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SIMS CHARACTERIZATION OF NITROGEN DOPING OF LCLS-II-HE PRODUCTION CAVITIES*

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Abstract

The thermal diffusion of nitrogen into the surface of niobium has been shown to yield superior low-loss SRF performance. An effective solution was identified and promptly employed in the production of cryomodules for LCLS-II. With added experience and R&D, a modified process was chosen for use in the upgrade for LCLS-II-HE. Largely motivated by this circumstance, supporting research has significantly refined the technique for making calibrated secondary ion mass spectrometry (SIMS) measurements of the N concentration depth profiles produced by production processes. Standardized reference samples were included with four HE production cavities in their N-doping furnace runs. We report the calibrated dynamic SIMS depth profiles of N, C, and O for these samples, together with the cryogenic acceptance test performance of the associated cavities. Interpretation and comparison with similar samples acquired in other furnaces highlights the importance of intentional process quality control of furnace conditions.

SIMS ANALYSIS OF NIOBIUM

Sample Preparation

Over the past several years a standardized Nb sample preparation process has been developed at Jefferson Lab to facilitate high quality SIMS characterization of the surfaces produced by various candidate SRF cavity preparation methods. The key characteristics are: fabrication from cavity sheet stock, dimensions standardized for multiple loading in custom SIMS sample holder and custom electropolishing sample holder that assures only single face exposure to electrolyte, annealing of the samples to obtain grain sizes (~200 μm) to enable SIMS sampling of only single grains (since sputter rates vary with grain orientation), planarization of the sample face to ~5 nm via chemical/mechanical polishing and electropolishing, with minimum disturbance of the lattice of the surface grains. Such surface planarization is necessary in order to obtain uniform sputter depth and thus maximize the depth resolution during SIMS sputter profiling.

Development of SIMS Quantification Techniques

There having been no prior work refining dynamic SIMS technique on Nb matrix, this became the subject of the PhD dissertation efforts of J. Tuggle and J. Angle at the Nano Characterization and Fabrication Lab (NCFL) of Virginia Tech. Method sensitivities and vulnerabilities were explored and refined such that measurement errors on contaminant species concentrations approaching 10% have been realized. [1-4]

SAMPLING PRODUCTION PROCESS

Having recognized a vulnerability to potential process variation with "tightness" of the cavity "caps" that can restrict N_2 flow into the cavity during doping [5], we arranged to have standard prepared samples included with the doping furnace run of four LCLS-II-HE cavities at RI Research Instruments GmbH. Our purpose was to sample the doping variability within the routine production process.

A single standard Nb sample was included inside each of two cavity envelopes during each of two routine N-doping production furnace runs. The samples experienced the same N_2 pressure and temperature profile as that cavity's interior surface. The standard protocol for N-doping for the LCLS-II-HE project is heating at 800 °C for 3 hours under high vacuum conditions followed by 2 min exposure to ~33 mbar N_2 gas while sustaining 800 °C. Then the nitrogen gas is evacuated and the furnace heat is removed, and contents are allowed to cool down under vacuum. Between preparation at Jefferson Lab and placement in cavity, and then also between removal from cavity and transport to analysis, the samples were stored in concave base sample holders to protect the key surface. The HE production cavities sampled were CAVR076, CAVR142, CAVR144, and CAVR151.

SIMS CHARACTERIZATION

The four samples were shipped to the NCFL for analysis with a Cameca 7f dynamic SIMS system. Depth concentration profiles were measured on three randomly selected niobium grains on each sample. Secondary ion yields indicating atomic N, O, and C concentrations within each Nb grain were calibrated against a similar standard sample ion-implanted by Kroko. The obtained concentration profiles are presented in Fig. 1.

The sputter times and current were the same for all sampled grains. The grain orientation dependence of sputter rates produces the variation in sampled depths. With these samples we were seeking to acquire profiles to a depth of at least 10 μm.

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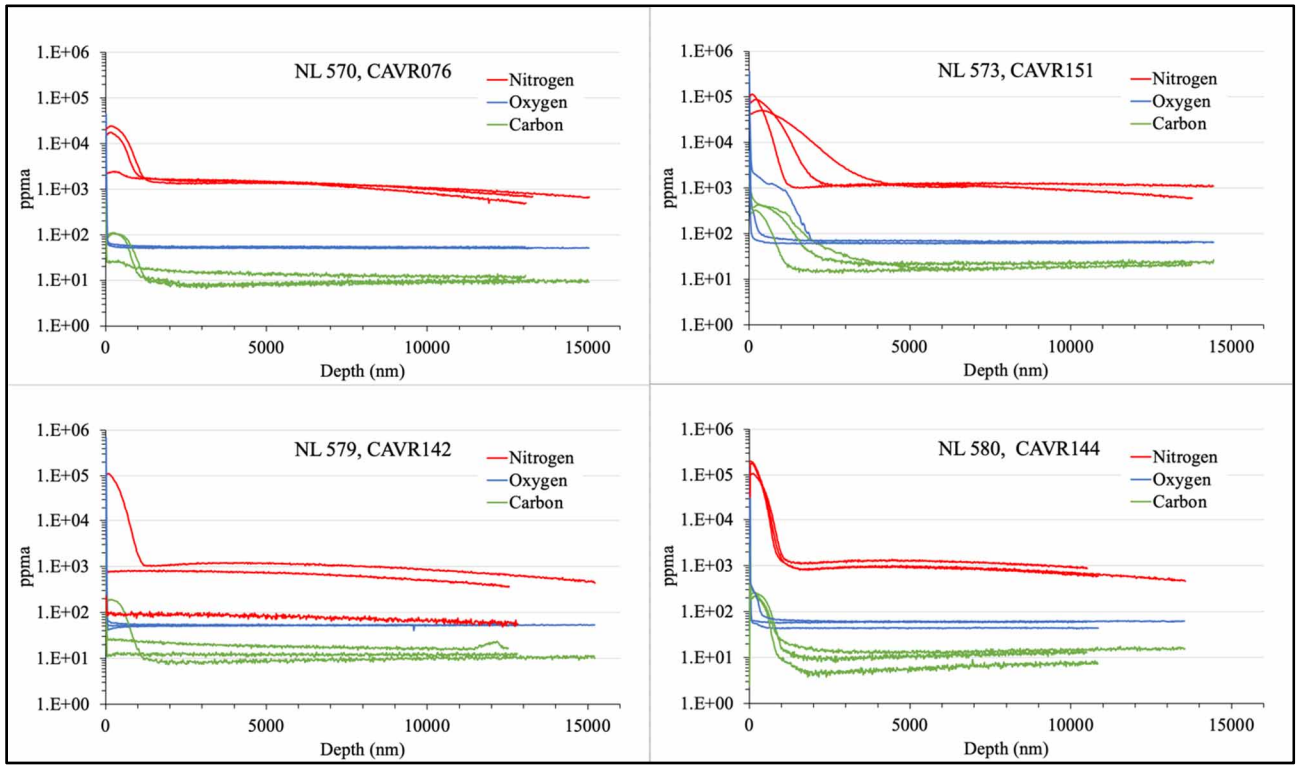

