

# INVESTIGATION OF LOW-LEVEL NITROGEN IN NIOBIUM BY SECONDARY ION MASS SPECTROMETRY

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## Abstract

Understanding the improvement of the SRF cavity quality factor (Q) by low-level nitrogen addition (“N-doping”) is attracting much attention from researchers. Precise, repeatable measurement of the nitrogen profile in the parts-per-thousand to parts-per-million range is vital. Secondary Ion Mass Spectrometry (SIMS) is the method of choice because of excellent sensitivity and depth resolution. Accurate quantification must consider sample properties, such as surface topography and crystal structure, as well as calibration of the instrument and data analysis. We report a SIMS study in which, SRF-grade niobium sheet equivalent, polycrystal and single crystal coupons were N-doped.

## INTRODUCTION

New and robust characterization programs are needed in order to elucidate N-doping and any thorough investigation of N-doping must include SIMS. It is the only available technique to combine acceptably low detection limits with depth information, giving concentration as a function of depth. However, accurate quantification with SIMS is non-trivial, requiring standards and SIMS experiments as opposed to straight forward analysis common to other analytical techniques. This is due to matrix effects, differential sputtering, surface topography, achieving acceptable backgrounds and other complications.

### Matrix Effects

SIMS obtains information by directing a beam of primary ions onto the surface of interest and measuring the mass distribution and intensity of the ejected (secondary) ions. [1] Secondary ion yields can vary five or six orders of magnitude across the periodic table and also several orders of magnitude depending on the bulk material (matrix). Because of this, quantification cannot be based on relative signal intensities only. An implant standard must be created for each species of interest by implanting it into the matrix of interest. Its depth profile can be acquired and dose information can be used to calculate a relative sensitivity factor (RSF) for that species in that matrix. A reference signal from the matrix (here, Nb) is used to adjust for instrumental factors. Example analyses of nitrogen implants in both poly and single crystalline material appear in Fig. 1.

### Depth Resolution

Depth resolution is the ability to distinguish between atoms from one depth over atoms from a different depth.

Good depth resolution makes SIMS a must-use technique for N-doping. However, many factors may affect depth resolution. Penetration depth of primary beam, raster and gate size, knock-on, crater shape are instrument controlled and require meticulous forethought in choice of analysis conditions.

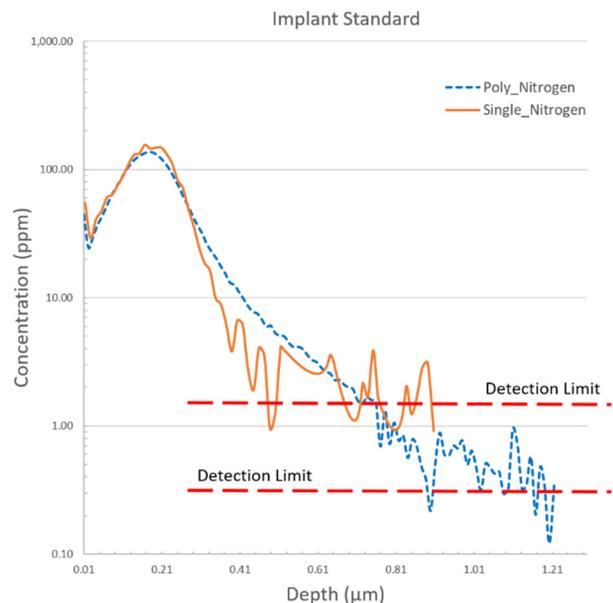


Figure 1: Depth profile of implants used to calibrate N for both polycrystalline and single crystal material.

There are also multiple factors affecting depth resolution which are sample dependent [1]. For example, differing sputter rates between grains of different crystal orientation directly affect the depth resolution achievable in a SIMS analysis. The problem can be reduced by using large grain Nb relative to SIMS crater size. Crater size and grain size must both be taken into consideration. Smaller crater sizes may be used to provide faster analysis when doing relatively deep measurements, but have a negative effect on depth resolution and detection limits due to contributions of the crater edge to the signal. A balance must be found for relative crater, analysis area and grain size. While both implants in Fig. 1 were created and analyzed under the same conditions, the single crystal depth profile shows a sharper implant peak and quicker drop to detection limit, indicative of better depth resolution. Depth resolution was estimated using roughness measurements and TRIM calculations and found to improve from ~109 nm for the polycrystalline implant to ~12 nm for the single crystal implant.

Surface topography may also negatively affect depth resolution and repeatability. As a crater is sputtered, the original surface topography carries down and may increase. It was seen to have a large effect on samples with only a buffered chemical polish (BCP) finish. Nanopolished (NP) samples were found to have much better repeatability in nitrogen measurements and accordingly were used exclusively.

