

FUNDAMENTAL SIMS ANALYSES FOR NITROGEN-ENRICHED NIOBIUM

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Abstract

In order to fully understand nitrogen addition techniques it is vital to have a full understanding of the material, including the content, location, and speciation of nitrogen contained in the treated Nb. In this work Secondary Ion Mass Spectrometry (SIMS) is used to elucidate content and location. Dynamic SIMS nitrogen analysis is reported, for the first time, for “as-received” cavity grade niobium from three separate suppliers. In addition, a number of method and instrumental issues are discussed including depth resolution, detection limit, and quantification.

INTRODUCTION

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]. Of all analytical techniques including various types of SIMS (TOF, NanoSIMS, etc.) dynamic SIMS instruments, such as the CAMECA IMS-7f, have the lowest detection limits, making dynamic SIMS the instrument of choice when concerned for trace element quantification.

SIMS analysis requires proper sample preparation and method development in order to correctly quantify results. When conducting SIMS experiments, matrix effects, differential sputtering, surface topography, acceptable backgrounds, and other complications all must be considered. For a brief discussion of SIMS issues and the development of a method for the analysis of N in Nb please see Ref. [2]. For a more in depth discussion of SIMS method development in general please see Ref. [1].

EXPERIMENTAL

Sample Preparation

Unless otherwise noted all samples are 3 mm thick cavity grade niobium, cut to 10 x 10 mm coupons with “NanoPolished” surfaces. Normal BCP surface finishes have been found to be insufficiently smooth and produce poor depth resolution due to surface topography [2]. Standards used for quantification were prepared by ion implantation with ¹⁴N to a dose of 1X10¹⁵ atoms/cm² at 160 keV and ¹⁶O to a dose of 2x10¹⁵ atoms/cm² at 180 keV.

SIMS Instrumentation

SIMS analyses were collected on a CAMECA IMS-7fGEO magnetic sector instrument. A Cs⁺ primary ion

beam was used and rastered over an area of 150 x 150 μm with a 63μm diameter analysis area. An impact energy of 15 kV (10kV source/-5kV sample) was used with a current of 100nA. Negative secondary ions of ⁹³Nb¹⁴N⁻ were detected, while ⁹³Nb⁻ was used as a reference signal. Data were collected, in at least two locations, on each sample to verify repeatability. Figure 1 shows a schematic of the CAMECA 7f instrument.

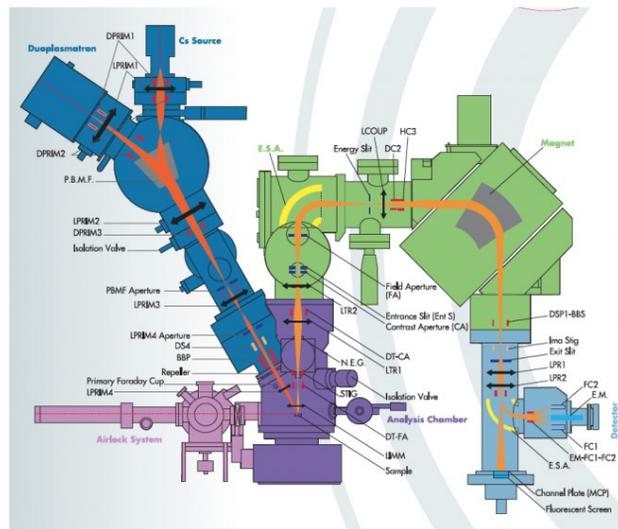


Figure 1: Schematic of CAMECA IMS-7fGEO [3].

Quantification

The most common method for quantifying SIMS depth profiles is by utilizing ion implant standards. The ion of interest can be placed in the matrix of interest at a known dose by the ion implanter. Quantification is achieved by depth profiling the implant standard and using this data to calculate a relative sensitivity factor (RSF). The RSF can then be used to quantify the species of interest in depth profiles of the sample material. All concentrations were reported in atomic ppm and denoted by ppm(a). Ion implants are also useful to determine the detection limit of the method/instrument.

