

PLASMA ETCHING RATES AND SURFACE COMPOSITION OF BULK NIOBIUM TREATED IN Ar/Cl₂ MICROWAVE DISCHARGE*

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Abstract

To achieve theoretically predicted values of the accelerating fields in superconducting radiofrequency (SRF) cavities, their inside surface should be fairly smooth and free of impurities. Thus, surface preparation is the critical step in production of SRF cavities. Plasma etching process is a dry chemistry technique that can be used to achieve these requirements. It is based on interaction between reactive halogen species produced in the glow discharge and the surface. During this process, volatile Nb halides are evaporated from the surface of Nb, removing the mechanically damaged and contaminated layer. We present a treatment of bulk Nb samples in the Ar/Cl₂ microwave discharge. We have shown that etching rates of bulk Nb as high as 1.5 μm/min can be achieved without introducing impurities in Nb. The rate dependence on various discharge parameters and reactive gas composition is presented. Surface composition and topology measurements were carried out before and after plasma treatment to determine level of impurities and surface roughness. Optimal experimental conditions determined on samples will be applied on single cell cavities, pursuing improvement of their RF performance.

INTRODUCTION

Although plasma etching of Nb thin films has been used in production of Josephson tunnel junctions [1], there are no reports on actual plasma treatment of bulk Nb used for SRF cavities. In discharge plasmas, Nb interacts with chlorine (Cl) and fluorine (F) producing volatile Nb halides. Physical-chemical properties of basic Nb compounds are compiled in Table 1. Reactive species (Cl and F radicals and ions) are produced in pulsed d.c., RF, or microwave glow discharges through collision processes. They interact with Nb on the surface producing volatile compounds that are removed from the surface in the flow of reactive gas. The production of reactive species and, consequently, Nb removal rate is determined by discharge parameters such as input power, pressure, temperature, electron concentration, etc. In our experiments, two different reactive gases and discharge systems were used. For proof-of-the principle, a BF₃ plasma was applied to disk shaped bulk Nb samples in a repetitively pulsed d.c. diode system [4]. Surface roughness characterization of plasma treated samples showed that their roughness was smaller compare to BCP treated samples.

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The primary objective of the plasma etching process in our experiment is to remove the top 100 μm of the bulk Nb surface that could contain impurities and be mechanically damaged. Therefore, etching rates of the order of 1 μm/min are desirable. Literature on plasma etching of Nb thin films shows that etching rates in Cl containing reactive gases is always higher than etching rate in only F containing reactive gasses [5]. Therefore, we performed experiments using Cl₂ as the reactive gas in a microwave (MW) glow discharge system, which is efficient in Cl radical production and evaporation of etching products from the Nb surface.

Table 1: Physical and Chemical Properties of Nb Compounds of Interest for Plasma Etching Process [2,3]

Compound and color	T _{m.p.} [K]	T _{b.p.} [K]	T _c [K]	ΔH _o [kJ/mol]	Vapor pressure at 350 K [Pa]
Nb gray	2741	5017	9.2		
NbO gray	2210		1.2	-405.8	
NbO ₂ white	1040			-796.2	
Nb ₂ O ₅ white	1780		die.	-1899.5	
NbF ₅ colorless	352	512		-1813.3	331.8
NbCl ₅ yellow	477	520		-796.3	14.1
NbN gray	2300		16.2	-233.7	
NbC gray	3773	4573	9.8	-137.6	
NbS ₂ black			6.1		

EXPERIMENTAL SET-UP

The microwave glow discharge system is an electrodeless, “barrel” type reactor that uses a 2.45 GHz microwave radiation source to produce the discharge. Experimental set-up is schematically presented in [6]. The energy transfer from the MW electric field to the gas is more efficient than in commonly used RF discharges, resulting in higher electron and radical density in the discharge. In addition, MW discharges can be stably produced at pressures above 1 Torr and maintain higher gas temperatures compared to RF discharges. We placed disk-shaped Nb samples in a quartz tube, directly above the magnetron antenna where the energy transfer was most efficient. All experiments were performed in an Ar/Cl₂ discharge with various concentrations of Cl₂ in the gas mixture.

