

# WET OXIDATION OF AN EPITAXIAL NIOBIUM FILM

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## Abstract

Freshly ion-milled surfaces of epitaxial niobium film were exposed to humid environments and then depth profiled for contaminants by Secondary Ion Mass Spectroscopy (SIMS). Two exposures were used: 30% humid laboratory air, and heavy water vapour in argon.

## INTRODUCTION

This study is part of our long-range program to develop better deposited film SRF accelerator cavities[1]. It was designed to examine the uptake of oxygen and hydrogen by a niobium film when exposed to dampness typical of cavity handling and storage conditions.

A bare niobium surface left exposed in the laboratory will quickly begin to absorb light elements. Its outermost few nanometers oxidizes, tending to passivate the surface. Niobium SRF cavities are typically oxide-passivated before exposure to lab air. In recent detailed studies of oxidation processes in niobium films, Hellwig [2] found that the effectiveness of the passivation layer depends on the history of the oxidation process, and on the initial substrate surface condition. He also found very little hydrogen to be absorbed during atmospheric oxidation.

Hydrogen is known to enter the niobium metal of a typical RF cavity during polishing and cleaning operations, and is thought to be uniformly distributed throughout the niobium lattice at room temperature [3]. At low temperature it tends to move to the surface, there condensing into islands of normally conducting niobium hydride. The resulting "Q-disease" is traditionally avoided by rapid cooling to operating temperature, thus freezing the hydrogen into the lattice before it can diffuse to the SRF surface.

Interest in the interaction of moisture with the niobium lattice is further stimulated by the success of a recent innovation in SRF cavity preparation, in which a bulk niobium cavity is heated to 120 C for 48 hours just before testing [4]. The interest arises because this is the wrong temperature to affect movement of contaminants in a free lattice, and because the required time is much longer than expected for simple evaporation of surface water.

## EXPERIMENTAL PROCEDURE

We compare absorption of contaminants from laboratory air by a freshly ion-milled niobium surface with the absorption of contaminants by an oxidized niobium surface, using depth profiling by SIMS.

This profiling process systematically mills away the metal surface. It thus makes a local pit or crater, and samples the secondary ions emitted as it mills away the surface of the crater floor. In our experiments, we can readily expose a fresh surface to a chosen atmosphere as follows: interrupt the profile at a chosen depth, move the sample out of the SIMS main vacuum chamber into the forechamber, let a moist atmosphere into the forechamber for a chosen time, then pump down, return the sample to the main chamber and continue depth profiling. SIMS can be made sensitive to hydrogen, and has excellent depth resolution.

We report here two separate series of measurements made on the same film sample. In the January 2003 series we recorded profiles of  $H^1$ ,  $C^{12}$ ,  $O^{16}$ , and  $Nb^{93}$  from the surface through the full depth of the film. Profiling was interrupted at depth 56 nanometers, to expose the freshly milled surface to lab air at 20 C and 30% relative humidity for 23 hours before completing the profile. A similar run of this series lengthened the exposure to 11 days. The tempting hypothesis that both the oxygen and the hydrogen come from water absorption by the niobium surface was examined in the May 2003 series of profiles. In these runs, the fresh surface was exposed not to air, but to an atmosphere of argon that had been bubbled through heavy water,  $D_2O$ . In the May series  $H^1$ ,  $H^2$  ( $D^2$ ),  $C^{12}$ ,  $O^{16}$ , and  $Nb^{93}$  were profiled.

Our epitaxial niobium film sample was produced at Cornell by magnetron sputtering onto an A-cut single crystal sapphire substrate [1]. After sputtering and cooling down, it was stored in a Drierite [5] box for 2 days before the January measurements began, and again between the January measurements and the May measurements.

SIMS studies were done at Surface Science Western (SSW), University of Western Ontario in London, Canada. The Cameca IMS-3f ion microprobe was set to detect negative secondary ions emitted by the current surface layer. The primary beam of positive cesium ions at 10 kV continuously ion-milled away the surface, while secondary ion rates were recorded as a function of milling time. The process made a 250 micron square crater, whose final depth was determined subsequently by a Tencor P-10 surface profilometer, and used to infer SIMS profile depth from the recorded ion-milling time. During SIMS profiling, secondary ions were accepted from only the central 60 micron diameter spot of the 250 micron square surface of the crater floor. Profiles with a depth range of 50 to 100 nm used a primary ion current of 10 na, and some deeper ranging profiles used currents of 100-200 na.

