

Crystallinity in niobium oxides: A pathway to mitigate two-level-system defects in niobium three-dimensional resonators for quantum applications

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Materials imperfections in Nb-based superconducting quantum circuits—in particular, two-level-system (TLS) defects—are a major source of decoherence, ultimately limiting the performance of quantum computation and sensing. Thus, identifying and understanding the microscopic origin of possible TLS defects in these devices will help develop strategies that eliminate them, which are key to superconducting qubit performance improvement. In this paper, we demonstrate an order-of-magnitude reduction in two-level system losses in three-dimensional superconducting radio frequency (SRF) niobium resonators by a 10-h high vacuum (HV) heat treatment at 650 °C, even after exposure to air and high-pressure rinsing (HPR). X-ray photoelectron spectroscopy (XPS) and high-resolution scanning transmission electron microscopy (STEM) reveal an alteration of the native oxide composition regrown after air exposure and HPR and the creation of nanoscale crystalline oxide regions, which correlates with the measured tenfold quality factor enhancement at low fields of the 1.3 GHz niobium resonator. Tunneling spectroscopy measurements show a pronounced proximity effect that further confirms the presence of metallic layers on the niobium surface.

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I. INTRODUCTION

Superconducting niobium resonators, originally developed for particle acceleration with exceptionally high quality factors ($Q > 10^{10}$ – 10^{11}), are gaining attention in quantum computing applications [1–5]. These resonators are excellent candidates for storing quantum information as quantum d-level systems (qudits) due to their remarkably long lifetimes of up to several seconds and their extensive accessible Hilbert spaces, which provide the potential for direct encoding of qudits and offer advantages over the two-level qubit encoding [3–5]. Niobium SRF cavities have also been proven very useful in studying the losses in two-dimensional superconducting qubits and measuring

them with a high level of accuracy, such as in the work of Checchin *et al.* [6] using a 3D niobium cavity to isolate the silicon substrate and quantify its loss contribution. In another study, Romanenko *et al.* [7,8] used bulk Nb SRF cavities as a three-dimensional (3D) resonator and showed that two-level-system (TLS) defects present in the niobium native oxide dominate the losses in 3D resonators below 1.4 K and at low fields in a similar manner to what has been observed in 2D superconducting qubits [8,9]. In this sense, niobium cavities can be seen as a tool to investigate the microscopic origins of TLS defects in Nb-based quantum devices and a platform on which to experiment with different approaches to suppress these loss channels in niobium 2D qubits.

Upon exposure to air, niobium forms an amorphous oxide layer with varying stoichiometries that is known to host TLS defects [7–12]. Recent studies on three-dimensional niobium resonators have shown that these native oxide layers contribute substantially to the degradation of quality factors (Q), reducing it to about 2×10^{10} in 1.3-GHz cavities [7,8,10] in the TLS-dominated regime

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at low accelerating fields ($\leq 10^{-2}$ MV/m). One way of increasing this quality factor has been demonstrated using high vacuum annealing from 340–450 °C and durations from 2.5 h up to 5 h, after which the cavity is maintained in a vacuum environment to prevent reoxidation [7,10,13]. While effective, this method is impractical for quantum computing and sensing applications due to the need for sustained vacuum conditions. Another approach for suppressing two-level system losses has been reported by Kalboussi *et al.* [14], where the 3D resonators have been coated with a thin layer of aluminum oxide using atomic layer deposition (ALD), followed by a heat treatment at 650 °C for 10 h. This resulted in the reduction of the niobium native oxide while keeping the niobium metal passivated by the ALD layer. Even though this approach offers an air-stable improvement in the low-field quality factor, it is worth noticing that the amorphous Al_2O_3 deposited by ALD itself exhibits (like all other dielectric materials) TLS losses that should ideally be avoided.

In this article, we report air and water-stable improvement of the low-field quality factor of a niobium single cell 1.3-GHz cavity after thermal treatment at 650 °C for 10 h in high vacuum (HV). We also achieve some of the best performances reported for 1.3 GHz niobium 3D resonators after air exposure and high-pressure rinsing (HPR) in the TLS-dominated regime with a Q_0 of 9×10^{10} , at low fields ($\leq 10^{-2}$ MV/m) corresponding to a resonator lifetime $\tau \sim 15$ s.