Detection Limit

Analysis of elements at low concentration, requires insuring the detection limit of the method and instrumentation is acceptable; i.e., lower than the subject species concentration. This is especially true when analyzing atmospheric species such as nitrogen and oxygen, which are ever present in some amount. It can be difficult to know whether a baseline value for a sample is due to the species of interest

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within the sample or simply background instrument contamination. One way to empirically determine the nature of a detected signal is by conducting a raster reduction test. First a matrix level signal and impurity species of interest are collected at a larger raster. The raster is then collapsed while keeping the beam current and analysis area constant; 100nA and 63 μm were used for the example here. If the raster is collapsed from 250 x 250 μm to 150 x 150 μm , as was the case in Fig. 2. This will cause the matrix signal to increase by a factor relative to the change in raster size. In the case of our example it will increase by a factor of approximately three. If the species of interest increases this same amount, then the detected signal originates from the sample, with little background input. If the species of interest increases, but less than the matrix level signal, then there is some impurity detected from the sample, but it is near the detection limit. If the signal does not change, then no impurity was detected and the detection limit is at least a factor of four better than before raster collapse.

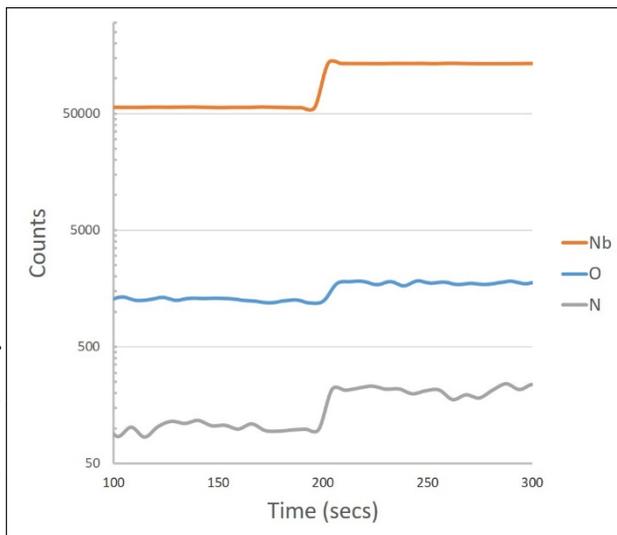


Figure 2: Raster reduction to check signal source for nitrogen and oxygen.

The “as received” materials have relatively low concentrations of both N and O making it necessary to check the origin of the species. A raster reduction was done each day “as-received” samples were analyzed. In Fig. 2 we can see the raster reduction from an analysis day, the nitrogen detected is still well above the baseline for the method/instrument, proving the nitrogen signal measured is from the sample. The oxygen signal however appears to be approaching the detection limit and has some contribution from outside the sample.

Depth Resolution

For bulk nitrogen measurements in raw materials or N-doped witness coupons, the highest priority for a SIMS analysis method is detection limit and proper quantification. However, with the recent move towards nitrogen infusion, measuring nitrogen in low concentration near the surface (≤ 40 nm) with relatively high depth resolution be-

comes a concern [4]. TOF-SIMS instruments are particularly good at high depth resolution and shallow analysis with depth resolution less than 1 nm in ideal cases [5]. However, dynamic SIMS is capable of better detection limits and ~ 3 nm depth resolution in the ideal case [6]. SIMS instruments cannot be optimized simultaneously for depth resolution and sensitivity [7]. In addition, nitrogen negative ion yield is virtually zero under many analysis conditions, requiring detection of molecular species ($^{93}\text{Nb}^{14}\text{N}^-$) and relatively high sputter rates in order to achieve sufficient detection limits [8]. With the need to analyze near surface N-infusion samples, depth resolution with the current method, must be determined under conditions that provide a sufficient sensitivity.

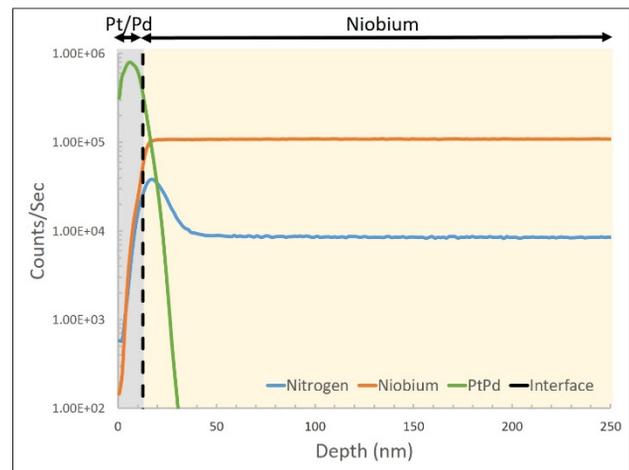


Figure 3: Depth profile of N-doped niobium with EP surface. Specimen was sputter coated with Pt/Pd prior to depth profiling.

