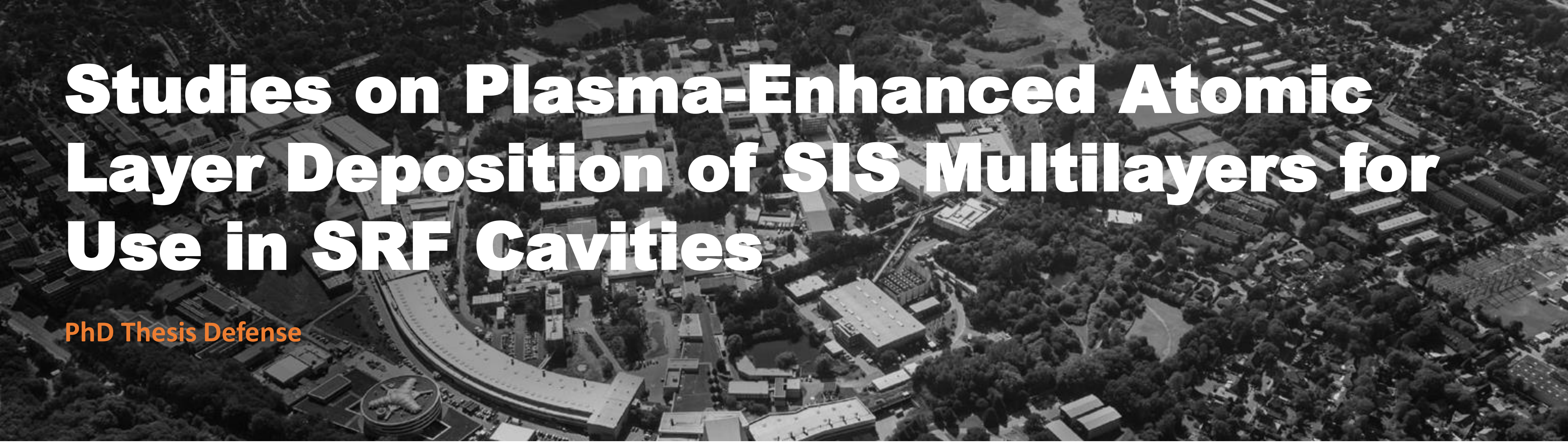


Studies on Plasma-Enhanced Atomic Layer Deposition of SIS Multilayers for Use in SRF Cavities

PhD Thesis Defense

Isabel González Díaz-Palacio

Universität Hamburg

05.03.2025

Superconducting RF (SRF) cavities for beam acceleration

1.3 GHz 9-cell TESLA cavity

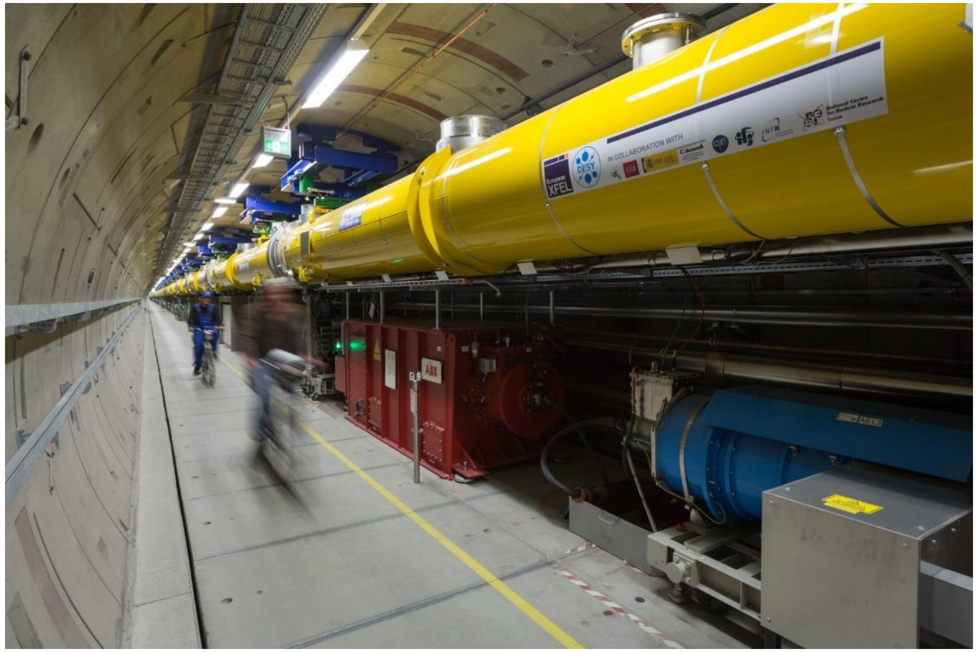
$\sim$ 1 m

ILC Technical Design Report (2013)

$\sim$ 20 cm

Quality factor: $Q_0 \propto \frac{1}{R_S}$ Accelerating gradient: $E_{acc} \propto B_{RF}$

Operating at 2K in the Meissner state

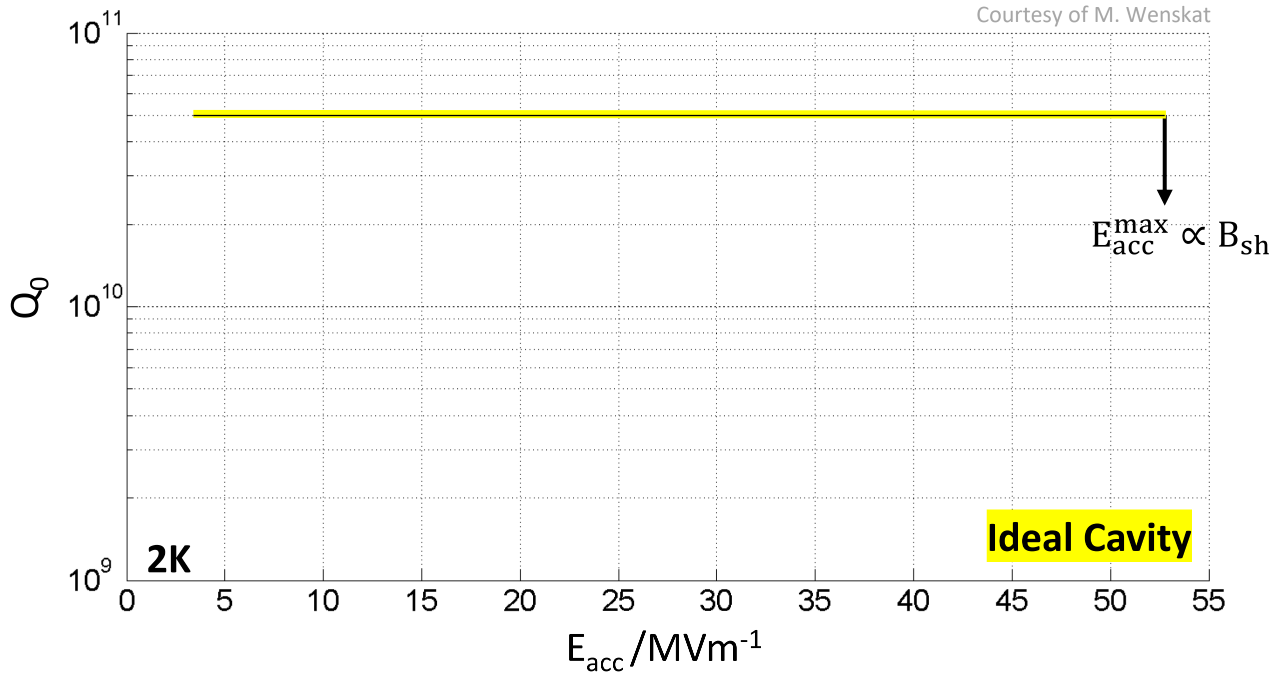


Cryomodule in the Eu-XFEL tunnel https://media.desy.de/

Nb is the material of choice for SRF cavities

Niobium
- $B_{c1} \approx 180$ mT < $B_{sh} \approx 220$ mT< $B_{c2} \approx 400$ mT
- $T_c \approx 9.2$ K
- good thermal, mechanical, and chemical properties

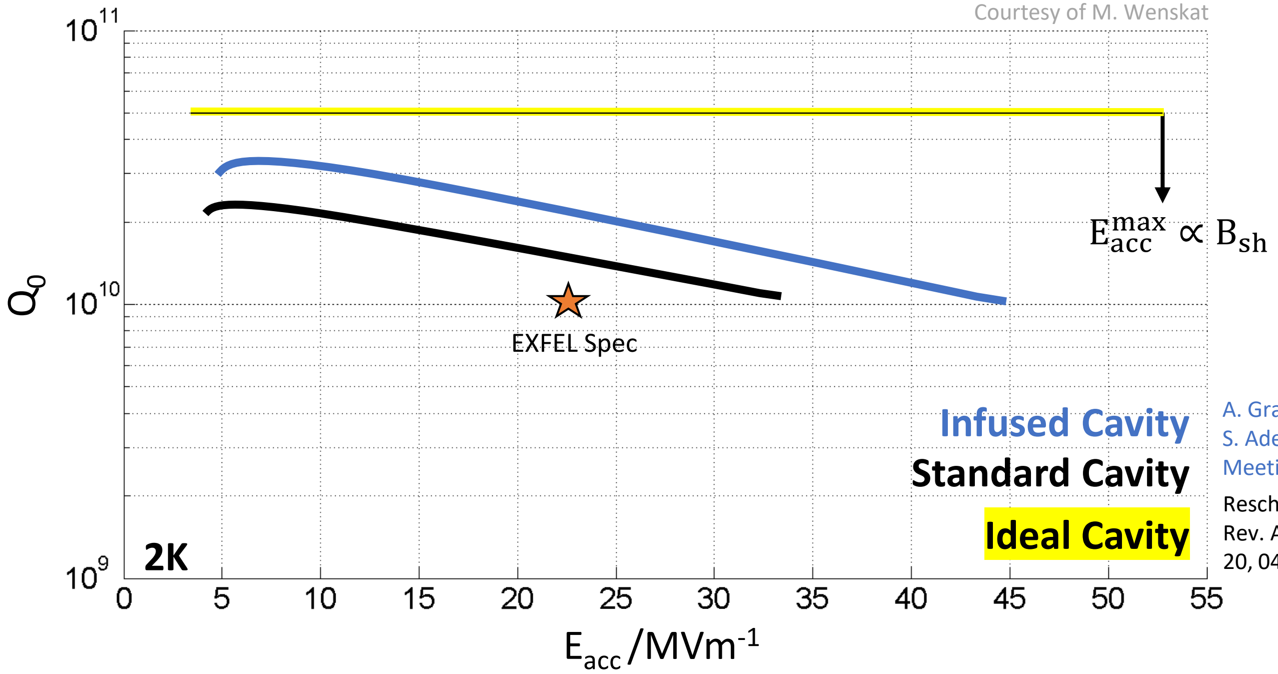
Quality factor: $Q_0 \propto \frac{1}{R_S}$ Accelerating gradient: $E_{acc} \propto B_{RF}$



Cavity surface treatments are crucial for the RF performance

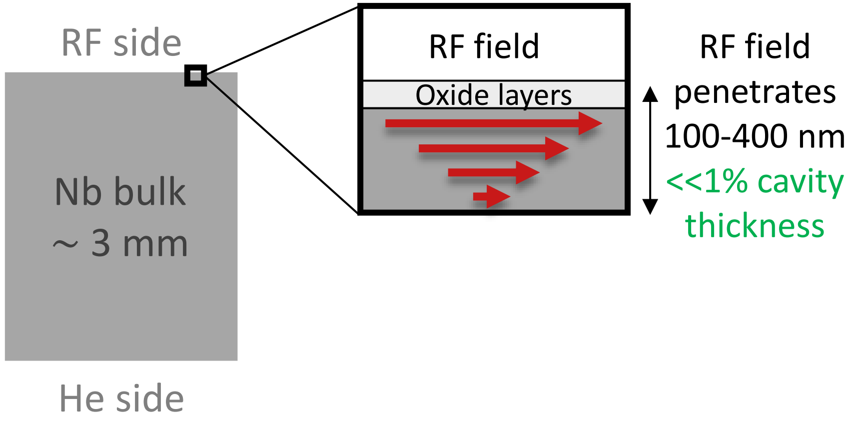
Niobium
- $B_{c1} \approx 180$ mT < $B_{sh} \approx 220$ mT < $B_{c2} \approx 400$ mT
- $T_c \approx 9.2$ K
- good thermal, mechanical, and chemical properties

Quality factor: $Q_0 \propto \frac{1}{R_S}$ Accelerating gradient: $E_{acc} \propto B_{RF}$



