Tunneling Study of SRF Cavity-grade Niobium

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Abstract—**Niobium, with its very high HC1, has been used in superconducting radio frequency (SRF) cavities for accelerator systems for 40 years with continuous improvement. The quality of cavities (Q) is governed by the surface impedance RBCS, 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 method and how it can help understanding SRF cavity performances. 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 delta=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 SCRF cavities performances have been continuously improved to reach now reproducible quality factor of 10^10 and max accelerating field E of 30 MV/m. However, unresolved mysteries among which High field Q-slope and its mitigation by a mild baking treatment remain 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 a heretofore unrecognized contributor 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 characterize the tunneling barrier itself, here the niobium insulating oxides 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 getting ride of the oxides: A uniformly 2nm thick Alumina film has been deposited by 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 exposed.

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 or single crystals 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 24h - 48h) 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 then a more complex set of oxides with a continuum of gradually increasing oxygen concentration NbO_X from interstitial
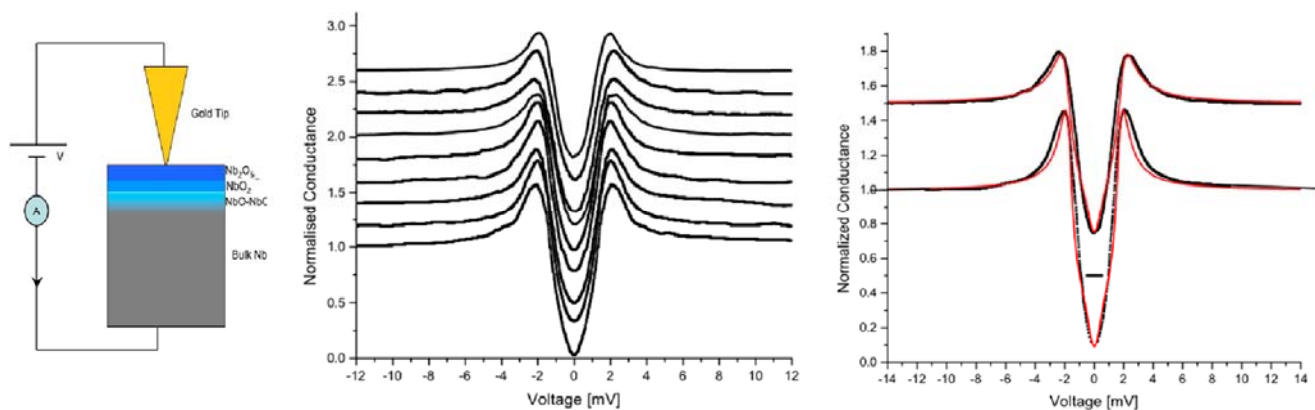
Fig.1. Left: schema of the point contact experiment. Center: 10 conductance curves measured at 1.7K on a baked Nb single crystal, the conductance curves has been shifted by 0.2 vertically for more clarity. Right: Average conductance curves shifted by 0.5 for more clarity, for a baked (bottom) an unbaked (top) Nb sample, in red the corresponding fits with the Shiba theory.

oxygen (x<1) near the bulk niobium, up to the top most Nb_2O_5 (x=2.5). Oxygen vacancies in the Nb_2O_5 (NbO_X with 2<x<2.5) create Nb4d1 ions that carried 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 oxygen vacancies concentration. At this point it is worth noting that, in fact, Halbritter [3] was the first to propose the existence of such impurities in the Nb2O5 and built a model based on these localized charges to explain part of the RF cavity performances. It turns out that these localized charges are also magnetic impurities.

Several mechanisms can lead to a broadening of the DOS: proximity effect due to a metallic overlayer, strong structural disorder that induces a mean free path $l << \xi$, the superconducting coherence length (35 nm for Nb). However all these effects will 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 higher energies 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 state develops 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% for an unbaked sample and 0.13% for a baked sample. The total amount of quasiparticles inside the gap can be calculated by integrating conductance curves between $+\Delta$ and $-\Delta$. 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 is in good agreement with the ratio of the Quality factor Q at low field for unbaked and baked cavities.

