Argonne NATIONAL LABORATORY

... for a brighter future

Nanofabricated Superconducting RF Composites: The surface composition and morphology matters!

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U.S. Department of Energy

UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

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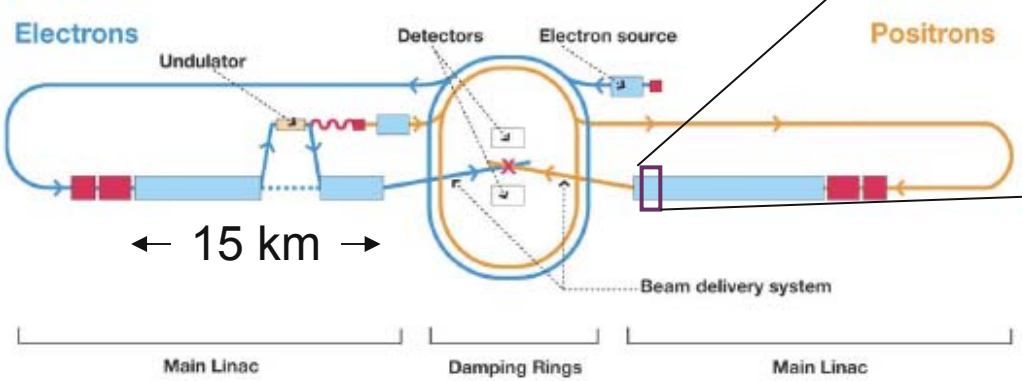
ANL-Accelerator LDRD

Superconducting Radio-Frequency (SRF)

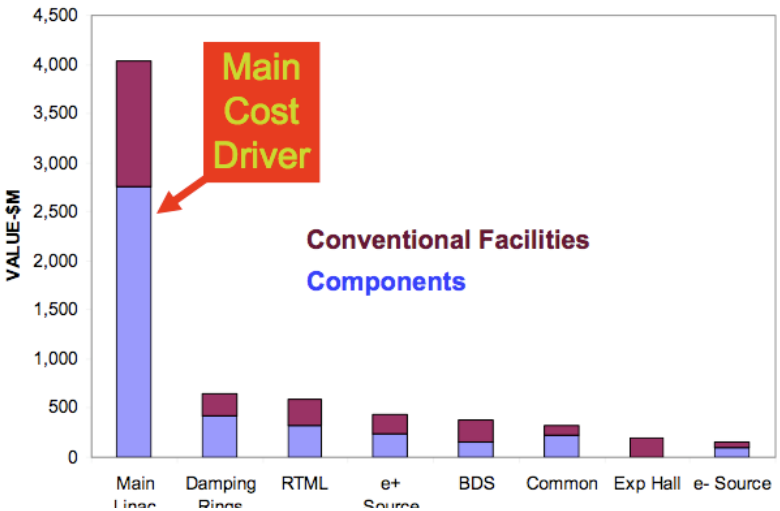
- Department of Energy – Office of Science
  - DOE-OS is in the particle accelerator business (ILC ($19B), AEBL($0.4 B), NSLS-2($0.5B) , SNS($1.8B), APS, APS-ERR, etc.)
  - Orbach to HEPAP 2/22/07 "DOE is committed to continuing a vigorous R&D program of accelerator technology SCRF is a core capability having broad applicability, both to the ILC and to other future accelerator-based facilities as well. Out FY2008 request for ILC R&D and SCRF technology confirms this commitment"



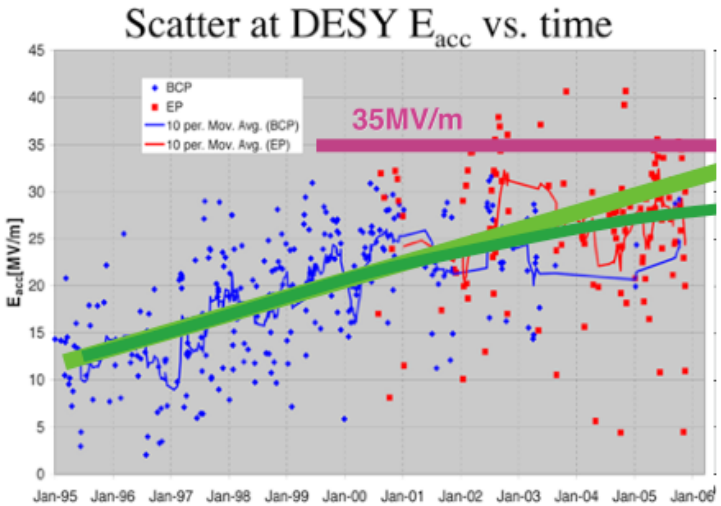
1 m

- 30 km of ultra pure Nb bellows
- 2 K
- very high electrical and magnetic fields

Current and future SCRF Projects have two difficulties



- Cost
  - Most of the cost is in the linacs



- Performance.
  Not just gradient

Single region
~100 cavities

Three regions
~120 cavities

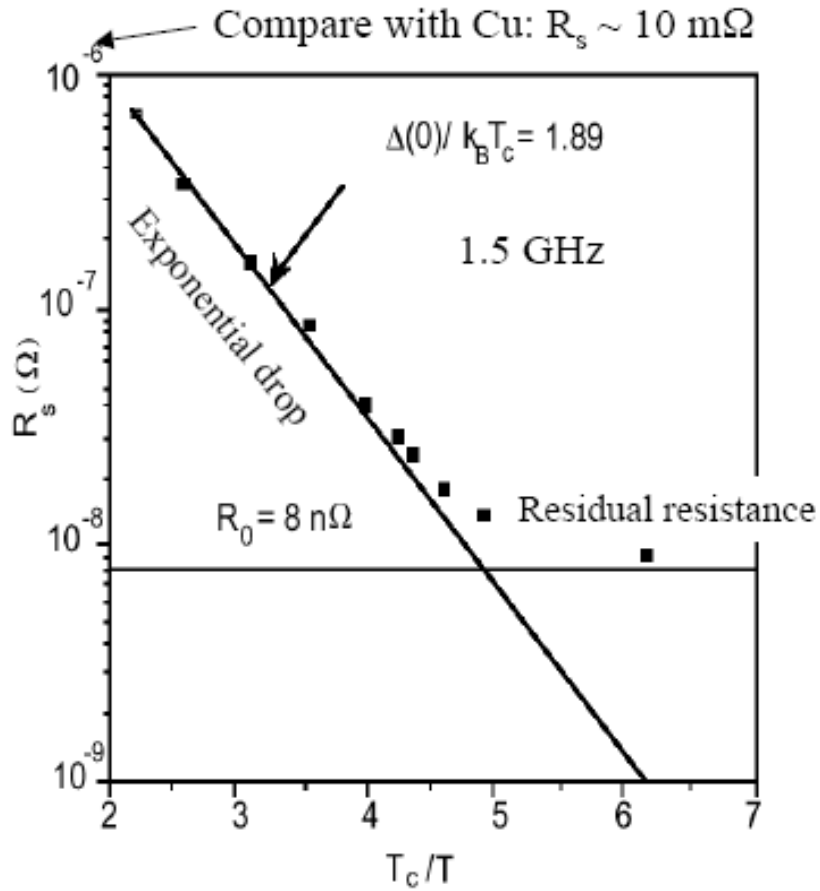
RF Resistance in Superconductors – Key Cost Driver

At RF frequencies, the resistance of a sc is finite because Cooper pairs have inertia -> unpaired electrons feel an electric field

$$R_s = A_s \omega^2 \exp\left(-\frac{\Delta(0)}{k_B T}\right)$$

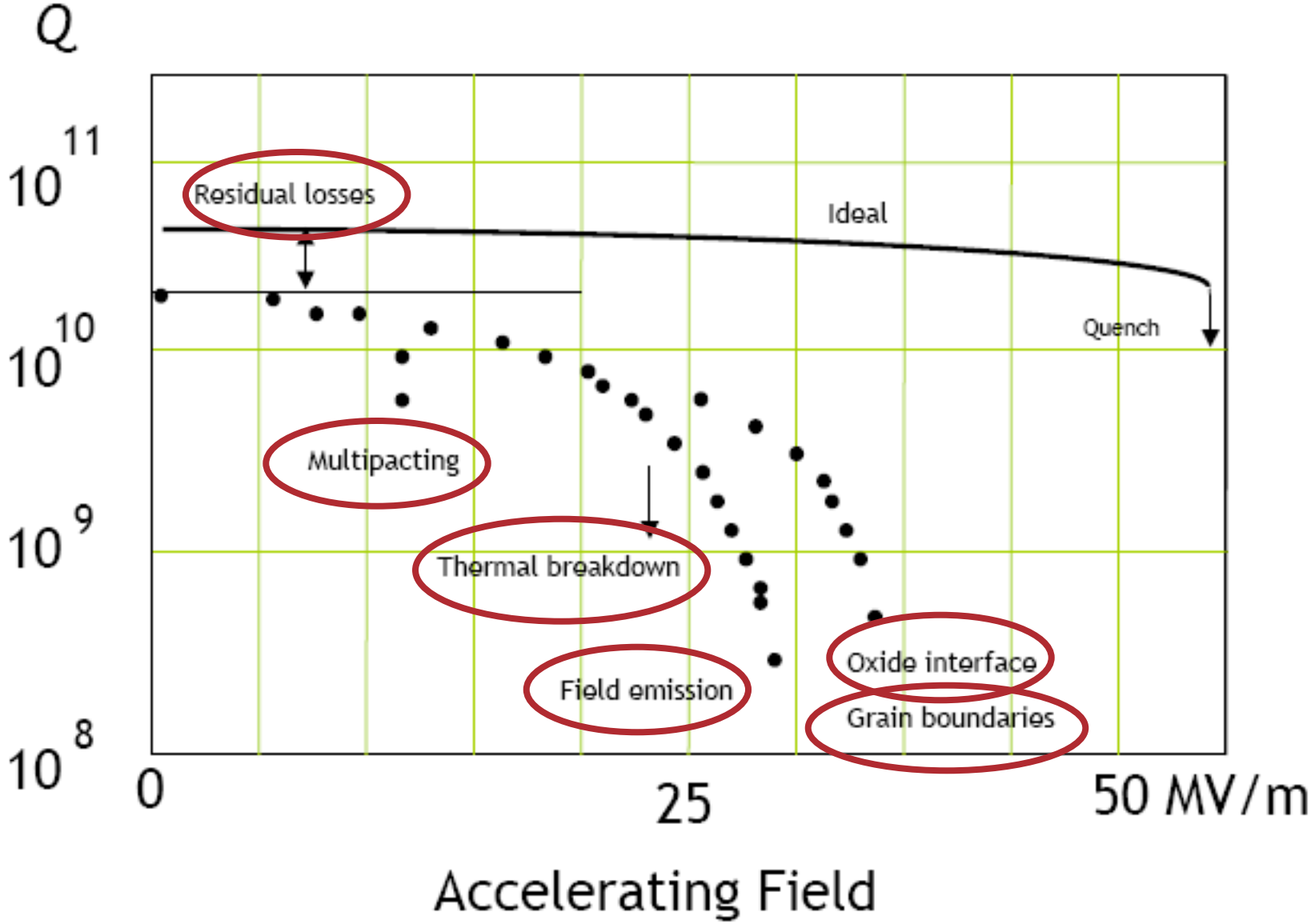
More resistance the more the sc pairs are jiggled around

More resistance the more unpaired electrons are excited



The surface quality of the SCRF cavity is crucial!

Several Processes limit current performance



How structures fail

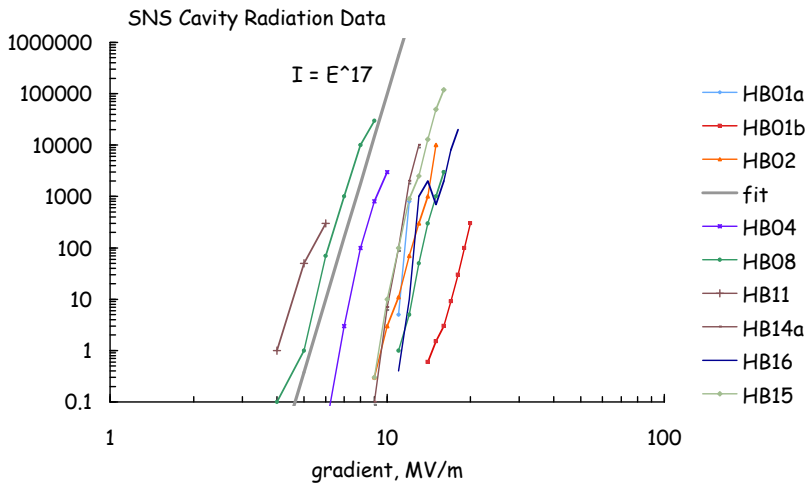
Field emission
Field emitted electrons heat and quenches the superconductor.

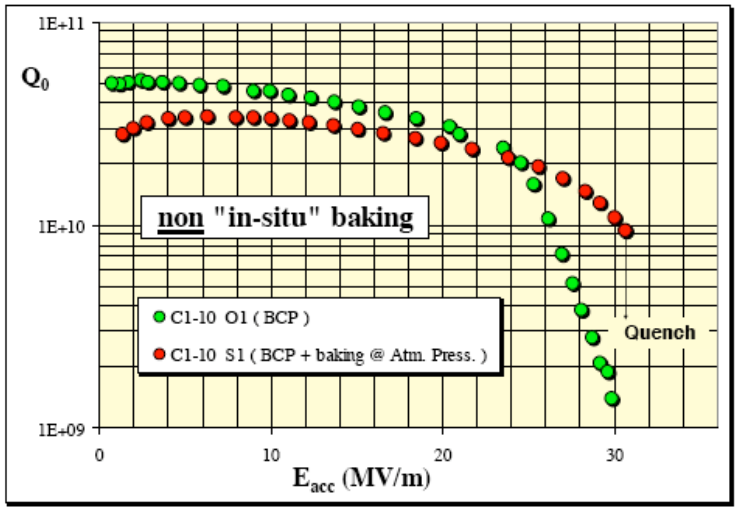
Multipactor
Resonant amplification of low energy electrons.

Quench fields
Cavities quench when ***B*** > 180 mT

High field Q-slope
Cavity losses rise with impurities and defects.

Thermal
Increased thermal conductivity stabilizes quenches.

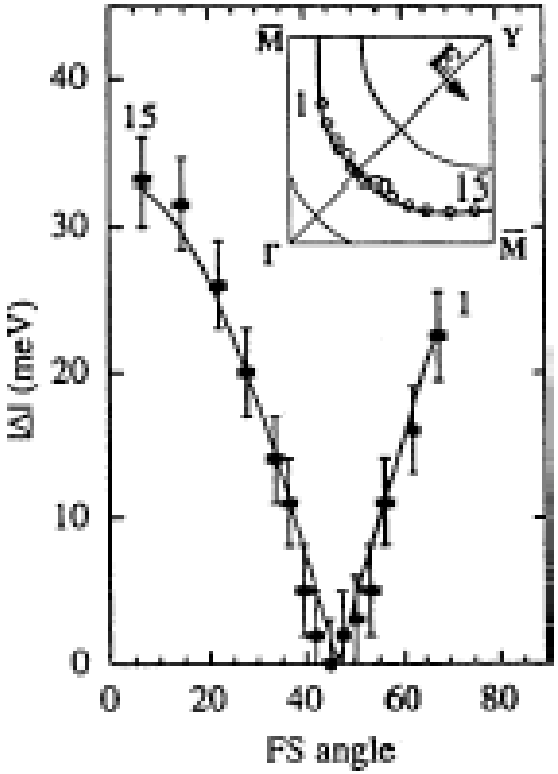




Why Nb?

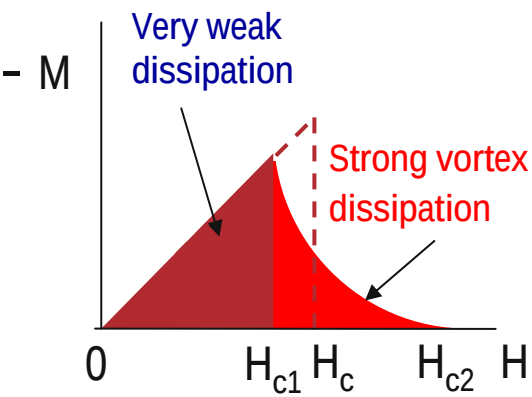
- **BCS surface resistance:**
  - ***Rs ∝ λ4exp (-Δ/kBT)***

- **Minimum Rs**
  - **-> maximum Δ**
  - **maximum Tc ≅1.87Δ/kB**
  - **minimum London penetration depth λ**
  - **Highest lower critical field**

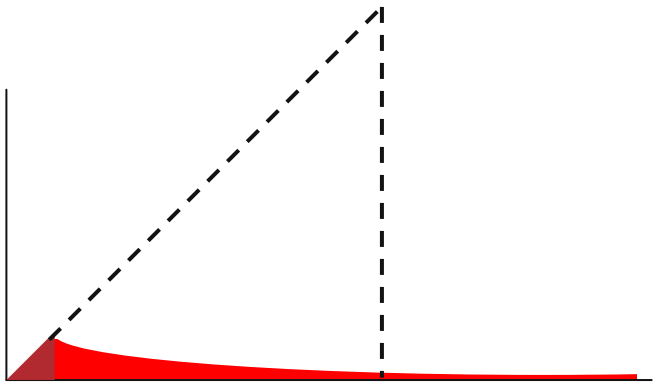


Vanishing Δ(k) = 0 along [110] directions in HTS

Nb, Because it works best! (the highest H_{c1} of any material)



Nb



Higher-H_c SC

Very weak dissipation at $H < H_{c1}$ ($Q = 10^{10}$-10^{11})
Q drop due to vortex dissipation at $H > H_{c1}$

Nb has the highest lower critical field H_{c1}

$$H_{c1} = \frac{\phi_0}{4\pi\lambda^2}\left(\ln\frac{\lambda}{\xi} + 0.5\right)$$

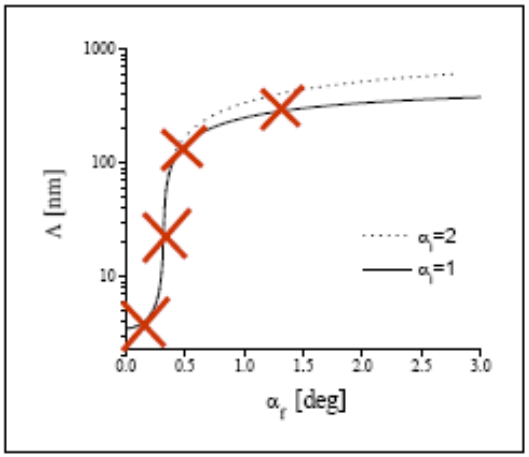
Thermodynamic critical field H_c (surface barrier for vortices disappears)

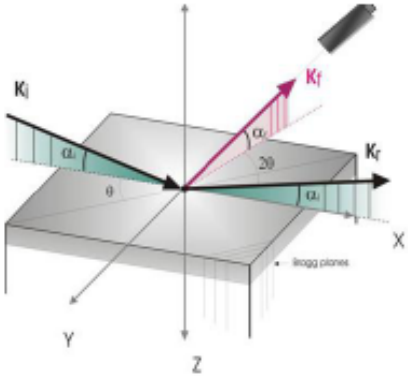
$$H_c = \frac{\phi_0}{2\sqrt{2}\pi\lambda\xi}$$

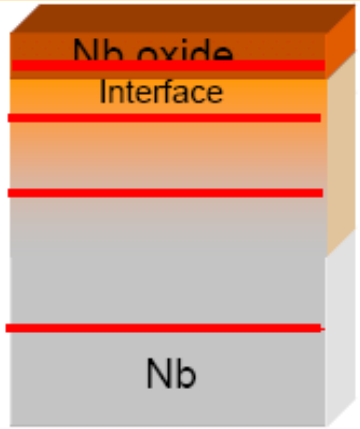
Material	T_c (K)	$H_c(0)$ [T]	$H_{c1}(0)$ [T]	$H_{c2}(0)$ [T]	$\lambda(0)$ [nm]
Pb	7.2	0.08	na	na	48
Nb	9.2	0.2	0.17	0.4	40
Nb_3Sn	18	0.54	0.05	30	85
NbN	16.2	0.23	0.02	15	200
MgB_2	40	0.43	0.03	3.5	140
YBCO	93	1.4	0.01	100	150

Nb, No surface scientist would choose it!