A. Grassellino and S. Aderhold. TTC Meeting (2016)

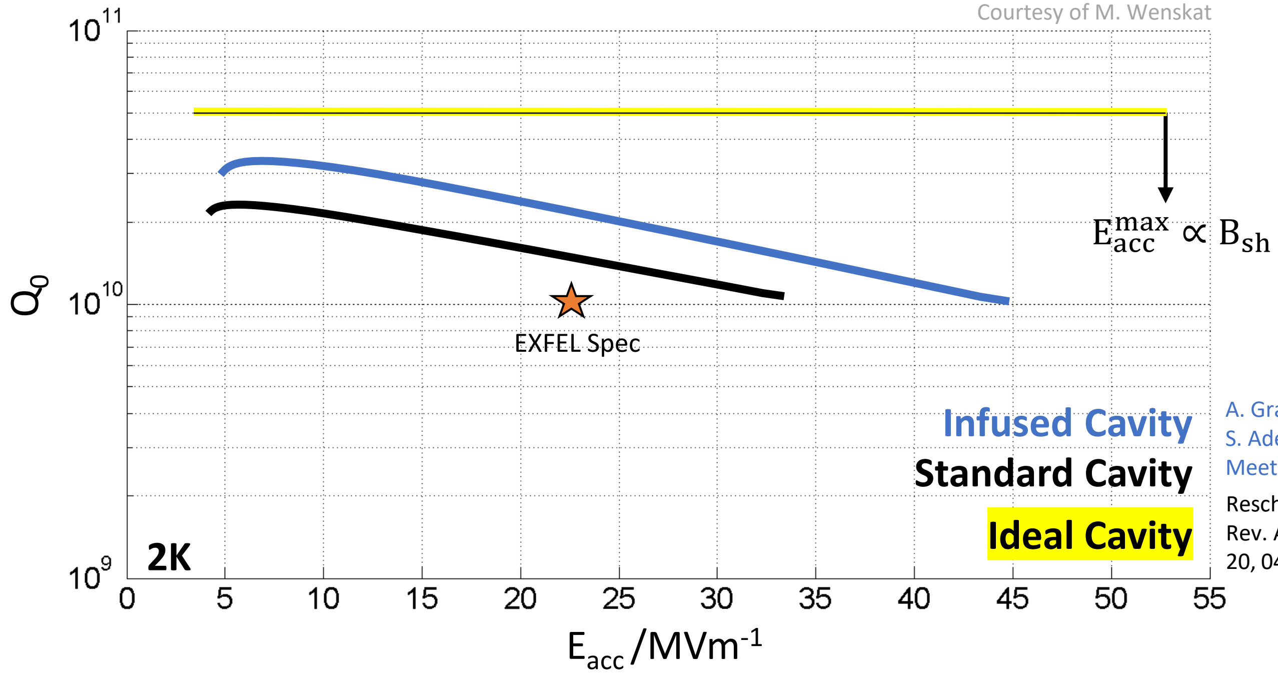
Reschke et al., Phys. Rev. Accel. Beams, 20, 042004 (2017)



Cavity surface treatments are crucial for the RF performance

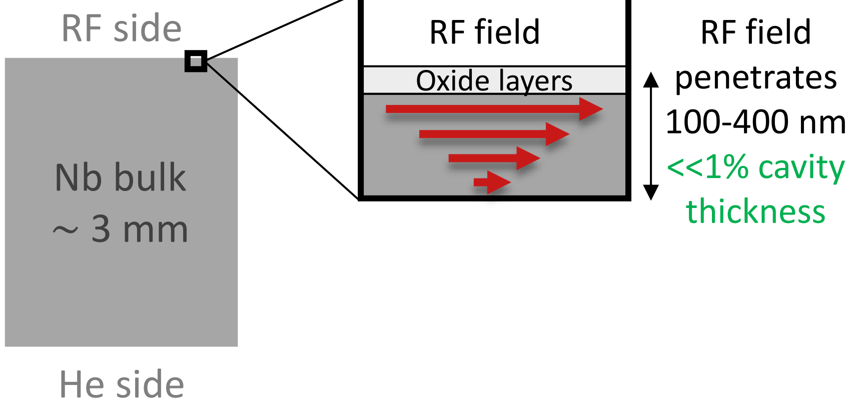
Niobium
- $E_{acc}^{max} \sim 50 - 55\ \mathrm{MV/m}$
- $B_{c1} \approx 180$ mT < $B_{sh} \approx 220$ mT< $B_{c2} \approx 400$ mT
- $T_c \approx 9.2$ K
- good thermal, mechanical, and chemical properties

Quality factor: $Q_0 \propto \frac{1}{R_S}$ Accelerating gradient: $E_{acc} \propto B_{RF}$



A. Grassellino and S. Aderhold. TTC Meeting (2016)

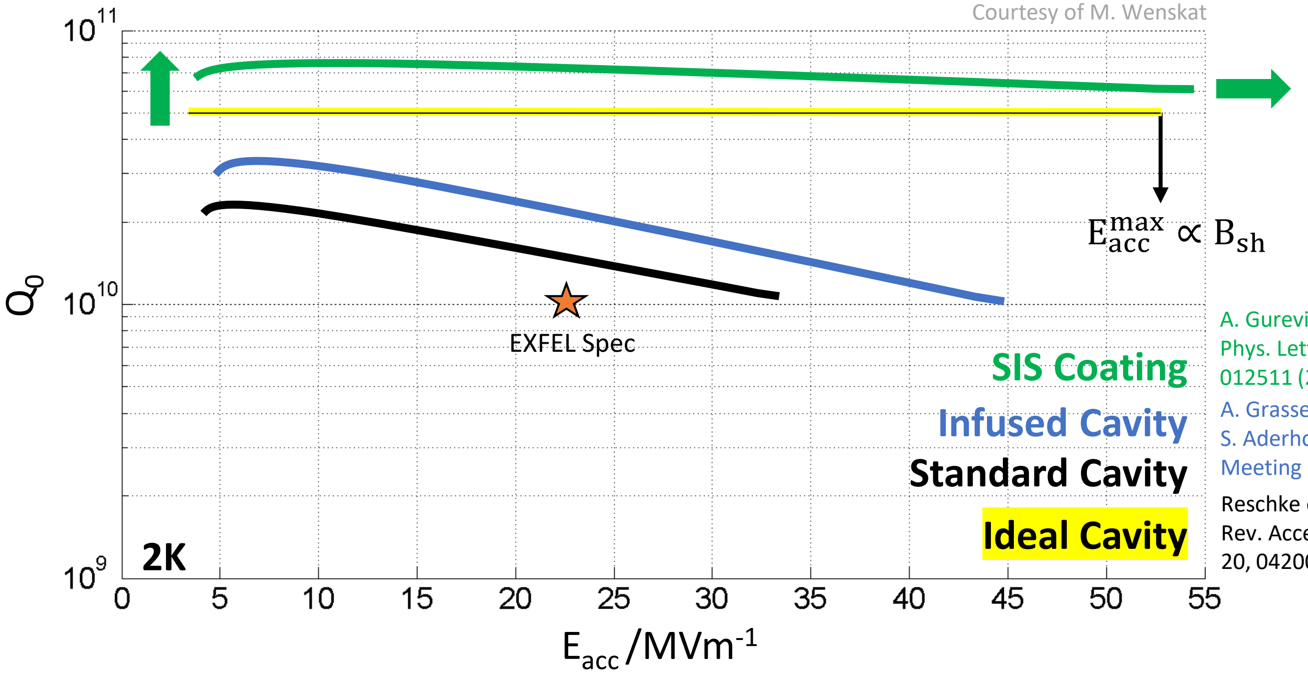
Reschke et al., Phys. Rev. Accel. Beams, 20, 042004 (2017)



Higher accelerating gradients demand → **new strategies beyond bulk Nb**

Pushing SRF cavities performance beyond Nb limits: SIS coating

Quality factor: $Q_0 \propto \frac{1}{R_S}$ Accelerating gradient: $E_{acc} \propto B_{RF}$

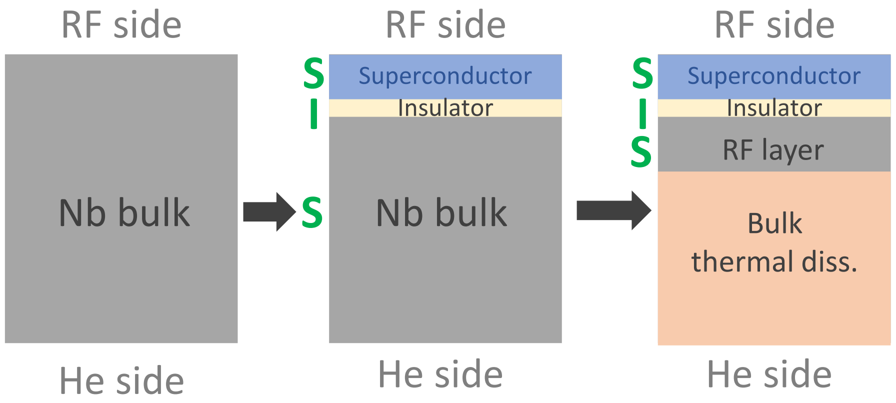


A. Gurevich, Appl. Phys. Lett. 88, 012511 (2006)

A. Grassellino and S. Aderhold. TTC Meeting (2016)

Reschke et al., Phys. Rev. Accel. Beams, 20, 042004 (2017)

Modify the RF surface coating **superconductor-insulator-superconductor** (SIS) multilayers



Future?

S-layer for potential reduction of surface resistance

$B^{Nb}_{c1} \approx 180$ mT ; $B^{Nb}_{c2} \approx 400$ mT

- **Higher $Q_0 \propto \frac{1}{R_S}$**

$$R_S = R_{BCS}(T) + R_{res}$$

Superconductor	Tc (K)	ρ_n ($\mu\Omega$cm)	B_{c1} (mT)	B_{c2} (mT)	λ (nm)
δ-NbTiN	17.8	35	30	20000	150-200
δ-NbN	17.1	70	20	15000	200-350
Nb_3Sn	18.3	50	50	30000	80-100

C.Z. Antoine SRF 2019 Tutorials

Material candidates for I-layer

- I: **AlN**, Al_2O_3, MgO, etc

$$\mathbf{B_{c1}^{layer} > B_{c1}^{Bulk}}$$

$$\mathbf{d_{S-layer} < \lambda_L}$$

SIS multilayers as shielding for Nb cavities

$B^{Nb}_{c1} \approx 180$ mT ; $B^{Nb}_{c2} \approx 400$ mT

- **Higher $\mathbf{Q_0} \propto \frac{1}{R_S}$**

$$R_S = R_{BCS}(T) + R_{res}$$

Superconductor	Tc (K)	ρ_n (μΩcm)	B_{c1} (mT)	B_{c2} (mT)	λ (nm)
δ-NbTiN	17.8	35	30	20000	150-200
δ-NbN	17.1	70	20	15000	200-350
Nb_3Sn	18.3	50	50	30000	80-100

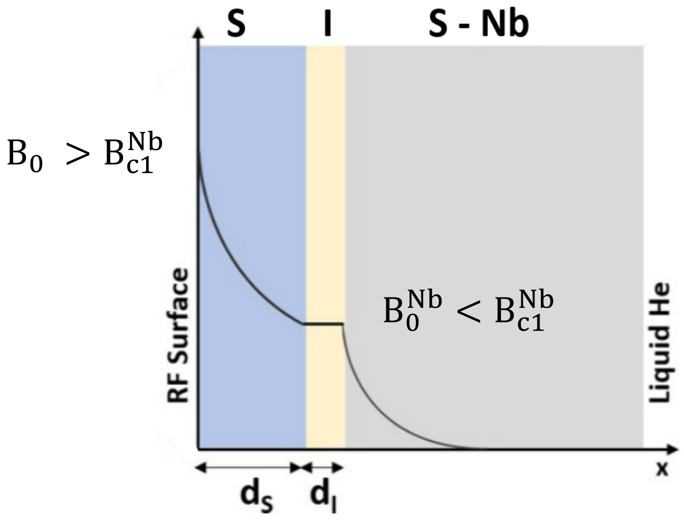
C.Z. Antoine SRF 2019 Tutorials

Material candidates for I-layer
- I: **AlN**, Al_2O_3, MgO, etc

$$\mathbf{B^{layer}_{c1} > B^{Bulk}_{c1}}$$

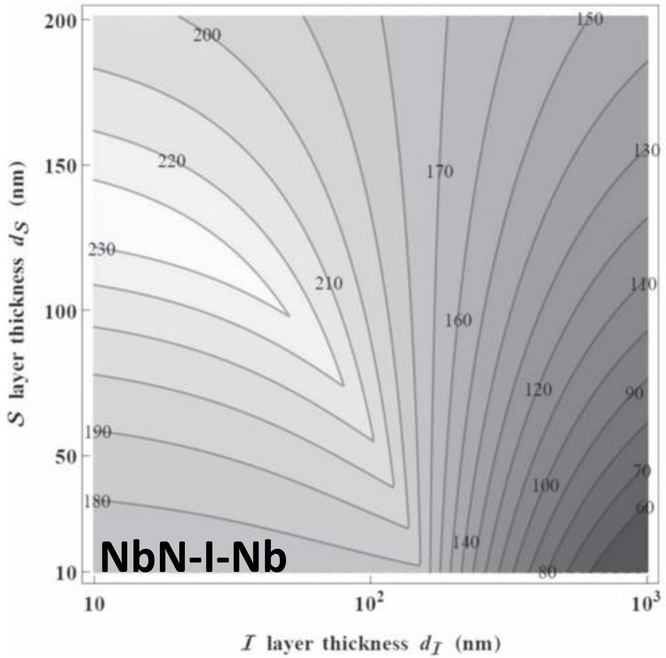
$$\mathbf{d_{S-layer} < \lambda_L}$$

- **Higher $\mathbf{E_{acc}} \propto B_{RF}$**



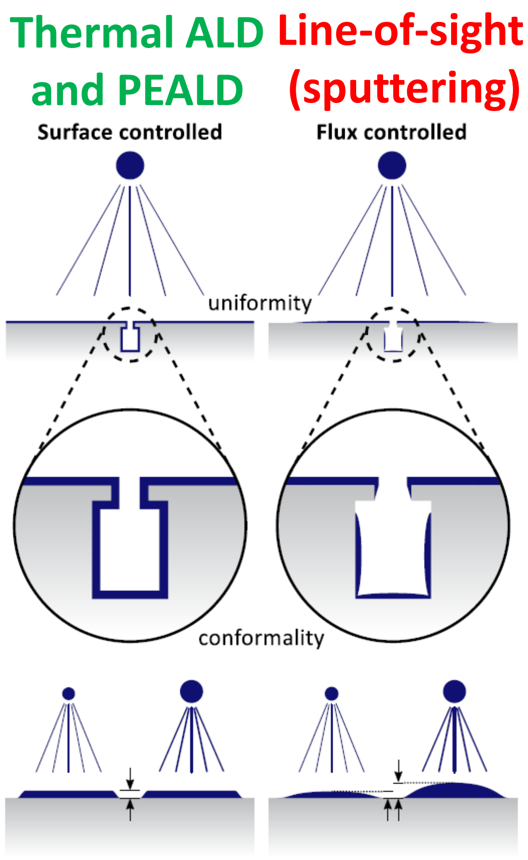
The shielding effect increases with the number of multilayers $\mathbf{(SI)^N - S}$

