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SIMS SAMPLE HOLDER AND GRAIN ORIENTATION EFFECTS *

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Abstract

SIMS analyses for “N-doped” materials are becoming increasingly important. A major hurdle to acquiring quantitative SIMS results for these materials is the uncertainty of instrument calibration due to changes in sample height either from sample topography or from the sample holder itself. The CAMECA sample holder design allows for many types of samples to be analyzed. However, the cost is that the holder faceplate can bend, introducing uncertainty into the SIMS results. Here we designed and created an improved sample holder which is reinforced to prevent faceplate deflection and thereby reduce uncertainty. Simulations show that the new design significantly reduces deflection from 10 µm to 5 nm. Measurements show a reduction of calibration (RSF) uncertainty from this source from 4.1% to 0.95%. Grain orientation has long been suspected to affect RSF determination as well. A bicrystal implant standard consisting of [111] and [001] grains was repeatedly rotated 15° in between analyses. It was observed that 20% of the analyses performed on [111] grains exhibited anomalously high RSF values likely due to the changing of the grain normal with respect to the primary Cs^+ beam.

INTRODUCTION

Superconducting radio frequency (SRF) cavities are particle accelerating structures renowned for their extreme efficiency. Nb SRF cavities rely on maintaining the superconducting state in the extreme conditions of high peak magnetic fields. Therefore, great care has been taken to avoid contaminants like carbon, nitrogen and oxygen [1]. Interestingly, over the last decade it was discovered that intentionally “doping” these cavities with nitrogen (interstitial alloying of the surface Nb) can improve the quality factor (Q_0) by a factor of three with continual improvements being made [2].

Today, ongoing research is performed by scientists globally to further improve the performance of SRF cavities, with great attention directed towards nitrogen doping [3]. Changing N-doping diffusion times and temperatures can substantially influence the interstitial N concentration and affect the superconducting properties. Because the RF penetration layer is ~100 nm, determination of nitrogen concentration is needed with high depth resolution.

Secondary Ion Mass Spectrometry (SIMS) is the ideal choice to quantify the concentration of nitrogen. SIMS utilizes a primary ion beam, such as Cs^+, to bombard the surface of a sample, causing the surface to sputter away at a controlled rate[4]. The removed material is also ionized and extracted into a secondary ion beam where the contents are detected over time by the mass spectrometer. Initially, the intensity of the secondary ions is given as the output for detection. Implantation standards are used to convert the intensity to concentration. These standards are materials of the identical matrix as the experimental samples, i.e niobium, which have been dosed with a known amount of impurity atoms by ion implantation. Analysis of the implant standard generates the relative sensitivity factor (RSF) which acts as a calibration factor to determine concentration of impurities, i.e. nitrogen [4-7].

Commercial/traceable implant standards do not exist for niobium-based materials and must be fabricated by ion implantation labs. Virginia Tech and JLab undertook a major study to evaluate factors which lead to uncertainty of RSF determination [7]. It was determined that sample topography had the most profound effect in increasing RSF uncertainty. The sample topography effects were found to be mitigated by adjusting the dynamic transfer contrast aperture (DTCA) in between analytical scans. This change alone, decreased RSF uncertainty from 40% to 10% with large grain single crystals exhibiting values from 2-8%.

Another major finding was that the sample holders were sensitive to the loading force. Variations in the loading force causes uncertainty in RSF determination by changing the working distance between sample and secondary ion extraction optics. Samples loaded into the sample holder are held in place by friction by compressing copper springs between the sample and a backing plate (Fig. 1). Varying the number of springs causes the faceplate to deflect differently which changes the working distance of the sample, subsequently changing the focal point and extraction of the primary and secondary beam, respectively [7, 8]. The observable effect is the change in the detection of the matrix signal which adversely affects the RSF determination. Depending on the significance of this effect, altering the DTCA in between scans will not solve this problem. Therefore, a new SIMS holder was designed and machined to limit working distance variation to generate the most accurate quantitative SIMS results for N-doped niobium.

It has been hypothesized that grain orientation could also affect the determination of the RSF as well as quantitation of nitrogen in niobium [9]. However, it has been observed that the effect is more likely to occur in [111] grains with respect to normal and tends to coincide with increased matrix counts. The effect which causes the RSF values to shift in niobium matrices has yet to be properly documented.

