Residual Oxygen on Nb Heated to 500 C

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Abstract

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Abstract

The superconducting accelerating cavities for the International Linear Collider will be constructed of high-residual resistivity ratio (RRR) niobium sheet. Excessive oxygen within the skin depth (several microns) will reduce the RRR and increase resistive losses. We measure the thickness of this oxide layer, following bakeout simulation, to be about 0.5 nm thick. The results suggest that this layer will very slowly disappear from the top five nm at 500°C.

INTRODUCTION

Niobium sheet material for superconducting rf cavities for International Linear Collider (ILC) fabrication is very pure high-RRR (residual resistivity ratio) and very low interstitial oxygen content. However, the fabricated cavity has a native niobium pentoxide layer which must be removed prior to cooling down to superconducting temperature; otherwise, the oxide layer disturbs the rf current flow within the skin depth.

It has been suggested that an extended low-temperature (up to 400°C) bakeout of the completed multi-cell structure may remove the oxide or, at least, dissolve and disperse it to low concentration in the bulk. X-ray photoelectron spectroscopy (XPS) is ideal for following the valence states of the Nb surface (< 5 nm) layer. The XPS system in the Physical Electronics group at SLAC is ideal for real-time monitoring of the surface condition during a reproduction of the bakeout heating. In addition, curve-fitting of high resolution XPS core level spectra can identify the thickness and valence of the oxide present before and after the heating process. Therefore, the bakeout idea was tested with several samples of Nb sheet material, starting at 400°C, while monitoring the surface oxide.

EXPERIMENTAL DETAILS

The system (a Vacuum Generators ESCALab II) is composed of two coupled stainless steel ultra-high vacuum (UHV) chambers where the pressure is in the low 10^{-10} Torr scale in the measurement chamber and high 10^{-9} Torr scale in the loadlock chamber. Samples, individually screwed to a carrier plate, are loaded first onto an aluminium transfer plate and placed into the loadlock chamber, evacuated to the low 10^{-8} Torr scale, and transferred into the XPS measurement and sample-heating chamber.

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Figure 1: XPS measurement system. Analysis chamber (1), loadlock chamber (2), sample plate entry (3), sample transfer plate (4), rack and pinion travel (5), sample plate stage (6), XYZΦ Omniax™ manipulator (7), sample on manipulator (8), electrostatic energy analyzer (9), x-ray source (10), SEY/SEM electron gun (11), microfocus ion gun (12), sputter ion gun (13), to pressure gauges and RGA (14), to vacuum pumps (15), gate valve (16).

The sample to be measured is then installed onto a special manipulator arm, Omniax™. This manipulator features heating of the loaded sample, the temperature of which is recorded by two type-C thermocouples. The back of the sample is heated by electron bombardment. This is achieved by high voltage-biasing a tungsten filament emitter negatively with respect to the sample.

XPS measurements were made using a non-monochromatized Al k-alpha electron bombardment x-ray source and hemispherical electrostatic electron energy analyzer. The XPS data were collected with the analyzer operating in the constant analyzer pass energy mode, with a total instrument energy resolution 0.75eV FWHM for "fingerprint" survey spectra and 0.5eV for individual core level measurements. Photoelectrons were collected by the analyzer from a 4x4mm² sample area at 15° from surface normal. Binding energies (BE) are referenced to the analyzer Fermi level. Intensity data is recovered from about the outermost 5 nm of surface.

XPS core level "profiles" can be collected during heating. Nb 3d and O 1s spectra were accumulated for 0.2s each, along with sample temperature, in a cycle. Successive time cycles were collected without dwell. Each profile was processed to display the core level peak height, above background, versus time. The 5+ valence of the Nb core

was used as representative of niobium pentoxide, the native terminal oxide of Nb. Reference XPS core level measurements from a clean 100 nm thick (effectively bulk) anodized Nb₂O₅ layer on Nb permitted the conversion of XPS Nb 5+ valence intensities to equivalent niobium pentoxide thicknesses.

Candidate Nb sheet samples were provided by Cornell University. The 0.75" diameter by 0.050" thick samples were made of high-RRR buffer chem-polished (1:1:2, cold acid) material. About 100 microns of material was removed per side.

