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DELIVERABLE REPORT

Deposition of SC multilayers on cavities

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ABSTRACT

Superconducting radio frequency (SRF) cavities are a cornerstone infrastructure of particle accelerators. Current fabrication (bulk niobium) technology is reaching its material intrinsic limits and new materials and structures are needed to both decrease the operation and construction cost while preserving or even improving their performances.

The approach described in this task consist in depositing by Atomic Layer Deposition (ALD) superconducting multilayers and adhesion/diffusion barriers on coupons and cavities in order to increase superconducting cavity performances (Quality factor and accelerating gradient).

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Executive summary

Superconducting radio frequency (SRF) cavities are a cornerstone infrastructure of particle accelerators. Current fabrication (bulk niobium) technology is reaching its material intrinsic limits and new materials and structures are needed to both decrease the operation and construction cost while preserving or even improving their performances.

The report describe the achievement in task 9.4 of the work package 9: Innovative superconducting thin film coated cavities. This task aims at depositing by Atomic Layer Deposition (ALD) superconducting multilayers and adhesion/diffusion barriers on coupons and cavities in order to increase superconducting cavity performances (Quality factor and accelerating gradient).

We first describe (section 2) the work done on adhesion/diffusion barriers deposited by ALD with thermal treatments as means to control de top surface chemical composition/structure and study its influences on bulk Nb cavity performances. This aspect has direct implication for Qubits applications. The outcome of this work seeded international collaboration and world record high quality factors at low accelerating fields as well as multipacting mitigation by ALD on bulk Nb cavities.

In the following section 3, we demonstrate the use of ALD of TiN to suppress successfully the multipacting inside SRF cavities. This was possible owing to the atomic scale control of the TiN film thickness that in turn enabled us to tune precisely the thin film resistivity and total electron yield.

In the fourth section, we summarize the results obtained on the thermal stability of ALD protective layers deposited on Cu coupons for post deposition by HIPIMS or classical sputtering techniques of Nb and Nb3Sn thin films. We will present as well the first deposition on a Cu cavity provided by CERN. We successfully developed several oxide layers that are stable up to 700°C for 2 hrs in vacuum with no detectable Cu diffusion through the barrier.

The fifth section is focused on the results obtain on superconducting multilayers deposited by ALD on Nb coupons and cavities. We demonstrate the increase of the vortex penetration field with a multilayer on ellipsoids and, to our knowledge, the world first successful attempts at coating SRF cavities with a superconducting multilayer. We have successfully suppress the delamination previously encountered on large Nb coupons and SRF cavities, preventing us from reliably testing the multilayer approach. In parallel, we are applying the findings from the section 3 to stabilize the NbTiN layer upon annealing at high temperature.

The last section (section 6) summarize the tunneling spectroscopy achievements and ongoing projects. This unique apparatus is operational and numerous samples have been measured and analysed.

The homemade ALD system dedicated to cavity coating (Milestone 40) is operational; we have successfully coated uniformly ten 1.3 GHz niobium cavities and one Cu cavity.

1 Introduction

In this deliverable report, we first describe (section 2) the work done on adhesion/diffusion barriers deposited by ALD with thermal treatments as means to control de top surface chemical composition/structure and study its influences on bulk Nb cavity performances. This aspect has direct implication for Qubits applications. The outcome of this work seeded international collaboration and world record high quality factors at low accelerating fields as well as multipacting mitigation by ALD on bulk Nb cavities.

In the following section 3, we demonstrate the use of ALD of TiN to suppress the multipacting inside SRF cavities. This was possible owing to the atomic scale control of the TiN film thickness that in turn enabled us to tune the thin film resistivity and total electron yield.

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The fifth section is focused on the results obtain on superconducting multilayers deposited by ALD on Nb coupons and cavities. The main outcomes is the successful delamination mitigation previously encountered on large Nb coupons and SRF cavities, preventing us from reliably testing the multilayer approach. In parallel, we are applying the findings from the second section to stabilize the NbTiN layer upon annealing at high temperature.

The last section (section 6) summarize the tunneling spectroscopy achievements and ongoing projects. This unique apparatus is operational and numerous samples have been measured and analysed.

The homemade ALD system dedicated to cavity coating (Milestone 40) is operational; we have successfully coated uniformly nine 1.3 GHz niobium cavities and one Cu cavity.

I will conclude on scientific outreach (papers, patent, and conferences), interactions with the other tasks of WP 9 and future perspectives.

2 Control of Nb surface properties by ALD

The control of the niobium surface chemical composition and structure is central to the Quality factor improvement of superconducting resonators in the low field regime, dominated by two level systems defects. Previous work emphasized the dominant role of native Nb_2O_5 in RF losses. To mitigate this source of losses I proposed to use protective layers with controlled thickness, chemical composition and structure synthesized by ALD on Nb samples and 1.3 GHz cavities with post annealing treatments in high vacuum.

We have investigated the processes stability (thermal treatments, chemical stability and high pressure rinsing) of various layers deposited by ALD first on Nb coupons then on Nb cavities. Some of the results are summarized below:

2.1 Al_2O_3 THIN FILMS

Al_2O_3 thin films deposited on Nb were stable up to 650°C for 10 hrs in high vacuum and prevented the re-growth of Nb_2O_5 upon air exposure and HPR. XRR and XRD measurements showed that the Al_2O_3 films remained amorphous after annealing up to 800°C but densified progressively from 3±0.1 to 3.4±0.1 g/cm^3 losing Hydroxyl groups and improving the loss tangent. Higher temperature annealing up to 800°C however led to inconsistent results: for some samples annealed for 2 to 3 hrs, a small amount of Nb_2O_5 was present after air exposure. Only one sample annealed for a shorter amount of time (1/2 hr at 800°C) showed Nb_2O_5 free surface. We therefore decided to limit the post annealing temperature to 650°C. The optimized recipe was applied on two Nb cavity and the RF tests showed in both case a factor 2 increase of the Q factor (figure 1) as compared to the baselines from 10^{-4} MV/m up to ~ 18 MV/m where a multipacting barrier occurred. This Q factor in the Two level system (TLS) defects dominated regime below 1MV/m can be explained by a reduced amount of TLS in a 10 nm thick amorphous Al_2O_3 as compared to a 6.5 nm thick amorphous Nb_2O_5 layer. This work was published last year in Applied Physics Letter [1, CP1].

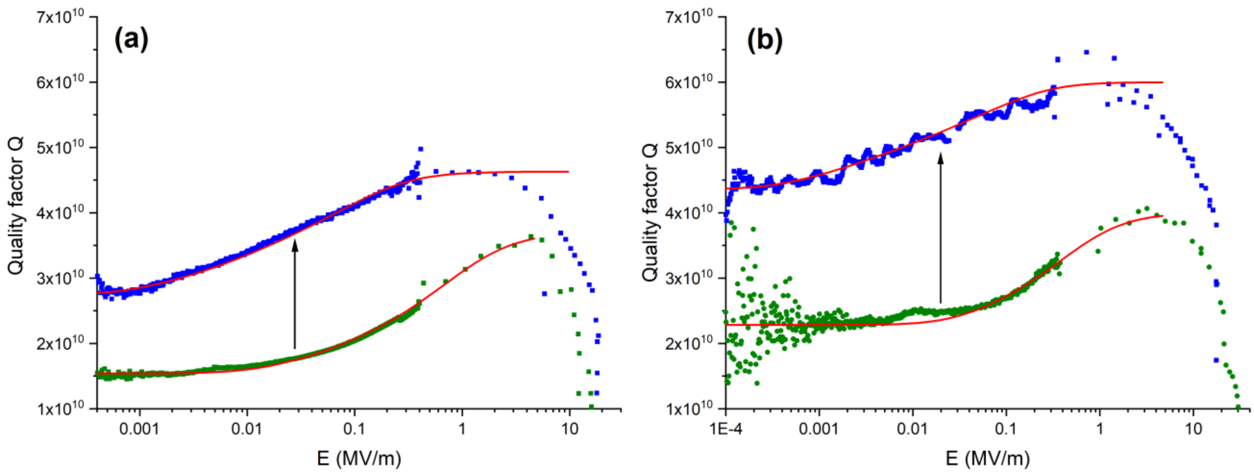

Figure 1: RF tests at 1.4K of two Nb cavities coated with 10 nm Al_2O_3 and post annealed at 650°C for (a) 4 hrs and (b) 10 hrs).