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Here we created an experiment in which [001] and [111] grains are analyzed in 15° increments to determine if certain rotational axes influence grain orientation effects.

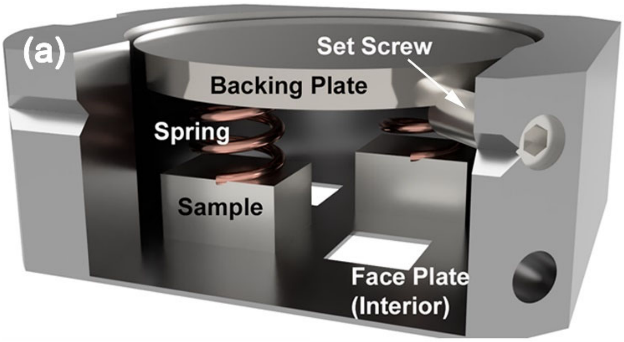

Figure 1: Depiction of a loaded CAMECA 7f Geo sample holder. Samples are placed into position and held in place by compressing copper springs between the sample and the backing plate. The force applied can cause deflection of the face plate resulting in an observable change in the niobium matrix signal and the RSF. (Reproduced from J. Angle et. al. 2021)

Design

The default holder for the CAMECA IMS 7f Geo, as provided by the manufacturer, is constructed of stainless steel and contains a 25mm cavity with a 0.1 mm tantalum faceplate (Fig. 1).

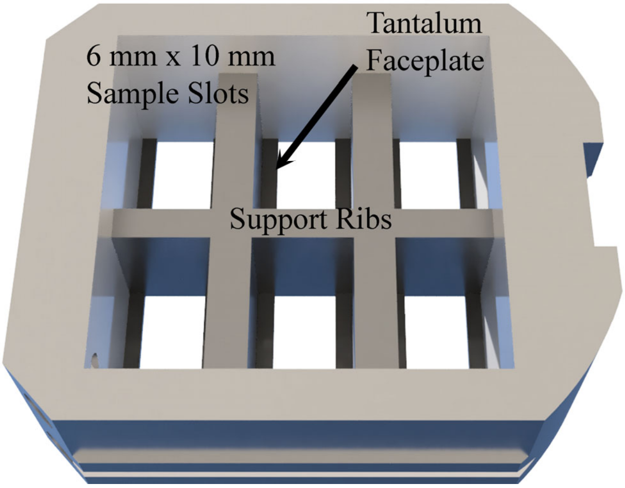

Figure 2: Depiction of the newly fabricated SIMS sample holder for niobium cavity samples. Each sample is individually supported by structural ribbing to prevent the faceplate from deflection due to sample loading. The individual ribbing also ensures that constant force is applied independent of the number of samples loaded.

The tantalum acts as a high strength foil to limit deflection when pressure is applied. However, the faceplate is only supported around the circumference, thus deflection is inevitable. Additionally, the force applied to the faceplate can vary depending on the number of samples in the holder thereby making the working distance inconsistent. The new sample holder is designed to maximize the number of samples which can be analysed while supporting the faceplate to resist deflection.

Typical N-doped samples provided for analysis are 6 mm × 10 mm and 3 mm thick. The 7f Geo has a maximum stage travel of ~ 23 mm × ~ 23 mm. Using these constraints, 2 mm ribs were introduced to support the holder. The structural ribs are offset into the holder to allow the backing plate to rest and compress the springs with constant force. A tantalum faceplate with a thickness of 0.01mm was spot welded to the holder to contain the samples within the holder. Figure 2 shows a diagram of the proposed new SIMS sample.

RESULTS AND DISCUSSION

The holder designed was created using the computer aided design (CAD) software Autodesk Fusion 360. A major advantage to using this software is that static loading of component parts can be simulated. Therefore, to determine the significance of using a new sample holder, the standard CAMECA design was modelled in conjunction with the new proposed design for Nb samples. The database in use was not equipped with tantalum as a simulateable material, so the properties of 404 stainless steel, which has a similar elastic modulus, were substituted. To determine the loading force, an MTS 30 kN load frame was used in compression to determine the force applied to the faceplate using the CAMCECA copper loading springs depressed to 12.5 mm. It was found that the four springs combined would apply no greater than 2 N of force to the faceplate. This value was used as a maximum value to simulate the force exerted onto the faceplate of each holder. The static stress simulator via Autodesk Fusion 360 was used to calculate the displacement of the faceplate of each holder using 2 N of total applied force. The results indicated a maximum deflection of 10 µm for the standard CAMECA design with the new design only deflecting 5 nm (Fig. 3).