**Detection Limit**

For low concentration analysis it is imperative to have low background signal from the species of interest in the instrument. This requires special attention to be paid when the species of interest are atmospheric such as nitrogen. Since nitrogen is a large component of our surrounding environment it can be difficult to eliminate from a high vacuum environment. A special sample holder for the Cameca7f was designed and machined in order to analyze as many samples at once as possible, thus reducing instrument exposure to atmosphere and normalizing the instrument conditions for as many samples as possible at one time. Analysis of samples were not started until an instrument vacuum of  $\sim 3 \times 10^{-10}$  Torr was achieved. In addition a cold probe surrounding the sample and cooled via liquid nitrogen was used to condense any gas directly surrounding the sample in vacuum. Implant standards can be used to determine detection limits for a given analysis and current instrument condition. The detection limit at time of analysis is marked on Fig. 1. The vacuum condition of the instrument was slightly worse during analysis for the single crystal analysis shown here and a significant loss in detection limit is observed.

Table 1: Summary of Sample Treatments

Sample	History
U42	Preprocess
U48	800C 2h, 400C 10m, 400C 20m N (20-25Torr), Naturally Cooled
U49	800C 2h, 500C 10m, 500C 20m N (20-25Torr), Naturally Cooled
U71	800C 2h, 600C 10m, 600C 20m N (20-25Torr), Naturally Cooled
U52	800C 2h, 700C 10m, 700C 20m N (20-25Torr), Naturally Cooled
U56	900c 1h, 900c 10m , 900c 10m N (20-25Torr), Naturally Cooled

**EXPERIMENTAL**

*Samples/Treatments*

The material for the present study was 10 mm square coupons cut by electrical discharge machining from trimmings of the 3 mm thick niobium sheet used to make SRF cavities (“RRR grade”). Typical grain size was in the 50  $\mu\text{m}$  to 100  $\mu\text{m}$  range (“polycrystals”). Coupons were prepared into conditions typical of cavity production: BCP, centrifugal barrel polishing (CBP) and electropolishing (EP). The coupons were also specially metallographically polished (NP) before doping.

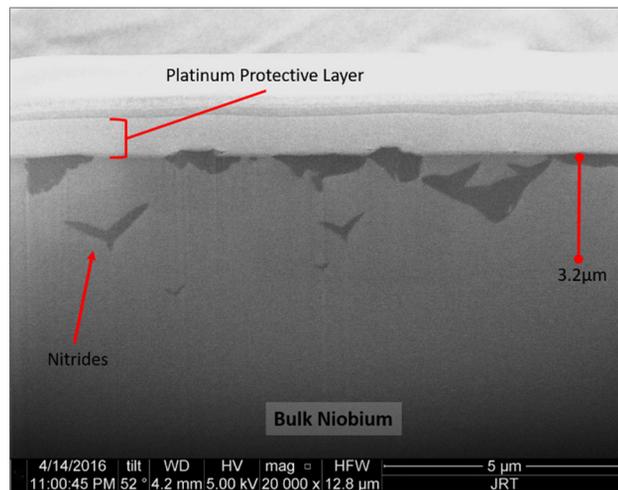


Figure 3: Cross section of U56 equivalent sample.

Six coupons were prepared under different doping conditions. The oven profile includes a high temperature bake, short time for temperature equilibrium to the doping temperature and then a few minutes of nitrogen exposure at 20-25 Torr. After nitrogen exposure the samples were allowed to naturally cool in the oven. Specifics on the treatment of each sample can be found in Table 1.

Standards were prepared by ion implantation with  $^{14}\text{N}$  to a dose of  $1 \times 10^{15}$  atoms/cm<sup>2</sup> at 180 keV. Implant standards were treated to the same preprocess surface preparations as the sample coupons prior to implantation.

*Dynamic SIMS*

SIMS analyses were collected on a CAMECA IMS-7fGEO magnetic sector instrument. A  $\text{Cs}^+$  primary ion beam was used and rastered over an area of  $150 \mu\text{m}^2$  with a  $63 \mu\text{m}$  diameter analysis area. An impact energy of 15 kV (10kV source/-5kV sample) was used with a current of 100 nA. Negative secondary ions of  $^{93}\text{Nb}^{14}\text{N}$  were detected, while  $^{93}\text{Nb}$  was used as a reference signal. Data were collected at multiple locations on each of the coupons.

