

INITIAL TESTS OF ATOMIC LAYER DEPOSITION (ALD) COATINGS FOR SUPERCONDUCTING RF SYSTEMS*

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Abstract

Atomic Layer Deposition (ALD) is a technique for synthesizing materials in single atomic layers[1]. We are studying ALD as a method for producing highly controlled surfaces for superconducting RF (SCRf) systems. We have begun tests of ALD coatings of single cells that will involve RF measurements of a cell before and after ALD coating at Argonne. In addition to the tests on complete cells, we are also beginning a program of point contact tunneling measurements to determine the properties of the superconductors at the interface between the bulk niobium and the oxide layer. Herein we describe the method, and ongoing initial tests with single cell resonators and small samples.

GRADIENT LIMITS

Niobium, with its very high H_{c1} , has been used in SCRf cavities for accelerator systems for almost 40 years with continuous improvement in its properties. We are now able to produce cavities approaching the intrinsic theoretical limit for Nb. It can be argued that further progress in SCRf demands pursuit of a radically different approach to materials processing.

Nonetheless, practical limitations must be addressed when large scale production is involved. The performance of some mass produced SCRf structures can be significantly reduced from the limits achieved in laboratory tests. In many cases, the nature of these limits and the mechanisms responsible for them are not well understood.

Atomic Layer Deposition (ALD) is a convenient, already widely-applied technique for synthesizing single component coatings or multilayers composed of different materials. We can use ALD either to build up composite superconductors like those proposed by Gurevich[2], or simply to apply a protective layer on the surface of an RF structure. For instance, if we can create a film with much lower secondary emission coefficient (dry oxide, TiN) we could prevent the occurrence of multipacting.

ATOMIC LAYER DEPOSITION

ALD is a self-limiting, sequential process that can deposit conformal films of a broad range of materials onto substrates of varying compositions. ALD is similar to

chemical vapor deposition (CVD), except that ALD breaks the CVD reaction into two separate half-reactions, keeping the precursor vapors separate during each reaction. For instance, Al_2O_3 ALD is performed using alternating exposures of trimethylaluminum (TMA) and water vapor. ALD is based on self-limiting surface reactions, which makes achieving atomic scale thickness control possible. Consequently, atomic layer thickness control is easily achieved. The films are nearly pinhole free, and roughness even tends to decrease with thickness for some ALD materials. Stoichiometry can be controlled precisely as well, since atom rearrangement requires only a few atomic distance migration. Deposition rates can reach a few microns / hr, and many ALD reactions can be performed near room temperature.

In SCRf applications, ALD seems to offer a number of useful options. Capping or insulating layers can be applied to protect the surface from impurities coming either from the surface or from the bulk. The surfaces produced by ALD can be nano-smooth to avoid field emission, applied in protective layers to avoid quenches, chemically pure to avoid contamination or defects, applied on almost any structure, which allows design freedom, and applied *in-situ*, to avoid contamination during assembly. Since only the top few hundred monolayers of the superconductor are active parts of an RF superconductor, the ability to produce these surfaces precisely and reproducibly will be valuable. Since ALD coatings can be relevant to almost all aspects of SCRf limiting behaviour, we feel a productive experimental program on this topic can be realized.

A wide range of metals, metal oxides, nitrides or more complex compounds can currently be grown using known ALD chemistry, however none have been applied to SCRf before the present work. ALD growth of materials such as superconducting NbN have been reported[3], and schemes for MgB_2 ALD are possible.

COATING OF NIOBIUM SAMPLES

We describe here our first results for depositing ALD Al_2O_3 and TiN on Nb samples. Although these layers can be a starting point toward more complex structures like the insulator-superconductor multilayers already mentioned [2], we might already find application with a one-component coating. Indeed, ALD grown Al_2O_3 can be a useful insulator/capping film. Its amorphous structure is

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very dense, very stable and forms a diffusion barrier even at high temperature.

