Tunneling Study of SRF cavity-grade niobium

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***Abstract*—Niobium, with its very high H_{C1}, has been used in superconducting radio frequency (SRF) cavities for accelerator systems for 40 years with continual improvement. The quality factor of cavities (Q) is governed by the surface impedance R_{BCS}, which depends on the quasiparticle gap, delta, and the superfluid density. Both of these parameters are seriously affected by surface imperfections (metallic phases, dissolved oxygen, magnetic impurities). Loss mechanism and surface treatments of Nb cavities found to improve the Q factor are still unsolved mysteries. We present here an overview of the capabilities of the point contact tunneling spectroscopy and Atomic layer deposition methods and how they can help understanding the High field Q-drop and the mild baking effect. Tunneling spectroscopy was performed on Nb pieces from the same processed material used to fabricate SRF cavities. Air exposed, electropolished Nb exhibited a surface superconducting gap Δ=1.55 meV, characteristic of clean, bulk Nb, however the tunneling density of states (DOS) was broadened significantly. Nb pieces treated with the same mild baking used to improve the Q-slope in SRF cavities revealed a much sharper DOS. Good fits to the DOS are obtained using Shiba theory suggesting that magnetic scattering of quasiparticles is the origin of the degraded surface superconductivity and the Q-slope problem of Nb SRF cavities.**

***Index Terms*—Tunneling spectroscopy, niobium, RF cavity, magnetism.**

I. INTRODUCTION

FOR over three decades, the SRF cavities performances have been continually improved to achieve reproducibly quality factor of 10^{10} and maximum accelerating gradient E of 30-35 MV/m. However, unsolved mysteries remain, among which High field Q-slope and its mitigation by a mild baking treatment and prevent cavities from reaching the intrinsic Niobium limit believed to be around 50-55 MV/m. The interactions between Nb surface superconductivity and the native oxides are complex and not fully understood; a fundamental investigation of the microscopic mechanisms by which oxygen and the complex set of niobium oxides influence cavity performance seems now to be unavoidable. We will present first, a tunneling spectroscopy study of the mild baking effect on cavity-grade electropolished Nb samples that identify magnetic impurities as up to now unrecognized contributors to the dissipation mechanism at the surface of Nb. In the second part, we will present preliminary data on the high bias part of the conductance spectrum (>30 mV) that characterizes the tunneling barrier itself, in this case niobium insulating oxide Nb_2O_5. In the third part, we will present the Atomic Layer Deposition technique and the first attempts to improve the Nb surface superconductivity by eliminating the oxides; a uniformly 2 nm thick alumina film has been deposited by atomic layer deposition (ALD) on niobium sample and followed by a high temperature heat treatment in ultra high vacuum (UHV). In conclusion, the first results obtained on alumina coated cavities and the future projects associated with ALD will be presented.

II. MAGNETIC IMPURITIES AND THE MILD BAKING EFFECT

As we reported previously [1] tunneling measurements on cavity-grade Nb directly probe the surface superconductivity. Our results provide new insights into the Q-slope problem and the baking effect. Air exposed, electropolished poly- and single-crystal samples reveal a surface gap parameter characteristic of clean, bulk Nb (Δ=1.55 meV) but the tunneling density of states (DOS) is considerably broadened. Samples treated using the same mild baking step that reduces the Q-slope (e.g. 120 °C for 24 h – 48 h) show much sharper DOS and reduced zero-bias conductance (Fig.1 center and right) and this effect prevails whether the sample is baked in air or in vacuum.