As the amount of TLS defects, and therefore quality factor values at low fields, depend on the thickness of the Al_2O_3 layer, I proposed to investigate the process stability (post annealing, HPR) of various layer thicknesses from 10 nm down to 2.5 nm. XPS analysis showed that for all the thickness investigated the Al_2O_3 film was preventing NbOx regrowth after HV annealing and air exposure. After HPR, however, only films thicker than 4 nm were able to prevent NbOx growth (figure 2), indicative of a O/OH diffusion through the Al_2O_3 thinnest films. We tested a 2.5 nm thick film on a cavity, post annealed without HPR. The RF tests failed due to an antenna breakdown. This cavity will be re-tested soon. Another 1.3 GHz Nb cavity was coated with 5 nm of Al_2O_3 and sent for post processing and RF testing at FNAL. We do not have the results yet.

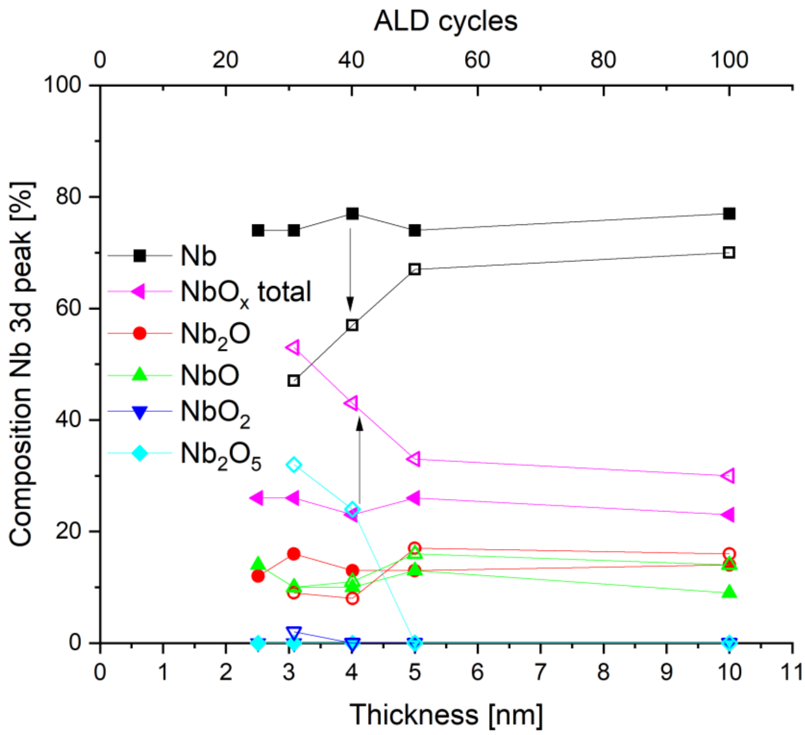

Figure 2: Niobium chemical composition measured by XPS after annealing at 650°C for 10 hrs in HV (full symbols) and HPR (open symbols) for different film thickness.

The high gradients RF tests on Al_2O_3 thin film coated Nb cavities reveal a strong multipacting barrier at around 18 MV/m due to the large Secondary electron yield of Al_2O_3 as compared to Nb_2O_5. We have successfully developed a method based on ALD of thin TiN films to mitigate multipacting phenomenon in SRF cavities [2] as described in the next section.

2.2 ZrO_2 THIN FILMS

The crystalline nature of the protective layer also influences the density of TLS defects; in consequence, I choose to investigate ZrO_2 that grows crystalline by ALD, in contrast to the amorphous Al_2O_3. ZrO_2 is extremely chemically stable, and according to the Ellingham diagrams more stable than Nb_2O_5 and NbO from 100 to 2000 K. We first assessed the thermal stability of a 10 nm thick ZrO_2 film deposited on EP Nb and found that ZrO_2 is stable up to 900°C for 3 hrs, with a sharp Nb metal/ZrO2 interface after air exposure and HPR. The absence of NbOx layers as probed by XPS is an improvement over the Al_2O_3 capping layer that always showed NbOx sub oxides (Nb_2O and NbO) at the interface.

Following our experience with Al_2O_3, we showed that ZrO_2 films thinner than 5 nm did not prevent Nb_2O_5 from reappearing upon air exposure and/or HPR, setting a lower limit on the thinnest film we can effectively use on a cavity (figure 3 (a)). TEM cross section investigation revealed a crystalline and uniform 5 nm ZrO_2 film and confirmed the sharp and oxygen free interface between metallic Nb and ZrO_2. After insuring a uniform film thickness across a cavity profile, two Nb cavities were coated with 5 nm of ZrO_2, one was sent to FNAL and one was processed here at CEA. The RF test at CEA showed an 80% improvement of the Q factor at low and medium fields up to a few MV/m. We are awaiting for the FNAL test results. We plan to redo one ZrO_2 deposition and RF test to confirm this result.

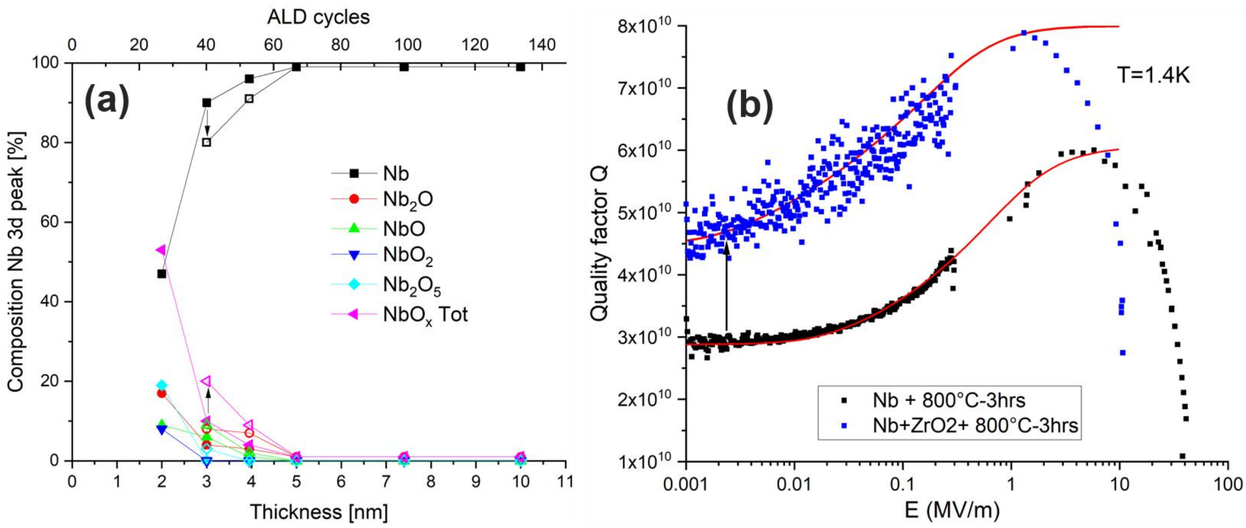

Figure 3: (a) Niobium chemical composition measured by XPS after annealing at 650°C for 10 hrs in HV (full symbols) and HPR (open symbols) for different film thickness. (b) Preliminary RF tests of a Nb cavity coated with 5 nm of ZrO_2 and post annealed at 800°C in HV with HPR.

