

SURFACE STUDIES OF PLASMA PROCESSED Nb SAMPLES*

P. V. Tyagi[#], M. Doleans, B. Hannah, R. Afanador, C. McMahan, S. Stewart, J. Mammosser, M. Howell, J. Saunders, B. Degraff, S-H. Kim, SNS, ORNL, Oak Ridge, TN, USA

Abstract

Contaminants present at top surface of superconducting radio frequency (SRF) cavities can act as field emitters and restrict the cavity accelerating gradient. A room temperature in-situ plasma processing technology for SRF cavities aiming to clean hydrocarbons from inner surface of cavities has been recently developed at the Spallation Neutron Source (SNS). Surface studies of the plasma processed Nb samples by Secondary ion mass spectrometry (SIMS) and Scanning Kelvin Probe (SKP) showed that the NeO₂ plasma processing is very effective to remove carbonaceous contaminants from top surface and improves the surface work function by 0.5 to 1.0 eV.

INTRODUCTION

Field emission (electron emission) is one of the prime factors to limit the performance of superconducting radio frequency (SRF) cavities during operation at high accelerating gradient [1]. Many of the SNS (spallation neutron source) SRF cavities are also limited by the field emission and operating below their design accelerating gradient [2]. Surface contaminants (e.g. hydrocarbons) located at top surface of high E-field regions of the SRF cavities (e.g. iris) are believed to be one of the main culprits for the field emission. These contaminants can act as field emitters during the cavity operation at high E-field. Many times, good cavities working at high accelerating gradient tend to degrade over the time during operation and start to show field emission. In order to recover the cavity performance while they are installed in the accelerator tunnel, currently rf conditioning and/or He processing are the most common in-situ processes employed on the cavities and sometimes cavities performance is recovered. However, these processes are not effective all the times and there is no clear understanding of the cleaning mechanism of these processes developed so far.

Therefore an effective in-situ processing is the most demanding for the cleaning of cavity surface to recover cavity performance while they are installed in the accelerator tunnel. Recently, a room temperature in-situ plasma processing [3] for cleaning of the hydrocarbon residues from cavity surface has been successfully developed at SNS for high beta (HB) SRF cavities. A couple of plasma processed cavities have shown significant improvement in the accelerating gradients with reduced electron activities during the cold tests [4].

At SNS, plasma ignition in a desired cell of the SNS HB cavity (6-cells) is achieved utilizing the combination of different modes of the cavity under a continues flow of

fundamental gas. Ne gas is the choice of fundamental gas to ignite the plasma and tune in a desired cell of the cavity. After plasma is tuned in a desired cavity cell, O₂ is introduced as a cleaning agent to oxidize hydrocarbons from cavity surface. The oxidized hydrocarbons (volatile) are continuously pumped through the cavity pumping system. The cavity pumping system is equipped with a residual gas analyser (RGA) which is used to monitor the gases coming out of the cavity during the plasma processing.

In order to understand plasma chemistry at cavity surface, we have carried out detailed experimental studies on Nb samples. Surface characterizations of Nb samples were carried out by secondary ion mass spectrometry (SIMS) for chemical analysis at top surface and scanning kelvin probe system (SKP) for workfunction (WF) measurements. In this article, we report the results from these surface studies.

INCREASE WF TO REDUCE FIELD EMISSION

WF measurements of Nb surface are not yet very common in the SRF community to evaluate Nb surface quality after various surface processing. However, WF of Nb surface plays an important role for field emissions in the SRF cavities as it is directly related to the field emission via Fowler-Nordheim law (eq.1).

$$j \propto \frac{E_s^2}{\phi} \exp\left(-\frac{a \times \phi^{\frac{3}{2}}}{E_s}\right) \quad (1)$$

Where, j is current density, ϕ is the surface WF and E_s is surface enhanced electric field; $E_s = \beta E$ ($\beta > 1$), where β is known as field enhancement factor. It is believed that the onset of field emission at lower than expected field (for constant β) may be associated with the low work function contaminants present at top surface. Hence, higher WF is desirable to lower the field emission after the plasma processing of Nb surface.