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 low temperature; the growth of a thicker [5], more stable NbO_2 Peierls insulator, non magnetic by nature, acting as a protective layer. NbO_2 prevents then 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 of cavity performance to various surface treatments such as air or vacuum baking, air exposed for one year, successive water rinses etc...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) that do 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 []. The detailed mechanism of the anodization growth seems to be well understood and based on the Camberra-Mott process that depends on the oxygen mobility and local electric field. It is probable that the growth of the first nanometers of Nb_2O_5 are almost defect free, whereas as the thickness of the oxide layer increases, the growth start to become more difficult leading to an increase of oxygen vacancies concentration at the interface with the niobium and to the re-apparition of the Q-slope above ~50 nm. X-ray fluorescence or X-ray magnetic circular dichroism experiments could be relevant techniques to enlighten the defect composition of anodized Nb_2O_5.
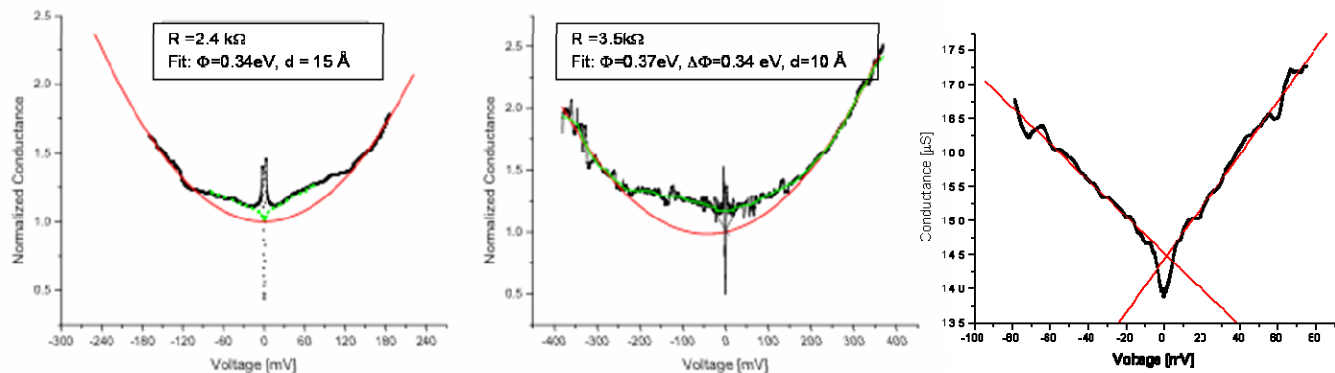
Fig.2. High bias conductance curves on electropolished cavity-grade niobium sample. Parabolic fits using the Dynes-Brikman theory are in red with the corresponding parameters. Left: baked in UHV at 120C for 24h, middle: unbaked and freshly electropolished, right: typical linear slope conductance observed 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 on Figure 2, the tunneling conductance curves were measured up to 350 mV for a baked (left) an unbaked (right) cavity grade Nb sample. 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 [6] theory are shown in red and depends on 3 parameters; the thickness d of the barrier, or here the Nb_2O_5, the average work function Φ or height of the barrier and its asymmetry $\Delta\Phi$. If for both baked and unbaked Φ is approximately the same ~0.35 eV, in agreement previous measurement on niobium [7], the thickness however change 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).

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 amount of additional states can be calculated by integrating the difference of the red and green curves shown in Fig. 2 Left and middle, it gives: 42 for the baked sample and 80 for the

unbaked sample. The baking seems to have reduced the number of additional states inside the barrier, perhaps by the local rearrangement f oxygen vacancies inside the oxides. This preliminary observation comforts Halbritter hypothesis [3]. A more detailed study of the conductance in this region reveals a linear increase of the conductance that seems to depend on the oxide thickness but not on the temperature. Several tunneling mechanisms can explain this linearity, among which the double hoping process through localized states or the presence of localized paramagnetic moments [8] in the barrier. If it is too early to discard one for the other, it comforts us nonetheless regarding the localized nature of these states. The same behavior has been found on transition metal oxides such as Vanadium oxides, Chromium oxides, Titanium oxides [9], etc…all of which show magnetic properties.

Further High voltage studies on baked and unbaked sample are being carried on.

IV. ATOMIC LAYER DEPOSITION AND HIGH TEMPERATURE BAKING

Atomic Layer Deposition (ALD) [10] is a method of synthesizing materials in single atomic layers that can achieve growth rate of a few microns/hr. We are studying an alternative solution to remove the oxides from the Niobium surface by ALD coating cavity-grade electropolished Nb samples with a uniform 2-3nm Al_2O_3 protective overlayer and heat them in UHV at high temperature [11]. The coated samples were baked in vacuum at temperature ranging from 250-500 C and the XPS spectrum of the Nb3d core level was measured simultaneously. 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 1.6K.