Niobium oxides have been widely studied in their bulk, crystalline form: Nb_2O_5 is an insulator with a band gap > 4 eV, NbO_2 is a weak Peierl semiconductor with a gap of 0.1 eV, and NbO is metallic and superconducting below 1.4 K. Beyond these three main categories, each of these oxides has the unique property to stabilize a substantial off-stoichiometry. A pristine air-exposed Nb surface develops a more complex set of oxides with a gradually oxygen concentration (x<1) near the bulk niobium, up to the top most Nb_2O_5 (x=2.5) increasing oxygen concentration NbO_X from interstitial. Oxygen vacancies in the Nb_2O_5 (NbO_X with 2<x<2.5) create $Nb4d^1$ ion that carry an unpaired electron. These ions defects can then be seen as localized charge and spin. Cava et al. [2] showed that indeed, sub- stoichiometric bulk crystalline Nb_2O_5 develops magnetic moments and metallicity, both increasing with the concentration of oxygen vacancies.

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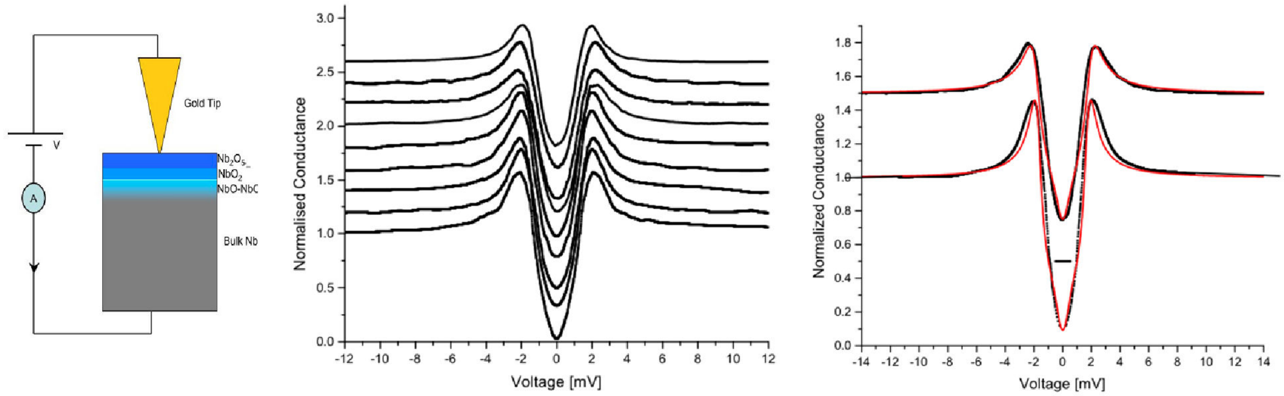

Fig. 1. Left: schematic of the point contact experiment. Center: 10 conductance curves measured at 1.7K at different locations on a baked Nb single crystal. Right: average conductance curves for baked (bottom) and unbaked (top) Nb sample, in red the corresponding fits with the Shiba theory.

At this point it is worth noting that, in fact, Halbritter [3] was the first to propose the existence of such impurities in the Nb_2O_5 and built a model based on these localized charges to explain part of the RF cavity performance. It turns out that these localized charges are also magnetic impurities.

Several mechanisms can lead to a broadening of the DOS: a proximity effect due to a metallic overlayer, a strong structural disorder that induces a mean free path $l << \xi$, where ξ is the superconducting coherence length (35 nm for Nb). However all these effects would also decrease the gap amplitude and shift the quasiparticles peaks to lower energy. This is in contradiction with our results that show (Fig 1 Right) a shift of the peaks to energies higher than the bulk Nb gap Δ=1.55 meV. To our knowledge only one mechanism can explain these results: pair-breaking caused by inelastic scattering on magnetic impurities.