Kubo 2017 *Supercond. Sci. Technol.* **30** 023001



The SIS multilayer approach requires experimental validation

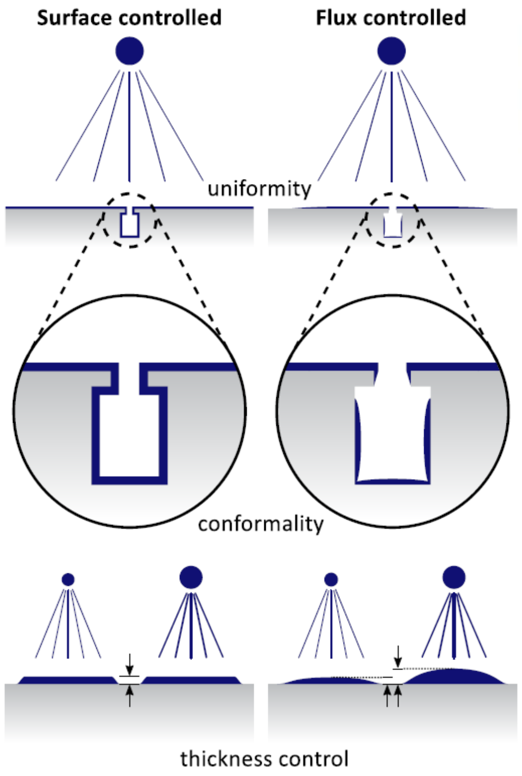
Smooth, homogeneous, and conformal deposition is required



Arts, K. (2021) Eindhoven University of Technology

Line-of-sight: difficult to scale up to cavity geometry

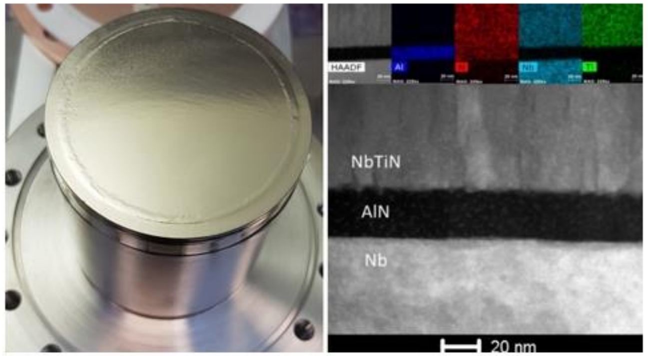
Thermal ALD and PEALD | **Line-of-sight (sputtering)**



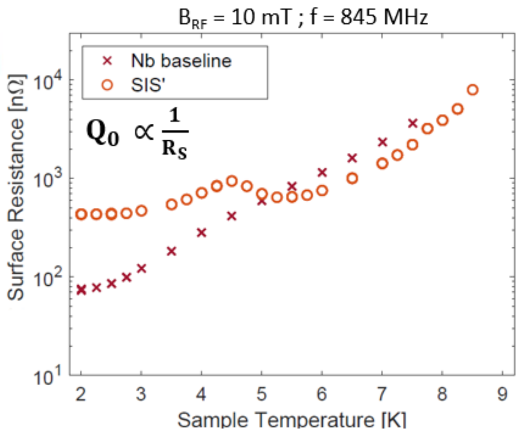
Arts, K. (2021) Eindhoven University of Technology

Progress on planar samples

AlN-NbTiN by DC magnetron sputtering

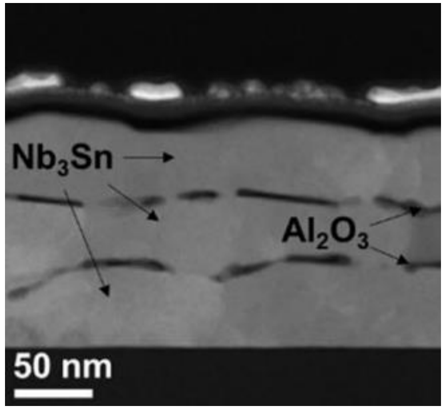


S. Keckert (2019), Dissertation, Universität Siegen



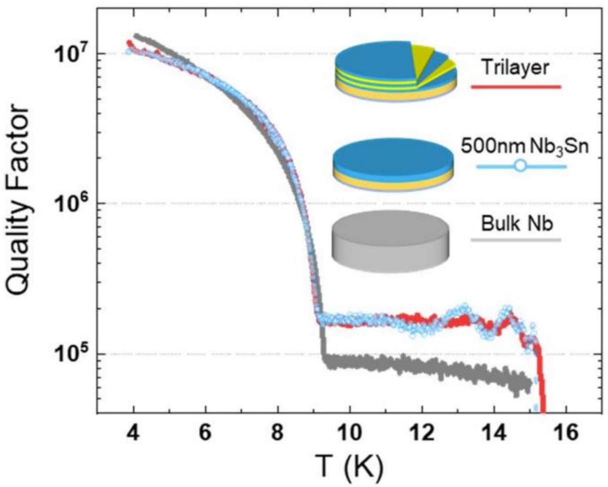
Nb_3Sn/Al_2O_3

by DC magnetron sputtering



Sundahl, C., *Sci Rep* **11**, 7770 (2021)

B_{RF} = 30 µT ; f = 11.4 GHz

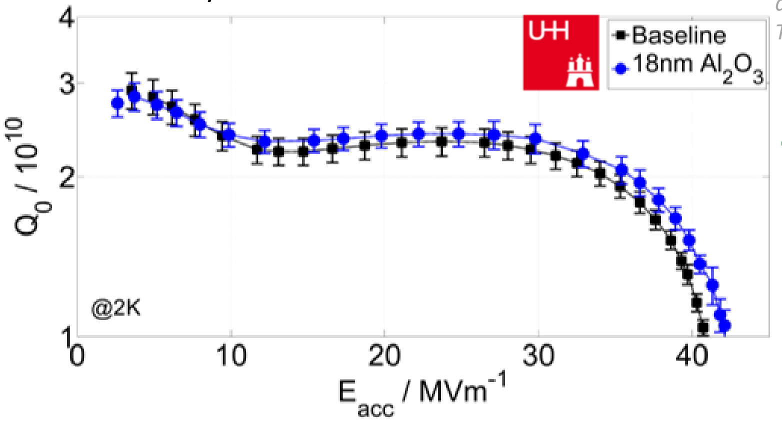


Thermal ALD and PEALD: easier to scale up to cavity geometry

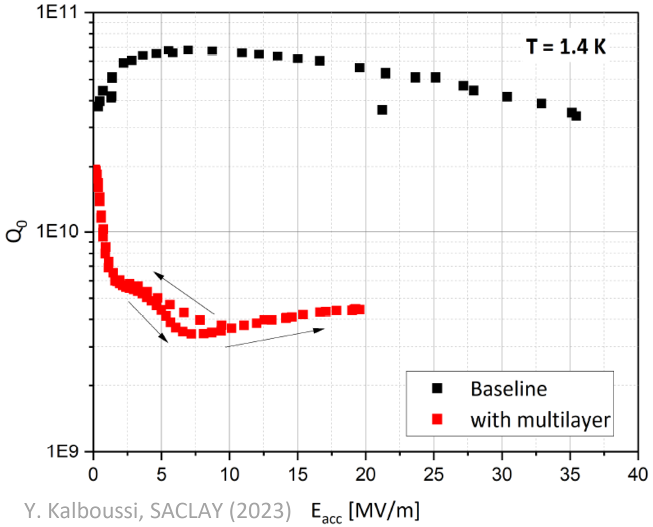
Progress on cavities

Al_2O_3 by thermal ALD

Marc Wenskat *et al* 2023 *Supercond. Sci. Technol.* **36** 015010



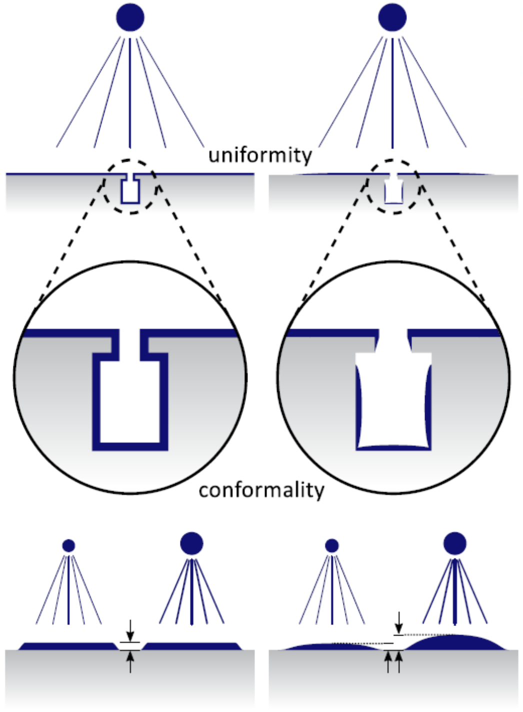
NbTiN/AlN by thermal ALD



Y. Kalboussi, SACLAY (2023)

Thermal ALD and PEALD
Surface controlled

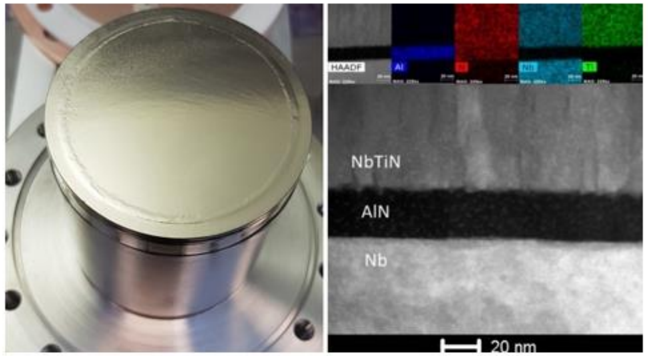
Line-of-sight (sputtering)
Flux controlled



Arts, K. (2021) Eindhoven University of Technology

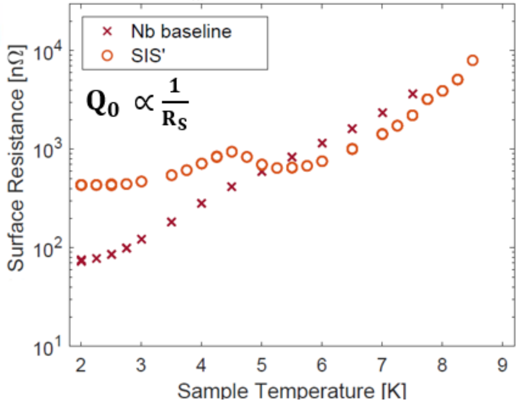
Progress on planar samples

AlN-NbTiN by DC magnetron sputtering



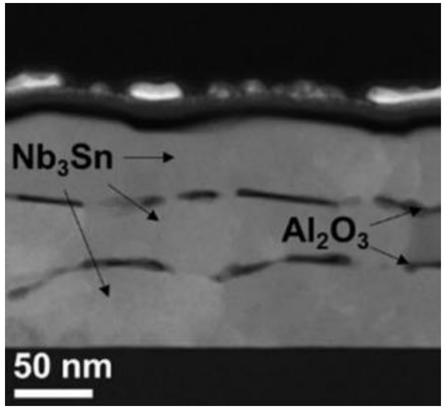
S. Keckert (2019), Dissertation, Universität Siegen