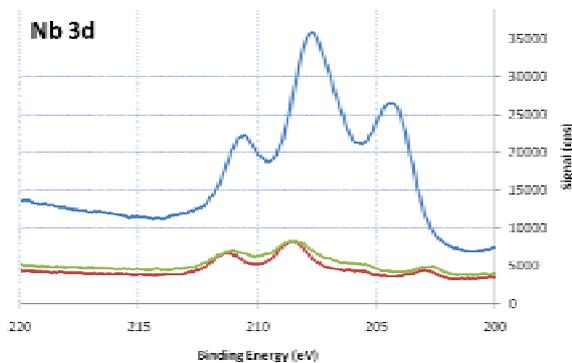


Figure 1: XPS spectra comparing a pristine Nb sample (No ALD, topmost curve) that has been air oxidized (20h at 200°C) to a sample that has been ALD coated with 3.5nm Al_2O_3 (red, lowest curve) and then similarly oxidized (green, middle curve). Coating dramatically limits the growth of Nb mixed oxides.

The TMA exposures for Al_2O_3 ALD should tend to reduce Nb oxide. In principle, we can further heat treat Nb at higher temperature (500-800°C) and eliminate the niobium oxide. The oxygen atoms that have not reacted with aluminum will diffuse into the bulk of the niobium, and the alumina prevents oxygen penetration from the ambient (atmosphere or residual gases). The heat-treated alumina will be hydroxide free; hence we expect its secondary emission coefficient to be very low. Thus, with a single-component capping film, we could improve two different aspects of usual SRF problems.

We anticipate that hydroxyl-terminated alumina surfaces may be subject to multipacting, based on the working history of aluminium cavities, thus we are considering the use of a material to use on the top surface. TiN is expected to reduce secondary emission by increasing the work function of the surface, however this material requires a much higher deposition temperature than alumina, and other materials could also serve this purpose.

Experimental Details

Niobium samples were cut out from Nb sheets used for cavity fabrication. As it was desired to track the deposition with ellipsometry (at least during the initial stage) all of the pieces were mechanically polished to near mirror finish, and a subset of these were further electropolished to remove near-surface defects and contamination.

The procedure used to grow alumina is as follows:

1. Trimethylaluminum (TMA) is introduced in the preparation chamber. One monolayer adsorbs on the surface (chemisorption) releasing methane.
2. The chamber is purged with nitrogen (to clear the excess TMA and the methane).
3. Water vapor is allowed inside the chamber. It reacts spontaneously with the chemisorbed aluminium

compound forming a hydroxide, and releasing methane.

4. The chamber is purged again with N_2 .
5. Repeating the complete cycle several times allows growing a well characterized alumina film of precisely determined thickness.

It takes about 10 minutes to complete up to 5 nm of alumina growth on Nb. Note that the reactants and buffer are pumped away at one end of the reactor tube, and a continuous flow of gas over a set of samples to be coated is ensured. After coating, analysis of the samples is performed by x-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry. Select samples are studied by point contact tunnelling.

A slight difference (~10% in thickness) is observed on mechanically-polished only samples versus electropolished ones. This is likely a nucleation effect and depends on the initial surface structure and how it is chemically terminated.

In figure 1, the protective effect of an Al_2O_3 coating on a Nb sample is demonstrated. An uncoated sample is air oxidized for 20 hours at 200C, and substantial oxide-related features appear in the XPS spectrum (top), indicating a relatively thick mixed oxide. A sample that has been coated by ALD with 3nm of Al_2O_3 grown at 150C, on the other hand, shows little change upon the same heat treatment cycle (bottom two spectra).