The Shiba theory [4] describes the effect of bulk-diluted paramagnetic magnetic impurities on the superconducting DOS in the strong coupling limit: additional quasiparticles' states develop at an energy ε inside the gap where ε is a parameter that depends on the coupling strength (the weak coupling limit, or Abrikosov-Gorkov theory, is given by ε=1). The scattering rate of quasiparticles, $\alpha=\Gamma/\Delta$, where Γ is the quasiparticles lifetime, broadens the DOS and shift the peaks to energies E> Δ (Fig. 1 Right). The best fit gives Δ=1.55 meV, ε=0.62, $\alpha_{Unbaked}$=0.3 for an unbaked sample and Δ=1.55 meV, ε=0.62, α_{baked}=0.2 for a baked sample. From these parameters, we can extract the corresponding concentration of magnetic impurities and find 0.2 at.% for an unbaked sample and 0.13 at.% for a baked sample. The total number of quasiparticles inside the gap can be calculated by integrating conductance curves between +Δ and -Δ. We find the ratio of the areas for baked and unbaked curves to be equal to ~1.5, the dissipation mechanism of a baked sample is then reduced by the same amount with respect to an unbaked sample. This result seems in good agreement with the ratio of the quality factor Q at medium field for unbaked and baked single crystal cavities [5].

The microscopic origin of the mild baking effect and the related decrease of magnetic scattering can be explained by a simple mechanism; Irreversible local rearrangements of oxygen in the niobium oxides occur even at such a low temperature, for instance the growth of a thicker [6] and more stable NbO_2 Peierls semiconductor which is non magnetic by nature. NbO_2 acts as a protective layer and prevents partially the superconducting pairs from being scattered by magnetic impurities present in the Nb_2O_5 located on top of NbO_2. As the probability of a pair to tunnel through an insulator decreases exponentially with its thickness, the drop off of magnetic impurities concentration, as felt by the superconductor, requires only a few Angstrom thick stoichiometric NbO_2.

This irreversible modification of the oxide layer induced by the mild baking treatment provides also an explanation for the reported stability [7] of cavity performance to various surface treatments such as air or vacuum baking, air exposed for one year, and successive water rinses. Several experimental results however seem to be inconsistent with this hypothesis, for instance the growth of Nb_2O_5 by anodization up to a certain thickness (~50 nm) does not modify the post-baking improvements. If it is hard to imagine that the thin stoichiometric NbO_2 layer is unperturbed by the anodization, it is nonetheless well known that anodized Nb_2O_5 contains less oxygen vacancies than the fast grown wet oxides [8]. The detailed mechanism of the anodization growth seems to be well understood and based on the Cabrera-Mott process [9] that depends on the oxygen mobility and local electric field. It is probable that the growth of the first nanometers of Nb_2O_5 is almost defect free, whereas as the thickness of the oxide layer increases, the growth starts to become more difficult leading to an increase of oxygen vacancies concentration at the interface with the niobium and to the reappearance of the Q-slope for Nb_2O_5 layers above ~50 nm. X-ray fluorescence or X-ray magnetic circular dichroism experiments could be relevant techniques to elucidate the defect composition of anodized Nb_2O_5.