ETCHING RATES

Etching rate is calculated from the change in the sample's mass before and after exposure to the discharge. It depends on the concentration of reactive species in gas above the surface of Nb samples. Thus discharge parameters that determine production of reactive species influence etching rate. Etching rate dependence on concentration of reactive gas, pressure in reaction chamber and input power density was investigated. Previously, statistical errors of the determined etching rates were estimated to be approximately 7% and it is indicated on the each graph.

Concentration

In the case of plasma etching based on chemical interaction between the substrate and reactive gas, the etching rate is directly proportional to the amount of reactive gas in the system. In Figure 1, it is shown that etching rate increases with increasing proportion of Cl_2 in the gas mixture. The experimentally determined contribution of Ar sputtering to the etching rate is small compared to the chemical etching rate and could be neglected. It is important to notice that small concentrations, up to 3 volume percent of Cl_2 in the gas mixture, give an etching rate higher than the etching rates achieved with pure Cl_2 in a RF discharge [5].

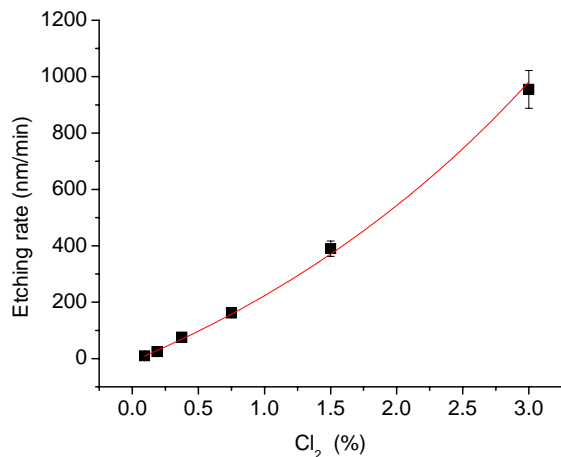


Figure 1: Niobium etching rates as a function of Cl_2 percentage in the Ar/Cl_2 plasma. Solid line presents the fitting curve. Experimental conditions: total flow 196 sccm, pressure in reaction chamber 340 mTorr, and input microwave power 491 W.

Pressure

Chlorine radicals and ions are produced in the glow discharge through Cl_2 collisions with high energy electrons. The rate of radical production, and consequently the etching rate, depends on the input power and pressure. Increasing pressure in the reaction chamber increases the total amount of Cl_2 molecules present in the reaction chamber and consequently the collision rate and the production of Cl radicals. Due to the higher

concentration of reactive species, the maximum etching rate is increasing up to 1.5 $\mu\text{m}/\text{min}$. We present this result in Figure 2. One can see that at pressures above 1 Torr the etching rate becomes constant. One possible explanation for this behavior is the change of the rate-controlling step in the plasma etching mechanism with increasing pressure in the reaction chamber. At lower pressures, the rate-controlling step is the production of reactive species in the discharge. Thus, the etching rate is increasing with pressure. At higher pressures, the amount of reactive species that can be absorbed on the Nb surface becomes constant since Nb surface has only a limited number of active centers that can absorb Cl_2 molecules and radicals. Under these conditions, volatile product formation becomes the dominant rate-controlling step and the etching rate becomes constant.

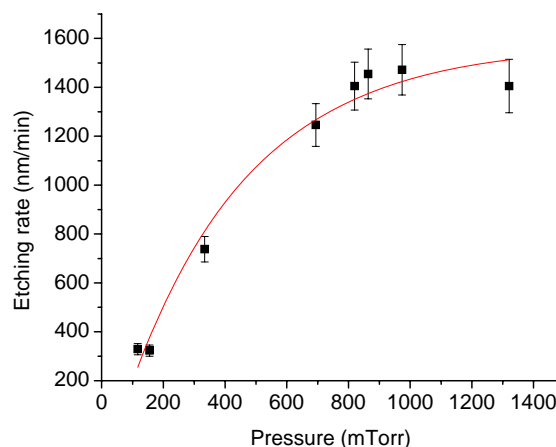


Figure 2: Niobium etching rates as a function of pressure in reaction chamber. Experimental conditions: 3% Cl_2 in the gas mixture and input microwave power 491 W.