B_{RF} = 10 mT ; f = 845 MHz



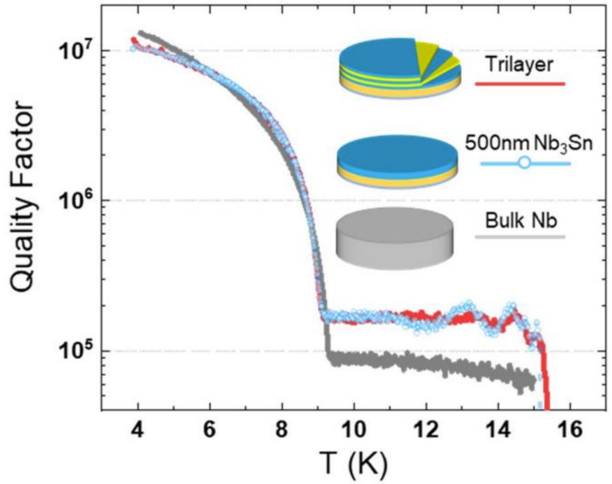
Nb_3Sn/Al_2O_3

by DC magnetron sputtering



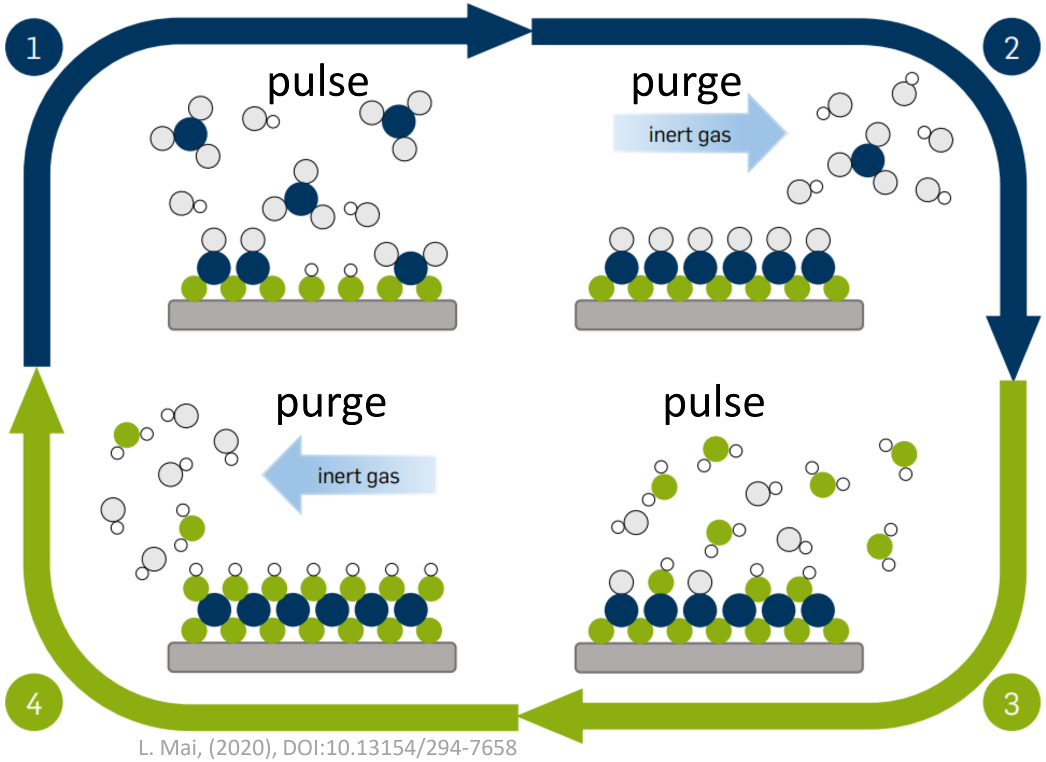
Sundahl, C., *Sci Rep* **11**, 7770 (2021)

B_{RF} = 30 µT ; f = 11.4 GHz



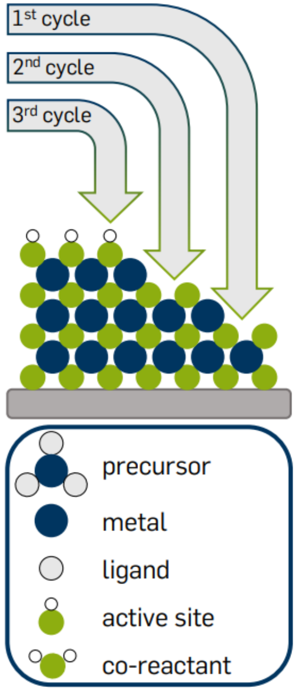
Thermal ALD vs plasma-enhanced ALD (PEALD)

Thermal ALD cycle



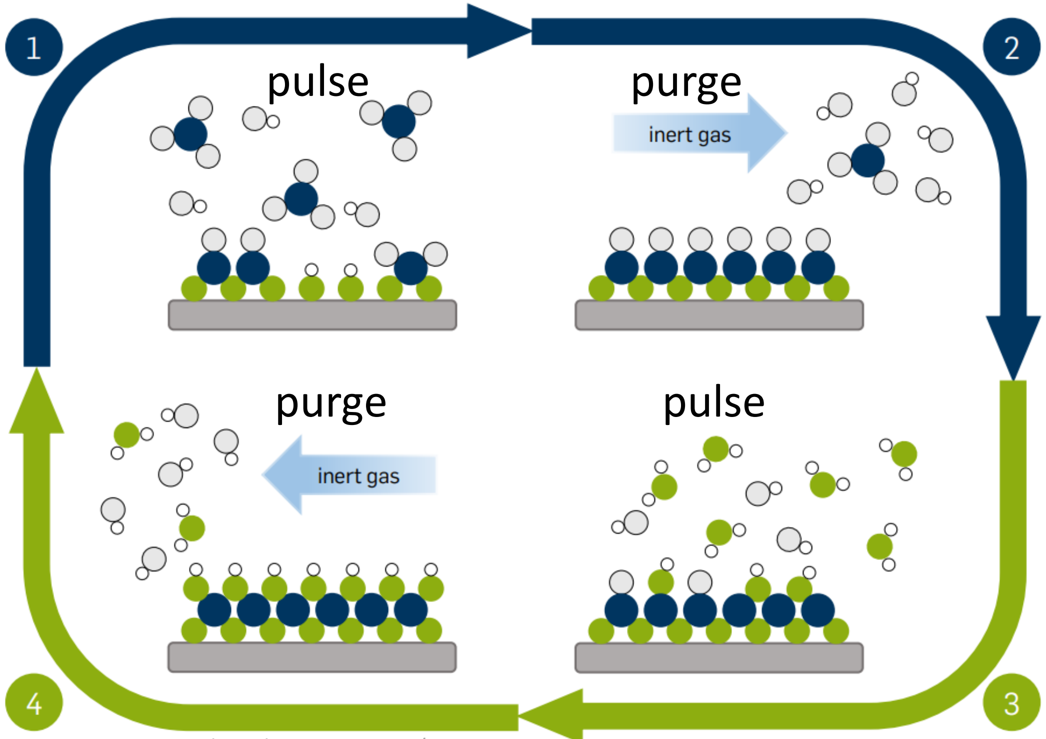
L. Mai, (2020), DOI:10.13154/294-7658

Growth per cycle (GPC)



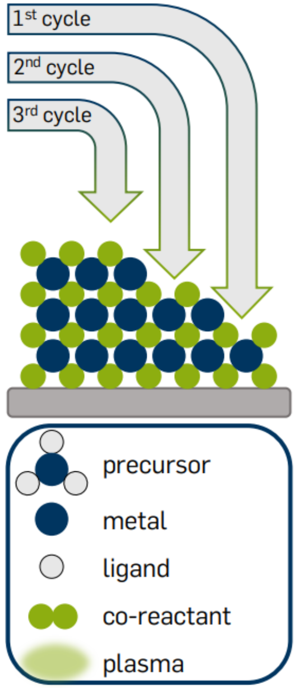
Thermal ALD vs plasma-enhanced ALD (PEALD)

Thermal ALD cycle

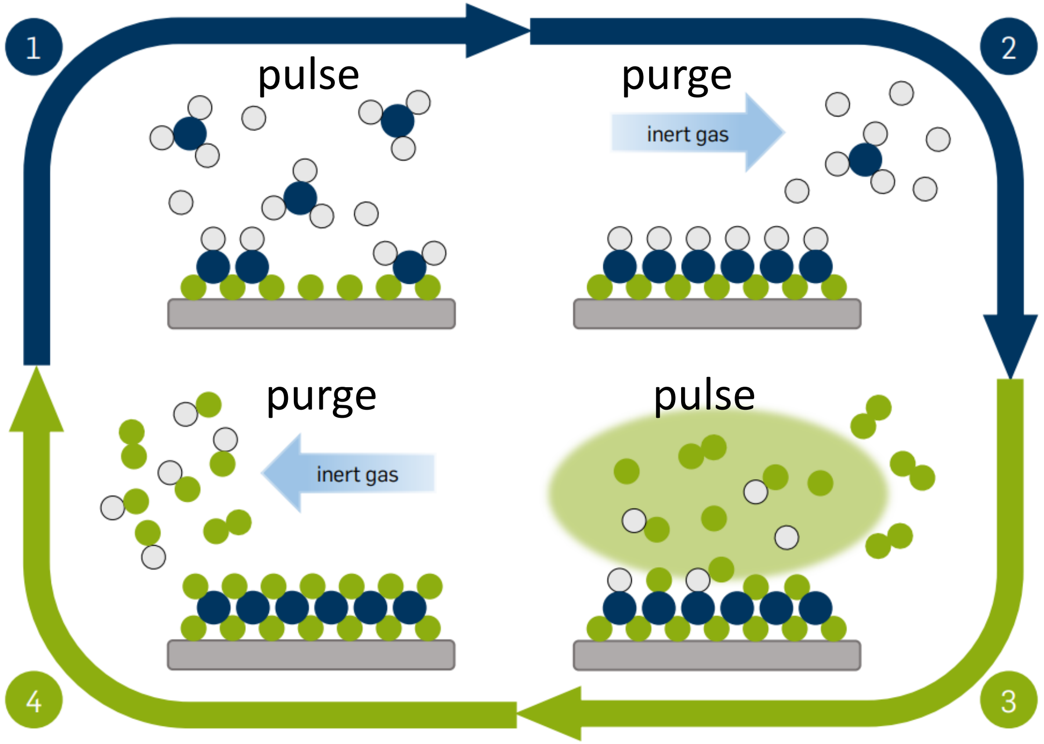


L. Mai, (2020), DOI:10.13154/294-7658

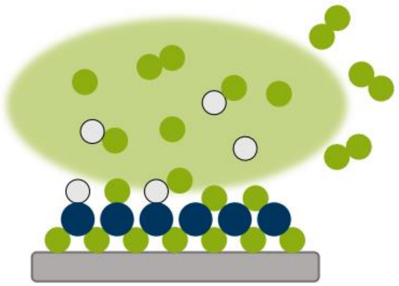
Growth per cycle (GPC)



PEALD cycle



The role of plasma species in PEALD

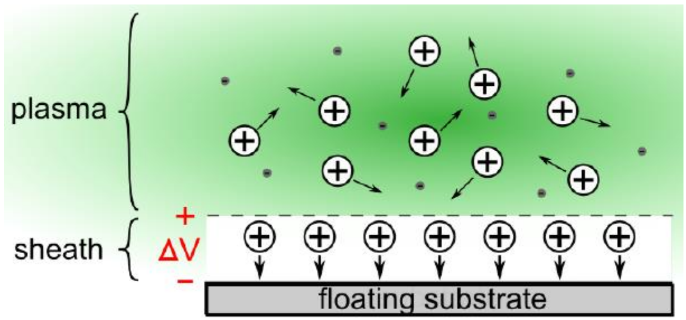


Plasma species

e⁻ — ions — excited species — **radicals**

deliver high **reactivity** and energy to the surface without heating the substrate

the flux of ions is anisotropic



Kessels, E. (2023) PEALD AVS Seminar

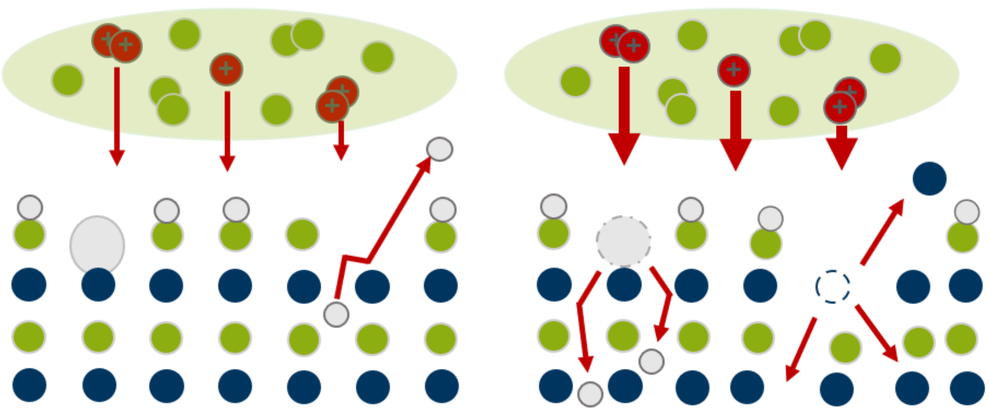
MERITS

- ✓ Reduced deposition temperature
- ✓ Increased choice of precursors
- ✓ Improved material properties
  (*better crystallinity, denser films, reduced impurities*)

LIMITATIONS

- Plasma-induced damage (ions, radiation)
- Conformality limited (radical recombination, ion flux)
- Additional complexity

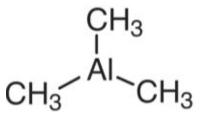
Beneficial effect **Detrimental effect**

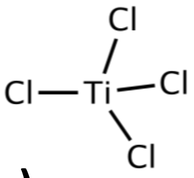


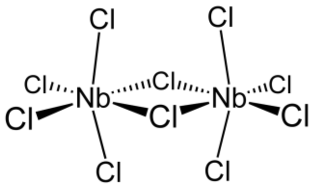
Thermal ALD vs PEALD of AlN and NbTiN

Thermal ALD cycle

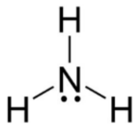
1 **TMA** **$TiCl_4$** **$NbCl_5$**







3 **Ammonia (NH_3)** = =



AlN **TiN** **NbN**

NbTiN Supercycle

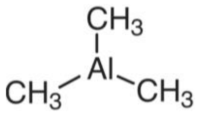
*combine individual ALD cycles

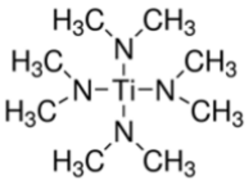
Drawbacks

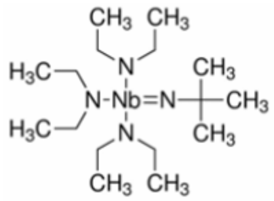
- Deposition temperature 450 °C
- Additional reducing Zn pulse
- HCl byproducts and Cl impurities
- $NbCl_5$ etches TiN – more TiN cycles