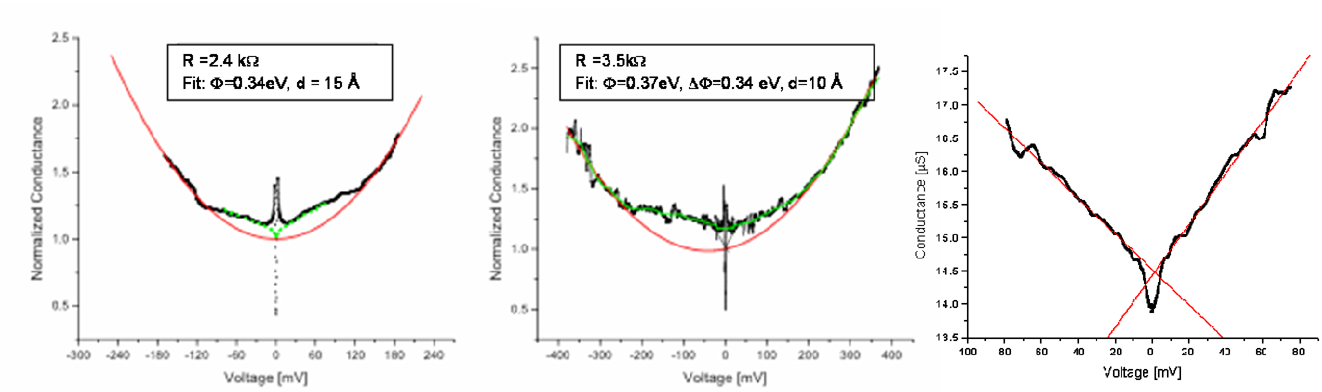

Fig. 2. High bias conductance curves on an electropolished cavity-grade niobium sample. Parabolic fits using the Dynes-Brikman theory are in red with the corresponding parameters. Left: baked in UHV at 120C for 24h, middle: unbaked and freshly electropolished, right: typical linear slope conductance observed on all samples, in this case T=9.7K > Tc

III. High bias and the tunneling barrier

As we showed in the previous section, for bias voltage around the Fermi level the tunneling spectroscopy probes the superconducting DOS. At bias $V>>\Delta$ (1.55 meV) however, the conductance spectrum reveal the properties of the tunneling barrier itself, that is the native insulating oxides on the surface of electropolished niobium coupons.

Preliminary results are shown in Fig.2. The tunneling conductance curves were measured up to 350 mV for a baked (left) and an unbaked (middle) cavity grade Nb samples. In each case, a first region can be distinguished: a parabolic-like increase of the conductance that reflects the trapezoidal shape of the tunneling barrier. Fits using the Brikman-Dynes [10] theory are shown in red and depend on 3 parameters; the thickness d of the barrier, in this case the Nb_2O_5, the average work function Φ, and its asymmetry $\Delta\Phi$. The work function Φ for both baked and unbaked sample is approximately the same, ~0.35 eV, in agreement with previous measurement on niobium [11]. The thickness however changes significantly. The unbaked sample was cooled down to 4.2 K 10 h after the electropolishing, whereas the baked sample spent 1 day on the experimental bench after the 24h baking in UHV. The corresponding thicknesses extracted from the fits are in agreement with measurements of the growth rate in air of the Nb_2O_5 done by Halbritter on niobium single crystal (110) [3].

Perhaps more interesting is the clear deviation from the parabolic behavior at lower voltages, indicative of additional states in the barrier that spread between ~ 0 and 200 mV for the unbaked sample and between 0 and 120 mV for the baked sample. Similar high bias measurements (not shown here) on niobium pentoxide-free oxide show a flat conductance followed by the usual parabolic increase. We can deduce that these states are present in the Nb_2O_5 and probably due to the localized states mentioned earlier. The total number of additional states, calculated by integrating the difference of the red and green curves shown in Fig. 2 (left) and (middle), is reduced by a factor of 2 after baking. This might be due to local rearrangement of oxygen vacancies inside the oxides. This preliminary observation supports Halbritter hypothesis [3]. A more detailed study of the conductance in this region reveals a linear increase that seems to depend on the oxide thickness but not on the temperature, to be published. Several tunneling mechanisms can explain this linearity, among which are the double hopping process through localized states, or the presence of localized paramagnetic moments [12] in the barrier. While it is too early to discard one for the other, the localized nature of these states is established. The same behavior has been found on transition metal oxides such as vanadium oxides, chromium oxides, titanium oxides [13] etc. all of which show magnetic properties.

Further study on baked and unbaked sample will continue.

IV. Atomic layer deposition and high temperature baking

Atomic layer deposition (ALD) [14] is a method of synthesizing materials in single atomic layers that can achieve a growth rate of a few microns/hr. We are studying an alternative solution to remove the oxides from the Niobium surface using ALD by coating some cavity-grade electropolished Nb samples with a uniform 2-3nm Al_2O_3 protective overlayer and heating them in UHV at a high temperature [15]. The coated samples were baked in a vacuum of 2.10^{-9} Torr at temperature ranging from 250-500 °C and the XPS spectrum of the Nb3d core level was measured during heating. After each thermal treatment the samples were transferred in air to the point contact apparatus and the surface superconducting DOS was probed by tunneling spectroscopy at a temperature of 1.6 K.

