

## TOF-SIMS STUDY OF NITROGEN DOPING NIOBIUM SAMPLES\*

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### Abstract

Nitrogen doping treatment with the subsequent electropolishing (EP) of the niobium superconducting cavity can significantly increase the cavity's quality factor up to a factor of 3. The nitrogen doping experiment has been successfully repeated and demonstrated on both single cell and 9-cell cavities and the best nitrogen doping recipe has been searched. But the mechanism of the nitrogen doping effect remains unclear. Nitrogen doping study on niobium samples was carried out in Peking University. The niobium samples were manual processed to avoid heat generation. The experiment condition is close to that of the Fermilab. After the nitrogen doping treatment, the samples were mildly electropolished with the thickness of 1.3 $\mu\text{m}$ , 1.9 $\mu\text{m}$ , 3.3 $\mu\text{m}$ , 4.2 $\mu\text{m}$ , 5.1 $\mu\text{m}$ , 5.9 $\mu\text{m}$  and 7.0 $\mu\text{m}$ . The time of flight secondary ion mass spectrometry (TOF-SIMS) measurements show that the samples directly after nitrogen doping have a much higher nitrogen concentration in the depth of about 90nm. When the EP removal is larger than 1.3  $\mu\text{m}$ , the samples' impurity elements is remarkably reduced and their distribution is similar to each other. Also the measured results to some extent prove that EP removal can introduce H to the niobium surface.

### INTRODUCTION

Quality factor  $Q$  is one of the most important factors of radio-frequency niobium superconducting cavities. High quality factor can efficiently decrease the cryogenic load of superconducting cavities, and the post treatment has an important influence on the cavities' radio-frequency performance. The average unloaded  $Q_0$  of linac coherent light source (LCLS-II) 9-cell 1.3GHz cavities and cryomodules were set to be exceeding  $2.7 \times 10^{10}$  at a gradient of 16MV/m at 2K [1]. It means that the surface resistance of the cavity is less than 10n $\Omega$ , and the standard surface treatment procedures including a combination of chemical treatments like electropolishing (EP), buffered chemical polishing (BCP) and heat treatments [2] cannot meet this requirement. Grassellino [3, 4, 5] from FNAL has reported a new surface treatment, nitrogen doping, that can systematically improve the quality factor of radio-frequency niobium superconducting cavities up to a factor of about 3 compared to the standard surface treatment procedures. Nitrogen doping consists of three steps, namely heat treatment at 800 $^{\circ}\text{C}$  for several minutes in a nitrogen atmosphere of about 25 mTorr, heat treatment at 800 $^{\circ}\text{C}$  for several minutes in high vacuum and EP removal of cavity material to several microns.

After that Cornell University [6] and JLAB [7] have successfully repeated and demonstrated the nitrogen doping experiment on both single cell and 9-cell cavities. On one hand, Cornell University and JLAB together with FNAL have been searching for the best nitrogen doping recipe [8, 9]. A widely accepted one is the so called "Fermilab 2/6", that is 800 $^{\circ}\text{C}$  degasing for 3 hours in high vacuum, then heat treatment at 800 $^{\circ}\text{C}$  for two minutes in a nitrogen atmosphere of about 25 mTorr, with the subsequent heat preservation of six minutes in high vacuum. After that the cavity was EP removed 5 $\mu\text{m}$  to obtain the best performance. On the other hand, fundamental understanding of the nitrogen doping mechanism is being carried out extensively, but yet remains unclear. But more and more studies [10, 11, 12, 13] show that hydrogen content may play an important role in the remarkable increase of the quality factor of superconducting niobium cavity after nitrogen doping treatment. The nitrogen impurities can reduce the diffusion coefficient of hydrogen in nitrogen doped niobium [14], but exorbitant nitrogen content may degrade the quality factor of the superconducting niobium cavity. The cavity directly after nitrogen treatment shows the quality factor of the order of  $10^7$ [3], for the possible poorly superconducting nitrides on the cavity inner surface [15]. Nitrogen doping study on niobium samples was carried out in Peking University to seek the physical explanation of it. In the first stage, the niobium samples, with different EP removal, have been analysed using TOF-SIMS to measure their depth profiles of impurity elements, which can be helpful to understand the nitrogen doping effect.

