

# INVESTIGATION ON DEPTH PROFILING OF NIOBIUM SURFACE COMPOSITION AND WORK FUNCTION OF SRF CAVITIES\*

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## Abstract

The niobium samples were prepared by different surface treatments that commonly applied for the superconducting RF cavities preparation, as the following of electrochemical polishing, the buffered chemical polishing and high temperature annealing. In order to understand the property of niobium surface, especially the relationship between the composition and the work function value, the X-ray and ultraviolet photoelectron spectra depth profiling has been studied. The intensity photoelectrons signals of O1s, C1s and the Nb3d were identified for composition of the niobium oxide and the hydrocarbon contamination. And the work function of sample surface was measured via the means of the ultraviolet photoelectron spectra band width. To make a depth profiling, the sputtering of Argon ions was used to remove surface material gradually under by control the sputtering times. The results shown that the value of work function strongly depends on the chemical composition.

## INTRODUCTION

The electrons load effects, such as the multipacting (MP) in the low field gradient and field emission occurred at the higher gradient, have adverse impact for superconducting RF operating to higher gradient and reliability. During the SRF cavities design and preparation, the multipacting effect can be eliminated by optimizing geometry of the inner conducting wall.

The field electrons emission is the tunneling effect that the electrons are pulled out from the inside material to the outside vacuum. The emission density is under control of the electric field enhancement factor on the surface and the work function of conducting wall material. The surface treatments, such as the chemical polish and high pressure rinsing by the DI water, are developed a lot to reduce the surface enhancement factor successfully. In the recent years, plasma in-situ cleaning for the elliptical cavities revealed that the field emission effect can be relieved, as the results of the surface composition modified and the work function improvement [1-2].

The changing of carbon contamination and the niobium oxides on the outmost surface as the main issues of cavities treatment, such as chemical polish, the high temperature annealing and the low temperature baking, have been studied under the in situ condition experiment for niobium samples from literatures [3-5]. Meanwhile, the cavities surface is hardly keeping a similar state with sample in situ condition during the surface preparation. To understanding the real station of SRF cavities, the niobium samples were prepared following the sequence of the cavity treatment, and the depth profiling was studied.

\* Work supported by National Natural Science Foundation of China (91426303, 11505255)

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## SAMPLE PREPARING

Square shapes, 10mm \*10mm width, 3mm thick high with purity niobium (RRR>250) were cut from the niobium sheet used to fabricate the SRF cavities. To remove the surface damage layer and the metal impurities from the wire cutting progress, the buffered chemical polish (BCP) was used in the first step. The BCP solution was 1:1:2 volume mixture of HNO<sub>3</sub>(69%), HF(40%) and H<sub>3</sub>PO<sub>4</sub>(80%), and keep the temperature under 20 °C during the reaction. 150 μm thickness was removed, the surface roughness value monitored by the peak-to-valley (PV) and the arithmetic average (Ra) was 4.0μm and 0.7μm.

To increase the roughness to better, the electrochemical polish (EP) was used after the BCP treatment. The EP solution was 1:9 volume of HF(40%) and H<sub>2</sub>SO<sub>4</sub>(98%), the current density was about 35mA/cm<sup>2</sup>. The Figure 1 shows that Ra roughness can reduce to constant value about 100nm above 150μm thickness removed. Finally, the samples polished to Rz of 0.6μm and Ra of 100nm.

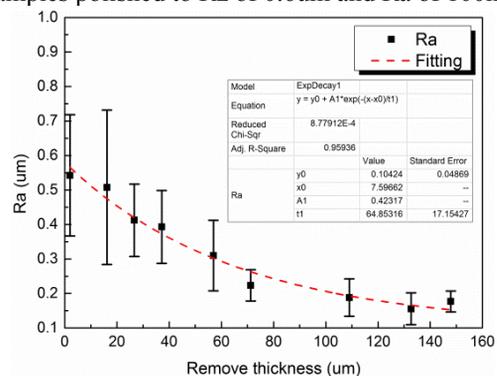


Figure 1: The arithmetic average roughness independence with the surface thickness remove by the EP treatment, the electric parameters set at 10V and 35mA/cm<sup>2</sup>.

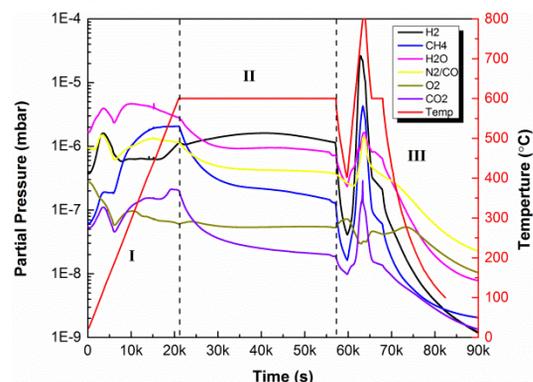


Figure 2: Temperature and partial data during the annealing treatment.

