

SURFACE OXIDES ON Nb AND Nb₃Sn SURFACES: TOWARD A DEEPER UNDERSTANDING*

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Abstract

Surface oxides on Nb and Nb₃Sn SRF cavities, as a thin “dirty” layer, could be critical to their performance as suggested by recent theory. Although these oxides have been studied in the past, we intend here to provide a deeper understanding based on a systematic study on coupon samples that have been processed under the different conditions currently used in SRF cavity treatments. Our aim is to obtain a more complete picture of the oxide evolution. This then might help to explain the observed cavity performance variation, and might allow designing a process to achieve a designed, optimized surface with controlled oxides types and thickness. We find that the surface oxides are in amorphous phase that exhibits normal conducting behaviors, while the pentoxide further degrades with time. Also, we observed a thin hydroxide layer on the outermost surface and possibly Nb(OH)_x motifs in the bulk. Moreover, distinctive oxide structures were found in Nb₃Sn samples from vapor diffusion, electroplating, and sputtering. The semiconducting SnO_x appeared through the oxide depth in vapor diffused Nb₃Sn, while a ~1 nm SnO_x layer merely exists at the outermost surface of electroplated Nb₃Sn.

INTRODUCTION

The role of oxygen in superconducting radio-frequency (SRF) cavities is not clear yet. We intend to investigate the surface oxides and the oxygen impurities after different acid and heat treatments. Surface oxides that are likely a normal conducting phase on the superconducting surface are theoretically critical to the RF performance due to the proximity effect [1]. Route toward a perfect surface is believed to be either a dielectric oxide or a normal conducting oxide of desired thickness (and electrical properties). However, it is challenging to achieve such perfect oxide surfaces.

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Although numerous studies [2-7] have systematically characterized the surface oxides and investigated the oxidation process on Nb surfaces, applying the learnings from these materials investigations to fabricating a surface oxide layer under a controlled manner on a cavity scale is not straightforward. Ereemeev [8] examined the RF response to removal and re-growth of surface oxides via baking and air exposure under modulated pressure and time, but the understanding of these results was not fully clear. The discrepancies he observed between repeated treatments and between their oxide characterization and the corresponding RF results, suggest one probable cause – the variation in treatment environment. This motivates us to gain a deeper understanding of the surface oxide structure on Nb after different processing conditions.

Also, new SRF materials such as Nb₃Sn push the need of surface oxide studies on these surfaces [9, 10]. For example, Porter [9] observed a two-gap behavior on the BCS resistance versus temperature curve for the Nb₃Sn cavities, which indicates a possible influence from the surface oxides.

Moreover, new processes such as low- and mid-temperature bakings together with nitrogen infusion and doping bring about our attention on the complexity of involvement of multiple impurities in the material system (at least oxygen and nitrogen). For example, the nitrogen infused niobium done by Koufalis [11] showed absolutely higher oxygen concentration than nitrogen concentration by several orders of magnitudes within several hundreds of nanometers in depth. Recently, Fermilab also confirmed this observation. It is necessary to understand the role of oxygen in the nitrogen-doped/infused and other baked niobium.

In this work, we present the oxide and oxygen results from Nb and Nb₃Sn coupon samples that were processed or made by multiple treatments.

EXPERIMENTAL

Nb samples were prepared using ozone, long time O₂/N₂ soaking, nitrogen doping, HF soaking, electropolish (EP), and buffered chemical polish (BCP). The sample information and treatment details are summarized in Table 1.

Table 1: Summary of Niobium Sample Treatment Conditions

Sample ID	S1				S2	S3	S4
Step #	T1	T2	T3	T4	T1	T1	T1
Treatment	BCP	HF acid soaking for 30 min	Second BCP for 30 min	Ozone exposure for 3 days	100 μm EP	EP + 800 C degas + RT O ₂ /N ₂ flow for >1 day	EP + 800 C degas + “2/800” nitrogen doping + 5 μm light EP
Air exposure time	Several months	Several days				Several months	

Sample 1 (S1) was used to examine 4 different treatments, which minimized possible sample variation. These results showing clear sensitivity to the corresponding processing conditions also confirmed that the surface roughness of the Nb samples barely affects accurate structural and depth determination via X-ray photoelectron spectroscopy (XPS). The other three samples (S2-4) were prepared for their specific treatments, that include a series of typical processes used in the SRF cavity preparation.