Calibration is always a concern with SIMS because the secondary emission ratio varies from element to element.

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## RESULTS

Moreover it can be substantially enhanced by the presence of oxygen in the film, with the oxygen's effect probably depending on its state of chemical bonding. To illustrate this effect, we note that the concentration of niobium should be almost constant, with a slight dip in a heavily contaminated surface layer, as is typically observed in a surface that has been exposed to air for days. On the other hand, profiles starting at a newly exposed surface show an *enhanced* counting rate for Nb<sup>93</sup> in the first 5 or 10 nm, which is caused by the increased sensitivity. None of the data shown here have yet been corrected for this effect, so for the profiles H<sup>1</sup>, H<sup>2</sup>, and C<sup>12</sup> you should allow for a factor like that required to make the Nb<sup>93</sup> profile a straight horizontal line, perhaps with a dip in the first few nm.

The effect of exposure to laboratory air at 30% relative humidity for 23 hours is quite noticeable, as may be seen from Figure 1. Here the vertical profiles begin (depth = 0) at the surface of the recently sputtered film. The film had been stored for two days in air at atmospheric pressure but in a plastic box packed with Drierite[5]. It shows a strong oxygen signal falling off a factor of 10 in the first 5 nm, another factor of 5 in the subsequent 15 nm, and a factor of 3 in the next 35nm. Hydrogen is very mobile in the lattice at room temperature, and is usually uniformly distributed throughout, except for a tendency to have escaped into the atmosphere from the near surface layer.