### SAMPLE PREPARATION AND NITROGEN DOPING EXPERIMENT

#### Sample Preparation

To avoid heat generation, instead of wire electrodischarge machining (EDM), the niobium samples were manual processed. Firstly, niobium strips with the dimensions of about 40mm $\times$ 4mm $\times$ 2.8mm, were cut out from the same niobium plate using the same saw. Secondly, the niobium strips were polished smoothly on 180-grit sandpaper, 300-grit sandpaper and 1200-grit sandpaper. The samples' treatments were attempted to replicate that of the cavities' to the extent possible. So the niobium strips were etched by EP 1:9, with the depth of about 150 $\mu\text{m}$ , to remove a mechanical damage layer and surface contaminations introduced during handling. Taking into account the higher oxygen content in the mixed acid surface layer which may result in a bad etched surface and the convenience of cutting down the polished samples without damaging the surfaces to be measured,

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trenches were engraved on the niobium strips at certain position, as can be seen in Figure 1.

Before the heavy EP removal of 150 $\mu\text{m}$ , the niobium strips were cleaned in the following steps:

- Degreased in a solution of ultrapure water and detergent with ultrasonic agitation for 10 minutes.
- Rinsed in the ultrapure water with ultrasonic agitation for 5 minutes.
- Rinsed in the anhydrous alcohol with ultrasonic agitation for 5 minutes.
- Dried by blowing nitrogen to the surface of the niobium strips.

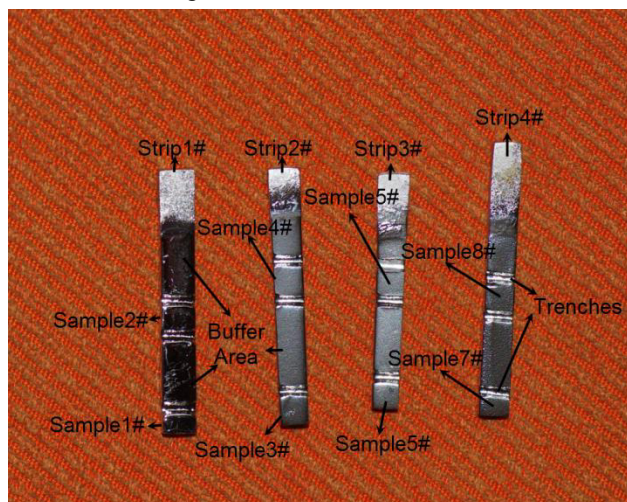


Figure 1: Niobium strips after heavy EP with the removal of 150 $\mu\text{m}$ . Each strip offers two experimental samples, as it can be seen in the picture.

Micrometre calliper was used to directly determine the EP removal. By measuring the depth of the niobium strips inserted into the mixed acid, the surface area of the strips into the mixed acid can be calculated. Therefore, the EP removal can be tested and verified by weighting method. So far, a total of six niobium strips have been heavily electropolished with the removal of about 150 $\mu\text{m}$ , and the details of the electropolishing is listed in Table 1. After the heavy EP removal, the niobium strips were rinsed with ultrapure water and anhydrous alcohol again and kept in the vacuum environment for nitrogen doping experiment.

Table 1: The Details of the Heavy Electropolishing

Niobium Strip	EP Removal/ $\mu\text{m}$
Strip 1#	154.4
Strip 2#	154.5
Strip 3#	149.5
Strip 4#	142.8
Strip 6#	155.4
Strip 7#	124.3

### Nitrogen Doping Experiment

The nitrogen doping experiment of the niobium samples were carried out in a muffle furnace using a high purity quartz tube as protective tube, taking the advantage of high purity quartz tube's good thermal and chemical stability at high temperature. We upgraded and improved the muffle furnace's vacuum sealing system. Its preliminary pressure is  $6 \times 10^{-5}$  Pa, which can meet the requirement of nitrogen doping experiment. Each quartz boat can be placed inside two niobium strips, which were leaned against the edge of the quartz boat to ensure the adequate processing of nitrogen doping treatment as shown in Figure 2. At last, a total of four niobium strips, labelled as Strip 1#, Strip 2#, Strip 3# and Strip 4#, were placed inside two quartz boats. And the boats were put in the middle area of the quartz tube for experiment.

