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

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Abstract

Oxide layer structure on the surfaces of niobium (Nb) can be studied by continuously monitoring peaks of the secondary ions of Nb and its relevant oxides as a function of time during depth profiling measurements employing a secondary ion mass spectrometer (SIMS). This is based on the fact that different oxides have different cracking patterns. This new approach is much simpler and easier for studying oxide layer structure on Nb surfaces than the conventional approach through deconvolution of oxide peaks obtained from an x-ray photoemission spectrometer. Eventually it can be developed into an in-situ tool for monitoring the oxide layer structure on Nb surfaces prepared by various procedures. Preliminary results of SIMS measurements on the surfaces of Nb samples treated by buffered electropolishing and buffered chemical polishing will be reported.

1 INTRODUCTION

Understanding oxide layer structure on niobium (Nb) surfaces is important for performance optimization of the superconducting radio frequency (SRF) cavities based on Nb. In the past, surface chemical information of Nb has been studied mainly by x-ray photoelectron spectroscopy (XPS). However, due to the difficulty in deconvolution of the obtained oxide peaks and the possibility that oxide layer structure on Nb surfaces may vary with different surface processing techniques employed, detailed information regarding the oxide layer structure, such as, for instance the thickness of Nb suboxides and their chemical states, is still not completely clear up to now. Attempt [1] has been made to establish a data base for XPS measurements and then to use principal component analysis method for performing analyses on the data base to extract information about the oxide layer structure. It may take some time before the data base can be fully set up.

Here I present a new approach for studying the surface oxide layer structure by means of a dynamic secondary ion mass spectrometer (SIMS) through continuously monitoring various secondary Nb and its oxides peaks when Nb surfaces are under bombardment by argon (Ar) ions. It is shown that under certain conditions, the removal rate on Nb surfaces can be slowed down and the secondary ion signals of Nb and its oxides are still strong enough to guarantee a good signal/noise ratio. Dynamic SIMS results are supported by the results [2] obtained using a static SIMS for Nb sample treated by buffered electropolishing (BEP) [3], implying that this approach is suitable for employing both static and dynamic SIMS systems.

2 EXPERIMENT

Nb samples used in this studied were obtained from the same sheet to ensure having the same original conditions. Some of them were cut into 20X20 mm^2 squares for buffered chemical polishing (BCP). BCP was done using the standard acid mixture of 48% HF, 69% HNO_3, and 84% H_3PO_4 at a volume ratio of 1:1:2. Roughly 120 μm was removed from the sample surface. After BCP, samples were rinsed by DI water, followed by ultrasonic cleaning for 20 minutes. Finally sample surface was blown dry via a nitrogen gun before being put into the SIMS observation chamber.

BEP treatment was done employing the setup described in reference 3. A thickness of 120 μm was also removed from the sample surface for all BEP treated samples for consistence and easy comparison to those treated by BCP. After BEP, samples were cleaned in the same procedure as that for BCP samples.

Dynamic SIMS measurements were done using a home made system described in reference 4 with Ar^+ as the primary ion beam. The static SIMS system used was a commercial TRIFT II from Physical Electronics with a newly installed Au^+ as the primary ion beam to enhance the sputtering rate.

3 RESULTS AND DISCUSSION

It is well known that Nb surface is always covered by a thin Nb_2O_5 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 NbO_2^+ 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 NbO_2^+. The maximum in the Nb^+ peaks in Fig.1 is believed to be a result of the following three

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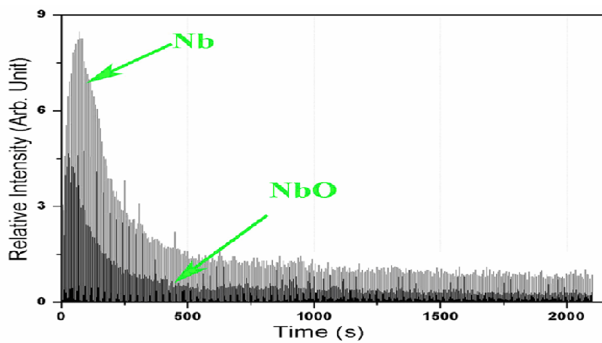

Fig.1: Typical depth profile plot for investigating oxide layer structure on the surfaces of Nb treated by BEP.

