

RECENT XPS STUDIES OF THE EFFECT OF PROCESSING ON NB SRF SURFACES*

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Abstract:

XPS studies have consistently shown that Nb surfaces for SRF chiefly comprise of a few nm of Nb₂O₅ on top of Nb metal, with minor amounts of Nb sub-oxides. Nb samples after BCP/EP treatment with post-baking at the various conditions have been examined by using synchrotron based XPS. Despite the confounding influence of surface roughness, certain outcomes are clear. Lower-valence Nb species are always and only associated with the metal/oxide interface, but evidence for an explicit layer structure or discrete phases is lacking. Post-baking without air exposure shows decreased oxide layer thickness and increased contribution from lower valence species, but spectra obtained after subsequent air exposure cannot be distinguished from those obtained prior to baking, though the SRF performance improvement remains.

INTRODUCTION

The use of surface spectrometers, dominantly XPS, to examine the Nb surface nano-layer began to be reported more than 25 years ago and continues to the present day [1-20]. The surface chemistry of niobium is dominated by high reactivity toward oxygen [3, 20]. The outermost layers are always found to be Nb₂O₅, suboxides: such as NbO₂, NbO, and Nb₂O are also known and, in various combinations and morphologies, are proposed to be between the Nb₂O₅ and the underlying metal [4-7,13]. In order to understand how composition varies with depth, angle-resolved XPS (ARXPS) and variable photon energy XPS provide a damage-free method, in contrast to unavoidable radiation damage with sputter profiling [13], which have been largely used to analyze variation with depth [22].

In the preparation of niobium cavities for SRF accelerator cavities, surface damage and contamination are removed by chemical etching and followed by post-etch treatments. The two widely practiced etch technologies are buffered chemical polish (BCP) and electropolish (EP).

A low temperature (110 ~ 140°C), 48 hrs *in-situ* baking under ultra-high vacuum has been successful applied as a

final preparation of Nb SRF cavity by several laboratories over the last few years. The benefits reported consist mainly of an improvement of cavity quality factor and a recovery from the high field “Q-drop” [23-28]. Non *in-situ* baking studies also show that baking in the air at atmospheric pressure have been carried out with same efficiency [25]. Recent studies of low T baking conducted on large-grain single cell cavity shown that *in situ* baking at 120°C for only 3 hrs was sufficient to reduce most of the hot spots up to a quench field [24].

However, high gradient “Q-drop” and its empirical cure by low T baking are still not well understood [25-26]. A number of models have been proposed as described in ref [27]; none of them is able to fully account for all the observations.

In this study, samples undergone same BCP/EP treatment, as is done in cavity productions, are subjected for a series of surface roughness and chemistry studies. The BCP treated single crystal Nb samples have been post-baked at different temperatures, durations and atmospheric conditions. Synchrotron based XPS has been used to characterize the surface chemistry for each of the conditions and to improve understanding of the phenomenon.

EXPERIMENTAL PROCEDURE

Sample preparation

12 mm diameter Nb single crystal disk samples were saw cut from 3.175 mm thick Nb large-grain sheet used for fabricating large grain cavity—the technology recently developed at Jefferson Lab [29]. 12 mm diameter and 3 mm thick polycrystalline Nb disk samples were cut from the same Nb sheet used to make SRF cavities, having purity of 99.9999% according to the vendor-Wah Chang. After ultrasonic degreasing for 20 minutes, BCP treated samples were etched in a fresh 1:1:2 solution - mixture of HNO₃ (69%), HF (49%) and H₃PO₄ (85%) by volume for 100 minutes at room temperature removing a weight equivalent to about 200 μm of material, this has been found to eliminate any trace of mechanical machining from the surface[30,31]. EP treated samples were etched with a fresh 1:9 mixture of HF (49%) and H₂SO₄ (96%) with a 50 mA/cm² operational current density at temperature around 35 °C and same amount of removal achieved. To remove acid residue and particles on samples introduced during handing, the samples were

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ultrasonically rinsed in deionized water immediately following BCP/EP. After rinsing, the samples were air dried and material removal was confirmed by weight loss.

