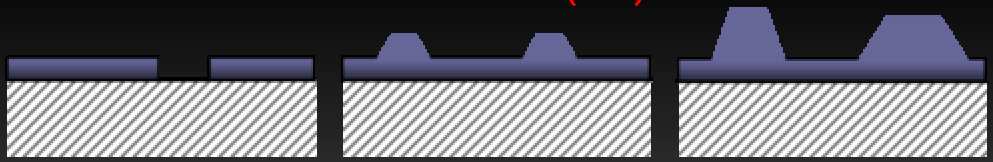


(ii) 2-D or layer-by-layer growth, also known as **Frank–van der Merwe (FVDM)** mode

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.

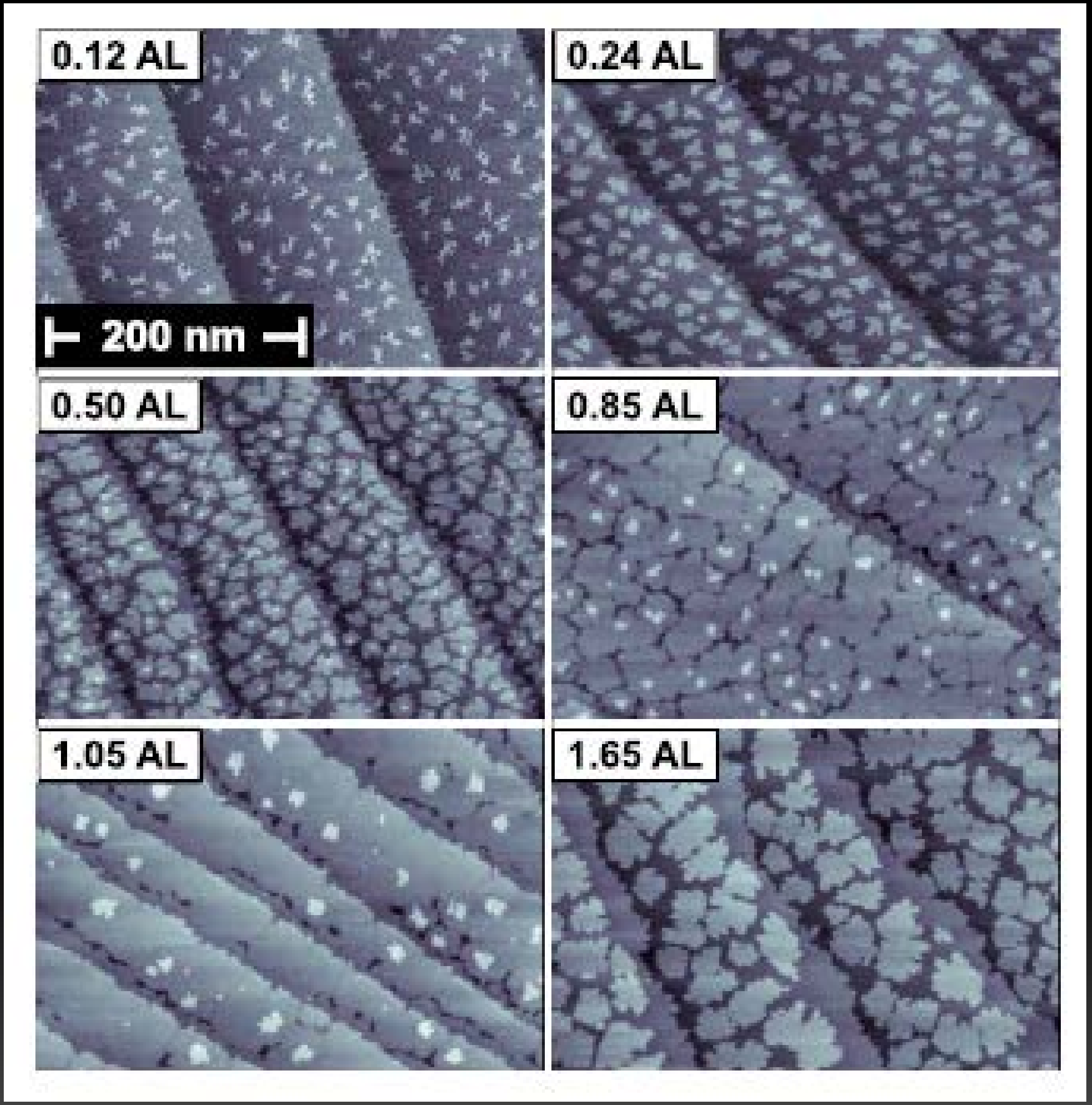


The film nucleation depends first and foremost on the nature of the material deposited (metal…)

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.

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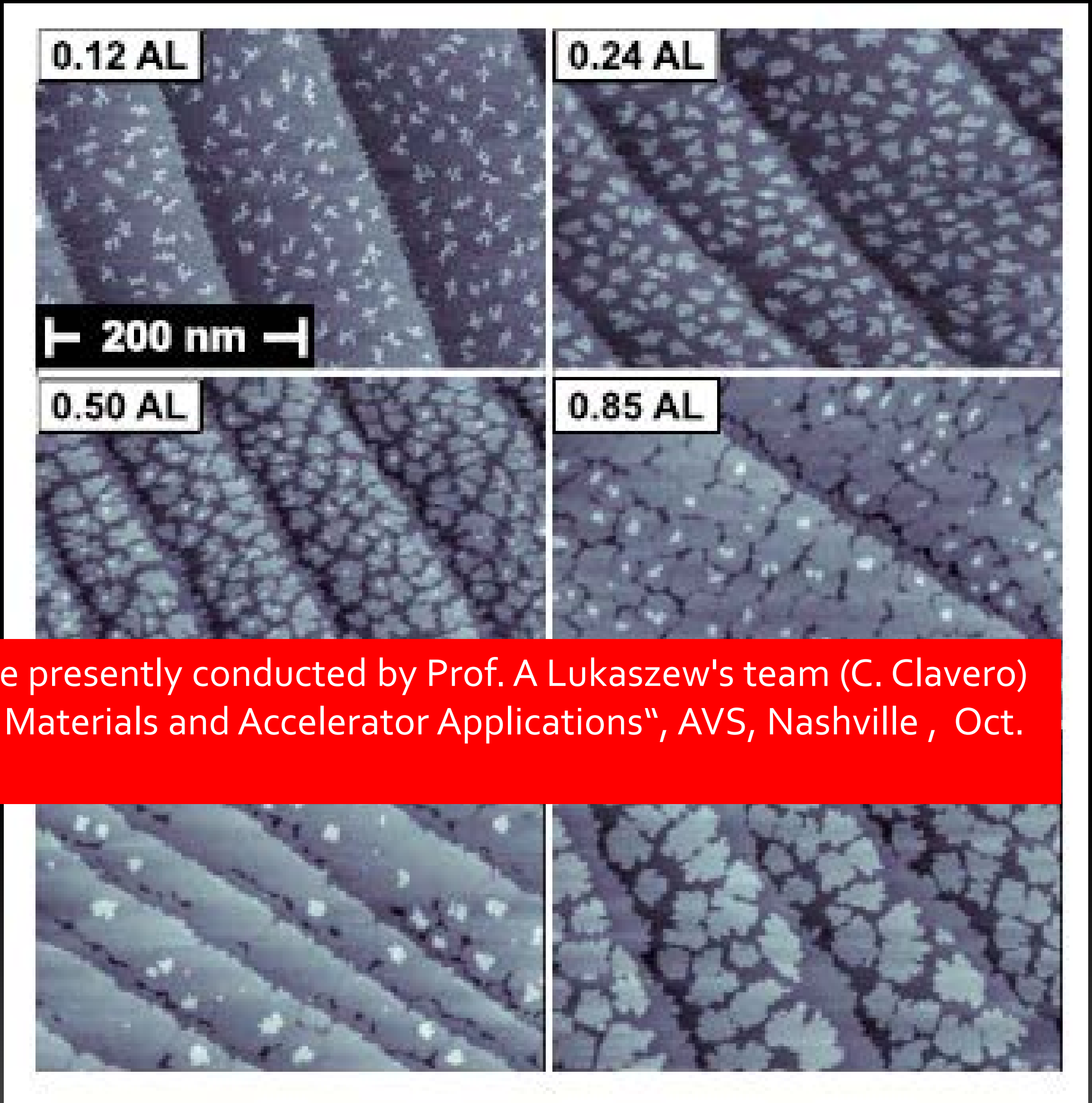

Similar studies for Nb growth on Cu are presently conducted by Prof. A Lukaszew's team (C. Clavero) "Surface Science for Future Electronic Materials and Accelerator Applications", AVS, Nashville , Oct. 30 -Nov 4, 2011