Experimentally, the new holder was tested to determine RSF variance as a function of position on the holder. A silicon wafer dosed with 2×10^{15} atoms/cm^2 at 160 keV was fractured into six segments which were then loaded into the sample holder. To remove any debris from the fracturing process, the surface was rinsed with ethanol and blown dry with nitrogen. The sample holder was then loaded in to the CAMECA 7f Geo and allowed to evacuate overnight. SIMS was performed using a Cs$^+$ primary ion beam with an accelerating voltage of 5kV and an impact energy of 8 keV utilizing a beam current of 25 nA. The beam was rastered over an area of 150 µm × 150 µm area and data were collected from a 63 µm × 63 µm area in the center of the raster. ^{28}Si^{14}N$^-$ secondary ions were detected in conjunction with a ^{28}Si$_4^-$ reference signal.

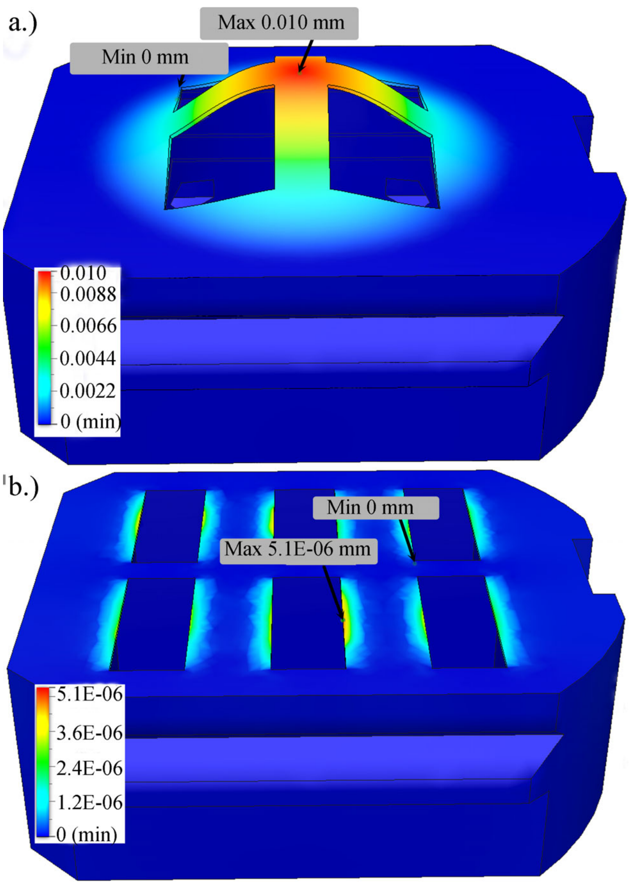

Figure 3: Static stress simulations of the a.) standard CAMECA 4 slot sample holder vs. the b.) newly designed 6 slot Nb SRF cavity sample holder. Using the new design suggest that sample deflection could be reduced from 10 µm to 5 nm.

Table 1: SIMS Results for N-Doped Si Implant Standard

	CAMECA Holder		New Holder	
Spot	**$^{28}Si_4$ Counts x10^5**	**RSF X10^{20}**	**$^{28}Si_4$ Counts x10^5**	**RSF X10^{20}**
A	2.17	1.332	3.37	1.024
B	1.86	1.347	3.45	1.002
C	1.78	1.455	3.50	1.007
D	2.06	1.328	3.32	1.017
E	1.94	1.386	3.82	1.001
F	1.95	1.295	3.26	1.002
Avg.	**1.96**	**1.35**	**3.45**	**1.008**
StDev	**0.14**	**0.06**	**0.20**	**0.01**
%RSD	**7.1**	**4.1%**	**5.7**	**0.95%**

SiN^- was monitored as the indicator for N, since the secondary ion yield for N^- is negligible. As the objective of this experiment is to evaluate the effect of the holder, the DTCA was not adjusted between runs. The results are summarized in Table 1. Static stress simulations agreed with the hypothesis that the Cameca-style four-sample holder would deflect substantially more than the new six-sample holder designed with support ribs. It was further observed that matrix signal counts increased and RSF valuesdecreased for the new holder. The RSF for the new six-sample holder was found to exhibit an uncertainty 0.95% RSD for single crystals installed with common orientation.