Cavity coating

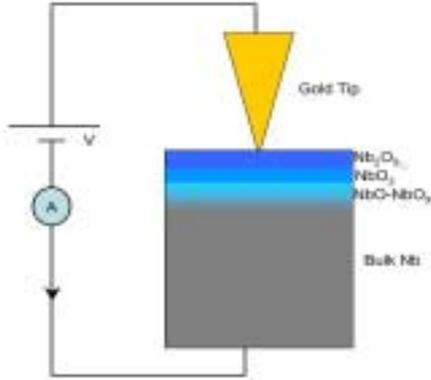
We have immediate plans for cavity coating. The concept is for the cavity to act as the deposition chamber since the whole surface will be coated, and only moderate heating (under 300 °C) is necessary. In a first step, alumina and TiN or a similar material will be tested to observe their impact on the cavity performances, especially in regard to field emission and multipacting. In the second project stage, we will deposit superconductors such as NbN, Nb_3Sn , or MgB_2 .

POINT CONTACT TUNNELING

The superconducting RF surface impedance (R_{BCS}) depends on two intrinsic properties: the quasiparticle gap parameter, Δ , and the superfluid density, n_s . Both of these parameters can be seriously affected in Nb by surface imperfections such as metallic phases (e.g. NbO), dissolved oxygen, or magnetic scattering of the quasiparticles. Tunnelling spectroscopy is an ideal, surface sensitive probe as the quasiparticle current measures Δ while the Josephson current can be used to measure n_s . Proximity effect theory helps to explain the experimental observations.

We report here some preliminary measurements on SRF cavity-grade Nb using point contact tunnelling. This technique allows a point-to-point local probe of the Nb surface and, since the Nb_2O_5 layer serves as the tunnel barrier (Figure 2), information on its properties are also found from the high bias tunnel conductance.

Figure 2: Schema of a point contact junction between a gold tip and a niobium sample. The electronic properties



of the niobium and its oxides are probed by measuring $I(V)$ and $dI(V)/dV$ curves.

Figure 3 shows the dynamic conductance curves, dI/dV vs. V , for point contact junctions on Nb using an Au tip. Nb monocrystalline samples were taken from large grain material of the same high purity from which SRF cavities are formed. In one case, the Nb was electropolished and exposed to laboratory air (upper curve in figure 3). Then the same Nb piece was given a low temperature anneal, 120 °C for 48 hours in air (bottom curve in figure 3). This annealing is similar to the heating step used to reduce the Q-slope on real cavities, since it has been shown that baking is effective when performed under vacuum or in air[4]. (Note that the same sample was also baked under vacuum and exhibited similar behavior).

The conductances reveal a clear energy gap parameter, $\Delta = 1.55$ meV, indicative of bulk Nb, but the BCS density of states indicates some additional smearing (beyond that originating from the temperature at 1.6 K).

The only mechanism we can identify which would give rise to such additional smearing is magnetic scattering (parameterized by Γ_{SF}) which we suspect originates from the surface oxide layers. It is well known that reduced (defective) oxides, e.g., $Nb_2O_{5-\delta}$, $NbO_{2-\delta}$, exhibit magnetic moments. It is intriguing that the baked Nb reveals sharper energy gap features, **indicating a decrease of magnetic scattering**. The origin of this effect is not known at present but it suggests that the annealing is causing some oxygen diffusion and the formation of stoichiometric, non-magnetic Nb oxide layers. Fits using Shiba theory are in good agreement with measurements [5]. (Shiba theory is an extension from BCS theory that takes into account the scattering of quasiparticles on magnetic impurities).

Figure 4 shows the tunneling conductances from air-exposed Nb samples that have been coated with 30 nm ALD Al_2O_3 . There is no difference in the energy gap region compared with the uncoated Nb, and this indicates that the ALD causes no deleterious effects on the surface superconductivity. However, the tunnel barrier analysis

from high bias conductance data clearly reflects the different barriers associated with Nb_2O_5 compared with Nb_2O_5/Al_2O_3 . In the former case, the barrier height is about 300 mV, typical of Nb_2O_5 , whereas in the latter the barrier height has an average value of 4.5 V, typical of Al_2O_3 .