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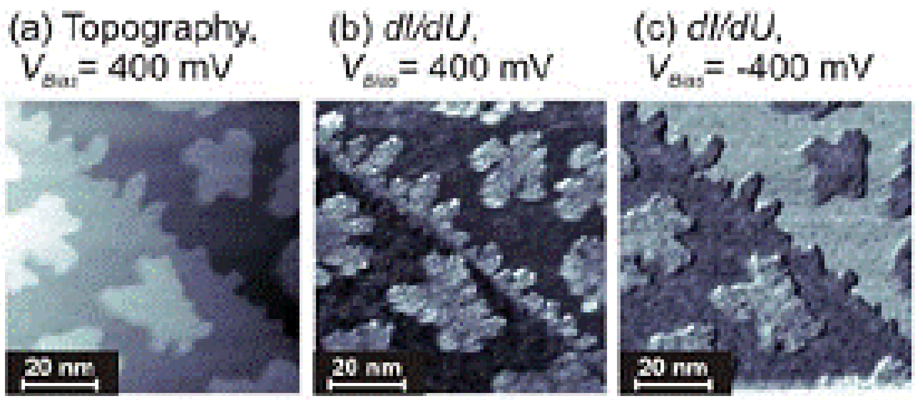
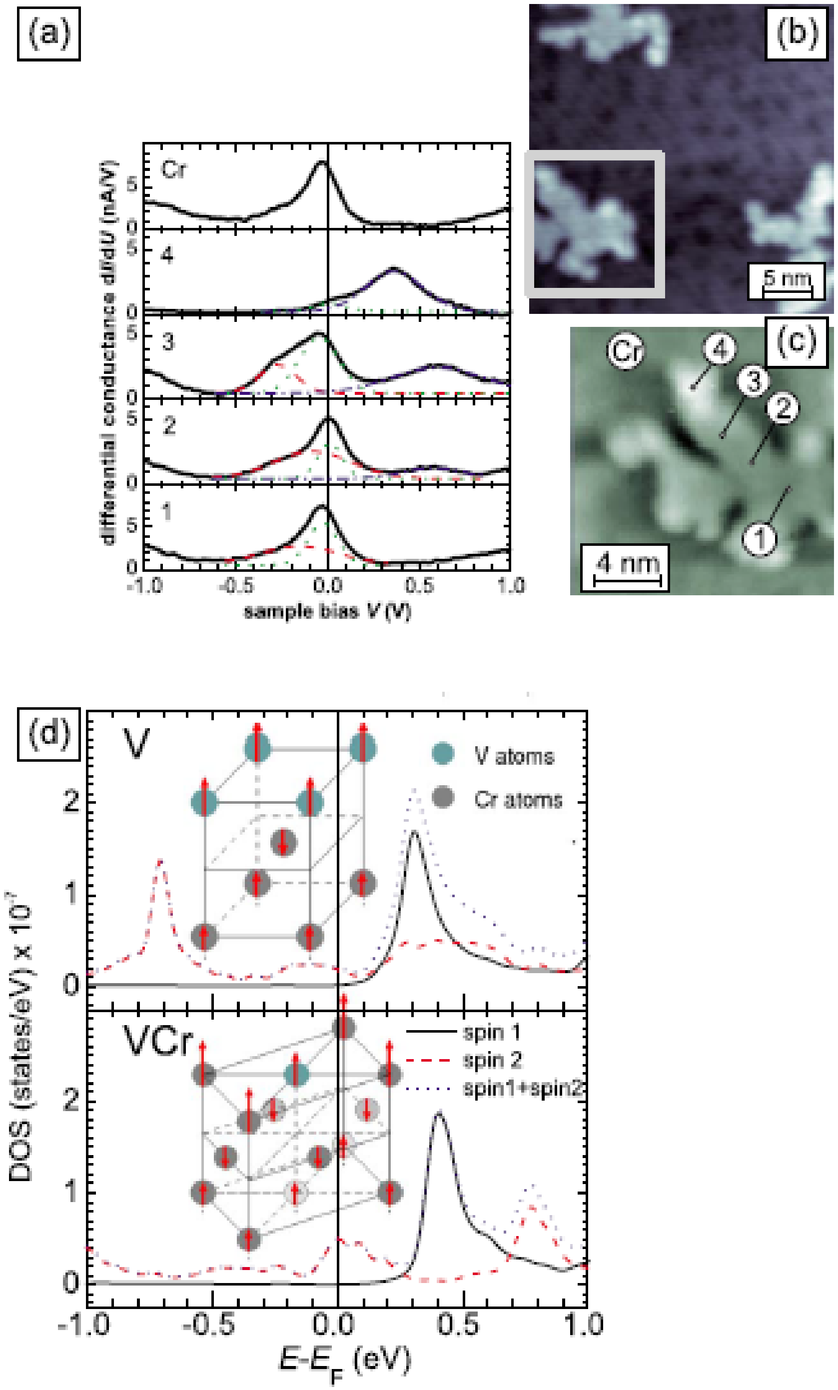
Once template has been formed, homo-epitaxy.

STM/STS studies-Proximity effects



STM images of V sub-monolayer on Cr. (a) Topography, (b) chemical contrast dI/dU map and (c) spin resolved dI/dU map corresponding to 0.24 AL V coverage.

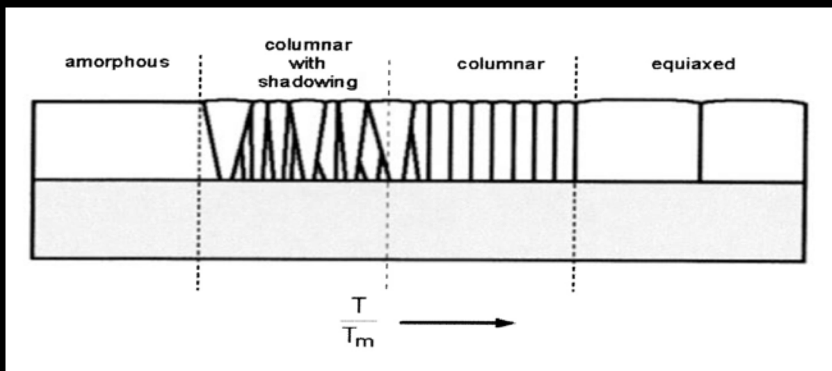
C. Clavero, M. Bode, G. Bihlmayer, S. Bluegel and R. A. Lukaszew, "Island assisted interface alloying and magnetic polarization at submonolayer V/Cr interfaces". Phys. Rev. B 82, 085445 (2010).



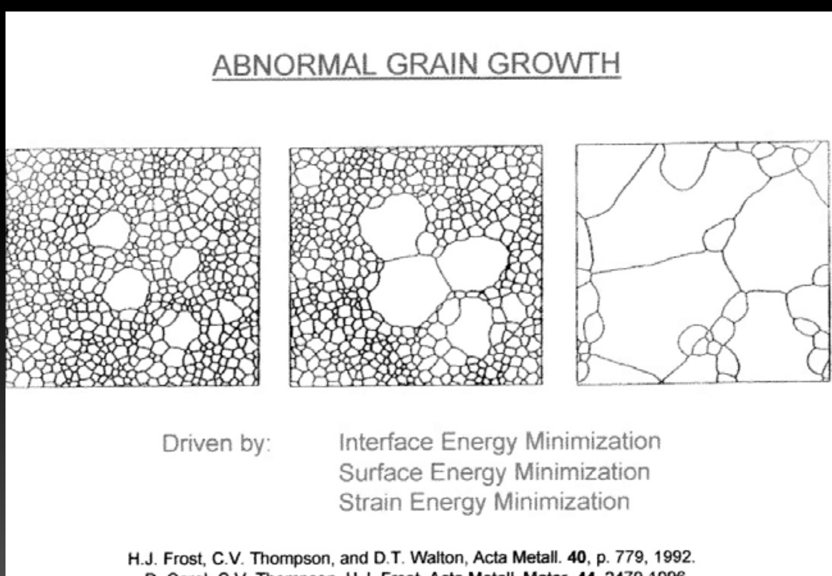
(a) Differential conductance curves measured on the substrate at different positions on one of the islands for 0.09 AL coverage.
(b, c) are topographic images.
(d) DOS simulations for a single V AL on Cr(001) and for a single AL of equi-atomic CrV alloy on Cr(001).
(PRB 82, 085445, 2010)

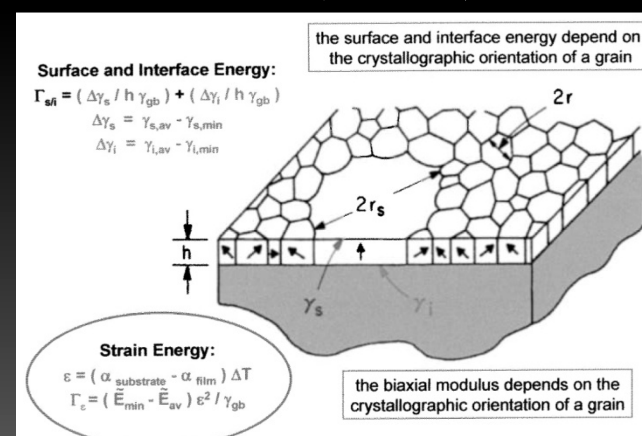
Subsequent Film Growth

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)

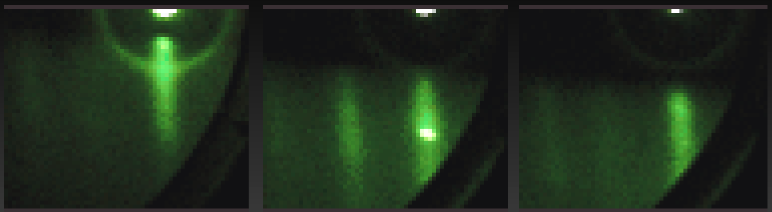




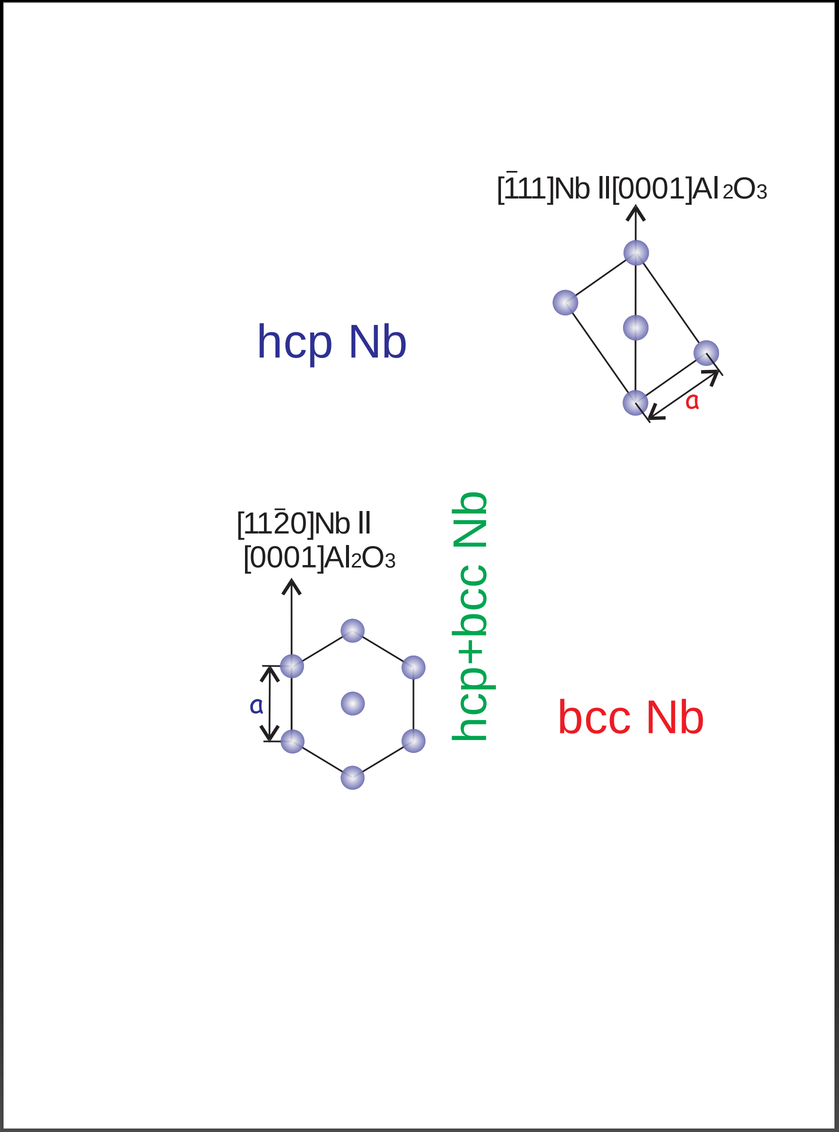
Early stages of Nb growth on Al_2O_3

Using Reflection high energy electron diffraction (RHEED), a **hexagonal Nb surface structure** was observed for the first 3 atomic layers followed by a strained *bcc* Nb(110) structure and the lattice parameter relaxes after 3 nm.