2.3 Ta_2O_5 THIN FILMS

In parallel, we also investigated with FNAL the possibility to coat a Ta_2O_5 thin film inside Nb cavities. Tantalum oxide are known to host lower TLS defects concentration and Ta resonators have twice higher quality factor than Nb ones in the quantum regime. At CEA, we synthesized Ta_2O_5 by ALD and showed that 800°C or 900°C post annealed lead to diffusion of Nb into the Ta layer. FNAL further optimized the post annealing treatment that led to a preserved Ta_2O_5 layer without inter diffusion and the minimal amount of NbOx at the interface.

Following this work we optimized the grow recipe to obtain a uniform layer on a cavity profile and coated a Nb cavity with 10 nm of Ta_2O_5 that was sent back to FNAL for post processing and RF tests at ultralow temperature. We are awaiting for the test results.

2.4 NATIVE NIOBIUM OXIDE IMPROVEMENT

In addition to the ALD protective layer work summarized in the previous sections, we also investigated a method to optimize the native niobium oxide itself, trying to find processes that would reduce as much as possible the TLS losses and hence the amount of Nb_2O_5. I tested the annealing at 650°C for various amount of time in vacuum of an air-exposed niobium (coupons and cavities) as a way to re-order to residual NbO layer at the top surface. The XPS analysis on coupons showed the presence of a Nb_2O layer at the interface between the Nb and the Nb_2O_5. Moreover, the amount of Nb_2O_5 was greatly reduced after HPR as compared to a sample electropolished + HPR (figure 4 (a)). TEM cross sections analysis revealed a thin oxide layer of 4 nm after HPR instead of 6.5 nm on a reference sample electropolished + HPR. TEM also showed the presence of NbO crystals within the native oxide layer; in some locations, the native oxide was only composed of crystalline NbO without Nb_2O_5. We tried also a higher temperature annealing up to 800°C but the XPS analysis showed no difference with a Nb samples EP + HPR.

We applied these processes (650°C and 800°C) on two Nb cavities. After 650°C annealing in High vacuum, the RF tests showed a world record high quality factor (Q~10^{11}) at low field amplitude after air exposure and HPR (figure 4 (b)). Whereas after an 800°C annealing, the low RF field quality factor was no different from a baseline RF test with a value of ~ 2.10^{10}. These experiments confirm the dominant role of amorphous Nb_2O_5 in RF losses and the associated TLS defects. These results also pave the way for new and more optimized air stable treatments of Nb superconducting films used in the Qubits community. This work is to be published in Physical Review Applied [3] and a patent have been submitted.

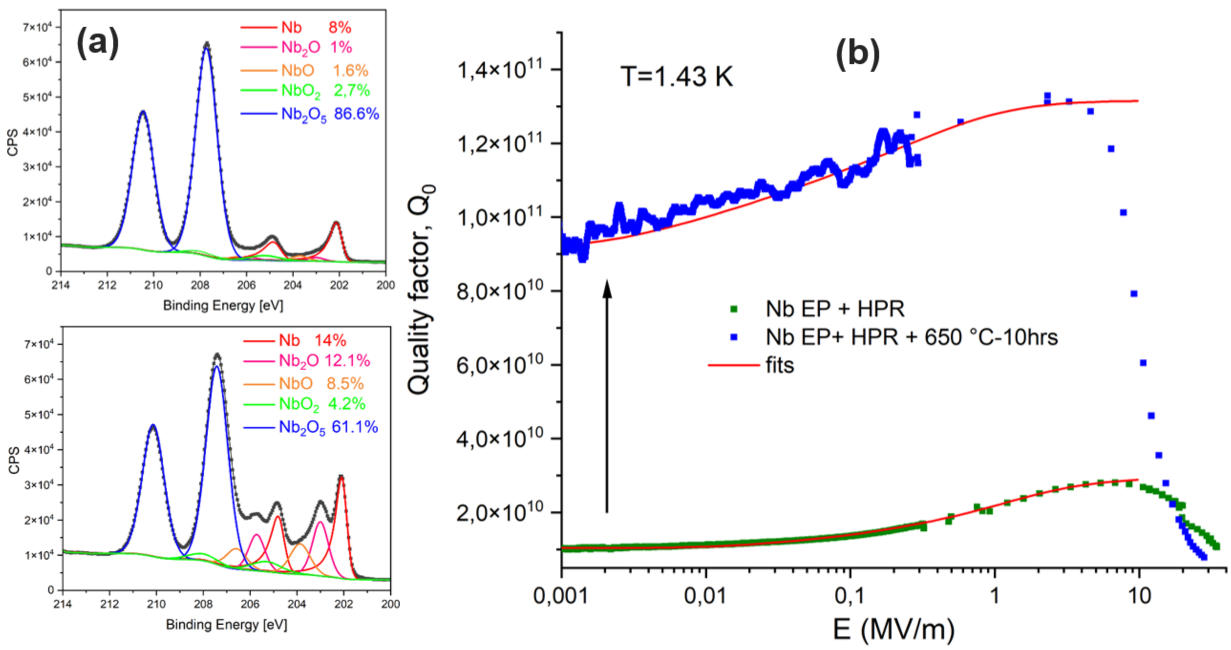

Figure 4: (a) comparision of the Nb peak chemical composition byu XPS between a referenced Nb EP + HPR sample (top) and a Nb EP post annealed at 650°C with HPR (bottom). (b) The corresponding RF tests of a cavity with the same treatments.

2.5 Conclusion and prospects

We demonstrated that the combination of ALD and post annealing steps open new opportunities to control the surface chemical and structural properties that strongly influence the RF performances of superconducting resonators. The next step involves applying this method to 2D superconducting thin films in Qubits units.

3 Multipacting mitigation in SRF cavities

We have investigated the use of Atomic Layer deposition (ALD) to mitigate multipacting phenomena inside superconducting radio frequency (SRF) cavities used in particle accelerators while preserving high quality factors in the 10^{10} range. The unique ALD capability to control the film thickness down to the atomic level on arbitrary complex shape objects enable the fine tuning of TiN film resistivity and total electron emission yield (TEEY) from coupons to devices. This level of control allows us to adequately choose a TiN film thickness that provide both a high resistivity to prevent Ohmic losses and low TEEY to mitigate multipacting for the application of interest. The methodology presented in this work can be scaled to other domain and devices subject to RF fields in vacuum and sensitive to multipacting or electron discharge processes with their own requirements in resistivities and TEEY values.