NeO₂ PLASMA PROCESSING TO REMOVE HYDROCARBONS AND INCREASE WF

Plasma Processing of Nb Samples

Sample preparation

Nb samples used for studies were prepared from a Nb sheet of similar residual resistance ratio (RRR) as of SNS HB cavities are fabricated. Disc type samples were first EDM wire cut out from the Nb sheet followed by mechanical polishing using a grinder polisher [5]. SiC grinding papers of different grit sizes were used to obtain coarse grinding to fine polishing. After the mechanical

* Work supported by SNS through UT-Battelle, LLC, under contract DE-AC05-00OR22725 for the U.S. DOE.
#tyagipv@ornl.gov, pvttyagi@gmail.com

polishing, samples were subjected to the clean room work which involves cleaning with isopropanol followed by ultrasonically rinsing in the DI (deionized) water for 15 min.

Sample plasma processing methodology

A barrel type plasma reactor located inside the microwave housing was used for the plasma processing (see Fig. 1) of Nb samples. The microwave housing contains a 2.4 GHz rf source with a controllable power unit to control the microwave power. The entire microwave plasma processing unit was provided by SPI supplies [6]. There are two ports in the plasma reactor in order to connect a gas feed system for introducing process gases into the plasma reactor and a pumping cart for continuous pumping during the plasma processing. The pumping cart contains a residual gas analyser (RGA) for the analysis of the gases coming out of the reactor during the plasma processing. The gas feed system contains multiple gas input lines with variable leak valves for each line and an output line to be connected to plasma reactor. The gas feed system can be connected to multiple gas cylinders and provide an adequate gas mixture at required total pressure in the plasma reactor. In order to monitor the gas pressure in the gas feed and plasma reactor, pirani gauges were installed in the gas feed system and outlet port of the plasma reactor.



Figure 1: Microwave plasma processing set-up with gas feed system (sample inside the barrel is shown in inset).

Typically, a base pressure of Ne gas in the range of ~130-140 mtorr is maintained for plasma ignition in the cavity-cells. Due to strong electro-negative nature of O₂, the O₂ concentration is kept up to ~2% of the total Ne pressure for maintaining the plasma stability. Similar conditions of gas pressures and mixtures were used for the plasma processing of Nb samples with NeO₂ gas mixture in the microwave system. Additionally, we had observed a significant microwave heating of the plasma reactor during longer plasma processing, therefore, we used short microwave cycle of 30S and multiple microwave cycles to mitigate the heating effect and

undesired oxidation of the Nb surface. Figure 2 shows the Ne plasma in the microwave plasma reactor.



Figure 2: Ne plasma ignited in the microwave plasma reactor.

Hydrocarbons removal after NeO₂ plasma processing of Nb samples

SIMS [7] was employed for the chemical analysis of top surface of Nb samples and depth profiling of the hydrocarbon impurities before and after the plasma processing. SIMS process involves sputtering of the top surface and analyses of the secondary ions generated during the sputtering process. Our SIMS equipment [8] utilizes primary beam of Ga⁺ ions for sputtering of the sample surface and a quadrupole mass filter for mass analysis. A typical SIMS spectrum consists of two mass spectra of positive and negative ions generated during the sputtering of the sample surface. A quantitative analysis of the elements present at top surface by SIMS is very difficult as intensity of a mass peak in the SIMS spectra depends on various factors such as ion escape probability, sputtering yield of different elements etc. [7].

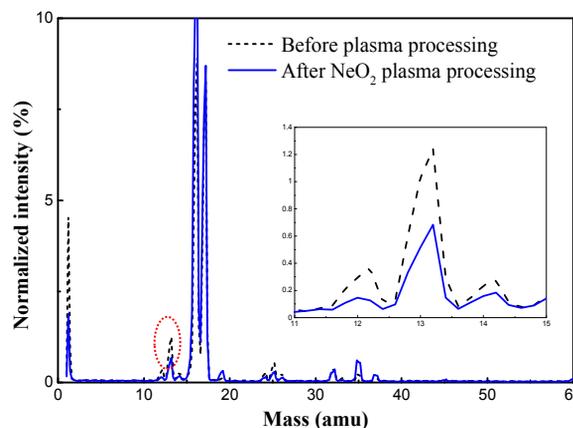


Figure 3: Negative SIMS mass spectra of Nb surface before and after plasma processing. Inset shows the zoomed spectra of C⁻ and CH⁻ before and after plasma processing.