PEALD cycle

1 **TMA** **TDMAT** **TBTDEN**







3 **H_2/N_2** = =

AlN **TiN** **NbN**

NbTiN Supercycle

*combine individual ALD cycles

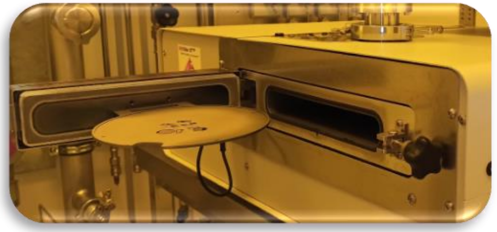
Benefits

- Lower deposition temperature < 300 °C
- Potential impurities are C and H
- Expected higher crystalline order

Growing AlN-NbTiN multilayers by PEALD on planar substrates

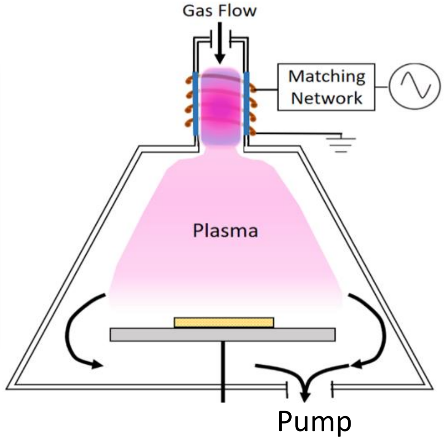
<u>PEALD setup:</u> GEMStar XT-P remote inductively-coupled plasma (**ICP**)

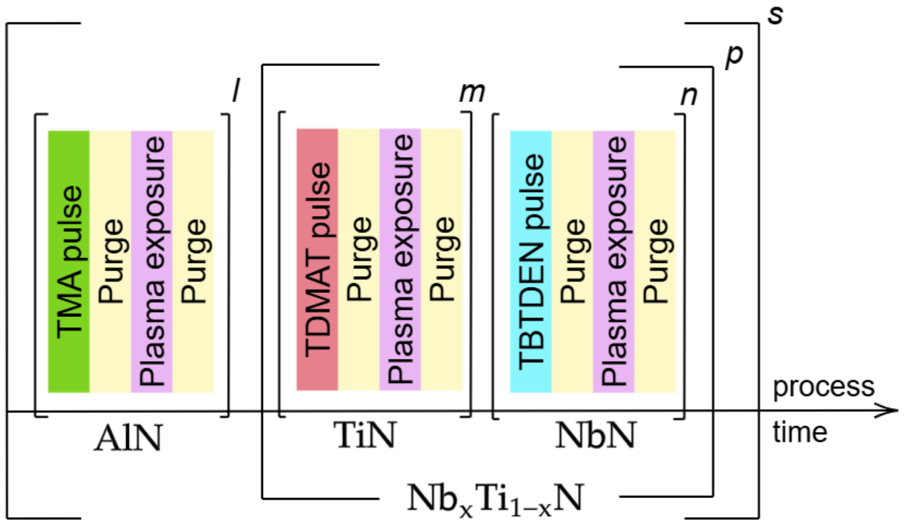
Deposition at 250 °C



Planar substrates

Boris *et al.*, J. Vac. Sci. Technol. A 38, 040801 (2020)



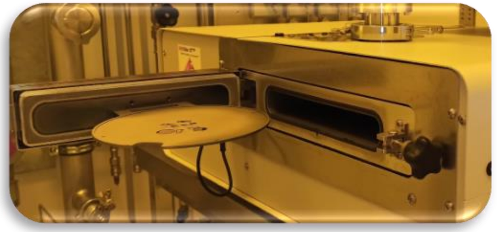


Supercycle

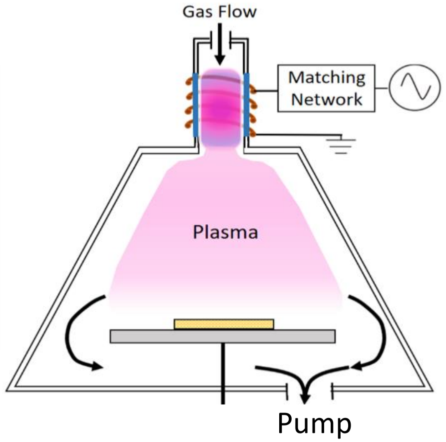
Growing AlN-NbTiN multilayers by PEALD on planar substrates

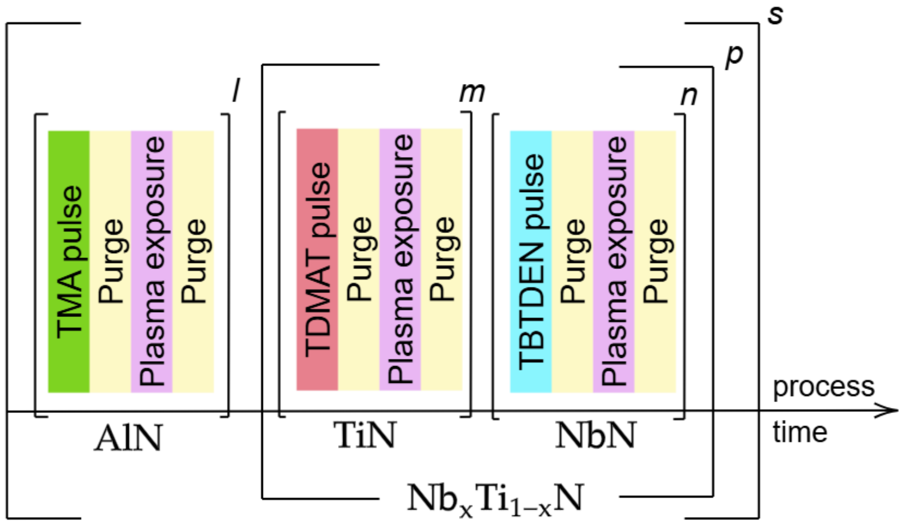
PEALD setup: GEMStar XT-P remote inductively-coupled plasma (**ICP**)

Deposition at 250 °C



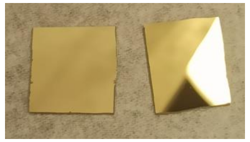
Boris *et al.*, J. Vac. Sci. Technol. A 38, 040801 (2020)





Supercycle

Planar substrates



Si wafers: XRR, EDS, XPS, XRD, ETO, VSM, SEM, STEM, AFM

Standard cavity surface preparation

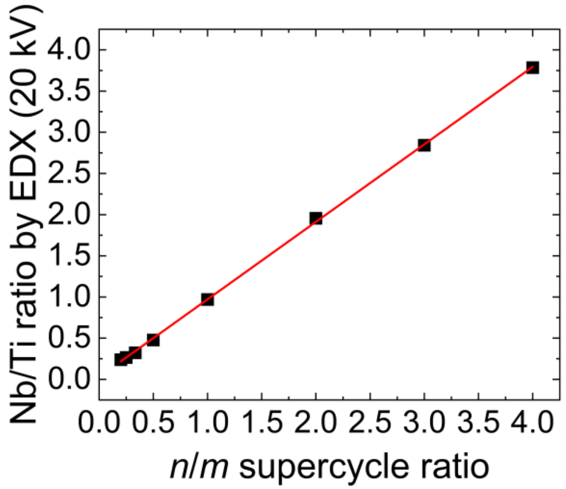
Nb substrates: SAED, STEM, SEM, EDS, VSM, T_c station

Characterization

Tailoring NbTiN films

- $Nb_xTi_{1-x}N$ films of various compositions varying the ratio of NbN to TiN cycles (*n* to *m*) inside the supercycle

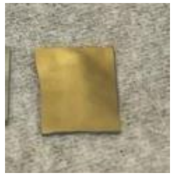
V. Palmieri SRF Workshop 2001

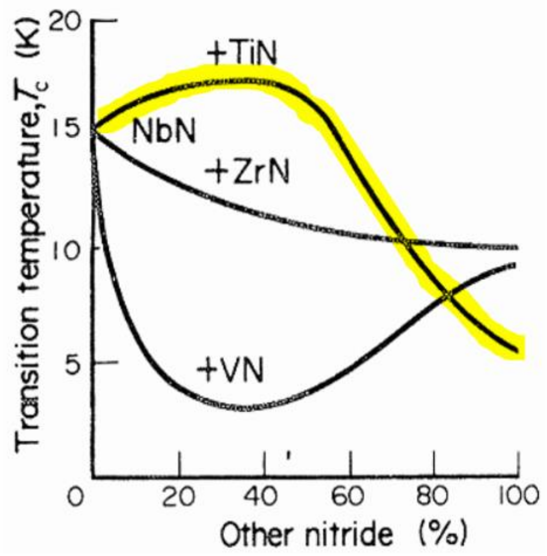


PEALD offers good control over the elemental composition

Optimal composition

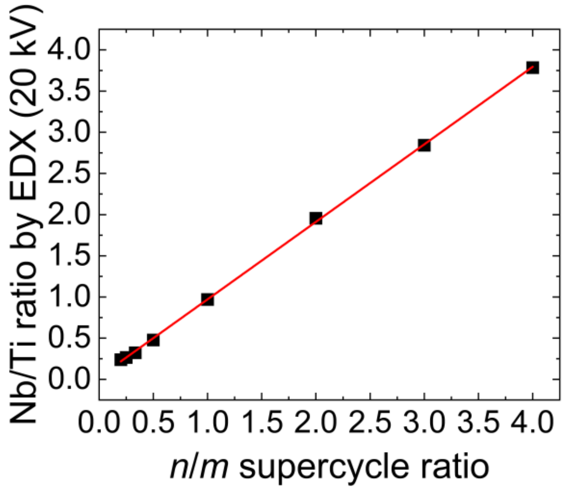
$Nb_{0.75}Ti_{0.25}N$





Tailoring NbTiN films

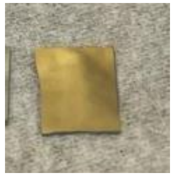
- $Nb_xTi_{1-x}N$ films of various compositions varying the ratio of NbN to TiN (*n* to *m*) inside the supercycle



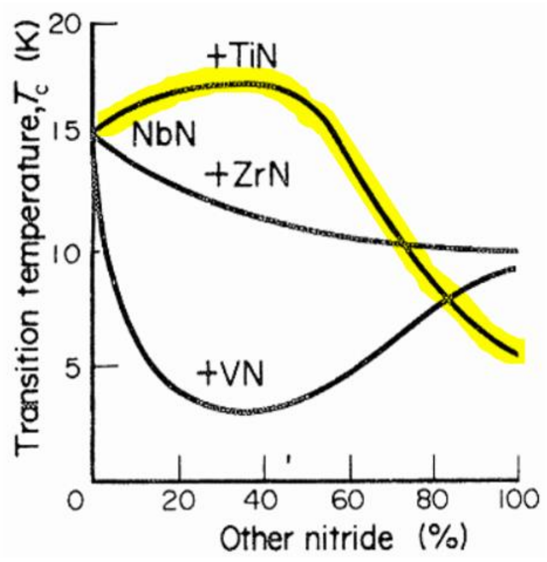
PEALD offers good control over the elemental composition

Optimal composition

$Nb_{0.75}Ti_{0.25}N$

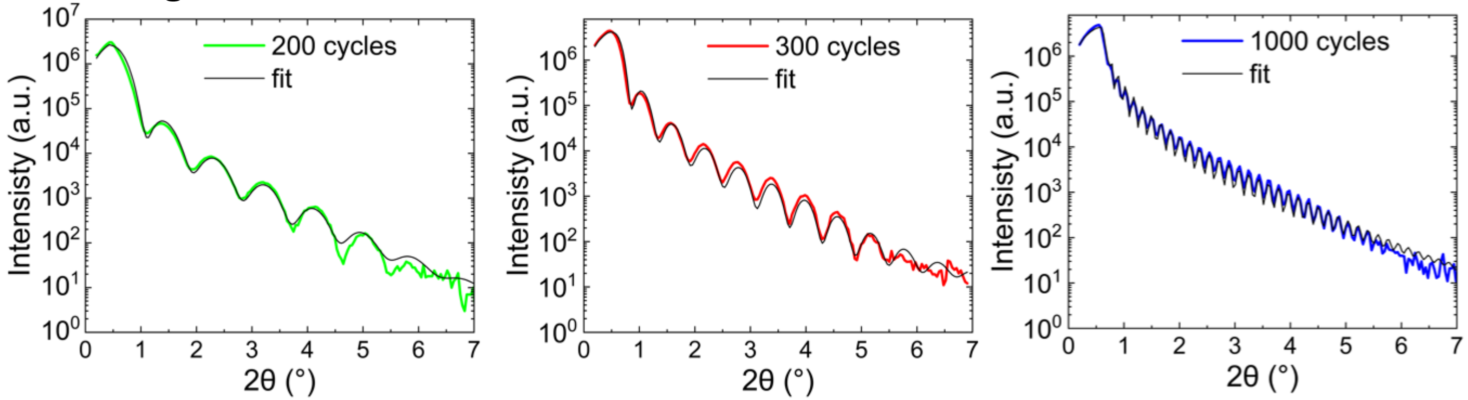


V. Palmieri SRF Workshop 2001



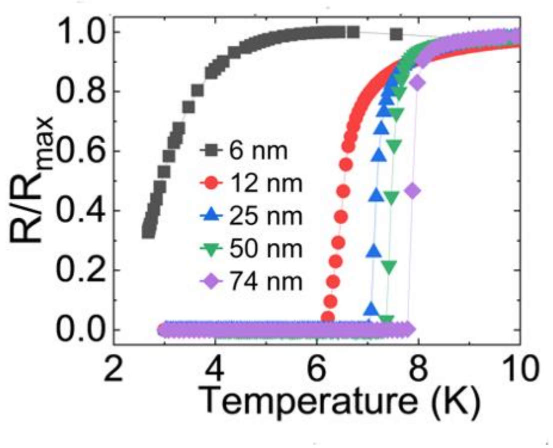
- GPC determination: $\text{GPC}_{\text{Supercycle NbTiN}} \approx 1 \times \text{GPC}_{\text{TiN}} + 3 \times \text{GPC}_{\text{NbN}}$