3.1 Tuning the resistivity and the TEEY by ALD

The TiN films were deposited on a 9 nm thick film of ALD Al_2O_3. The resistivity of the as-deposited TiN films displayed in Figure 5 (a) were measured with four point probes at room temperature. The bulk resistivity is 63 μΩ.cm and start increasing below 10 nm. For films thinner than ~ 0.8 nm the resistivity values were too high for our set up to be measured (> 106 μΩ.cm). Attempts to fit the data with Fuchs or Mayadas theories that take into account various electron diffusion mechanisms (grain boundaries, point defect and surfaces scattering) did not succeed because the experimental resistivity values increase faster than what is predicted by the theory. This can be explained by the change in chemical composition probed by XPS with an increasing insulating TiO_2 component as the film thickness decreases.
The TEEY of the as deposited bilayer Al_2O_3-TiN was measured for various TiN films thicknesses. The TEEY measured as a function of primary electron energy from 11 to 1800 eV. All the TEEY

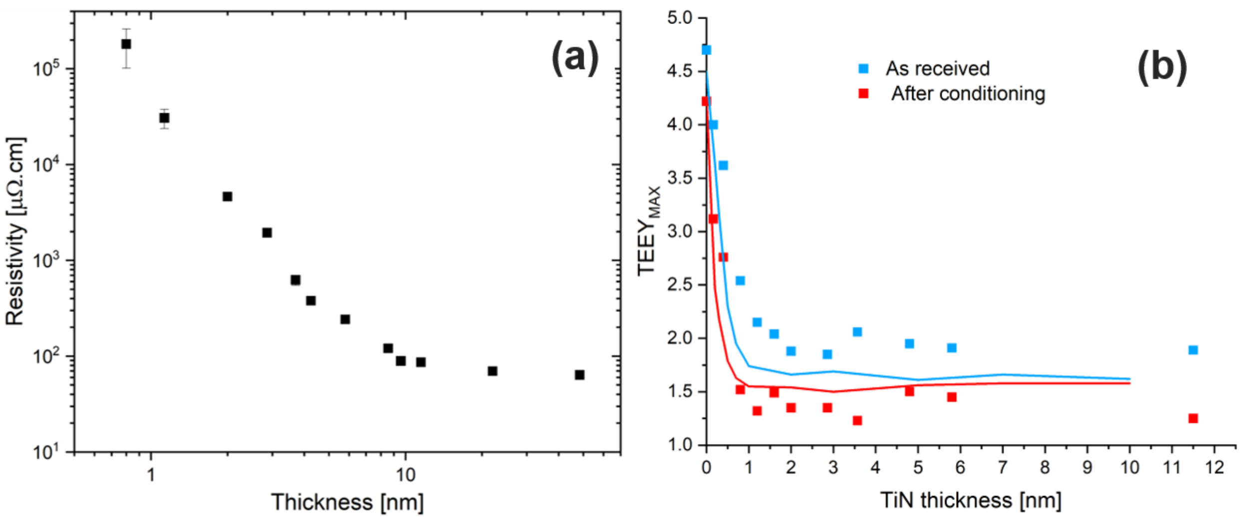

Figure 5: Dependence of the TiN film (a) resistivity and (b) TEEY on the TiN film thickness. The solid lines are fits using the MICROELEC module code developed to simulate electron transport.

curves shows a typical shape where the TEEY first increases with the energy of the primary electrons until it reaches a maximum value of TEEY $_{MAX}$ at energy E_{max} and decreases again upon increasing the primary electron energy. Using the measured film thicknesses, we can extract the maximum TEEY as a function of TiN film thickness represented in Figure 5 (b). Starting from the bare 8.5 nm Al_2O_3 film, the maximum TEEY (TEE $_{MAX}$) is 4.65 ± 0.05 at around E_{max} = 320 eV, in agreement with previous literature results with ALD Al_2O_3. As the TiN thickness is increased, the TEEY$_{MAX}$ decreases exponentially to saturating values of 1.87 and 1.25 before and after conditioning for films thicker than ~ 2 nm or 50 ALD cycles.

3.2 CAVITY TEST RESULTS

In order to test the multipacting mitigation approach using a thin TiN layer deposited by ALD, a first attempt was made to deposit 10 nm of Al2O3 inside a 1.3 GHz cavity followed by a post annealing at 650°C for 10 hrs in high vacuum (in the 10^{-6} mbar). The purpose of such deposition and annealing procedure is described in [1]. This process was repeated twice on the same cavity with a reset of the surface by chemical etching in between the Al2O3 ALD depositions and post annealing. For both RF tests after deposition and post annealing, a strong multipacting barrier reproducibly occurred at 15-18 MV/m and could not be processed, preventing us from reaching higher accelerating fields. Following standard SRF cavity-testing procedures, a high pressure rinsing is carried out prior to each RF tests presented in this section.

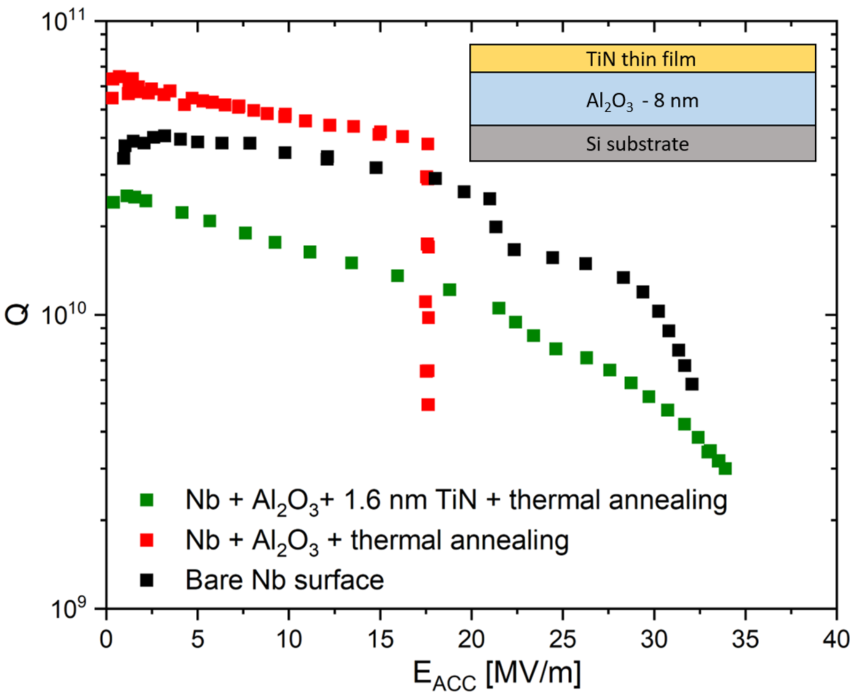

Figure 5c: RF tests of a bare niobium cavity (black), coated with 10 nm of Al2O3 and post annealed at 650°C for 10 hrs (red) revealing the strong multipacting barrier. In green, the same cavity with an additional 1.6 nm of TiN deposited by ALD, supressing the multipacting.

We deposited two different thicknesses of TiN on previously tested Al2O3-coated and annealed Nb cavities. The RF performances after a 5 nm (230 ALD cycles) TiN film coating revealed significantly degraded quality factors (Q) with respect to the Al2O3-coated cavity baseline; the Q values are decreased by over 2 orders of magnitude down to 10^8 and correspondingly the surface resistance increases 330 times to 2200 nΩ. The second RF test was conducted after a 1.6 nm (40 ALD cycles) TiN coating and the measurements are shown in Figure 6. The quality factor is now in the 10^{10} range, two orders of magnitude higher than for the previous RF test with a 5 nm TiN coating. Correspondingly, the surface resistance decreases from 2200 nΩ down to 10.8 nΩ at low temperature upon reducing the TiN thickness from 5 to 1.6 nm. Importantly, the multipacting barrier at 18 MV/m disappeared, extending the range of accelerating gradient from 18 MV/m up to 35 MV/m and recovering the bare Nb RF maximal E_{ACC} performance (black curve in Figure 5c).

