Atomic layer deposition of superconducting films and multilayers for SRF

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Multilayer thin films for SRF


- Potential path to high $E_{\text{acc}}$ and high $Q_0$
Atomic layer deposition (ALD)

A thin film synthesis process based on sequential, self-limiting surface reactions between vapors of chemical precursors and a solid surface to deposit films in an atomic layer-by-layer manner.

Advantages:
- Atomic-level control of thickness and composition
- Smooth, continuous, pinhole-free coatings on large area substrates
- No line-of-sight limits → excellent conformality over complex shaped surfaces

Coat inside Nb SRF cavity with precise, layered structure → ALD
ALD thin film materials

- Oxide
- Nitride
- Phosphide/Arsenide
- Sulphide/Selenide/Telluride

- Element
- Carbide
- Fluoride
- Dopant
ALD superconductors?

- Oxide
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- Element
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- Fluoride
- Dopant

Except in one paper, superconductivity has been ignored...
- Reported $T_c = 10$ K for NbN [Hiltunen, et al., Thin Solid Films 166, 149 (1988)]
Superconductors by ALD

Goal for SRF is a material with a $T_c$ higher than bulk Nb (9.2 K)

- **Niobium Silicide: NbSi**
  - $\text{NbF}_5 + \text{Si}_2\text{H}_6$
  - $\text{NbF}_5 + \text{SiH}_4$

- **Niobium Carbide: NbC**
  - $\text{NbF}_5 + \text{Al(CH}_3\text{)}_3$
  - $\text{NbCl}_5 + \text{Al(CH}_3\text{)}_3$

- **Niobium Carbo-Nitride: NbC$_{1-x}$N$_x$**
  - $\text{Al(CH}_3\text{)}_3 + \text{NbF}_5 + \text{NH}_3$
  - $\text{Al(CH}_3\text{)}_3 + \text{NbCl}_5 + \text{NH}_3$

- **Molybdenum Nitride: MoN**
  - $\text{MoCl}_5 + \text{NH}_3$
  - $\text{MoCl}_5 + \text{Zn} + \text{NH}_3$

- **Niobium Titanium Nitride: Nb$_{1-x}$Ti$_x$N**
  - $(\text{NbF}_5, \text{TiCl}_4) + \text{NH}_3$
  - $(\text{NbCl}_5, \text{TiCl}_4) + \text{Zn} + \text{NH}_3$

- **Iron Selenide: FeSe$_x$**
  - $\text{FeCl}_3 + \text{Se(Et}_3\text{Si)}_2$
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Viscous flow ALD reactor

Key features:

- Inconel 600 reactor tube (superior corrosion resistance)
  - Halide precursors (NbCl$_5$, TiCl$_4$, etc.)
- All-welded precursor inlet manifold (reduced sites for potential leaks)
  - Oxygen contamination in nitride films
Thin film characterization

- X-ray photoemission spectroscopy (XPS)
- X-ray reflectivity (XRR)
- X-ray diffraction (XRD)
- Synchrotron grazing-incidence x-ray diffraction (GIXRD)
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- DC electrical transport (down to 1.6 K)
- SQUID magnetometry

- Atom probe tomography (APT) [Seidman, NU]
- Rutherford backscattering spectroscopy (RBS) [Evans Analytical]
Molybdenum nitride: MoN

Effects of intermittent Zn pulse

- Chemistry: MoCl$_5$ + NH$_3$ versus MoCl$_5$ + Zn + NH$_3$ at 450°C
- Hexagonal MoN in both cases, higher density & change in texture with Zn
MoN: Superconducting $T_c$ (SQUID)

Addition of Zn leads to:

- ~2x increase in $T_c$ (equivalent thickness)
  - Peak $T_c = 7.5$ K for 25 nm film

- Decrease in RT resistivity
  - 200 $\mu\Omega$-cm without Zn
  - 120 $\mu\Omega$-cm with Zn

- No chlorine, zinc observed by XPS
- Could be related to film density
  - 88-93% of bulk (9.2 g/cm$^3$)
- Could be due to hydrogen:

  Without Zn: $\text{MoCl}_5 + 3\text{NH}_3 \rightarrow \text{MoN} + 5\text{HCl} + \text{N}_2 + 2\text{H}_2$

  With Zn: $\text{MoCl}_5 + \text{Zn} + \text{NH}_3 \rightarrow \text{MoN} + \text{ZnCl}_2 + 3\text{HCl}$
Niobium titanium nitride: Nb$_{1-x}$Ti$_x$N