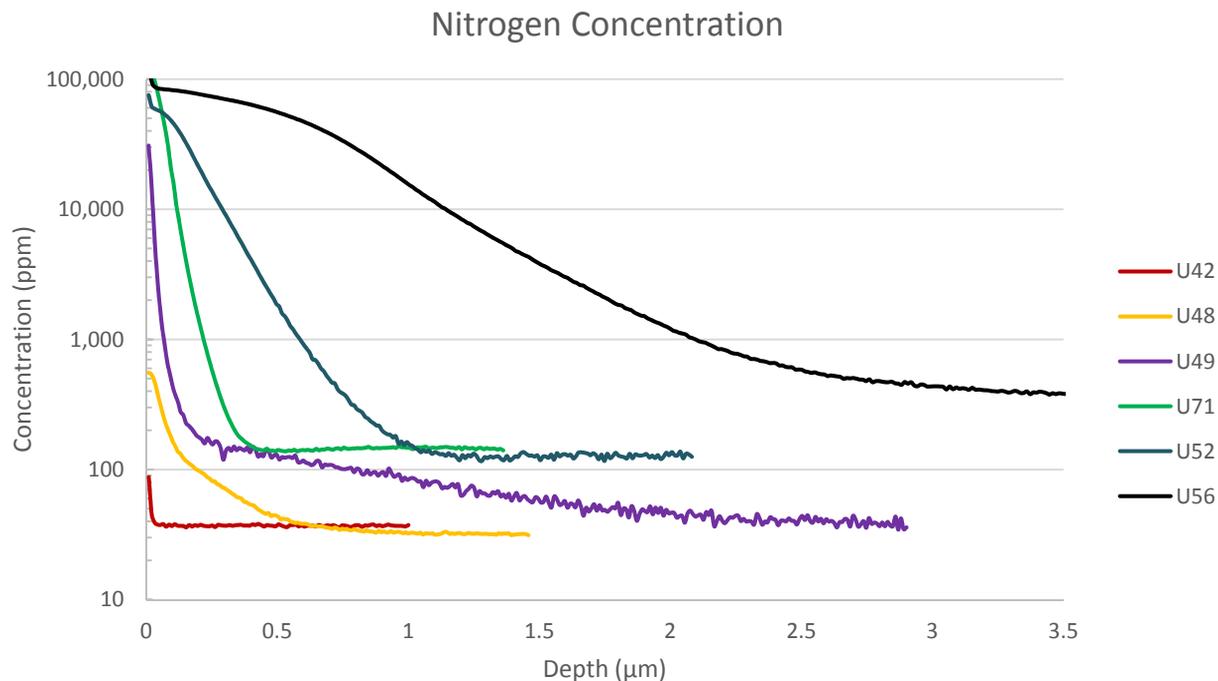


Figure 2: Nitrogen concentration with respect to depth for each sample. Data is an average of multiple analyses per sample.

## RESULTS AND DISCUSSION

The nitrogen data from several analyses from each sample coupon were averaged together to produce the graph in Fig. 2. The concentration of nitrogen can be seen to be higher at the surface, decrease and then level out at a baseline nitrogen value for each sample. The high nitrogen region at the beginning of each profile seems to correspond to the thickness of nitrides formed at the surface during the doping process. A cross section of a U56 equivalent coupon can be seen in Fig. 3. The nitrides in the cross section correspond well to the fall off of nitrogen in the SIMS data for U56.

(baseline) is of great interest. In order to get baseline nitrogen measurements for each sample the last 50 data points from each analysis were averaged together and then averaged with multiple analyses from each sample. Figure 4 shows the average baseline nitrogen concentration and error calculated for each sample. For further discussion of data from this work please see Ref. 2.

## CONCLUSION

The ability of secondary ion mass spectrometry to depth profile at high sensitivity makes it a vital part of the effort to understand N-doping in niobium. A SIMS method for the measurement of nitrogen in doped niobium coupons has been developed and shown to be repeatable. This method allows direct measurement of nitrogen concentrations in witness samples that are a direct reflection of functional cavities.

## ACKNOWLEDGMENT

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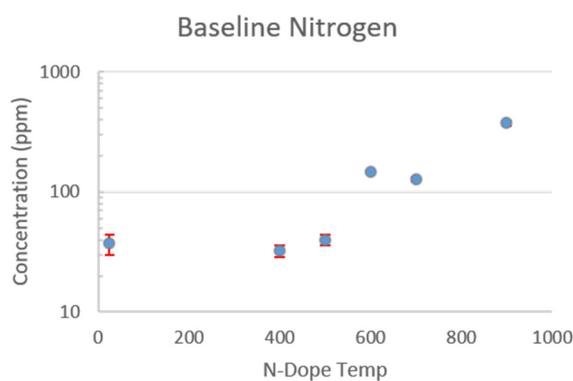


Figure 4: Baseline nitrogen concentrations with calculated error.

Since microns of material are removed from cavities post doping by EP, the nitrogen concentration at depth