We found reproducibly that a low temperature baking from 220-380C 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
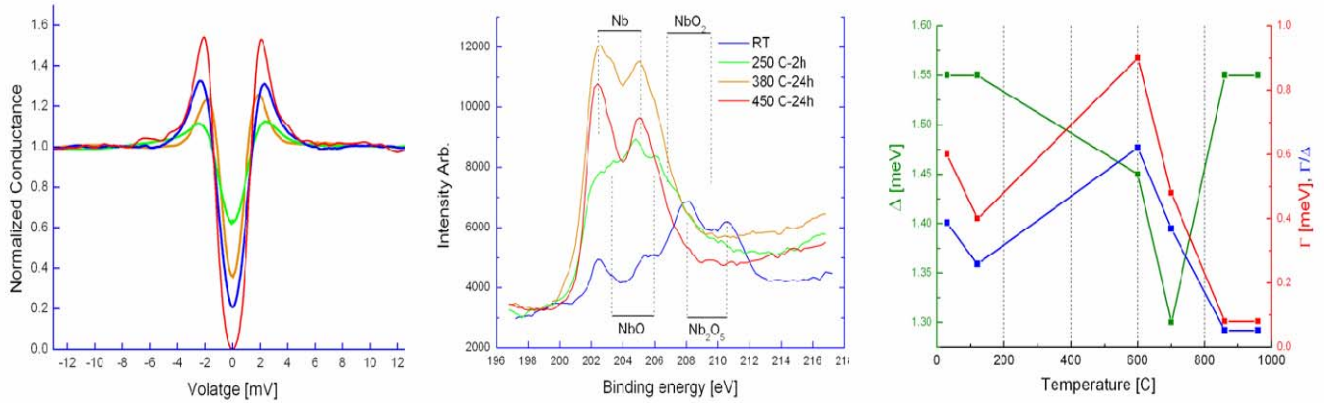
Fig.2. Left: Tunnel conductance curves at 1.7K. Center: corresponding XPS spectrum. Left: evolution of the gap and inelastic scattering parameter as a function of the baking temperature

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. 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, while baking the situation is more complex and well-known deleterious effects (massive injection of oxygen into Nb) do occur as well as other elastic processes that could lead to a filling of the gap.

To extract 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 of ~ Ghz frequency, only electrons with a few Micro-volts energy above 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.

For unbaked coated samples, the tunneling conductance spectrum is identical to 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), the XPS spectrum shows a reduction of Nb_2O_5 into sub-oxides, besides oxygen diffuses 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 $\Gamma=0.9$ meV and the decrease of the gap $\Delta=1.35$ meV, extracted from the fit of the conductance spectrum, indicates an important surface pollution of the superconducting niobium. At higher baking temperature: 380 C during 20h (in orange), the surface oxides are now composed mostly of metallic oxides NbO and NbOx (x<1) with a small amount of NbO2. The tunneling conductance curve reveals a pronounce decrease of the superconducting gap down to $\Delta=1.3$ meV, consistent with the presence of a thicker metallic overlayer on top of niobium [12]. As interstitial oxygen diffuses on several mm $>> \lambda$ for the baking parameters, a cleaning of the interface oxides/Nb leads to the decrease of the inelastic scattering parameter $\Gamma=0.35$ meV. Finally for temperature above 450 C during 20h (in red), the XPS spectrum shows that niobium oxides are now composed of pure NbO together with a sharpening of the metallic niobium peaks Nb^o. The related tunneling spectrum shows a recovering of the bulk Niobium gap $\Delta=1.55$ 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: $\Gamma=0.08$ 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 infers 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 [13] 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 $\Delta=1.55$ 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 the evolution of the superconducting parameters, Δ and Γ are in agreement with the cavity performance baked under the same conditions [14]. Higher baking temperature will be tested in order to improve the superconducting DOS, aiming at a perfect BCS superconductor with no smearing parameter or additional states inside the gap. However, a maximum baking temperature is imposed by the Alumina overlayer stability. If for T<800 C a 2-3 nm amorphous Al2O3 layer is stable, for higher T the Alumina transforms into a crystalline Alpha phase stiffer, building nanocrystals and cracks. Above T=1000 C the protective layer vaporizes.
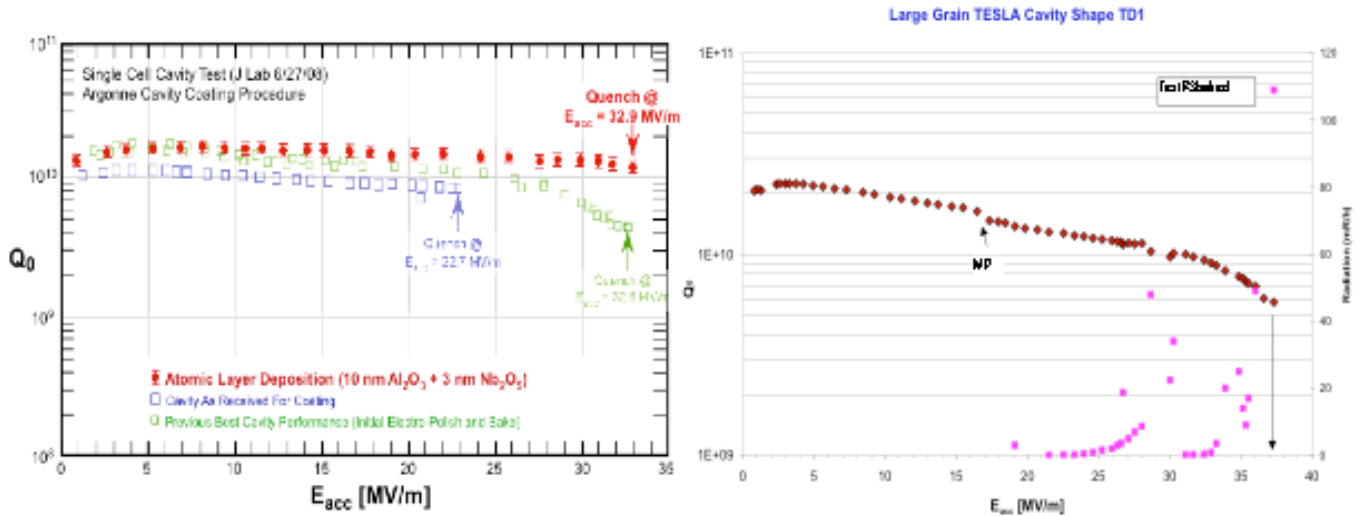
Fig. 4. Left: RF performance test on a 1.3 Ghz cavity, in bleu cavity as received, in green the best test ever done with this cavity: electropolished and baked, red: the ALD coated cavity. Right: baseline of the future cavity to be coated.

