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SURFACE ENGINEERING BY ALD FOR SUPERCONDUCTING RF CAVITIES

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Abstract

Atomic Layer Deposition is a synthesis method that enables a unique control of thin films chemical composition and thickness over complex shaped objects such as SRF cavities. This level of control opens the way to new surface treatments and to study their effect on RF cavity performances. We will present coupon and, in some cases, preliminary cavity results, from various surface engineering routes based on the deposition of thin oxides and nitrides films combined with post annealing treatments and study their interactions with the niobium. At CEA Saclay, three main research directions are under investigation:

1. Replacing the niobium oxides by other surface layers (Al_2O_3, Y_2O_3, MgO) and probe their effect on the low and high field performances,
2. Doping with N and combine approaches (1) and (2).
3. Optimizing the superconducting properties of NbTiN-AlN multilayers on Nb and Sapphire.

More details on the results presented in this paper can be found in the Phd. theses by the main author.

INTRODUCTION

For approximately five decades, bulk niobium resonators have been the backbone of superconducting particle accelerators. Thanks to the continuous research efforts made by the superconducting radio frequency (SRF) community, niobium cavities provide today reliably exceptional performances with accelerating gradient higher than 40 MV/m (TESLA shape — 1.3 GHz). Nonetheless, niobium cavities still witness performance degradation when exposed to high fields and are approaching their theoretical limits dictated by the Niobium's superheating field H_{sh}, the ultimate limit of the Meissner state. To keep up with future SRF facilities requirements in terms of quality factors and accelerating gradients as well as to improve their quality factor in the quantum regime, we aim at exploring a new technological pathway to enhance the performances of SRF cavities through functionalizing their inner surface with thin film coatings. Due to its complex shape, coating an SRF cavity demands a fine tuning of the film's chemical and structural properties and a thickness uniformity down to the nanometric scale. One very promising deposition technique to achieve these requirements is atomic layer deposition (ALD). ALD is a chemical phase deposition technique based on sequential and self-saturating gas-surface reactions. Two or more chemical precursors are introduced to the surface separately, one at a time, following a cycle. An ALD cycle is typically composed of four steps:

- Pulse of precursor 1, allowing the first gas-surface reaction.
- Purge of precursor 1, allowing the evacuation of excess precursor 1 and the reaction products of the first gas-surface reaction.
- Pulse of precursor 2, allowing the second gas-surface reaction.
- Purge of precursor 2, allowing the evacuation of excess precursor 2 and the products of the gas-surface reaction.

Thus, after each pulse, a monolayer of precursor reacts with the surface and after each cycle, a monolayer of about 1 Å of the desired material is deposited, which guarantees atomic-level control of the thickness.

METHODS

In this study, we present the results of different ALD coatings performed on both samples and cavities using the two home-made thermal ALD systems. The coatings on coupons were performed using the research-scale ALD system which is a viscous-flow thermal ALD reactor with a 5 cm diameter deposition chamber. The reactor temperature was maintained between 60 °C and 450 °C by an external computer-monitored resistive heater system. Several K-type thermocouples were placed along the length of the flow tube to ensure the temperature homogeneity. A constant flow of ultrahigh-purity nitrogen (UHP, 99.999%) at 200 sccm with a pressure of 1.5 mbar was used to transport reactant to the substrate. The ALD system is also equipped with a residual gas analyser (RGA) device to help the control of the chemical reaction inside the deposition chamber. In order

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to coat SRF cavities with the optimized recipes obtained on coupons, a second ALD system is built with a custom-made vacuum oven that allows the coating of SRF cavities (mainly 1.3 GHz and 0.7 GHz) under controlled atmosphere.

In the scope of this research project, we deposited by thermal ALD several materials, mainly oxides and nitrides using standard ALD recipes, Table 1 summarizes the chemical precursors that have been used. Pulses of 1 to 2 seconds were used whereas the purge time was 15 to 20 seconds.