Depth-sensitive diffuse scattering in the near surface region: first results

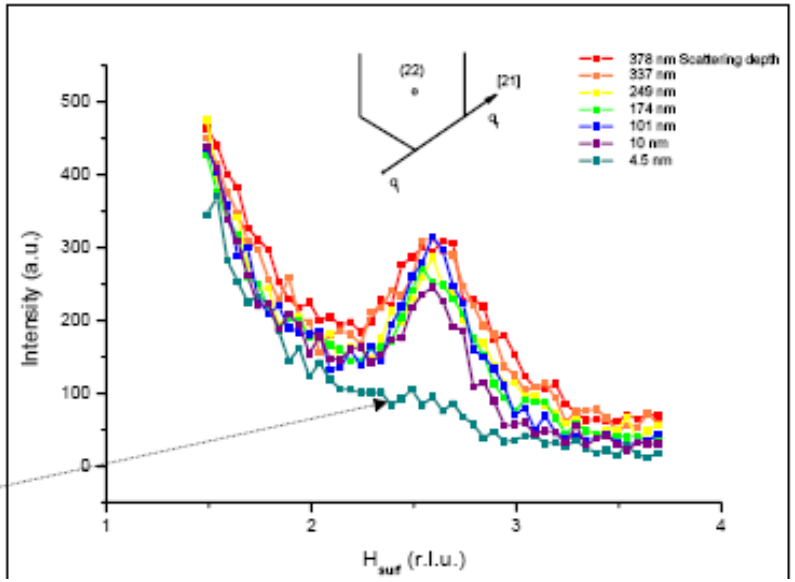






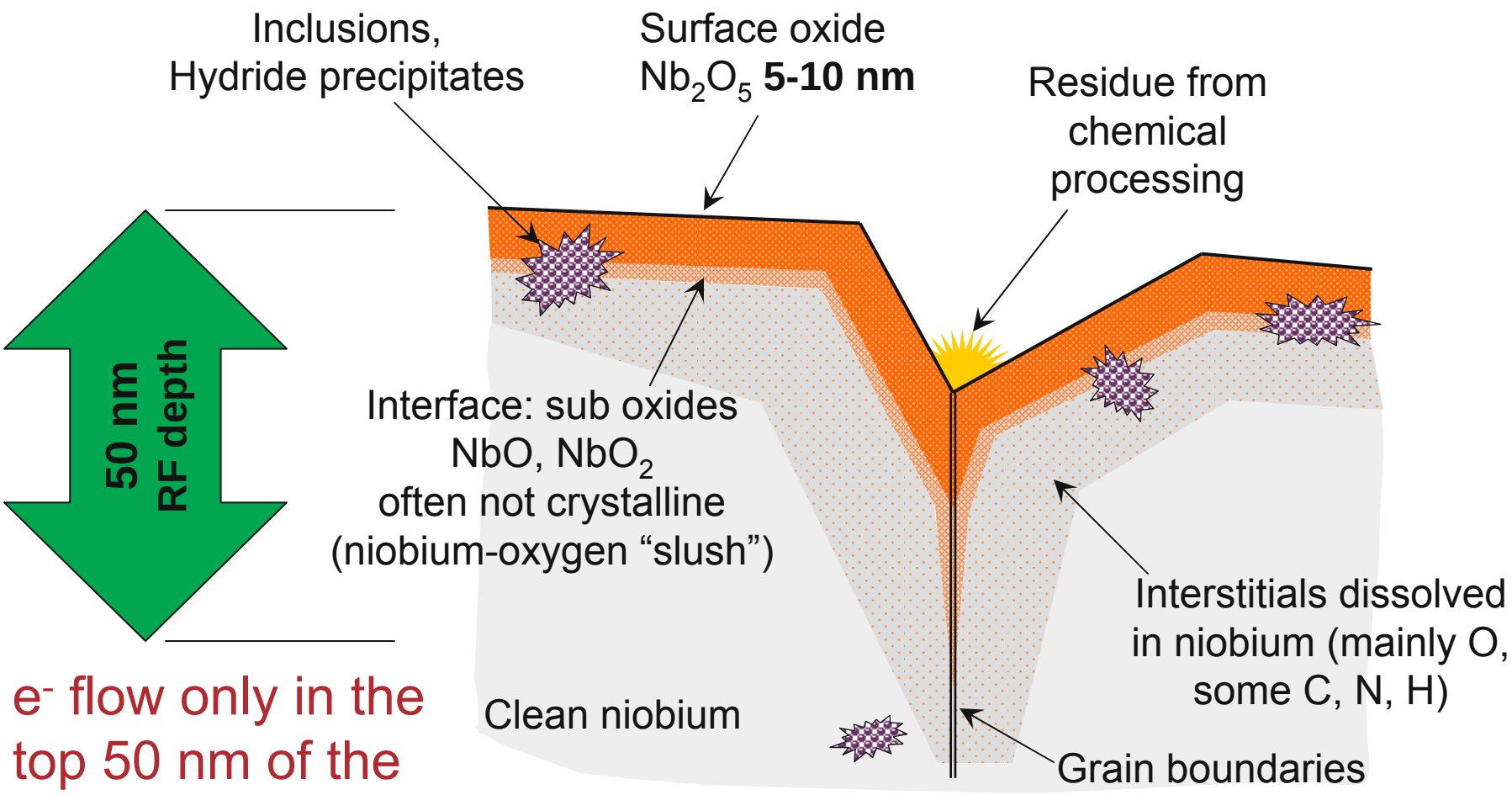
Scattering depth $\Lambda = f(\alpha_f, \alpha_i)$

Diffuse scattering intensity evolution for different scattering depths.



Inside the oxide : no signature of the distorsion

Pollution at niobium surfaces



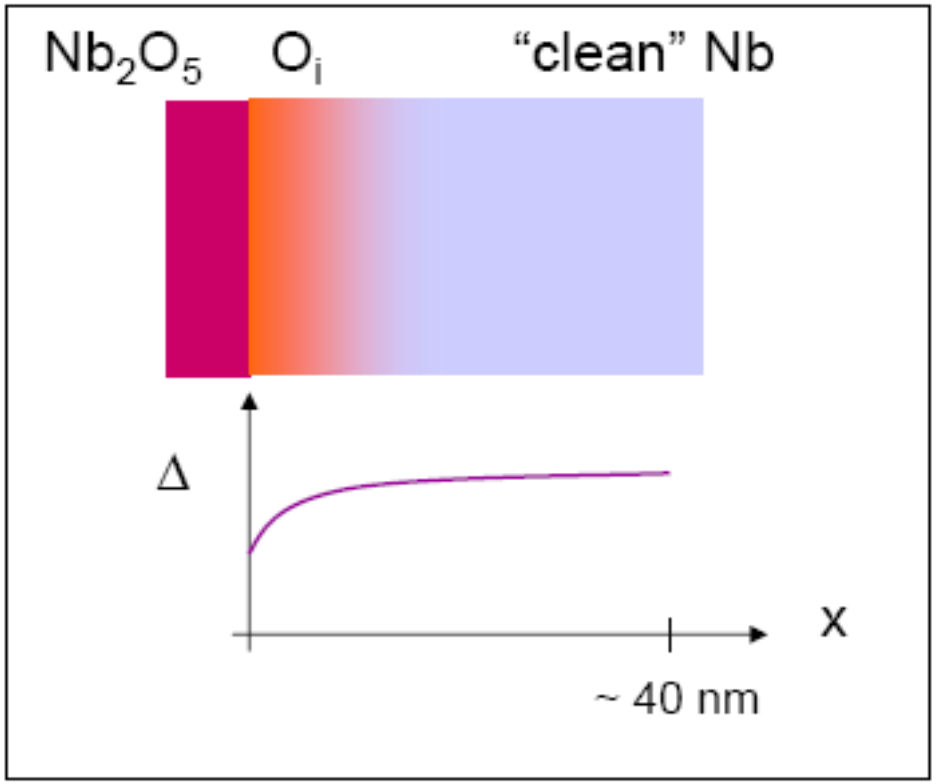
e^- flow only in the top 50 nm of the superconductor in SCRF cavities!!!

Slide courtesy of C. Antoine

Oxygen – So what?

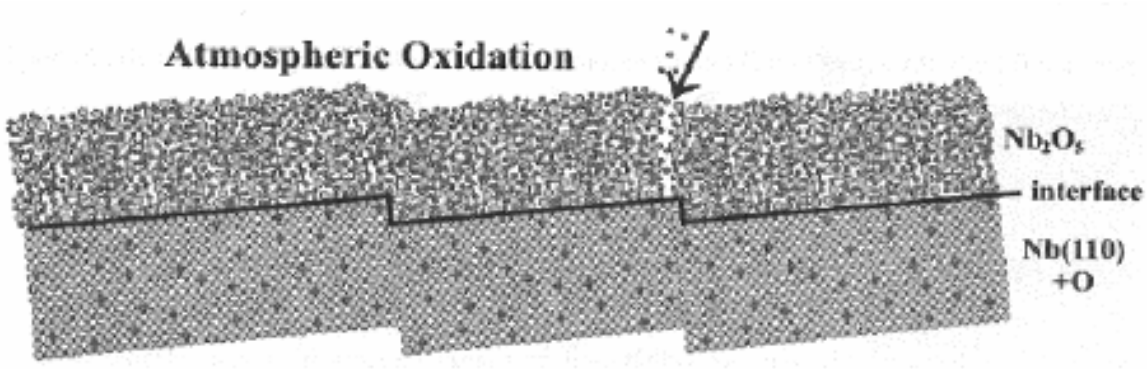
- **How does O_i influence superconductivity ?**
- $[O_i]$ might affect very locally the superconducting gap Δ (d_{char} ~ 1nm) [*Gurevich*]

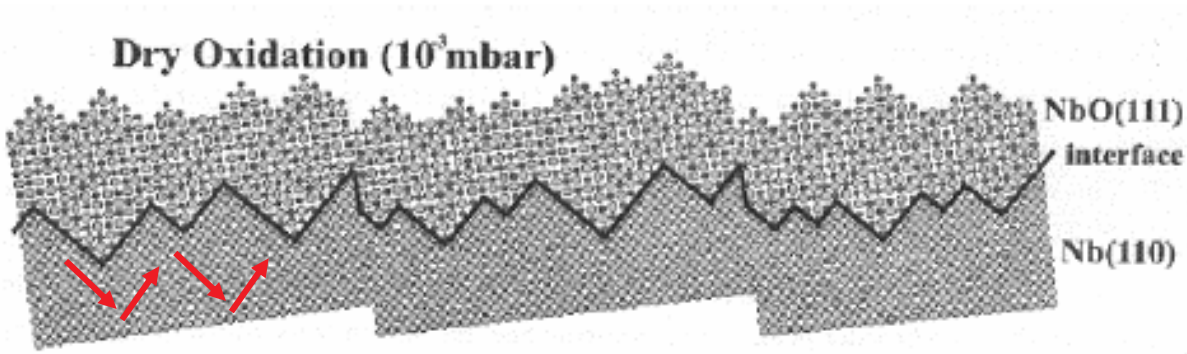
$$Rs \sim e^{-\Delta/T}$$



Grain boundaries are worse

Clean interface ?



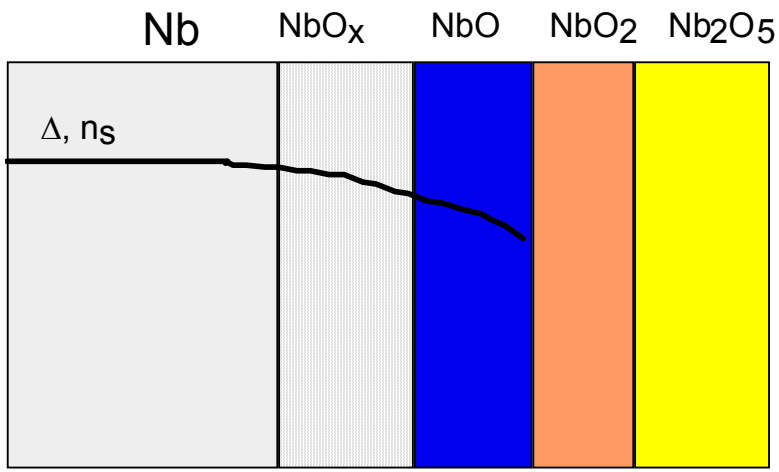


Current Flow

from [Hellwig, 2000]

SRF Impedance is a Surface Effect

Depends on two fundamental properties: the energy gap Δ and the superfluid density n_S. These are altered by proximity effects and magnetic scattering.



$$R = R_{BCS} + R_{res}$$

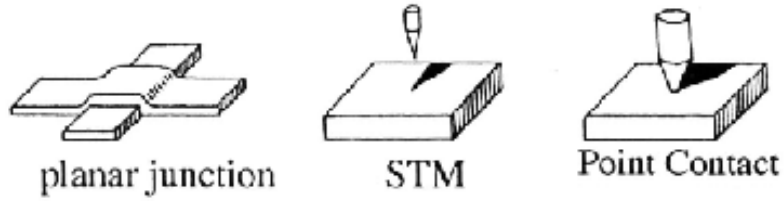
$$R_{BCS} = C\lambda_L^4\omega^2 l \exp(-\Delta/kT)$$

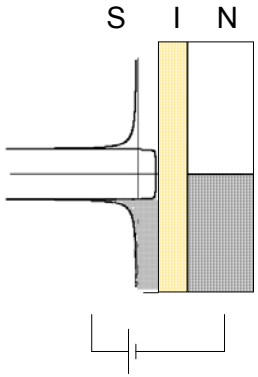
$$\lambda_L^2 = m/\mu_0 n_S e^2$$

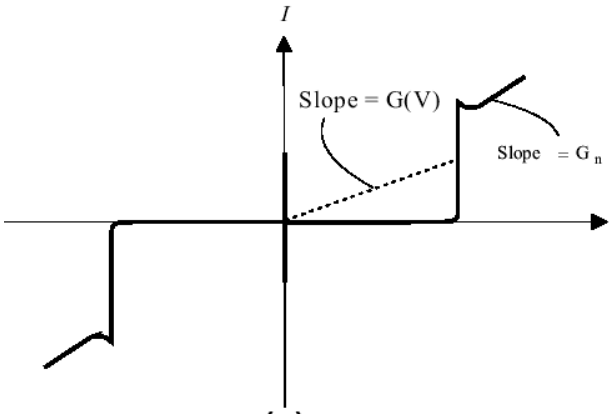
Experimental Goals

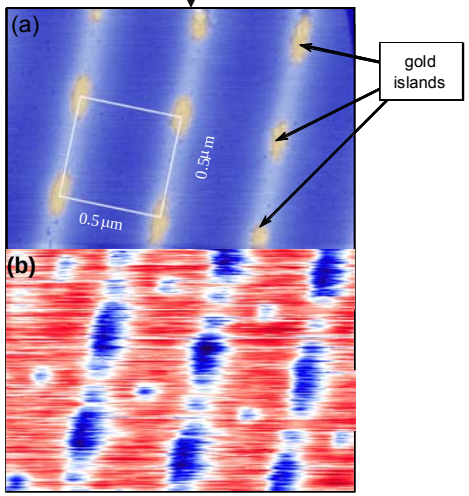
- *Measure Δ and n_S at the surface*
- *Tunneling Spectroscopy is ideal*
- *Explore ALD oxide coatings*