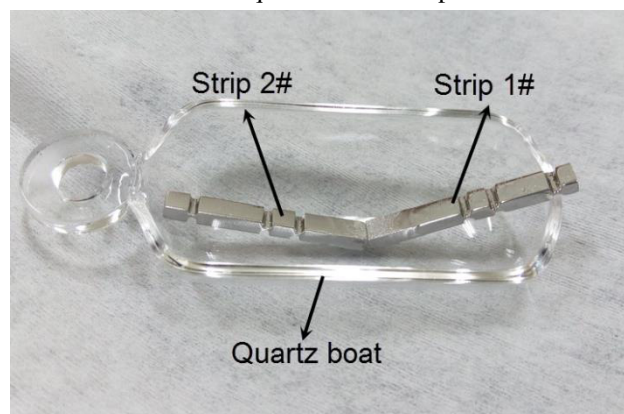


Figure 2: The niobium strips were leaned against the edge of the quartz boat to ensure the adequate processing of nitrogen doping treatment.

The ambient temperature was 23 $^{\circ}\text{C}$  and the pressure in the furnace before heat treatment was  $1.3 \times 10^{-4}$  Pa. Taking into account the security concerns of the furnace itself and its heating requirements, the heating process from room temperature to 800 $^{\circ}\text{C}$  was divided into six stages:

- From room temperature to 300 $^{\circ}\text{C}$  in 60 minutes;
- Heat preservation of 30 minutes at 300 $^{\circ}\text{C}$ ;
- From 300 $^{\circ}\text{C}$  to 600 $^{\circ}\text{C}$  in 60 minutes;
- Heat preservation of 30 minutes at 600 $^{\circ}\text{C}$ ;
- From 600 $^{\circ}\text{C}$  to 800 $^{\circ}\text{C}$  in 67 minutes;
- Heat preservation of 188 minutes at 600 $^{\circ}\text{C}$ .

On the whole, it takes 247 minutes to heat the furnace from room temperature to 800 $^{\circ}\text{C}$ . The heat preservation at 300 $^{\circ}\text{C}$  and 800 $^{\circ}\text{C}$  helps to degas impurity such as hydrogen absorbed by the strips during EP. Owing to the degassing process of the niobium strips at high temperature, the pressure of the furnace changed to  $1.8 \times 10^{-3}$  Pa when the temperature reached 800 $^{\circ}\text{C}$ . After 180 minutes of heat preservation at 800 $^{\circ}\text{C}$ , the pressure fell to  $8.3 \times 10^{-4}$  Pa. Before the heat treatment, the gas conduit has been purged with nitrogen gas. When the time of heat preservation at 800 $^{\circ}\text{C}$  reached 180 minutes, the valve and the mass flowmeter were opened at the same time. Then the pressure of the furnace rose to 4.7Pa quickly from  $8.3 \times 10^{-4}$  Pa at the gas flow rate of 31.7sccm.

The furnace was heat preserved at 800°C for two minutes in a nitrogen atmosphere of 4.7Pa. After that the valve and the mass flowmeter were closed at the same time, maintaining the same temperature for six minutes to let the nitrogen diffuse into the niobium. In this process, the pressure of the furnace fell to less than 10<sup>-3</sup> Pa within one minute. After six minutes of thermal diffusion, the furnace was turned off to cool down naturally. Figure 3 shows the temperature and pressure during the nitrogen doping treatment.

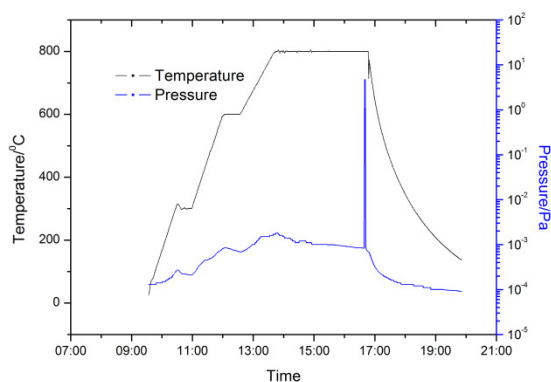


Figure 3: The temperature and pressure during the nitrogen doping treatment.

