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# FIRST DIRECT IMAGING AND PROFILING TOF-SIMS STUDIES ON CUTOUTS FOM CAVITIES PREPARED BY STATE-OF-THE-ART TREATMENTS*

A. Romanenko†, Y. Trenikhina, M. Martinello, D. Bafia, A. Grassellino
Fermi National Accelerator Laboratory, Batavia, IL 60510, USA

*Abstract*

Small amounts of interstitial impurities in the penetration depth of superconducting radio frequency (SRF) cavities have a dramatic effect on the quality factors and maximum accelerating gradients. Here we report the first TOF-SIMS studies of cutouts from cavities prepared by all modern surface treatments, which allow a direct correlation of the impurity distribution with the observed cavity performance. Imaging capability of our instrument allows to avoid the possible issues associated with the ``ghost'' depth profiles appearing as a consequence of particulate surface contamination, which likely caused the inconclusive SIMS results on e.g. oxygen diffusion in the past.

## INTRODUCTION

One of the most important tasks for further progress in SRF is establishing a direct correspondence between the near-surface impurity profile and the observed cavity performance. A lot of studies tried to establish that with many aspects clarified up to date (see e.g. [1] for a review). The most direct method though is based on first testing the cavity and then cutting out the samples from cavity walls, possibly further guided by temperature mapping. There have been only a couple of brief secondary ion mass spectrometry (SIMS) studies reported on *cutouts* so far in the context of nitrogen doping [2, 3] and nitrogen infusion [4, 5].

In this contribution we report the first such systematic studies allowing for several conclusions, most notably a direct confirmation of the oxygen diffusion involvement in the 120C baking mechanism. We have found that 120C baking for 48 hours leads to an introduction of a >~50 nm deep oxygen reach layer right underneath niobium oxide, also accompanied by the modified hydrogen-related signals ($NbH_x$, OH). We also re-confirm that nitrogen doping and infusion lead to the nitrogen-rich layers on different depth scales.

## CAVITY RESULTS

We have prepared, measured, and cut several 1.3 GHz TESLA shape fine grain high RRR Nb cavities with the following (last) surface treatments:

- 800C 3 hrs degassing + 20 um EP (1-cell TE1AES008)
- EP + 75C 3 hrs + 120C baking for 48 hrs (1-cell TE1AES009)
- Nitrogen doping using 2/0 recipe (2 min of $N_2$ injection) followed by 5 um EP (9-cell CAV018)
- Nitrogen infusion at 120C for 48 hours (1-cell TE1PAV012)

The results of the corresponding cavity tests at 2K are shown in Fig. 1.

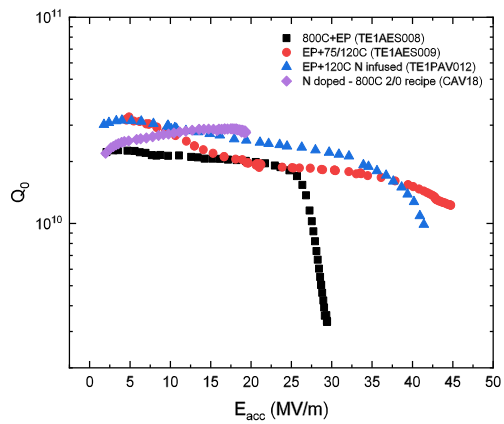


Figure 1: $Q(E_{acc})$ curves at T=2K of the cavities used for cutout studies.

For most of the 1-cell tests the cutout locations have been guided further by the temperature mapping data, and performed using the previously established procedures [6] to preserve cleanliness and avoid any heating. For a 2/6 N-doped 9-cell cavity we have also extracted samples from different cells (equatorial area – see Fig. 2) to study if there is any variation in the nitrogen concentration.

Figure 2: 9-cell 2/0 N doped cavity (left) with equator samples extracted from each cell. Single cell with cutouts from various locations and a typical sample is shown on the right.