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The high temperature annealing to degas hydrogen is an effective method to overcoming the Q-slope for SRF cavities operation at higher gradient. The niobium samples were annealed in the tube furnace with 600 OC for 10 hours. A quadrupole mass spectrometry was installed for residual gas analysis, the data shown in the Figure 2. The background vacuum is better than 1E-4 Pa.

Following the standard SRF cavities preparation, the sample were polished again, called light EP about 20um to remove the other metal impurities induced from the furnace. After that, the high pressure DI water rinsing was use to remove the surface particles and dusts.

### XPS AND UPS EXPERIMENTS

The x-ray photoelectron spectroscopy and the ultraviolet photoelectron spectroscopy were undertaken on the high base vacuum pressure chamber bellow 1E-9torr. Al K $\alpha$  x-ray line (1486.7eV) and the He I (21.22eV) ultraviolet line were used as exciting radiation source. Because of high energy of x-ray photoelectrons, XPS analysis can provide chemical composition of surface to about 6nm below the surface. And, the lower energy of ultraviolet line, it was very sensitive to the few molecular or several atom layers of outmost surface, which was very useful to investigate the valence state of surface.

Additional device of an Argon ion gun working at 2 keV with scan the sample surface of 3.5mm\*3.5mm was used to remove the surface material by ion bombard sputtering. By means of different sputtering times, the depth information was profiled. The Figure 3 and Figure 4 is correspond to the Nb3d and C1s.

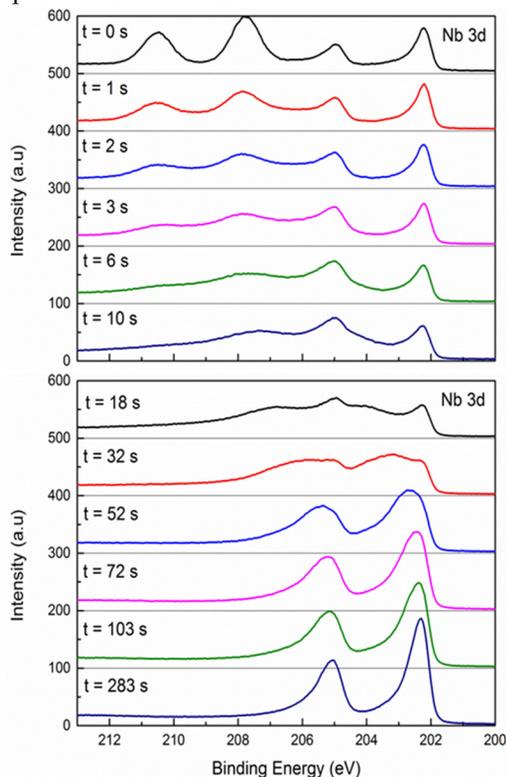


Figure 3: XPS spectra of Nb 3d shift dependence on the Ar+ sputtering time.

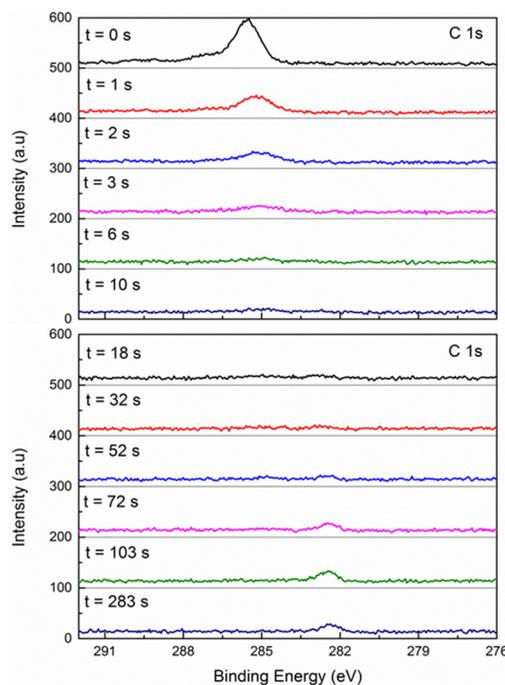


Figure 4: XPS spectra of C 1s shift dependence on the Ar+ sputtering time.