We found reproducibly that a low temperature baking from 220-380 °C leads to reduced superconducting features: a gap $\Delta<$ 1.55 meV and an increased inelastic scattering parameter that fills the gap with normal electrons and increases the dissipation. At temperature above 450 °C, however, Δ recovers the bulk niobium gap value of 1.55 meV and the inelastic scattering parameter decrease drastically down to 0.08 meV.

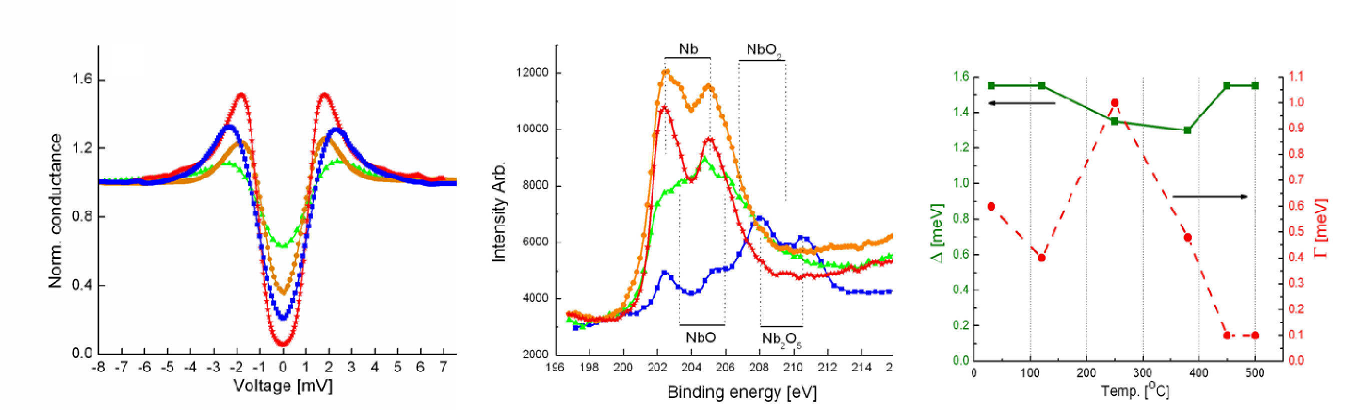

Fig. 3. Left: Tunnel conductance curves measured at 1.7K after each temperature treatment (color labels: red stars corresponds to 450 °C for 24 h, orange circles to 380°C for 24 h, green triangles to 250 °C for 2h and blue squares for room temperature). Center: corresponding XPS spectrum. Right: evolution of the gap (solid green) and inelastic scattering parameter, Γ (dash red) as a function of the baking temperatures.

In the present study, we observe a shift of the quasiparticle peaks to voltages above the bulk Nb energy gap of 1.55 meV, suggesting an inelastic scattering mechanism. However, baking is complex; in addition to inelastic scattering, well-known deleterious effects occur which could lead to a filling of the gap, such as the massive injection of oxygen into niobium, and other elastic processes.

Extracting the proportion of inelastic and elastic scattering mechanisms is beyond the scope of this paper and perhaps impossible. As a consequence, we think of Γ as a broadening parameter that gives a quantitative estimate of the deviation of the measured superconducting DOS from an ideal one. Perhaps more significant, in the presence of an RF magnetic field at few GHz, only electrons with a few μeV energy around the Fermi level will couple significantly and dissipate. The number of such states inside the gap can be extracted from the value of the zero bias conductance (ZBC), or as the ratio: Γ/Δ, within the phenomenological Dynes model [16].