V. CAVITY RADIO FREQUENCY TEST

We tested the Atomic layer deposition process on a 1.3 GHz niobium cavity from Jlab. The cavity where inserted into the ALD line and coated with 10nm an Alumina layer covered after by 3nm of niobium pentoxide Nb2O5 to avoid multipacking effect. During the deposition process, the cavity was wrapped with heating tape and baked at 200C for ~30 mn, the outside walls of the cavity were air exposed. The precursor used to deposit the multilayer structure were carried by a constant flow of ultra pure nitrogen, the gas precursor for the alumina was trimethyl aluminum with a pulse of 1 s followed by a pumping time of 5 s then the oxidizing agent, water, was sent for 1s and pumped during 5s too. A total of 50 cycles were needed to grow a 10nm thick layer of amorphous Al_2O_3. Immediately after the precursor $Nb(OC_2H_5)_5$ was sent with a pulse of 2s follow by a purge of 5s, and then water for 1s and a purge of 5s. The growth of 3 nm of amorphous Nb_2O_5 required 30 cycles. Fig.4. Left, summarize the RF test before (in bleu) and after the ALD coating (in red), without any high temperature baking.

This first result proves clearly that not only 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 suppressed almost completely the Q-slope up to the quench at 32.9 MV/m as compared to the best test ever done on this cavity (green). The improvement with respect to the as received cavity is clear: the Quality factor is increased by a factor of 3, the maximum accelerating field Emax by a factor of 1,5. We are still investigating the possible reasons for such improvements and further ALD coating test will be done. It is worth noting that the as received cavity showed significant field emission at high field whereas the ALD coated cavity, none. The simplest explanation would be that, as amorphous alumina has an excitation band gap of ~ 5-7 eV, the conformal protective layer uniformize and increase 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 among which elemental niobium, metal oxides, nitrides or more complex compounds can be achieved by ALD or by plasma assisted ALD (PEALD), even superconductors such as NbN has be successfully grown with a critical temperature of 15.75 K quite near the bulk value (16 K). The next step is now to build, first on cavity grade niobium coupons, the multilayer structure proposed by Gurevich [16], alterning alumina layer ~20 nm thick with NbN layer of 150 nm thick. Other superconductors could be grown to such as V3Si (17K), Nb3Ge (20K), MgB2 (40K) etc…

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