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

M. Pellin, J. Elam, J. Moore, J. Norem, ANL, Argonne, IL 60439 USA
C. Antoine, CEA/Saclay
L. Cooley, Fermilab
T. Prolier, J. Zasadzinski, IIT
R. Rimmer, JLab

Abstract

Atomic Layer Deposition (ALD) is a method of synthesizing materials in single atomic layers. We are studying this technique as a method of producing highly controlled surfaces for superconducting RF systems. We have begun tests of ALD coatings of single cells that will involve RF measurements of a cell before and after 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. We describe the method, and tests we are beginning 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. We are now able to produce cavities approaching Nb's intrinsic theoretical limit. The only way to make the SRF technology further progress is to conceive radically different approach.

We also have to address practical limitations when we deal with large scale production. The performance of some structures can be significantly reduced from the lab achieves limits. In many cases the nature of these limits and the mechanisms responsible for them are not well understood.

.Atomic Layer Deposition is a convenient technique that can synthesize single layers. We can use it either to built up composite superconductors like those proposed by Gurevich [1], or simply use it to put a protective layer on a RF structure surface. For instance, if we can get a film with much lower secondary emission coefficient (dry oxide, TiN) we could prevent multipacting occurrence.

ATOMIC LAYER DEPOSITION

Atomic Layer Deposition is a self-limiting, sequential surface chemistry that deposits conformal monoatomic-films of materials onto substrates of varying compositions. ALD is similar in chemistry to chemical vapor deposition (CVD), except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separate during the reaction. ALD film growth is self-limited and based on surface reactions, which makes achieving atomic scale deposition control possible. By keeping the precursors separate throughout the coating process, atomic layer control of film grown can be obtained as fine as ~ 0.1 angstroms per monolayer. The films are nearly pinhole free, and roughness even tends to decrease with thickness. Stoechiometry is quite easy to master since atoms rearrangement requires only a few atomic distance migration. Growth rates can be a few microns / hr and the reactions usually take place 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 in a known way should be valuable. Since ALD coatings can be relevant to almost all aspects of SCRF limiting behaviour, we feel a rich experimental program is possible.

In principle a wide range of metals, metal oxides, nitrides or more complex compounds can easily be achieved. Even superconductors like NbN or MgB_2 have been reported in literature.

COATING OF NIOBIUM SAMPLES

We report here our first attempts to deposit 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 [1], we might already find application with a single layer. Indeed Al_2O_3 can be a useful insulator/capping layer. Its amorphous structure is very dense, very stable and forms a diffusion barrier even at high temperature.

Once Al is deposited on Nb, it should tend to reduce Nb oxide. We can further heat treat Nb at higher temperature (500-800 °C) and totally get rid of the niobium oxide.. The oxygen atoms that haven't reacted with aluminum will diffuse toward the bulk of the niobium, and the

---

* Supported by USDOE

norem@anl.gov

alumina will prevent oxygen penetration from outer atmosphere. The heat treated alumina will be hydroxide free; hence we expect its secondary emission coefficient to be very low. Thus, with a single capping layer we could improve two different aspect of usual SRF problems.

We anticipate that alumina surfaces may be subject to multipactor, 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 changing 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. Since we need to follow the deposition rate with ellipsometry (at least during the initial stage) some of them were mechanically polished, or mechanically polished and then electropolished.

The cycle used to build up Alumina is the following :

1. Trimethylaluminum (TMA) is introduced in the preparation chamber. One monolayer gets adsorbed on the surface (chemisorption).
2. The chamber is purged with nitrogen (to get rid of the excess TMA.
3. Water vapour is allowed inside the chamber. It discomposes spontaneously the adsorbed aluminium compound into a hydroxide, releasing methane.
4. The cycle is completed with another N_2 purge.

The cyele is repeated for each layer. It takes about 10 minutes to complete ~ 100 nm of alumina on Nb. Slight difference (~10% in thickness) is observed on mechanically polished samples vs electropolished ones. The coating process is monitored with XPS, ellipsometry and crystal microbalance.

Cavity coating

We have further plans for cavity coating. In principle the cavity can act as the deposition chamber since the whole surface will be covered and only moderate heating is necessary. Nevertheless we felt that the external surface must be protected from atmosphere and we are building a set up that will allow to treat the whole cavity. In a first step, Alumina and TiN will be tested in order to observe its impact on the cavity performances, especially in regard to field emission and multipacting. Then we will try to deposit superconductors like Nb_3Sn, NbN or MgB_2

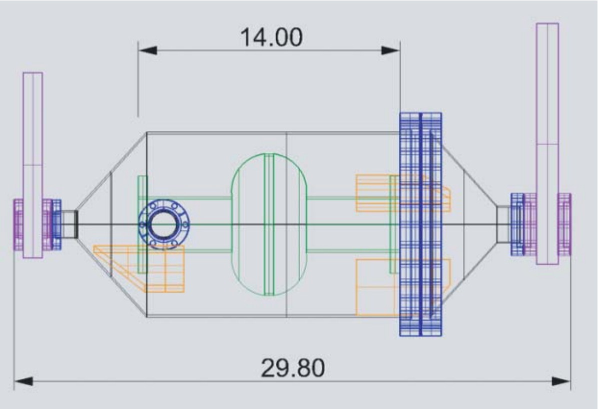

Figure 1: deposition chamber for 1.3 5 GHz cavities

POINT CONTACT TUNNELING

The superconducting RF surface impedance, RBCS, 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 imperfection such as metallic phases (e.g. NbO), dissolved oxygen, 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 (Fig.1); information on its properties are also found from the high bias tunnel conductance.