For an interface, depth resolution can be given as the change in depth between 84% and 16% of the maximum signal [1, 5]. In order to measure depth resolution, an interface was created by sputter coating a N-doped/EP surface witness sample with ~ 15 nm of platinum and palladium (80/20 by weight). This created an interface in the resulting depth profile (Fig. 3) which could then be used to calculate the depth resolution. The depth resolution was calculated using the leading and trailing edge of the interface and found to be 6.0 and 6.4 nm respectively. Figure 3 shows a depth profile of a Pt/Pd coated sample with the physical location of the interface marked by the dashed line.

RESULTS AND DISCUSSION

As-Received Cavity Material

N-doped cavities have shown differing performance during post process testing. One potential cause could be differing amounts of interstitials present pre-process. In an effort to understand varying performance from N-doped cavities, “as-received” cavity grade niobium was analyzed for nitrogen and oxygen content, establishing a baseline level for cavity material niobium for the first time.

Material was used from three suppliers; Wah Chang, Tokyo Denki, and Ningxia. Samples were marked W, T and

N respectively, with numbers representing different lots of material. SIMS conditions used were the same as in previous studies [2]. A nitrogen and oxygen implant standard was used for quantification and raster reduction was used to verify the signal source. The analysis results can be found in Figure 4 along with the calculated error for each. Concentrations of nitrogen and oxygen in samples prepared to LCLS-II specs were found to be 1-2 ppt(a) and 300-500 ppm(a) respectively. In all cases the amount of nitrogen in “as-received” samples was found to be more than an order of magnitude lower. Oxygen concentrations across all samples were found to be 34.4 ± 14.5 ppm(a) with a maximum of 71.6 ppm(a). Nitrogen concentrations were found to be 34.1 ± 13.0 ppm(a) with a maximum value of 68.4 ppm(a).

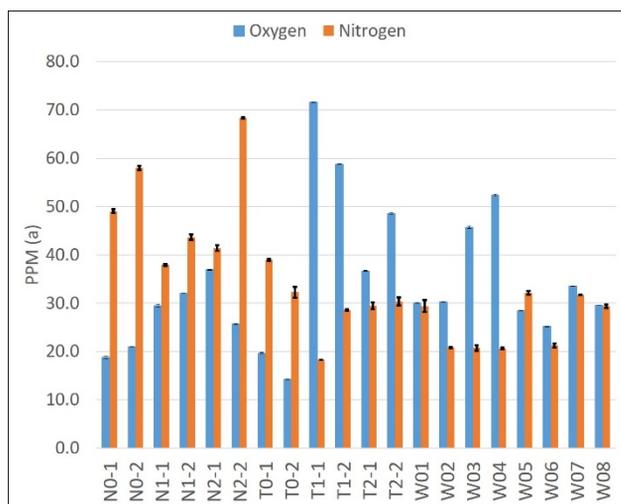


Figure 4: Oxygen and Nitrogen quantification with error for “as-received” samples.

Bi-Crystal Materials

Bi-crystalline samples were prepared at Jefferson Lab. These samples are 10 x 10 mm and have been cut from very large grain material in such a way to include a single grain boundary through the middle of the coupon. During SIMS analysis of the bicrystalline samples, a difference was observed from one side of the grain boundary to the other, giving rise to the question of whether grain orientation has an effect on the doping process. SIMS analysis was performed on each side of the central grain boundary within a few hundred microns of the boundary itself. A graphical representation of analysis placement can be seen in Fig. 5 along with optical images of the analysis craters. All four craters were sputtered under the same conditions for the same length of time. Lighter colored (shinier) crater bottoms are generally indicative of a smoother crater. In this case, side one craters have an average roughness of 63 nm, while side two craters are smoother at 43 nm. Variation in sputter rate, clear here from the final depth of analysis (Fig. 5), is a known phenomenon and was found to be 1.3 nm/sec for side one and 3.6 nm/sec for side two.