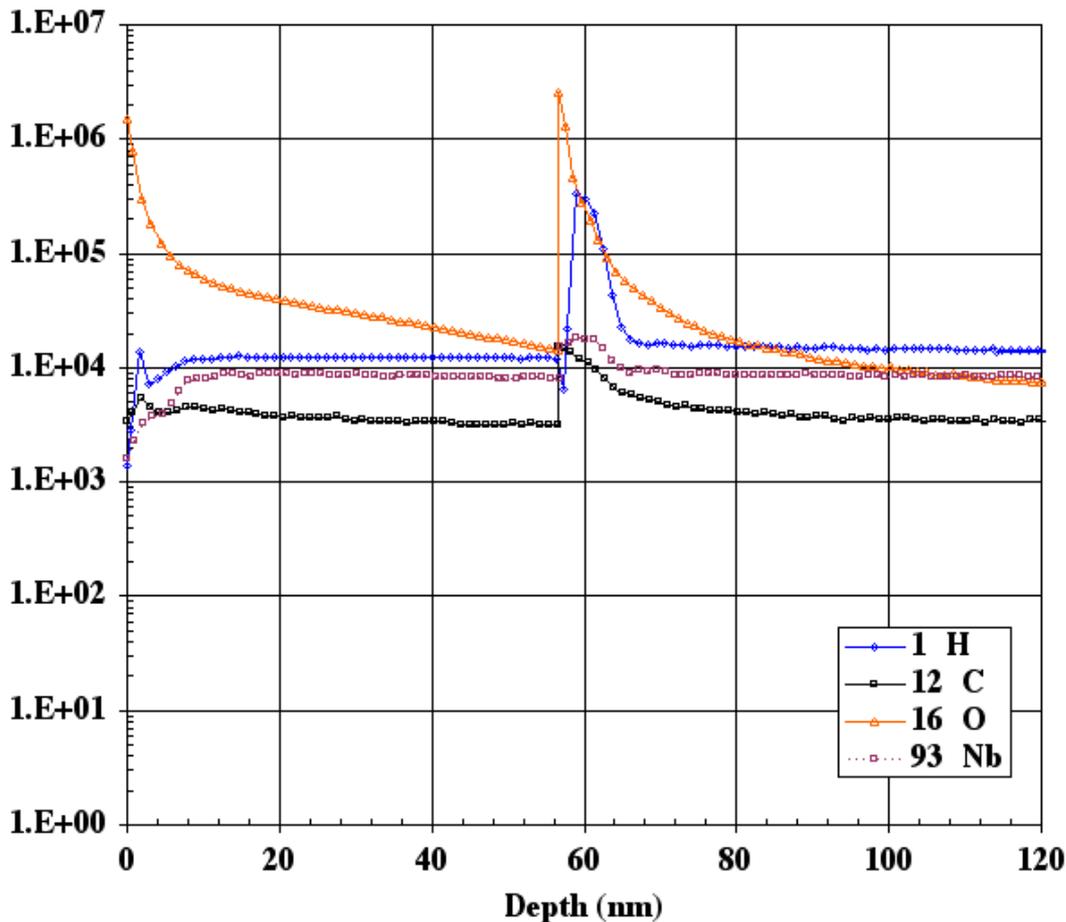


Figure 1: Profiles stopped at 56 nm for 23 hour exposure of milled surface to laboratory air at 30% relative humidity.

After the interruption at 56 nm and the exposure to laboratory air at 30% relative humidity, there is an abrupt rise in the oxygen concentration, while hydrogen and carbon (even after allowing for an oxygen enhancement of the secondary emission ratio as mentioned above) also show very striking peaks. Hydrogen has only escaped the lattice in the 2 or 3 nanometers nearest the surface, and a peak in its concentration remains in a layer a few nanometers deeper than the region with the highest oxygen concentration. In this deeper region oxygen should

be present not in niobium pentoxide, but in NbO and suboxides.

To see how stable the hydrogen peak is at room temperature, we looked to see if such a peak would remain after many days. Figure 2 shows the contamination of a similar new surface after an exposure to the same laboratory air for 11 days. The profiles taken while the fresh surface was being milled were recorded, but are not shown. That ion milling was done at 100 nanoamps, and the concentration scales are different. A further difference

from Figure 1 is that this milling was pursued deeper into the film to 310 nanometers before stopping for exposure to air for 11 days. Note that the beginning depth for the profiles shown in Figure 2 is thus 310 nm. However, the

effects exhibited are very similar. There is a hydrogen peak below the surface, which has remained there for 11 days without spreading uniformly through the lattice.

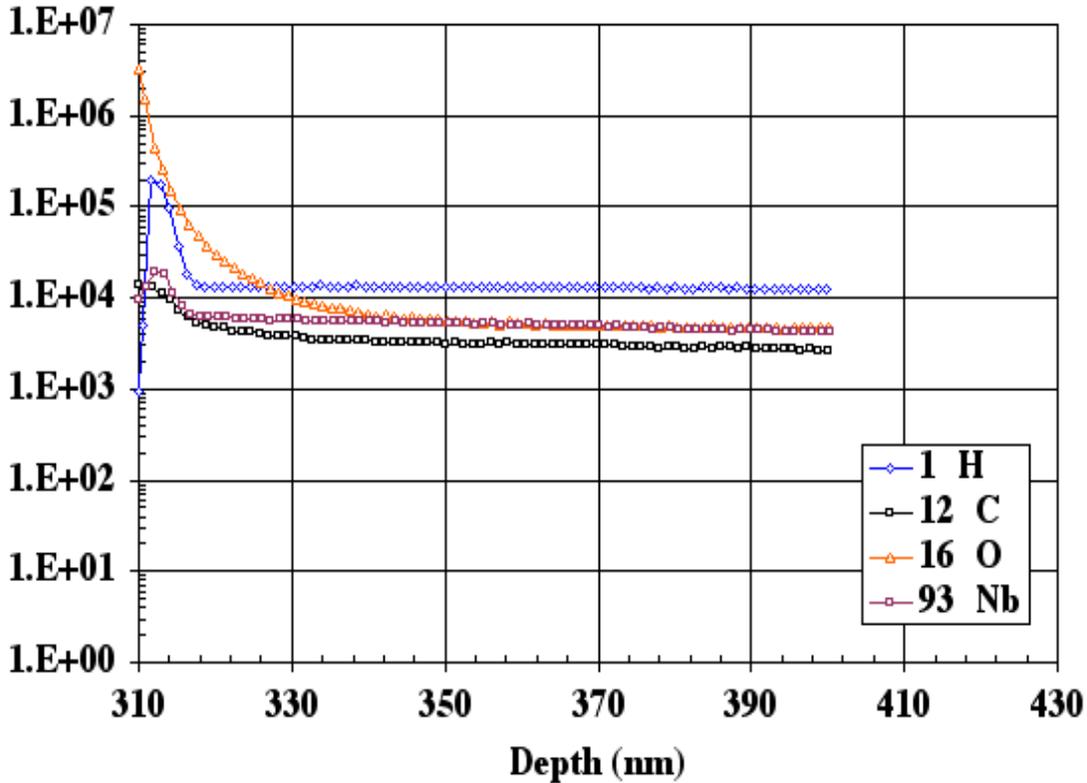


Figure 2: Profiles stopped at 310 nm for 11 day exposure of milled surface to laboratory air at 30% relative humidity