Surface Morphology

Optical images were taken with HIROX KH-3000VD High Resolution Digital Video Microscopy System. Profilometry measurements were obtained with a stylus profilometer (KLA-Tencor: P-15) equipped with a 2 μm diameter tip. The samples were scanned in three different regions with a scan size of 200 μm \times 200 μm and 1000 μm \times 1000 μm . AFM measurements were performed using a commercial AFM (Digital Instruments: Nanoscope IV) in a tapping mode using silicon tips with a diameter of 10 nm. The samples were scanned in three different regions with scan sizes of 20 μm \times 20 μm , 40 μm \times 40 μm , and 100 μm \times 100 μm . Our results shows that EP treated single crystal Nb sample gives the best finish, however across 40 μm \times 40 μm scanning area, 100 nm scale roughness remained as shown in Figure 1.

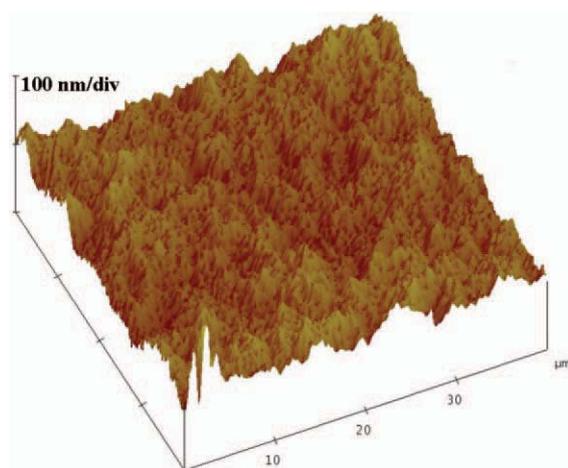


Figure 1. AFM image of EP single crystal sample

Angle resolved XPS vs. Variable photon energy XPS

Synchrotron based XPS experiments reported here were undertaken on the soft x-ray undulator beamline X1B at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). This beamline is equipped with a spherical grating monochromator and focusing mirrors to attain a spot size of about 100 μm \times 30 μm . The location of the illuminated area remains constant as photon energy is changed. The photon energy ranges from 100 eV to 1600 eV, attainable energy resolution can be less than 0.1 eV. Samples were freshly rinsed with reagent-grade isopropanol, before being introduced to the beamline vacuum chamber and pumped to a base pressure below 10^{-10} torr [32].

We used variable photon energy XPS to gain an alternative view of how composition varies with depth. We also collected angle-resolved data at fixed photon energy to better understand the relationship between the

two approaches; results from BCP treated single crystal materials are shown in Figure 2 a, b.

Comparing the Nb 3d spectra (Figures 2a, 2b) measured at varying angle and photon energy; we find the intensity from metal Nb changes more quickly with the latter. A further advantage is that the variable photon energy experiment always views the same column of material, without regard to local topography, in contrast to the effect of tilting the sample for ARXPS, which inherently views different columns. While the difference is real, the impact is certainly insignificant for truly planar surfaces, but may not be so for the topography resulting from BCP etching [22, 32].

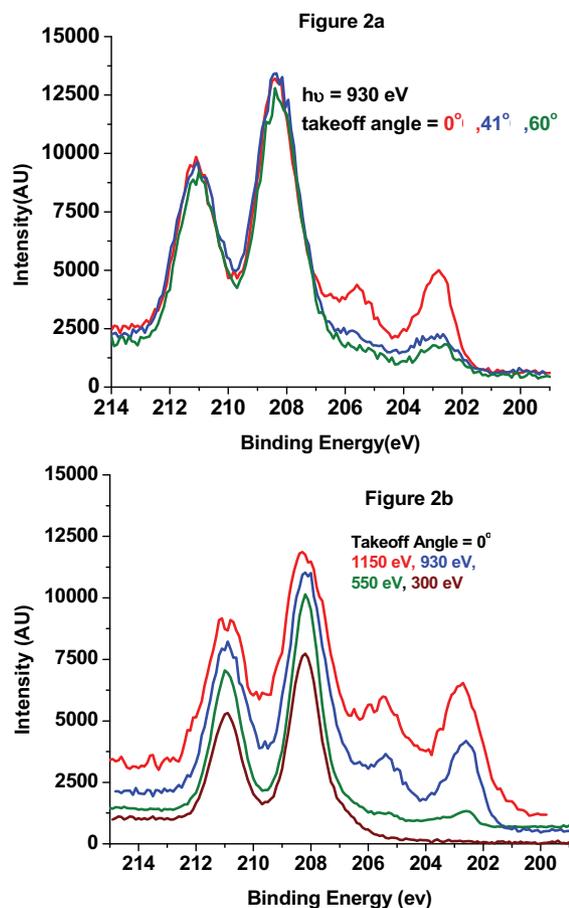


Figure 2. Variable angle (a) and photon energy (b) Nb 3d spectra for BCP treated single crystal Nb sample.