RHEED images for the hexagonal phase at the third atomic layer. Patterns repeat every 60 .



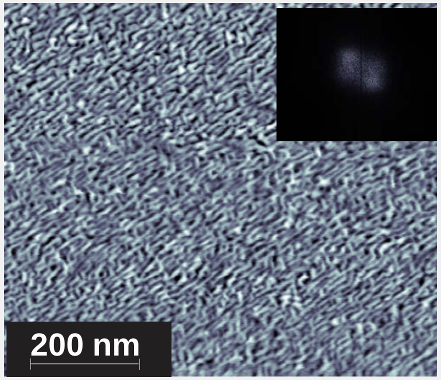
0 deg 30 deg 60 deg

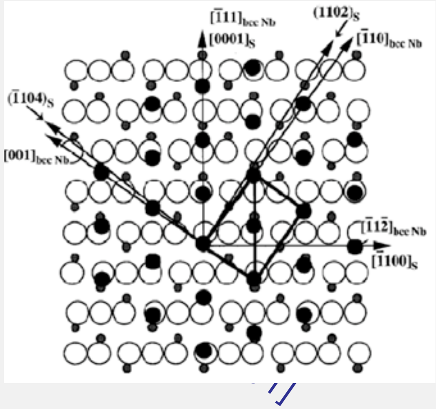


A. Lukaszew et al. , College of William & Mary

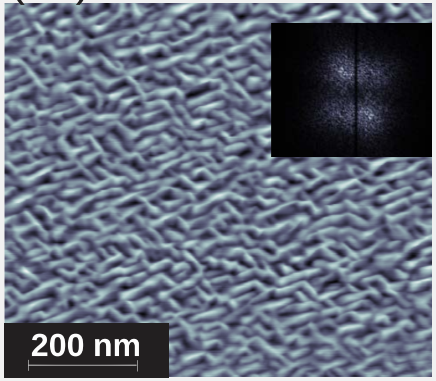
Subsequent Nb growth on a-plane sapphire : biaxial anisotropy in the surface features.

(a) 30 nm Nb

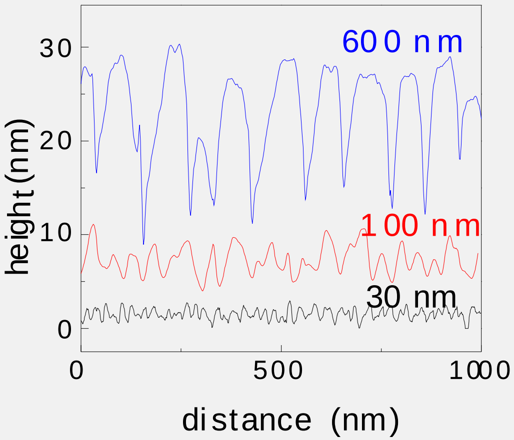




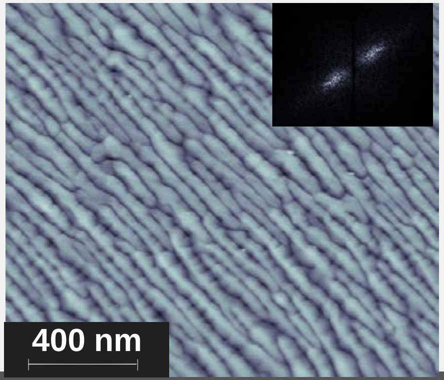
(b) 100 nm Nb

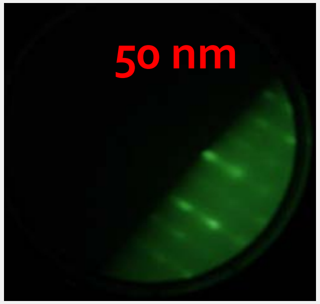


(d)

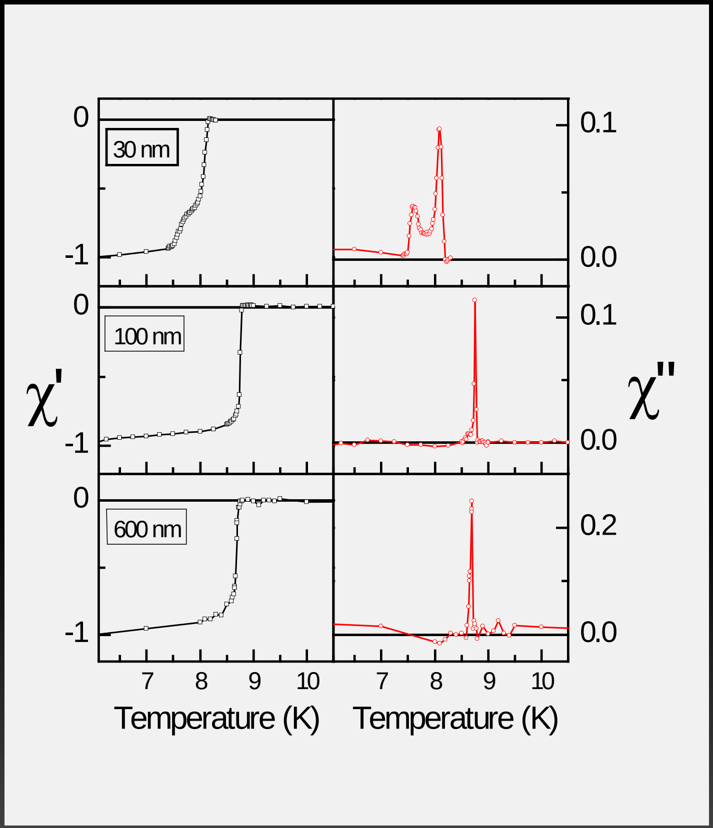


(c) 600 nm Nb



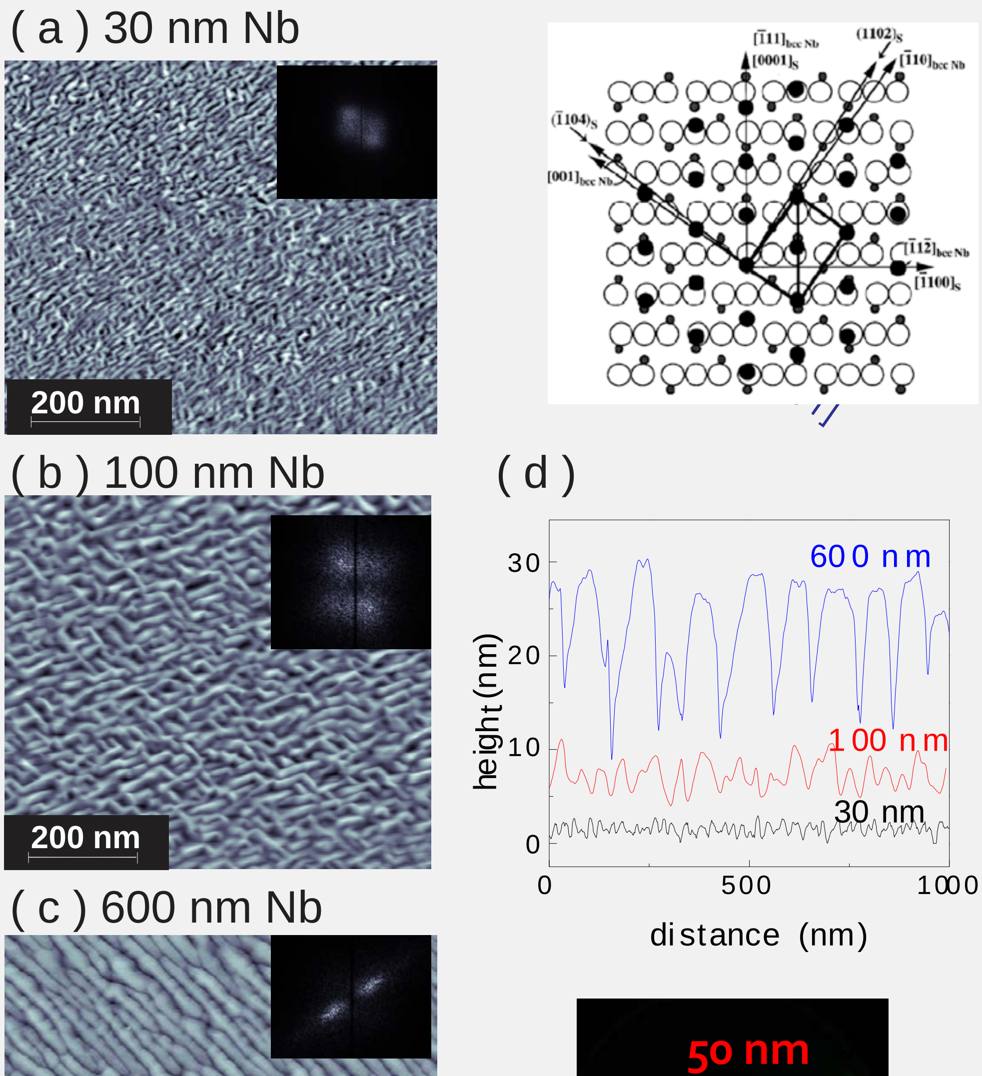


Susceptibility AC measurements



$$\chi(\omega)=\chi'(\omega)+i\,\chi''(\omega)$$

A. Lukaszew et al. , College of William & Mary



Subsequent Nb growth on a-plane sapphire : biaxial anisotropy in the surface features.

