

PLASMA TREATMENT OF BULK Nb SURFACE IN THE Ar/Cl₂ DISCHARGE*

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Abstract

The preparation of the cavity walls has been one of the major challenges in the superconducting radio-frequency (SRF) accelerator technology. Therefore, constant research and development effort is devoted to develop surface preparation processes that will improve roughness and lower the level of impurities, like hydrogen or oxygen, embedded in bulk Nb, having in the same time reasonable etching rates. Plasma based surface modification provides an excellent opportunity to achieve these goals. We present Ar/Cl₂ discharge treatment of bulk Nb where we achieved etching rates comparable to the rates obtained with the electropolishing method without introducing impurities in Nb. The current experiments were performed on disk shaped Nb samples, exposed to plasma produced in a microwave discharge system. Surface composition and topology measurements were carried out before and after plasma treatment. Upon determining optimal experimental conditions on disk shaped samples, we will apply the same procedure on the single cell cavities, pursuing improvement of their RF performance.

INTRODUCTION

There is no report on plasma treatment of bulk Nb used for SRF cavities, even though plasma etching of Nb thin films has been readily used in production of Josephson tunnel junctions [1]. In discharge plasmas containing chlorine or fluorine radicals, the bulk Nb surface interacts with these radicals producing volatile Nb halides. The production of reactive species and, consequently, the Nb removal rate is determined by discharge parameters such as input power, pressure, temperature, electron concentration, etc.

Taking into account volatile Nb halides properties, we carried out experiments in two discharge systems. For proof-of-principle, BF₃ plasma was applied to Nb samples in a repetitively pulsed d.c. diode system. Results showed [2] that the surface smoothness was improved compared to BCP treated sample.

Currently we are pursuing a series of experiments in a microwave glow discharge system using Cl₂ as a reactive gas. Plasma etching of Ta₂O₅ [3], a chemically similar compound to Nb₂O₅ present on the surface of bulk Nb, showed that using Cl₂ gives same the results regarding etching rate and surface smoothness as etching with F compounds. In the same time, the products of the reaction

are environmentally safe and can be easily scrubbed after exiting the system. We measured the surface characteristics of the Nb sample before and after exposure to the discharge in order to compare the results. We determined favorable etching rates, impurity content and roughness.

In a parallel effort, we are developing a plasma chemical kinetic model of the Ar/Cl₂ plasma interaction with the Nb surface combining available experimental data with our calculations. Our aim is to understand the etching kinetics and Nb surface modification in order to optimize the process with respect to etching rate and surface roughness.

EXPERIMENT

Experimental set-up of the discharge system

The microwave cavity discharge system, shown in Fig. 1, is a typical “barrel” reactor [4], capable of maintaining discharges at pressures above 1 Torr [5]. In the microwave discharge, the high energy transfer efficiency from the microwave electric field to the gas results in high electron and high radical densities in the plasma. These plasma conditions are more favorable for plasma etching than for sputtering processes. Also, the higher gas temperature in the plasma contributes to a higher rate of chemical reactions and vaporization of Nb chlorides. The Nb samples are placed in the quartz tube of a reaction chamber. Low background gas pressure is achieved using a system of mechanical and turbo molecular pumps, both corrosive gas resistant. The gas in the reaction chamber has high constant flow rates, so that reactive species lost due to the chemical reaction can be replenished and products of the chemical reaction removed away from the sample. The gas flow control is achieved through flow meters connected to a controller. For processes that demand more than one reaction gas, a mixing chamber is placed in front of the reaction chamber to facilitate a better mixing of the gases. The experimental set-up is connected to a spectrometer with the CCD camera for emission spectroscopy measurements. Emission spectroscopy is used as a process monitoring technique as well as a tool to determine the reaction mechanism of the plasma etching process.

Diagnostic techniques

We used an analytical scale with 0.01 mg precision to determine the samples' mass. We determined the presence of different elements on the surface using a low vacuum scanning electron microscope (SEM) JSM-6060LV. We performed a more detailed composition analysis X-ray

