Plasma treatment of bulk niobium surface for SRF cavities[☆]

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Abstract

Pulsed electric discharges were used to demonstrate the validity of plasma surface treatment of superconducting radio-frequency cavities. The experiments were performed on disc-shaped Nb samples and compared with identical samples treated with buffer chemical polishing techniques. The results of several standard surface analytical techniques indicate that plasma-treated samples have comparable or superior properties regarding the surface roughness and composition.

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1. Introduction

The preparation of cavity wall surfaces has been one of the major challenges in superconducting radio-frequency (SRF) accelerator technology. Accelerator performance depends directly on the physical and chemical characteristics of the SRF cavity surface [1]. The objective of the present research is to minimize the surface roughness and the presence of Nb oxides that may cause the degradation of SRF cavity characteristics. In the present experiments, plasma sheaths were used as metal-to-discharge interfaces to generate an adequate environment for the transformation of Nb oxides or other impurities from the Nb surface into removable volatile compounds. In addition, employing electric discharge provides a unique opportunity to study oxide-free Nb surfaces right after processing without exposure to air. This approach also allows control of the

final phase of the SRF surface passivation involving plasma-controlled oxidizing or nitriding processes. The Nb halogenides have boiling points in the temperature range that is easily obtainable in the discharge plasmas [2]. Therefore, the gasses containing halogen atoms like SF₆, CF₄, CH₂F₂, or Cl₂ are suitable candidates for Nb surface treatment. Although all these gasses are toxic and/or corrosive, the concentrations used in plasma etching processes are much smaller than the concentration of acids used in buffer chemical (BCP) or electrochemical polishing (EP) [3].

Thin films of niobium and niobium pent-oxide treated in reactive discharge plasmas have been described in literature [4–13]. The plasma treatment processes were based on the formation of volatile niobium fluorides. Other gasses were rarely added to the reaction mixture. The etching rates show large variations, from a few nm/min to a few hundreds of nm/min, even in cases in which the same type of etching gas was used. This is a consequence of different preparation techniques of Nb thin films and different experimental conditions in the reaction chamber. Pressure, flow rate, and power density vary substantially from experiment to experiment. The only common feature in

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all experiments was the use of 13.6 MHz radio-frequency (RF) power supplies typically in the parallel-plate reactors [14]. These limited empirical results were a starting point for the study of bulk niobium surface modification with low-pressure discharge plasmas.

In this paper, we present the preliminary results on the proof-of-principle test on bulk Nb disks. BF_3 was used as reactant gas in the parallel-plate type reactor. We describe the procedure of sample preparation, the experimental system, some processing diagnostics, and methods of sample characterization. The preliminary results on samples and comparison with a BCP-treated sample are presented.

2. Experiment

2.1. Sample preparation

The bulk Nb used for fabrication of SRF cavities comes in the form of metal sheets covered with a thin layer of oxides. The Nb samples used in this experiment were 1" or 2"-diameter disks machined from the same high residual resistance ratio Nb sheet. The residual resistance ratio for used sheet was 300. All samples were degreased before plasma processing and in the case of large mechanical damage of the surface, mechanically polished. After processing under different plasma conditions, the surfaces of these samples were compared.

The repetitively pulsed DC diode system (PLAD) [15,16] operating in the voltage range 100 V–20 kV at repetition rate between 500 Hz and 10 kHz was used for the proof-of-principle of bulk Nb plasma etching. In most of the reactive RF-plasma systems, deposition and etching are occurring at the same time. Therefore, control of the surface is not easily accomplished. In the DC pulsed system, deposition is minimized and etching is controlled by the bias pulse width and frequency. The reactor can be used in two operational modes: in the bulk mode and in the sheath mode. In the bulk mode, the sample is connected to the cathode, which is negatively biased to generate the pulsed plasma, while the hollow cathode and the anode are grounded. In the sheath mode, shown in Fig. 1, the sample is also connected to the cathode, but the hollow cathode is charged by connection to the same high voltage as the cathode.