RESULTS AND DISCUSSION

Surface Chemistry (before and after low T baking)

Figures 3a, 3b show a common picture of Nb 3d spectrum before and after 120°C, 48 hrs *in-situ* baking. After baking, the top Nb₂O₅ layer is partially transformed into sub-oxides which are directly observed from decreasing Nb⁵⁺-associated doublet intensity and increasing of suboxides-associated peaks. Less than 1 nm of sub-oxide layer thickness is measured through variable photon energy Nb3d spectra [22], but an explicit layer

structure or detection of discrete phases is still lacking. The total oxide layer becomes thinner with baking, observed from the increasing of Nb^0 doublet intensity (Detailed deconvolution procedure and species-related peak separations as in Figure 3a, 3b will be reported shortly).

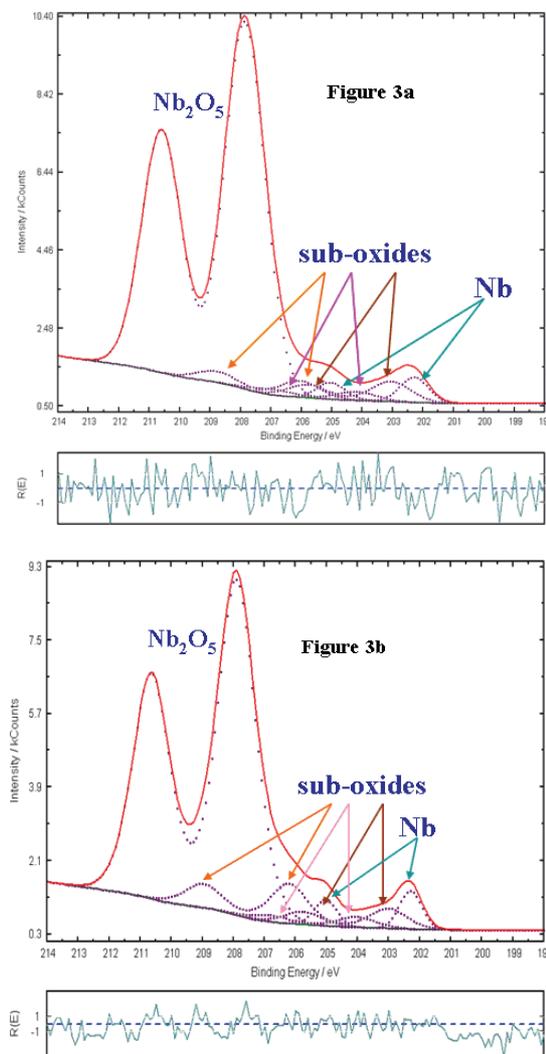


Figure 3. Deconvoluted Nb 3d spectrum (a) before and (b) after low T baking.

Effect of baking temperature

Measurements of low field superconducting parameters suggest that oxygen diffusion was involved in the effect of low-temperature baking. A model based on reduced lower critical field due to higher interstitial oxygen near the surface has been refined to provide an explanation for “Q-drop” and the baking effects [24]. A recent study has shown that 3 hrs, 160°C *in situ* baking achieved same effect as that of 120°C for over 48 hrs baking [25].

In order to investigate baking effect on the surface, the samples have been *in situ* baked at 120°C for 12 hrs, at 160°C for 3 hrs and 12 hrs respectively. Low T baking was conducted in the sample preparation chamber of

multi-spectroscopy facility of X1B with the pressure of low value of 10^{-9} torr. We find that 160°C, 3hrs baking causes almost the same amount of Nb_2O_5 to transform to suboxides as that of 120°C, 12 hrs, and a long baking duration for higher temperature helps more Nb_2O_5 transformation. The corresponding Nb 3d spectra before/after 120°C, 12 hrs and 160°C, 3 hrs baking; before/after 120°C, 12 hrs and 160°C, 12 hrs baking are shown in Figure 4a and 4b.