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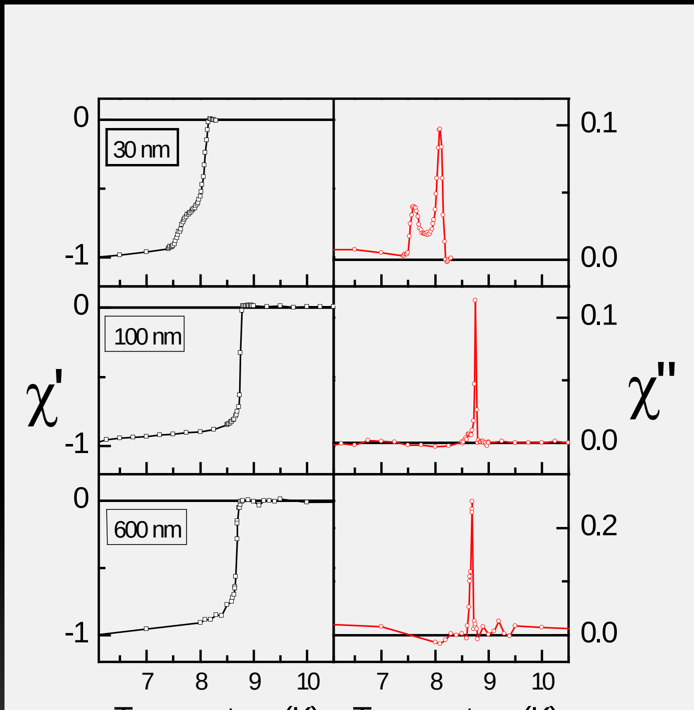


THPO047: Growth Mode and Strain Effects in the Superconducting Properties of Nb Thin Films on Sapphire

Cesar Clavero, Douglas Barry Beringer, Rosa A. Lukaszew, William Roach, Jonathan Skuza (The College of William and Mary, Williamsburg, VA), Charles E. Reece (JLAB, Newport News, VA)

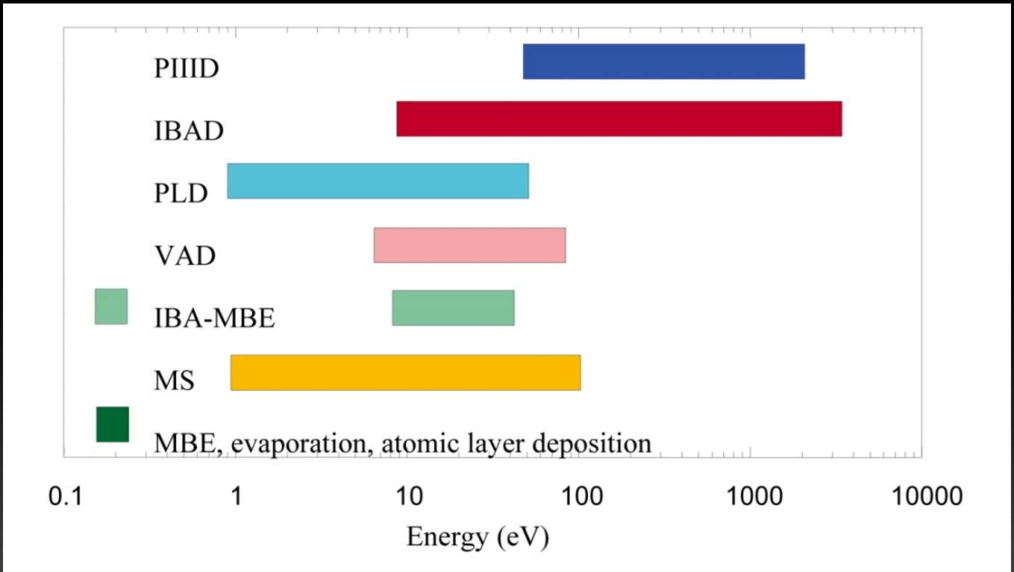
Deposition Techniques

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**.

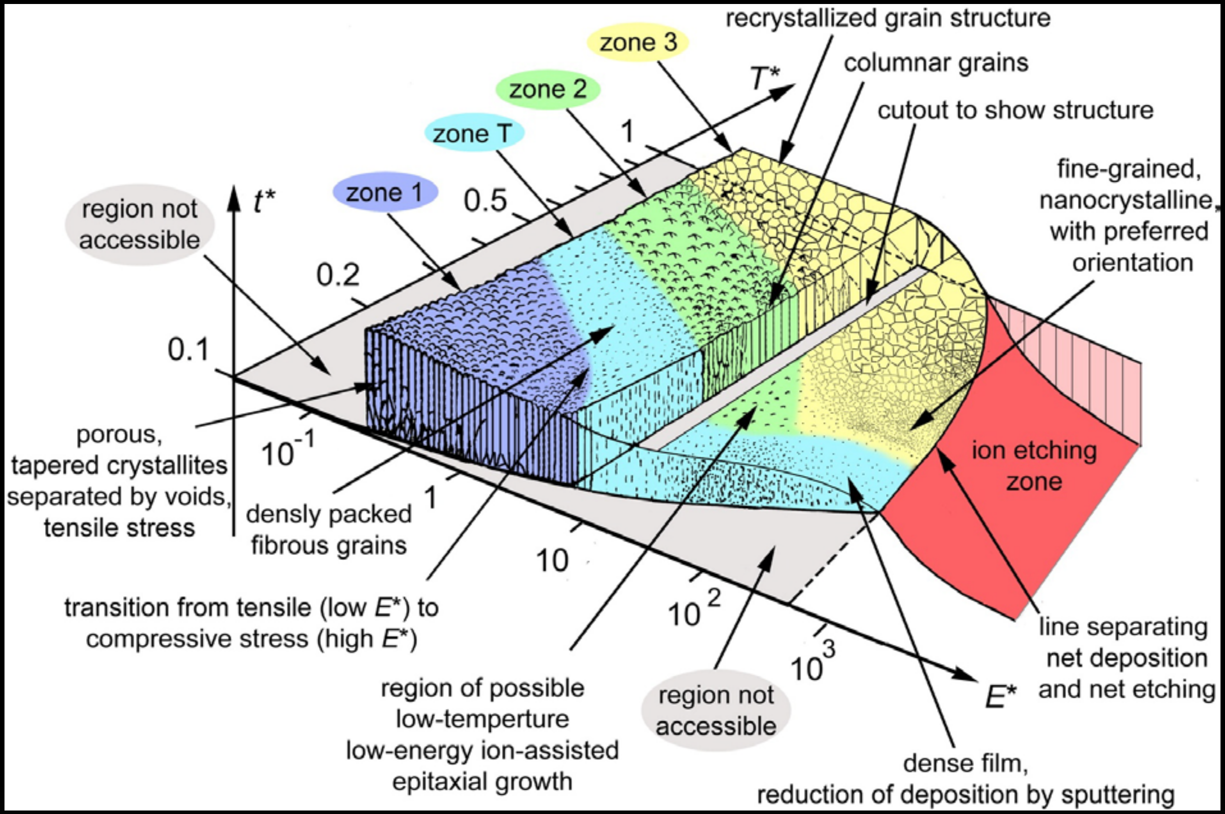
Without energetic atoms, only the substrate temperature influences the processes of physi- and chemisorption, thermal desorption, nucleation, nuclei dissociation, surface diffusion, and formation of specific nucleation sites.



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!

Deposition Techniques



Generalized Structure Zone Diagram

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

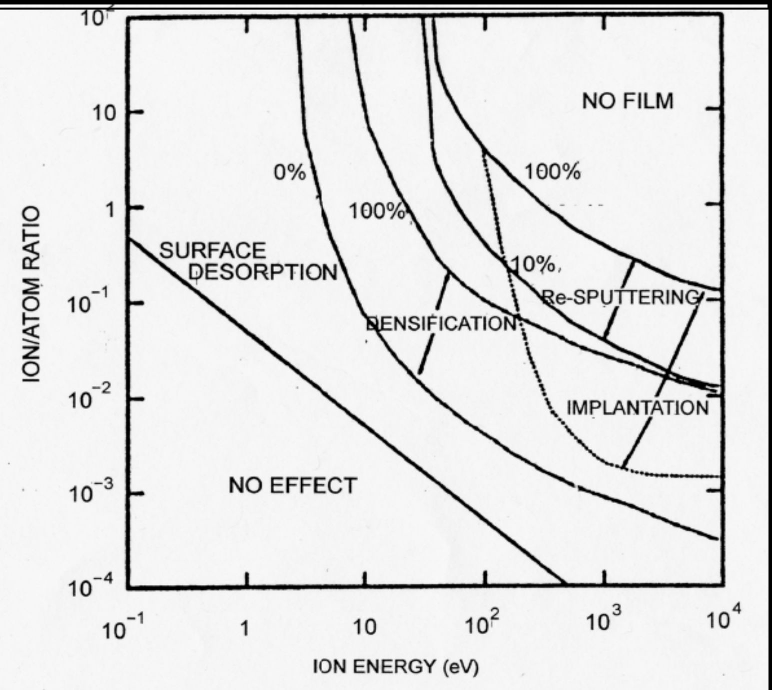
ENERGETIC CONDENSATION: HiPIMS, CED (Vacuum Arc Dep.), ECR...

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.**

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

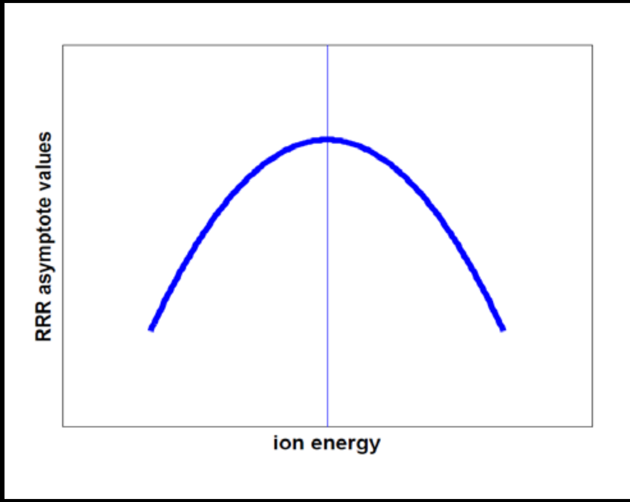
- **Promotion of surface diffusion of atoms**
- **Surface displacement** (epitaxial growth)
- **Bulk displacement** cascades :defects followed by re-nucleation
- Post-ballistic thermal spike → **atomic scale heating , annihilation of defects** followed by **re-nucleation** (transient liquid, **large 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.

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

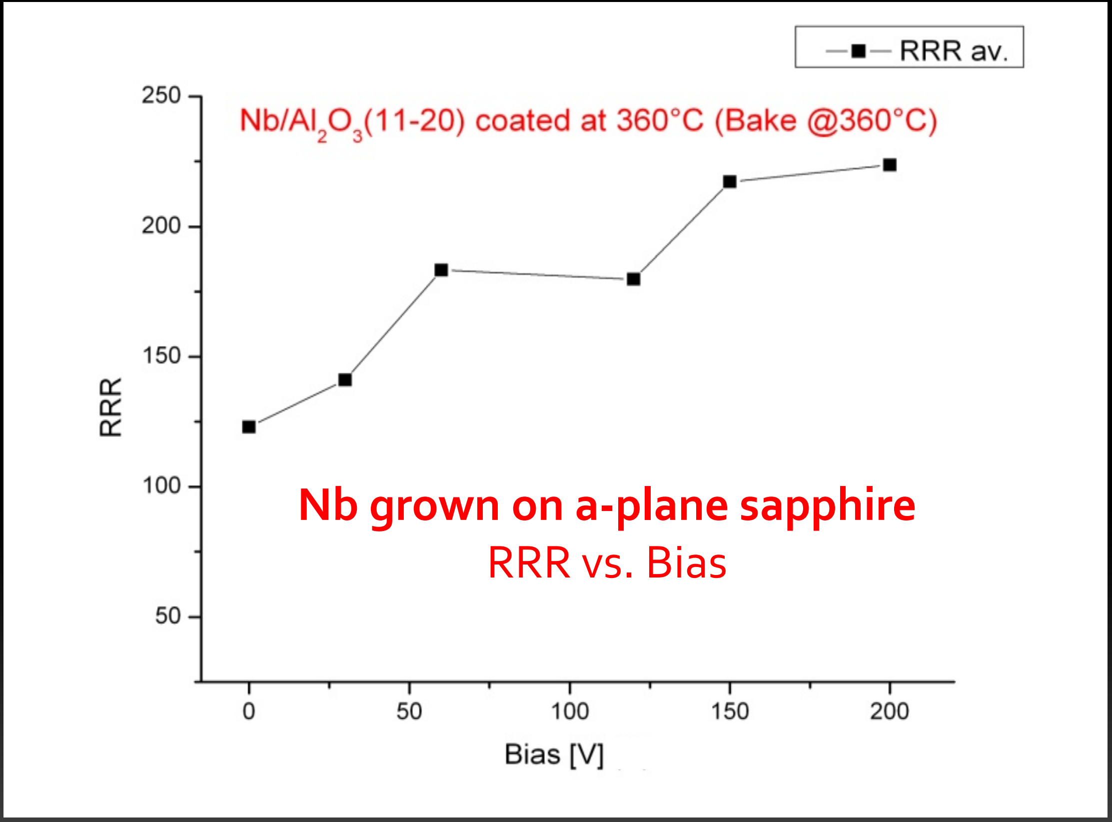


As a result of these fundamental changes, energetic condensation allows the possibility of controlling the following film properties:

- 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.