## TOF-SIMS RESULTS

We have used the Fermilab state-of-the-art IONTOF time-of-flight secondary ion mass spectrometry (TOF-SIMS) dual beam system. The liquid bismuth ion beam ($Bi^+$) was used for secondary ion measurements, while the cesium ($Cs^+$) gun of 1 keV energy was used for the sputter

* Work supported by the US DOE Office of High Energy Physics.
† aroman@fnal.gov

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erosion during depth profiling. An extremely important capability of modern TOF-SIMS systems in general and our system in particular, distinguishing this study from most of previously reported studies, is the utilization of the full 3D and imaging information to make sure that the obtained depth profiles are not affected by any artifacts, such as the particles on the surface. Many past studies using e.g. dynamic SIMS suffer from such a lack of spatial information, which could lead to possible false profiles. The most recent study using a similar modern system has been reported in [7] for a set of non-cutout samples prepared by BCP and colloidal silica polishing.

In Fig. 3 an example of the dual beam analysis containing the full 3D information used for eliminating possible artifacts is shown. The images of total counts of $Nb_2O_5^-$, $O^-$, and $NbN^-$ are shown, along with the extracted XY, YZ, and XZ cross-section images through specified planes containing the particle.

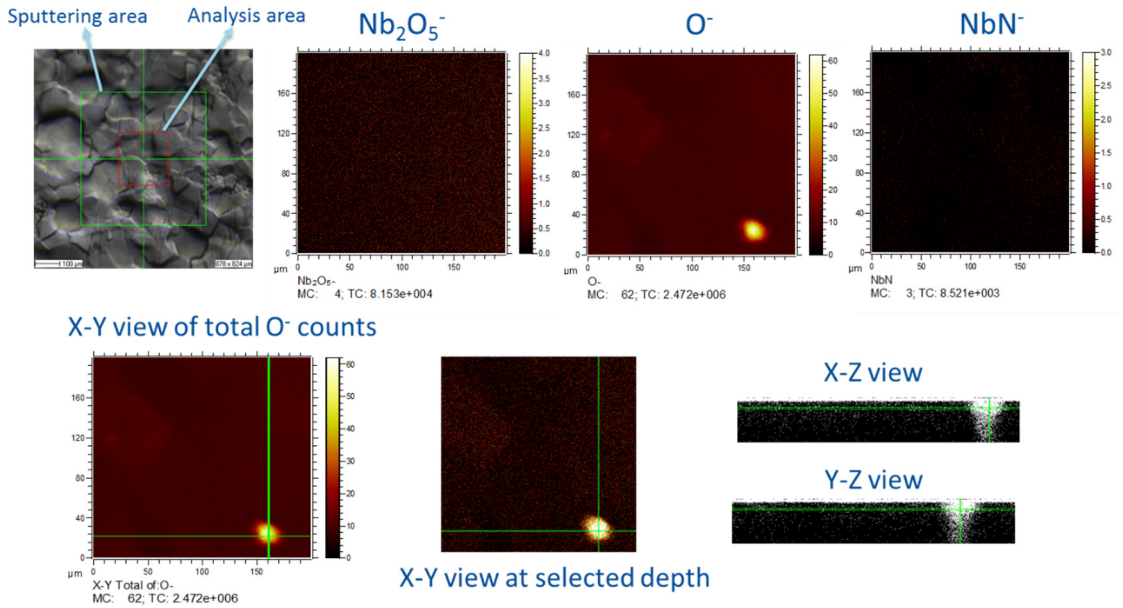


Figure 3: Examples of the secondary ion images obtained in the analysis area for the depth profiling. The capability of post-processing based on the full 3D information allows avoiding any areas with the particulate contamination.

Subsequent analysis of the images and elimination of the areas of particulate contamination from the dataset used for reconstructing depth profiles is the key step in avoiding the appearance of the artifact depth profiles.

## *Oxygen*

A very important finding is the difference in the oxygen concentration right underneath the oxide between the EP and EP 120C baked cavity cutouts, as shown in Fig. 4.

Several spots have been analyzed on the cutout from TE1AES008 (EP cavity) and a cutout from TE1AES009 (EP+75/120C 48 hrs) and compared based on the $O^-$ signal normalized point-by-point over the $Nb^-$ signal. We have found a 100% reproducibility and no spot-to-spot-variation.