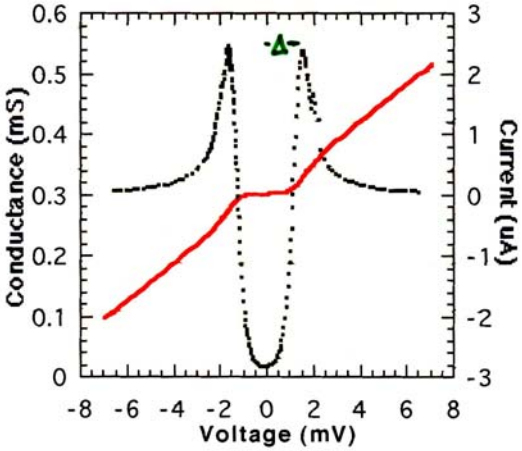
Tunnel Junction Types











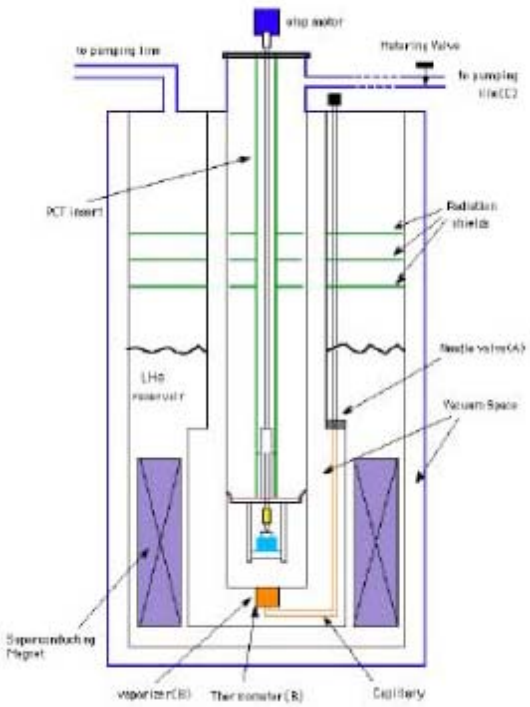
$Nb/Al/Al_2O_3/Nb$

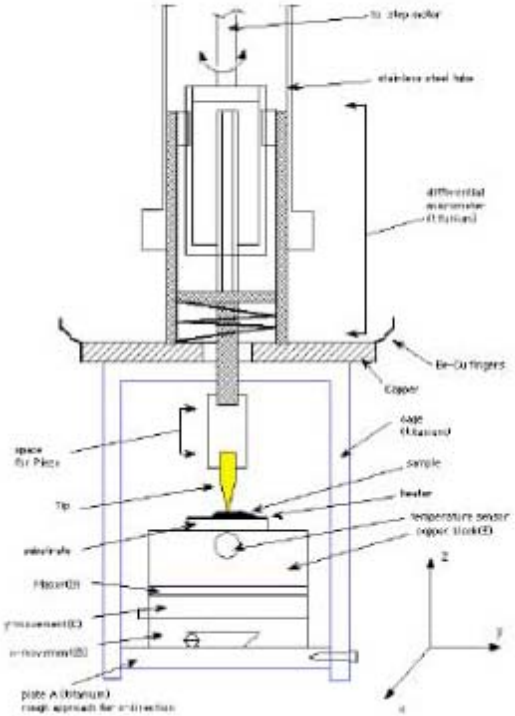
Au islands on $NbSe_2$

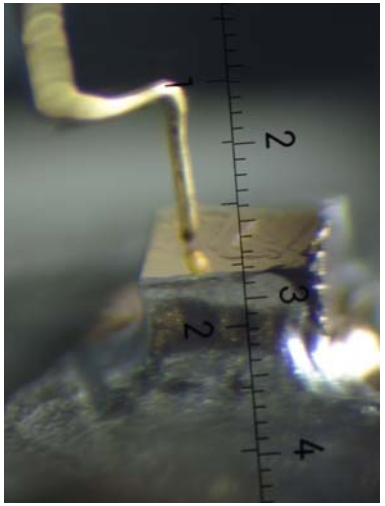
UHV annealed Nb foil (2200 C)

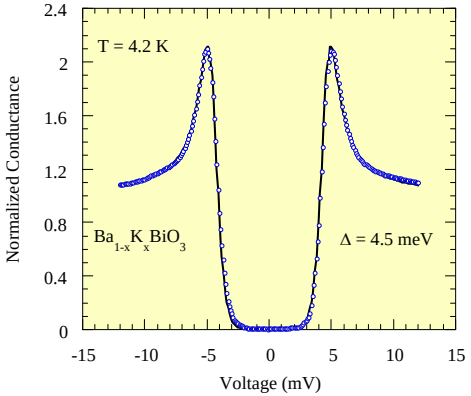
Point Contact Tunneling Spectroscopy

- Au tip touches the surface insulator
- Native surface Nb_2O_5
- ALD surface Al_2O_3+TiN









Example of BCS DOS In BKBO measured by PCT

Tunneling Spectroscopy Laboratory (Prolier, Zasadzinski, Grey, 212)

STM Vacuum Tunneling on "Clean" Nb: Field Emission cleaned

Appl. Phys. Lett., Vol. 73, No. 20, 16 November 1998

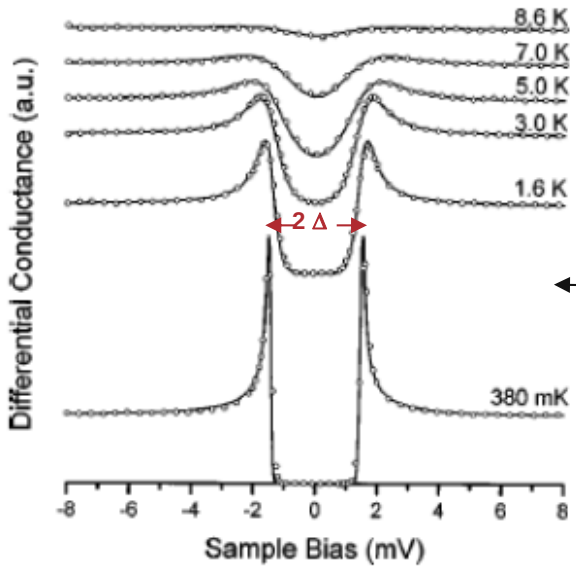
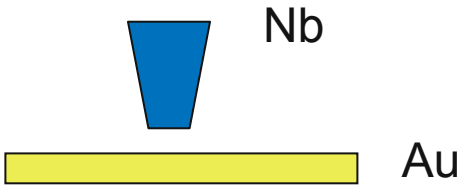


FIG. 2. Measured differential conductance spectra (circles) for tunneling between a Nb tip and a Au surface at several temperatures. The spectra are displaced vertically from each other for clarity. The solid lines are the calculated conductance using a BCS DOS with $\Delta_{tip}(0) = 1.47$ meV and the temperatures shown. The excellent agreement of the data and the calculations confirms that the temperature dependence of the tip DOS is very similar to that of bulk Nb.



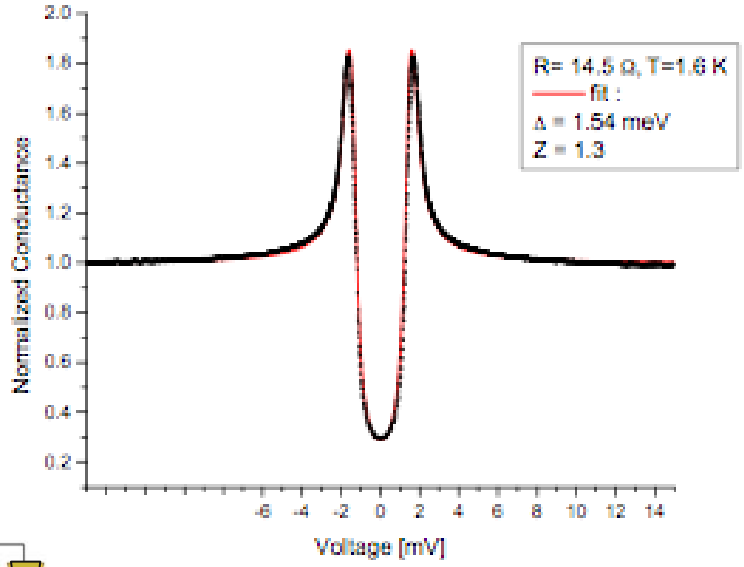
This is the shape we expect to see from tunneling into clean Nb. Bulk energy gap is Δ= 1.55 meV.

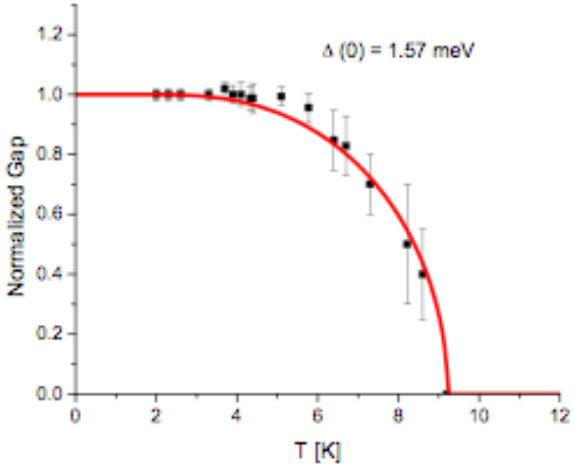
Shape can be fit assuming condensed matter physics, here a BCS DOS.

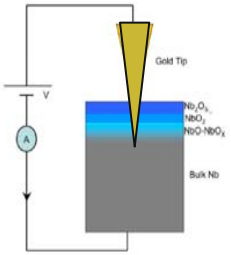
- *Field Emission Cleaning is poorly understood (leading to variations in Point Contact Tunneling curve)*
- *Evidence of proximity effects*
- *Reduced surface superconductivity*

Low Resistance Point Contacts on cavity grade Nb

Here the probe tip Perforates Oxide layers plunging into Nb metal
Data fit is similar to that found for field desorption cleaned Nb tip.



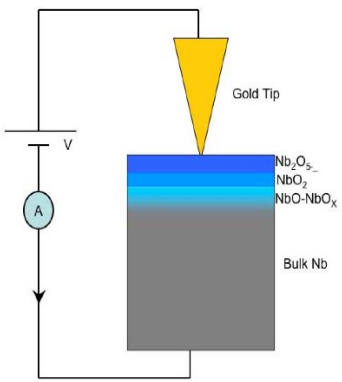




Baked Nb Crystal

PCT Tunneling Data - **Ohmic** contacts

$Nb_2O_{5-\delta}$, $NbO_{2-\delta}$ are magnetic

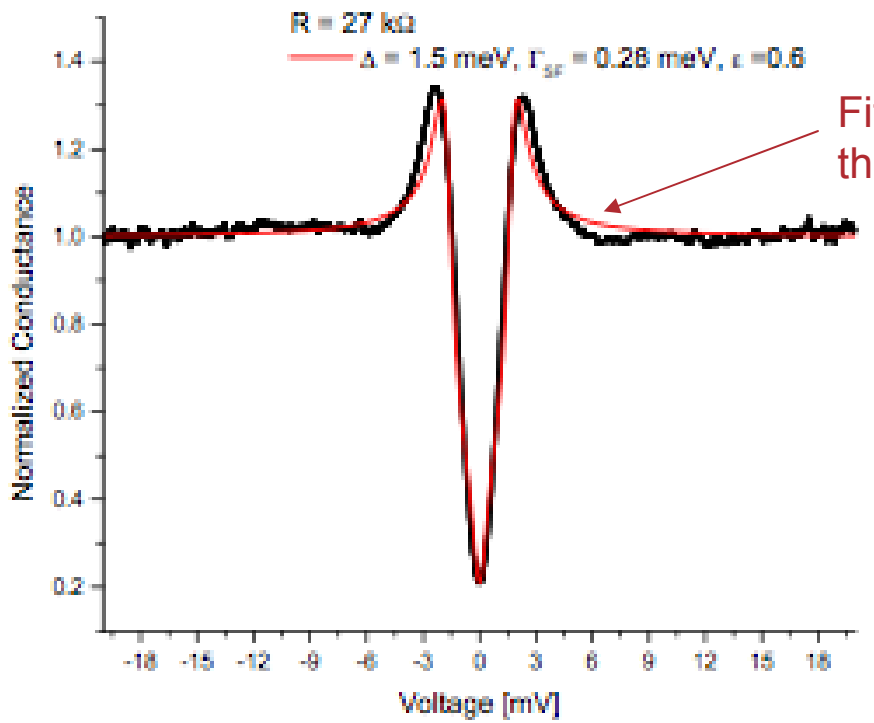


Conductance vs Voltage Curve

- Δ is still characteristic of bulk Nb
- Shape is "triangular"
- Conductance minimum 0.2

-> New Condensed Matter Physics

Evidence of Magnetic Scattering



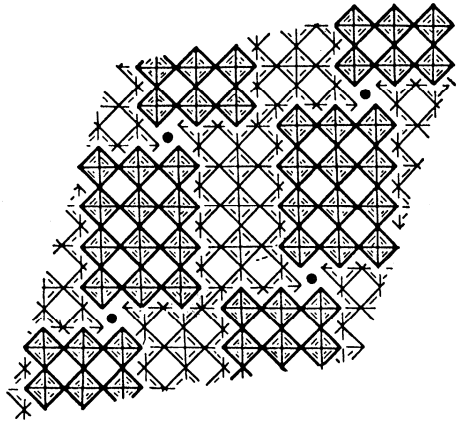
Fit using Shiba theory

The structure of "niobium oxide" is more subtle than previously acknowledged, and its properties, therefore, are more complex than presently appreciated!

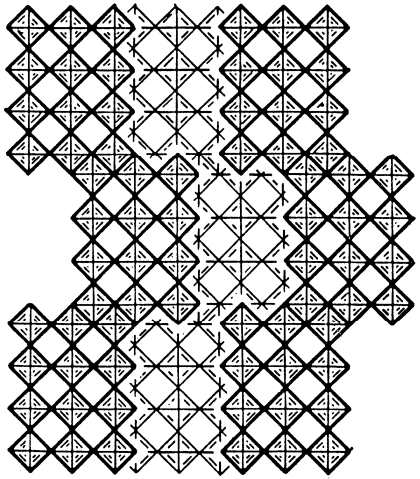
PHYSICAL REVIEW B VOLUME 44, NUMBER 13 1 OCTOBER 1991-I

Electrical and magnetic properties of $Nb_2O_{5-\delta}$ crystallographic shear structures

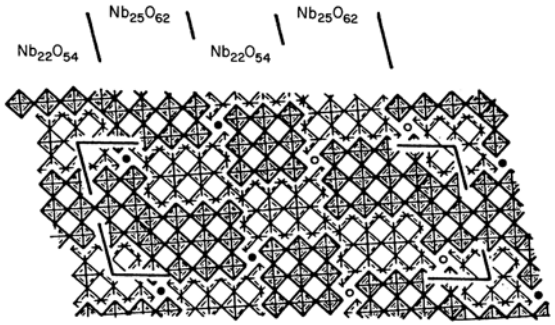
R. J. Cava, B. Batlogg, J. J. Krajewski, H. F. Poulsen, P. Gammel, W. F. Peck, Jr., and L. W. Rupp, Jr.



Nb_2O_5
(= $Nb_{12}O_{30}$)



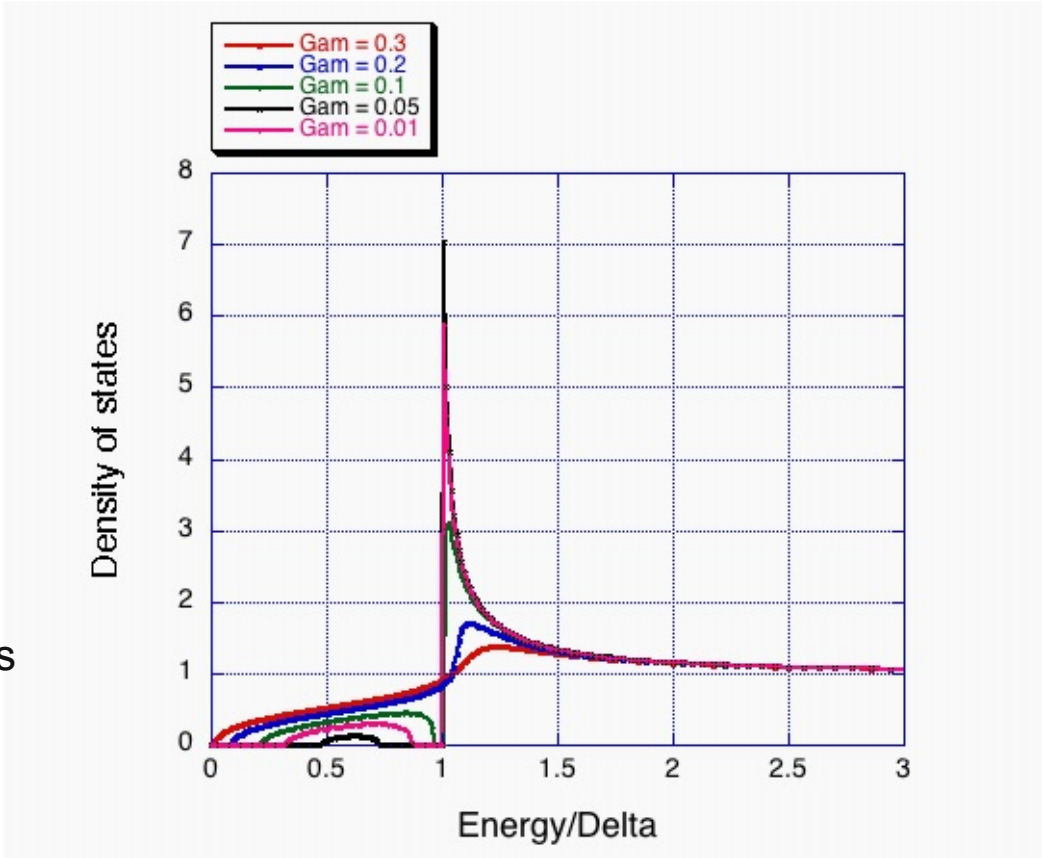
$Nb_{12}O_{29}$
T_{Neel} = 2.5 K



Shear structure of
22/54 + 25/62

Magnetic Dissipation

Scattering off magnetic interfaces or precipitates gives rise to Shiba states inside the gap. These cause dissipation (lowering Q).

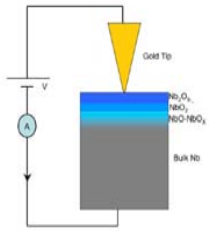


- As Cooper pairs move down the superconductor, they randomly strike the interface.

- Since magnetic electron coupling far exceeds Cooper pairing energies, the pairs often become decoupled and require energy to re-pair.