Effect of Ion energy, baking & coating temperatures

Nb grown on a-plane sapphire (ECR)



Nb grown on a-plane sapphire (Bias -120V) RRR vs. .Bake & Coating Temp.

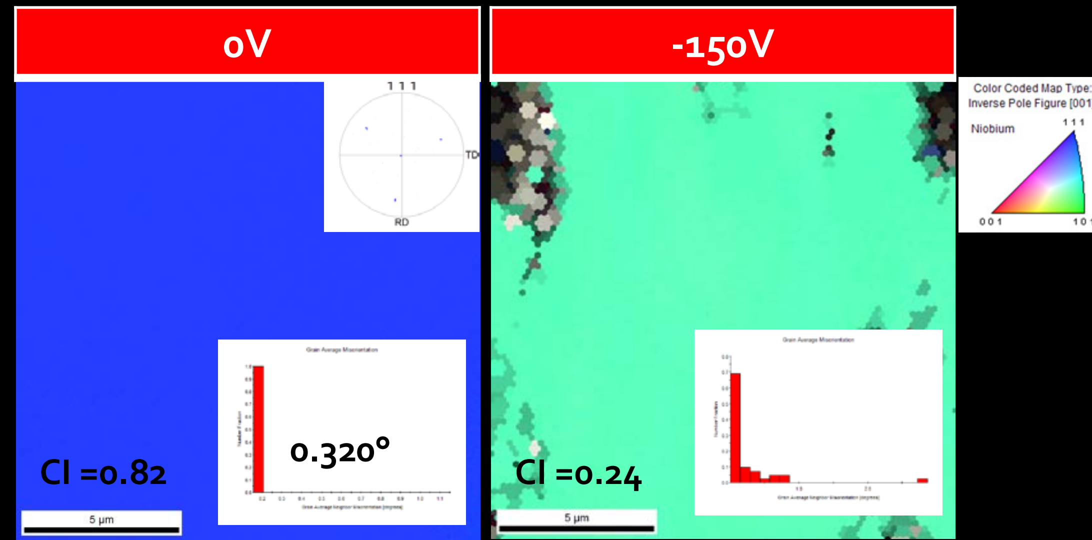
Bake Temp.	Coating Temp.	Bias [V]	Al_2O_3 (11-20)
360°C	360°C	-120	**179.8**
360°C	500°C	-120	189
700°C	360°C	-120	**348**
500°C	360°C	-120	348
500°C	500°C	-120	**488**

Nb (110) on (11-20) Al_2O_3

30' coating, pressure during coating ~2.5e-8Torr

Film Nucleation

Influence on ion energy on ECR film on Al_2O_3 (0001):switch from [111] to [110] above -90V bias (>154eV)

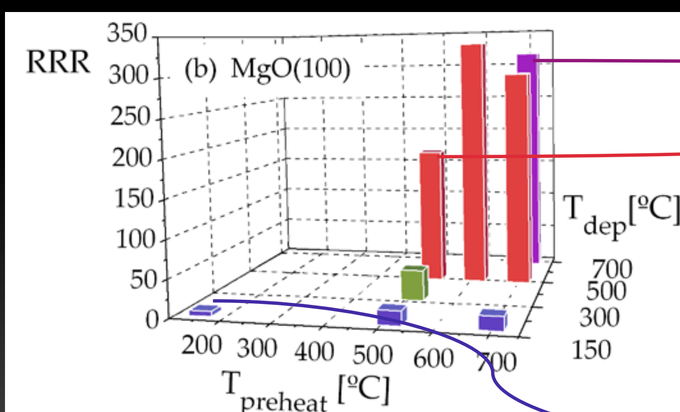


MBE Nb films on (0001) sapphire grow along (111) at 900°C, but (110) at 1100°C.

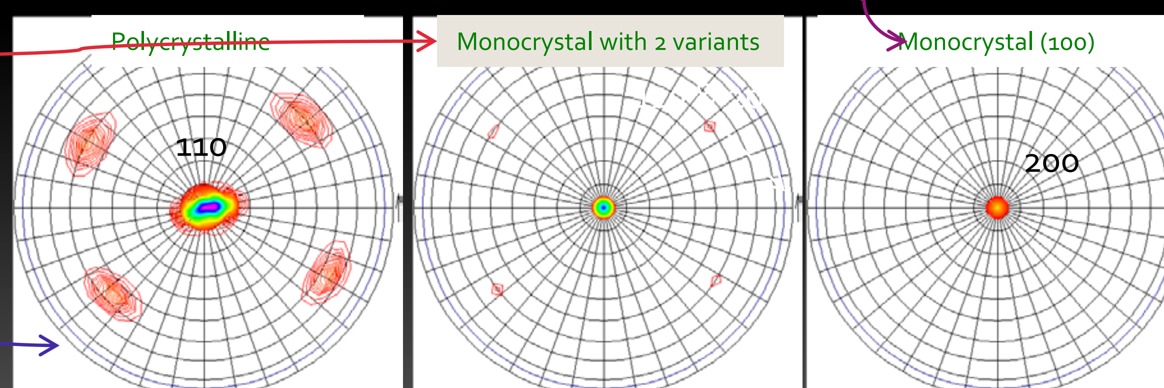
5000x, 15 µm x 15µm, 0.1 µm step

T. Wagner et al., J. Mat. Res. Vol. 11, n°5, pp. 1255-1264 (1996), Mat. Res. Symp. Proc, Vol. 440, pp.151-156, (1997)

Influence on temperature on CED films on MgO (100): switch from (110) to (200) @700°C



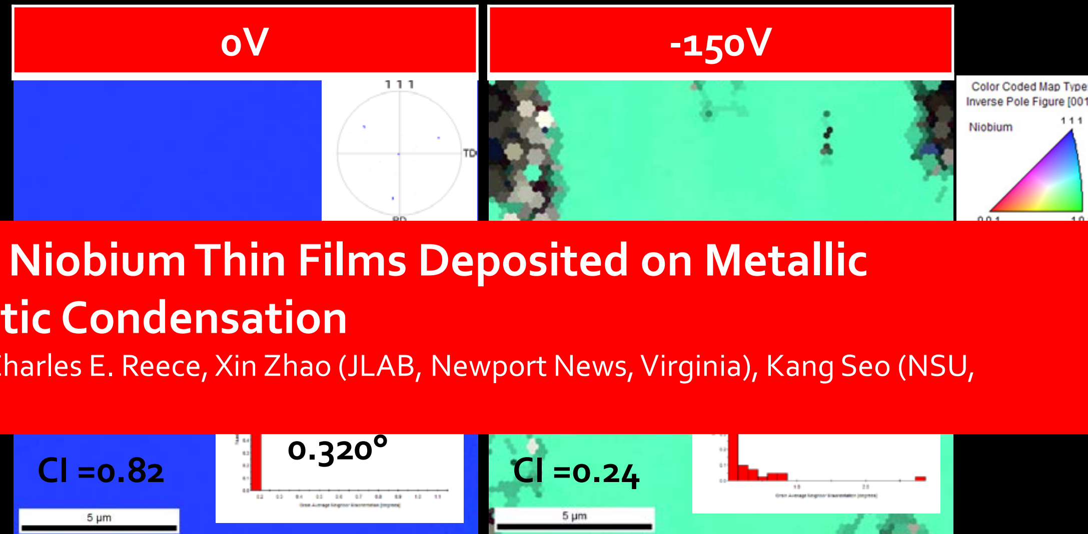
AASC



RRR=7, 150°C | RRR=181, 500°C | RRR=316, 700°C

Film Nucleation

Influence on ion energy on ECR film on



THPO064 Structural Properties of Niobium Thin Films Deposited on Metallic Substrates by ECR Plasma Energetic Condensation

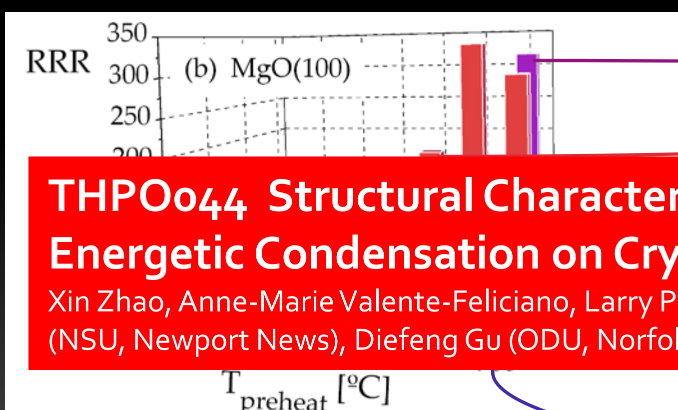
AASC, Anne-Marie Valente-Feliciano, Larry Phillips, Charles E. Reece, Xin Zhao (JLAB, Newport News, Virginia), Kang Seo (NSU, Newport News), Diefeng Gu (ODU, Norfolk, Virginia)

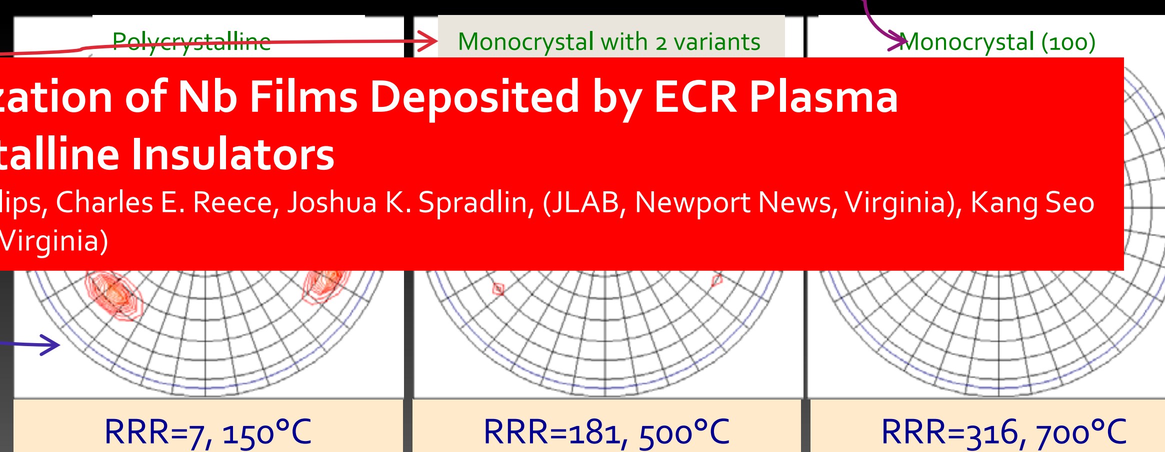
MBE Nb films on (0001) sapphire grow along (111) at 900°C, but (110) at 1100°C.