3.3 CONCLUSION AND PROSPECTS

We have investigated the ALD growth TiN film thickness dependence of the TEEY, chemical composition and resistivity. The ALD growth mechanisms explained by a simple model lead to an incomplete surface saturation of the TiN for films thinner than 1.5-2 nm. Consequently, the $TEEY_{MAX}$ values can be understood as a linear combination of the Al2O3 and the TiN $TEEY_{MAX}$ respective values. For film thicker than 2 nm, the surface is fully covered with TiN and the TEEYMAX values saturate. The TiN film resistivities increase exponentially below 10 nm ranging from 63 μΩ.cm in the bulk limit to over 105 μΩ.cm for 1 nm thick film. The careful selection of a suitable set of $TEEY_{MAX}$ and resistivities values by finely tuning the TiN film thickness enabled the suppression of the multipacting phenomena observed in SRF cavities while maintaining the high quality factor of the superconducting resonators in the 10^{10} range. The results presented here prove that the ALD-based surface engineering is a viable technological route to successfully mitigated multipacting in SRF cavities that could be applied to various cavities shapes. Besides, the scalability of ALD from coupons to real device, is an opportunity to apply this method to other particle accelerator devices such as drift tubes or power couplers, and other RF devices used in satellites for instance with their own optimal resistivities and TEEY values requirements. This work was published last year [2].

4 Diffusion barriers and adhesion layers on Cu

The deposition of superconducting layers on Cu substrates is of primary importance for future superconducting cavities with reduced amount of expensive materials, increased operation temperature and enhanced thermal conductivity. Several issues remain to be solved and explored: the generation of thermo-currents arising from the direct metal-metal contact can be responsible for trapped flux when thermal gradients are present. In addition, the Cu surface and its oxides seems to be sensitive to prolonged air exposure that can lead to superconducting thin films delamination. The deposition temperature of the superconducting layers, technique-dependent, influences the quality of the superconducting film quality (grain size etc…); higher deposition temperature often lead to better structural properties. Elevated deposition temperature however can also cause thin film delamination. Finally, external mechanical stress caused by cavity tuning for instance can also lead to film delamination. In order to tackle these problems we decided to investigate the thermal and chemical stability of insulation oxide layers deposited by ALD on electropolished Cu substrate provided by CERN for post deposition by HIPIMS (or sputtering) of thin superconducting films at various growth temperature from 150°C to 700°C [4].

We investigated several oxide layer with different chemical composition, structure and thicknesses.

4.1 Al_2O_3 ON EP CU

We started our investigation with Al_2O_3 thin film deposited by ALD on EP Cu substrates. We deposited 5, 10, 15 and 20 nm of Al_2O_3 and carried out HPR test and post annealing in vacuum. Depth profile XPS analysis indicates that all layer thicknesses resist the HPR process (1 ½ hr at 90 bar) and the post annealing up to 700°C for 2 hrs in high vacuum, without copper diffusion through the Al_2O_3 film (figure 6 (c)). A first set of samples coated with different thicknesses were sent to CERN for Nb deposition by HIPIMS (~6 microns) at 150°C. MEB, diffraction and tunneling spectroscopy showed that the Nb films structural (figure 6 (a) and (b)) and superconducting properties are identical with and without Al_2O_3 layers.

From these results, an EP 1.3 GHz Cu cavity was sent from CERN to be coated at CEA with 15 nm of Al_2O_3. After the deposition, the cavity was sent back for Nb HIPIMS deposition. After the HPR step part of the niobium film delaminated from in one of the beamtubes. As of know the reason for

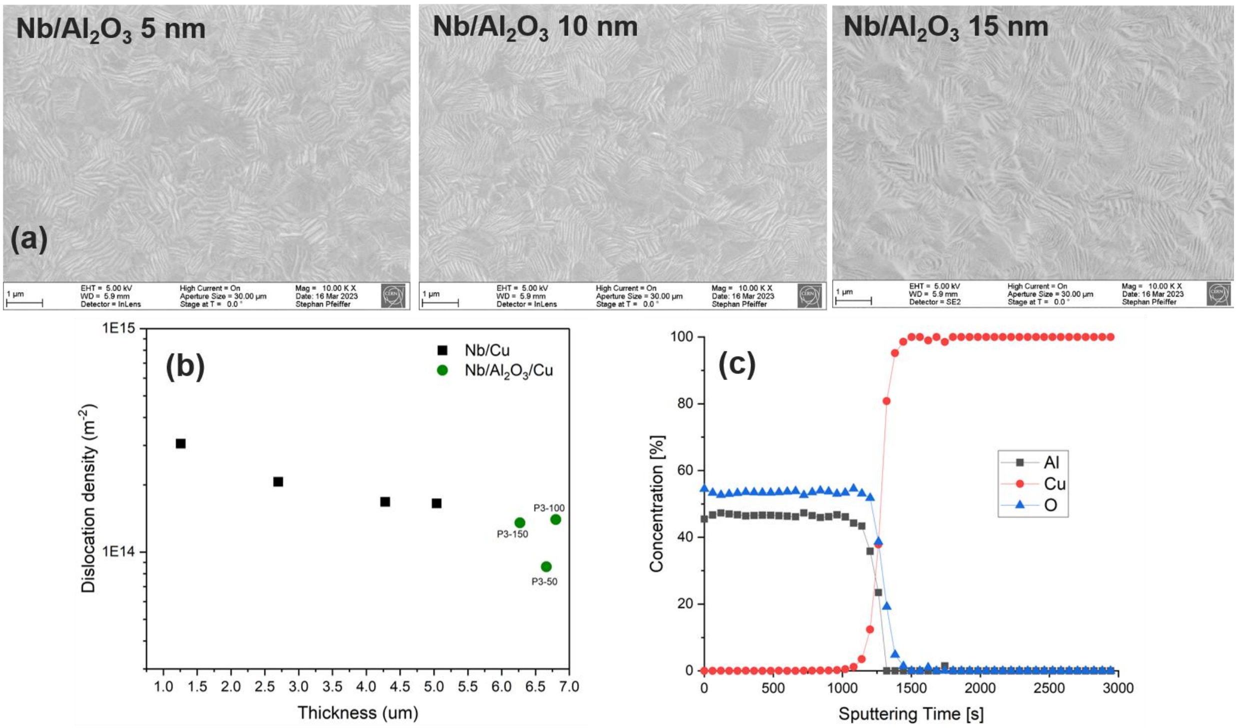

Figure 6: (a) MEB images of 6-6.5 µm Nb films deposited by HIPIMS on 3 different Al_2O_3 layer thickness on EP Cu. (b) dislocation density extracted form the XRD fits and (c) XPS depth profile of a 15 nm thick Al_2O_3 film deposited on Cu after annealing at 700°C for 2hrs and HPR.

that delamination in that specific area is unclear. It is planned that another EP Cu cavity will be sent to CEA and coated again.

4.2 ZrO_2 ON EP CU

Following the Al_2O_3 work, I also investigated the use of ZrO_2 on EP Cu as a passivation layer. Several thicknesses were deposited on EP Cu substrates: 10, 20 and 50 nm. After annealing the substrates at 700°C for 2 hrs, the thickest film showed clear cracks whereas the thinner films 10, and 20 nm remains intact (figure 7 (a)). XRD and MEB revealed that the crystalline structure of the ZrO_2 evolves with the film thickness; the grain size and the crystalline fraction increases with the film thickness. At this moment we postulate that the difference in thermal expansion coefficient between the Cu and the crystalline ZrO_2 is responsible for the cracks observed in the thickest film, whereas thinner and more amorphous (or smaller grain size) films have a higher elastic limit that can accommodate the thermal expansion coefficient differences. MEB images also revealed the presence of "holes" like structures (figure 5 (a) right) that were also present prior to the annealing step.