In the nitrogen doping experiment described above, the argon gas was not ventilated to the furnace to mitigate the pollution of the niobium strips from residual gases during cooling down. So strip 6# was used to verify the role of argon gas during the cooling down. It experienced the same experiment procedure before the cooling down. The only difference is that argon gas was flown into the quartz tube during the cooling down. Also the niobium strip 7# was used as a reference which had the same heat treatment process without nitrogen gas flowing into the quartz tube. However, due to time constraints, strip 6# and strip 7# were not analysed by TOF-SIMS.

**Mild EP**

EP removal after nitrogen doping treatment significantly influences the cavity’s radio frequency performance. So it’s important to know the distribution of impurity elements layer by layer. After nitrogen doping treatment described above, the niobium samples were mildly electropolished from 0µm to 7µm, with a one micron interval. In the stage of mild EP, the micrometre calliper cannot be used to directly determine the EP removal precisely. By calculating the surface area of the strips into the mixed acid, the total amount of charge needed to get a certain EP removal can be estimated. Then the current of the EP will be recorded with a certain time interval. When the cumulative charge reaches the predetermined value, the corresponding electropolishing process can be stopped. Also, the weighting method can still be used to test and verify the EP removal.

In the specific mild electropolishing process, the EP current was recorded with a 20 seconds interval. The

dependence of EP current on time is shown in Figure 4 as an example during the step of EP with the removal of 2µm.

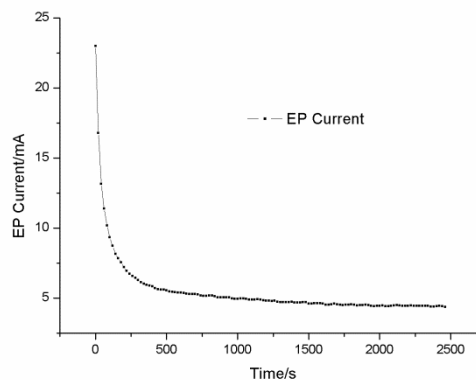


Figure 4: EP current dependence on time is shown as an example in the 2µm EP stage. The EP current was recorded with a 20 seconds interval.

The cumulative charge can be calculated:

$$Q = \sum_{k=1}^N i_k \times \Delta t$$

Then the EP removal would be:

$$\Delta d[\mu m] = \frac{Q[C]}{e \times 5 \times N_A} \times 93[g] \times 10000$$

$$\Delta d[\mu m] = \frac{Q[C]}{8.66[g/cm^3] \times A[cm^2]} \times 10000$$

Where  $e=1.602 \times 10^{-19}C$ , is the elementary charge,  $N_A=6.02 \times 10^{23}$ , is the Avogadro constant, 5 refers to the niobium atom existing in the form of pentavalent, A refers to the surface area of the strips into the mixed acid. The EP removal calculated from the recorded current and that from the weighting method agrees well, and the details of the mild EP are listed in Table 2.

Table 2: The Details of the Mild Electropolishing

Niobium Sample	EP Removal/µm
Sample 1#	0
Sample 2#	1.3
Sample 3#	1.9
Sample 4#	3.3
Sample 5#	4.2
Sample 6#	5.1
Sample 7#	5.9
Sample 8#	7.0

The samples after mild EP were rinsed with ultrapure water and anhydrous alcohol and kept in the vacuum environment for TOF-SIMS analysis.