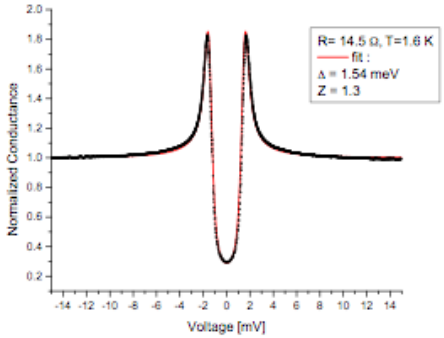
- Because of the different energy scales, even weakly magnetic layers will add significant dissipation!

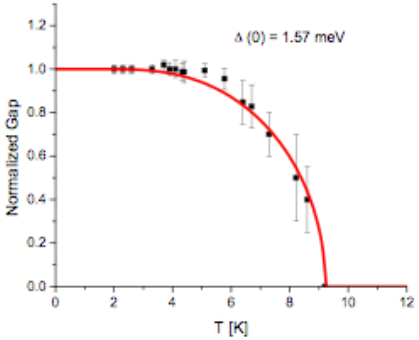
Point Contact Tunneling – where are the magnetic scatterers?



Magnetic impurities must be in the oxide layer!

Nb "Metal" PCT

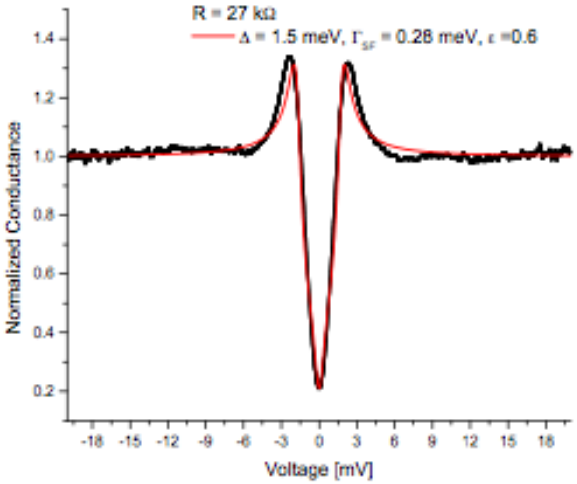




Low Resistance Point Contacts on Nb

Tip Perforates Oxide layers, data can be fit without magnetic scattering.

Nb Oxide PCT



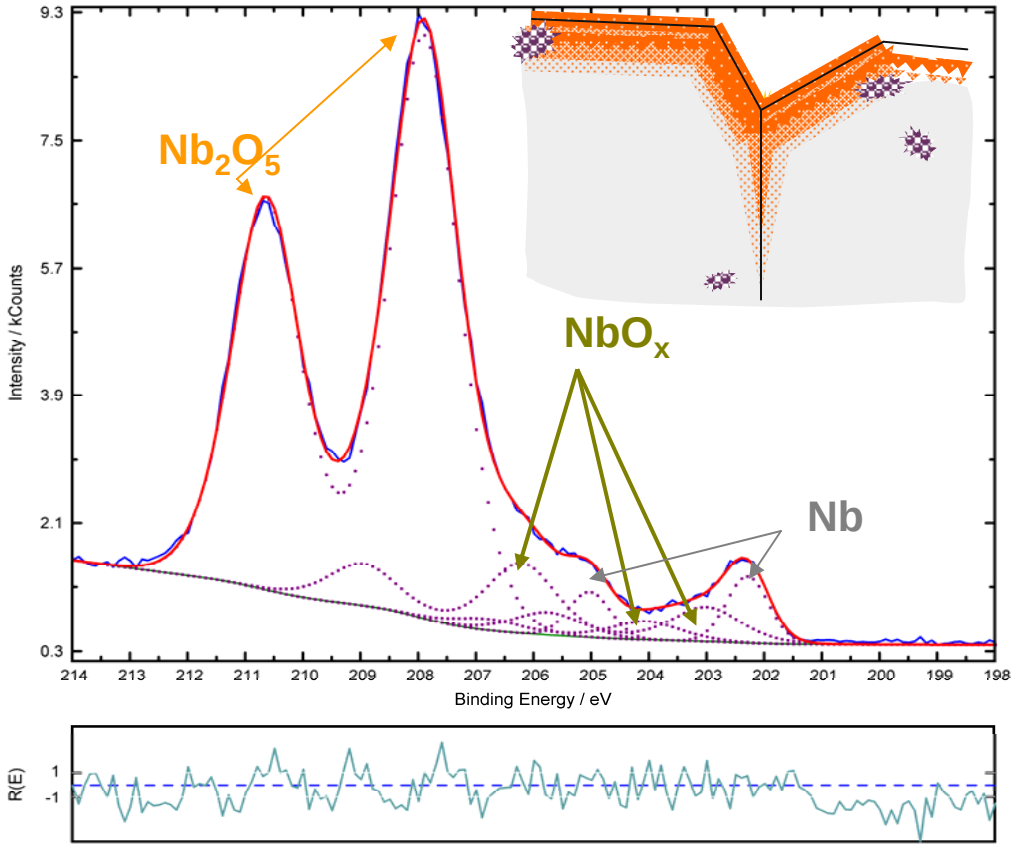
Ohmic Point Contacts on Nb

Electrons tunnel through the oxide layers, data can only be explained with magnetic scattering.

X-ray Photoelectron Spectroscopy: a Surface Probe of Nb Oxidation

Nb samples supplied by FNAL!

Dielectric Nb_2O_5
$Nb_2O_{5-\delta}$, $NbO_{2-\delta}$ are magnetic
NbO_x (0.2 < x < 2),metallic
NbO_x precipitates (0.02 < x < 0.2)



X-Ray Photon in; e^- out

- Energy of the electrons is related to the electronic states of atoms in the surface

Nb 3d

(3/2-5/2 spin orbit doublet)

- Doublet shifts (is perturbed) with Nb oxidation state
- Cleaned polished samples have a mixture of oxides
- XPS sampling depth has an e folding length of ~10 of nms
- Dotted lines are a deconvolution of the signal from atoms of different oxidation state.

Low Temperature Vacuum Bake Reduces Magnetic Oxides

$Nb_2O_{5-\delta}$, $NbO_{2-\delta}$ are magnetic

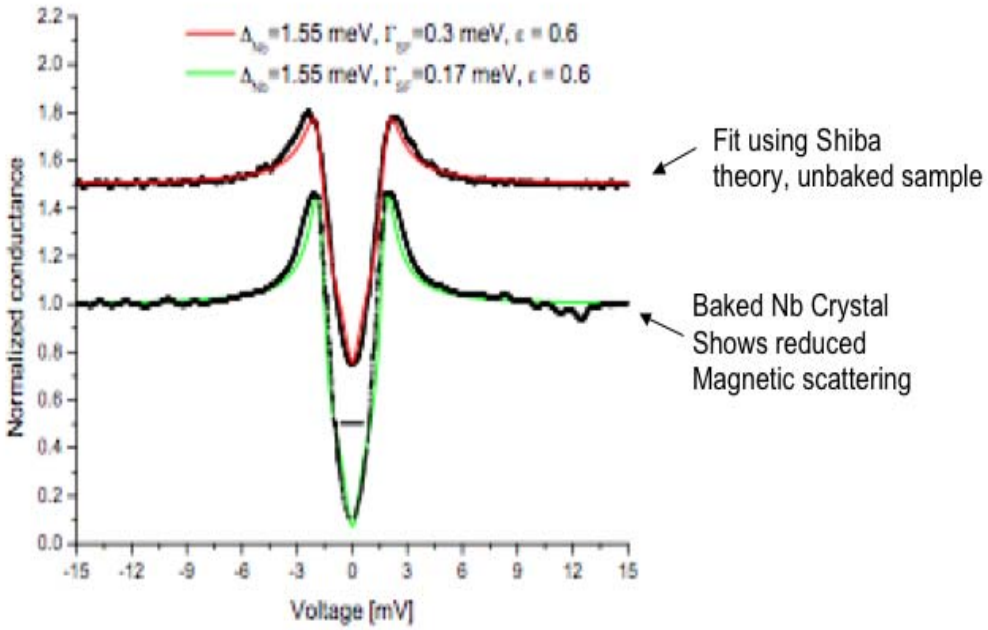
- **Can explain positive effects of both air *and* vacuum anneal**
- **Small changes in oxygen stoichiometry make a major difference**
  - **Dry vs wet oxidation**
  - **Initial surface condition**

Baking can be used to reduce (*not eliminate*) magnetic scatter losses!

(Green fit vs. red fit)
Curves offset for clarity.

XPS shows small changes in Nb Oxidation State

Mild Baking effect
120C during 24 h



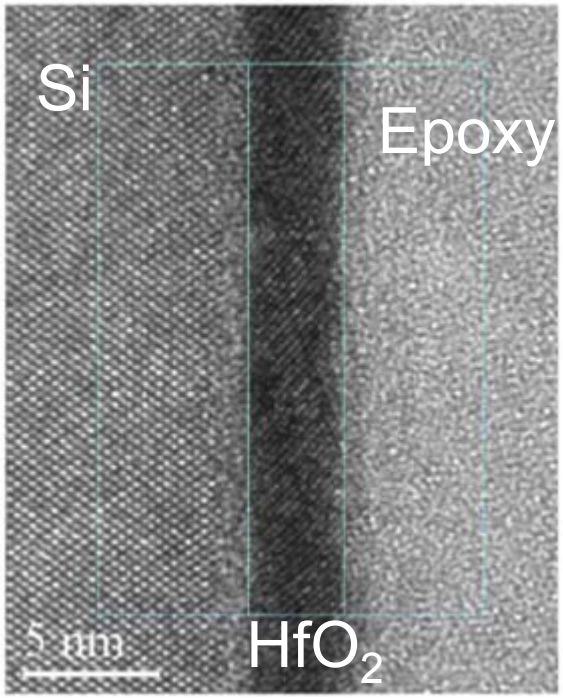
Summary

- PCT is revealing the bulk Nb gap ~1.55 meV but broadened DOS
- Evidence of magnetic scattering, data well fit by Shiba theory
- Baked Nb shows reduced magnetic scattering
- New model proposed for baking effect, oxygen diffusion fills vacancies

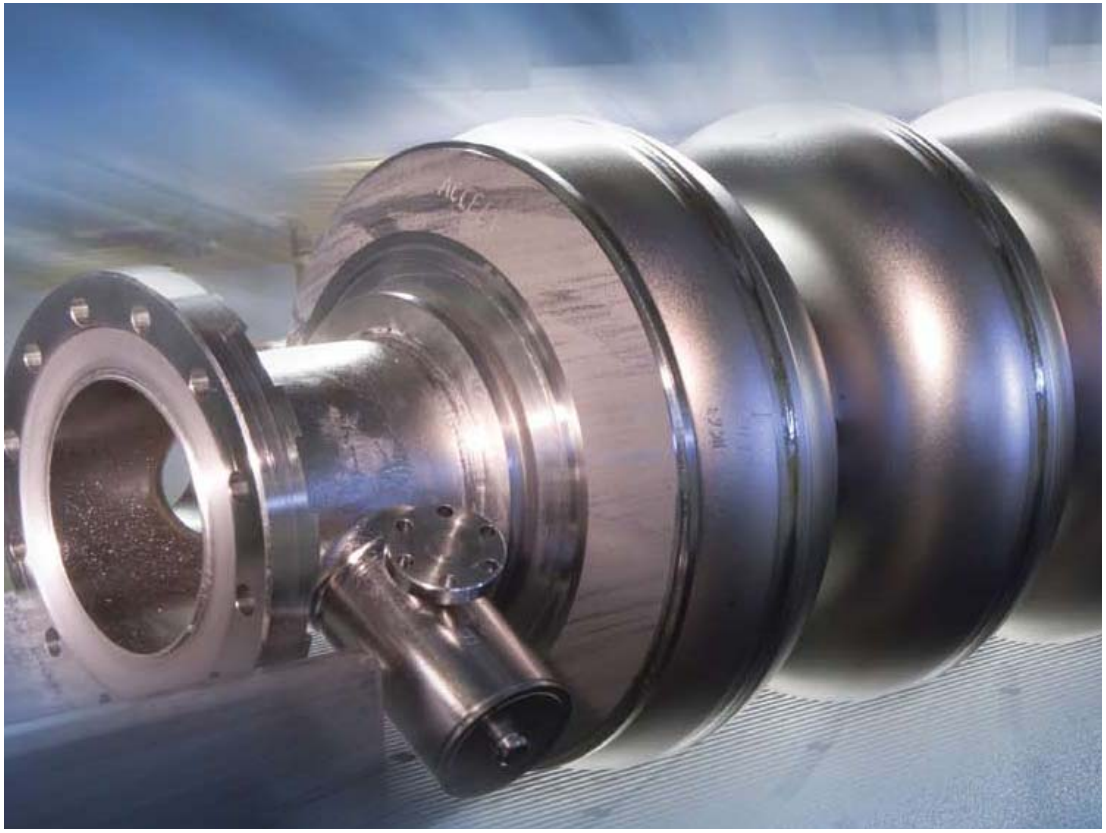
Along the way to a solution

- Niobium is from a surface scientists point of view a difficult material to deal with.
  - Extremely reactive.
  - Native Oxide is complex and passivates poorly
- Semiconductor Industry – a clue
  - Silicon is reactive but oxide is simple and passivates well (but has a low dielectric constant)
  - Gate dielectric oxides are now being used on Si metal (and being produced by ALD)

- Grow a dielectric oxide with superior properties to the Niobium Oxides
  - Simple - non-interactive with the sc layer
  - Passivating (stable surface, protective of the Nb metal underneath)



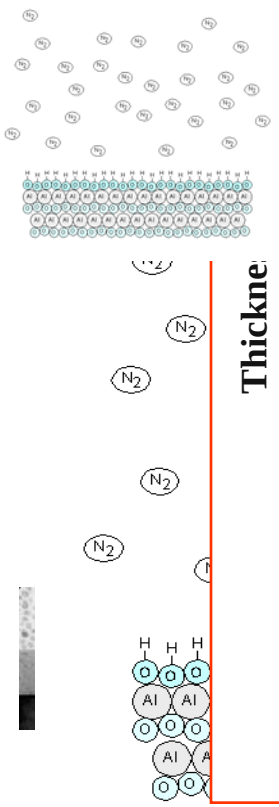
How can I grow/coat such complex objects?



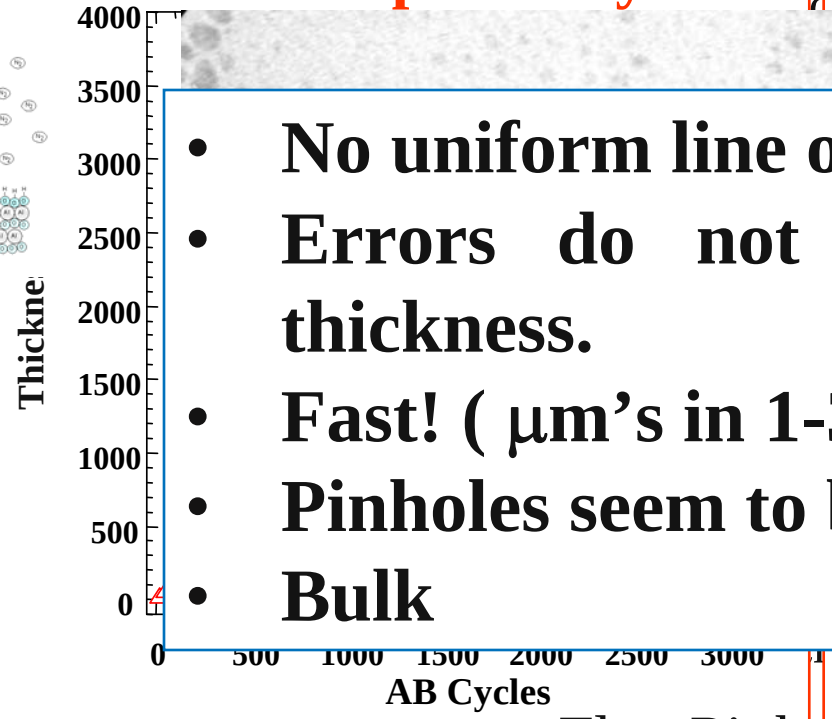
Atomic Layer Deposition

- Atomic Layer by Layer **Synthesis** Method similar to MOCVD
- Used Industrially
  - Semiconductor Manufacture for "high K" gate dielectrics
    - *"Abrupt" oxide layer interfaces*
    - *Pinhole free at 1 nm film thicknesses*
    - *Conformal, flat films with precise thickness control*
  - Electroluminescent displays
    - *No line of sight requirement*
    - *Large area parallel deposition*
- Parallel film growth technique; Inside of large tubes can be done at once.