The sheath operational mode, used for the present experiment, maximizes the plasma density. These conditions are more favorable for plasma etching. The samples were processed under three different conditions listed in Table 1. The BF_3 flow rate was held constant at 5 sccm.

In-situ mass spectrometry of the reactor gas, residual ions, and afterglow ion composition was used for process characterization. The residual gases spectrum measurement was done during the plasma on and off. The resulting spectrum is an average measurement over many pulses. Alternatively, sampling of the positive ions was timely synchronized with two different stages of the pulsed plasma

discharge: pulse-on and afterglow stages, presented in Fig. 2. The sampling period was 5 μs while the interval of applied pulse was 20–50 μs .

For comparison purposes, we used an Nb sample processed with BCP, one of the typical chemical polishing used on SRF cavities. This sample was treated with BCP 1:1:1 (49% HF, 69% HNO_3 , 85% H_3PO_4) with material removal in excess of 250 μm .

2.2. Surface characterization

All samples were transported to the diagnostic system exposed to room temperature air more than the 10 h before surface analysis. Therefore, they are all covered with the layer of niobium pent-oxide [17]. Current experiments, subject of future publication, will focus on chemical composition analysis of the samples' surface. The surface morphology investigation was performed with four different techniques: optical microscopy, surface profilometry, scanning electron microscopy, and scanning probe microscopy.

For the optical microscopy investigations, a Hirox KH-3000 VD high-resolution video microscope with a magnification of 10×350 was used to obtain qualitative comparison of details from the surface of the samples. The instrument is capable of observing non-flat samples by taking images from different focal planes and digitally merging them into a single image with extended depth of focus. The variable angle of illumination adds to the visual effects depicting the surface roughness in more graphic detail. This feature was used to make images of the surfaces presented in this work. The option to measure the height was used for estimation of inclusion depths and other features observed on the surface. This procedure consists in the separate focusing of two areas of different height (i.e., a ridge compared to a valley) and reading the vertical distance between two focal planes. This vertical distance is referred as height in Table 2.

Complementary surface analysis was performed with the surface profilometer KLA TENCOR P-15. The profilometer has a MH2sr head configuration with applied force between 1 and 50 mg. The sensitivity of the head is 0.5 μm . Four millimeter long 2D scans were performed with the vertical resolution limited to 0.02 nm due to the tilt of the samples. The integrated software can determine the standard deviation from a smooth surface.

The analysis and comparison of sample surface morphology and composition were made with an AMRAY 1800 scanning electronic microscope combined with an EDAX 9800 X-ray system. Different magnifications, point and area average composition analyses were performed.

Tri-dimensional imaging and surface roughness analysis were performed using a scanning probe microscope (multimode SPM, Veeco) operating in the tapping mode. The scanned area was $10 \times 10 \mu\text{m}^2$.

Fig. 1. Scheme of the pulsed DC reactor [15].

Table 1
Experimental conditions in PLAD reaction chamber

Sample #	Pressure (mTorr)	Voltage (kV)	Power density (W/cm ²)
1	20	1.20	0.3
2	28	1.95	0.6
3	250	0.54	0.012

3. Results

3.1. Process characterization

A typical residual gas spectrum during plasma etching compared with the reactor gas spectrum when there is no Nb sample in the reaction chamber is given in Fig. 3. The typical mass spectrum for BF_3 plasma (peaks BF_3^+ at 68,

BF_2^+ at 49, BF^+ at 30, F^+ at 19, and B^+ at 11 atomic units) is present in both spectra. In Fig. 3b, a set of relatively intense peaks in the region between 16 and 20 atomic units is present. These peaks suggest high release rates of oxygen and hydrogen from the Nb surface. A prominent peak at 28 atomic units may suggest a significant amount of boron hydroxide. There is a small intensity peak on 93 atomic units, indicating the presence of Nb^+ ions in the reaction system during plasma etching. The intensity of the NbF_5 fragments' ions is small in comparison with the predominant BF_3 fragments' ions.