For unbaked coated samples, the tunneling conductance spectrum is identical to that of the uncoated samples, implying that the coating procedure didn't affect the surface superconducting DOS. This first result is in agreement with preliminary RF test done on coated cavities (see section 4). At 250 °C for 2h (green line in Fig. 2 center), the XPS spectrum shows a reduction of Nb_2O_5 into sub-oxides; in addition oxygen diffusion on a distance of the order of λ, thus increasing the oxygen concentration and the dissipation in the induced current layer. The strong increase of the inelastic parameter Γ=0.9 meV and the decrease of the gap Δ=1.35 meV, extracted from the fit of the conductance spectrum, indicates an important surface pollution of the superconducting niobium. At higher baking temperature; 380°C for 20h (orange line in Fig. 2 center), the surface oxides are now composed mostly of metallic oxides NbO and NbOx (x<1) with a small amount of NbO_2. The tunneling conductance curve reveals a pronounced decrease of the superconducting gap down to Δ=1.3 meV, consistent with the presence of a thicker metallic overlayer on top of niobium [6]. For this baking parameters interstitial oxygen diffuses on several mm >> λ, a cleaning of the interface oxides/Nb leads to the decrease of the broadening parameter Γ=0.35 meV. Finally for temperature above 450 °C during 20 h (red line in Fig. 2 center), the XPS spectrum shows that niobium oxides are now composed of pure NbO together with a sharpening of the metallic niobium peaks Nb^o indicating that a the sub-oxides had partially disappeared. The related tunneling spectrum shows a recovering of the bulk Niobium gap Δ=1.55 meV and a decrease of the zero bias conductance to less than 5%, indicative of a strong reduction of the normal electrons inside the gap: Γ=0.08 meV. The XPS spectrum reveals a sharpening of the Nb peak, indicative of a further decrease of the oxide layer thickness. The overall evolution of total niobium oxides amount is confirmed by the atomic percentage of oxygen inferred from the survey spectrum taken at each temperature. The saturation of the superconducting parameters, as well as the NbO peak intensity above 450 °C, indicate a more stable and ordered NbO phase, discovered by Hellwig [17] for similar high temperature baking. This would lead to a thin, clean metallic overlayer on top of the bulk niobium, with no interstitial oxygen at the interface. In such a case, Arnold theory and previous experiments showed that the superconductivity is fully induced in a thin, clean NbO metallic overlayer without any reduction of the underneath niobium gap Δ=1.55 meV. The coated cavity baked at this temperature should show better performances, close to the ideal limits of a perfect Nb superconductor.

It is interesting to see that there is a correlation between the evolutions of the superconducting parameters, Δ and Γ measured on niobium coupons and the evolution of the Q factor and Tc values measured on Nb cavities baked under the same conditions [18]. Higher baking temperature will be tested in order to improve the superconducting DOS, aiming at an ideal BCS superconductor with no smearing parameter or additional states inside the gap. However, a maximum baking temperature is imposed by the alumina overlayer stability. For T<800 °C a 2-3 nm amorphous Al_2O_3 layer is stable, but for higher T the Alumina transforms into a crystalline α phase, building nanocrystals and cracks. Above T=1000 °C the protective layer vaporizes.