Table 1: Thermal ALD Recipes Used in This Work

Film	Precursor 1	Precursor 2	Deposition temperature
Al_2O_3	H_2O	TMA	250 °C
Y_2O_3	H_2O	$Y(MeCp)_3$	250 °C
MgO	H_2O	$Mg(MeCp)_3$	250 °C
NbN	NH_3	$NbCl_5$	450 °C
TiN	NH_3	$TiCl_4$	450 °C
AlN	NH_3	$AlCl_3$	450 °C
ZrN	NH_3	$ZrCl_4$	450 °C

ALD DEPOSITED OXIDES FOR SRF CAVITIES

Ever since the emergence of niobium-based superconducting applications such as superconducting cavities and Josephson junctions, niobium oxides seemed to play a crucial role in their performance. Their growth mechanism and their different properties have been widely studied in order to understand how they affect superconductivity [1]. Niobium is naturally passivated by a layer of native oxide about 5 nm thick. This oxide is known to be defective and have poor thermal stability. It has also been considered responsible for the reduced performance of SRF cavities as a source of magnetic impurities. Preliminary studies by Proslier et al. [3] also showed that replacing the defective native niobium oxide with an ALD-deposited alumina film improved the performances of RF cavities.

At CEA, one of our objectives is to functionalize the surface of the niobium by depositing a multilayer structure. This will involve putting the cavity through several thermal cycles at high temperatures. It is therefore necessary to protect the massive Nb from uncontrolled impurity diffusion such as nitrogen. The insulating diffusion barrier chosen must have a high thermal stability to replace effectively native niobium oxides and eventually be the basis of the multi-layered structure. It is also crucial for this diffusion barrier to have a low dielectric constant so that it is transparent for RF waves and does not cause additional losses. In this study, we performed the deposition of 10 nm of three different diffusion barriers Al_2O_3, Y_2O_3 and MgO, all known to have high thermal stability and good insulating properties. We then tested their thermal stability following heat treatments under vacuum up to 800 °C. The X-ray Photoelectron Spectroscopy (XPS) analyzes showed that the Al_2O_3 and Y_2O_3 [4] layers are the most suitable for replacing the native oxides of Nb. As a matter of facts, after the ALD deposition followed by heat treatment at 650 °C for 4 hours, the XPS signal of 3d Nb is almost entirely composed of metallic Nb and shows only 5% of NbO contribution.

We tested this approach on a niobium cavity. The deposited Al_2O_3 followed by annealing at 650 °C for 4 hours increased the quality factor of the cavity at low and medium accelerating fields but has generated a multipacting barrier at 18 MV/m (see Fig. 1). We have also noted that this approach improves the performance of the cavities at very low fields which is of great interest to the Qubits community which aims to increase their T1 coherence lifetime and therefore their quality factor at very low fields (down to a few photons).

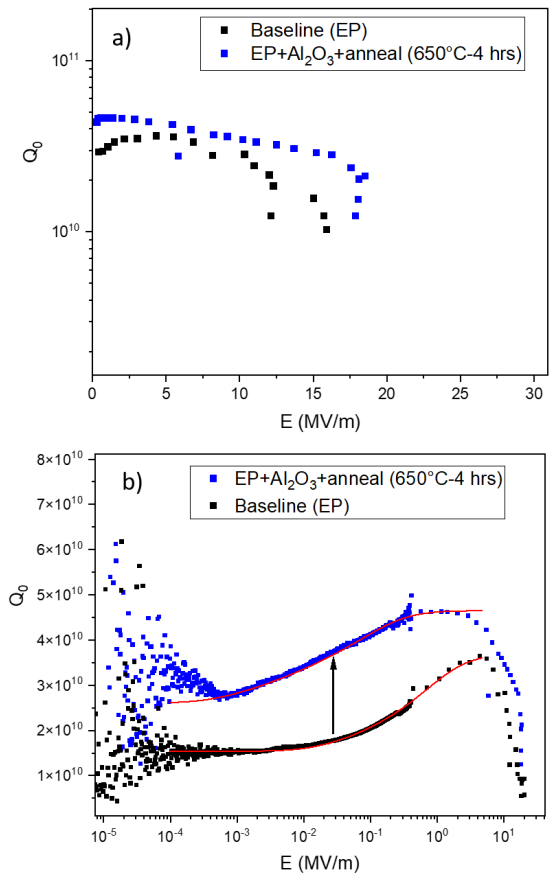

Figure 1: RF test results of the 1.3 GHz bulk niobium cavity in a) high field regime and b) low field regime. The black curves are the results of the bare Nb cavity after electropolishing. The blue curves represents the cavities performances after the ALD coating with 10 nm of Al_2O_3 followed by an annealing of 4 hours at 650 °C in UHV.