Depth profiling XPS show a sharp ZrO_2-metallic copper interface after annealing and the absence of Cu diffusion through the oxide layer (figure 7 (b)). MEB, XRD and optical investigation revealed that the most promising two thinnest films (10 and 20 nm) candidates resisted the HPR process step.

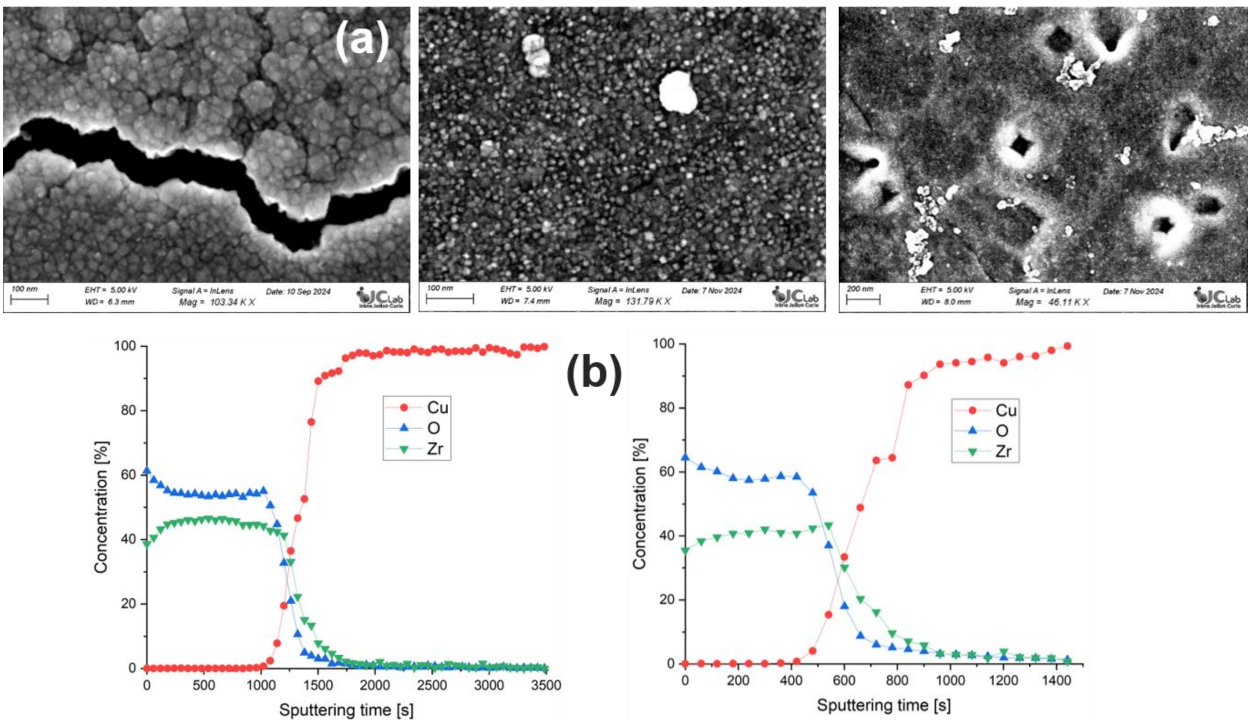

Figure 7: From left to right: (a) SEM images of a 50, 20 and 10 nm thick ZrO2 film deposited on Cu and post annealed at 700°C for 2hrs. (b) Depth profile XPS of a 20 and 10 nm ZrO2 film annealed at 700°C for 2hrs.

4.3 ZrO_2/ Al_2O_3 AND $ZrAlO_x$ THIN FILMS

In order to further accommodate the difference in thermal expansion coefficient, I proposed to explore a combination of crystalline and amorphous layers with the two alloys systems: ZrO_2 and Al_2O_3. A bilayer ZrO_2 (20 nm)/ Al_2O_3 (5nm)/Cu and a 20 nm intermixed alloy of ZrO_2: Al_2O_3/Cu with the ratio 4:1 were deposited on EP Cu substrates (figure 8 (a)). Both films resisted the post annealing and HPR steps. XPS depth profiling showed preserved sharp interfaces in the bilayer and with the Cu substrate (figure 8 (b)). XRD measurements after the annealing step revealed a crystalline ZrO_2 layer on amorphous Al_2O_3, whereas the intermixing alloys remained amorphous. This difference in crystallinity between the two samples may lead to different growth properties and response to external mechanical stress of superconducting films deposited on top.

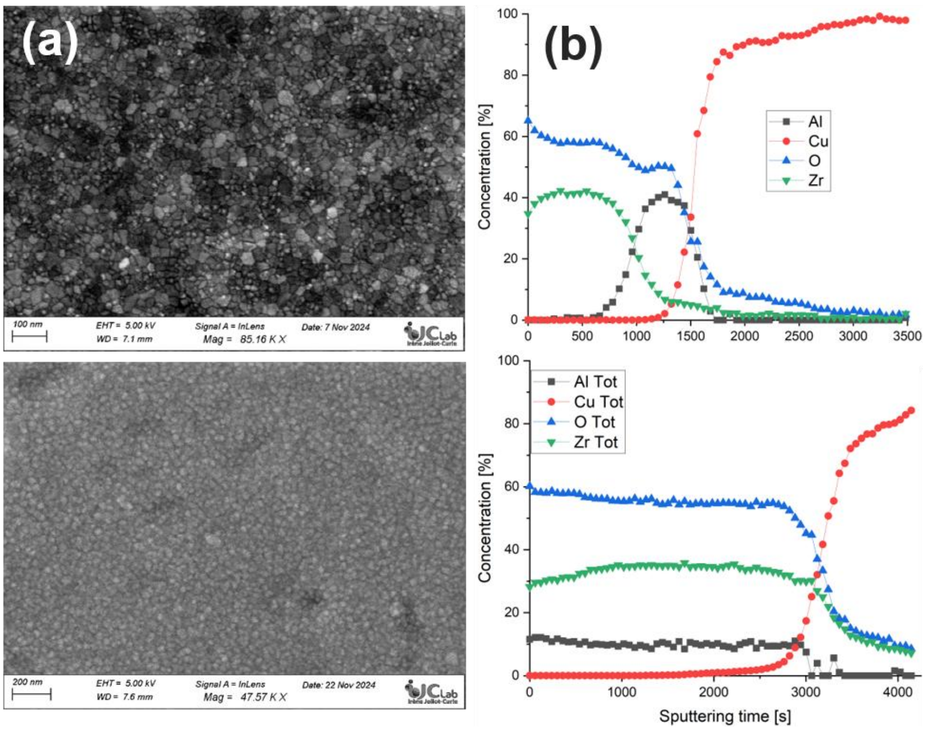

Figure 8: (a) MEB images of a bilayer ZrO2 (20 nm) /Al2O3 (5 nm) on Cu post annealed at 700°C for 2 hrs in HV and (b) the corresponding XPS depth profiles.

