INVESTIGATION OF OXIDE LAYER STRUCTURE ON NIOBIUM SURFACES USING A SECONDARY ION MASS SPECTROMETER*

Andy T. Wu+...Nb+, NbO+, and NbO2+. The maximum in the Nb+ peaks in Fig.1 is believed to be a result of the following three oxide layers. It is well known that Nb surface is always covered by a thin Nb2O3 layer that is dielectric. In between the dielectric layer and bulk Nb, there must be some suboxide layers. It is these suboxide layers that may create losses to Nb SRF cavities, since they may not be superconducting at the operational temperature of a particle accelerator. Therefore, the suboxides are the main focus of SIMS depth profile measurements.

Typical SIMS depth profile measurements are done through continuous monitoring Nb+, NbO+, and NbO2+ peaks as shown in Fig.1. Variations in surface oxide layer structure are reflected from the variations in the ratios between secondary ion peaks of Nb+, NbO+, and NbO2+. The maximum in the Nb+ peaks in Fig.1 is believed to be a result of the following three

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Fig. 1: Typical depth profile plot for investigating oxide layer structure on the surfaces of Nb treated by BEP.

Contributions: 1) Nb$_2$O$_3$ layer on the surface of a Nb sample is dielectric although thin. Therefore there is a certain amount of charging effect that reduces Nb$^+$ yield. 2) It is well known in the field of SIMS measurements that oxides on the surfaces of metals can enhance positive secondary ion yields significantly due to the decreasing in ionization potentials. For Nb, an enhancement factor of more than 85 has been recorded [5]. 3) The lower the oxygen concentration in a unit sputtered layer, the lower are the secondary positive ion yields.

Most of the times, the surface oxide layer was sputtered away in less than 100 seconds. It was therefore a little too quick to extract meaningful information regarding the variations in oxide layer structure from the cracking pattern (although in principle it still could be done with a faster SIMS system). I found that under certain conditions the sputtering process could be slowed down significantly as shown in Fig. 2. It was not so easy to find the locations on Nb surfaces that might exhibit this slow sputtering process, since these locations had to be crack, defect, and even scratch free so that no passages existed for the charges created by the sputtering process to dissipate. Since the dielectric Nb$_2$O$_3$ layer is usually about 6 nm, some visible scratches may therefore have even thinner Nb$_2$O$_3$ layer, which can be served as charge dissipation channels. However, on several Nb samples treated by BEP and BCP we could find these slow sputtering locations and they were reproducible.

Several issues have to be answered before this technique can be developed into a quantitative tool for measuring the thickness of various oxides on Nb surfaces. First of all, we have to know how much variation in the peak ratios between Nb$^+$, NbO$^+$, and NbO$_2^+$ reflects a change in oxide layer structure from, for instance, Nb$_2$O$_3$ to NbO$_2$. Secondly, cracking patterns of other possible suboxides, such as Nb$_2$O$_3$ and NbO$_2$ and NbO, have to be determined unambiguously. Thirdly, the requirement on the stability of the primary ion beam has to be established. Fourthly, the best set of parameters, such as beam energy, beam current, beam size, etc, for the primary ion source suitable for the technique described here have to be determined for each SIMS system.

Despite all these, this technique can still be used for qualitative analysis such as, for instance, quality control on Nb SRF cavity production. Suppose there is a witness sample attached to an Nb cavity that undergoes the standard cavity treatment procedure during cavity production. Before RF test, the witness is demounted and then measured by SIMS as described above. For a cavity with the best RF test result, there will be a matching depth profile that can be used as the standard for comparison. Therefore, by doing SIMS measurements using the technique described above on a witness Nb sample, one can predict whether the cavity has a good surface oxide layer structure by comparing the obtained pattern with the standard one.

Slow sputtering process was also seen on BCP112 treated Nb samples. A typical example is shown in Fig. 3. I noticed, however, it was easier and more frequent to reach the slow sputtering conditions on BEP treated samples than on BCP treated ones. This is presumably attributable to the following two reasons: 1) Nb surfaces treated by BEP are typically two orders of magnitudes smoother than those treated by BCP in terms of RMS [2]. Smoother surfaces allow more homogeneous sputtering. 2) By comparing Fig. 3 with Fig. 2, one can see that the secondary ion peaks start to decrease dramatically at a time about 200 seconds earlier than the counterparts in Fig. 2. Since the experimental parameters adopted for obtaining Fig. 3 are exactly the same as those for Fig. 2,
this difference implies therefore that the oxide layer on the surface of this BCP treated Nb is thinner than that on the surface of BEP treated one. Thinner oxide layer means more vulnerable for creating cracks or scratches, leading to less chance to detect the slow sputtering process due to the reasons already discussed above.

Since it is a significant advantage to slow down the sputtering process during depth profiling measurements, it is very naturally to think about using a static SIMS for this purpose. Fig.4 shows a typical static SIMS spectrum where the intensities of the peaks of Nb⁺ and its relevant oxides are plotted as a function of time [2]. The spectrum was obtained from measurements on the same BCP treated Nb sample as that used for Fig.2. A newly installed pulsed 22 keV Au⁺ source was used as the primary ion beam that was operated at 2 nA over an area of 50X50 μm². As expected, there are well defined plateaus for the intensities of the peaks of Nb⁺, NbO⁺, and NbO₂⁺ just as those shown in Fig.2 and Fig.3. One clear difference between the static and dynamic SIMS results is that the peak intensities in static case start to decrease at a time about 1100 seconds later than the counterpart in Fig.2, although the primary ion beam density is the static case is comparable to the 85 uA/cm² adopted for dynamic SIMS. Since Au⁺ is a relatively new primary ion source for the SIMS community, detailed information regarding the interactions between Au⁺ and the solid surface under its bombardment is still unknown. This prevents us from further discussion on this subject. Nevertheless, static SIMS results confirm the results observed using a dynamic SIMS, implying therefore that the technique described here can be done using both static and dynamic SIMS systems.

Quantitative calculation of the secondary ion yields from an oxidized Nb surface is done to compare with the experimental results based on the following empirical formula developed by Plog et al [6]:

\[ S = S_0 M(m,q) \exp[-(G^0 - K - \alpha q)^2 / 2\gamma^2], \]

where q is the total charge of the fragment in question, n is the oxidation state, K = q+2n, M(m,q) is the mass and its relevant oxides are universal parameters with values of 0.024, 235, 2.4, and 0.98 respectively, G^0 is lattice valence that depends on the valency stage of the metal at the surface [6], α is a target parameter varying from one metal to another. In the case of cleaned Nb kept in UHV with a few monolayers of oxide coverage, G^0 and α are determined to be 4.05 and 0.95 respectively [6]. The calculated results are shown in Fig.5. Examining Fig.2, we can see that NbO⁺ peak is higher than Nb⁺ just before the sharp falling down, implying therefore the existence of a thin layer of niobium suboxide in the BEP processed sample similar to the few monolayers of oxide formed on a clean Nb surface kept in UHV, which are presumably NbO. On the other hand, on BCP treated Nb samples peaks of Nb⁺ are always the strongest as shown in Fig.3.

![Calculated Spectrum](image)

**Fig.5:** Calculated secondary ion yields based on an empirical formula developed in ref.6 (see text for details)

### 4 CONCLUSION

A technique based on SIMS has been developed to study the oxide layer structure on Nb surface. Further study is needed before this technique can be used for quantitative characterizations.

### 5 REFERENCES