NbTiN-BASED MULTILAYER STRUCTURE

In order to experimentally test the theory proposed by A. Gurevich [5], a study of the ALD growth of NbTiN and AlN films as well as the deposition of multilayers of NbTiN (50 nm)/AlN (7 nm) on bulk Nb samples and sapphire wafers was undertaken. For the deposition of NbTiN films, a combination of NbN and TiN cycles at 450 °C was used [6]. The chemical composition of NbTiN films is tuned by changing the number of cycles of TiN and NbN in the ALD recipe.

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Figure 2 shows the chemical composition of NbTiN films obtained from XPS analysis as a function of the ALD ratios of NbN and TiN cycles. We have observed an etching phenomena of the TiN deposited by the $NbCl_5$ pulse. This etching explains the slow increase in the Ti content in the films when increasing the number of TiN cycles in the ALD recipe.

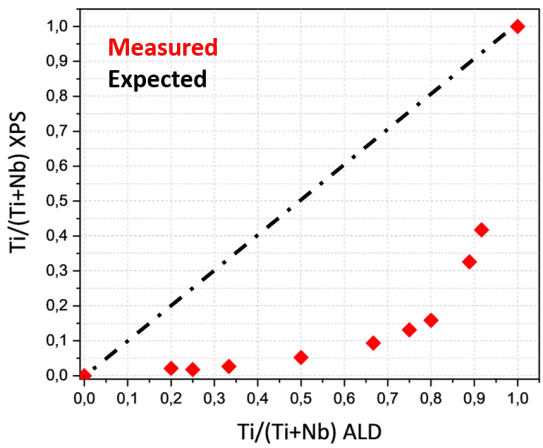

Figure 2: The chemical composition of NbTiN films obtained from XPS analysis as a function of the ALD ratios of NbN and TiN cycles (in red). The dashed line presents the expected composition from the TiN and NbN ratios used in the ALD recipe.

The resistivity of the NbTiN films decreased linearly when increasing the Ti content in the films whereas the critical temperature measurements showed that the NbTiN films have a T_c around 7 or 8 K without any clear dependence with the chemical composition. To understand the origins of such low T_c, complementary characterizations such as X-ray diffraction and Rutherford backscattering spectroscopy have been performed on the NbTiN films and revealed that the NbTiN films are nitrogen rich which results in smaller lattice parameters than expected and modest superconducting temperatures.

Subsequently, several post-deposition heat treatments have been tested to get rid of the excess nitrogen and increase the T_c. The vacuum level was maintained in the 10^{-6} mbar range during the annealing in a custom made resistive-walls vacuum oven with passive cooling. The thermal treatments turned out to be very effective on bilayer coted sapphire samples: The critical temperatures were greatly enhanced from 8 K at best to 15.5 K as it can be seen on Fig. 3. The resistivity of the films was also significantly lowered [1].

The annealing at 900 °C during 10 min have been found to be the most effective on AlN-AlN bilayer coated on sapphire. XPS analysis on NbTiN-AlN bilayer coated on Niobium coupons showed signs of inter-diffusion between the NbTiN-AlN layers and the Niobium substrate. Since niobium is a getter material, inter-diffusion is more likely to occur on niobium substrate than on sapphire substrate. Based on our XPS and SEM analysis, it seems that when annealing NbTiN-

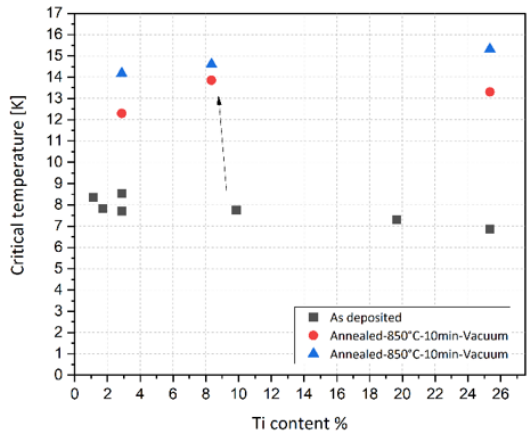

Figure 3: The critical temperature of the NbTiN films after different annealing treatments measured on sapphire substrates as a function of the Ti content.