4.4 Y_2O_3 AND YSZ ON CU

One of the first layer I attempted to grow on Cu substrate was Y_2O_3. Crystalline as grown by ALD, I deposited 2 different thicknesses: 40 and 80 nm. These layers resisted the HPR step and were sent to CERN for Nb_3Sn deposition without further analysis. Both samples showed delamination, more pronounced on the thicker 80 nm sample. X-ray diffraction, MEB and tunneling spectroscopy carried out on Nb_3Sn/40 nm Y_2O_3/Cu and a referenced sample Nb_3Sn/Ta/Cu showed on both samples difference phases of Nb_3Sn with varying Sn composition and superconducting gaps values on the surfaces. These variations were more pronounced on the Y_2O_3 coated sample. From the investigations we did on the ZrO_2 sample, it is very likely that thick Y_2O_3 layers cracks upon annealing them at the high temperature required for Nb_3Sn deposition. Therefore, I grew recently a thinner 10 nm Y_2O_3 layer that did not present cracks upon annealing it at 700°C for 2 hrs in HV.

I also investigated the growth of YSZ (Yttria stabilized Zirconia) doped with 7% of ZrO_2. A 22 nm thick YSZ layer was grown on an EP copper substrate. SEM showed that the film present some cracks after annealing it at 700°C for 2 hrs in HV. As we have other thin films alloys that seems to work on Cu substrates, I decided to stop the Y_2O_3 /YSZ investigation.

4.5 Conclusion and prospects

We demonstrated that several layers alloys and thicknesses deposited by ALD are compatible with post deposition parameters by HIPIMS and DC magnetron sputtering of Nb and high Tc superconductors such as Nb_3Sn. The future work will focus on the deposition of Nb_3Sn and Nb by HIPIMS on ALD coated Cu coupons; eight coupons with the various successful ALD layer structures previously described were sent to CERN. We will conduct structural and chemical analysis of the deposited thin films along with HPR tests prior to Cu cavity coating.

5 Superconducting multilayers

A pathway towards decreasing the construction and operation cost of particle accelerators is to increase significantly the accelerating gradient of SRF cavities. One pathway proposed by Alex Gurevich is to deposit a multilayer structure: superconductor/insulator on top of the bulk superconductor inside the SRF cavities [R1]. Such structure is predicted to delay the vortices penetration into the bulk superconductor underneath and hence increase the maximum acceleration field. For several years now, we are investigating this approach at CEA using thermal ALD of NbTiN as the superconductor and AlN as the insulator.

5.1 NbTiN-AlN multilayer

We successfully grew NbTiN on AlN structure by thermal ALD on Nb, sapphire coupons and Nb 1.3 GHz cavities [T1, CP3, CP4]. By varying the growth parameters, we can control the Ti and Nb content of the films. The as grown superconducting properties were about 8 to 9 K, significantly lower than the expected 17K for bulk NbTiN. We investigated post-annealing parameters in HV on a 50 nm thick NbTiN film to improve the superconducting properties and found that 900°C was necessary to reach Tc of 15 to 16 K. XRD, TEM, SQUID and tunneling spectroscopy measurements showed that when applying the same annealing process on Nb coupons and on Sapphire samples the superconducting transition is larger (between 12.5 to 15 K) on Nb than on Sapphire (15 K to 16 K ±0.1 K). EELS analysis reveal that some N from the multilayer diffused into the Nb underneath, a phenomenon that does not occur on Sapphire. We can conclude that the widening of the superconducting transition could be due to variations of the nitrogen concentration in the NbTiN film grown on Nb. Despite this behaviour, we were able to measure the first vortex penetration field (H_{PEN})

on NbTiN/AlN coated Nb ellipsoids provided by Tobias Junginger from Victoria University as a function of the NbTiN thickness. From a baseline of 170 mT obtained on bare Nb, the H_{PEN} increases continuously as the NbTiN layer thickness increases from 42 to 91 nm, reaching 213 mT that represent a 26% increase in H_{PEN} (Figure 9).

Prior to testing thicker NbTiN to reach higher H_{PEN}, we have to tackle the N diffusion issue on Nb samples. In this respect, we are investigating the growth of a diffusion barrier on Nb prior to depositing the NbTiN/AlN multilayer. We have tested a promising candidate but the results need to be confirmed before reporting them.

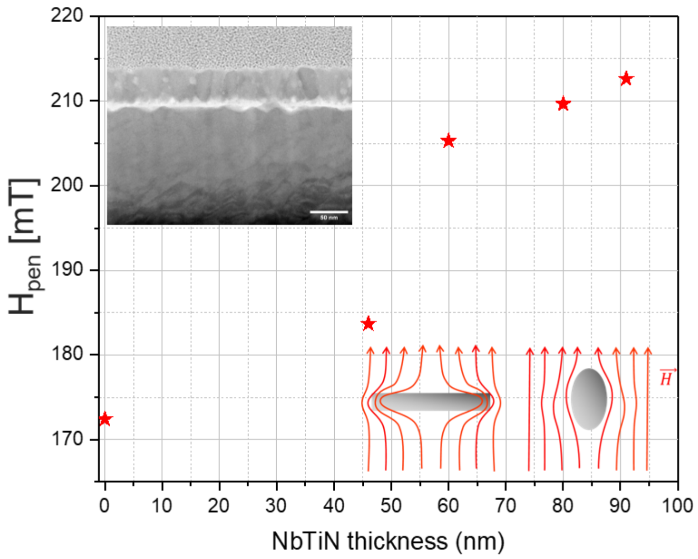

Figure 9: First vortex penetration field measured by SQUID on Nb ellipsoids.
The insert shows a TEM cross section of a 42 nm thick NbTiN/AlN on Nb sample.

5.2 NBTIN-ALN ON NB CAVITIES

We have investigated the growth uniformity of NbTiN-AlN multilayer on 1.3 GHz cavity profile and found that with growth parameters identical to the ones used on coupons the uniformity of the layers was better than 5%. Following this results we coated two niobium 1.3 GHz cavities with 50nm NbTiN/7 nm AlN. Both depositions were a success (figure 10 (a)). After annealing the cavities however we noticed extensive delamination on the beamtubes (figure 10 (b)). After finding a leak on one of the precursor channel, we fixed it, open the ALD system and cleaned up all the parts prior to putting it back together. We then tested again the multilayer deposition and annealing steps on larger EP Nb coupons and tubes and found no delamination. The ALD system is now ready to attempt another multilayer deposition on a 1.3 GHz cavity, after we confirm the N diffusion barrier results mentioned previously.

We are expecting 6 GHz cavities from INFN for SIS multilayer deposition at CEA and RF testing at INFN.

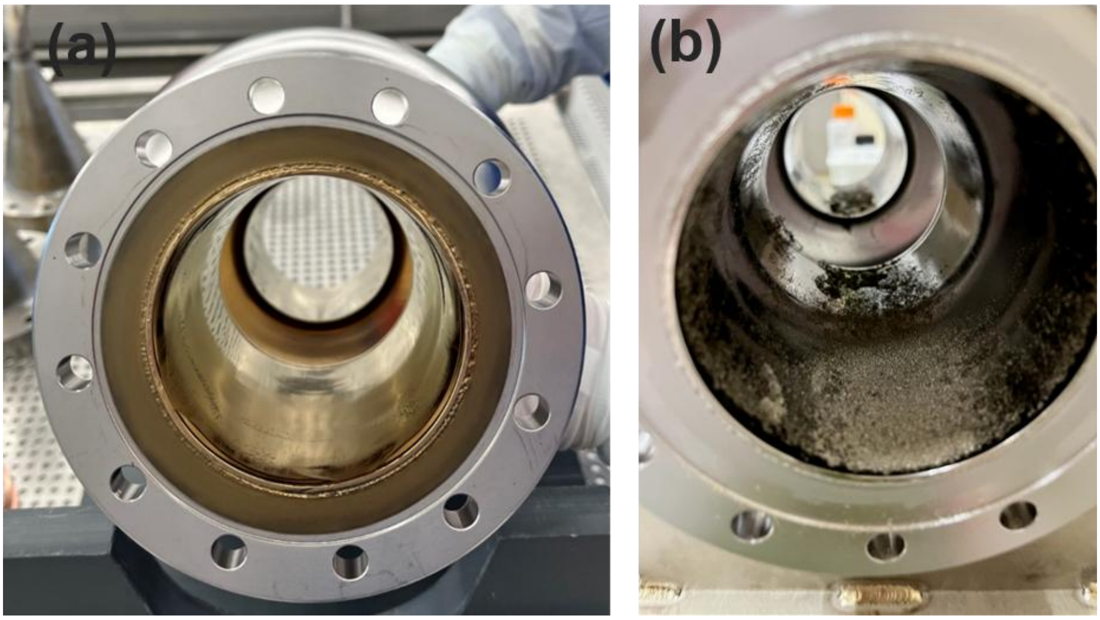

Figure 10: a 1.3 GHz Nb cavity coated with a bilayer NbTiN/AlN (a) before and (b) after annealing in HV.