Grain Orientation Dependence

SIMS performed on experimental samples are most commonly large grain polycrystalline specimens which tend to be preferentially oriented in either the [111] or [001] crystal orientations with respect to normal. An extensive study in Angle *et al.* 2021, showed that higher uncertainty existed for polycrystalline niobium over single crystals, exhibiting 12%, and 2% uncertainties, respectively. While the increase in uncertainty is expected with increasing the complexity of the system, the cause is still unknown. SIMS analysis of cavity witness samples have shown that certain grains will exhibit uncharacteristically higher matrix signals, which appear to cause a reduction in the calculation for nitrogen concentration (Fig. 4). It has also been noted that this effect is most observed in the [111] crystal orientation, but not by a consistent factor. It was then hypothesized that rotating the sample about normal causes certain grains to generate higher count rates (orientation-dependent secondary ion yield), subsequently causing the RSF to change.

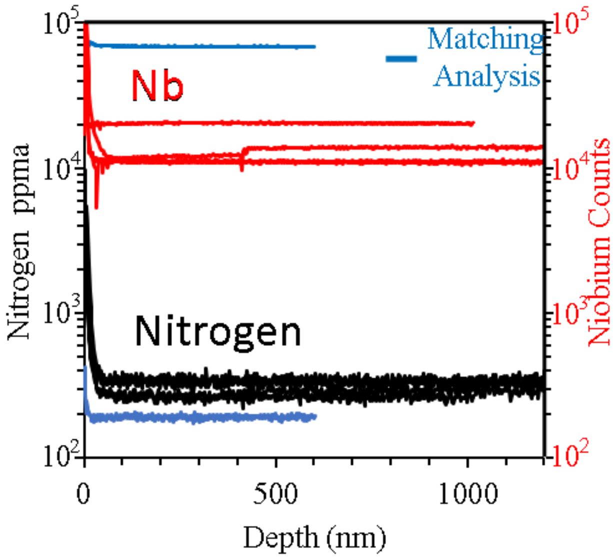

Figure 4: SIMS Depth profile of an experimental sample which showed anomalously high niobium matrix signal. It was observed that the analysis which showed the high matrix signal correlated with the lowest calculated nitrogen concentration.

To rotate the sample in the SIMS, a new holder was created. A stainless steel Cameca holder with a 16 mm sample window was repurposed for this experiment. Though made of stainless steel, the faceplate for this holder was made much thicker (0.35 mm) and more rigid than the 4-hole style holder. A custom disc insert was faced with a lathe to allow for a 16 mm circular portion to rest in the sample window. A 6 mm × 12 mm rectangular chamber with 0.75 mm lips was machined to allow for the sample to be loaded at the proper working distance. Markings were scribed every 15° to allocate specific rotations (Fig. 5a). The sample insert is rotated with a pair of tweezers and locked into place with a setscrew. The sample was held into place with a copper spring and a backing plate with approximately 2 N of force applied. To ensure that holder deflection would not factor into the RSF determination, a static stress simulation was also performed for this holder. The simulation suggested the holder would deflect 4.7 angstroms; therefore, holder effects are assumed to be negligible (Fig. 5b).