The oxygen absorbed by these newly milled surfaces could have come either from the air or the water vapour in it. As for hydrogen and carbon, there are hydrocarbons in laboratory air. The hydrogen could have come from the water vapour, from hydrocarbons or from the well-stocked hydrogen reservoir deep inside the lattice itself.

To examine these questions our next measurements used exposure to an atmosphere of humid argon, and where the humidity was introduced by bubbling the argon through heavy water, D<sub>2</sub>O. Thus its hydrogen was deuterium, and mass 2, rather than mass 1.

In Figure 3, we see surprisingly similar profiles, except for the addition of the deuterium profile in red. Before the pause for exposure (the first 62 nm), the deuterium profile is suppressed a factor of almost 7,000, as appropriate for the known natural abundance of deuterium.

After this brief 30 minute exposure to a heavy water humidified argon atmosphere, the deuterium signal has

already risen up to join the others. Just beneath the newly exposed surface at 62 nm, the O<sup>16</sup> profile rises 2 orders of magnitude, and the H<sup>1</sup> profile shows a very definite peak within the oxygen rich layer. Below it there is also a less distinct H<sup>2</sup> peak, and there is also a substantial C<sup>12</sup> peak.

Figure 3 also shows that deuterium has quickly diffused deep into the lattice, although the signal level diminishes slowly with depth. To see how the diffusion of deuterium had proceeded on a broader scale, we immediately made a new set of profiles whose axis was laterally displaced by several hundred microns from the vertical axis of those shown in Figure 3. These profiles are shown in Figure 4, where we see the deuterium signal is strong, but almost an order of magnitude below that shown by the profile beginning below the exposed fresh surface in Figure 3. Profiles in Figure 4 also show strong peaks in oxygen, carbon, hydrogen and deuterium in the near surface layers.

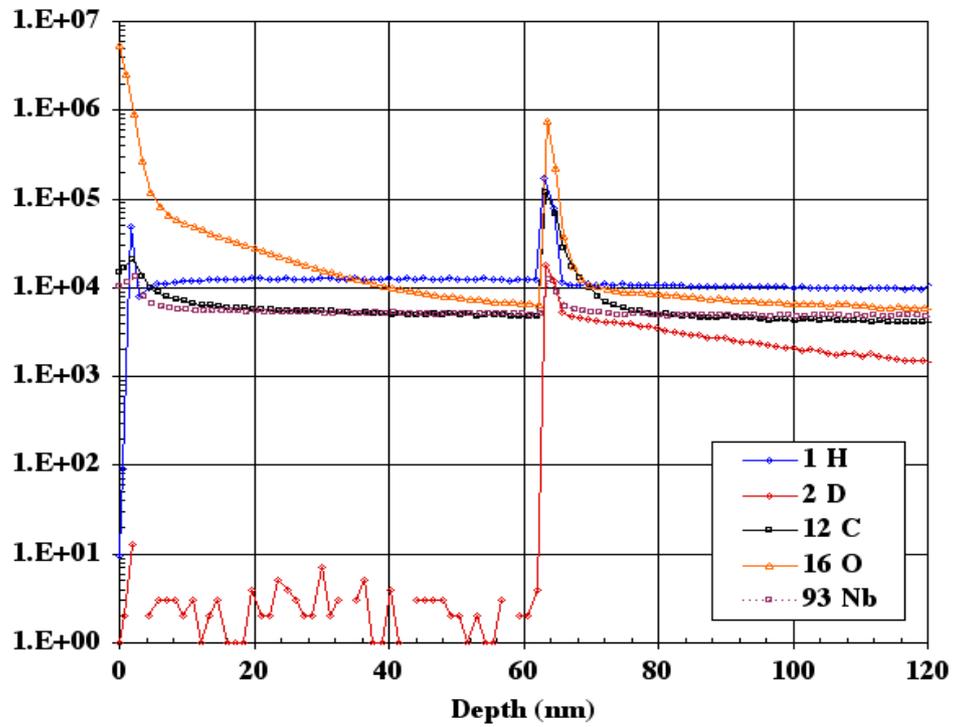


Figure 3: Profiles stopped at 62 nm for 30 minute exposure of milled surface to D<sub>2</sub>O in argon atmosphere.

