STUDY OF THE NIOBIUM OXIDE STRUCTURE AND MICROSCOPIC EFFECT OF PLASMA PROCESSING ON THE NIOBIUM SURFACE

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Abstract

A study of the niobium oxide structure is presented here, with particular focus on the niobium suboxides. Multiple steps of argon sputtering and XPS measurements were carried out until the metal surface was exposed. The sample was then exposed to air and the oxide regrowth was studied. In addition, three Nb samples prepared with different surface treatments were studied before and after being subjected to plasma processing. The scope is investigating the microscopic effect that the reactive oxygen contained in the glow discharge may have on the niobium surface. This study suggests that the Nb₂O₅ thickness may increase, although no negative change in the cavity performance is measured since the pentoxide is a dielectric.

INTRODUCTION

The work conducted at FNAL for the Linac Coherent Light Source-II (LCLS-II) 9-cell cavities [1,2] and at Oak Ridge National Laboratory by Doleans [3–6] for high beta cavities proved that plasma processing removes hydrocarbons from the cavity surface, increasing the niobium work function [7] and therefore mitigating field emission [8,9]. The processing uses a small percentage of oxygen in the glow discharge [10] to react with the hydrocarbons. For this reason, it is important to investigate if the presence of reactive oxygen in the plasma may be impacting the oxides that form the outermost layers of the cavity surface.

Here a comparative study of high RRR niobium samples prepared with different surface treatments and subjected to plasma processing is presented. The samples were analyzed via X-ray photoelectron spectroscopy (XPS) before and after plasma cleaning. The samples were inserted into a 9-cell cavity, on the iris of one end cell, and plasma processed for six hours using Ne-O₂ plasma.

To understand how plasma processing may affect the niobium oxide structure, it was necessary to start by investigating the niobium main oxide, Nb_2O_5 , and the other suboxides, through argon ions sputtering and oxide regrowth in air. Sample PH 36 was used for this scope. The combination of the two experiments allowed us to have a better understanding of the suboxides present on the niobium surface.

SPUTTERING EXPERIMENT ON Nb SAMPLE

Sample PH 36 is a high RRR niobium sample, prepared with bulk electropolish, followed by heat treatment at 800 °C



Figure 1: XPS Nb3d spectrum measured on sample PH 36 before starting the sputtering experiment. The sample's surface shows full, self-limited oxidization. As expected, the Nb₂O₅ doublet is the main feature present in the spectrum.

for 3 hours and further 20 μ m of EP removal. This sample, along with PH 35 (used in the plasma processing experiment), received a 5-minute hydrofluoric acid (HF) rinse in order to remove a calcium carbonate contamination that was found on the samples surface. The HF rinse strips the oxide from the surface and allows to regrow a new oxide layer [11–14].

Sample PH 36 was analyzed with XPS one week after the HF rinse, allowing the sample surface to reach full self-limiting oxidization (as confirmed by the measurement shown in Fig. 1 carried out on the sample prior to starting the sputtering experiment). Cycles of sputtering and measuring were repeated at different time intervals, for a total of 600 s of sputtering time. In addition, the sample was sputtered for another 600 s the following morning to remove possible NbO that may have formed on the sample surface during the night, while the sample was kept in high vacuum with active pumping (baseline pressure: 3×10^{-9} Torr). This final measurement is indicated as '600 s + 600 s' in the plots. The results of the measurement carried out during the sputtering experiment are shown in Fig. 2. Panel (a) in Fig. 2 shows a progressive shift in the position of the main doublet toward lower binding energy (BE) values. The shift indicates a gradual removal of the pentoxide and the emerging of the suboxides, until the metal peak is the dominant feature in the spectrum. It is believed that NbO may be artificially created during the sputtering process, as the Ar ions knock off preferentially the lighter oxygen atoms rather than the niobium, gradually reducing the Nb₂O₅ to NbO. In addition, the oxygen molecules present in the HV atmosphere will