By performing x-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM), we discovered that this thermal treatment changes the chemical and structural nature of the niobium oxides after reexposure to air and high-pressure rinsing. In particular, we reveal the appearance of crystalline regions in the native oxide layer, which is associated with low TLS contributions and explains the high quality factor measured.

II. EXPERIMENTAL DETAILS

In this study, we report rf results from a 1.3-GHz niobium cavity before and after annealing at 650 °C for 10 h in high vacuum (pressure $< 10^{-6}$ mbar). Before the thermal treatment, the cavity underwent a standard electropolishing process to prepare its surface [15], followed by a high-pressure rinsing with ultrahigh purity water under a pressure of 90 bar for 1.5 h [16]. Subsequently, the cavity was mounted for cryogenic testing in an ISO5 clean room environment. The cryogenic testing was performed in the Synergium vertical test facility at CEA, in which the cavity was submerged in a dewar of liquid helium and then cooled through pumping to 1.4 K. An rf test was conducted by employing a phase-lock loop to lock the cavity onto its resonance frequency, enabling the derivation of the intrinsic quality factor (Q_0) and field. The low-field region quality factor was measured using the cavity ring-down

method after the rf power was turned off, as described in Ref. [17]. After the test, the niobium cavity was introduced to the vacuum oven inside a titanium box with niobium caps on both cavity flanges to prevent oven contamination and underwent annealing at 650 °C for 10 h in a pressure lower than 5×10^{-6} mbar using a ramp of 6 °C/min. After cooling passively, the vacuum was broken in the oven and the cavity was transported to the clean room again and remained air-exposed there for a few weeks before undergoing a second high-pressure rinsing and preparation for the rf test.

In order to investigate the chemical, structural, and electronic properties changes on the niobium surface, x-ray photoelectron spectroscopy, transmission electron microscopy (TEM), and point contact tunneling spectroscopy (PCT) analyses were performed on two types of samples from air-exposed cavity-grade niobium coupons: (1) electropolished then high-pressure rinsed and (2) electropolished, high-pressure rinsed then annealed in the same conditions used for the cavity followed by a second HPR.

The XPS measurements were acquired using an Escalab 250 XI spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a monochromatic x-ray $\text{Al-K}\alpha$ source ($h\nu = 1486.6$ eV) and a charge compensation system. The diameter of the analytical spot size is 900 μm . The binding energies were calibrated against the C1s binding energy set at 284.8 eV. The spectra were treated using CASAXPS software [18].

For the STEM analysis, cross-section lamellae were prepared in a focused ion beam (FIB) microscope using a Ga ion source at the University of Lille. Note that, for the FIB preparation, the sample surface was first protected by a deposition of carbon followed by another layer of platinum and a standard lift-out procedure was performed. Bright field and high-angle annular dark-field (HAADF) images of the cross-section samples were acquired at LPS using a Nion Ultrastem 200 scanning transmission electron microscope operating at 100 kV. The probe convergence angle was 35 mrad. The tunneling spectroscopy was performed on a homemade apparatus at a temperature of 1.8 K, as described in Ref. [19].

III. RESULTS AND DISCUSSION

A. Resonator rf tests

Figure 1 shows the results of the rf tests performed on the 1.3-GHz niobium cavity at 1.43 K. The baseline rf test (green curve) shows the typical saturation of the quality factor Q_0 of air-exposed electropolished niobium cavities without any thermal treatments with values at low fields of around 1×10^{10} at 0.01 MV/m, as has been reported elsewhere [8,10,14] and which is characteristic of the presence of two-level systems. The blue curve represents the rf test after annealing the same niobium cavity at 650 °C for 10 h at high vacuum and exposing it to air for a