The ozone treatment was done using a Jelight 144AX UV ozone generator. The sample was placed at the minimum distance (~5 mm) away from the UV source. Moreover, the BCP, EP, HF soaking, degassing, and nitrogen doping followed the typical protocols.

These Nb samples were exposed to air after each treatment, which matches with the cavity scenario. The initial BCP polished (#S1T1), long-time O₂/N₂ soaked (#S3T1), and nitrogen doped (#S4T1) samples were placed in air for several months. All other samples were sealed in the plastic bag for several days before probed by XPS readily.

The Nb₃Sn samples were prepared by three different techniques – vapour diffusion [9, 12], thermal conversion from electroplated-Sn [13-16], and sputtering [17].

These Nb and Nb₃Sn samples were primarily characterized by XPS spectroscopy equipped with a UHV system (base pressure: ~10-10 Torr) and monochromatic Al k-alpha X-rays. The energy resolution is 0.6-0.9 eV, and the atomic resolution is 0.1 at.%. Depth profiling was done via sputtering by Ar ions. The minimum sputter rate was chosen, and the rate of 1.3 nm/cycle was determined. The sputter rate was calibrated by a 100 nm SiO₂ reference sample and a 2.4 μm thick Nb₃Sn film.

Some samples were also cross-sectionally imaged using FEI F20 and NION UltraSTEM 100 scanning transmission electron microscopes (STEM). Energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) under STEM were used to study the surface elements and structures.

RESULTS AND DISCUSSION

Niobium Surface Oxide Variation

Figure 1 shows the oxygen concentration profiles on Nb surfaces after the different treatments. Clearly, the surface oxides are extremely sensitive to specific treatments, leading to a large variation in structures.

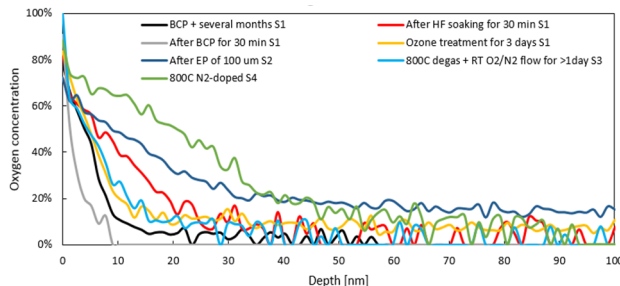


Figure 1: Oxygen concentration as a function of depth for Nb surfaces after different treatments.

The BCP samples (#S1T1 and #S1T3) after exposure to air for several days to months established the baseline of surface oxide structures. The relatively fresh BCP sample (#S1T3) showed the typical ~6 nm Nb₂O₅/NbO₂/NbO oxide stack without observing any oxygen in the Nb bulk that was reported in the literature [2-7]. With longer exposure time, we observed the partial decomposition of Nb₂O₅ ending with a large depth of oxygen impurities in the bulk and a thickened oxide layer in the BCP sample (#S1T1).

The EP (#S2T1) and HF soaked (#S1T2) samples unexpectedly exhibited excessively large oxygen concentration with thicker oxide depth and larger amount of oxygen impurities in the bulk as compared the BCP baseline. However, in earlier literature [18], the difference of surface oxides on BCP and EP niobium was not significant. Interestingly, decomposition of Nb₂O₅ did not appear in these two conditions, but instead, the thickness of Nb₂O₅ together with other oxides was enlarged.

The ozone treated (#S1T4) and long-time RT O₂/N₂ soaked (#S3T1) samples showed similar oxygen profiles that nearly resembled the BCP plus long-time air exposure baseline while introducing dramatic amount of oxygen impurities to the bulk region. One distinctive difference is the ozone treatment yielded the typical oxide stack with slightly increased oxide thickness, while the long-time O₂/N₂ soaked sample showed nearly none of Nb₂O₅ motifs. Note that the O₂/N₂ soaked sample was also placed in the air for several months, which suggests the decomposition of Nb₂O₅ is linked to the air exposure time (as no heat-related treatments were involved after air exposure). However, the nitrogen-doped sample (#S4T1) that was also exposed to air for several months did retain the Nb₂O₅ structure.

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The nitrogen-doped sample (#S4T1), besides capable to maintain a thick Nb₂O₅ layer on the surface, induced the thickest oxide stack and the largest amount of oxygen in the bulk as compared to all other samples studied. The nitrogen-infused sample studied by Koufalis [11] also showed similar behaviors. However, further investigation is required to confirm the excessive oxygen in the doped sample is from the doping, or from air exposure for several months, or from the light EP that is typically performed right after the doping.