5000x, 15 µm x 15µm, 0.1 µm step

T. Wagner et al., J. Mat. Res. Vol. 11, n°5, pp. 1255-1264 (1996), Mat. Res. Symp. Proc, Vol. 440, pp.151-156, (1997)

Influence on temperature on CED films on MgO (100): switch from (110) to (200) @700°C



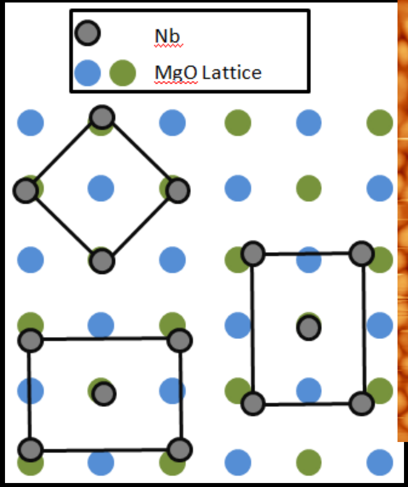


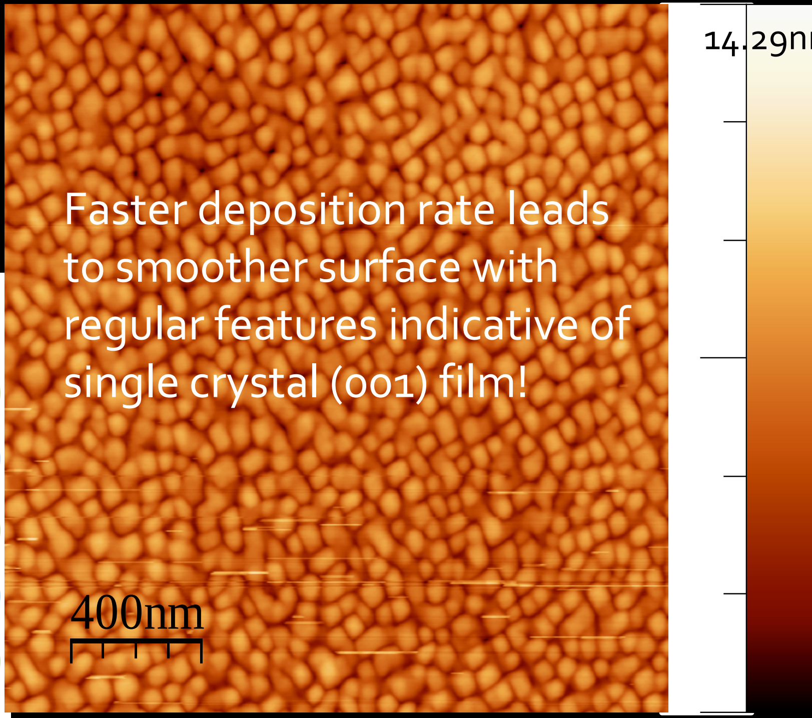
THPO044 Structural Characterization of Nb Films Deposited by ECR Plasma Energetic Condensation on Crystalline Insulators

Xin Zhao, Anne-Marie Valente-Feliciano, Larry Phillips, Charles E. Reece, Joshua K. Spradlin, (JLAB, Newport News, Virginia), Kang Seo (NSU, Newport News), Diefeng Gu (ODU, Norfolk, Virginia)

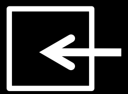
AASC

Nb on MgO(001)