Input Power Density

Plasma density increases with input power and accelerates the formation of free radicals. The etching rate of bulk Nb increased with the free radical concentration in the plasma, as shown on Figure 3, up to the optimal value of 2.0 W/cm^3 . Further increasing the power does not increase the etching rate significantly. This experiment was performed at constant gas flow and constant pressure in the reaction chamber, therefore the initial amount of Cl_2 molecules present during the experiment was constant. At some critical power density, the available fraction of Cl_2 molecules becomes smaller on the account of formed Cl radicals, and etching slows down. Additional confirmation for this finding is the fact that the etching rate is more dependent on variations of pressure (total amount of Cl_2) than on variations of power under constant pressure conditions (relative amount of Cl radicals in comparison to Cl_2).

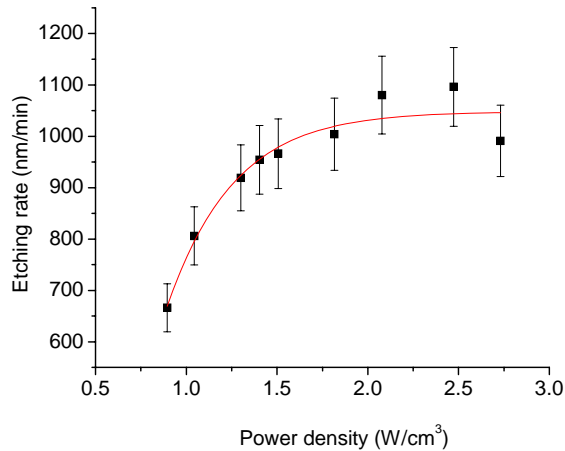


Figure 3: Niobium etching rate as a function of input microwave power. Experimental conditions: 3% Cl₂ in the gas mixture, total flow 196 sccm, and pressure in reaction chamber 340 mTorr.

IMPURITIES CONTENT

Surface composition before and after exposure to Ar/Cl₂ discharge was performed using X-ray photoelectron spectroscopy. An XPS survey spectrum does not show any other elements but Nb, O and C at the surface of Nb samples. Enlarged region of Cl 2s spectral line is presented on Figure 4. No Cl traces were found. High resolution spectra of Nb 3d and O 1s region were presented elsewhere [7]. High resolution spectra of Nb 3d line shows that oxide layer after exposure is thinner than native oxide layer before exposure. High resolution spectra of O 1s line shows that after exposure remaining O is in the shape of Nb oxides only. There are no adsorbed hydroxides on the Nb sample surface.

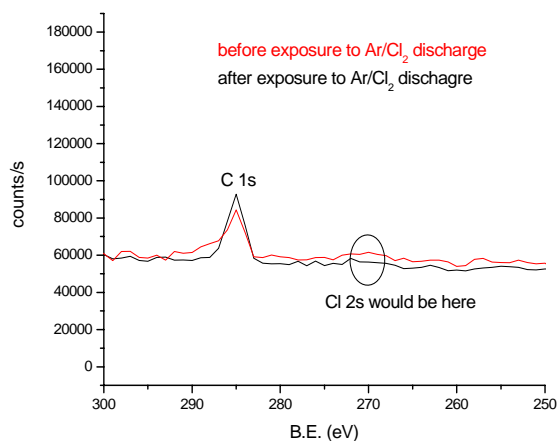


Figure 4: XPS survey spectral of 250 eV to 300 eV region.

CONCLUSION

- Microwave discharge treatment of Nb surfaces is a convenient, low-cost and potentially cleaner alternative to the presently used liquid acid etching techniques.
- We achieved etching rates up to 1.8 μm/min, comparable with wet etching processes.
- Surface composition analyses show that no impurities have been introduced into Nb during microwave discharge treatment.
- Work is in progress to adjust pressures and power density in a multi step process with the aim to obtain smoother surfaces.
- Development of the plasma etching process is combined with extensive quantitative spectral analysis with the aim to develop simple monitoring techniques and precise discharge diagnostics.
- Modified experimental set-up that includes 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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