The smallest fragments of hydrocarbons formed during the SIMS sputtering process are C^- (12) and CH^- (13) and observed in the SIMS negative spectrum. The mass peaks of C^- and CH^- in the negative spectrum are particularly of our interest as those represent the presence of hydrocarbon impurities at top of Nb surface

SIMS negative spectra of Nb surface before and after the plasma processing are displayed in Figure 3. Active plasma processing was carried out for 5 min over an hour of total plasma processing (short plasma processing). It can be seen from the Figure 3 that mass peaks of C^- and CH^- were drastically reduced after the plasma processing. This shows that NeO_2 plasma was very effective to mitigate hydrocarbon contaminants at top surface.

WF improvement after NeO_2 plasma processing

As discussed earlier, higher WF of Nb surface after plasma cleaning is desirable in order to mitigate the field emission caused by contamination present at cavity surface. In this regard, we had performed a systematic WF study on Nb samples after plasma processing. WF measurements (in air) were done utilizing a SKP system which works on the Lord Kelvin's principle and measures contact potential difference (CPD) between a probe and sample surface [9]. The absolute WF of the sample's surface can be calculated using following equation 2

$$\phi_{\text{sample}} = \phi_{\text{tip}} + \text{CPD}_{\text{sample}} \quad (2)$$

The reported WF of Nb is 4.3 eV [10]. However, a significant variation in the Nb WF from 3.8 – 5.2 eV has also been reported depending on Nb crystal structure, surface conditions and oxides [11,12]. We had carried out systematic WF measurements on the Nb samples before and after plasma processing. Our WF measurements had found a typical WF $\sim 4.8 \pm 0.1$ eV of as received Nb surface after mechanical polishing. Typical WF increase in the range of 0.5 to 1.0 eV is observed after NeO_2 plasma processing. The increase in the WF is mostly related to hydrocarbons (discussed later) cleaning by NeO_2 plasma processing and is helpful to mitigate field emission in the SRF cavities.

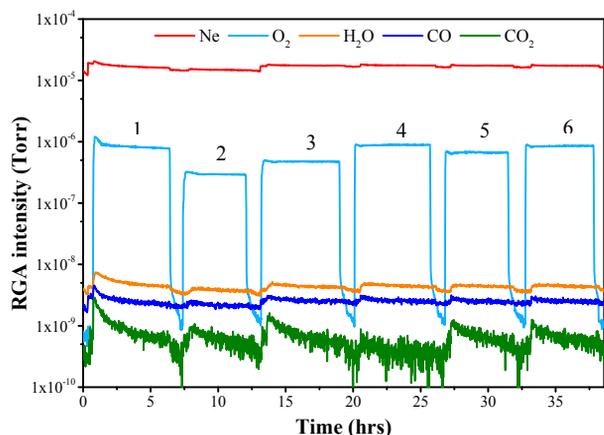


Figure 4: RGA spectrum obtained during the first time of plasma processing of each cell of SNS HB cavity. Cell number is mentioned in the figure.

Hydrocarbons Removal during NeO_2 Plasma Processing of SNS HB Cavity

An RGA spectrum obtained during the plasma processing (first time) of a SNS HB cavity (see Fig. 4) shows H_2O , CO and CO_2 as main by-products of the plasma chemistry. The CO and CO_2 peaks were continuously depleted during the plasma processing. This indicates the cleaning of hydrocarbons from top surface of cavity surface.

HYDROCARBONS RECOVERY AT Nb SURFACE IN VACUUM

Hydrocarbons Recovery on Cavity Surface in Vacuum

We had observed some recovery of the hydrocarbons signal in the RGA spectrum during the plasma processing of the same cavity again after 3 weeks. The cavity was kept under vacuum at room temperature during entire waiting time. Figure 5 displays the RGA spectrum obtained during plasma processing of same cavity after 3 weeks.