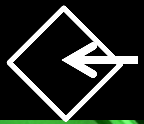




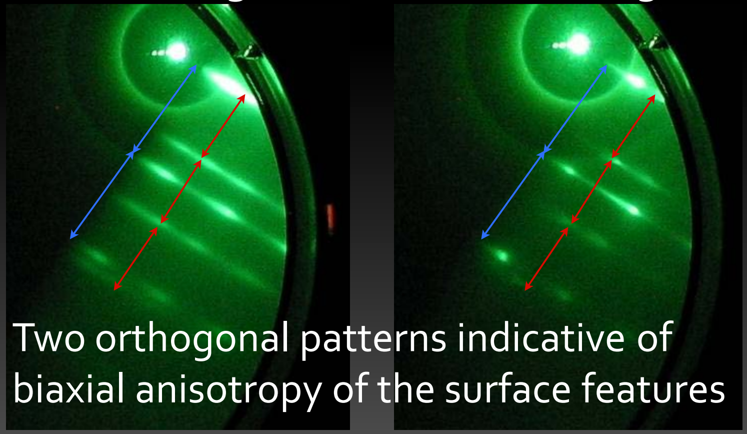
RRR = 46.5
RMS = 6.51 nm

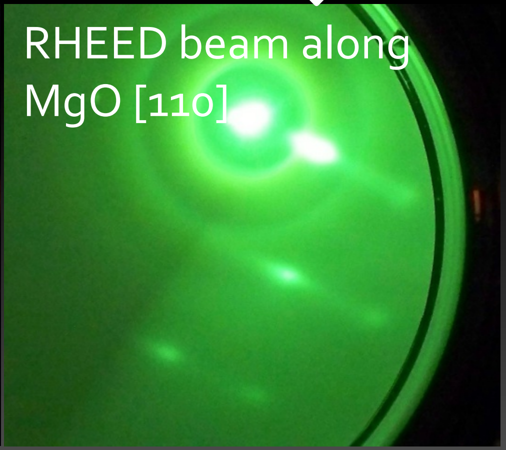


RRR = 165
RMS = 4.06 nm



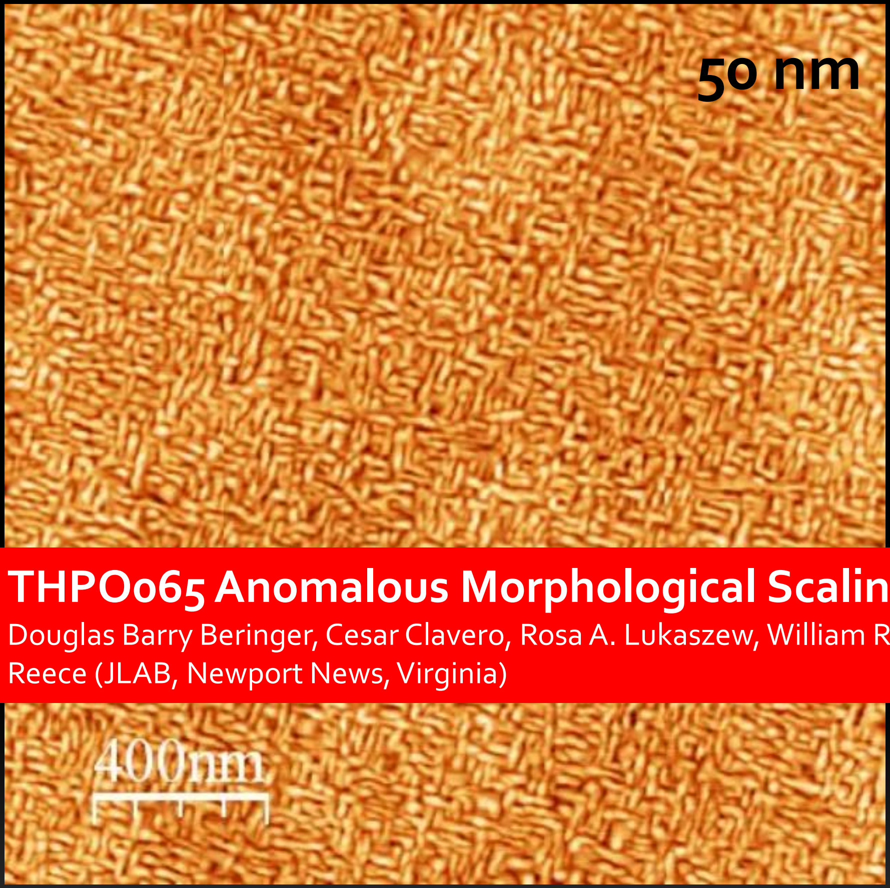
RHEED images for Nb(110) on MgO

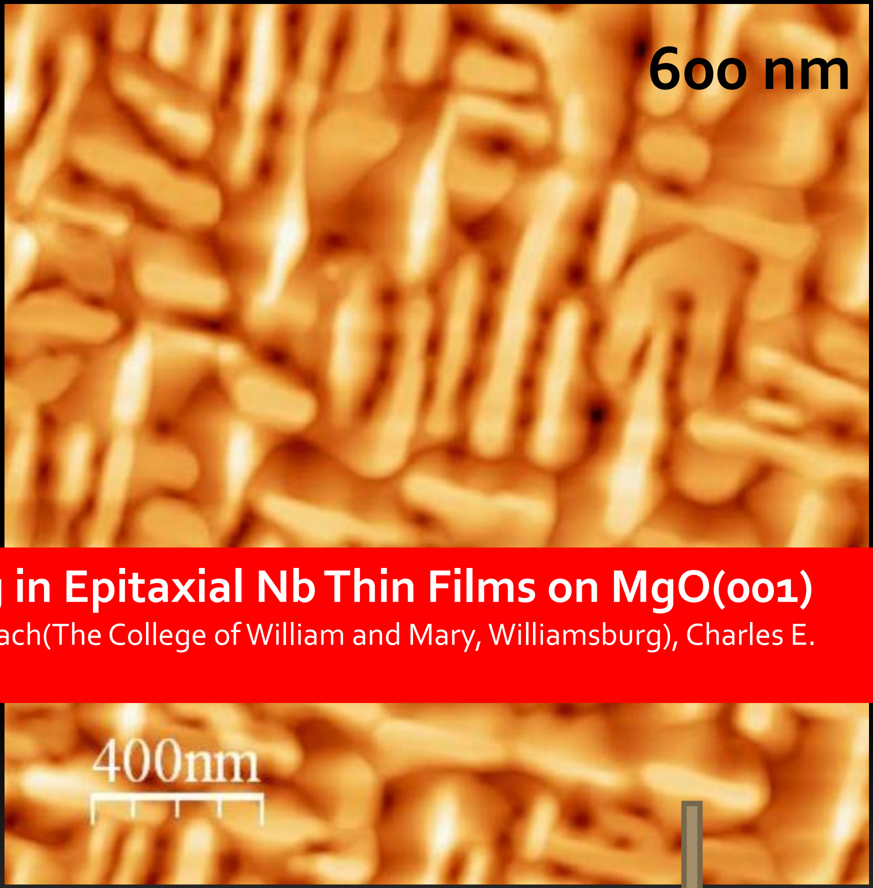




Same substrate but different growth rate lead to very different growth

Scaling of surface features





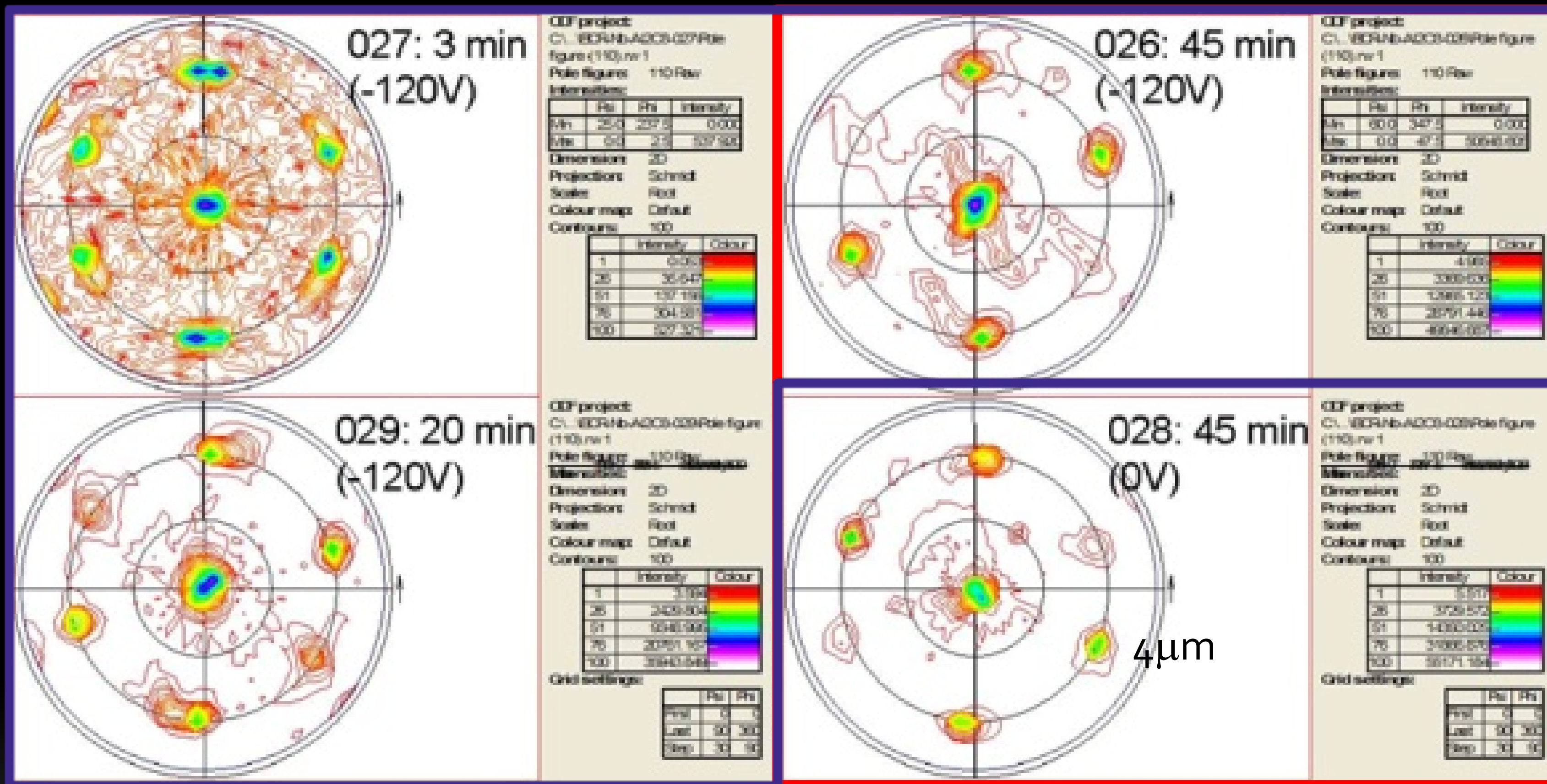
THPO065 Anomalous Morphological Scaling in Epitaxial Nb Thin Films on MgO(001)

Douglas Barry Beringer, Cesar Clavero, Rosa A. Lukaszew, William Roach(The College of William and Mary, Williamsburg), Charles E. Reece (JLAB, Newport News, Virginia)

Same scale in both images!
The surface features coarsen in the thicker film, but retain their overall symmetry

RRR = 46.5
RMS = 6.51 nm

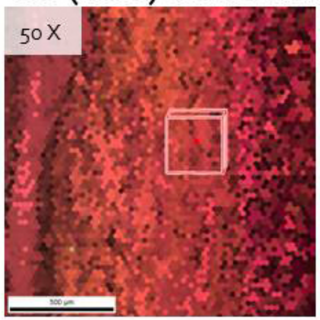
Evolution of Crystal Growth for Nb/Al_2O_3

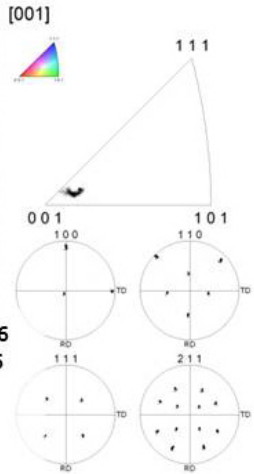


XRD pole figures show the presence of growth domains (rotation the poles of 70°)
As the film grows one growth variant prevails.

Nb on Cu single crystals

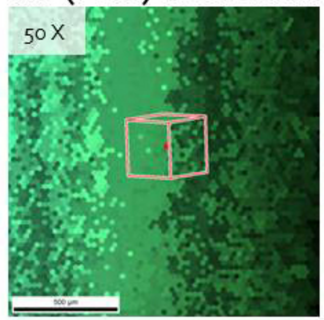
Cu (100) Substrate

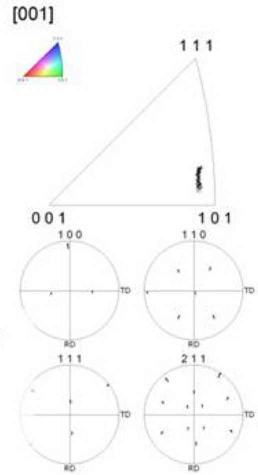




Average Confidence Index: 0.56
Average Image Quality: 646.66
Average Fit [degrees]: 1.19
Scan Area: 150 mm X 150 mm
Step Size: 10 µm

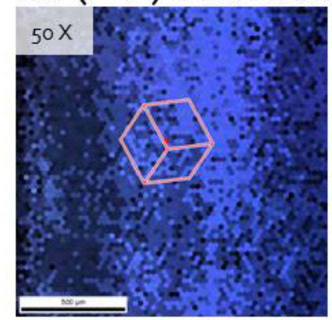
Cu (110) Substrate

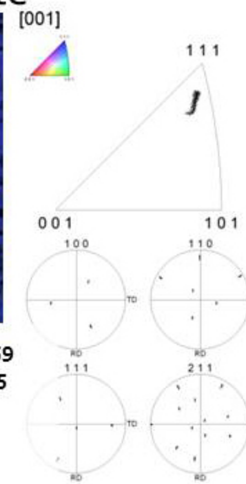




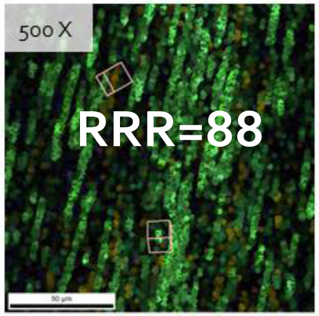
Average Confidence Index: 0.50
Average Image Quality: 730.73
Average Fit [degrees]: 1.26
Scan Area: 150 mm X 150 mm
Step Size: 10 µm

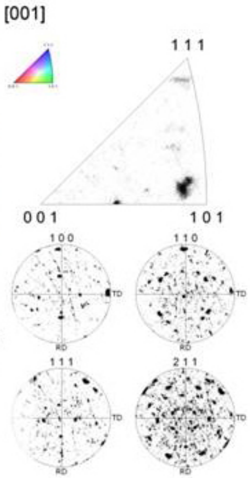
Cu (111) Substrate





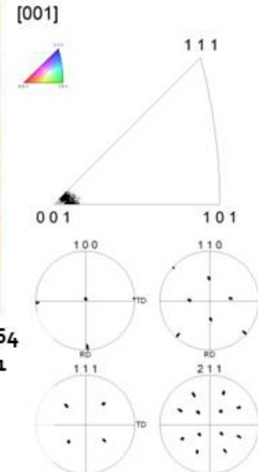
Average Confidence Index: 0.59
Average Image Quality: 608.85
Average Fit [degrees]: 1.09
Scan Area: 150 mm X 150 mm
Step Size: 10 µm





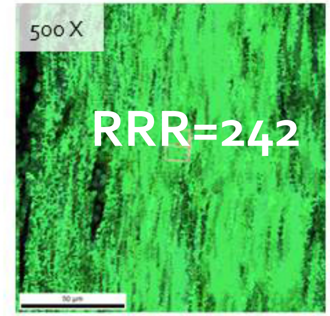
Average Confidence Index: 0.56
Average Image Quality: 646.66
Average Fit [degrees]: 1.19
Scan Area: 150 mm X 150 mm
Step Size: 10 µm

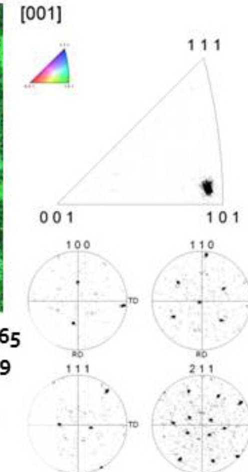
Nb (100)/ Cu (110)



Average Confidence Index: 0.64
Average Image Quality: 632.31
Average Fit [degrees]: 1.24
Scan Area: 150 mm X 150 mm
Step Size: 10 µm

Nb (110) / Cu (111)