E.g.: XRR curves for NbN films of various thicknesses



Low T_c limits as-deposited NbTiN films for SRF cavity application

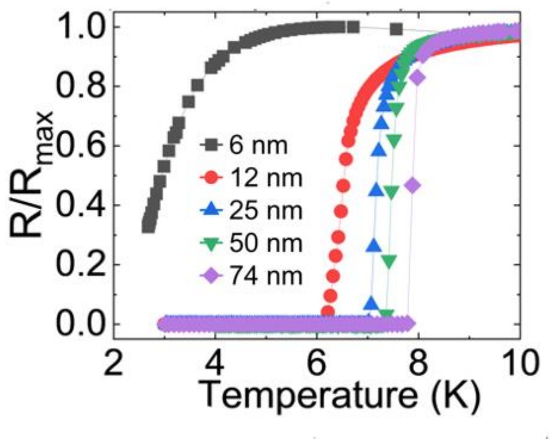
- Transport characterization revealed low T_c



PEALD $T_c^{NbTiN} < T_c^{Nb}$

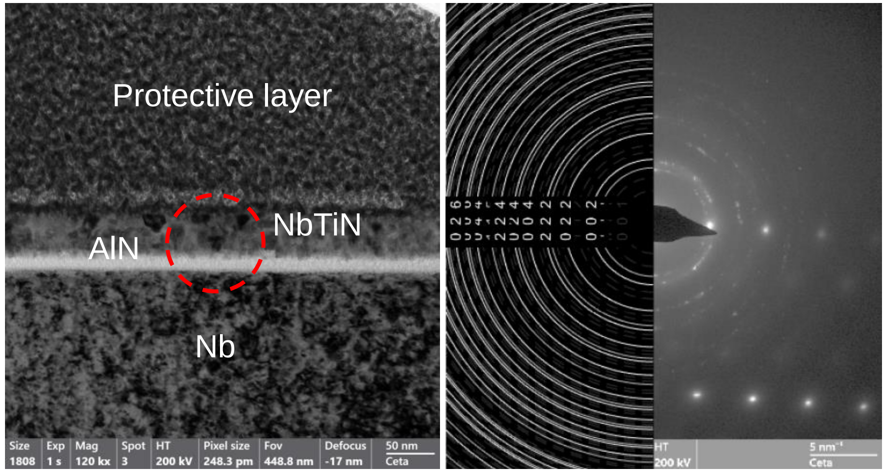
Low T_c limits as-deposited NbTiN films for SRF cavity application

➢ Transport characterization revealed low T_c



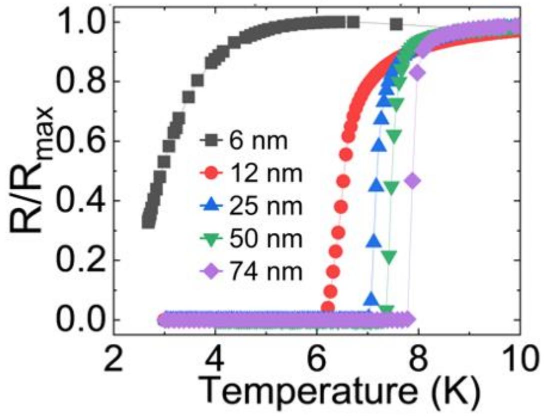
PEALD $T_c^{NbTiN} < T_c^{Nb}$

➢ Selected area electron diffraction (SAED):
ring indexing of the diffraction pattern → δ-NbTiN



Low T_c limits as-deposited NbTiN films for SRF cavity application

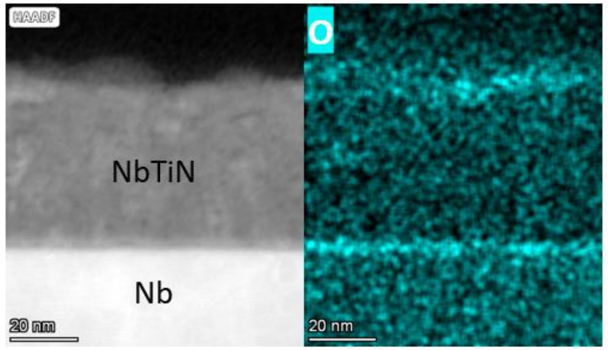
- Transport characterization revealed low T_c



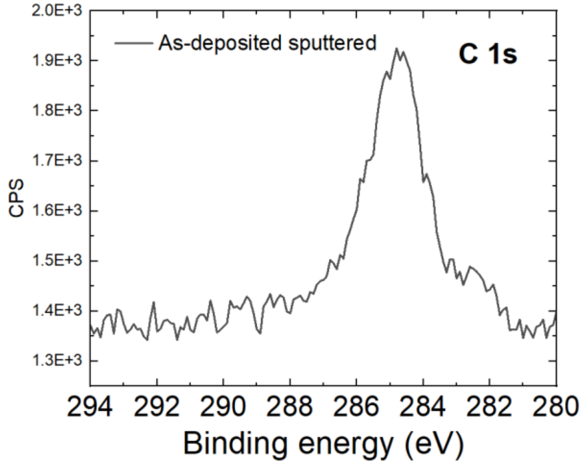
PEALD $T_c^{NbTiN} < T_c^{Nb}$

- Compositional analysis revealed oxygen and carbon contaminants

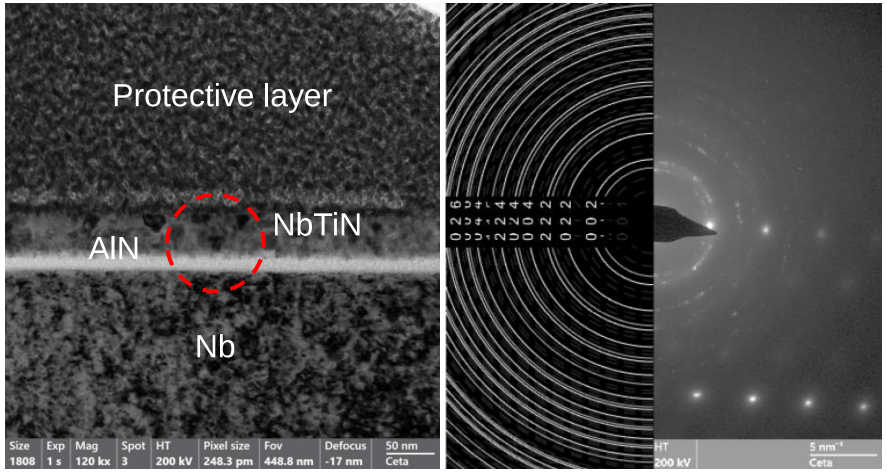
EDS elemental mapping



Carbon XPS peak

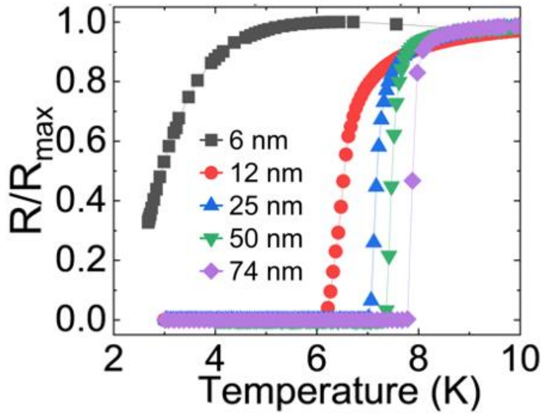


- Selected area electron diffraction (SAED): ring indexing of the diffraction pattern → δ-NbTiN



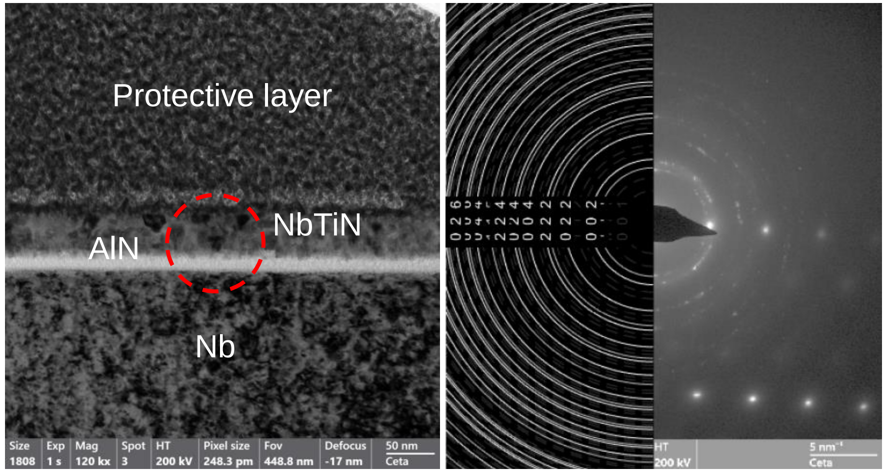
Low T_c limits as-deposited NbTiN films for SRF cavity application

- Transport characterization revealed low T_c



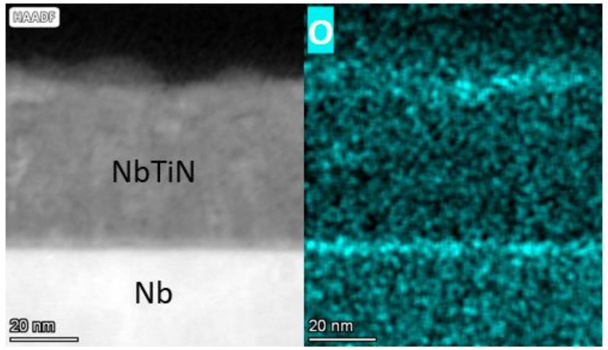
PEALD $T_c^{NbTiN} < T_c^{Nb}$

- Selected area electron diffraction (SAED): ring indexing of the diffraction pattern → δ-NbTiN

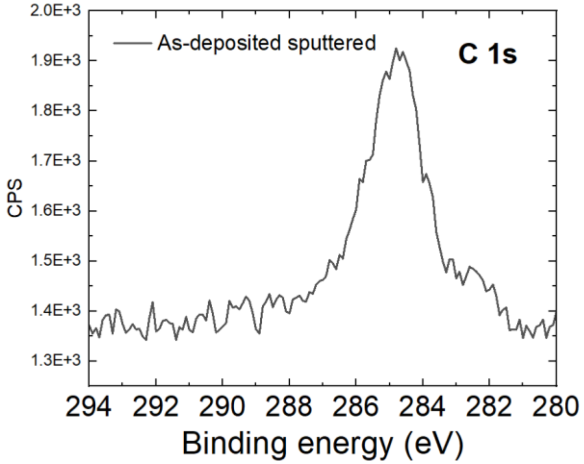


- Compositional analysis revealed oxygen and carbon contaminants

EDS elemental mapping



Carbon XPS peak



***As-deposited**: Si-NbTiN, Si-AlN-NbTiN, Nb-NbTiN, Nb-AlN-NbTiN

- x $T_c^{NbTiN} < T_c^{Nb}$
- ✓ Crystalline δ-NbTiN
- x Small grains – high density of grain boundaries
- x Impurities from PEALD process

Annealing is required to degas impurities and promote grain growth

Post-deposition annealing is necessary to meet SRF criteria

- Various annealing procedures were investigated

Optimized annealing:
Base pressure: UHV (10^{-8} mbar)
Temperature: $900 - 1000$ ℃
Duration: 1 h
Heating rate: 3 ℃/min
Atmosphere: vacuum

As-deposited vs Annealed

$\mathbf{T_c \approx 8\ K} \rightarrow \mathbf{T_c \approx 16\ K}$

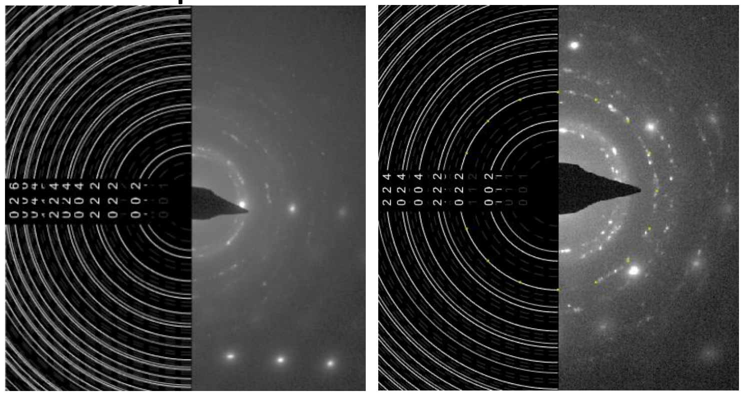
$\mathbf{B_{c1} \approx 15\ mT} \rightarrow \mathbf{B_{c1} \approx 98\ mT}$