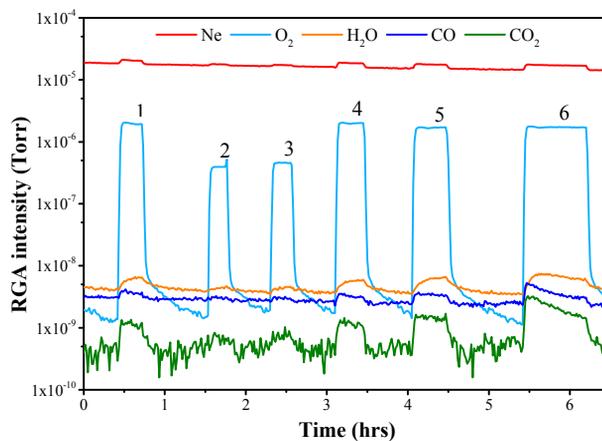


Figure 5: RGA spectrum obtained during the plasma processing of each cell of same cavity after 3 weeks. Cell number is mentioned in the figure.

Hydrocarbons Recovery on Sample Surface in Vacuum

SIMS depth profile of CH^- shows the recovery in CH^- at Nb surface after short plasma processing and waiting in vacuum for 15 min. Figure 6 combines the depth profiles of CH^- before plasma processing, just after plasma processing and waiting in vacuum for 15 minutes. It can be seen from the Figure 6 that high density of hydrocarbons was located at top surface of Nb sample within a nm of depth and NeO_2 plasma processing was effective to mitigate hydrocarbons only at top surface. The CH^- was fully recovered to initial level after waiting in the SIMS vacuum chamber for 15 minutes. This indicates that the hydrocarbons can recover at top surface

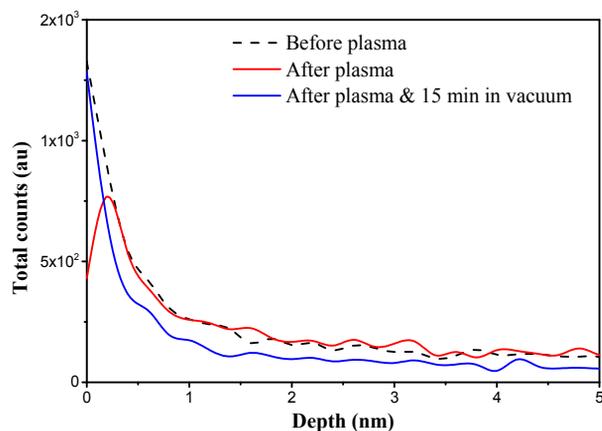


Figure 6: Comparison of CH⁺ depth profile at Nb surface before plasma, after short plasma processing and 15 min waiting in vacuum.

from underneath surface involving hydrocarbons diffusion process.

WF Degradation due to Hydrocarbons Recovery

We had observed the WF degradation of plasma processed (with NeO₂ plasma) Nb sample after waiting under vacuum. The WF of Nb sample was first increased by 0.6 eV just after NeO₂ plasma processing and dropped to its initial value after waiting in vacuum for few hrs. The WF degradation was probably due to hydrocarbons recovery as seen in SIMS depth profiling.

In order to evaluate the fact that one of the possibilities of the WF degradation is associated with the hydrocarbons at top Nb surface, artificial hydrocarbons could be generated using methane (CH₄) plasma processing on sample surface. In this regard, we had prepared a Nb sample and first subjected to NeO₂ plasma processing. A typical increase in the surface WF from 4.8±0.1 eV (before plasma processing) to 5.4±0.1 eV was measured after the NeO₂ plasma processing. Afterwards, we had carried out NeCH₄ plasma processing on Nb sample. The base pressure of Ne was maintained at 130 mtorr (similar to Ne base pressure for NeO₂ plasma processing) and CH₄ concentration was limited up to 2%. Total 4 cycles of plasma (2 min) were performed on Nb sample after NeO₂ plasma processing. The WF of Nb surface after the NeCH₄ plasma was measured 3.4±0.1 eV. Furthermore, we had re-processed the hydrocarbon contaminated Nb sample with regular NeO₂ plasma processing. The WF was again increased to 5.4 eV±0.1 similar to WF just after NeO₂ plasma processing and before NeCH₄ plasma processing. The WF study on Nb sample after NeCH₄ plasma processing confirmed that hydrocarbons can degrade Nb surface WF significantly and NeO₂ plasma processing can effectively clean hydrocarbons and increase the WF of Nb surface.