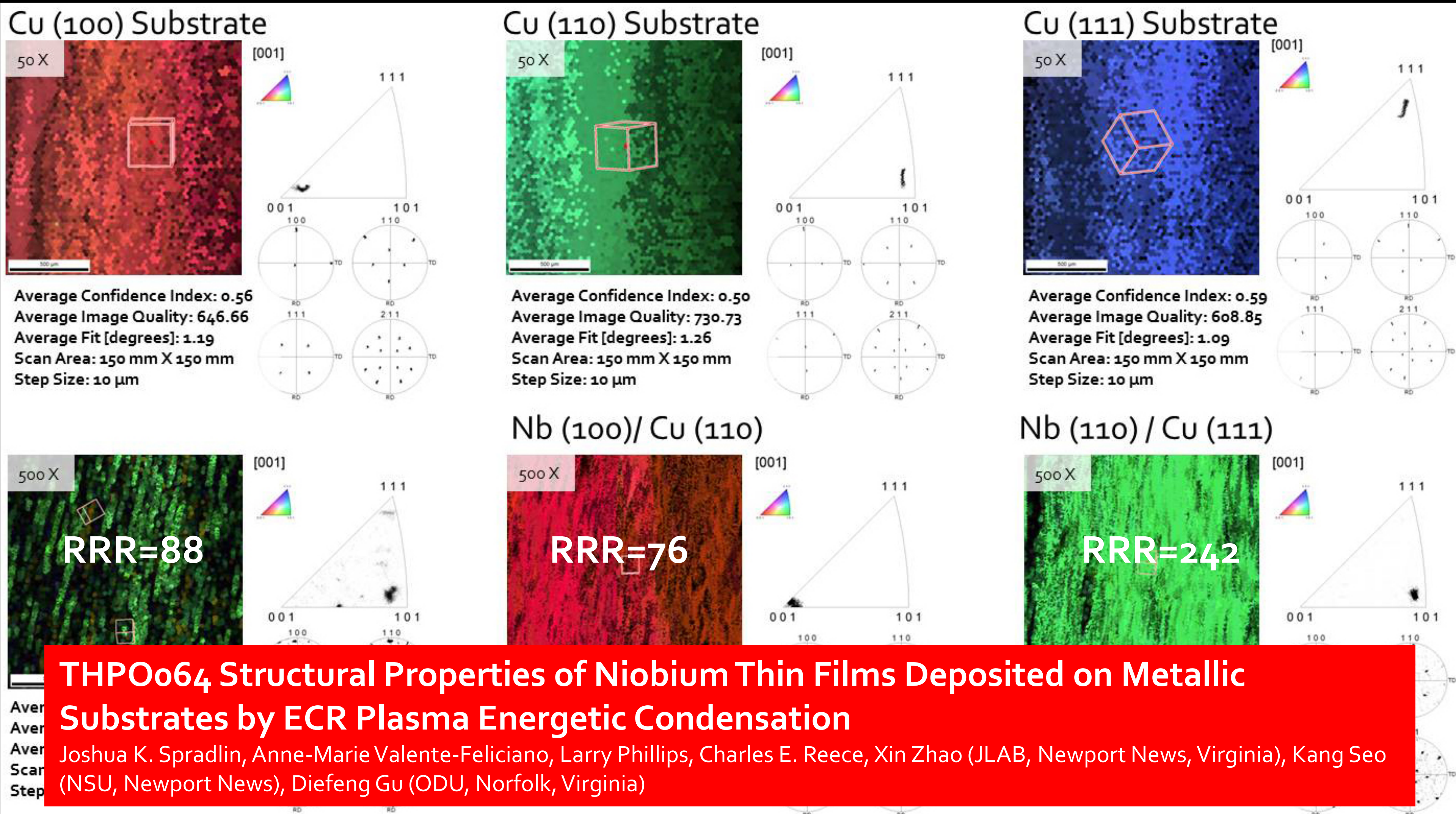


Average Confidence Index: 0.65
Average Image Quality: 397.29
Average Fit [degrees]: 1.03
Scan Area: 150 mm X 150 mm
Step Size: 10 µm

In the same run,

Nb/fine grain Cu	**RRR=82**
Nb/large grain Cu	**RRR=169**

Nb on Cu single crystals

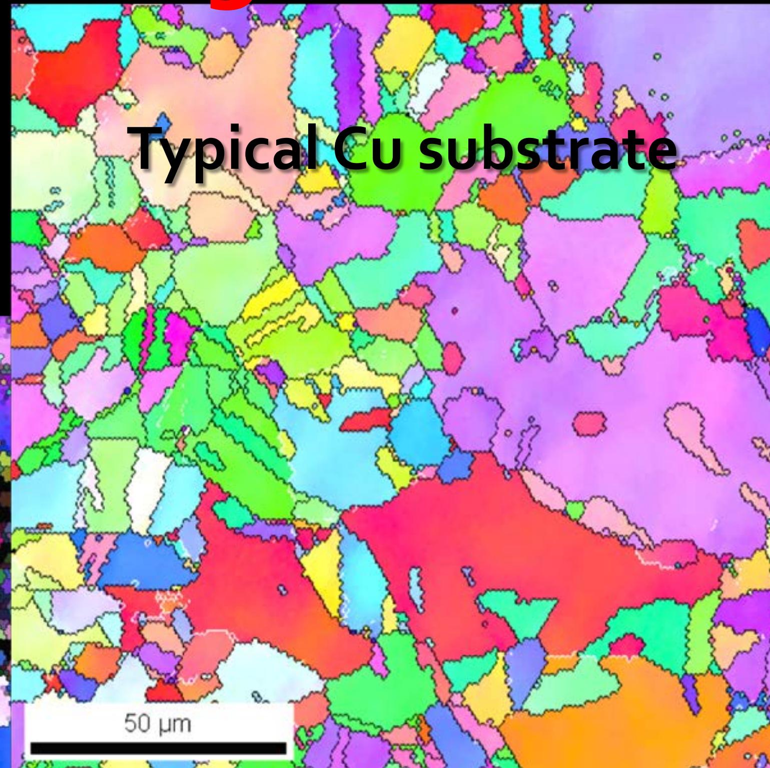


THPO064 Structural Properties of Niobium Thin Films Deposited on Metallic Substrates by ECR Plasma Energetic Condensation

Joshua K. Spradlin, Anne-Marie Valente-Feliciano, Larry Phillips, Charles E. Reece, Xin Zhao (JLAB, Newport News, Virginia), Kang Seo (NSU, Newport News), Diefeng Gu (ODU, Norfolk, Virginia)

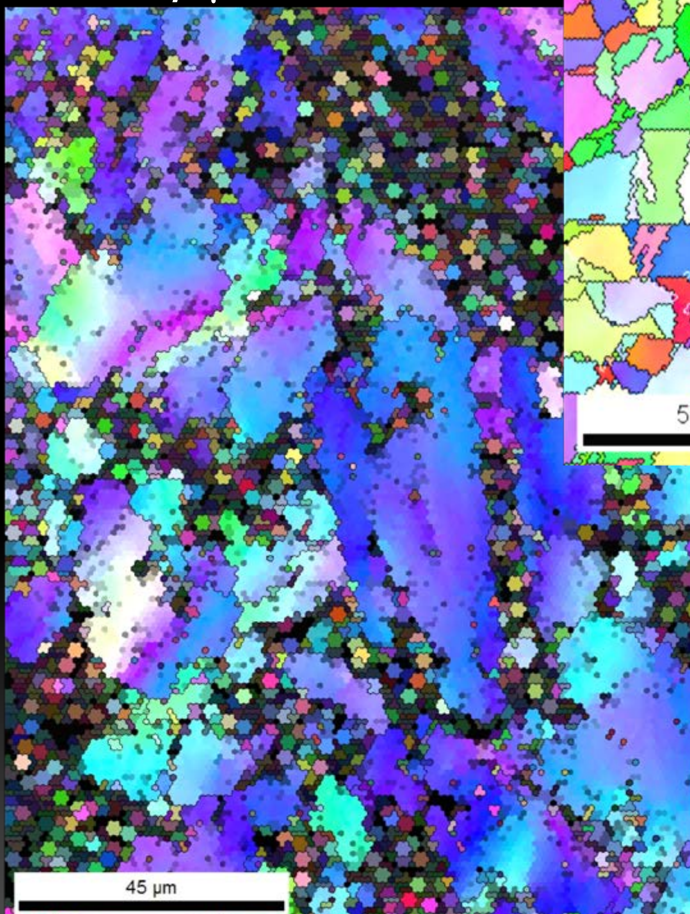
In the same run,	Nb/fine grain Cu	RRR=82
	Nb/large grain Cu	RRR=169

Effect of Bias Voltage for Nb on Cu



150 x 150 µm, 1 µm resolution, CI Avg. 0.71

Bias -120V, 2µm



Bias 0V , 4µm

Ab-normal growth
vith bias
vs.
columnar growth
without bias

120 x 150 µm, 1 µm resolution, CI Avg. 0.23

50 x 75 µm, 1 µm resolution, CI Avg. 0.16

CONCLUDING REMARKS

- Substrate preparation (cleanliness, annealing of defects…) is critical.
- The structure and morphology of the film are highly dependent on the substrate nature.

- Nucleation & Growth modes :

The Nb film structure can be tuned from columnar growth, ab-normal to equi-axial growth by varying the incident ion energy with the substrate temperature for temperatures lower than if using thermal process only.

Enable use of adequate substrates for cavities (Cu, Al…)

Growth of preferred orientation as function of energy, temperature and growth rate (and substrate):

Nb/ Al_2O_3 (0001) from (111) to (110)

Nb/MgO (100) from (110) to (100)

Towards Bulk-like Engineered Nb Films

3 sequential phases for film growth

- ✓ Film nucleation on the substrate (Nb, Al_2O_3, Cu; single crystal & polycrystalline)
- ✓ Growth of an appropriate template for subsequent deposition of the final RF surface
- ✓ Deposition of the final surface optimized for minimum defect density.

Some RRR values measured recently:

MgO (100)	585	CED
MgO(110)	424	ECR
MgO(111)	176	ECR
Al2O2 (11-20)	488	ECR
Al2O3(0001)	247	ECR
Cu fine grains	82	ARCO, ECR
Cu large grains	**289**	ECR
Cu(111)	242	ECR
Al2O3 ceramic	89	ECR
AlN ceramic	72	ECR
Fused silica	34	ECR
Borosilicate	30	CED

SRF Thin Films Collaboration

Jlab: C.Reece, A-M Valente-Feliciano, J. Spradlin, L. Phillips, X. Zhao, B. Xiao, A. Wu
W&M: A. Lukaszew, D. Beringer, W. Roach, C. Clavero , R. Outlaw, O. Trofimova
NSU: K. Seo
ODU: H. Baumgart, D. Gu
Black Labs LLC: R. Crooks
NCSU: F. Stevie, D. Batchelor
AASC:M. Krishnan, E. Valderrama

Under DOE HEP Grant ARRA & U.S. DOE Contract No. DE-AC05-06OR23177

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