The positive ion spectra shown in Fig. 4 have much lower intensity than the residual gas spectrum. It can be noticed that the plasma is much richer in heavier positive ions during the afterglow than during the pulse-on period. The dominant positive ions during the pulse-on period are B^+ , BF^+ , and BF_2^+ with intensity increasing with atomic

Fig. 2. Wave forms of the cathode potential (Wafer bias) and pulsed plasma density (Plasma) (modified from Ref. [16]).

Table 2
Height and size of features on the samples' surface determined by multifocusing of optical microscope

Sample	Height (μm)	Length (μm)
Untreated	8.0	57
BCP	3.3	64
1-plasma	2.3	5.4
2-plasma	1.4	3.7
3-plasma	3.5	7.3

unit. During the afterglow period, the intensity of BF^+ peak increases, while the intensity of B^+ and BF_2^+ peaks decreases. Also, a spectrum of ions with m/z ratio bigger than 60 atomic units is richer and more intensive than in the pulse-on period. One can conclude that the plasma reactivity is strong in both intervals. During the pulse-on period, the action of energetic ions should be expected to have a dominant effect, reminiscent of ion milling. The surface modification proceeds in the afterglow, but the action continues as reactive etching.

3.2. Surface characterization

3.2.1. Optical microscope and surface profilometer

Figs. 5(a, b, c) show the micrographs of the surface of samples: untreated (a), treated by BCP technique (b), and treated in PLAD system containing a mixture of Ar and BF_3 (c). The untreated sample (Fig. 5a) shows large features (more than $50\text{ }\mu\text{m}$ long) up to $10\text{ }\mu\text{m}$ high. The BCP-treated sample (Fig. 5b) has large but flattened features with sharp edges up to $3\text{ }\mu\text{m}$ high. The plasma-treated sample (Fig. 5c) shows that the features are smaller by an order of magnitude and more oblique, with an average height in the order of $1\text{--}2\text{ }\mu\text{m}$. Individual solitary features, more than $2\text{ }\mu\text{m}$ high, were also observed. Further analysis will be necessary to determine if these observed features are grains. For the purpose of this paper, they will be referred as large features.

(a)

(b)

Fig. 3. Sample 1: (a) reactor gas spectrum, and (b) residual gas spectrum when Nb sample is present in the PLAD system.

Using the multifocus ability of the microscope, we could compare two parameters on surface micrographs that could serve as measures of the surface roughness. One is the vertical distance between the highest and the lowest point in the observed optical field, labeled here as “height”. Another parameter is the average feature size. Values of these parameters are listed in Table 2.

We can relate the differences in the height and size of features on the plasma-treated samples surface to the effect of local electric field in the electric discharge. The surface of Sample no. 1 was exposed to fields greater than 1 kV/cm . At the features edges, the electric field could have been enhanced to 10 MV/cm , leading to locally increased erosion, with a smoothing effect as a consequence. Sample no. 3 presented in Fig. 6, shows different size and shape of the surface features. This sample was treated at high pressure (see Table 1) and effectively higher field due to the contraction of the sheath region in the plasma.

To determine the relevance of the optical microscope results, the roughness was also measured with a profilometer.

Fig. 4. Sample 1: (a) pulse-on positive ion spectrum, and (b) afterglow positive ion spectrum. Nb sample is present in the PLAD system.

Since the profilometer is a mechanical device, we chose an applied force of 0.5 mg to prevent any damage on the Nb surface. The surface roughness is described with two parameters: waviness (W_a) and roughness (R_a). The waviness refers to the tendency of the surface to form large-dimension shapes, while the roughness refers to the surface deviation from the large pattern. From Table 3, can be seen that the untreated sample shows the largest features of all measured samples. The BCP sample has a much smaller standard deviation (W_{RMS} and R_{RMS}) from the smooth surface than the untreated sample. All plasma-treated samples have the smallest measured standard deviation from the smooth surface.