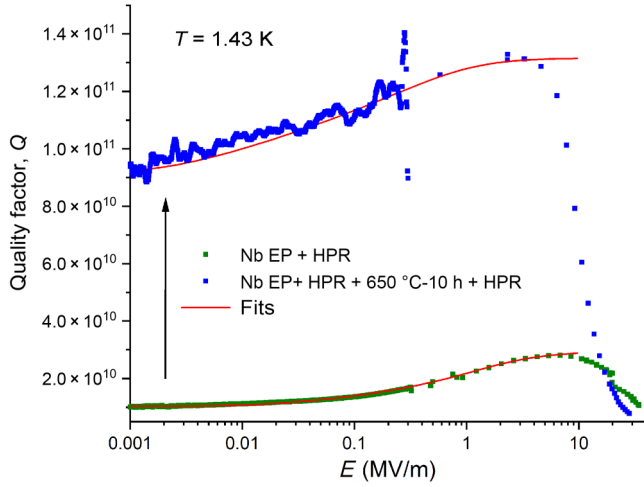


FIG. 1. Graph of Q_0 vs E for 1.3-GHz niobium cavity before and after annealing at 650 °C–10 h.

few weeks and high-pressure rinsing. After this treatment, the Q_0 saturation level increased approximately tenfold, attaining an unprecedented value of 9×10^{10} at saturation (0.001 MV/m) after air exposure and high-pressure rinsing.

It is worth mentioning that, among reported rf tests on bulk niobium cavities [7,8,10,14], this 10 h treatment at 650 °C showed one of the highest performances in the TLS-dominated regime. As a matter of fact, previous studies tested Nb cavities with different treatments and, in particular, annealing at 340 °C for 5 h, which showed improvements over the electropolished baseline with a quality factor value of 7×10^{10} at 0.01 MV/m [7,10]. This enhancement was ascribed to the complete dissolution of the native niobium pentoxide Nb_2O_5 during the annealing process. However, one needs to keep the cavity under vacuum to prevent Nb_2O_5 from regrowing upon exposure to air; otherwise, the cavity reexhibits electropolished (EP) performances. The fact that annealing the niobium cavity at 650 °C for 10 h results in significantly higher Q_0 , which is maintained after HPR and exposure to air, suggests that time-stable and irreversible modification has occurred at the niobium surface of the resonator.

The red lines in Fig. 1 are fits that use the interacting and noninteracting two-level-system model described in Ref. [20]. The fitting and the extracted TLS parameters are shown in Table I. The fit parameters for the baseline EP are consistent with the ones obtained in Refs. [14,20] for a niobium EP cavity with similar rf performances. The c

parameter that describes the saturating value of Q at very low electrical fields is more than ten times lower after the annealing. Following Ref. [20], the density of TLS defect, σ_{TLS} , and the dielectric losses, $\tan(\delta_{\text{TLS}})$, can be calculated from the fitting parameters assuming a dielectric constant for Nb_2O_5 of 30 and knowing the thickness of the oxides, as described later. These fitting values reveal an order-of-magnitude reduction in the TLS-defect density and losses in the annealed Nb cavity as compared with native niobium oxides present in the cavity baselines.

In order to identify the microscopic origins of these changes in the rf performances and TLS losses, we performed XPS measurements on niobium samples that underwent the same processes as the cavity, along with high-angle annular dark-field imaging and a fast Fourier transform (FFT) analysis.