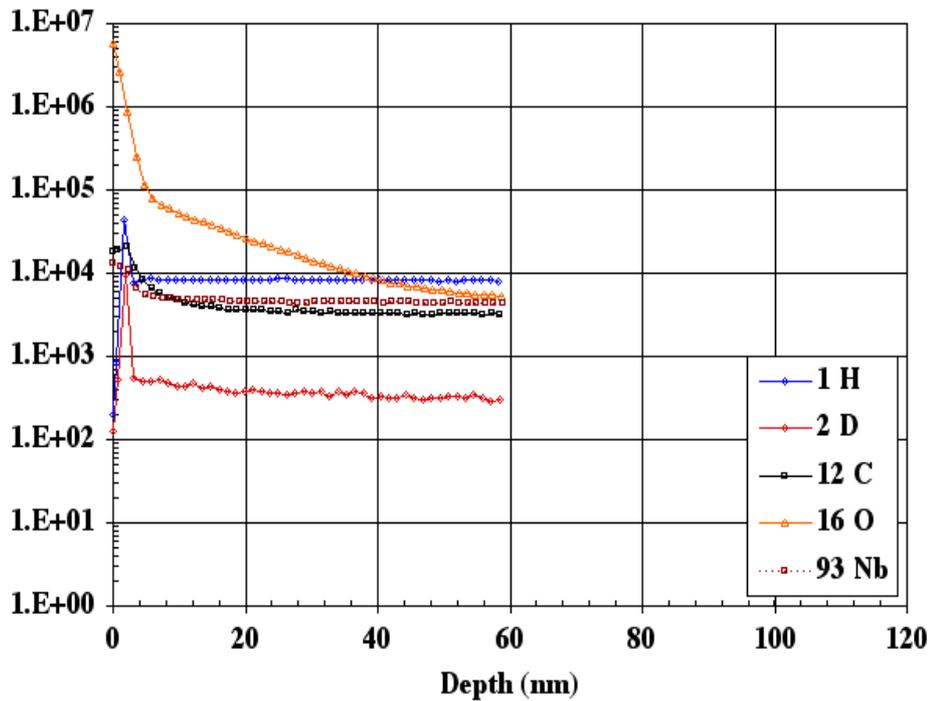


Figure 4: Control profiles, made minutes after the profiles shown in Figure 3, in a new crater displaced laterally by several hundred microns

## CONCLUSIONS

We see from Figure 3 that water vapour participates actively in oxidation of a freshly exposed niobium surface, even water vapour in an argon atmosphere. After this brief 30 minute exposure to heavy water vapour in argon, oxygen had begun to form its familiar surface layer, and to penetrate deeper into the lattice. The deuterium profile goes right through the film, but unlike hydrogen it diminishes with depth. Half a millimeter away (Figure 4) the deuterium signal is still weaker, so deuterium was still diffusing while the measurements were being made.

Hydrogen has a tendency to concentrate just under the oxidized surface. At room temperature it remains there for days. The  $H^1$  profile in Figure 3 suggests that part of it can come there from the hydrogen reservoir in the deeper lattice. Further work should examine this hydrogen peak's stability, and whether it can be dispersed by heating to 120 C for 48 hours. Further measurements should use "extra-heavy" water ( $H_2^{18}O$ ) to allow study of contamination of a niobium film through an oxide-passivated surface.

Freezing out the Q-disease by rapid cooling may solve only some of the problems caused by hydrogen in niobium cavities. The next step towards reliable high gradients may require more attention to hydrogen. For a beginning, SRF cavities could be kept in a desiccated environment. High pressure rinsing (HPR) could use some projectile other than water spray.

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- [5] "Drierite" is a commercial name for the common laboratory desiccant anhydrous calcium sulfate.