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Figure 2: Panel (a) shows the gradual decrease of the Nb_2O_5 doublet as the surface is sputtered and the emerging of the NbO peak, with a progressive energy shift toward lower binding energy values, until the metal Nb doublet is the main feature. Panel (b) shows the evolution of the O1s spectrum at the corresponding sputtering steps.

contribute to the NbO increase. Each step of the sputtering process was fitted and is shown in Fig. 3, confirming the gradual reduction of the Nb₂O₅ doublet in favor of the NbO, NbO₂ and, finally, the Nb metal peak. In order to adequately fit the measured spectra, it was necessary to add an additional peak P₁ which is attributed to a nonstoichiometric phase. The BE of the P₁ peak decreases at each sputtering step, suggesting that its chemical state is changing as the oxygen is removed from the lattice.

After 15 seconds of sputtering, four peaks are present in the spectrum, three of which are clearly identified as Nb₂O₅, NbO₂, and Nb. The fourth is identified as the nonstoichiometric peak P_1 that may be attributed to NbO_{1+x} . with 0 < < 1. After 45 seconds of sputtering, the NbO doublet is also measured as part of the spectrum. At 60 s the NbO becomes the dominant feature, with BE equal to 203.8 eV. After 300 s, four peak can be identified: NbO, metal Nb, and two additional peaks at 203 eV and 202.6 eV. The energy of the first peak suggests that it could be Nb_2O , in agreement with the value found in literature [15-17] and in particular with the observation of Delheusy [18], who finds this peak at 203.03 eV. The lower energy peak is assigned to P_1 , which may be expressed as $Nb_{2+x}O$. After a total of 600 seconds of sputtering, the measured spectrum is dominated by the pure metal peak; however, the NbO and Nb₂O and P₁ doublets are still present. The spectrum acquired the following morning, after an additional 10 minutes of sputtering ('600 s + 600 s') is the best measurement of the niobium metal peak achieved in this study. Nevertheless, a non negligible amount of NbO is still present on the sample surface. The '600 s + 600 s' was used to obtain the parameters necessary to fit the pure metal peak in all the XPS measurements taken on the four niobium samples used in these studies.

As for the O1s spectrum, as expected, a gradual decrease of the peaks was observed at each sputtering step. The spectrum measured on the oxidized sample is plotted in Fig. 4(a). The curve fitting shows the presence of three peaks attributed as niobium oxide (indicated as Nb–O), C–O, and C=O [19].



Figure 3: Nb3d spectra measured after each sputtering step (from 15 s in panel (a) to 600 s in panel (h)). In panel (i) is shown the final measurement done the following morning after an additional 600 s of sputtering). Each spectrum has been fitted and the peak decomposition is shown in the plots.



Figure 4: In panel (a) the O1s spectrum measured on the oxidized sample is plotted: peak fitting the data reveals that three peaks are present, identified as niobium oxide, C–O, C=O. Panel (b) shows the spectra measured after 15 seconds of sputtering with the ion gun. As expected, the intensity of the C–O, C=O is reduced as the adventitious carbon is being removed from the sample surface.

The peak identified as 'Nb–O' contains the signal generated by all the oxides' peaks, not only the Nb₂O₅. After 15 seconds of sputtering (Fig. 4(b)), the C=O was greatly reduced; the carbon signal is mainly due to adventitious carbon and as such is superficial. Increasing the sputtering time, the oxygen is gradually removed from the sample surface and also the intensity of the Nb–O peak decreases.

STUDY OF THE OXIDE GROWTH ON Nb SPUTTERED SAMPLE

Following the final 10 minutes of sputtering, the sample was extracted from the XPS analyzer chamber and exposed to air for 15 minutes in order to initiate the oxide regrowth in air. The exact position of the sample inside the analyzer

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chamber was recorded in order to remeasure the sputtered area each time.

After 15 minutes, the transfer chamber was evacuated and the sample was loaded into the analyzer chamber and measured again. The sample was then exposed to an additional 15 minutes of air and 45 minutes. Between the second and the final step, the sample was kept under high vacuum for 38 h. In total, the sample was exposed to: 75 min of air exposure + 90 min with active pumping from atmospheric pressure to HV + 38 h in HV.