ALD Reaction Scheme



Ellipsometry



- Film growth is linear with AB Cycles

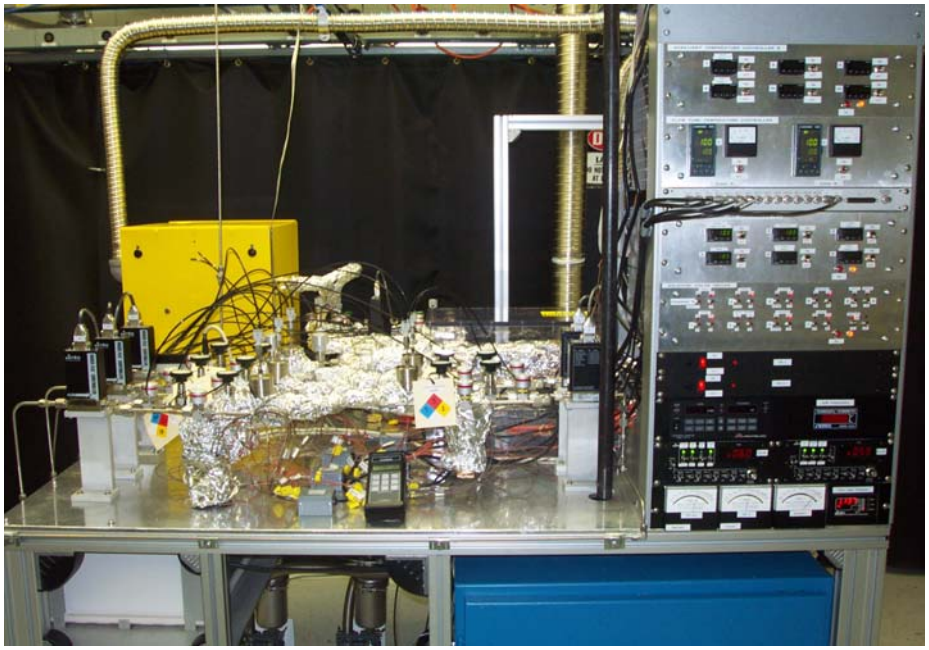
Atomic Force Microscopy

- RMS Roughness = 4 Å (3000 Cycles)
- ALD Films Flat, Pinhole free

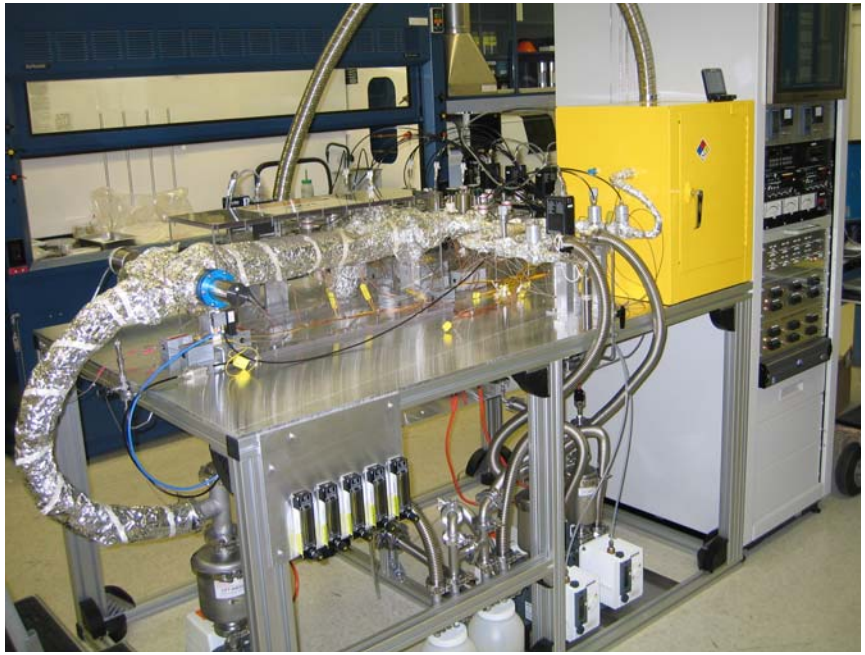
- **No uniform line of sight requirement!**
- **Errors do not accumulate with film thickness.**
- **Fast! (μm's in 1-3 hrs) and parallel**
- **Pinholes seem to be removed.**
- **Bulk**

- Flat, Pinhole-Free Film

ALD Flow Reactors

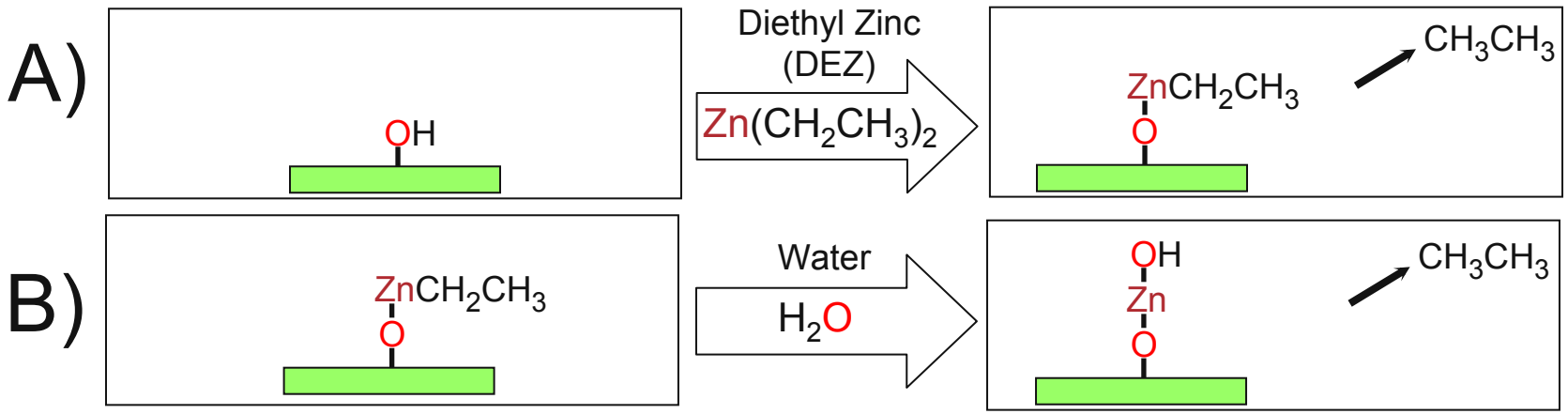


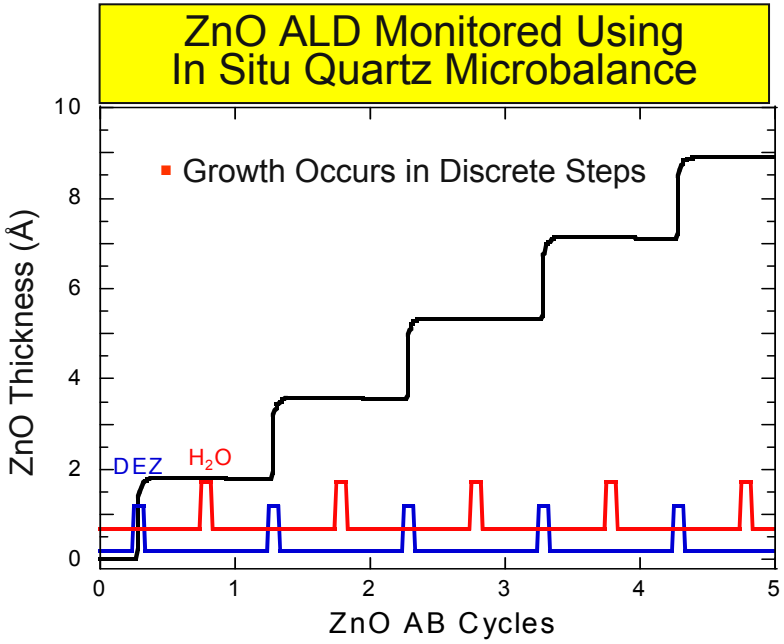
Bldg 200, MSD

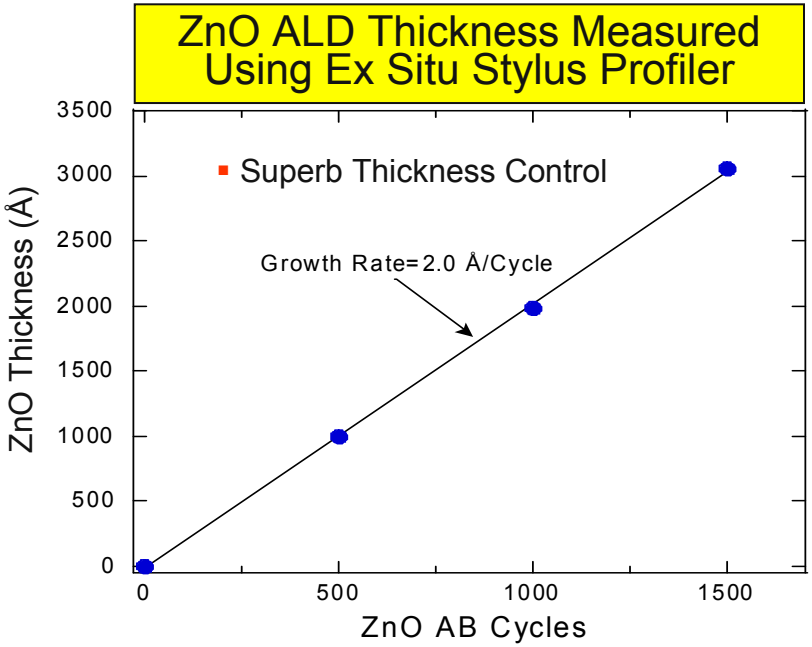


Bldg 362, ES

Atomic Layer Deposition of ZnO Films

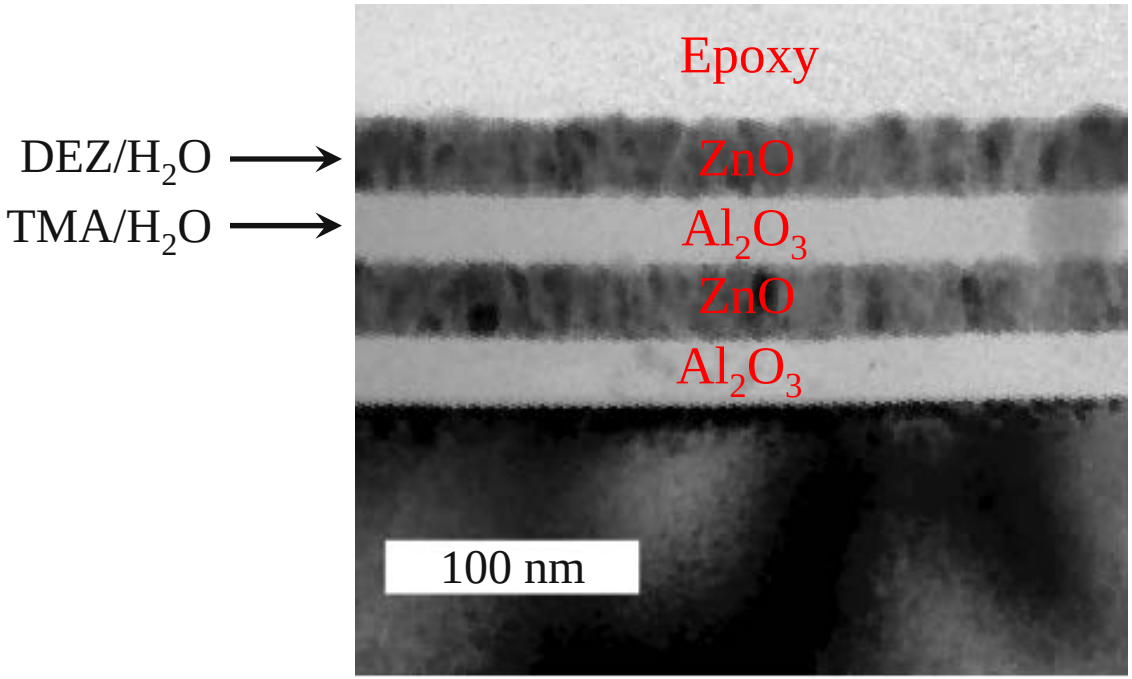






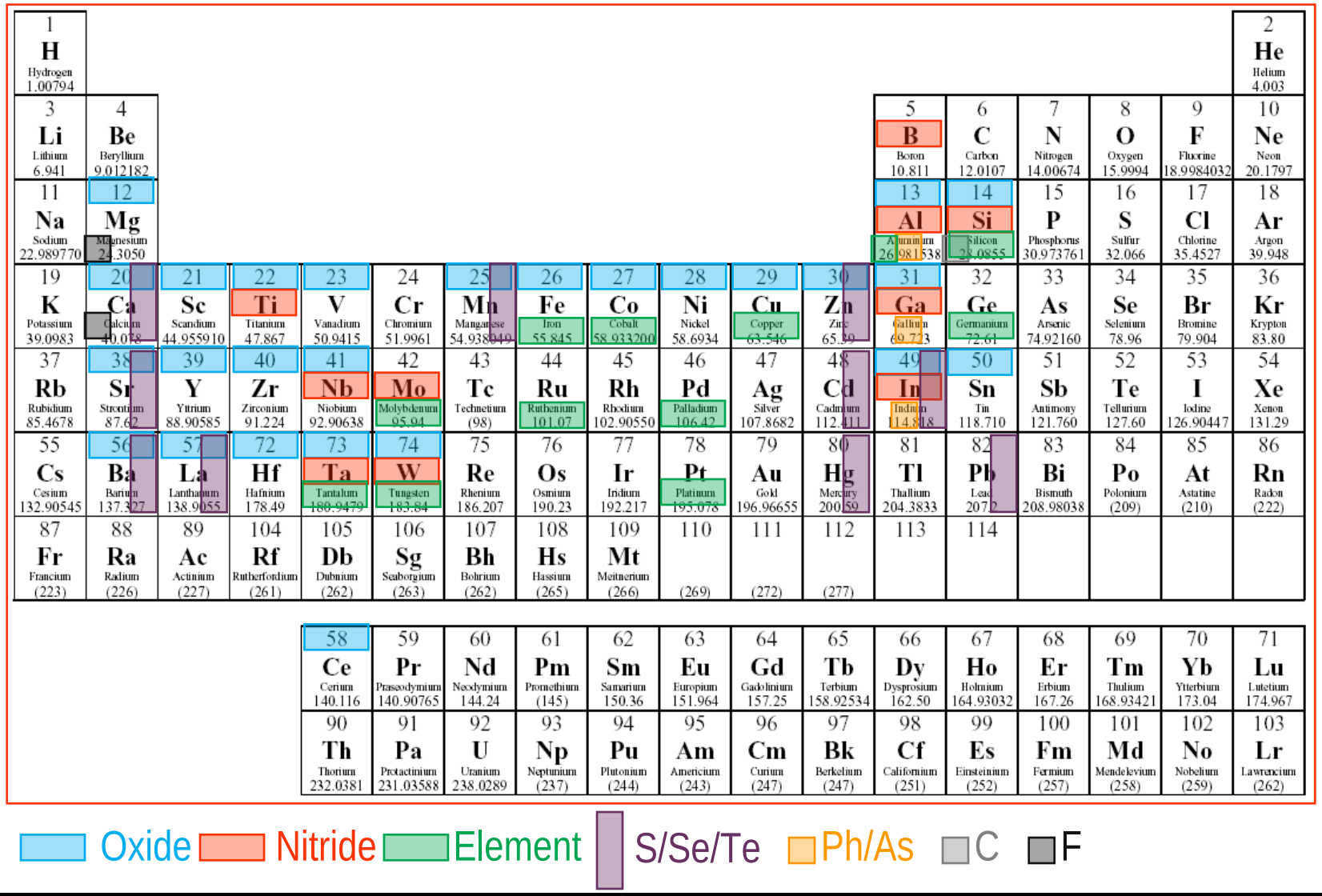
ALD Can Fabricate Complex Oxides, Multilayers, Alloys etc

Example: TEM of ZnO/Al_2O_3 ALD Multilayer



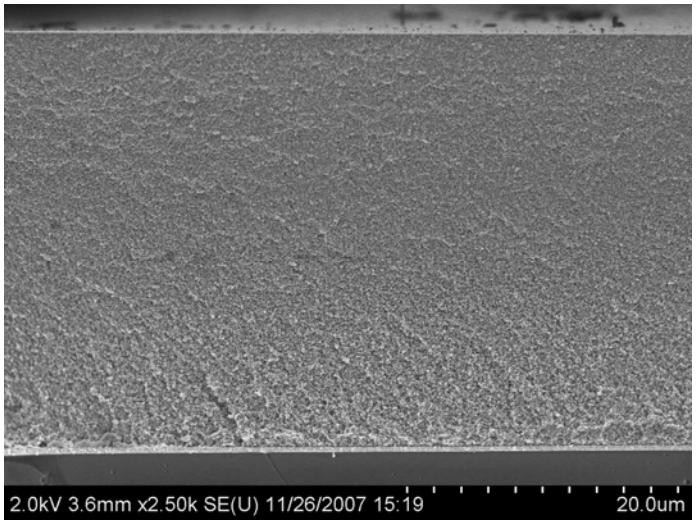
- Films Have Tunable Resistivity, Refractive Index, Surface Roughness, etc.