MITIGATION OF HYDROCARBONS RECOVERY

Mitigating Hydrocarbons Recovery using Longer Plasma Processing

In order to mitigate hydrocarbons recovery at Nb surface, effect of longer plasma processing was evaluated. The active plasma processing was carried out for 15 minutes over a total plasma processing of 3 hrs. SIMS depth profile of CH⁺ after longer plasma processing shows (see Fig. 7) that there was no hydrocarbons recovery at Nb surface after 15 minutes waiting in vacuum. The results from depth profile suggest that the longer plasma processing was helpful to mitigate hydrocarbons recovery by diffusion process from underneath surface.

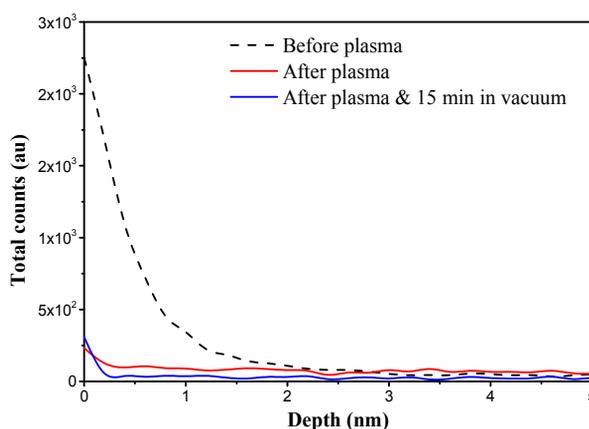


Figure 7: Comparison of CH⁺ depth profile at Nb surface before plasma, after longer plasma processing and 15 min waiting in vacuum.

However, from Figure 6 we had found that plasma processing is effective only at top surface. This means that the longer plasma processing can deplete the hydrocarbons within few nm utilizing natural hydrocarbons diffusion from underneath surface during the plasma processing. As hydrocarbons diffusion rate depends on concentration gradient (at constant temperature) [13], hydrocarbons diffusion process will be slower as hydrocarbons are continuously depleted from top surface. Hence, multiple plasma processing may offer a good way to deplete hydrocarbons within few nm of top surface and maintain higher WF over a longer period of time.

Mitigating WF Degradation over a Longer Time using Multiple Plasma Processing

In order to evaluate the fact that multiple plasma processing may help to slow down hydrocarbons recovery and maintain higher WF over the longer period of time, we have conducted a detailed WF study after multiple plasma processing. The WF study had confirmed that multiple plasma processing was very helpful to maintain higher WF over a longer period of time (see Fig. 8). The experimental conditions are summarized in Table 1.

Table 1: Summary of experimental conditions for WF measurements after multiple plasma processing

Experiments	Experimental conditions	Δ WF (eV)
1	Total 1.5 hrs. of active plasma and 15 hrs waiting in vacuum	-0.6 ± 0.1
2	Total 5 hrs. of active plasma and 15 hrs waiting in vacuum	-0.21 ± 0.1
3	Total 6.5 hrs. of active plasma and 24 hrs waiting in vacuum	-0.21 ± 0.1

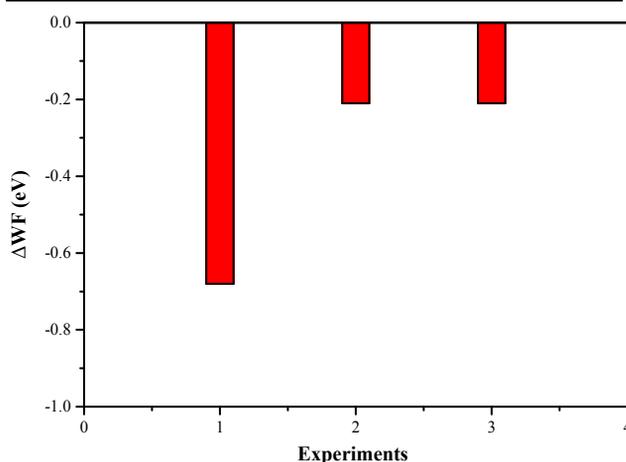


Figure 8: WF degradation in vacuum for different experiments mentioned in table 1. Multiple plasma processing was found beneficial for maintaining higher WF over a longer period of time.