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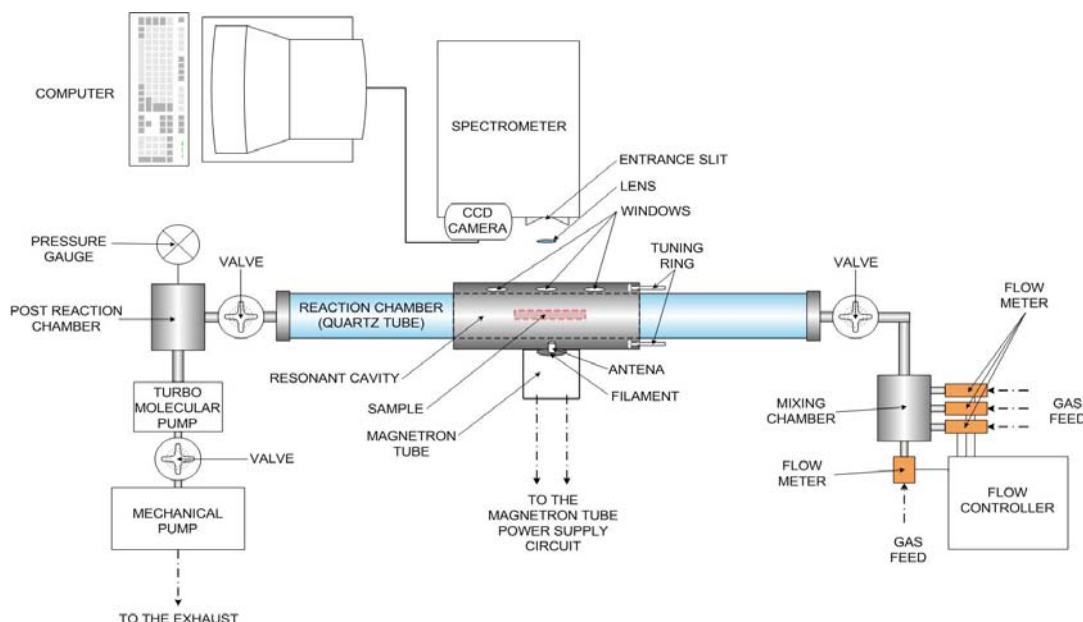


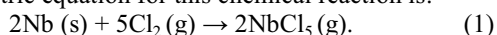
Figure 1: Microwave glow discharge system.

photoelectron spectrometer (XPS) Kratos Ultra with 15 μm spatial resolution and monochromatic Al K_{α} x-ray source. We measured the surface roughness using a tapping mode atomic force microscope (AFM) on 20 by 20 μm surface area.

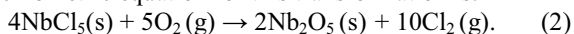
RESULTS

Etching rates

We determined the etching rates from the difference in sample mass before and after exposure to Ar/Cl_2 discharge. From Table 1, one can see that the etching rate increases with a higher amount of Cl_2 in the gas mixture. The dependence of the etching rate on the reactive gas concentration is an indicator of the chemical etching contribution to the Nb removal mechanism [3]. The stoichiometric equation for this chemical reaction is:



The mechanism of reaction is not fully understood. The reaction product NbCl_5 has a boiling point at 245°C [6], temperature that is easily achieved in microwave discharges. We found sublimed NbCl_5 molecules deposited in parts of the apparatus away from the cavity that are not exposed to discharge and consequently at lower temperature. The yellow colored NbCl_5 deposit turns to white Nb_2O_5 when exposed to air flow. The stoichiometric equation for this transformation is:



Having standard enthalpy of formation $\Delta H^\circ = -1899.5$ KJ/mol, Nb_2O_5 is more stable chemical compound than NbCl_5 with $\Delta H^\circ = -797.4$ KJ/mol. This thermodynamics characteristics favors binding of O_2 and release Cl_2 from deposit in the excess of oxygen.

In order to determine the contribution of sputtering to Nb removal from the surface, we exposed some Nb samples to pure Ar discharge. No measurable change in mass was found and consequently no etching rate was determined. Biasing the samples up to -300V did not give any measurable etching rate. This result is in accordance with the Nb low physical sputtering rate, since it has a high binding energy among atoms present on the surface [7].

Table 1: Experimental conditions and etching rates obtained during plasma treatment of disk-shaped Nb samples

Gas flow [sccm]		Pressure [mTorr]	Power density [W/cm ³]	Etching rate [nm/min]
Cl_2	Ar			
0.15	199.85	300	1	3
5.85	189.15	270	1	174
5.85	189.15	290	2	345
5.85	189.15	290	3	350
5.85	189.15	450	2	2500

The current experiment is not conclusive with respect to the physical sputtering contribution during Ar/Cl_2 discharge treatment of Nb surface. There is a possibility that the chemical reaction between adsorbed Cl radicals and Nb distorts the crystalline structure changing the binding energy and makes physical sputtering more favorable than in the case of pure Ar treatment. Emission spectroscopy measurements indicate that, during Ar/Cl_2 discharge treatment, clusters of Nb are present in the discharge. We will undertake further investigation to

determine the contributions of physical sputtering and chemical reaction on the total etching rate.

We investigated the influence of the other discharge parameters on etching rate and the results are also presented in Table 1. Increasing the power density increases the etching rate. This is related to more efficient collision processes in the discharge and a higher production rate of reactive Cl, which is directly proportional to the etching rate. Increasing the pressure also increases the etching rate, due to the increased amount of reactive Cl species that interact with the Nb surface. We will pursue additional measurements under same experimental conditions to verify results and establish statistics.

Surface composition

The samples exposed to Ar/Cl₂ discharge were cooled down to room temperature in the Ar flow and transferred from the discharge system to available analytical equipment exposed to air. The surface analysis was performed on SEM since it provides both morphology and composition of the surface. The qualitative analysis of the Nb sample surface composition showed no chlorine lines or any other impurities, except oxygen. Additional analysis was done on the yellow colored deposit from effluent gasses in cold region of reaction chamber. This deposit was transported to SEM facility without exposure to air. The composition analysis showed the presence of Nb and Cl in a proportion corresponding to NbCl₅ compound.