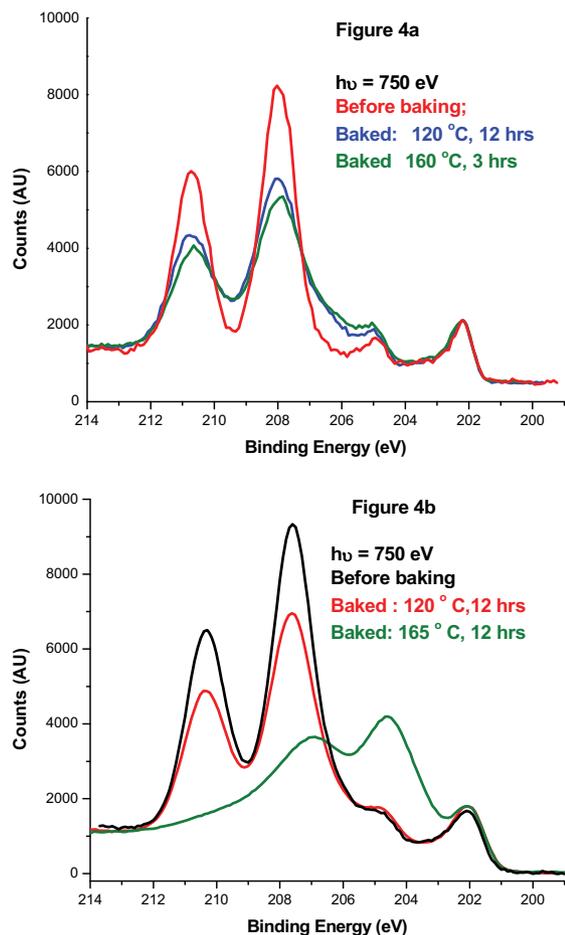


Figure 4. Nb 3d spectrum (a) before, after 120°C for 12 hrs, and 160°C for 3 hrs; (b) before, after 120°C for 12 hrs, and 160°C for 12 hrs.

Effect of baking duration

As introduced previously, *in-situ* baking for shorter duration (120 °C, 3 hrs) was surprisingly found to be sufficient to reduce most of the hot spots up to quench field. In order to find out the effect of baking duration for surface oxide, Nb samples undergone baking at 120°C at 3 hrs and at 12 hrs respectively have been investigated. We find more Nb_2O_5 transformation with the time as shown in Figure 5. Then after a few hours air-exposure, the change of oxide layer associated with Nb_2O_5 transformation observed disappeared and cannot be distinguished from those obtained prior to baking as indicated from Figure 6. However, a number of cavity studies show that the achieved improvement through low temperature is

maintained for over few months' air exposure. The results give evidence that the change of suboxides created by *in situ* baking is not responsible for the improved SRF cavity performance.

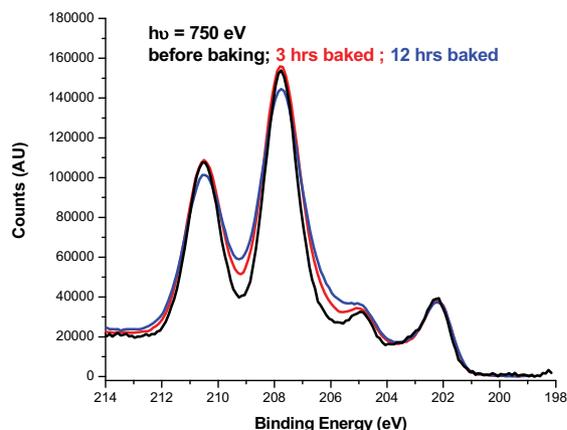


Figure 5. Nb 3d spectra before/after 120°C, 3 /12 hrs baking

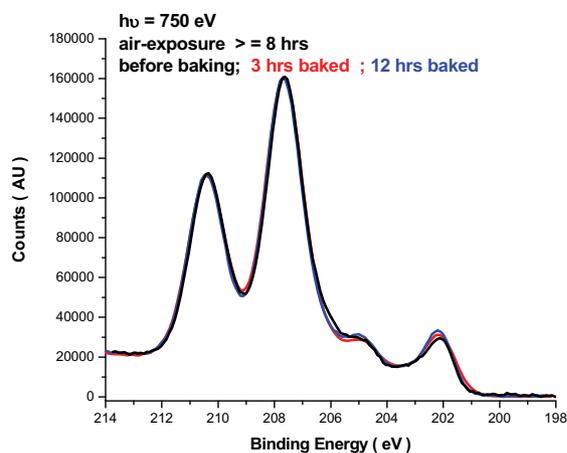


Figure 6: Nb 3d spectra after over 8 hrs air-exposure (*in situ* baked at different duration).