AlN layer on niobium substrate at 900 °C during 10 min, the NbTiN layers (initially nitrogen rich) ends up by losing too much nitrogen probably through diffusion into bulk niobium. This worsens the NbTiN film quality and causes cracks and thus a great deal of oxygen contamination.

At this point, further thermal vacuum treatments have been tested on niobium samples. By adjusting the temperature ramps and the duration of the annealing, we managed to optimize the annealing parameters for niobium. The best thermal treatment found consisted in heating the samples up to 800 °C with a fist ramp of 6 °C/min, then heating up to the set point of 900 °C with a ramp of 18 °C/min. The same ramps are then used immediately to cool the samples without spending any time at 900 °C. As a consequence, the bilayer-coated niobium spends only ≈5 min at temperatures higher than 850 °C, which results in an improvement of the crystalline structure (by losing the right amount of nitrogen) without impacting the thermal stability of the bilayer. This process have been tested on an ellipsoid Niobium sample coated with an AlN (7 nm) - NbTiN (45 nm) multilayer. Superconducting Quantum Interference Device (SQUID) measurement on the coated ellipsoid sample showed a first superconducting transition at 15 K corresponding to the T_c of the NbTiN films and a second transition at 9.2 K corresponding to the T_c of niobium. The coated ellipsoid showed also an increase in the first vortex penetration field of 13.4 mT. When increasing the NbTiN layer thickness to 60 nm, we measured an increase of 30 mT after the bilayer coating (see Fig. 4) which is in good agreement with Gurevich predictions [5].

After studying the HPR effect on the quality of the bilayer and performing several uniformity tests of the thickness of inside a 1.3 GHz copper cavity, a first 1.3 GHz niobium cavity have been coated with a bilayer of AlN (7 nm) -NbTiN (50 nm). After the coating, as it can be seen in Fig. 5, the cavity had a bright golden and uniform colour. The inner surface were mirror-like with no sign of defects.

The bilayer coated cavity was then annealed to enhance the critical temperature of the NbTiN layer in a similar manner

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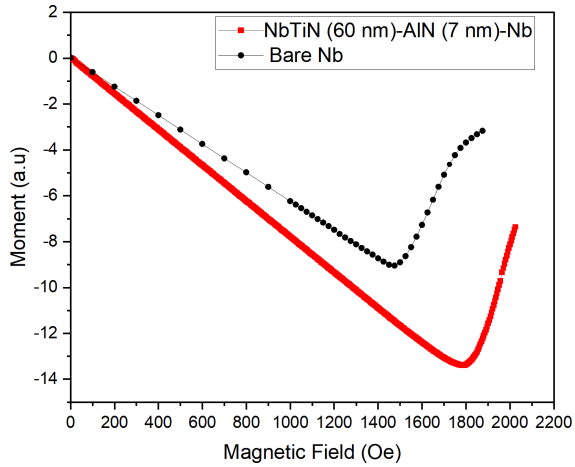

Figure 4: The first vortex penetration field of the ellipsoid sample before (black) and after the NbTiN-AlN (7 nm) coating + the post-annealing treatment (red).

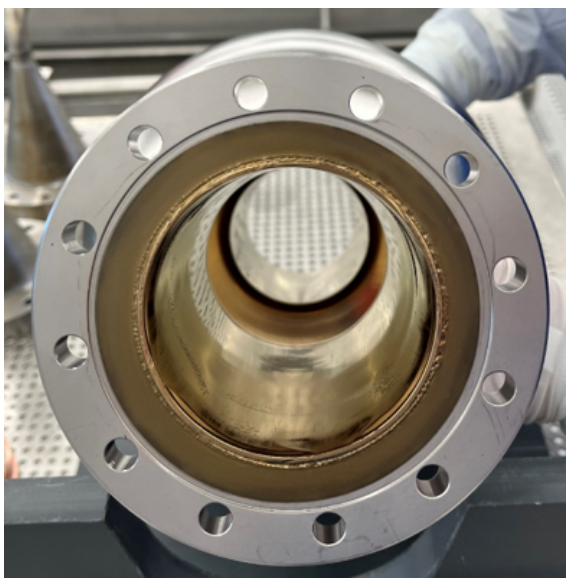

Figure 5: Picture of the 1.3 GHz niobium cavity after the AlN-NbTiN coating.