In Fig. 5, a comparison of oxygen distribution between all four treatments including doping and infusion is shown. Remarkably, nitrogen doping does not lead to any oxygen enrichment, which was suspected previously as a possible reason for an early quench.

Nitrogen infusion revealed the oxygen concentration tail extending over about ~100 nm.

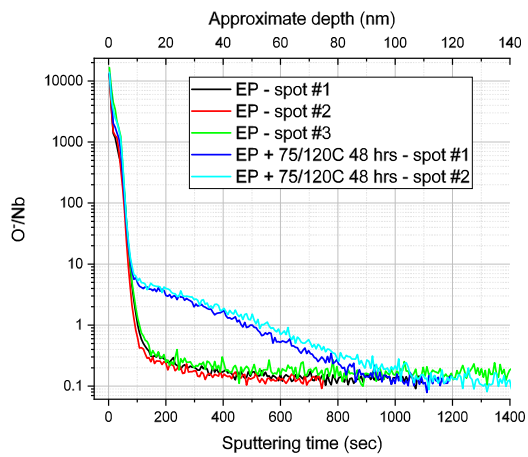


Figure 4: Oxygen depth profile comparison between the cavity cutouts showing the dramatic effect of 120C baking on the under-oxide oxygen concentration.

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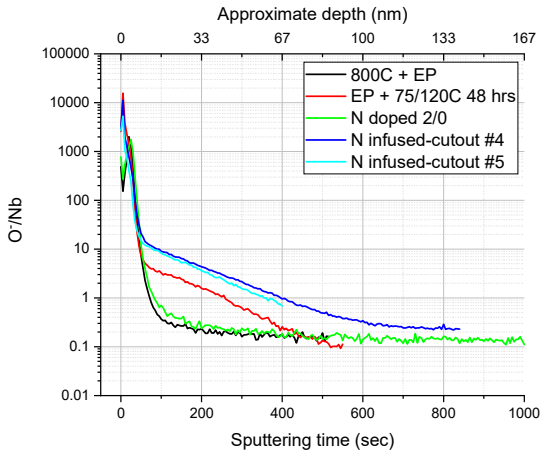


Figure 5: Oxygen depth profile comparison for EP, EP+120C, N-doped 2/0 +5 um EP, and 120C N-infused cutouts.

## *Nitrogen*

Nitrogen concentration profile was evaluated based on the $NbN^-$ ion signal, normalized to $Nb^-$ counts. The results are shown in Fig. 6. Nitrogen doping results in the almost constant depth profile (on the scale of tens of nanometers), with the changes in nitrogen concentration happening on the scale of micrometers (reported elsewhere, e.g. [2]).

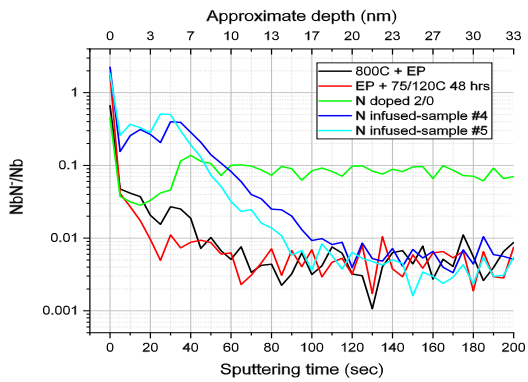


Figure 6: Nitrogen depth profile comparison between the doped, infused, and non-doped cavity cutouts.

In Fig. 7, a comparison between the nitrogen depth profiles ($NbN^-/Nb^-$) from three different grains on the same N-doped cutout is shown with the profiles being very similar to each other.

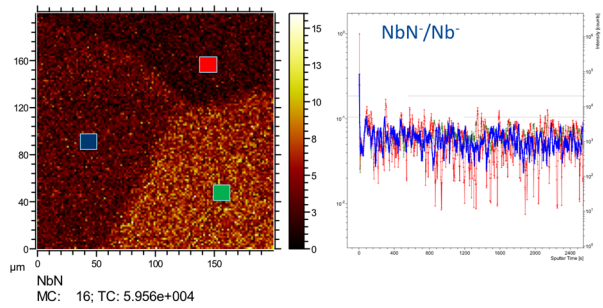


Figure 7: Comparison of NbN/Nb profile (right) for three neighboring grains (left). No concentration difference is observed.