Accurate Identification of the Oxygen-Related Structures

A challenge the author encountered is how to accurately determine the oxide structures and distinguish the oxygen interstitials (atomic absorption) and chemisorption in a niobium system. After carefully reviewing existing niobium oxide studies [2-7] and other metal oxidation studies [19], the fitting approach was determined as shown in Fig. 2.

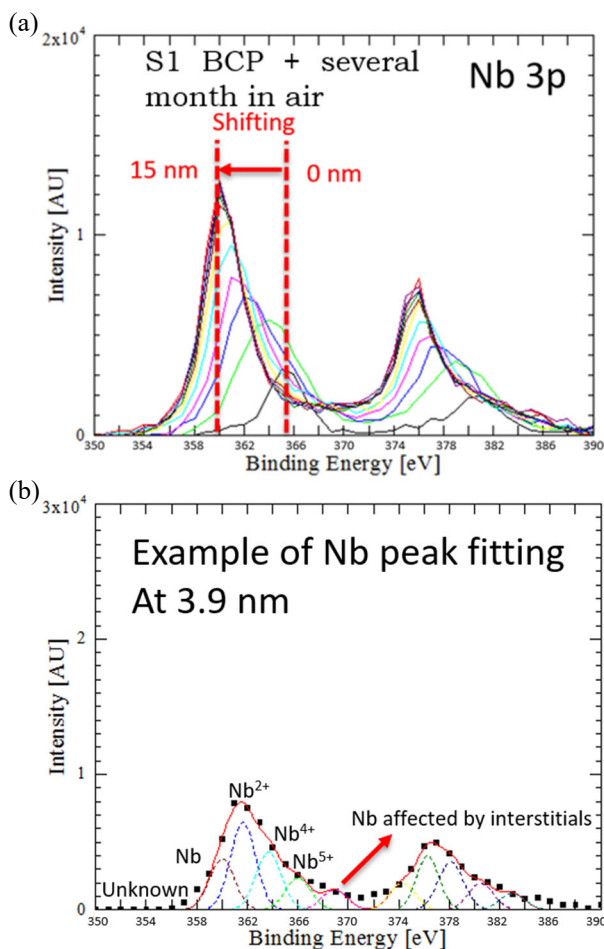


Figure 2: (a) Depth profiling of the BCP polished niobium surface that was exposed to air for several months. (b) Example of Nb 3p peak fitting of XPS spectrum taken at the 3.9 nm depth, showing the oxide and interstitial structures.

Both Nb 3p and Nb 3d photoelectrons are being studied depending on their instrumental sensitivity and calibration in different XPS systems used in this work, but their fitting

approaches barely differ. Figure 2 shows the metallic Nb and oxides Nb₂O₅, NbO₂, and NbO are assigned at the literature-reported binding energies, but Nb₂O, a defective NbO structure was not included in our fitting due to the concern of energy resolution for differentiating Nb₂O and NbO binding energies.

In addition, we further identified a new oxygen interstitial peak at a relatively higher binding energy based on analysis for other metal systems [19], and the validity was confirmed by comparing results from different niobium surfaces.

Also, we observed a new identified peak at the relatively lower binding energy. To confirm this peak is not from spectrum residues, we extensively examined high resolution XPS scans with different low pass energies and measurement cycles, which increases the measurement resolution while minimizing the measurement noise. Indeed, as shown in Fig. 3, the new identified peak is obvious on a 500 C heated niobium surface. Further depth profiling led to a decreased intensity of this peak but the peak persisted after 4.5 nm surface sputtering. We suspect this peak is assigned to Nb(OH)_x as the hydroxide motif was observed in the O 1s peak but on the surface region during room temperature scans.

Further analysis of this identified and possibly critical peak is ongoing, and a detailed structural analysis on oxygen-related structures for different acid- and heat-treated niobium samples are expected in the future work.