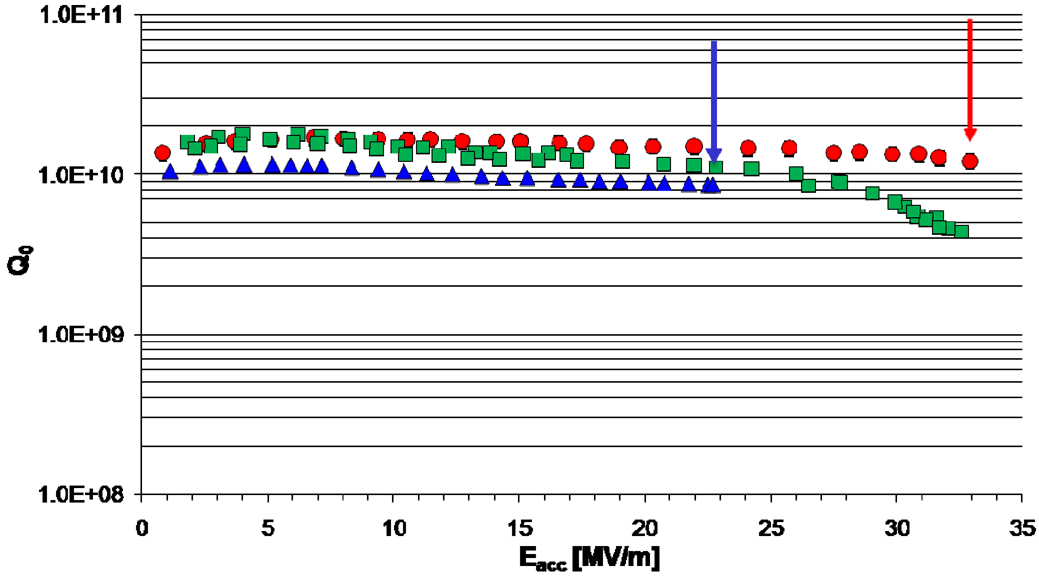

Fig. 4. RF performance test on a 1.3 GHz cavity, as received in blue: the blue arrow indicates the quenching field: 23 MV/m. The best test ever done with this cavity (green) after electropolished and baked, and after the ALD coating (red), the quenching field (red arrow) is 32.9 MV/m.

V. Cavity radio frequency test and field emission

We tested the atomic layer deposition process on a 1.3 GHz niobium cavity from Jlab. The cavity was inserted into the ALD line and coated with 10 nm an Alumina layer and then covered by 3 nm of niobium pentoxide Nb_2O_5 to avoid multipacting. Nb_2O_5 is known to have a much lower secondary electron yield than Al_2O_3, acting as a protective overlayer against multipacting. During the deposition process, the cavity was wrapped with heating tape and baked at 200 °C for a total time of 2 h, the outside walls of the cavity were air exposed. The precursors used to deposit the multilayer structure were carried by a constant flow of ultra pure nitrogen. The gas precursor for the alumina (trimethyl aluminum) was sent with a pulse of 2 s followed by a pumping time of 5 s, the oxidizing agent (water) was sent after with a pulse of 2 s and pumped during 5 s. A total of 100 cycles were needed to grow a 10 nm thick layer of amorphous Al_2O_3. The precursor $Nb(OC_2H_5)_5$ was sent Immediately after with a pulse of 5 s follow by a purge of 5 s, and then water for 2 s and a purge of 5 s. The growth of 3 nm of amorphous Nb_2O_5 required 60 cycles. Fig.4 Left, summarizes the RF test before (in blue) and after the ALD coating (in red), without any high temperature baking.

This first result proves clearly not only that the ALD layered structure didn't do any harm to the cavity, in agreement with the results in section III, but on top of that the Q drop at high field, visible on green curve, disappeared up to the quench at 32.9 MV/m. The improvement with respect to the as-received cavity (bleu) is clear: the quality factor is increased by a factor of 3, the maximum accelerating field Emax by a factor of 1.5. Whereas such improvements are due to the ALD coating itself, to the baking at 200 °C during the deposition process or to the high pressure rinsing is still unclear and we are currently coating more cavities to investigate the reproducibility of such results. It is worth noting that the green curve showed significant field emission at high field whereas the ALD coated cavity showed none. A simple explanation could be that, as amorphous alumina has an excitation band gap of ~ 5-7 eV, the conformal protective layer makes uniform and increases the work function on the inside cavity walls, preventing electrons from metallic defects in the native niobium oxides from escaping the surface.

In principle a wide range of metals, including elemental niobium, metal oxides, nitrides or more complex compounds, can be achieved by ALD or by plasma-enhanced ALD (PEALD). Even the superconductor NbN has been successfully grown with a critical temperature of 15.75 K close to the bulk value (16 K). The next step is now to build, first on cavity grade niobium coupons, the multilayer structure proposed by Gurevich [19], alternating alumina layers ~20 nm thick with NbN layers of 150 nm thick. Other superconductors could be also grown, such as V_3Si (Tc=17 K), Nb_3Ge (Tc=20 K), MgB_2 (Tc=40 K).

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