to that tested on niobium coupons. After the annealing, we observed film delamination especially at the beam tube. The cavity looked overall more metallic with some golden areas. It should be noted that during the annealing, we witnessed some vacuum degradation (the vacuum reached 10^{-5} mbar) due to the cavity degassing and the relatively small volume of the oven. Despite the unexpected film delamination on parts of the cavity, we tested the coated cavity under RF. The RF results are presented in Fig. 6. The cavity showed overall degraded performances compared to its baseline. The quality factor showed a high Q-slope in low fields: it decreased sharply from 2×10^{10} at 1 MV/m accelerating gradient to 5.109 at 1.5 MV/m. The surface resistance of the coated cavity showed very close values to the baseline measurement at 4 K. Nonetheless, the residual resistance turned out to be much higher at 2 K (30 nΩ while the bare niobium cavity had a surface resistance of ≈5 nΩ at the same temperature.

To rule out the effect of the vacuum degradation during the annealing step on the RF performances, the cavity was electro-polished to remove the ALD coatings and coated again with a bilayer of NbN (7 nm)–NbTiN (50 nm). For the second test, the cavity was annealed in the vacuum furnace dedicated to niobium cavities in operation in Supratech platform at IJCLab. The vacuum was successfully maintained below the 10^{-6} mbar. Nonetheless, we observed the same delamination and dust-like particles on the beam tubes as seen on the first trial. The RF test showed a slightly lower residual resistance than the first test.

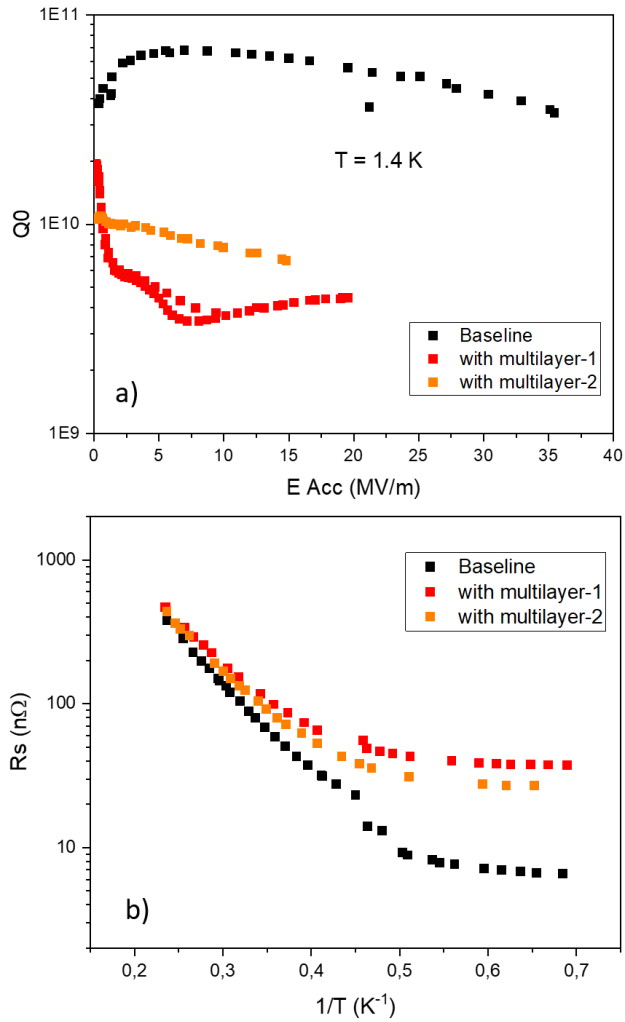

Figure 6: RF test results of the 1.3 GHz bulk niobium cavity: The bare EP cavity (black), the first test of the multilayer (red), the second test of the multilayer (orange).