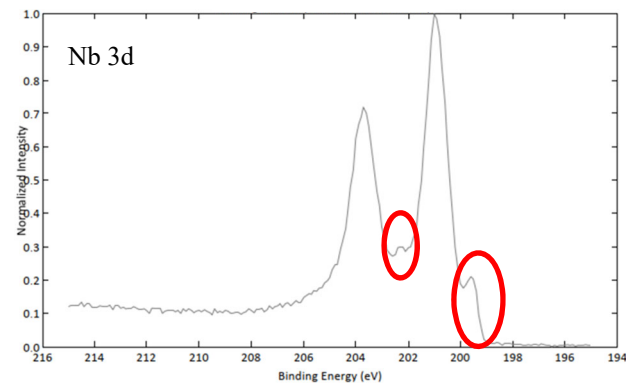


Figure 3: XPS Nb 3d spectrum taken under 500 C *in situ* heating, showing a new identified peak at the relatively low binding energy.

Oxide Variation on Nb₃Sn Surfaces

The multi-gap behaviors observed in Nb₃Sn SRF cavities draw our attention to examining the oxide structures on Nb₃Sn surfaces. Interestingly, we observed varied oxide structures on samples made by different techniques as shown in Fig. 4. The vapor-diffused sample showed mixed SnO_x and Nb₂O₅ on the outermost surface and some oxygen-deficient Nb and Sn oxides embedded with metallic Nb₃Sn at the underneath ~8 nm region. Note that SnO₂ and SnO are collectively assigned to SnO_x in this work due to the impossible deconvolution of their tiny binding energy difference.

By contrast, the electroplated-Sn converted Nb₃Sn surface showed a distinctive SnO_x layer at the outermost surface together with NbO_x embedded in metallic Nb₃Sn at the subsequent ~4 nm depth. STEM imaging with EDS and EELS analysis showed that these oxides are in an amorphous phase. Valence band profiling showed a normal-conducting or semiconducting pattern for the oxide layers. Further analysis is being conducted to accurately determine the electrical properties of the oxide layers.

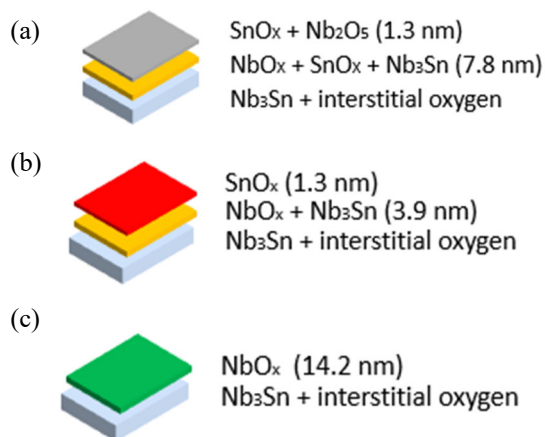


Figure 4: Surface oxide structures on Nb₃Sn samples made by (a) vapor diffusion, (b) thermal conversion of electroplated-Sn, and (c) sputtering.

Another important observation is the common presence of oxygen interstitials in the Nb₃Sn bulk region. The XPS scans observed deep oxygen presence in all Nb₃Sn samples studied. This observation was confirmed under STEM imaging of some samples (more imaging will be carried out). It should be noted here that the large surface roughness on Nb₃Sn surfaces could induce some measurement uncertainty, but the existence of such oxygen interstitials is valid due to the confirmation from atomic imaging.

Also, we found the sputtered Nb₃Sn again showed a distinctive oxygen structure that is a thick NbO_x layer on the surface without any SnO_x. Unlike other Nb₃Sn samples, we only obtained one dataset from the sputtered samples. Confirmation of this result is expected by other sputtering peers.

CONCLUSIONS AND FUTURE WORK

In summary, surface oxides on both Nb and Nb₃Sn surfaces are being systematically examined at Cornell. The Nb surfaces processed by different acid and heat treatments are reported. Large variation in the oxide structures is observed, showing the sensitive behavior during cavity preparation. Accurate quantification of oxide structure and thickness is being carried out. Detailed analysis together with new results from in situ heating-stage studies will be reported in the future.

Moreover, oxide variation is also observed on Nb₃Sn surfaces that are made from three different techniques. Efforts will be continued on characterization of surface oxides on new material systems [20].

Some open discussions include (1) how to create a standard acid and heat treatment procedure, (2) how to design the surface oxides in a controlled manner (ozone treatment was tested in this work), (3) what is the role of oxygen in the baked and nitrogen-doped/infused niobium, and (4) how does the oxide variation observed in this work affect the cavity performance. We aim to enrich our understanding in these four aspects in the future work.

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