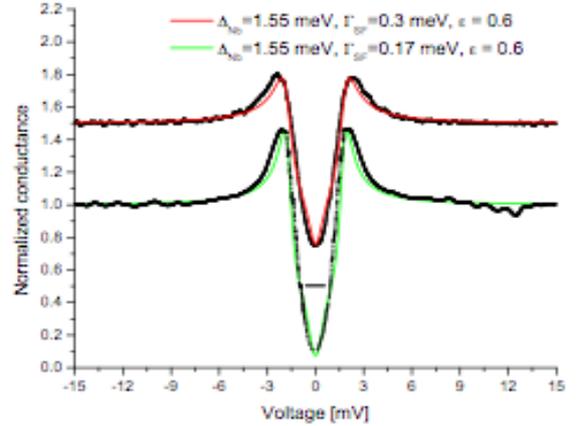


Figure 3: In black (bold): conductance curves measured at 1.65 K. In red (thin curve, top): Fit using Shiba theory for the EP unbaked sample and in green (thin curve, bottom) fit for the EP and baked sample. Γ_{SF} represents the inelastic scattering of the Cooper pairs by the magnetic impurities and ϵ is an impurity type-dependent parameter.

We will soon be testing high-temperature vacuum annealing of ALD-coated Nb and using point contact tunnelling to probe the surface superconductivity. The hypothesis is that the protective Al_2O_3 film will prevent external oxygen from diffusing into the bulk, so that the high temperature anneal will reduce and dissolve all oxygen coming from the Nb oxides deep into the bulk, leaving only an Al_2O_3/NbO bilayer on the Nb surface. Longer term, we plan to probe ALD grown superconducting films.

SUMMARY

We have begun a program to produce and evaluate superconducting surfaces using ALD and this paper summarizes some of the initial results of this effort. This program will have two parts: testing cavities coated with a variety of superconducting materials and configurations, and characterization of these materials using a variety of methods. ALD seems ideally suited to producing a wide range of superconducting surfaces, including multi-layered structures and different materials. Point contact tunnelling seems to be a useful way of determining the superconducting properties of these materials and preliminary data seems to show the effects of magnetic scattering in the oxide layers.

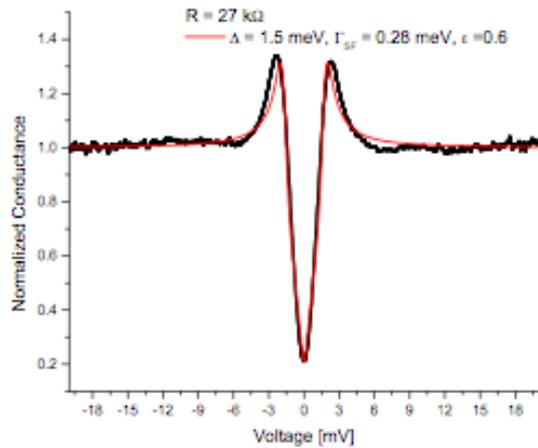


Figure 4: Conductance curve measured at 1.6 K on a Nb sample coated with 3 nm of Al₂O₃ by ALD. In red (thin), the fit using Shiba theory.

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REFERENCES

- [1] M. Ritala and M. Leskela, in Handbook of Thin Film Materials, edited by H S Nalwa (Academic Press, San Diego, 2001), Vol. 1, p. 103.
- [2] A. Gurevich, Appl. Phys. Lett. 88, 12511 (2006).
- [3] K-E. Elers, M. Ritala, M. Leskela et al., Appl. Surf. Sci. 82/83, 468-474 (1994).
- [4] B. Visentin, presented at the 11th Workshop on RF superconductivity, Travenmünde, 2003 (unpublished).
- [5] H. Shiba, Prog. Theor. Phys. 40, 435 (1968) and Prog. Theor. Phys. 50, 50 (1973)