RESULTS AND DISCUSSION

Pentoxide reference spectrum

The anodized pentoxide layer, shown in Figure 2, was fit using mixed Lorentzian-Gaussian lineshapes appropriate for dielectric material. The intensity of the Nb⁵⁺ 3/2 spin orbit-split line was then used as the bulk intensity in the oxide thickness conversion equation

$$d = -\lambda \cos \theta \ln(1 - I / I_{\infty})$$

where d is the oxide thickness, λ is the photoelectron inelastic mean free path, θ is the energy analyzer takeoff angle, I is the oxide overlayer Nb photoelectron intensity, and I_{∞} is the Nb photoelectron intensity from an "infinitely-thick" pentoxide. Curve-fitting of the data in Figure 2 provides the I_{∞} needed for processing the heating data. The leftmost component is the 3/2 line. This oxide line is used in our processing because it is well-separated from the Nb⁰ valence metallic Nb line.

water and hydrocarbons, stuck to the Nb. Also Na appears, completely masked by the overlayer prior to the heating. There is also a small amount (not identified on the figure) of Gd. It's source is possibly etch chemicals. What little is left of the carbon is present as NbC (identified by its binding energy, i.e., valence, and narrow lineshape), produced from the thermal energy of the heating process.

Heating experiments

The heating profiles for the two samples are presented in Figures 5-7 and 9. The first sample was heated for a long period at 400°C, cooled and re-heated. The second sample was heated for a shorter time to 500°C. The third for a long time at 500°C. The oxide thickness, resulting from the lower temperature, appeared to stabilize at ~0.4 nm (one monolayer of pentoxide is calculated to be 0.24 nm thick). Therefore, we tried the higher temperature on the second sample, to further reduce the final oxide layer level. Interestingly, that did not change the slope of the oxide thickness reduction.

Figure 5. Sample #1, Nb pentoxide 3/2 core level peak vs. T. Peak intensities are measured above background. The second heating occurred the next day, after sitting in 5×10^{-10} torr vacuum (95% H₂, 5% CO) overnight.

Figure 6. Sample #2, Nb pentoxide 3/2 core level peak vs. T. Peak intensities are measured above background.

Figure 7. Sample #2, total oxygen core level peak vs. T. Peak intensities are measured above background

In all cases, oxygen, either as pentoxide or as total oxygen (sum of all oxygen states) remained well above the inelastic electron background, right up to the highest temperature, see Figure 8.

Figure 8. O1s core level of sample #2, at 500°C.

There does appear to be a small downward slope for the total oxygen intensity, at 500°C, of the second and third samples (Figures 7,9), but not the first whose slope was flat at 400°C. Interestingly, the starting oxide layer thickness of the third sample is double that of the first. As noted above, the first two samples were fluorine-contaminated. The third sample was argon-ion sputter-cleaned, air-exposed and stored in a dry N₂-flushed container for several weeks. Except for oxide thickness, the heating behavior of sample 3 appears the same as samples 1 and 2, suggesting that the Nb surface was partially-passivated against oxidation by the fluorine in samples 1 and 2..

Figure 9. Sample #2, total oxygen core level peak vs. T. Peak intensities are measured above background.

High Resolution Spectra at 500°C

Figures 8 and 10 show high resolution spectra of sample 2, at 500°C. The Nb 3d and O 1s cores show considerable oxide detected, well above background, with valence 1+. The binding energy chemical shift in Nb is about 1 eV binding energy per oxidation number (1).

Figure 10. Curve fitted spectrum of sample #2, at 500°C, showing just two components, Nb⁰ (metal) and Nb¹⁺.

Figure 11. Nb spectrum of sample #2, as received. Comparison with Figure 2 shows that two principal components are present, Nb metal and Nb pentoxide.

The significance of this valence, 1+, is discussed at length in references 1-4. If the oxide is present as a compound, Nb₂O or NbO_{1-x}, the melting point will be much higher (~1200°C) than that of Nb₂O₅. We also curve-fitted sample 2 after cooling to RT, and obtained essentially the same component peaks result as we did at elevated temperature. The 1+ valence is not Nb₂O₅ temperature-related, at least up to 500°C.

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