Further composition analysis of the Nb sample was done with XPS. The results are shown in Fig. 2a. The survey spectra show only Nb, O and C characteristic lines. The source of C lines is environmental carbon deposited on the surface of samples during handling and transportation. We found no chlorine lines.

Figure 2b presents high resolution spectra of Nb, showing 3d_{5/2} and 3d_{3/2} doublet, separated by 2.75 eV [8]. This Nb doublet is highly sensitive to the oxide state of Nb. The peak at 201 eV corresponds to metal Nb which is Nb⁰ oxidation state. The most intense peak at 207 eV corresponds to Nb₂O₅ containing Nb⁵⁺ oxidation state. Between these two peaks are located unresolved peaks of Nb suboxides which oxidation states are Nb¹⁺, Nb²⁺, Nb³⁺, and Nb⁴⁺. In both spectra, before and after exposure to the discharge, Nb⁵⁺ is the most dominant oxidation state. However, the amount of suboxides is smaller after exposure. Deconvolution and detailed analysis should be performed.

Experiments with Nb samples in pure Ar plasma show that the discharge removes residues of organic solvents left on the surface during sample preparation. We expected a similar result for the sample exposed to Ar/Cl₂ discharge. Thus, we show O 1s line spectra in the Fig. 2c. According to Ref.[8], the high energy side wing contains unresolved peaks of Nb hydroxides and carbonyl group from solvent residues. The wing is significantly smaller after exposure to the discharge. The most intense peak is one that can be associated with the Nb oxides. Its surface

increases after exposure to the discharge. Additionally, deconvolution and detailed analysis should be performed.

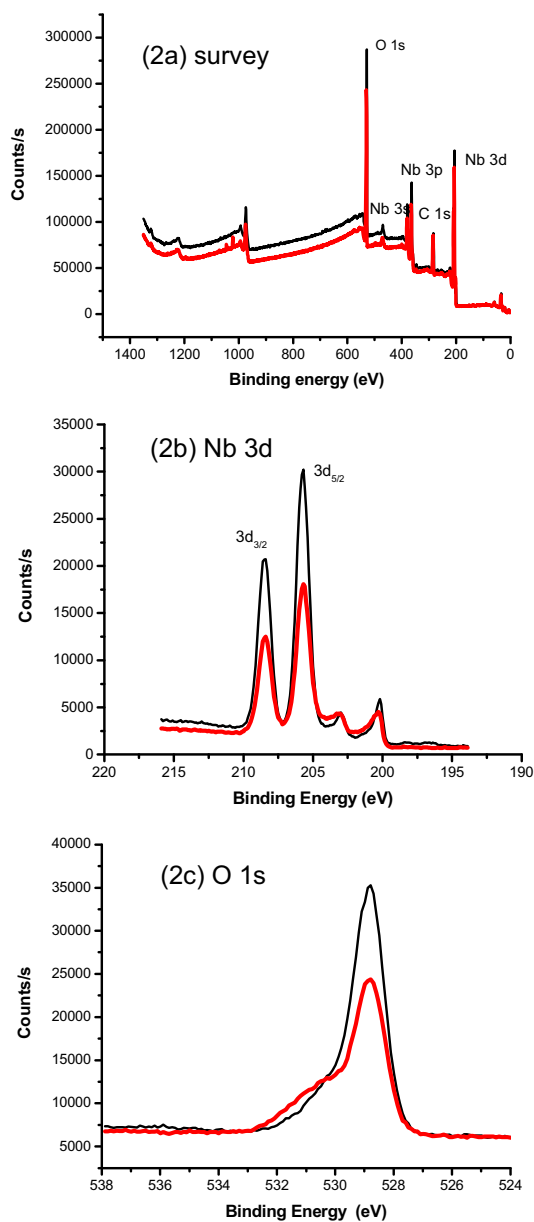


Figure 2: X-ray photoelectron spectroscopy of Nb sample surface: – before exposure; – after exposure.

Surface roughness

The current experiment shows that with increasing material removal rate from bulk Nb, the surface roughness increases. Based on AFM measurements, the root mean square of the surface roughness increases after exposure to Ar/Cl₂ discharge. To solve this problem, we are pursuing experiments with a higher pressure in the reaction chamber. In these conditions, we expect a smaller number of high energy ions and consequently lower physical sputtering, which damages surface.

CONCLUSIONS

- The microwave discharge treatment of Nb surfaces is a convenient, low-cost and less hazardous alternative to the presently used liquid acid etching techniques.
- In preliminary studies, we achieved etching rates up to 2.5 $\mu\text{m}/\text{min}$, comparable with electropolishing processes.
- The surface composition analyses show that no impurities have been introduced into Nb during the microwave discharge treatment.
- The work is in progress to optimize pressure and power density with the aim to obtain smoother surfaces.
- The development of the plasma etching process is combined with an extensive quantitative spectral analysis with the aim to develop simple monitoring techniques and precise discharge diagnostics.
- A modified experimental set-up that includes a single cell cavity has been built. It will be used to determine the influence of the plasma treatment on RF performance of the cavities.

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