Figure 1: Concentration profiles determined by SIMS of N, O, and C in single surface Nb grains of samples included in production N-doping heat treatments for four cavities for the LCLS-II-HE Project.

From review of these data, one may note several significant features:

- At the intended surface removal depth of 5 µm for LCLS-II-HE cavities, the N atomic concentrations are all quite consistently ~1000 ppma (0.1%), with one odd exception.
- The depth of the surface nitrides varies significantly among the sampled grains.
- Two grains on sample NL 579 show an absence of any surface nitride signature.
- Indicated surface C concentration structure correlates with that of N, which might be due to higher secondary ion yield from a nitride matrix compared with that of Nb.
- The O and C concentrations beneath the "disturbed" nitride layer are consistent with nominal starting material specifications, indicating insignificant uptake from the furnace vacuum conditions during "doping".
- The N diffusion profiles appear deeper than in previously reported conditions, presenting weak sensitivity to modest variations in local removal by electropolishing of the cavities.

CAVITY RF PERFORMANCE

The four cavities whose N-doping processing was sampled proceeded normally through the balance of the production process (which includes removal of 5 µm by controlled electropolish) and received their RF performance acceptance testing at Jefferson Lab and Fermilab. The 2 K performance of these four HE cavities is presented in Fig. 2. All meet the project's acceptance requirements. The cavity CAVR151 had a higher Q_0 prior to some quench processing which very likely induced some transient flux trapping, adding about 1 nΩ additional surface resistance for this test.

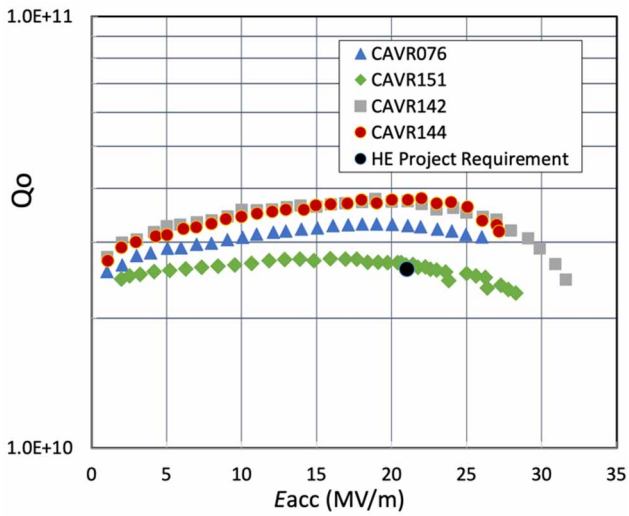

Figure 2: Acceptance test performance for the four HE production cavities with N-doping samples.

DISCUSSION

We were pleased to find negligible variation within the sample set of four cavities. We were also pleased to observe the negligible uptake of O and C from the production furnace runs. This contrasted with samples from runs in

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other vacuum furnaces [4]. We are attracted to speculate that the diffusion of N, O, and C are not independent and the low O and C present here is potentially responsible for the longer diffusion tail of N into the surface than previously reported using other vacuum furnaces.

The O and C concentrations beneath the "disturbed" nitride layer are consistent with nominal starting material specifications, indicating insignificant uptake from the furnace vacuum conditions during "doping".

The single low-N-concentration grain in sample NL579 stands as an anomaly. At present, our primary potential explanation is that this grain's sputtering geometry inadvertently created a "channeling" condition [3] that we have previously identified, which greatly alters the sputtered ion yields, spoiling the measurement calibration. This could in principle be confirmed by reanalyzing the same grain after rotation in the holder.

While there is clearly high variability of formation of the nitrides on the Nb surface during "doping", with sensitivities to Nb grain orientation [6], for purposes of the LCLS-II-HE project, 5 μm surface removal by electropolishing is sufficient to yield an excellent SRF surface.

CONCLUSION

The production processes used for the "doping" of the surface of LCLS-II-HE cavities with nitrogen appears stable and contributes to cavity performance that exceeds project requirements. We note, however that reproducibility of the actual nitrogen concentration profile is dependent on high quality furnace conditions. Also, grain-to-grain orientation variability may exist that gets integrated into the net whole-cavity performance.

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