**TOF-SIMS ANALYSIS**

The subtle material details of the niobium surface largely influence the surface resistance of niobium below

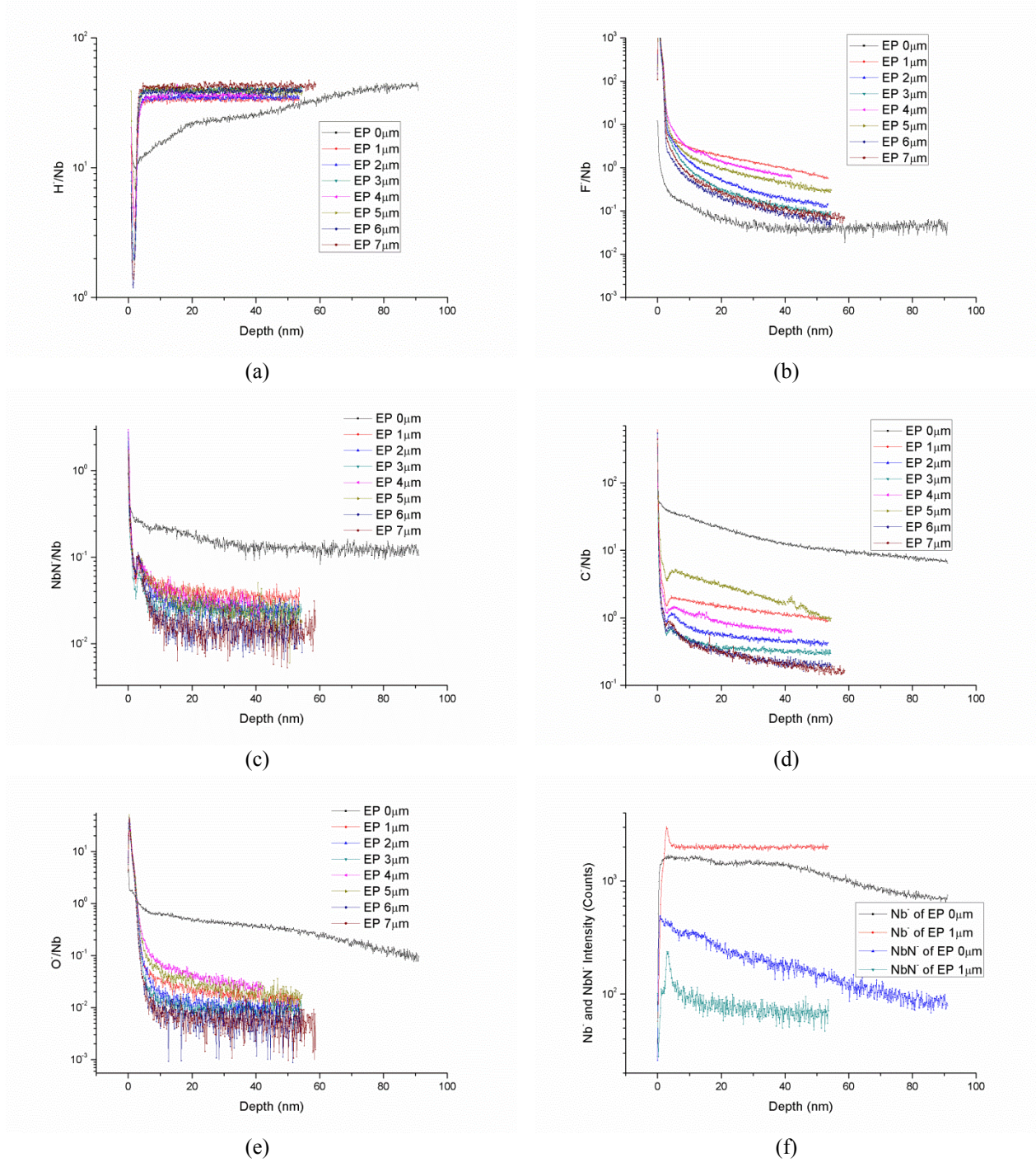


Figure 5: Depth profiles of H/Nb ratio (a), F/Nb ratio (b), NbN/Nb ratio (c), C/Nb ratio (d) and O/Nb ratio (e) measured in the eight samples. The specific abnormal depth profile of Nb<sup>-</sup> and NbN<sup>+</sup> in sample 1# is shown in (f), compared with that of sample 2#.