In Fig. 2 are shown 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 Fig.2). Then the same Nb piece was given a low temperature anneal, 120 C for 48 hours in air (bottom curve in fig.2). This annealing is similar to the heating step used to reduce the Q-slope on real cavities, since it has been shown that the baking is effective wherever it is done under vacuum or air [2]. (Note that the same sample was laso baked under vacuum and give similar behaviour).

The conductances reveal a clear energy gap parameter, Δ = 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).

.

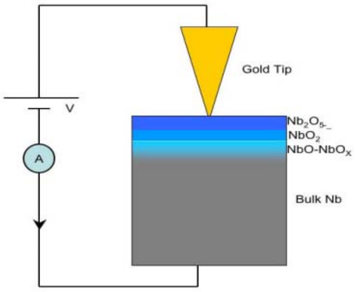

Figure 2: schema of a Point Contact junction between a gold tip and a niobium sample. The electronic properties of the niobium and its oxides are probed by measuring I(V) and dI(V)/dV curves.

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 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. (Shiba theory is an extension from BCS theory which takes into account the scattering of quasiparticles on magnetic impurities) [3].

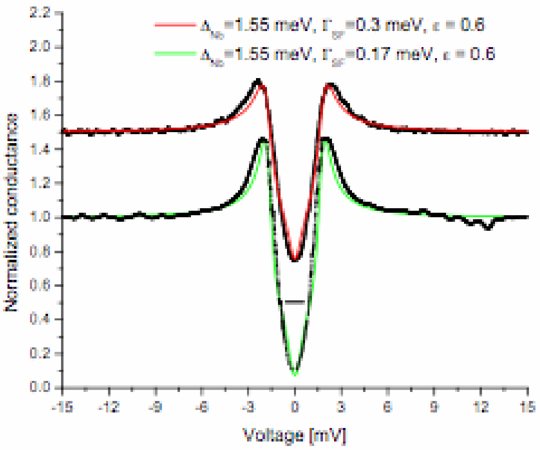

Figure 3: In black: conductance curves measured at 1.65 K. In red: Fit using Shiba theory for the EP unbaked sample and in green fit for the EP and baked sample.

SF represents the inelastic scattering of the Copper pairs by the magnetic impurities and ε is an impurity type-dependent parameter.

In Fig. 3 are shown the tunneling conductances from air-exposed Nb samples that have been coated with a few monolayers of Al2O3 using ALD. There is no difference in the energy gap region compared with the uncoated Nb and this indicates that the ALD deposition is having no additional 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.

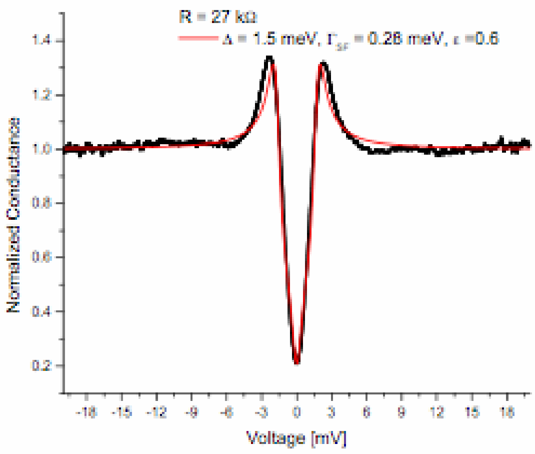

Figure 4: Conductance curve measured at 1.6 K on a Nb sample coated with 3nm of Al2O3 by ALD. In red, the fit using Shiba theory.

The next set of experiments will be to perform a high temperature anneal (up to 700 C) in vacuum of the ALD coated Nb plates and to use point contact tunnelling to probe the surface superconductivity. The hypothesis is that the protecting alumina overlayer will prevent external oxygen from diffusing into the bulk, the high temperature anneal will then reduce and drive all oxygen coming form the Nb oxides deep into the bulk, leaving only an Al_2O_3/NbO layer on the Nb surface.

ACKNOWLEDGEMENTS

This work was supported in part by the USDOE Office of High Energy Physics

REFERENCES

[1] A.Gurevich, "Enhancement of RF breakdown field of SC by multilayer coating". Appl. Phys.Lett., 2006. 88: p. 12511.
[2] B. Visentin. "Q-Slope at high gradient : review of experiments and theories". in 11th Workshop on RF superconductivity. 2003. Travenmünde
[3]. H.Shiba, Prog.Theor.Phys. 40, 435 (1968) and Prog.Theor.Phys. 50, 50 (1973)