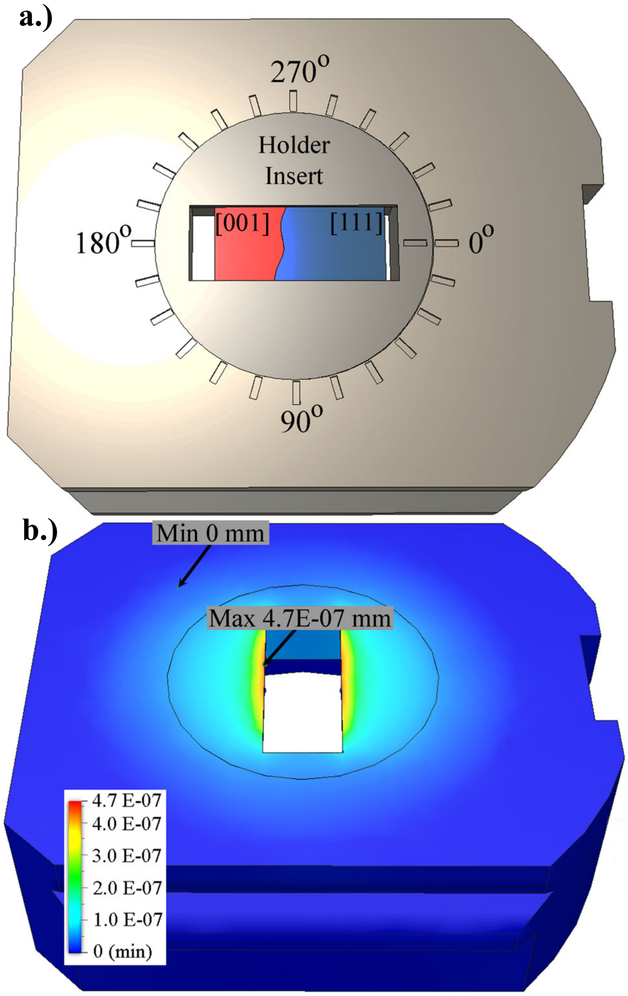

Figure 5: A.) Diagram showing the rotational analysis of the bicrystal implant standard. The holder insert is rotated and locked in place by a set screw. B.) Static stress simulations of the of the rotational holder showed negligible deflection.

SIMS was performed using the same analysis conditions of a Cs^+ primary ion with an 8 keV impact energy and 25 nA of beam current. A bicrystal implant standard with [111] and [001] normal grain orientation was chosen for this experiment. The implant standard was dosed with 2×10^{15} atoms/cm^2 of oxygen and nitrogen at 180 keV and 160 keV respectively. Following each analysis, the sample holder was removed, and the crater depth was determined with a Tencor AlphaStep 500 stylus profilometer. The insert containing the implant standard was then rotated 15° and the holder was then returned to the SIMS. Prior to the next analysis, the sample holder was held in the intro chamber for 1 hr with gentle heat from a heat lamp to remove water adhesion. This cycle was repeated until one full revolution was complete. The RSF was calculated at each rotation with results shown in Fig. 6. The results showed that sample rotation had no effect for the [001] crystal. The [111] crystal was found to have 75° window in which the nitrogen RSF value was observed to increase. This indicates that ~20% of arbitrary rotational scenarios will risk a deviation in nitrogen concentration quantification. Excluding the 75° window, the RSF was determined to remain generally constant with a value of $5.19\times10^{20} \pm 0.81 \text{ x } 10^{20}$. The maximum value for the 75° window was found to be 19.8×10^{20}. The value of proper pumping is shown in Fig. 7.

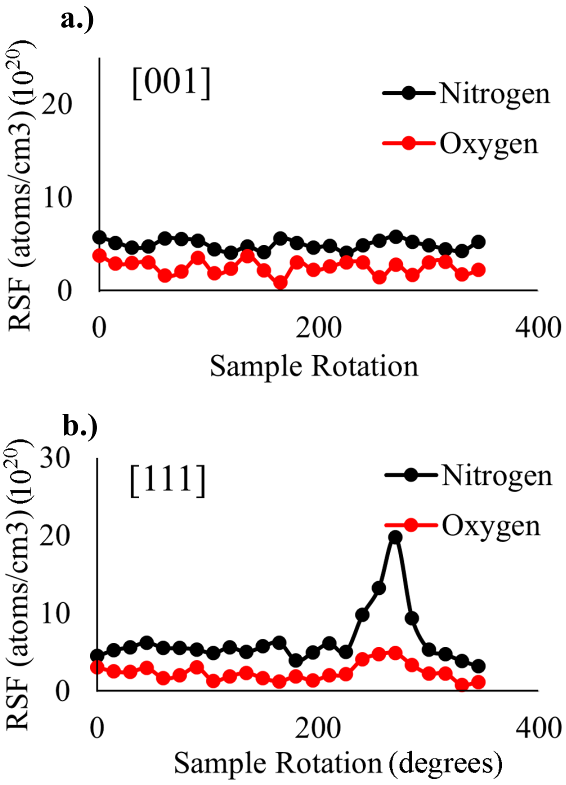

Figure 6: Plots show RSF value after rotating the implant standard in 15° degree increments. The results show that the [001] grain was largely unaffected by rotation. However, the [111] crystal was found to have increased RSF values over a 75° window.

