Improvement and protection of niobium surface superconductivity by atomic layer deposition and heat treatment

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A method to treat the surface of Nb is described, which potentially can improve the performance of superconducting rf cavities. We present tunneling and x-ray photoemission spectroscopy measurements at the surface of cavity-grade niobium samples coated with a 3 nm alumina overlayer deposited by atomic layer deposition. The coated samples baked in ultrahigh vacuum at low temperature degraded superconducting surface. However, at temperatures above 450 °C, the tunneling conductance curves show significant improvements in the superconducting density of states compared with untreated surfaces.

For several decades, the performances of accelerating niobium superconducting radio frequency (SRF) cavities have been continually improved to reach now a reproducible maximum accelerating field of ~30 MV/m and quality factor $Q$ above $10^{10}$. However, unresolved mysteries remain and prevent cavities from reaching the intrinsic Nb limits believed to be 55 MV/m. An SRF cavity is subject to an accelerating rf field $E(\omega)$ that induces an oscillating magnetic field $B(\omega)$ on the inner walls of the cavity. Penetration of the latter implies superconducting screening currents on a length scale $\lambda_{NB}$, the niobium penetration depth (~45 nm at $T=2$ K). The dissipation mechanisms are confined to a region of depth $\lambda_{SB}$ over which supercurrents interact strongly with the surface oxides. Up to recently, a detailed picture of these strong interactions and, in particular, the mechanisms by which oxygen influences the performance of niobium cavities was still missing.

The uncontrolled complex sets of oxides growing on the surface of air-exposed niobium lead to well-known problematic effects such as weakened superconductivity, proximity effects, or pair breaking phenomena. For niobium-based devices, submicron Josephson tunnel junctions or single electron transistors of these problems have been cured by capping a cleaned niobium surface with alumina. However, at present there are no realistic ways to remove the oxides from the inner wall of niobium cavities and to deposit a uniformly thin protective layer on a complex-shaped cavity. We propose an original approach to overcome these problems: the combination of the atomic layer deposition (ALD) technique with a subsequent annealing in ultrahigh vacuum (UHV). We probe the occurrence of surface oxides with x-ray photoemission spectroscopy (XPS) and the near surface superconductivity by tunneling spectroscopy.

Tunneling spectroscopy and XPS measurements were done on air-exposed cavity-grade niobium coupons capped with a protective alumina layer deposited by ALD. ALD is a self-limiting, sequential surface chemistry that has the unique ability to achieve uniform atomic scale deposition control on arbitrary complex-shaped substrates. The pinhole-free and dense structure of ALD made films make $\text{Al}_2\text{O}_3$ an ideal protective and diffusion barrier. Pieces of monocrystalline (110) and polycrystalline Nb were cut from larger sheets used to construct SRF cavities. These pieces were electropolished, cleaned with de-ionized purified water, and dried in air in a manner similar to that done on cavities. They were later introduced into the ALD reactor and coated with 3 nm of $\text{Al}_2\text{O}_3$ at a temperature of 120 °C under a flow of ultrapure nitrogen gas. A detailed description of the deposition process can be found in Ref. 6. The coated samples were baked in UHV at temperature ranging from 250 to 500 °C and the XPS spectrum of the Nb 3d core level was measured simultaneously. After each thermal treatment, the samples were transferred in air to the point contact apparatus and the surface superconducting density of states (DOS) was probed by tunneling spectroscopy at a temperature of 1.7 K as described elsewhere.

The evolution of the oxide’s composition and the superconducting DOS at the surface of a polycrystalline sample as a function of the baking temperature is shown in Fig. 1. For annealing temperature up to 380 °C, the tunneling spectroscopy [Fig. 1(a)] reveals degraded superconducting features as compared to unbaked samples (in blue) with a zero bias conductance (ZBC) as high as 65% of the normal conductance (measured at $V=12$ meV). Importantly, for an anneal at 450 °C for 24 h, the tunneling conductance becomes much sharper and the ZBC improves by a factor of 5 down to ~5%. In parallel, the XPS spectrum [Fig. 1(b)] that probes an ~3.5 nm depth on the surface shows a reduction in $\text{Nb}_2\text{O}_5$ to suboxides such as $\text{NbO}$ and $\text{NbO}_2$ below 450 °C (in green and orange), whereas at 450 °C 24 h the XPS unveils the presence of $\text{NbO}$ only with sharper metallic Nb peaks. The same reduction in the ZBC down to ~5% is found reproducibly on Nb single crystals [Fig. 1(c)] baked at...
The evolution of the gap coincides with the increasing peak 24 h, the superconducting DOS is strongly impaired, exhibiting a broadening of the energy gap may thus be a result of a proximity effect between the Nb and a thicker NbO. The corresponding variations in the inelastic scattering value $\Gamma$, jumping from 0.6 meV at 30 °C to 1 meV at 250 °C 2 h and decreasing back to 0.48 meV at 380 °C 24 h, do not seem to correlate with the oxide composition. This can be explained, however, by the competition between the strong oxide dissociation above 200 °C (Ref. 13) and the diffusion of oxygen into Nb. At 250 °C for 2 h, the diffusion length $L_{\text{diff}}$ calculated from the diffusion equation of oxygen into the bulk niobium is $120 \text{ nm} \sim 2\lambda_{\text{Nb}}$, whereas above 380 °C for longer time, 24 h, the diffusion is faster ($L_{\text{diff}} \approx 1 \text{ mm}$) and oxygen is driven far into the bulk. Consequently the $\Gamma$ value decreases. Interestingly, the evolution of the superconducting parameters correlates well with cavity performance after similar baking treatment. 14

Finally, for the highest baking temperature, >450 °C for 24 h, the total intensity of niobium oxide peaks composed of only NbO decreases drastically in agreement with Ref. 10 and with the idea that oxygen diffuses far into the bulk. This
result in a striking improvement in the superconducting properties: \( \Gamma = 0.1 \) meV and \( \Delta \) recovers the bulk Nb gap value of 1.55 meV. The saturation of the NbO peak intensity above 450 °C may be an indication of a more stable and ordered NbO phase, as proposed by Hellwig et al.,\(^{15}\) with a sharper NbO–Nb interface that would also contribute to improve the proximity effect of the superconducting DOS.

Higher temperature anneals will be carried out on coated niobium coupons to search for further improvements in the superconducting DOS, aiming at surface properties of an ideal Nb superconductor with no inelastic scattering and optimum Nb cavity performance.

In conclusion, the overall evolution of the superconducting parameters \( \Gamma \) and \( \Delta \), together with the oxide composition as a function of the baking temperature, can be explained by a competition between Nb-oxide dissociation and oxygen diffusion into the bulk. Such a model has been suggested for low temperature (\(<150 \) °C) anneals by Ciovati,\(^{15}\) but it has not been proven experimentally for high baking temperature. The close correlation of the results in Fig. 2(a) with cavity performance for the same temperature and baking time points to tunneling spectroscopy as a relevant tool to explain and predict cavity performance and inexpensively test various surface treatment protocols. A single cell 1.3 GHz cavity has been coated with 10 nm Al\(_2\)O\(_3\) and 3 nm Nb\(_2\)O\(_5\) (to avoid multipacking effect) and rf performance test will be conducted soon.

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