SUMMARY

A room temperature in-situ plasma cleaning technology for SNS HB cavities has been recently developed at SNS. Currently, plasma processing is aimed to target hydrocarbon impurities at top surface of cavities. Plasma processed cavities had shown significant improvement in the accelerating gradients with much reduced electron activities during the cold test. In order to understand the details of plasma surface chemistry, we had conducted a detailed surface study utilizing SIMS and SKP for chemical analysis and WF measurements respectively. Our studies with SIMS showed that the NeO₂ plasma processing is very effective to mitigate hydrocarbon contaminants from top surface of Nb sample. SIMS depth profile of CH⁻ had found that the NeO₂ plasma processing was effective to mitigate hydrocarbons only at top surface. However, hydrocarbons recovery on top surface of Nb sample from underneath surface of after plasma processing and waiting in vacuum was observed. Similar, hydrocarbon recovery on cavity surface was observed when a plasma processed cavity was subjected to plasma

processing after few weeks while cavity was kept under the vacuum at room temperature throughout the waiting time. In order to mitigate the effect of hydrocarbons recovery at top surface, multiple plasma processing was found advantageous. WF studies showed that the WF of Nb surface was increased from 0.5 to 1.0 eV after NeO₂ plasma processing and multiple plasma processing was found beneficial to maintain higher WF over a longer time period. The WF measurement of sample surface contaminated by the artificial hydrocarbons showed that hydrocarbons can significantly degrade the WF of Nb surface and can lead to field emission during cavity operation. However, it should be noted that NeO₂ plasma processing may not be effective to mitigate field emissions due to surface defects, mechanical imperfections etc. and can't modify β (field enhancement factor) due to such defects.

Based on the results from surface studies, it is clear that multiple plasma processing is a need to mitigate the hydrocarbons diffusion process and associated WF drop during the waiting time at room temperature under vacuum. As diffusion process depends exponentially on temperature [13], no hydrocarbons recovery at cavity surface is expected after a cavity is cooled-down to 2K. Hence, immediate cool-down of a cavity after the plasma processing is desirable in order to avoid the hydrocarbons recovery and WF degradation. However, in general, the cool down of a cryomodule takes few hrs therefore the strategy for plasma processing of a cryomodule may involve multiple plasma processing to allow suitable waiting time at room temperature after the plasma processing and the cryomodule cool down.

REFERENCES

- [1] Hasan Padamsee, "RF Superconductivity: Volume II" John Wiley & Sons.
- [2] M. Doleans et. al., SRF2013, Paris, France (2013).
- [3] P. V. Tyagi et. al., LINAC14, Aug 31-Sept 6, 2014, Geneva, Switzerland.
- [4] M. Doleans, Talk on "First cold-test results of plasma processed SNS High-beta SRF cavities", Aug 14, 2014, SNS, ORNL, USA.
- [5] Donald C. Zipperian, "Metallographic handbook" PACE Technologies Tucson, Arizona USA.
- [6] SPI Plasma Prep Jr, <http://www.2spi.com/>
- [7] John C. Vikerman and Ian S. Gilmore "Surface analysis: the principle techniques" John Wiley & Sons.
- [8] Scientific Analysis Instruments Limited, MiniSIMS TOF/alpha, user manual 1.2.
- [9] I. D. Baikie et al, Rev. Sci. Instrum., Vol. 69, No. 11 Nov '98.
- [10] H. B. Michaelson J. Appl. Phys. 48, 4729 (1977).
- [11] Jian Wang and Shao-Qing Wang, Surface Science, 630, 216-224 (2014).
- [12] R. Ballantini et. al., SRF1999, New Mexico, USA (1999).
- [13] James F. Shackelford "Introduction to Materials Science for Engineers" ISBN-10: 0133826651.