3.2.2. Scanning electron microscope

The results of the SEM analyses are presented in Fig. 7. The differences in pattern are consistent with the optical microscopy data. The sharp edges between features on the BCP-treated sample surface gives rise to strong electron

Fig. 5. Surface micrographs taken with KH-3000 digital microscope with magnification 10×350 : (a) an untreated sample, (b) BCP sample, 8-layer multifocus, and (c) plasma-treated sample (Sample no. 1), 3-layer multifocus.

emission shown by the narrow bright strips in Fig. 7a. The oblique shape of the features of the plasma-treated sample (see Fig. 7b) leads to more moderate electron emission, and the whole surface looks fuzzier, with few dominant details.

The point and area average composition analyses on the plasma-treated sample were performed by energy-dispersive

Fig. 6. Surface micrograph of Sample no. 3 from Table 1.

Table 3

Results of surface analysis performed by the profilometer

Sample	W_a (Å)	W_{RMS} (Å)	R_a (μm)	R_{RMS} (μm)
Untreated	235	285	0.930	1.125
BCP	141	169	0.323	0.476
1-plasma	20	26	0.246	0.309
2-plasma	23	27	0.195	0.240
3-plasma	11	16	0.295	0.353

X-ray analysis (EDX) and the corresponding spectra is shown in Fig 8. In addition to dominate Nb $L\alpha$ peak, a B $K\alpha$ and O $K\alpha$ peak can be noticed. The origin of B in the spectra is BF_3 , which is used as reactive gas for the plasma treatment of Nb surface.

3.2.3. Scanning probe microscopy

Tri-dimensional surface images of the plasma-treated sample and the BCP-treated sample are given in Figs. 9 and 10. They show similar pattern variation as the digital microscope and SEM images and confirm that smaller, oblique features tend to form on plasma-treated surfaces while large features, separated by sharp and deep edges tend to form on chemically polished surfaces.

The surface roughness parameters of the three samples, the average range in z -coordinate, root mean square (RMS) variation from the average z -coordinate, mean variation from the average z -coordinate R_a , and the effective surface area, are listed in Table 4. The plasma-treated samples have a much smaller range of the z -coordinate within the scanned area and other roughness parameters are comparable. The untreated sample had features too deep for a scanning probe microscope measurement (refer to Table 3).

Fig. 7. Surface micrographs obtained with scanning electron microscope: (a) sample treated with BCP technique—magnification 500 × and (b) plasma-treated sample (Sample no. 1)—magnification 1500 ×.

Fig. 8. Average-area EDX spectra of the plasma-treated sample (Sample no. 1).

The comparison between two plasma-processed samples shows that Sample no. 3 has consistently larger roughness parameters than Sample no. 1. This indicates a strong variation of surface quality depending on plasma conditions, as expected. The electric discharge plasma conditions have to be optimized in order to obtain the best surface characteristics.

Fig. 9. Three-dimensional image of the plasma-treated sample (Sample no. 1).

Fig. 10. Three-dimensional image of the BCP-treated sample.

Table 4
Results of surface analysis performed by the scanning electron microscope

Sample	Z range (nm)	RMS (nm)	R_a (nm)	Area (10^6 nm^2)
BCP	1213	151	105	101.24
1-plasma	677	131	112	101.85
3-plasma	985	155	116	102.10

4. Conclusion

The preliminary results of this study show that plasma-treated samples are comparable or superior to a BCP sample, both in the size of features and sharpness of the boundaries between individual features at the surface. Images obtained with the optical microscope, the scanning

probe microscope, and the scanning electron microscope show consistently the tendency of electric discharge plasmas to increase etching rates in the regions of enhanced electric field. This natural smoothing behavior leads to oblique shapes of the features and elimination of sharp edges.

The possibility of using other types of reactor and the formation of other volatile halogenides will be investigated in the near future. The proposed gas mixtures could contain reactive halogen gases other than BF_3 , for example Cl_2 . The higher temperature necessary for the evaporation of NbCl_5 can be more easily obtained in the barrel-type reactor working with microwave electric discharge generation. A barrel-type reactor, compatible with the single-cell SCF cavity, is under construction at Old Dominion University and the results will be presented in a future publication.

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