5.3 OTHER HIGH TC SUPERCONDUCTORS BY ALD

In parallel, we are also pursuing an effort to synthesize Nb_3Sn by ALD. This very preliminary work never attempted before. Some very recent chemistries successfully grew pure Ti and Sn so we decided to investigate pure Nb and Sn is 3 to 1 ratio. The precursors, ordered more than a year ago, arrived last week.

6 Tunneling spectroscopy

For over two years now, the tunneling spectroscopy set up is operational and a PhD thesis is ongoing. This homemade set up has the unique capabilities to measure the cartography of the superconducting surface properties of samples with native oxide layers over large area (~mm), as close as possible to real supercondutcing device conditions. We can also perform temperature dependence to extract the local critical temperature. This technique is complementary to other surface structural and chemical characterization techniques. Over 25 samples have been measured across several research area:

- Bulk Nb with various treatments and ALD capping layers in order to correlate the RF cavity performances and the cartography of the surface superconducting density of states.
- Nb films on Copper substrates in order to identify the reason for the lower accelerating gradient measured as compared to bulk Nb cavities.
- Nb, Ta films used for Qubits in order to understand coherence time limitations and propose technical solutions to overcome them.

- High Tc superconducting films such as NbTiN and Nb_3Sn on bulk Nb, Cu or Sapphire to assess optimal growth conditions prior to cavity testing.

The tunneling spectroscopy measurements are correlated with other surface characterization tools such as XPS, MEB, TEM in order to investigate the microscopic origins of non-ideal superconducting properties and, in some cases, provide technological route to improve their performances.

This experimental apparatus is on high demand from various institutions over the world (JLAB, STFC, INFN, CEA, ENS, FNAL) that provide samples for PCT measurements, indicating the importance of this technique for SRF and Qubits applications. This importance was further emphasize at the last thin film workshop by Alex Gurevich.

7 Future plans / Conclusion / relation to other IFAST work

Within the IFAST WP9 program, we have developed an operational ALD deposition system (Milestone 40) routinely used to deposit ALD layers or multilayers on 1.3 GHz SRF cavities in Nb or Cu. We can accommodate 0.7 GHz cavities as well as higher frequency such as 6 GHz cavities from INFN. We have coated cavities for CERN and FNAL and, with the recently signed agreement ICRADA between DOE and CEA, we plan to coat cavities from JLAB as well.

The tunneling spectroscopy apparatus is very often solicited to measure samples from IFAST and around the world collaborators. Although not directly funded by IFAST, this effort is partially funded by the EUROLABS project.

The presented results on the control of the niobium surface chemical and structural properties have demonstrated the opportunities offered by the ALD technique to the SRF program along with other research areas such as the quantum initiative [P1]. Our results lead to world record high quality factors at low RF field. The collaboration with institutions such as FNAL [CP5] and ENS attest of this interest. Besides a few more SRF cavities with one to two years, the future of this work will shift toward 2D thin film processes.

Subsequently, our work lead to the development of a method based on the ALD of TiN to suppress multipacting in SRF cavities and to another ongoing Ph.D. thesis to further investigate means to control the secondary electron yields by tuning the chemical composition of multilayer structure with space applications on satellites (CP2).

Our expertise on the interactions between the Nb and the ALD layers was applied to Cu materials. The results show that we successfully developed insulating diffusion barriers stable up to 700°C and HPR. In collaboration with CERN, the Nb post deposition was a success on coupons and preliminary cavity coated tests resulted in partial Nb film delamination. Future of this work is part of the ISAS project; we are going to test again ALD layer deposition on Cu cavities for Nb deposition and test Nb_3Sn deposition by HIPIMS on ALD coated Cu coupons.

Over the last years, the team has developed a process to grow and optimize the superconducting properties of NbTiN/AlN multilayers and demonstrated the enhancement of the first vortex penetration field as compared to bare Nb. We were the first to deposit a multilayer structure inside two SRF cavities. After a few technical drawbacks, we have finalize the work and within one year from now (provided we can conduct cryogenic RF tests) we will bring a definitive answer as to its practical application to SRF cavities.

We have processed (EP and post annealing) QPR samples from an IFAST collaborator at HZB that reached the highest performances ever measured [CP6]. CEA will also process three Nb cavities for STFC supported by EUROLABS project, applying electropolishing, thermal treatments and high pressure rinsing. These cavities will be used for supercondutcing film coatings at STFC.

In addition, the team has developed a new approach to construct and cool down SRF cavities with a 3D printing approach. We are the first to have demonstrated the efficient cool down to 4.2K of a 3.9 GHz 3D printed Cu cavity with cryocooler. The heat transfer liquid is Helium flowing through cooling channels imbedded into the cavity walls [5]. This work is ongoing.

In future work we are also developing 3D printing SRF cavities with several metals and integrated cooling channels within the cavity walls. The goal is to use liquid He as the heat transfer fluid flowing inside these channels and liquefied with cryocoolers. This development theme fits another IFAST WP, although we have not collaborated directly with them. These cavities will then serve as substrates for superconducting film deposition [RP2]. This project is supported by the French funding agency ANR Equipex. This equipment funding will allow for:

- The design and construction of a custom made cryostat to test the cooling dynamic of these cavities with cryocoolers and conduct RF tests.
- The design and construction of a HIPIMS deposition system to develop superconducting films deposition inside the 3D printed made cavities at 1.3 GHz,
- Build an upgraded RF testing facility to test more than one cavity at once and extend the range of testing frequency up to 6 GHz.
- Build a new chemical facility to electropolished other metals than Nb such as Cu and Al.

The R&D team working on these subjects has grown over the last two years:

- Yasmine Kalboussi has joined the team as a staff scientist after she completed her Ph.D. under the direction of Thomas Proslier
- Ivana curci is finalizing her Ph.D. thesis at the end of 2025, under the direction of Thomas Proslier
- Mathieu Lafarie is finalizing her Ph.D. thesis at the end of 2025, under the direction of Thomas Proslier
- Théo Dejob is a postdoctoral fellow working on ALD and HIPIMS.
- Fritz Motschmann is an Engineer working on the 3D printing design and construction of SRF cavities.
- Quentin Ponchon is an Engineer that worked on the 3D printing of cavities up to 2022.
- Mathieu Benko and Erwan Sellin are two long-term internship students working under the supervision of Y. Kalboussi, F. Eozenou and T. Proslier.
- Thomas Proslier has defended in June 2024 his Habilitation to direct research.

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