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2K. It's important to know the distribution of impurity elements in the nitrogen doping niobium layer by layer, especially for H and N. So TOF-SIMS was used to measure the impurity elements distribution in Tsinghua University. Cs<sup>+</sup> primary ion beam was used to detect elements such as H, N, C, O, F, and Nb since Cs enhances the negative ion yields. Because the surface resistance of the niobium below 2K depends largely on the penetration

depth of the rf field of the order of ~40nm, it's important to get the subtle material details within  $\lambda_L$ . To make the depth resolution high enough, the TOF-SIMS Cs<sup>+</sup> primary ion beam energy was reduced to 1keV. The current was maintained to 45nA throughout the analysis to make the sputtering rate of 1.14nm/s. The raster area was 300μm × 300μm with the detected area of 100μm × 100μm.

In order to prevent contamination, the analysis chamber

of the system was kept in the ultra-high vacuum (UHV) condition of  $8.8 \times 10^{-10}$  mbar. Under such vacuum condition, the detection limit is about 1at.ppm. The absolute content of each impurity element between different samples may have tiny difference. So the measured value of each impurity element was normalized in that of the niobium in the corresponding sample to characterize the element content changes after different treatment. During the measurement, both  $N^-$  and  $CsN^+$  did not have significant secondary ion yields, so  $NbN^-$  ions were used to characterize the nitrogen concentration distribution. The depth profiles of H, N, C, O, F, and Nb measured in the eight samples are shown in Figure 5.

For sample 1#, which did not receive mild EP, is the one directly after nitrogen doping treatment. The TOF-SIMS measurement shows that it has much higher nitrogen concentration in the depth of about 90nm. When the samples suffer the mild EP of more than 1.3 $\mu$ m, the nitrogen concentration was remarkably reduced, and the profiles become similar to each other. For samples that have been electropolished, there is a nitrogen peak near their surfaces with the same depth of 3-4nm, possibly due to the adsorption from air. But on the whole, the nitrogen concentration in the samples decreases with the increment of the EP removal. The nitrogen concentration of sample 2# near the surface is about four times larger than that of sample 8#. Also, it should be noticed that the measured Nb concentration in sample 1# significantly differs from those in the other samples, as can be seen in Figure 5 (f). But the Nb concentration change with depth is basically the same as that of NbN in sample 1#. The experimental results listed above reveal that nitrogen near the surface in sample 1# and in samples which were electropolished exists in different forms. Combined with SEM study on niobium samples directly after nitrogen doping, it is believed that nitrogen in sample 1# near the surface with depth of about 90nm exists possibly in form of nitride, while the nitrogen in other samples exists in the form of interstitial atoms.

It is puzzling that, the niobium sample directly after nitrogen doping treatment also has much higher oxygen and carbon concentrations near the surface than that of samples having been electropolished, just like the nitrogen signal. System leakage may lead to the diffusion of C and O into Nb at high temperature.

Figure 5 (a) shows that the hydrogen concentration in sample 1# without EP removal is lower than that of the other samples in the depth within 50nm from the surface. Because of the  $Nb^-$  yield decreases with decreasing nitrogen concentration in sample 1#, the H/Nb ratio increases with the depth. In fact, the measured H intensity in sample 1# is substantially constant beyond 30nm from the surface, and it is lower than that of other samples. So the experiment to some extent, provide evidence that EP can introduce hydrogen to the niobium.

The TOF-SIMS analysis of strip 6# and strip 7# is under way.

## CONCLUSION

Nitrogen doping study on niobium samples was carried out in Peking University. To know the distribution of impurity elements layer by layer, the samples after nitrogen doping were mildly electropolished with the thickness of 1.3 $\mu$ m, 1.9 $\mu$ m, 3.3 $\mu$ m, 4.2 $\mu$ m, 5.1 $\mu$ m, 5.9 $\mu$ m and 7.0 $\mu$ m. The TOF-SIMS was used to measure the impurity elements depth profiles. Combined with SEM study on niobium samples directly after nitrogen doping, it is believed that nitrogen in sample 1# near the surface with depth of about 90nm exists possibly in form of nitride, while the nitrogen in other samples exists in the form of interstitial atoms. System leakage may lead to the diffusion of C and O into Nb at high temperature, which results in the high oxygen and carbon concentrations of sample 1#. Besides, the experiment to some extent, provide evidence that EP can introduce hydrogen to the niobium.

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