$B_{c1}^{film} > B_{c1}^{bulk} = 30\ \text{mT}$

Annealed AlN-NbTiN multilayers meet SRF criteria

- **Enhanced crystallinity** for Si-NbTiN, Si-AlN-NbTiN, Nb-AlN-NbTiN (not for Nb-NbTiN)

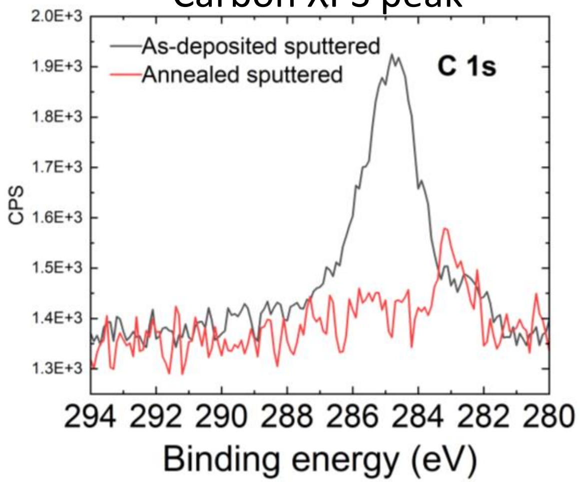
As-deposited | Annealed



δ-NbTiN

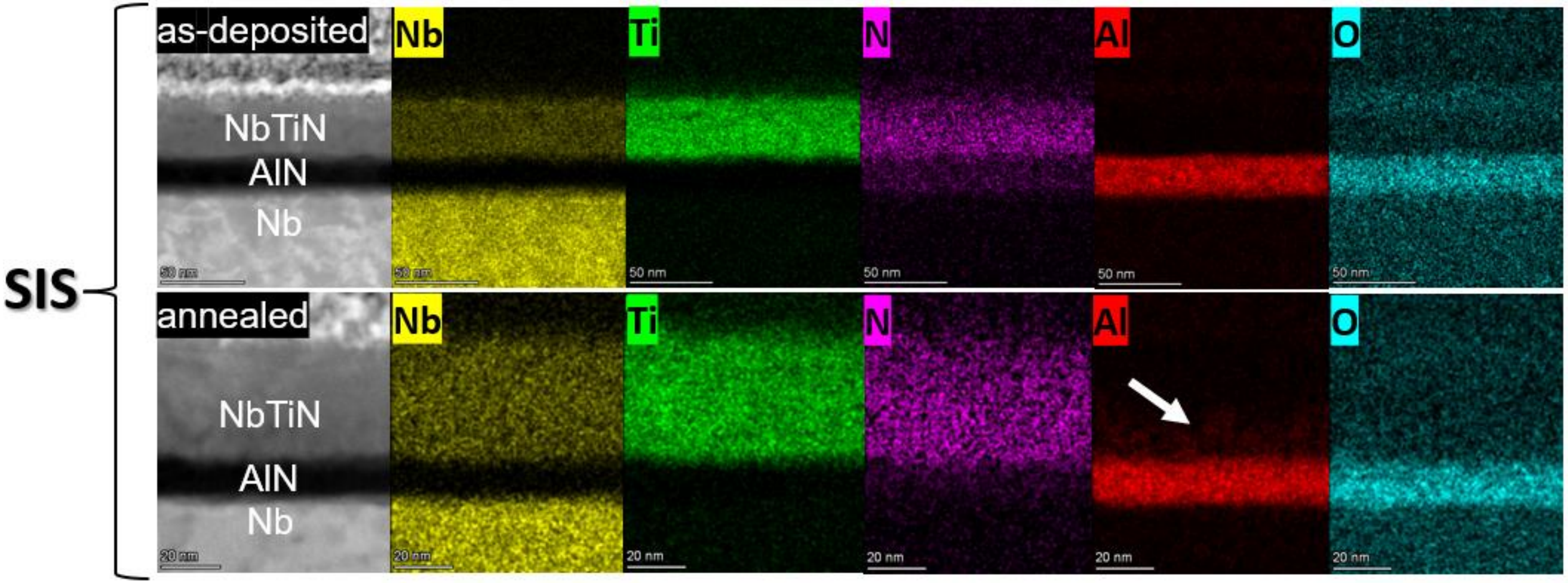
- Annealing results in **carbon degassing** (unclear for oxygen)

Carbon XPS peak



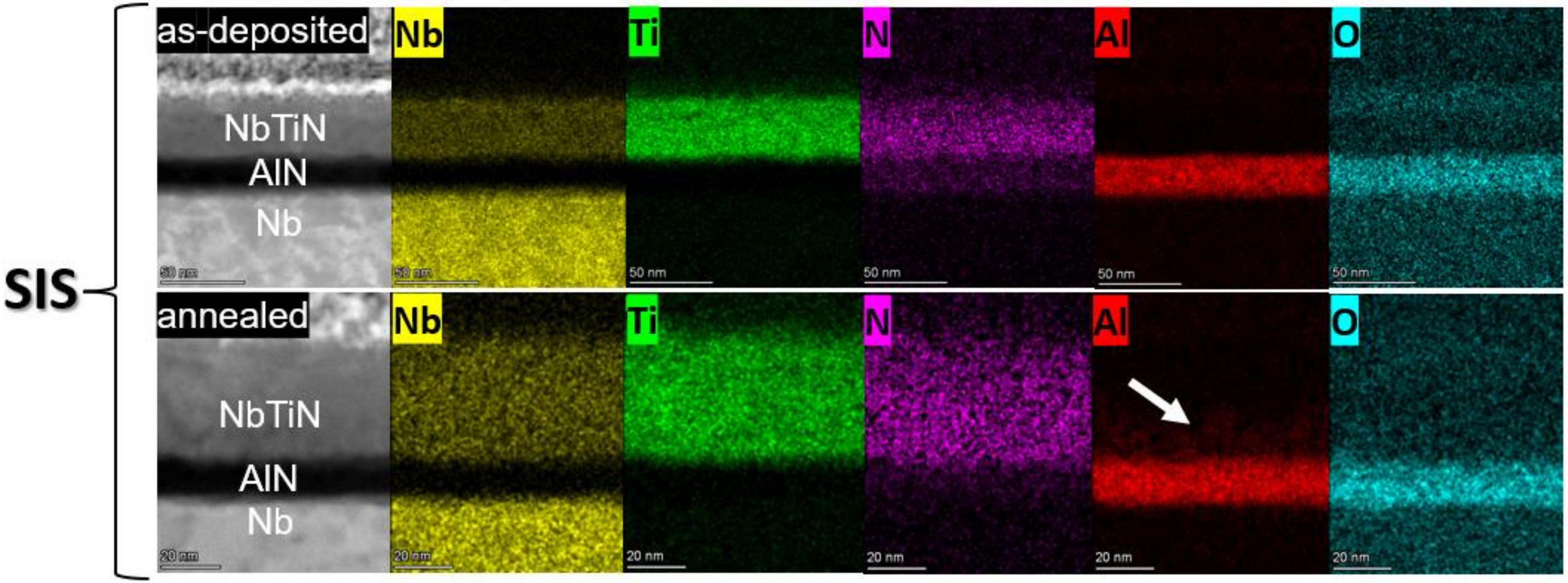
Annealing results in Al diffusion

- EDS elemental mapping indicated that annealing caused Al diffusion into the NbTiN film (also for Si substrate)

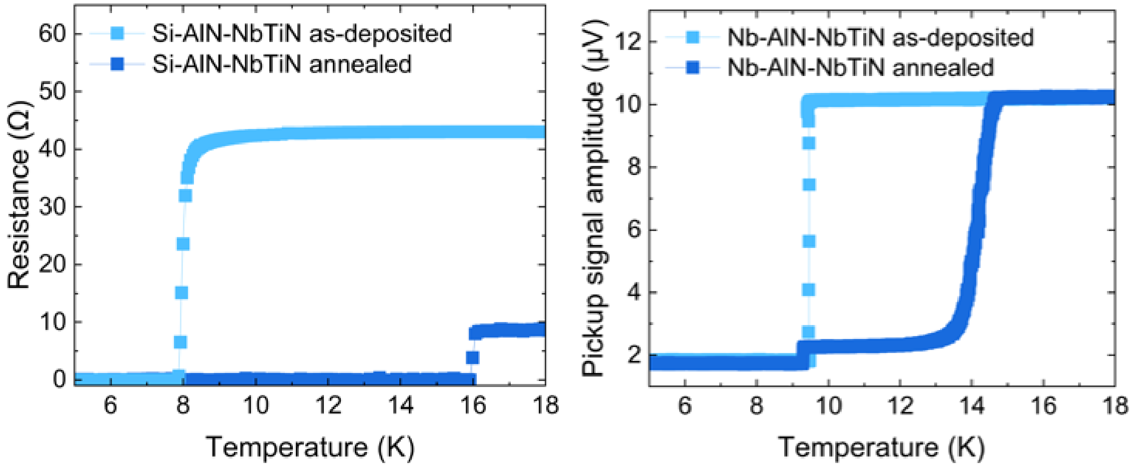


High T_c is reached regardless of Al diffusion

- EDS elemental mapping indicated that annealing caused intermixing at the AlN-NbTiN interface(also on Si substrate)

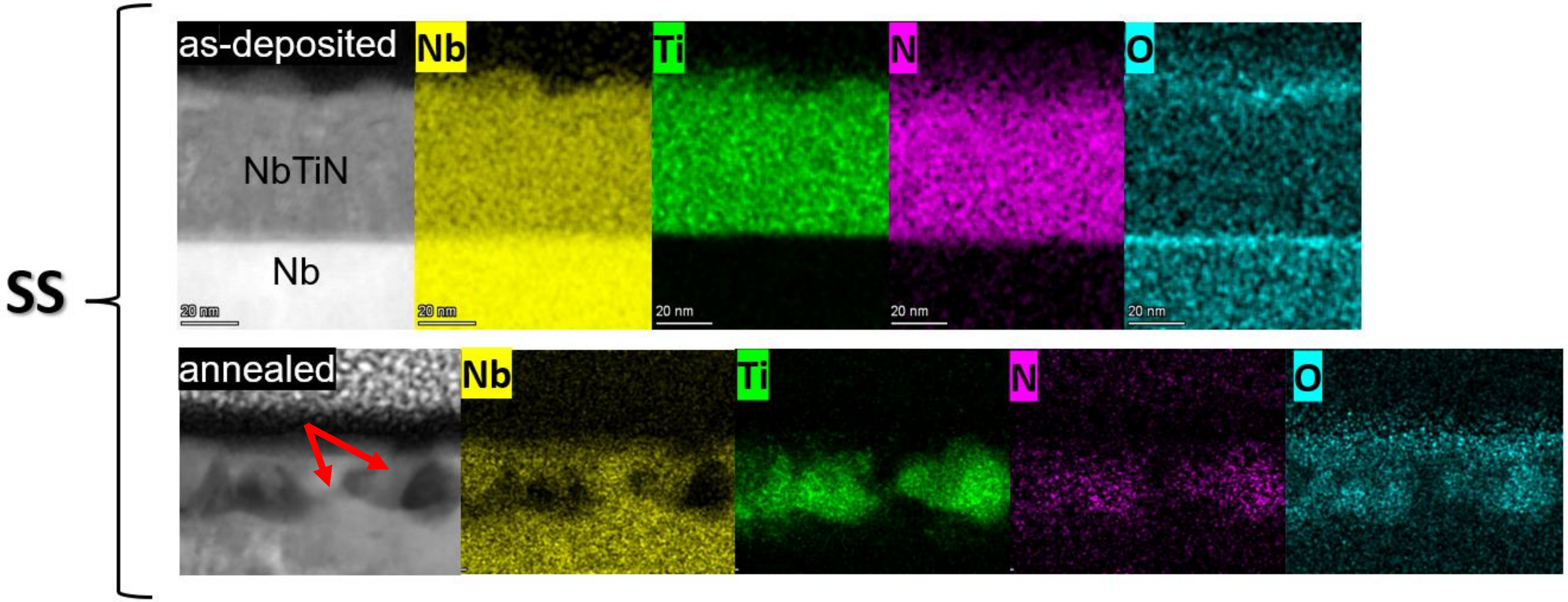


- Al diffusion does not prevent to achieve a high T_c



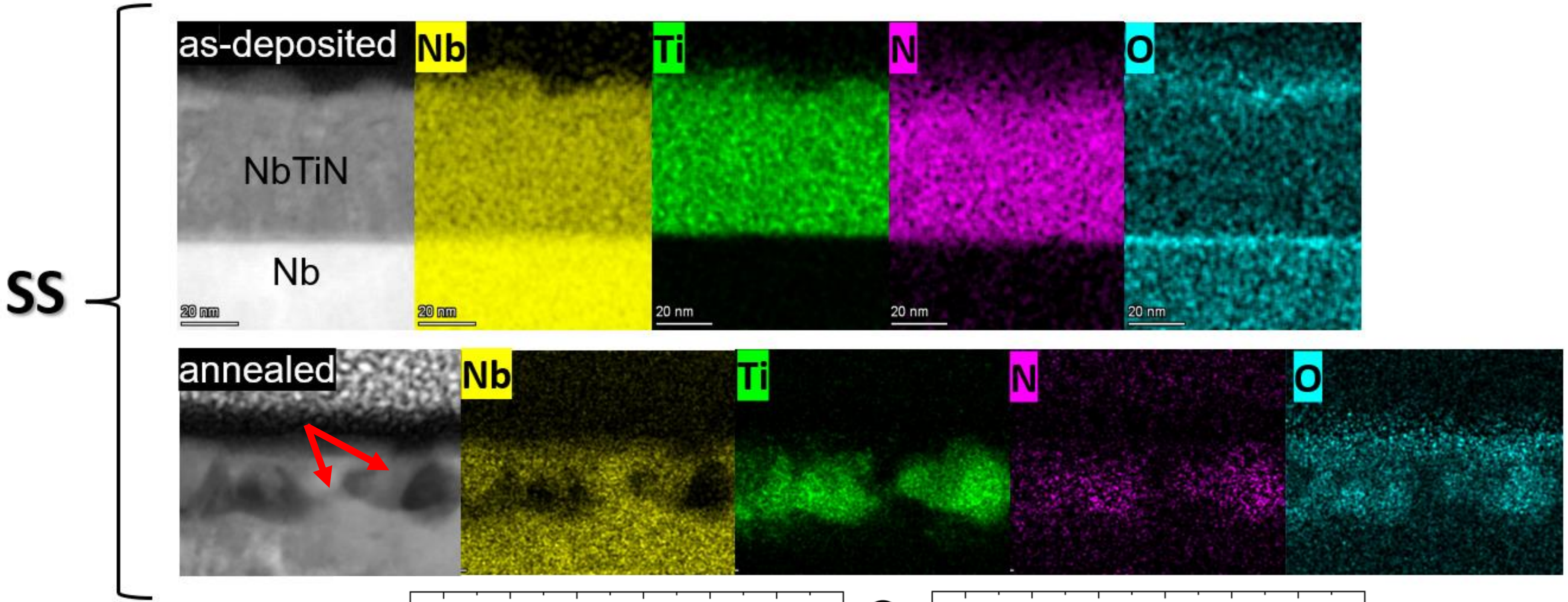
AlN layer is essential for the annealing success