Measurements with UPS were conducted after the XPS completed for each sputtering layers. Form the UPS spectrum, such as the Figure 5, the work function can be calculated by subtracting the energy of the incident photo (He I 21.22eV) from the difference between the Fermi level and the high binding energy cut off edge of secondary electrons [6]. Hence, the work function value is:

$$\Phi = h\nu - (E_{cut-off} - E_{Fermi}) . \quad (1)$$

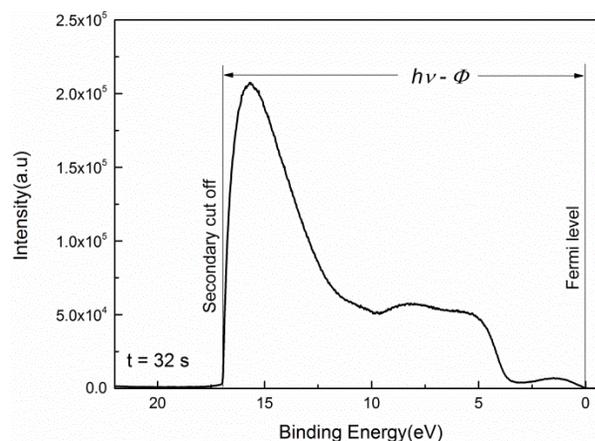


Figure 5: Niobium UPS spectra under the condition of argon ions sputtering for 32s with the energy of 2 keV.

### RESULTS

For the determine the atomic concentration C of the elements present on the niobium surface, the following equation can be used:

$$C_A = \frac{I_A / S_A}{\sum_{i=1}^N I_i / S_i} \quad (2)$$

Where  $I_A$  is the total intensity of element A from the XPS spectrum, and  $S_A$  is the sensitivity factor of A,  $N$  is the number of elements present on the surface. In our case, the value of sensitivity factor for niobium, carbon and oxygen elements is 2.921, 0.278 and 0.780 from the reference [5].

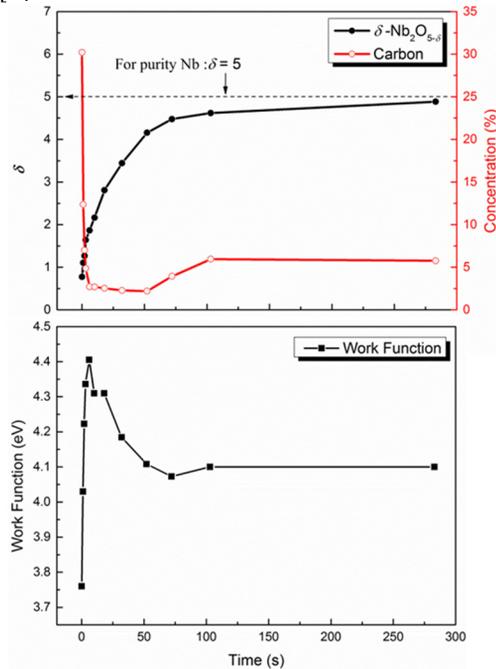


Figure 6: The concentration of Nb/O/C and work function under different sputtering times.

The highest valence oxide of niobium is niobium pent-oxide on the outmost layers of the surface, which has the high work function of 5.2eV compared with the metal purity niobium of 4.2 eV [4]. The atom number concentration of niobium and oxygen elements was normalized to the  $\delta$  in the formation of  $Nb_2O_{5-\delta}$ . Hence, the  $\delta$  was evaluated as the following:

$$\frac{2}{5-\delta} = \frac{C_{Nb}}{C_O} \quad (3)$$

Where, the  $C_{Nb}$  and  $C_O$  are evaluated from the Eq. 2. The number concentrations of the atom and the work function value with the depth profiling was shown in the Figure 6: The sputtering time is related to the depth from surface into inside of samples. It indicates that the concentration of the carbon contamination has a sharply decrease to the minimal level, and the work function to the highest value of 4.4eV. And with the  $\delta$  increasing, the work function value drop down gradually until the constant of 4.1 eV. The results indicate that the carbon contamination is likely to deteriorate work function, and while the niobium oxides seem have the diverse impact on the work function value. The compound of the niobium oxidation is analyzed by the peak fitting.

## DISCUSSION AND CONCLUSION

To identify the various oxide state of niobium, the chemical formation was assumed to be  $Nb_2O_5$ ,  $NbO_2$ ,  $NbO$ ,  $Nb_2O$ ,  $NbC_x$  and the purity Nb. The spectra was calibrated with the C 1s peak of graphite at 284.6. The principles for the peaks fitting: 1) the peaks of the all compounds were kept close to value from those literatures [3-5], 2) the spin split between for all species of Nb3d 5/2 and Nb3d 3/2 was set to 2.7eV [5], 3) the areas ratio of Nb3d 5/2 to Nb3d 3/2 was kept on 3:2. The background was subtracted by the Shirley type. This part of work was completed by the XPS Peaks4.1.