Samples extracted from the 9-cell cavity allowed also to observe that there is no cell-to-cell nitrogen concentration variation. This is shown in Fig. 8.

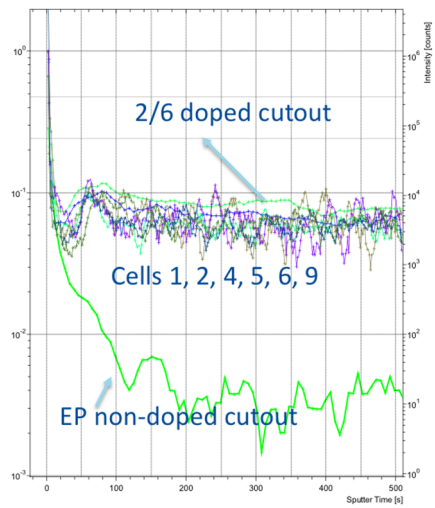


Figure 8: NbN/Nb profiles for cutouts from the equators of different cells of the 9-cell 2/0 N doped cavity showing little variation.

## *Hydrogen*

We were able to compare the hydrogen-related signal concentration and distribution between the samples as well. In order to minimize the background and to reveal the differences, the so-called 'interlaced' mode of operation of the TOF-SIMS instrument was used.

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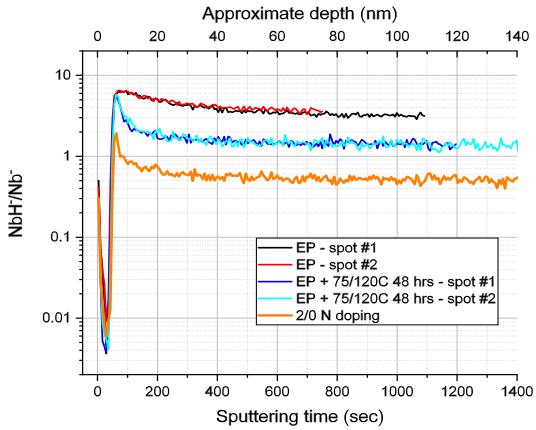


Figure 9: $NbH^-/Nb^-$ signal in interlaced mode for various cutouts.

The $NbH^-/Nb^-$ signal, which could be used as a measure of the free hydrogen concentration in the lattice, is shown in Fig. 9. The clear differences are observed with the EP cutouts showing the highest signal with 120C baking leading to the significant suppression underneath the oxide/metal interface (where concentrations are matching). Nitrogen doping reveals the lower overall signal and a depth profile shape similar to the 120C baked cutout.

Since the clear differences in the oxygen concentration were found, we have also evaluated the $OH^-/Nb^-$ signals, which we interpret as a measure of the oxygen-bound hydrogen signal. The resulting profiles are shown in Fig. 10.

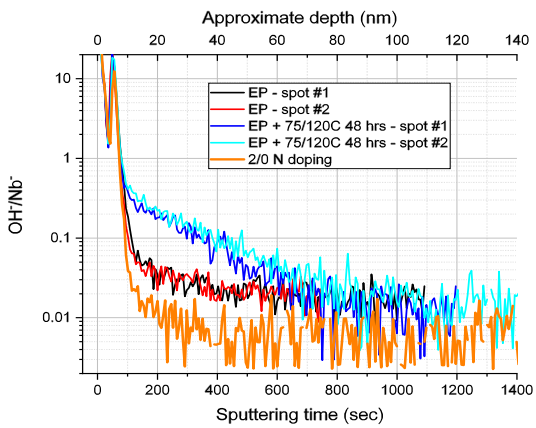


Figure 10: $OH^-/Nb^-$ signal in interlaced mode.

We note that the 120C baked cutouts reveal the increased $OH^-$ yield tail corresponding in depth with the $O^-$ enrichment from Fig. 4. In the nitrogen-doped cutout instead we observe no such signal.