Figure 5: Comparison of the three Nb3d measurements carried out during the oxide regrowth. In order to better compare the data, the background (extracted through curve fitting) was subtracted and the each curve was divided by its total peak area. The inset shows a zoom on the Nb₂O₅ and Nb peaks.

Figure 5 shows the comparison of the three Nb3d spectra measured after 15, 30 and 75 minutes of oxide regrowth in air. In order to better compare the data, the background (extracted through curve fitting) was subtracted and each curve was divided by its total peak area. As expected, the intensity of the Nb₂O₅ doublet increases as the pentoxide grows on the niobium surface, while the Nb peak intensity decreases. The ratio of the areas extracted through peak fitting is summarized in Table 1: the Nb2O5/Nb area ratio increases at each air exposure step, while the relative intensity of the suboxides remains approximately constant. Curve fitting the measured spectra (Fig. 6) reveals that five different chemical states are present on the sample near-surface region: Nb_2O_5 , the metal Nb peak and three suboxides: NbO2, NbO and Nb₂O. The observation that after 10 minutes of air exposure the oxide has not yet fully reformed is also in agreement with the findings of Posen et al. [20], who studied the performance of SRF cavities after medium-temperature bake and following 10 minutes of air exposure.

Table 1: Ratio Between the Areas of Each Oxide and the Nb Peaks Measured in the Nb3d Core Level Spectrum During Oxide Regrowth

Air exposure	Nb ₂ O ₅ /Nb	NbO ₂ /Nb	NbO/N	Nb ₂ O/Nb
15 min	0.87	0.12	0.36	0.08
30 min	0.99	0.14	0.41	0.11
75 min	1.00	0.15	0.40	0.07



Figure 6: Nb3d spectra measured during the regrowth of the oxide layer. Panel (a) shows the spectra measured after 15 minutes of exposure to air, panel (b) after a total of 75 minutes. Each plot also contains the results of the peak fitting, showing that in each step there are five peaks identified as Nb₂O₅, the metal Nb peak and NbO₂, NbO and Nb₂O.

XPS ANALYSIS ON Nb SAMPLES BEFORE AND AFTER PLASMA PROCESSING

The scope of this study was to identify possible differences in the oxide structure of three Nb samples prior and after plasma processing. Table 2 summarizes the different surface treatments used to prepare the Nb samples analyzed in this study. All the samples received bulk EP prior to the heat treatments. The average removal during bulk EP on these samples was 100 µm. Samples PH 35 and PH 36 also received a 5-minute hydrofluoric acid rinse after the final EP. Sample PH 35 was prepared using the LCLS-II N-doping recipe [21, 22], a second sample (PH 40) was treated with the recipe used for the LCLS-II HE verification cryomodule. The third sample (PH 45) was prepared without N-doping in order to study possible differences in the native oxide structure caused by the surface preparation and differences in the changes that may be induced by plasma processing.

Table 2: Sample Names and Preparations for the XPS Study of the Oxide Structure

Sample Name	Heat Treatment	Final EP
PH 45, PH 36	800 °C x 3 h	20 µm
PH 35	2/6 N-doping	5 µm
PH 40	2/0 N-doping	7 μm, cold

After the surface had time to fully oxidize, the three samples were analyzed with XPS and SEM/EDS; then, they were positioned inside a 9-cell cavity, on the iris of one end cell (as shown in Fig. 7(a)). The samples were plasma processed for a total of 6 hours, using the standard plasma parameters with oxygen partial pressure around 1 - 2.5% of the neon. According to the current plasma cleaning procedure developed for LCLS-II, each cavity cell is processed for approximately 2 hours. It was decided to process the samples for a longer time in order to exacerbate the effect that plasma processing may have on the niobium surface. The Nb3d spectra measured on the three samples before



Figure 7: Panel (a) contains a photo of the three niobium samples subjected to plasma processing. The samples are positioned on the iris of the end cell of a 9-cell cavity. A viewport, assembled on the cavity beamtube, allows to see the plasma and the samples. Panel (b) shows the Nb3d spectra measured on sample PH 45 after being subjected to plasma processing.