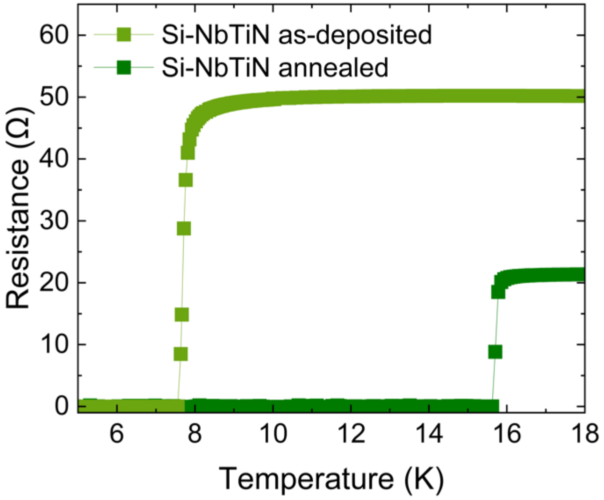
- EDS elemental mapping indicated Nb and Ti clusters caused by the annealing (not for Si substrate)

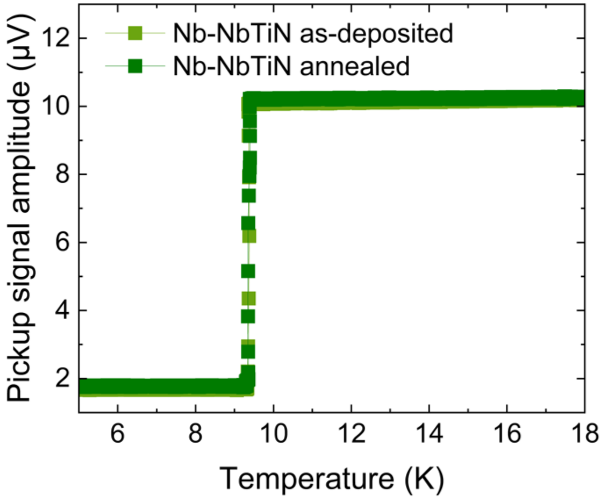


AlN layer is essential for the annealing success

- EDS elemental mapping indicated Nb and Ti clusters caused by the annealing (not for Si substrate)







- Nb and Ti clusters

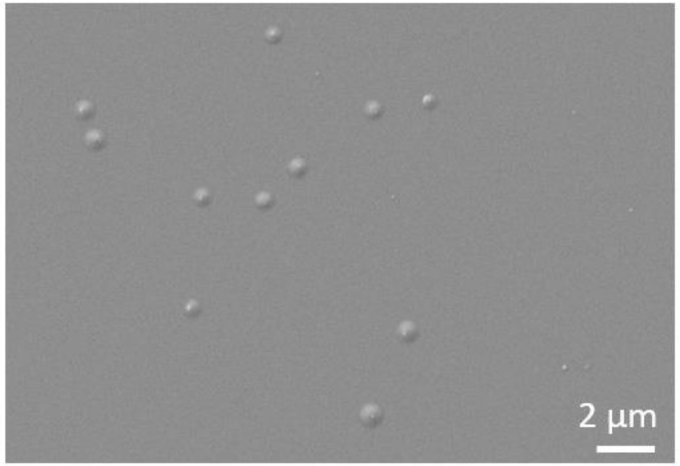
→ **no right phase formation**

→ **no high T_c**

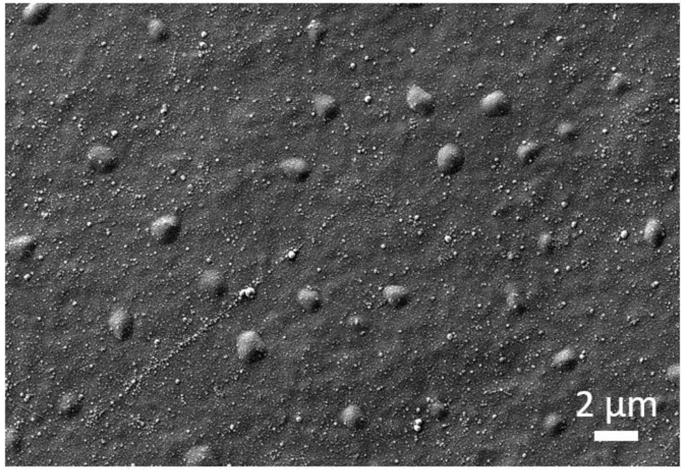
Morphological defects that could limit the cavity performance

➢ Blisters formation: Plasma-induced

On Si



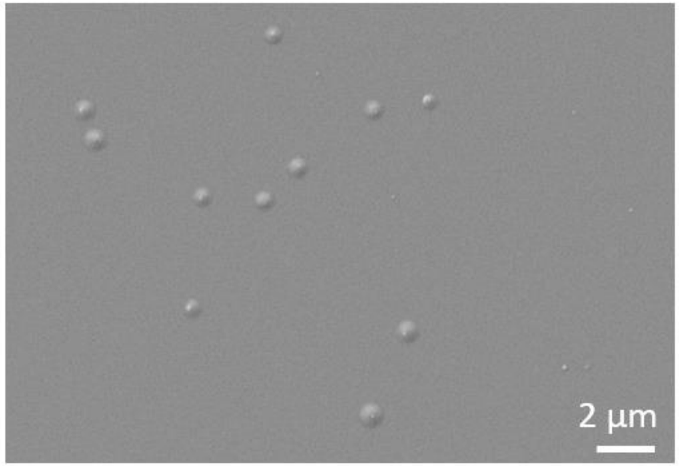
On Nb

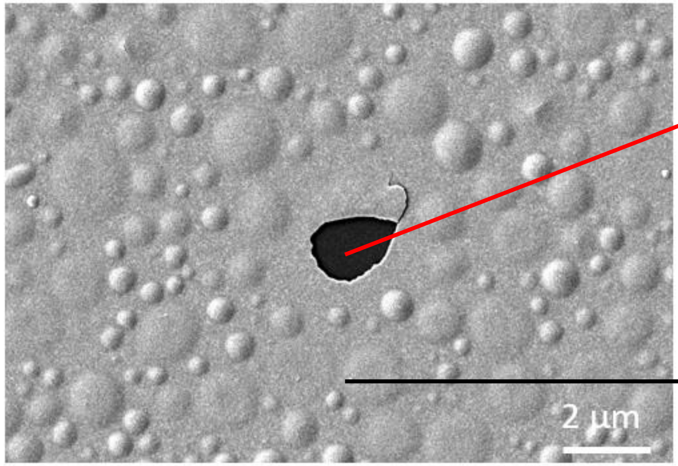


Morphological defects that could limit the cavity performance

- Blisters formation: Plasma-induced
- Annealing-induced defects

On Si

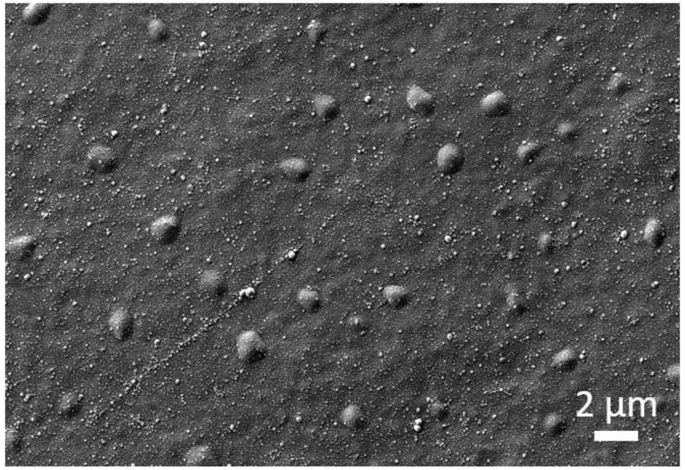


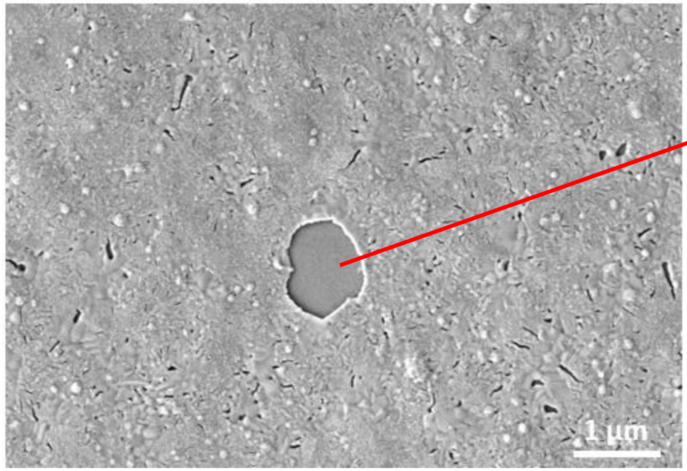


Blisters result in peel-off with annealing

Different thermal expansion coefficients between substrate and layers

On Nb





Blisters result in peel-off with annealing

No thermal expansion issues

Conclusions

Achievements

Synthesize AlN-NbTiN by PEALD

- ✓ On Si and on Nb (surface treated as SRF cavities)
- ✓ Tailor the NbTiN composition
- ✓ Characterizations: XRD, SAED, STEM, SEM, EDS, XPS, ETO, VSM, T_c station, XRR, SE, AFM

As-deposited films

- Low quality NbTiN (δ–NbTiN, $T_c^{NbTiN} < T_c^{Nb}$, $B_{c1}^{film} < B_{c1}^{bulk}$)
- Blisters formation

Post-deposition annealing

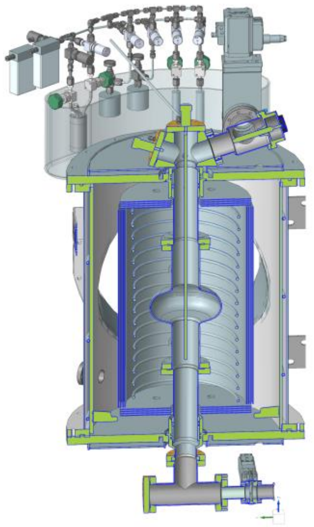
- Enhanced crystallinity and degas of impurities
- Films meet SRF criteria ($T_c^{NbTiN} > T_c^{Nb}$, $B_{c1}^{film} > B_{c1}^{bulk}$)
- AlN layer is essential for the annealing success
- Blisters result in peel-off

Next steps

Further characterization

- ✓ Multilayers resist HPR (standard cavity treatment)
- Thermal transmittance (ongoing)
- Flux trapping studies (ongoing)
- RF test with QPR or cavity (missing)

From planar substrates to 1.3GHz cavities (ongoing)



PEALD-SINGLE-CELL COATING SYSTEM

Acknowledgements

Committee members:

Prof. Dr. Michael Potthoff
Prof. Dr. Wolfgang Hillert
Prof. Dr. Robert H. Blick
Dr. Robert Zierold
Dr. Marc Wenskat

CHyN
Center for Hybrid Nanostructures

Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

DESY.

R. Blick‘s group

Dr. Carina Hedrich, Dr. Jun Peng, Vincent Strenzke, Kristian Deneke, Dr. Stefanie Haugg, Malte Siegmund, Rakshith Venugopal, and more.

W. Hillert‘s group

Dr. Getnet Kacha Deyu, Rezvan Ghanbari, Jonas Wolff, Lea Preece, Marco Voige, Chirag Banjare, Artem Zaidman, and more.

MSL SRF R&D group

Dr. Hans Weise, Dr. Detlef Reschke, Dr. Lea Steder, Dr. Christopher Bate, and more.