The fitting results are shown in the Figure 7 for different sputtering time. From surface to the inside niobium, the intensity of  $Nb_2O_5$  was gradually reduced, until it was disappeared at time of 32s. The thickness of  $Nb_2O_5$  is about 6nm for the normal state of niobium surface [4], the removing rate was deduced from 0.19 to 0.30nm/s. The  $Nb_2O$  signals appeared at the time of 32s, its concentration was increasing with the sputtering from 32s to 52s. The niobium carbide always existed for the depth profiling, combining the carbon concentration curve from in the Figure 6, the concentration of metallic carbide in the oxides layer is lower than its concentration in the metal purity niobium layer.

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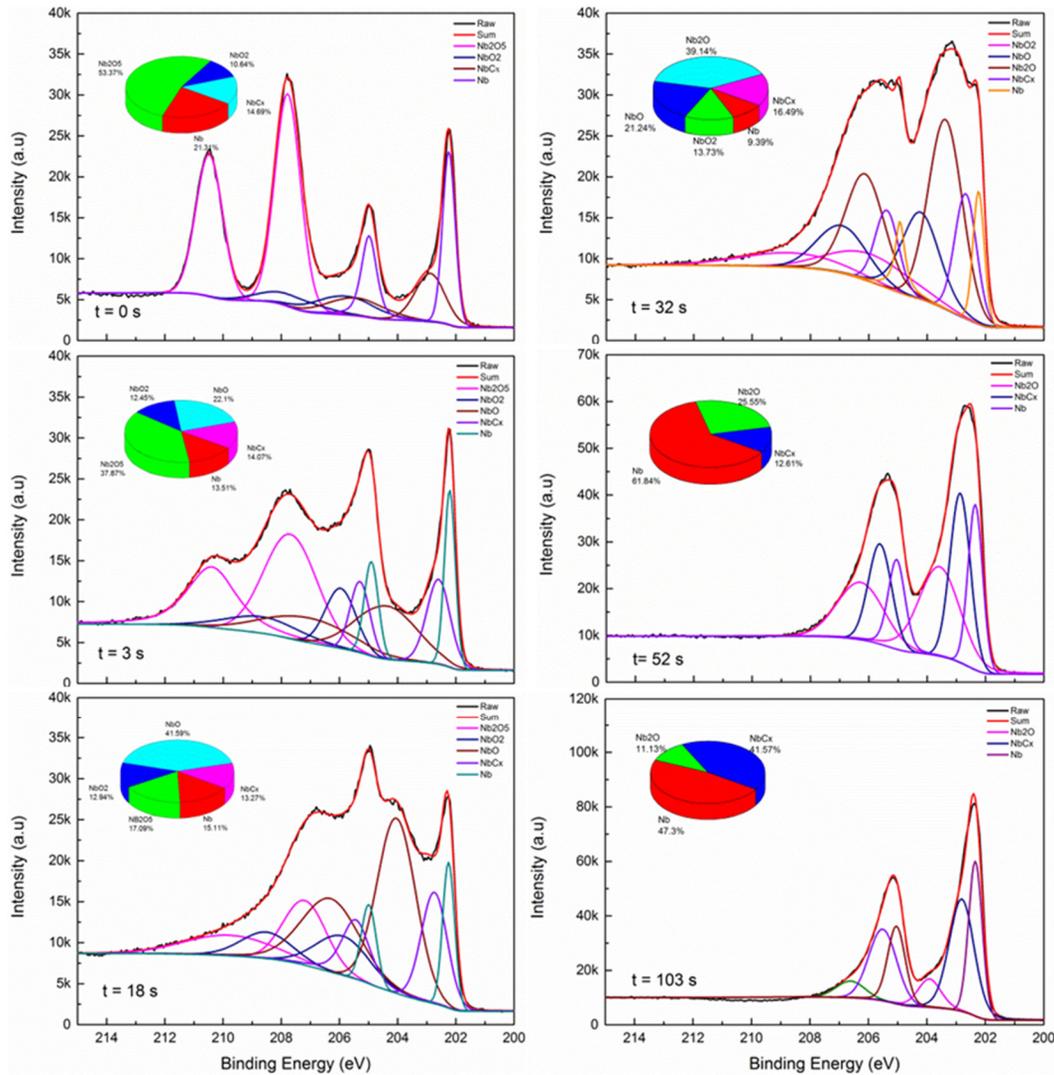


Figure 7: .Nb 3d peaks fitting results for different sputtering time.

### ACKNOWLEDGEMENT

This work is supported by National Natural Science Foundation of China (Y536070GJ0).

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