Further investigations are needed to understand the behaviour of the bilayer coated cavities in particular the measurement of the resonant frequency as a function of the temperature to look for the superconducting transition of the NbTiN layer. We also believe that an additional degassing step prior to the ALD coating is essential to prevent delamination from occurring.

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NIOBIUM DOPING BY ALD

In this part, we introduce a new approach to dope Nb cavities using ALD thin films followed by high temperature annealing. Our approach is to coat the SRF cavity with an ultra-thin film of metal nitrides or oxides (depending on the desired dopant) as a finite source of nitrogen or oxygen.

Then, the cavity is annealed at high temperatures to allow the diffusion of the doping atoms in the penetration depth of RF fields. Unlike oxygen or nitrogen, metal atoms (because they have a diffusion coefficient much lower than N and O) would remain on the surface and give rise to a new oxide passivating the niobium surface after exposure to ambient air without the use of a post-doping electropolishing treatment. The use of atomic layer deposition would guarantee a well-controlled, uniform amount of dopant thanks to its sub-nanometer thickness control. We would also benefit from the wide variety of possible coating layers offered by ALD. This may result not only in an alternative to the nitrogen doping technique discovered by Fermilab [7] but would also allow to experiment with other types of dopants and improve overall our understanding of the physics that governs the first tens of nanometers of the surface of a niobium cavity.

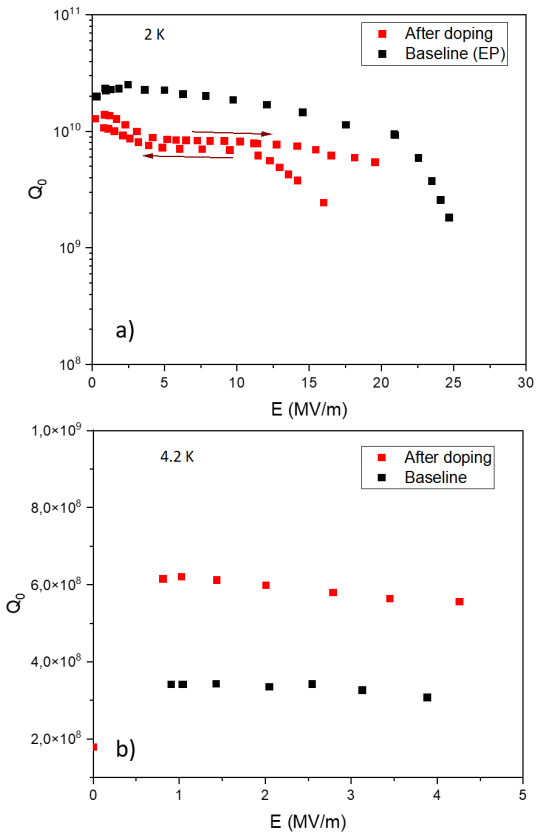

Figure 7: RF test results of the 1.3 GHz bulk niobium cavity: The bare EP cavity (black), the doped cavity (red) at 2 K (a) and 4.2 K (b).

As a first step in our exploration of this approach, we mainly focused on the doping of niobium with nitrogen in order to achieve doping levels similar to those obtained with the Fermilab method [7]. To do this, we tested the deposition of four different layers of metal nitrides TiN, AlN, NbN and ZrN as nitrogen source on niobium. The samples were then annealed at 900 °C for 3 hours under UHV to allow the diffusion of nitrogen in the niobium. For each film, we carried out analyzes by XPS and time-of-flight secondary ion mass spectrometry (TOF-SIMS) to monitor doping levels and examine the surface composition of samples after re-exposure to ambient air. We have seen that depending on the nitride layer (nature and thickness) used as a source of nitrogen, different levels of doping can be reached and we end up with different passivating layers after annealing. As a first experiment, we tested the doping of a cavity of niobium using a 5 nm film of NbN followed by annealing at 900 °C for 3 hours without electro-polishing. The RF test of the cavity showed an improvement of the quality factor at 4 K but a degradation at 2 K (see Fig. 7) due to the increase of the residual resistance. These preliminary results deserves further investigation in order to explain their microscopic origins.