Oxygen alloying has recently become an attractive alternative to nitrogen "doping". Therefore, investigation into oxygen RSF was included in this study. Oxygen was found to exhibit an increase around the same ~75° window and similarly impactful to the RSF value. The constant RSF average was found to be $2.36 \times 10^{19} \pm 0.60 \times 10^{19}$ with a maximum increased value of 4.92×10^{19}.

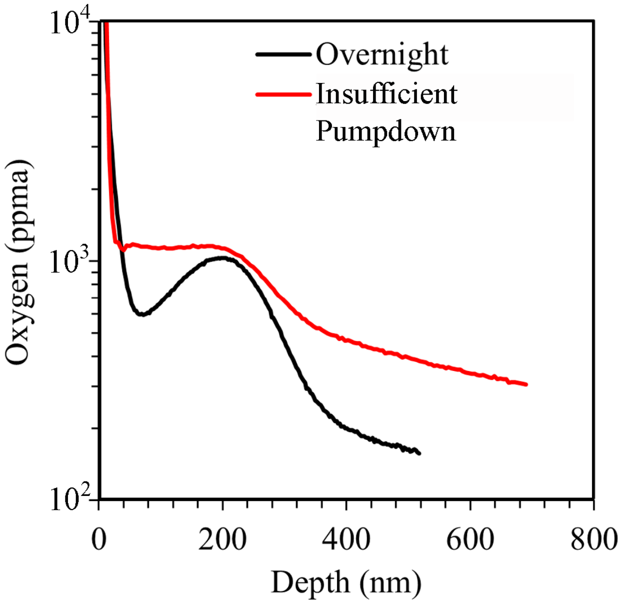

Figure 7: SIMS depth profile showing oxygen concentration as a function of depth. Analysis performed on the [111] crystal of the bicrystal implant standard. The above plot shows the importance of allowing the sample holder to pump down overnight to remove water adhesion and other adventitious oxygen.

CONCLUSION

Ongoing SIMS experimentation showed that working distance variation, if substantial, cannot be resolved by adjusting the DTCA between sample analyses. The changes in the working distance are caused by the deflection of the faceplate on the sample holder which ultimately adversely affects the calibration of the instrument and quantitation of the SIMS results. To mitigate this effect, JLab and Virginia Tech designed a new sample holder, specific to hold 6 mm × 10 mm × 3 mm niobium Nb samples. Support ribs were added to prevent the faceplate from deflection. Static stress simulations suggest this addition substantially reduced deflection of the face plate from 10 µm to 5 nm. Experimentally N-doped silicon wafers were analyzed to determine RSF variation due to the sample holder. It was determined that switching from the CAMECA standard SIMS holder to the improved sample holder could reduce RSF uncertainty from 4.1% to 0.95%.

Grain orientation effects were additionally investigated by rotating a bicrystal implant standard and recording the nitrogen RSF in 15° increments. It was observed that [001] grain remained unaffected by sample rotation, while the [111] grain saw an increase 5 times higher when rotated to particular critical configurations. This is attributed to the primary Cs^+ beam interacting 23° offset from the normal vector of the sample surface.

With increased interest in oxygen alloying, the oxygen RSF was also monitored. It was observed that the oxygen RSF also increased at the same critical rotational configuration, but not as drastic as the nitrogen RSF. In general, the oxygen RSF was found to vary more than nitrogen, yielding RSF uncertainties of 30% and 13% respectively. Due to the repeated removal of the sample and reduction of pump down time for the implant standard, water and other sources of adventitious oxygen were not adequately removed and is responsible for the increased uncertainty in this report.

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