### *Other Elements*

We have not observed in this preliminary analysis any systematic effects with the other impurities in the investigated samples. Further analysis is ongoing and will be reported elsewhere.

## DISCUSSION

It has been previously suggested that oxygen diffusion plays a role in the 120C baking effect (see e.g. [8]). One of the past proposed models for the high field Q-slope has been the 'oxygen pollution' model (see e.g. [9, 10]), requiring the oxygen-rich layer BEFORE 120C baking, which gets diluted/diffused away during the 120C bake.

We have found instead the absence of oxygen-rich layer in the EP cavity and the extended ~50-70 nm layer of oxygen-rich material underneath the oxide after the 75/120C 48 hrs baking, which is arguably the most important finding of our work. This confirms the involvement of oxygen diffusion in the 120C baking effect. However, our finding paints the opposite picture to the "oxygen pollution" model, namely signaling that the introduction of oxygen-rich layer is actually a *cure* for the high field Q-slope. This finding is consistent with the origin of the Q-slope being currently attributed to nanoscale niobium hydrides [11], as oxygen is a known effective trapping agent for the interstitial hydrogen thereby reducing the amount of free hydrogen and suppressing the hydride precipitation. The observed depth of the oxygen enrichment is also consistent with the previous oxypolishing, anodizing, and HF nanoprofiling studies on 120C baked cavities [12-15], as well as with the muon spin rotation studies on the cutouts [16].

It should be noted that the oxygen diffusion can also provide an alternative explanation to the observed increase in S-parameter in the positron annihilation studies [17], which was previously attributed mostly to the vacancy concentration changes.

We would also like to note that in one of the previous non-cutout studies focused on oxygen in niobium samples [18] an increase in the oxygen concentration right underneath the oxide has been observed, although at a somewhat higher temperature of 145C.

Remarkably, nitrogen-doped cavity cutouts do not show any excess oxygen contamination as compared to the non-doped material. This is important as one of the possible discussed origins of the lower quench fields in N-doped cavities has been a proposed oxygen contamination. Our data does not support this hypothesis.

Nitrogen-infused cutouts show an oxygen profile shape similar to the 75/120C cutouts, with a somewhat deeper penetration inside niobium. However, the 120C N infused cavity which was cut for these studies was prepared during the presence of the - later identified - oxygen leak in the furnace nitrogen supply line. Therefore, we cannot conclude if this oxygen profile would be present for the 'clean' nitrogen infusion, making it a subject of further future investigations.

Nitrogen distribution inside the cavity cutouts is consistent with the current understanding [2-5]. N-doped cutouts possess a nitrogen-rich layer extended over the scale of micrometers (see e.g. [2]), i.e. in the magnetic penetration depth the nitrogen concentration is practically constant. Nitrogen-infused cutouts have instead a very thin nitrogen-rich layer of about 10-15 nm underneath the oxide with the initial nitrogen concentration of about twice that of 2/0 N doped but dropping rapidly into the material.

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Samples from different cells on the 9-cell N doped cavity showed virtually identical nitrogen concentration, indicating that the nitrogen pressure and diffusion during the doping process is uniform enough.

## CONCLUSION

We have performed the first study of cutouts from cavities prepared by all the modern surface treatments using the state-of-the-art TOF-SIMS leading to several advances in understanding:

1) confirmed the oxygen diffusion involvement in the 120C baking effect; revealed lack of the oxygen-rich layer before and its emergence after the 75/120C 48hrs bake;

2) confirmed the nitrogen inward diffusion and the formation of the nitrogen-rich layer on the scale of ~10-15 nm during the 120C nitrogen infusion;

3) revealed the $NbH^-$ signal suppression in the near-surface area associated with the 120C baking;

4) revealed the possible oxygen trapping of hydrogen as witnessed by increased $OH^-$ signal in the 120C baked cutouts;

5) no oxygen contamination was found in N-doped cavity cutouts;

6) no nitrogen concentration variation was found between the different cells of the 2/0 N-doped 9-cell cavity;

7) no nitrogen concentration variation was observed between the different grains when normalized $NbN^-/Nb^-$ signals were considered.

## ACKNOWLEDGMENTS

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