Effect of air baking

As introduced previously, recent studies proposed that baking in air at atmospheric pressure could be carried out with the same efficiency as UHV condition, also the cavities surface treatment by oxygen plasma shows similar results as baking treatment [25]. Different temperature air-baking was also conducted on large grain single cell cavities to investigate the validity of oxygen diffusion model [27]. It was found that too high oxygen concentration near the surface, as obtained by baking the wet cavity in air at 180°C, is detrimental for the cavity performance and results in high interface and dielectric losses. XPS measurement has been done to investigate the surface oxide of samples baked at 120°C and 165 °C in air. We find that the higher baking temperature in air makes a thicker oxide layer, as shown in Figure 7. Almost

no signal of metal Nb could be observed from Nb 3d by using 750 eV photon energy (the attenuation lengths calculated is about 5nm [22]). A thicker oxide layer is obtained after air baking than after *in situ* baking at the same temperature, even after air-exposure, which could be clearly observed from the decreasing Nb⁰ doublet intensity, as shown in Figure 8.

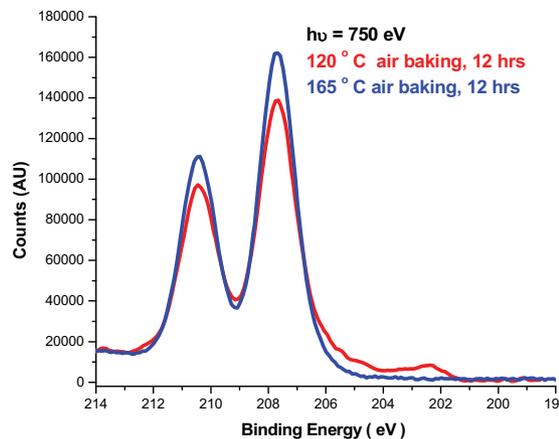


Figure 7. Comparison of Nb 3d spectra after 120°C and 165°C air baking

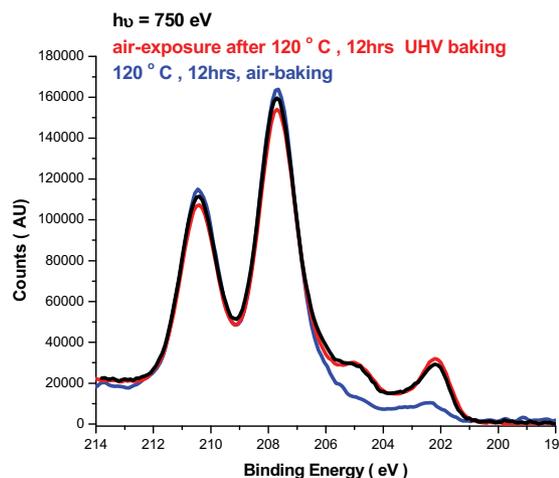


Figure 8: Nb 3d spectra after more than 8 hrs air-exposure of 120°C UHV and air-baked samples.

CONCLUSION

XPS studies shows that after baking, Nb₂O₅ is partially transformed into suboxides, the total oxide layer becomes thinner; but once air-exposed, the change of oxide layer observed after baking almost disappears, which gives evidence that the suboxides created by *in situ* baking are not responsible for improved SRF cavity performance, since cavities still keep good performance after new air-exposure that eliminates the created change of suboxides.

Compared with 120°C baking, higher baking temperature (160°C) transforms more oxide. 3 hrs, 160°C

baking makes almost the same amount of oxide transformation as that of 12 hrs, 120°C baking. Air baking produces a thicker oxide layer. Longer baking time at 120°C (3hrs ~12hrs) increases Nb₂O₅ reduction and transformation. So, from these XPS studies, the changes in the niobium oxide layer caused by low T baking appear to not play a big role in the observed performance improvement of niobium cavities.

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