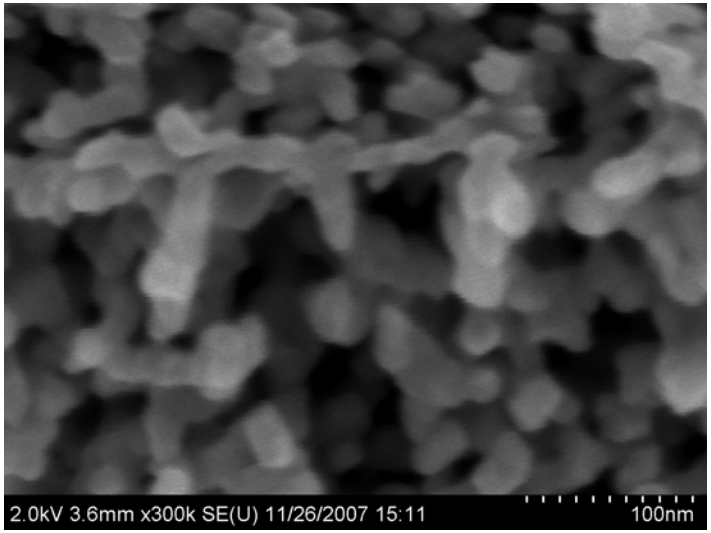
Demonstrated ALD A/B Reactions

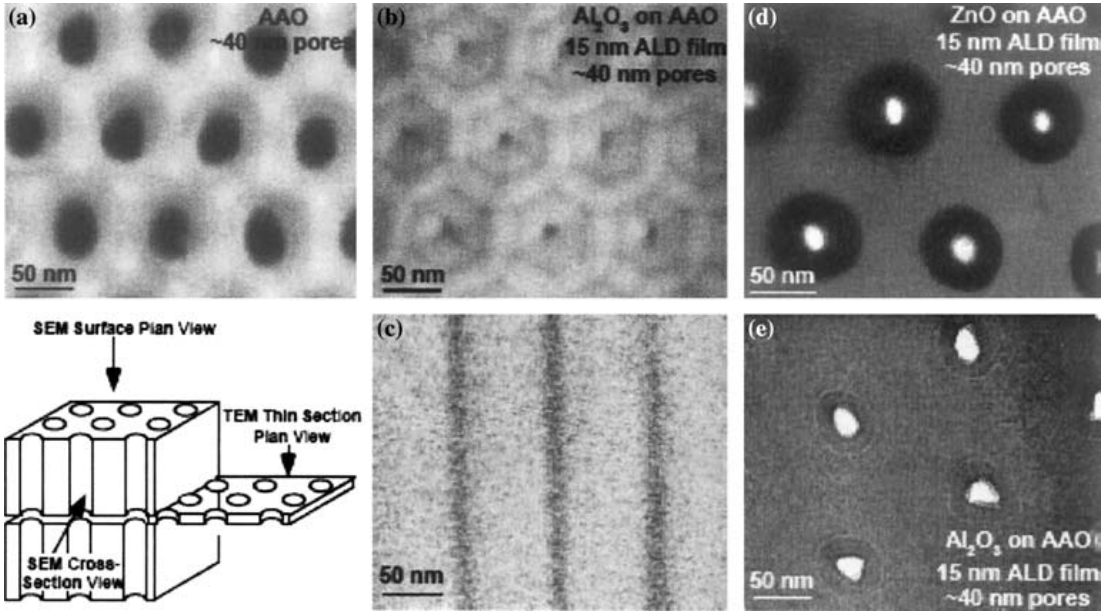


Conformal Coating – aspect ratio

- ALD has no trouble coating at aspect ratios exceeding 10000 - 1







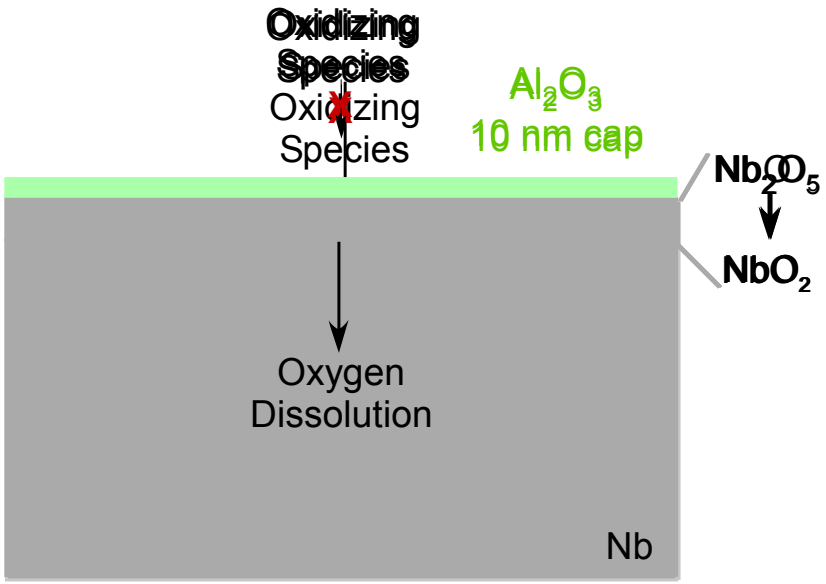
Martinson, Hamann, Hupp, Elam, Stair, Pellin NU/ANL

Al_2O_3 capping layers for Nb surfaces

- Surface behavior of Nb*
  - In air, Nb oxide layer
  - Annealed in vacuum

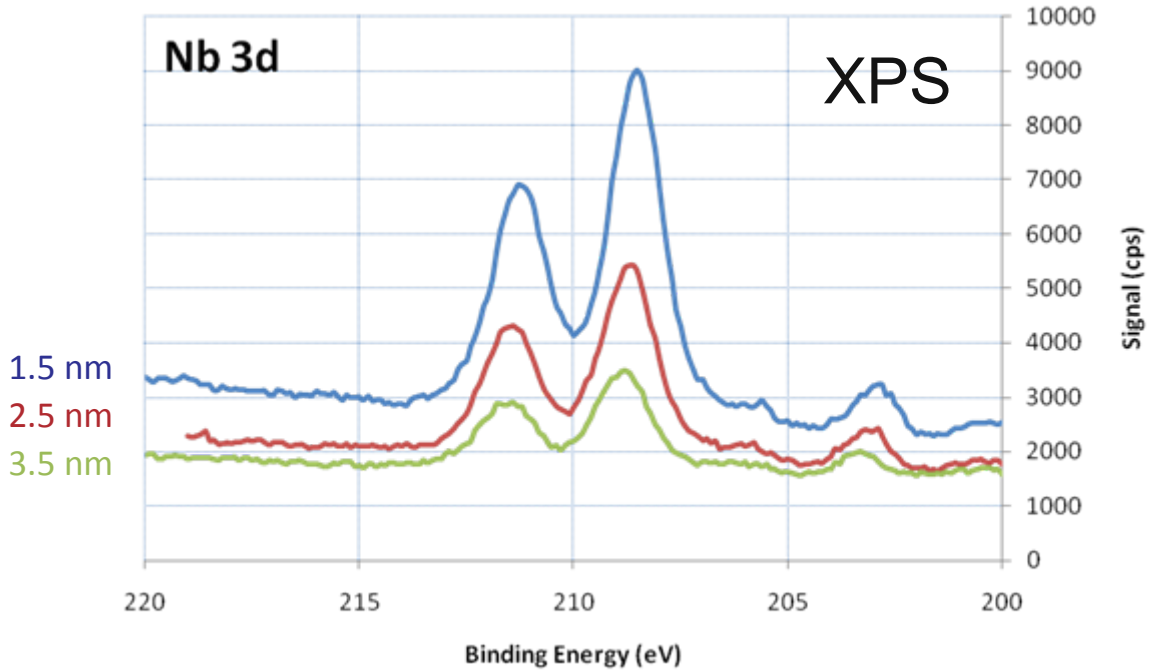
- Al_2O_3 Capping Layer
  - 10 nm
  - $Al(CH_3)_3$ alternating H_2O cycles
  - Room Temperature ->200 C deposition temperature
  - Annealed at (125 C to *860* C)

- Other caps? Conducting Oxides?



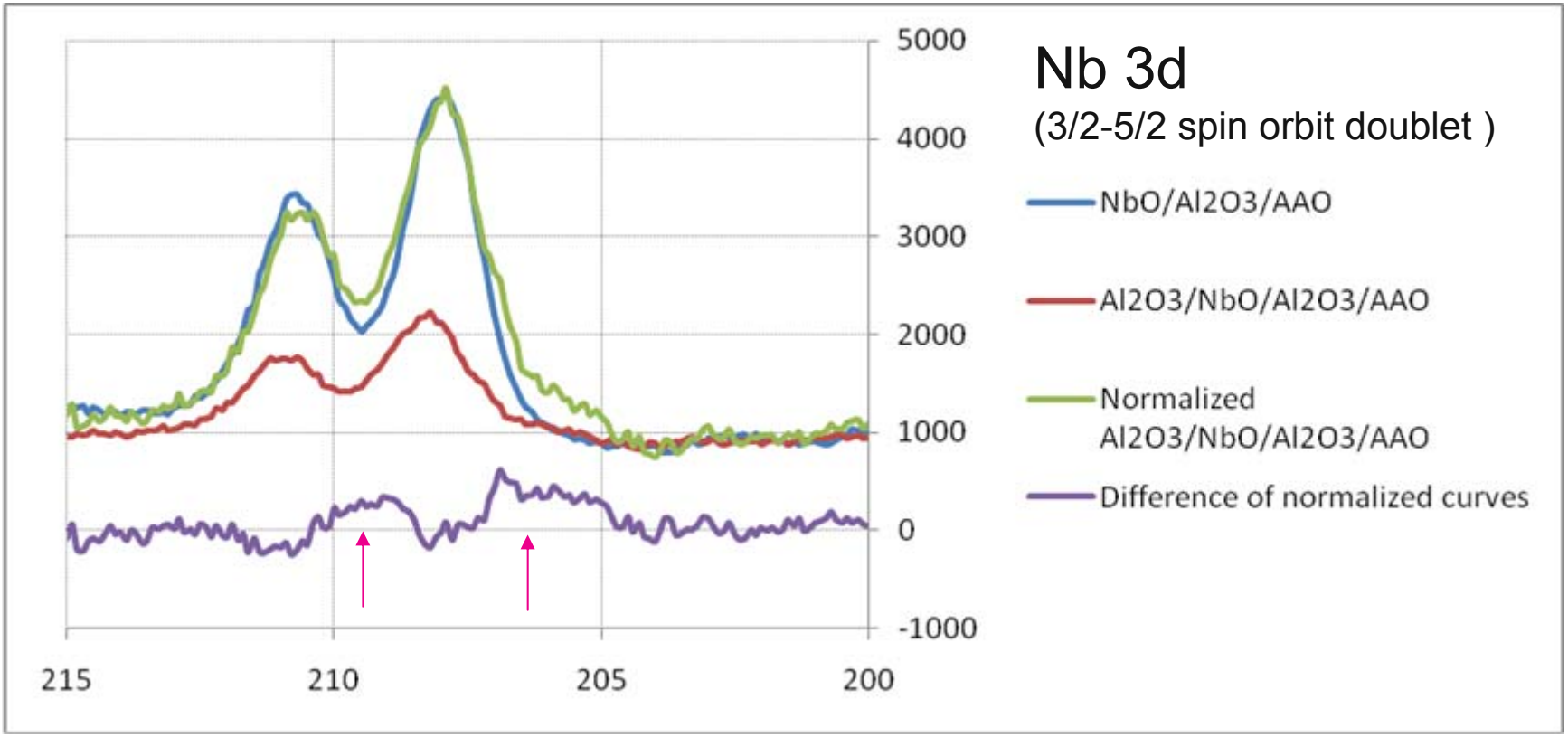
*Ciovati, APL, 89 (2006) 022507/1-3
Delheusy, Antoine et al, thesis work

Al_2O_3 deposited on Nb by ALD



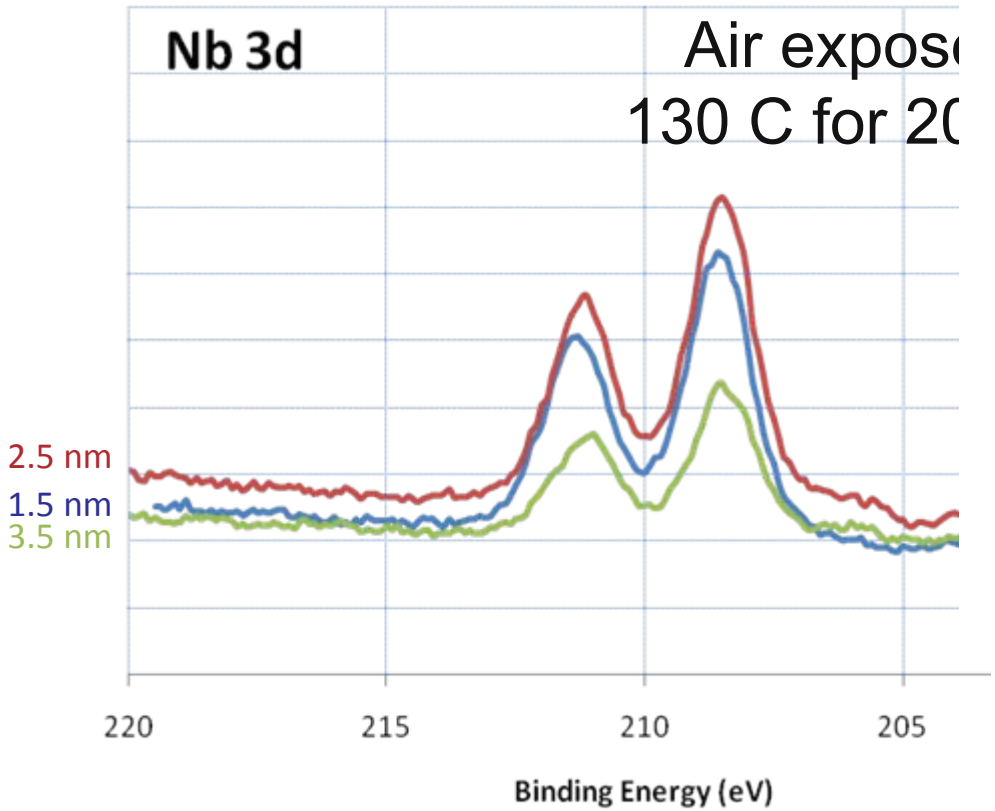
- Nb has a significant mixed native oxide layer that could affect SCRF cavity operation.
- Cavity grade Nb samples were mechanically polished to the micron scale followed by an electro-polish and atomic layer deposition of 1.5 nm to 3.5 nm alumina at 150C.
- Progressive attenuation of Nb 3d X-ray photoelectrons with increasing layer thickness indicates uniform growth.

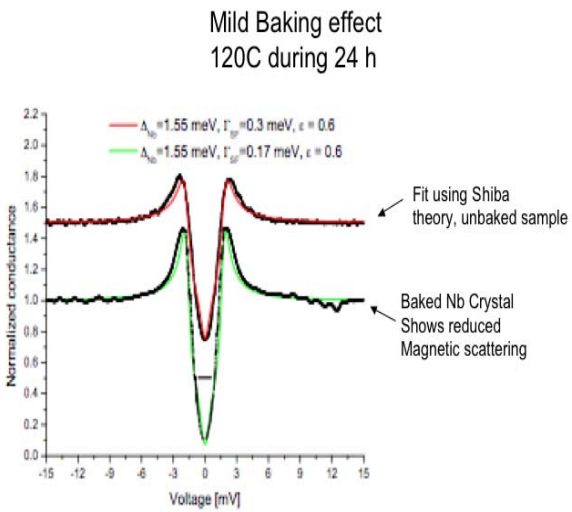
ALD reduction of Nb?



- All Nb spectra shifted from metal Niobia
- After ALD coating difference spectra reveal 2 eV shifted Nb
  - Interfacial Nb atoms are reduced.
  - Indicates our thermodynamic arguments are correct (Oxygen will stay in the Alumina Layer)

Heat treatment of ALD capped Nb – how thick a film is needed?

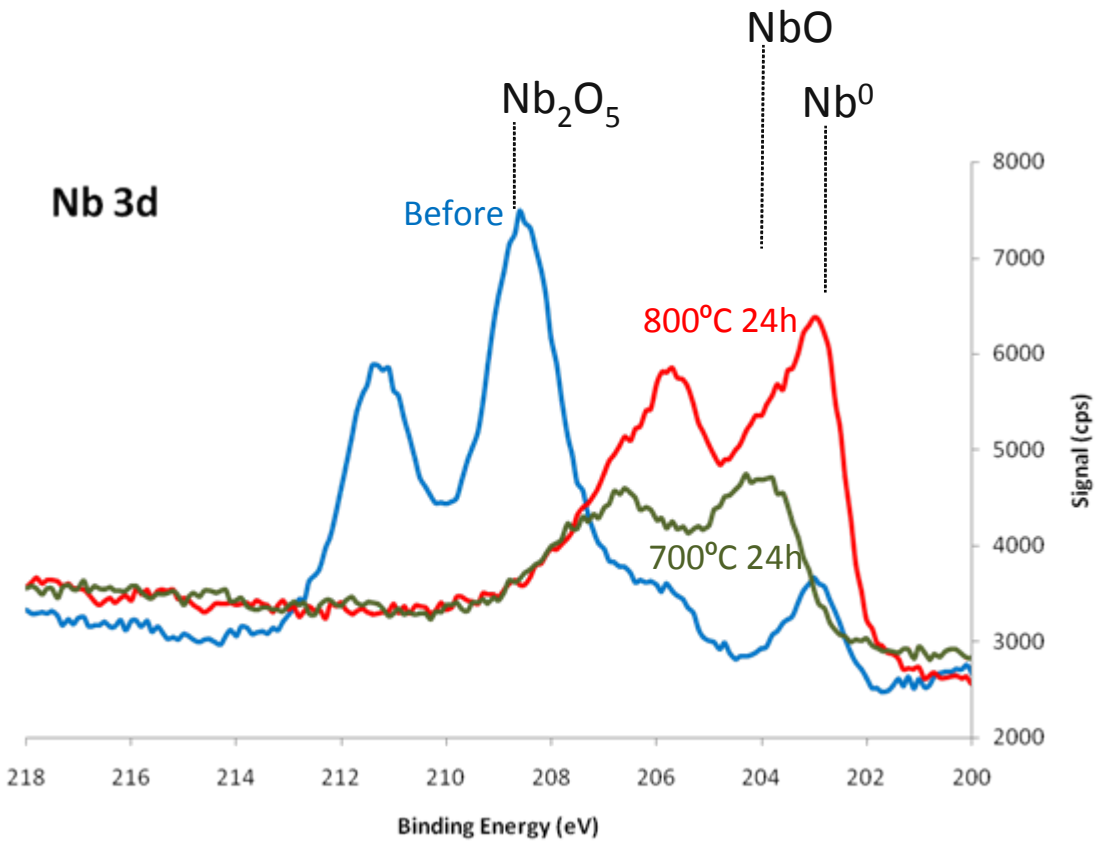




Baking can be used to reduce magnetic scatter) (Green fit vs. red fit)

- The 2.5nm and 3.5nm ALD-capped samples show slightly increased Nb signal – due to Al_2O_3 densification, but no increased oxidation
- 1.5 nm coating showed increased oxidation of underlying Nb (film rupture!)
- Concurrent Ellipsometry (not shown) is consistent with a change in the Niobia film refractive index (oxidation state structure).