In the same way, we explored Nb as a dopant source and a protective surface. Figure 8 represents the XPS analysis of a similar experiment done on 5 nm-ZrN coated niobium sample. The XPS profile shows no nitrogen in the surface of the niobium sample. It seems that the ZrN layer lost its nitrogen through diffusion toward bulk niobium. Upon re-exposure to air, the metallic Zirconium layers is transformed into a ZrO_2 layer as it can be also seen from the Zr 3d core level spectrum (see Fig. 8-b). Interestingly, the Nb showed no presence of niobium native oxides and showed only a pure metallic contribution on the Nb 3d core level spectrum. This results is particularly interesting as ZrO_2 is a relatively stable dielectric with potentially low losses under RF fields. This experiments will be soon tested on 1.3 GHz Nb cavity.

CONCLUSION

The main purpose of this work have been to suggest and explore new routes to functionalize the inner surface of niobium RF cavities in quest of improving their performances. Through the use of ALD-deposited oxide layers, we managed to compare their thermal stability with niobium native oxides and we were able to test their effect on niobium cavities performances. The Al_2O_3-coated niobium cavity showed enhanced quality factors in particular in the low field regime which is of huge interest to the Qubits community. One of our main goals through this research project was to explore the multilayered SIS (superconductor-insulator-superconductor) structure suggested in [5]. To that end, we developed a ALD-deposited bilayer based on aluminium nitride AlN as an insulator and niobium titanium nitride NbTiN as a superconductor with critical temperatures up to 16 K. This multilayer have been optimised to meet with niobium cavities requirements and was implemented for the very first time in niobium 1.3 GHz cavities.

Moreover, we tested a novel route to dope niobium cavities using ALD-deposited thin films as a dopant source followed by a subsequent annealing. We discussed our first

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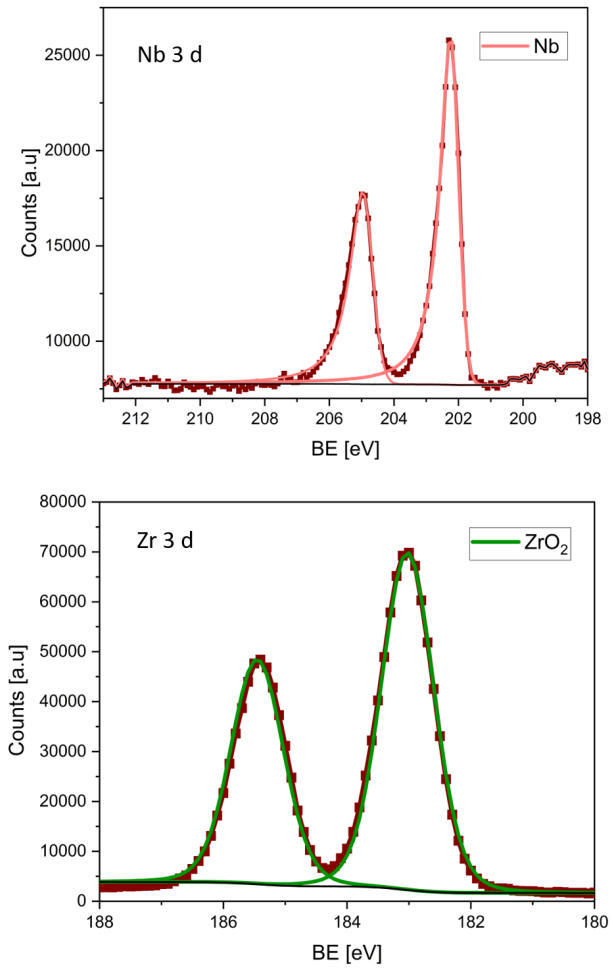

Figure 8: a) The Nb 3d core level spectra on the ZrN coated sample after annealing at 900 °C-3 hours. b) The Zr 3d core level showing ZrO_2 contribution at BE =183 eV.

set of measurement performed on both niobium coupons and 1.3 GHz cavity which showed encouraging results in particular at 4.2 K.

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