- Chemistry: (NbCl$_5$:TiCl$_4$) + Zn + NH$_3$ at 450°C, 500°C
- Can vary Ti content with NbCl$_5$:TiCl$_4$ ratio (1:2 ~ 20% TiN)
  - Cubic $\delta$ phase in all films

With increasing TiN
- Peaks shift to higher angle
- Density decreases
  - 7.2 g/cm$^3$ (1:0)
  - 5.7 g/cm$^3$ (1:4)
- RT resistivity decreases
  - 380 $\mu$Ω·cm (1:0)
  - 130 $\mu$Ω·cm (1:4)

Impurity content: 0.05 atom % Cl

Are they good superconductors?
Optimized growth of Nb$_{1-x}$Ti$_x$N

- Achieved superconducting $T_c$=14 K, **40% higher than any other ALD film**
- Nearly 5 K higher than Nb
Nb$_{1-x}$Ti$_x$N-based superconductor-insulator structures

**Aluminum nitride: AlN**
- Oxygen-free insulator, stable interface with Nb(Ti)N
- Good thermal conductivity (285 W/m-K)
- Similar structure to Nb(Ti)N
  - 0.27% mismatch between in-plane spacing of (0001)-oriented AlN and (111)-oriented NbN
- Can be grown with AlCl$_3$ and NH$_3$ at same temperature as Nb(Ti)N
  - No thermal cycling between deposition steps

- NbN/AlN multilayers grown previously by sputtering
**Nb_{1-x}Ti_{x}N / AlN: X-ray reflectivity**

- Density ~5% higher with AlN
- Roughness ~2x higher with AlN
- Change in thickness/cycles (difference in nucleation delay)
**Nb\(_{1-x}\) Ti\(_x\)N / AlN multilayers**

- 40 nm Nb\(_{0.8}\)Ti\(_{0.2}\)N / 15 nm AlN (single bilayer and 2x stack)
- 80 nm Nb\(_{0.8}\)Ti\(_{0.2}\)N / 30 nm AlN (single bilayer and 2x stack)
  - Quartz, Si(001), 100 nm SiO\(_2\)/Si(001), 30 nm Nb/Sapphire, and cavity-grade Nb

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Optimized Nb\(_{1-x}\) Ti\(_x\)N/AlN ALD growth process (\(T_c = 14\) K) is now ready for coating Nb SRF cavities
- Will enable testing the effects of S-I multilayer on cavity performance

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![Graph showing magnetization vs. temperature](image-url)
Scaling ALD to coat cavities

New ALD system currently being assembled

- Clean room 100 environment
- Up to 650°C in UHV (10e-8 Torr)
- *In situ* processing
- Accommodate single-cell ILC cavities

Klug | SRF2011 Hot Topic: Medium Field Q-slope and Paths to high-Q operation | 26 July 2011
Fe-based superconductors: Initial studies of FeSe$_x$

Promising new Fe-based superconductors (FeSe$_{1-x}$Te$_x$)
- $T_c$ reported up to 37 K
- Remain superconducting in high magnetic fields (>45 T)

New custom precursors for Se, Te (J. Schlueter, S. Sullivan ANL)
- (Et$_3$Si)$_2$Te / (Et$_3$Si)$_2$Se
- (tBuMe$_2$Si)$_2$Te / (tBuMe$_2$Si)$_2$Se

$$(R_3Si)_2Te(g) + MCl_2(g) \rightarrow MTe(s) + 2R_3SiCl(g)$$
Summary

- Growth of single-phase hexagonal-MoN at 450°C
- Demonstrated ~2x increase in $T_c$ in MoN with intermittent Zn dose ($\text{MoCl}_5 + \text{Zn} + \text{NH}_3$)
- Optimized growth of $\text{Nb}_{1-x}\text{Ti}_x\text{N}$ to achieve superconducting $T_c = 14$ K, 40% higher than any other ALD film and ~5 K higher than Nb
- Demonstrated successful ALD growth of $\text{Nb}_{1-x}\text{Ti}_x\text{N}/\text{AlN}$ S-I multilayers on flat substrates (Si, SiO₂, Sapphire, Nb)
- Assembly of new UHV ALD system for coating 1-cell ILC cavities
- New precursors for Fe-based superconductors ($\text{FeSe}_{1-x}\text{Te}_x$)
- Plasma-enhanced ALD system now online and in use
Thank you for your attention