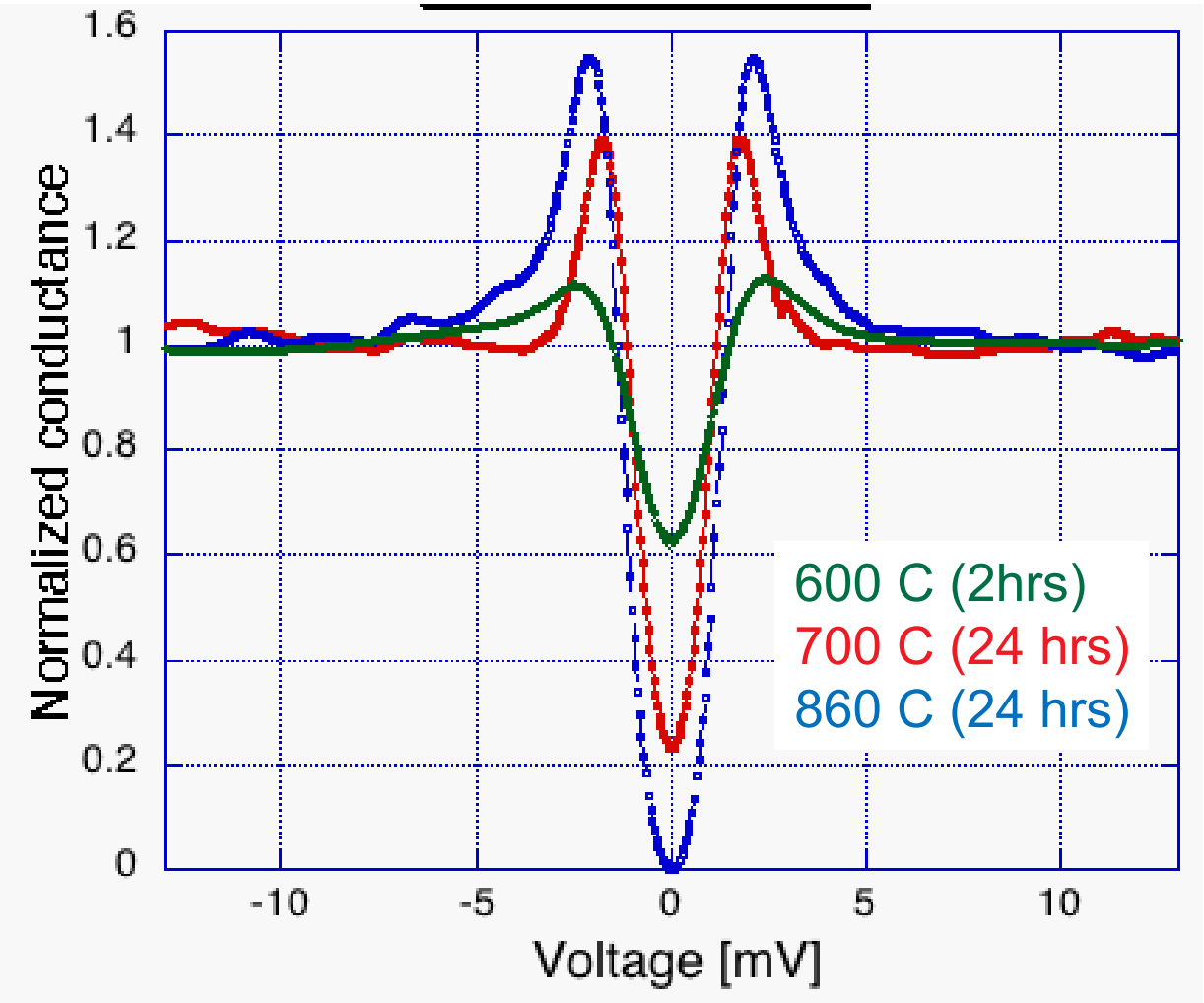
Alumina barrier layer coating – Higher temperatures show significant reduction of underlying Niobium Oxide)



Nb 3d spectra show reduction of oxide with protective ALD coating + heat treatment

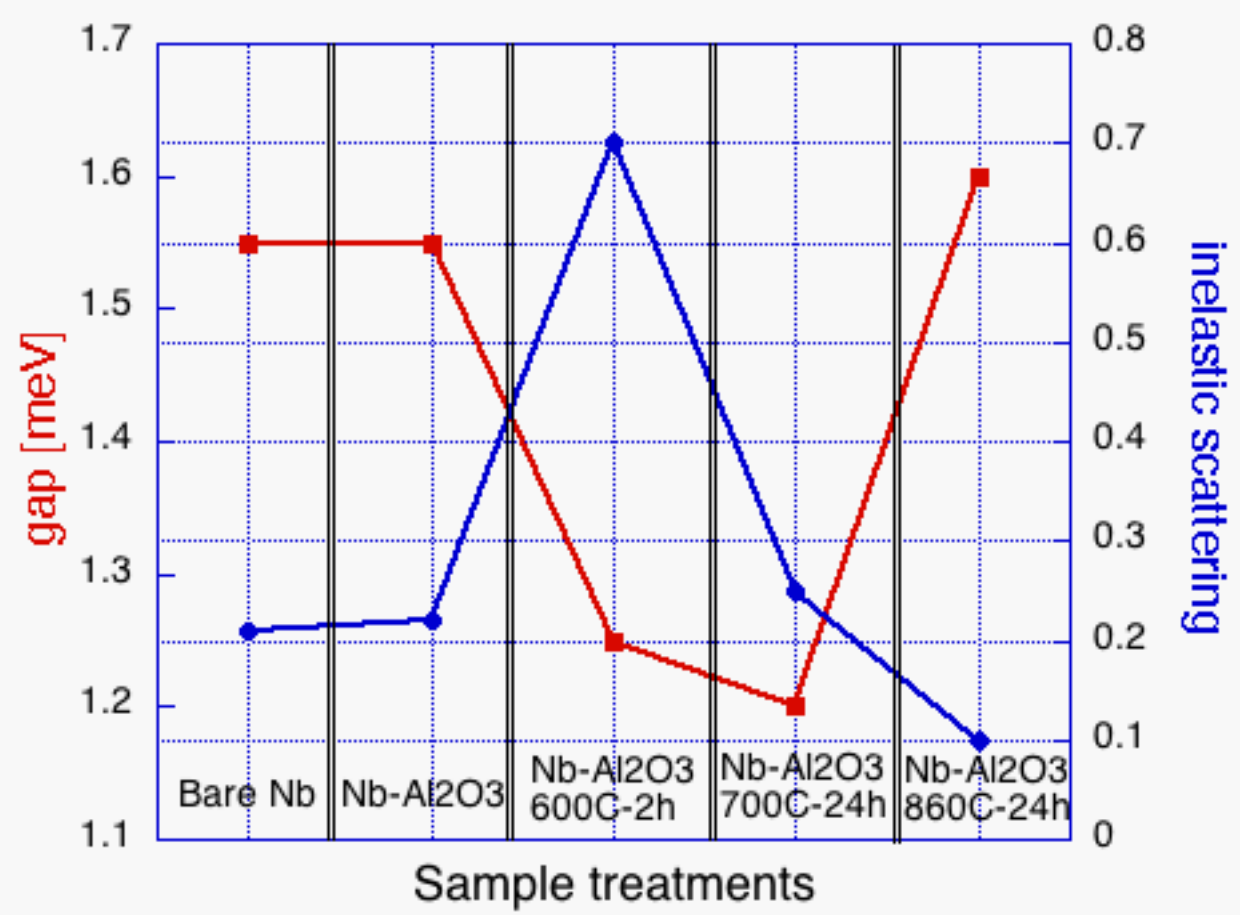
Ohmic Contacts -> Magnetic Losses can be eliminated

- High Temperature Baking of Al_2O_3 (3 nm) overcoated Nb coupon



Summary of baking results

- ALD Capping can stabilize and improve Nb cavity surfaces



Conclusions

- Magnetic Oxides are present and lossy!
- Current cavity post process bake
  - reduces *Oxygen Vacancies* decreasing magnetic oxides.
  - Effect happens for vacuum or air bake

- Preprocess H bake may set up the strain inducing the vacancies.
- ALD alumina capping allows control of oxidation layers with baking.

- Cavity Coating is proceeding.
  - Have a J Lab Cavity (Fermi by December 15)
  - Clean Room Procedures have been established (thanks M. Kelly)
  - ALD Machine design complete.
  - Delay caused by need to anneal at high T (860 C) w/out adding particles.

- The effort is just starting. Going forward there are many opportunities to significantly increase both Q and gradient (even beyond currently accepted materials limits).

How structures fail

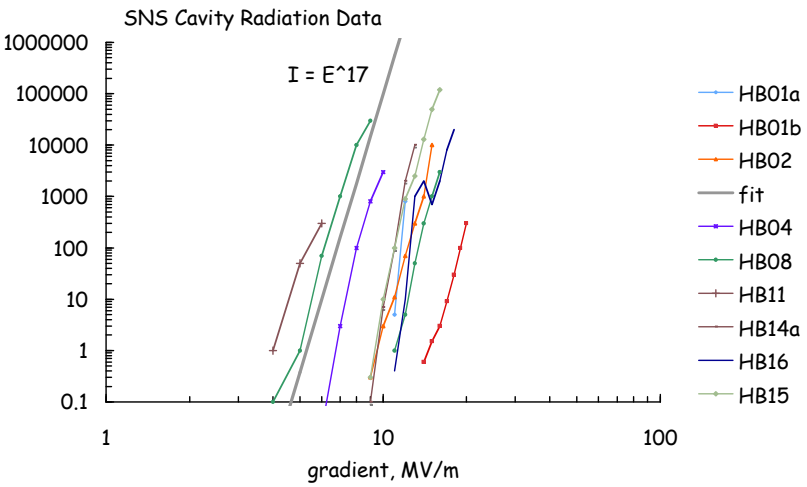
Field emission
Field emitted electrons heat and quenches the superconductor.

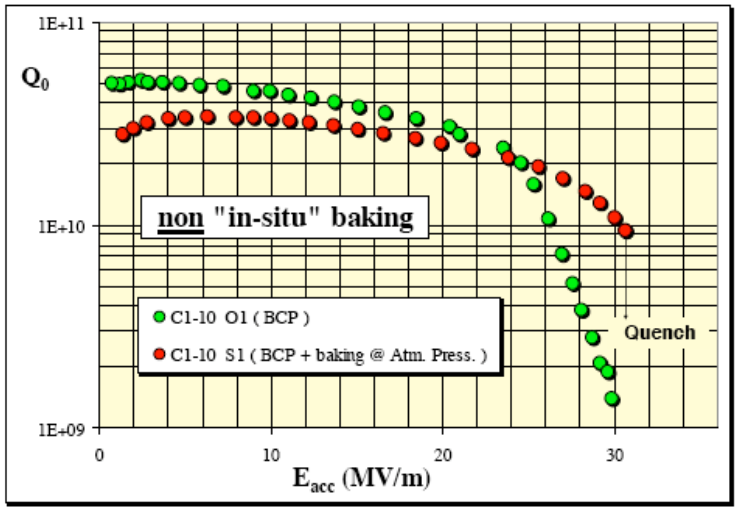
Multipactor
Resonant amplification of low energy electrons.

Quench fields
Cavities quench when $B > 180$ mT

High field Q-slope
Cavity losses rise with impurities and defects.

Thermal
Increased thermal conductivity stabilizes quenches.





Conformal Coating Removes Field Induced Breakdown

Nb ALD Coating

- Synthetic Development Needed
- Radius of Curvature of all asperities

(when polishing is not enough)

ALD can reduce field emission!

- Could allow separation of superconductor and cavity support materials

(allowing increased thermal load, better mechanical stability)

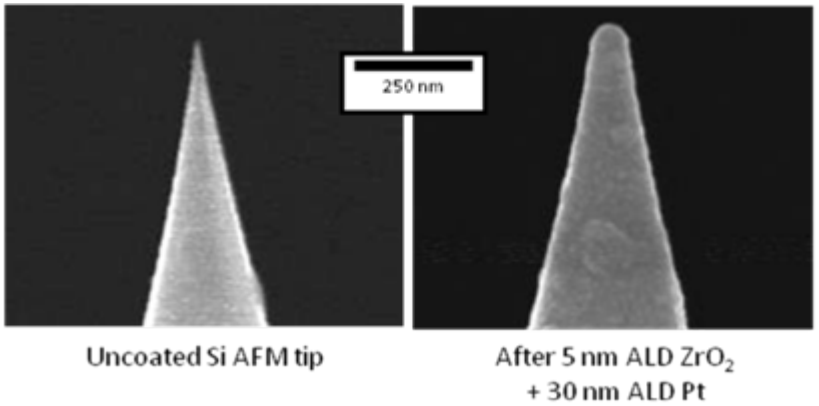
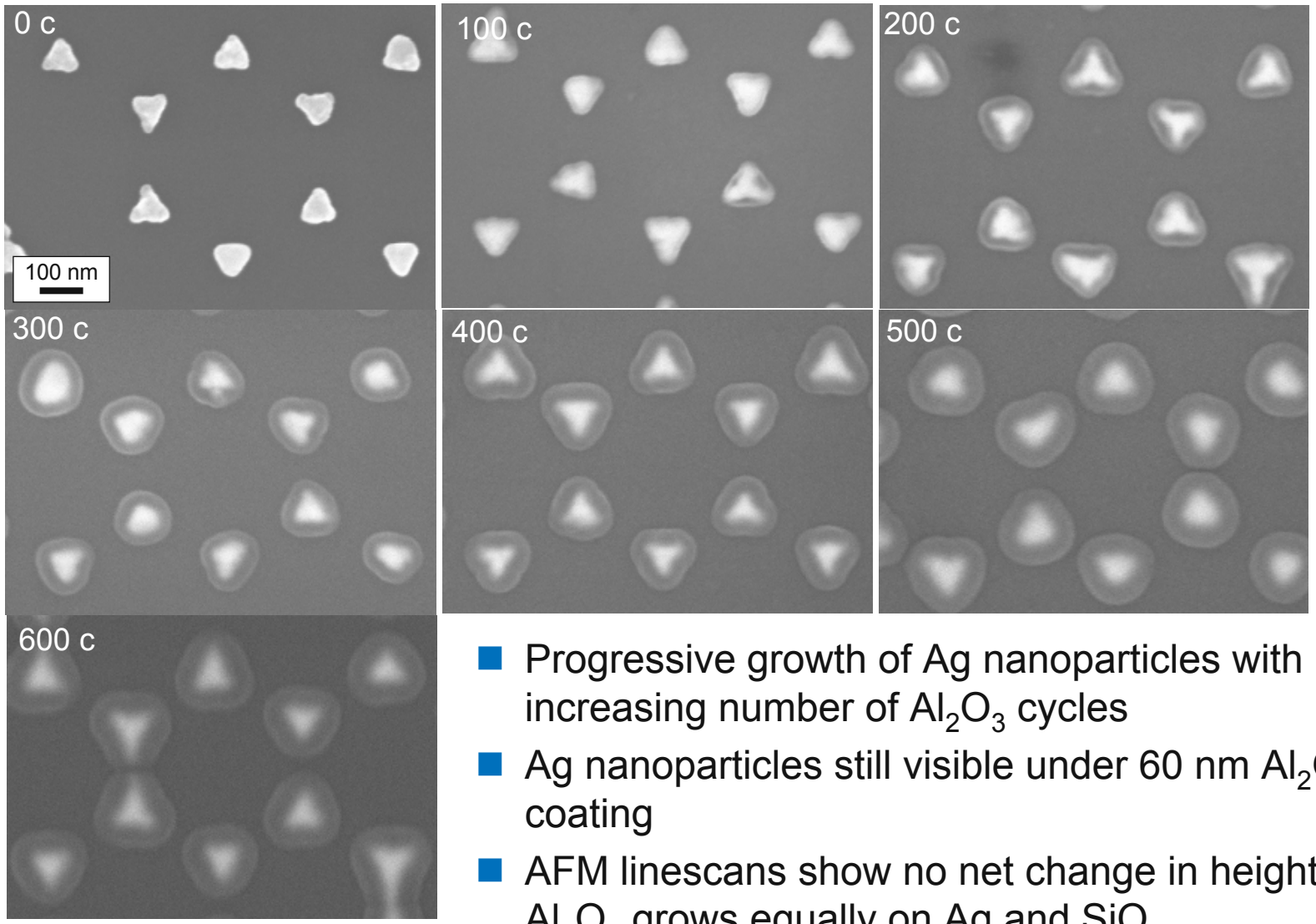


Figure 3: Scanning Electron Microscope images of nearly atomically-sharp tips, before and after coating with a total of 35nm of material by ALD. The tip, initially about 4 nm, has been rounded to 35nm radius of curvature by growth of an ALD film. Rough surfaces are inherently smoothed by the process of conformal coating.

Normal conducting systems (μ cooling, CLIC) can also benefit.

- ~100 nm smooth coatings should eliminate breakdown sites in NCRF.
- Copper is a hard material to deposit, and it may be necessary to study other materials and alloys. Some R&D is required. This is underway.
- The concept couldn't be simpler. Should work at all frequencies, can be *in-situ*.

SEM of LSPR Surfaces Following Al_2O_3 ALD



- Progressive growth of Ag nanoparticles with increasing number of Al_2O_3 cycles
- Ag nanoparticles still visible under 60 nm Al_2O_3 coating
- AFM linescans show no net change in height → Al_2O_3 grows equally on Ag and SiO_2

Multipactering

- Surface secondary electron emission needs to be low.
- The interior surface can be ALD'ed with Pt for instance to reduce electron runaways.