Figure 8: Nb3d spectra measured on the three niobium samples before and after being subjected to plasma processing. The spectra here are plotted as measured, without accounting for possible charge effect shifting.

and after plasma processing are shown in Fig. 8. All three samples showed an increase in the intensity of the Nb₂O₅ peak relative to the intensity of the Nb metal peak. Using the areas extracted through curve fitting with the Aanalyzer software [23], the relative increase in the Nb₂O₅ area for the three samples was estimated as 200% - 260%.

The increase in the pentoxide peak and the decrease in the metal signal suggest that the oxide thickness is increased. The niobium oxide is normally self-limiting and creates a passivating layer on the niobium surface, protecting the surface from interactions with the environment. However, the gas plasma mixture contains a small percentage of oxygen that can be dissociated and ionized, creating highly reactive O^+ ions that can impact on the niobium surface. Once chemisorbed, if the oxygen ions have sufficient energy, they can diffuse into the oxide lattice up to the interface with the niobium where they can cause the nucleation of new oxide clusters, as Delheusy explained in her dissertation [18].

The increase in oxide thickness is not expected to affect the performance of SRF cavities since Nb_2O_5 is a dielectric: it does not participate to the superconducting state and it is transparent to the RF current. While a consistent increase in the pentoxide peak intensity is measured in the three samples, no particular change in the suboxide peaks is detected when comparing the spectra acquired before and after plasma processing. Figure 7(b) shows the fitted Nb3d spectrum measured on sample PH 45 after plasma processing.

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Another feature that is visible in all Nb3d spectra measured on the plasma processed samples is a reduction of the energy difference ΔE between the Nb₂O₅ peak and the Nb metal peak. This reduction is more pronounced in samples PH 45 and PH 40, less in PH 35. Further analysis are needed to investigate this effect and understand if it is caused by plasma processing. If the reduction in BE is confirmed to be a physical phenomenon caused by plasma cleaning, one possible explanation could be that the introduction of oxygen vacancies in the pentoxide lattice during plasma processing may decrease the Nb₂O₅ BE. Cava *et al.* [24] showed that the pentoxide can exist as Nb₂O_{5- δ}. However, further studies are needed to better understand the possible ΔE reduction and what the cause could be.

CONCLUSION

The measurements carried out on sample PH 36, during the sputtering steps and during the following oxide growth, allowed to understand the different suboxides that can be present in the near-surface region of polycrystalline niobium. Although some features, like the abundance of NbO in some steps or the nonstoichiometric P₁ phases, may be artificially created by the sputtering process, they provide insight on the possible chemical states that can be present in niobium samples. The oxide growth study on the sputtered surface provided interesting insight on how the oxide is formed on a pristine surface and how its growth rate depends on the total thickness of the oxide structure.

The three samples subjected to 6 hours of plasma processing showed an increase in the intensity of the Nb₂O₅ doublet relative to the intensity of the Nb metal peak, suggesting that the oxide layer thickness may increase. The highly reactive oxygen ions present in the plasma can impact on the niobium surface and may be able to diffuse through the Nb_2O_5 , causing the formation of new oxide clusters at the interface between the metal and the oxide. A change in the energy difference between the pentoxide peak and the metal peak is observed in all three samples. After plasma processing, the ΔE is reduced, suggesting that the Nb₂O₅ BE may decrease. One hypothesis is that plasma processing may introduce oxygen vacancies in the Nb₂O₅ lattice, reducing its BE. Further studies are needed to quantify the change in oxide thickness and better investigate the possible shift in BE. Subjecting the samples to varying duration of plasma processing may help studying these phenomenona. Despite these peculiar effects, plasma processing does not cause any reduction in the cavity performance: Nb₂O₅ is a dielectric, therefore it should be transparent to RF and furthermore it does not participate to the niobium superconducting state.

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