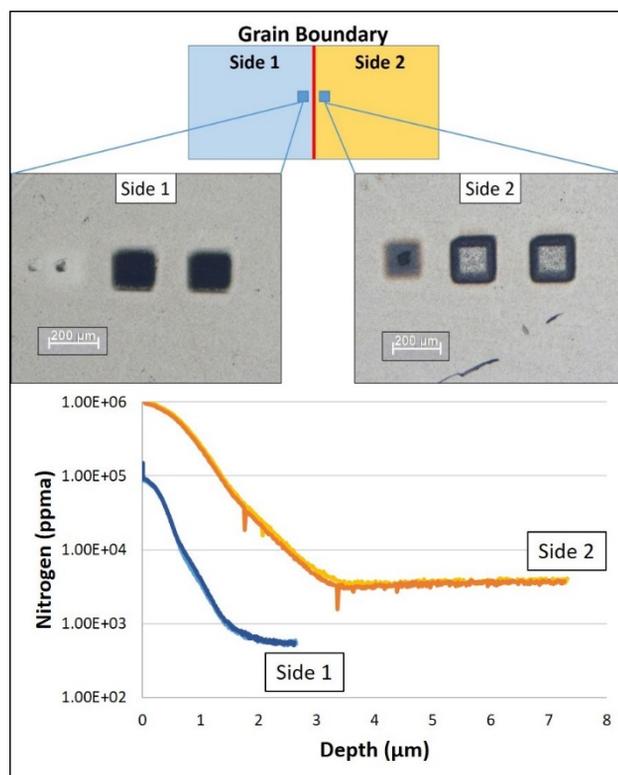


Figure 5: Illustration of crater placement, optical images of craters, and depth profile data from SIMS analysis of N-doped bicrystal sample.

Figure 5 also shows the depth profile data from all four craters. A clear difference can be seen in the profile from one side of the grain boundary to the other. Side two shows a higher initial nitrogen concentration from nitrides and thicker nitride layer. The baseline nitrogen concentration also shows an approximately 10-fold increase for side two. As crystal orientation is the only differentiating characteristic between the analysis points it must be tied to the differences seen in the data, either through instrumental or sample variation. The orientation of each side of the bicrystal was measured utilizing electron backscatter diffraction (EBSD). Figure 6 shows inverse pole figures for both. Despite the large difference seen in the depth profile data, only a relatively small difference can be seen in crystal orientation between the two areas.

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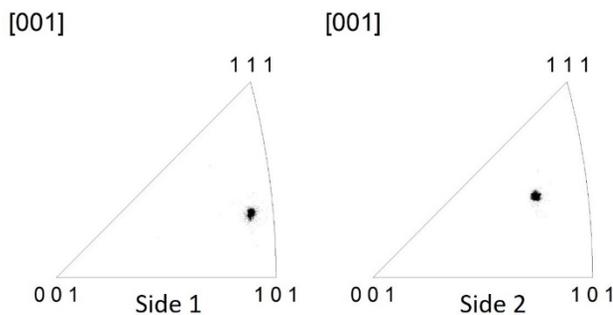


Figure 6: Inverse Pole Figures (IPF) representing the average orientation of side 1 and side 2 of the bi-crystal sample.

As mentioned, orientation is known to affect sputter rate during SIMS analysis [1]. The relative ion yield may also be affected causing differences in quantification. On top of that, niobium is a body centered cubic structure, which should not exhibit diffusion rate differences based on orientation. This suggests the differences seen in nitrogen concentration in the bicrystalline sample may be instrument related rather than the orientation having some effect on N-doping. However, the niobium nitride formed on the surface during doping plays a vital role in the uptake of nitrogen into the bulk niobium [9] and the orientation dependence for the formation of this nitride can be clearly seen. (Fig. 7 A and B) If there are orientation dependences for the N-doping process, the implications are far reaching for the production of N-doped cavities and deserve further investigation. Currently samples have been prepared and small spot analysis SIMS is being used for further investigation of orientation effects.

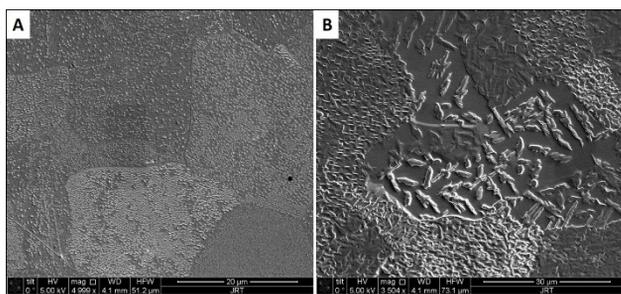


Figure 7: Image showing surface of 700 oC N-doped sample (A) and lightly sputtered (focused ion beam) area of 900 oC N-doped sample. Both show clear differences in nitride formation from grain to grain.

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. For the first time nitrogen and oxygen concentrations have been reported for “as-received” cavity grade niobium material. Oxygen and nitrogen concentrations across all samples were found to be 34.4 ± 14.5 ppm(a) and 34.1 ± 13.0 ppm(a) respectively. Specific values can be found in Figure 4.

Differences in SIMS measurements have been observed between crystal orientations. Further study is currently be-

ing conducted to determine whether this is completely attributable to instrument variation or orientation based variation in the N-doping of the sample.

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