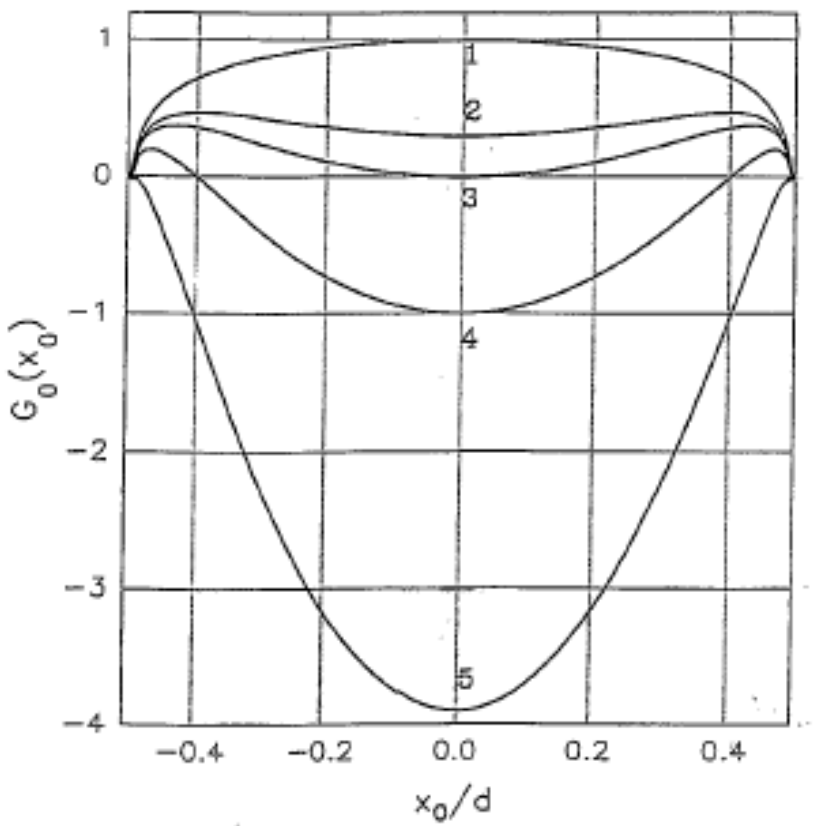
Enhanced lower critical field and surface barrier in films

Use thin films with d < λ to enhance the lower critical field

$$H_{c1} = \frac{2\sqrt{2}\,\phi_0}{\pi d}\left(\ln\frac{d}{\xi} + 0.07\right)$$

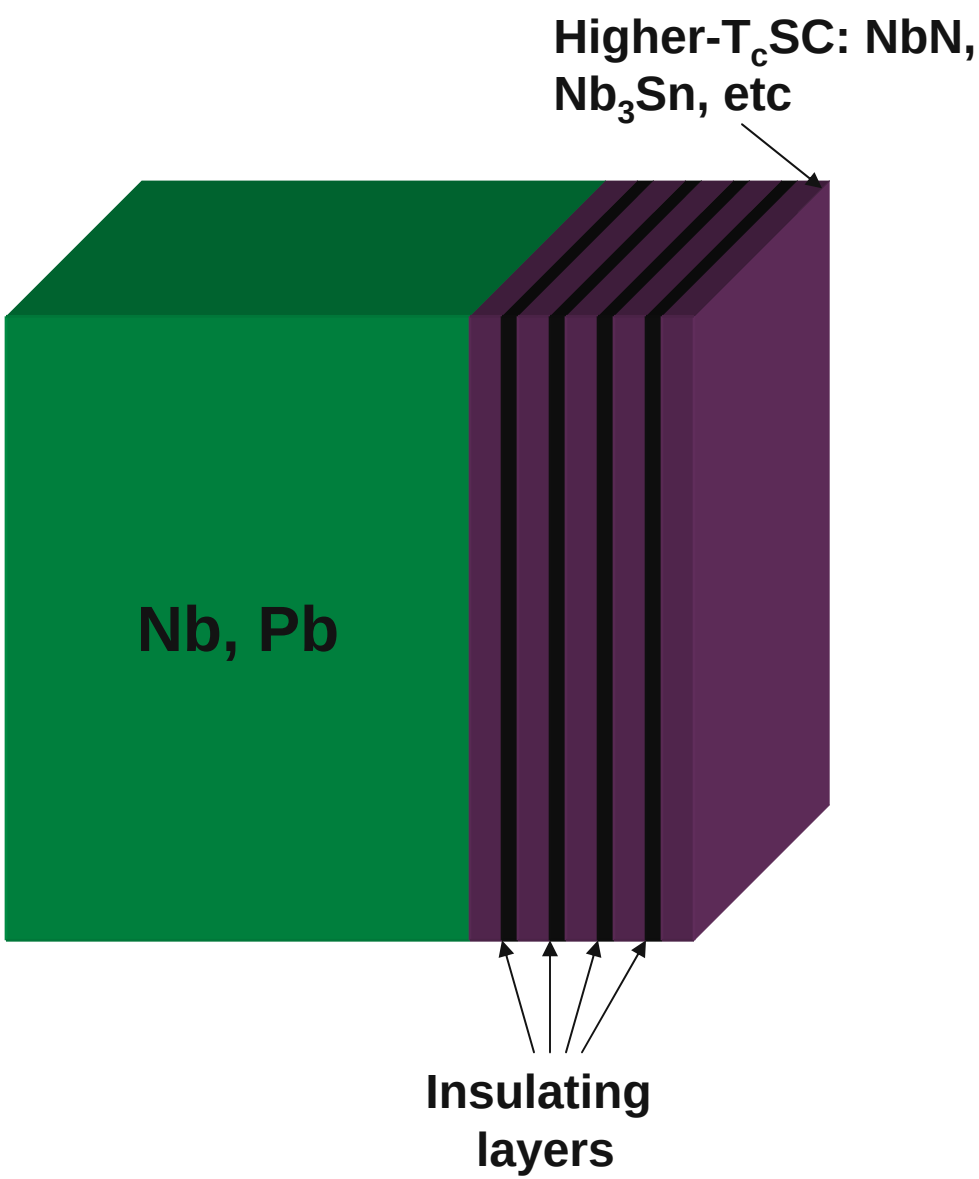
$$H_s = \frac{\phi_0}{2\pi d \xi}$$

Field at which the surface barrier disappears



Example: NbN (ξ = 5nm) film with d = 20 nm has H_{c1} = 4.2T, and H_s = 6.37T, Much better than H_c = 0.18T for Nb

How one can get around small H_{c1} in SC cavities with $T_c > 9.2K$? AG, Appl. Phys. Lett. 88, 012511 (2006)



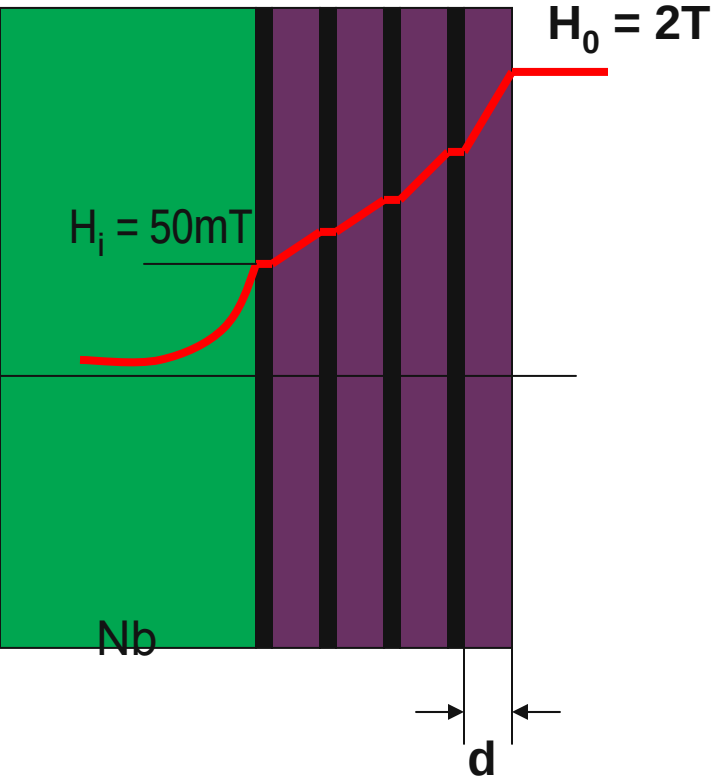
Multilayer coating of SC cavities: alternating SC and insulating layers with $d < \lambda$

Higher T_c thin layers provide magnetic screening of the bulk SC cavity (Nb, Pb) without vortex penetration

For NbN films with d = 20 nm, the rf field can be as high as 4.2 T !

No open ends for the cavity geometry to prevent flux leaks in the insulating layers

How many layers are needed for a complete screening?



Example: Nb_3Sn layers with d = 30nm
λ_0 = 65 nm and H_{c1} = 2.4T

Peak rf field H_0 = 2T < H_{c1}

Internal rf field H_i = 50 mT (high-Q regime)

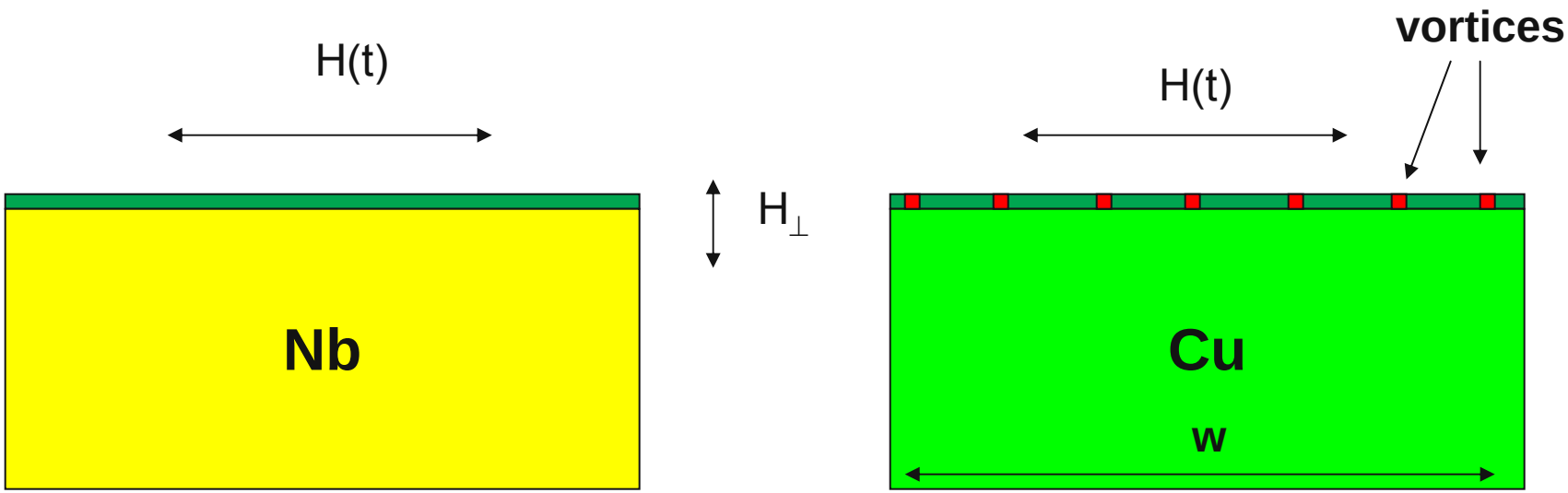
$$H_0 \exp(-\frac{dN}{\lambda_0}) = H_i \qquad \Rightarrow \qquad N = \frac{\lambda_0}{d} \ln \frac{H_0}{H_i}$$

N = (65/30)ln(40) = 8

Strong reduction of the BCS resistance by Nb_3Sn layers due to larger Δ and shorter λ:

$$R_s \propto \frac{\mu_0^2 \omega^2 \lambda^4 \Delta n_0}{k_B T p_F} \left[\ln\left(\frac{\Delta}{\hbar\omega}\right) + C_0 \right] \exp\left(-\frac{\Delta}{k_B T}\right)$$

Why is Nb_3Sn on Nb cavity much better than Nb_3Sn on Cu cavity?



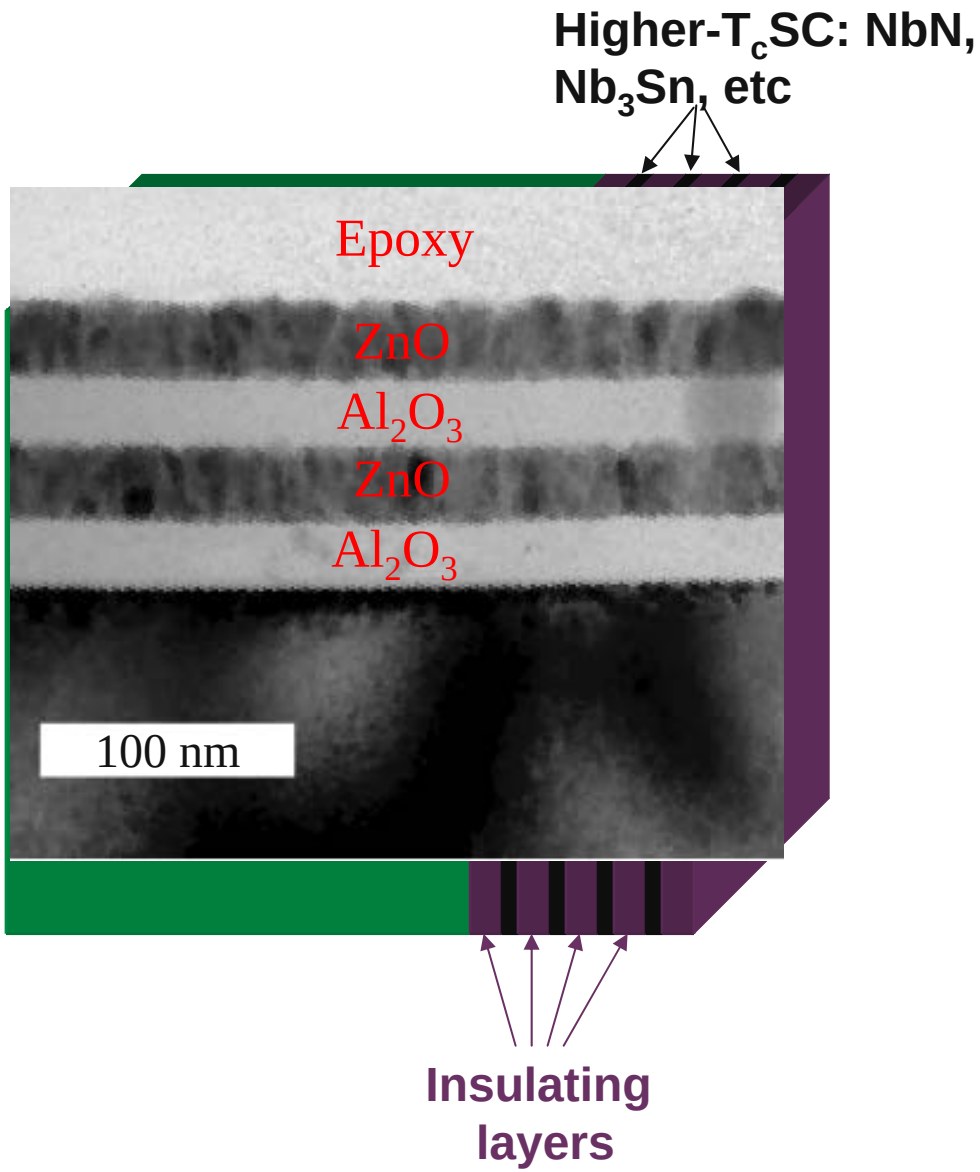
Nb_3Sn/Nb cavity is much better protected against small transverse field components than Nb_3Sn/Cu cavity

Meissner state persists up to $H_\perp < H_{c1}^{(Nb)}$

Meissner state is destroyed for small $H_\perp < (d/w)H_{c1}^{(Nb3Sn)} << H_{c1}^{(Nb3Sn)}$ due to large demagnetization factor $w/d \sim 10^3$-10^5

Q and Gradient Beyond Bulk Material Properties

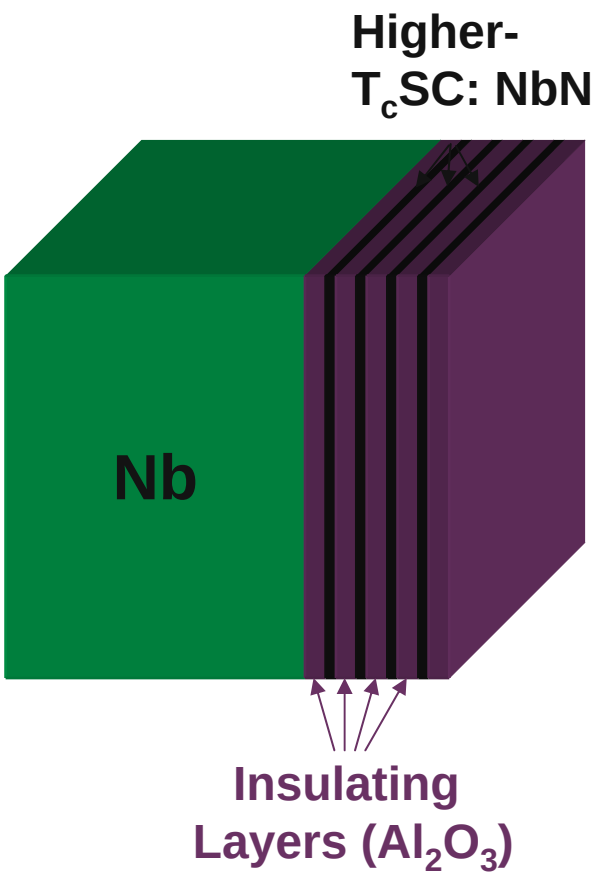
- Build "nanolaminates" of superconducting materials
- ~ 10- 30 nm layer thicknesses
- Significantly improved properties over any "simple" superconductor.
  - 10 fold acceleration gradient improvement
  - 3 fold Q factor (heat load) improvement



Overall Reaction (T = 400 C):

$$3NbCl_5 + 5NH_3 \rightarrow 3NbN + N_2 + 15\ HCl^*$$

- ALD Growth Rate ~ 0.03 nm/cycle NbN per cycle
- NbN ALD nucleates well on Al_2O_3 or SiO_2
- Need to find synthesis conditions for "clean" deposition
- Need to control crystallinity



Van Hoornick et al, Journal of the Electrochemical Society 153 (2006) G437.
Alén et al, Thin Solid Films 491(1-2) (2005) 235.

Separately, the collaborations attack fundamental questions associated with the niobium surface

- Atomic layer deposition
  - Is it possible to passivate niobium permanently to eliminate the problematic variations of niobium oxides?
  - It is possible to exceed the intrinsic SRF limits of niobium?
  - Is it possible to smooth out rough spots?
- Oxidation kinetics
  - Can we understand / predict effects of exposure to air, humidity, and vacuum vs. temperature and time ?
  - Do different niobium crystallographic directions affect the kinetics?
- STM / STS + XPS
  - Are there clear changes of the niobium superconducting gap with respect to location and pollutant?

Coordinated effort has produced a compelling discovery and a potential pathway for breakout

- It is natural for the collaborations to cross-fertilize
- Discovery: the superconducting gap profile can only be explained if *some oxide is magnetic*!
  - Magnetic niobium oxides were known, e.g. early days of HTS
  - Magnetic transitions occur at ~2.5 K for one of the oxides
- Baking (a common post-process fix-up) changes the magnetic oxide content
  - STM of ALD coatings, possibly also in baked spoke cavity (Kelly)
- Implication: since magnetism is antagonistic to superconductivity, magnetic niobium oxide would easily break Cooper pairs and initiate hot spots