contributions: 1) Nb_2O_5 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_2O_5 layer is usually about 6 nm, some visible scratches may therefore have even thinner Nb_2O_5 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_2O_5 to NbO_2. Secondly, cracking patterns of other possible suboxides, such as Nb_2O_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,

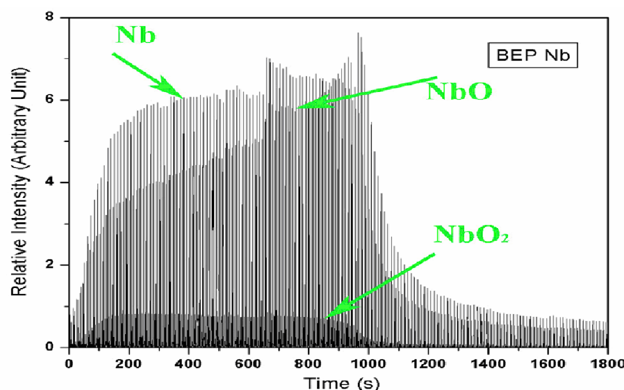

Fig.2: Typical slow sputtering process observed on a BEP treated Nb sample.

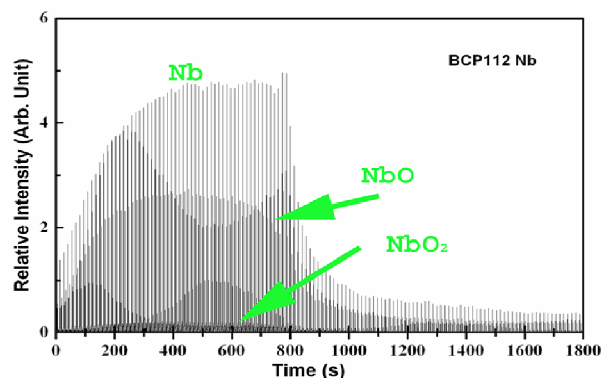

Fig.3: Typical slow sputtering process observed on a BCP treated Nb sample.

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 BEP 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 μm^2. As expected, there are well defined plateaus for the intensities of the peaks of Nb^+, NbO^+, and NbO_2^+ 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/cm^2 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]:

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

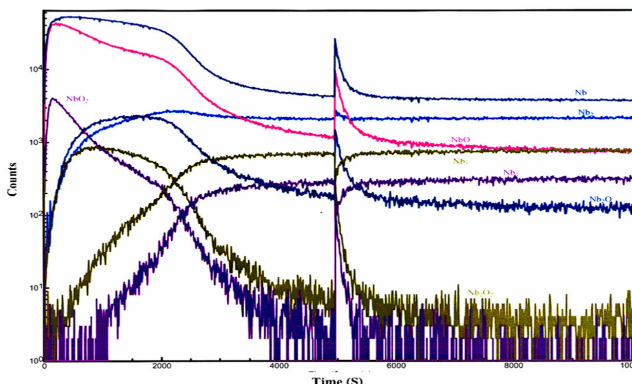

Fig.4: Intensities of the peaks of Nb^+, Nb_2^+, and their various oxides as a function of time observed on a BEP treated Nb by a static SIMS (see text for details). The peaks near 5000 seconds are artifacts due to a suspension and resumption of the measurements.

where q is the total charge of the fragment in question, n is the oxidation state, K=q+2n, $M(m,+1)=(m/m_0)^{-1}$ where m is the mass of the fragment in question, S_0, m_0, t, and γ 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.

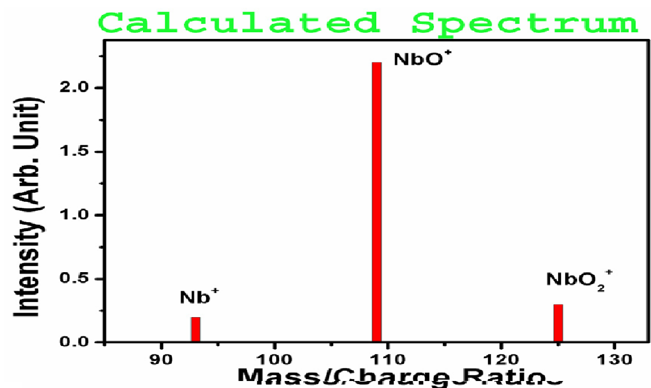

Fig.5: Calculated secondary ion yields based on an empirical formula developed in ref.6 (see text for details)

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.

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