B. Chemical and structural analysis of the

1. Nb surface

Fig. 2 summarizes the surface analysis obtained on a cavity-grade electropolished Nb sample that underwent a high-pressure rinsing without any thermal posttreatment. XPS provides a detailed analysis of the Nb oxidation state and chemical environment. High-resolution spectra of the Nb 3d core levels were recorded using a constant pass energy of 20 eV. In order to fit the peaks, we used an asymmetrical line shape for the metallic component of the Nb 3d core levels and symmetrical mixed Gaussian-Lorentzian line shapes to fit the other chemical states. An area constraint of 3:2 was applied to the spin-orbit doublets of Nb 3d_{3/2} and Nb 3d_{5/2} levels and their binding energies were set apart by 2.7 eV. Finally, the valence state of every peak was identified by its binding energy from the literature [21,22]. The binding energy ranges for Nb 3d_{5/2} in different valence states are as follows: 202.2 ± 0.05 eV, 203.1 ± 0.2 eV, 204.3 ± 0.5 eV, 205.5 ± 0.2 eV, and 207.6 ± 0.1 eV, which are considered as Nb, Nb_2O , NbO, NbO₂, and Nb_2O_5 , respectively. The results of the peak fitting for Nb 3d chemical states are shown in Fig. 2(a). We observe that the surface is composed mostly of Nb_2O_5 (86.6%), a small fraction of suboxides, such as Nb_2O (1%), NbO (1.6%), and NbO₂ (2.7%), and metallic niobium (8%). This oxide composition is typical of an uncoated electropolished Nb sample subject to a high-pressure rinsing with a native oxide composition dominated by Nb_2O_5 , which is in agreement with previous studies [14,21,22].

TABLE I. Fitting parameters using the interacting and noninteracting TLS model [20].

Treatments	c [C^2/J]	E_C [V/m]	ξ	$1/Q_{\text{non-TLS}}$	σ_{TLS} [cm^{-2}]	$\tan(\delta_{\text{TLS}})$
Baseline EP	1.6×10^{-23}	1.4×10^4	200	3.4×10^{-11}	3.7×10^{11}	1.7×10^{-3}
EP + 650 °C–10 h	8.5×10^{-25}	2×10^3	600	0.76×10^{-11}	1.9×10^{10}	1.5×10^{-4}

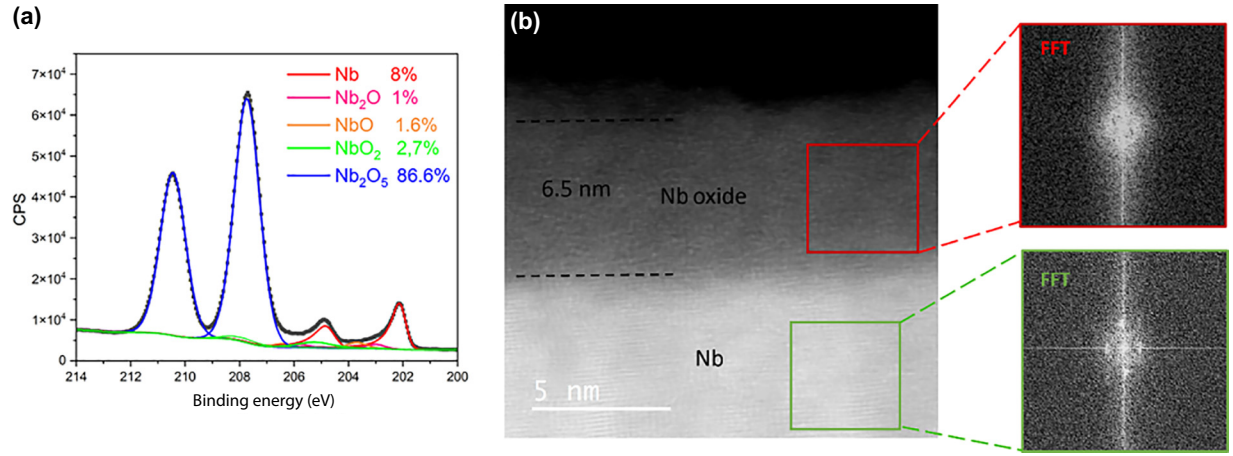


FIG. 2. (a) XPS spectrum of Nb-3d core levels of electropolished niobium + HPR. (b) HAADF imaging and local FFT analysis on electropolished Nb + HPR.

The HAADF image in Fig. 2(b) shows a uniform oxide layer of 6.5 nm on top of the crystalline niobium substrate. A local FFT analysis confirmed that the native oxide layer is amorphous while the niobium substrate is crystalline, with a cubic ($Im\bar{3}m$) lattice. The average thickness of niobium's native oxide layer after exposure to air is typically around 5 ± 1.5 nm [23,24], although this varies significantly depending on the surface preparation and oxidation conditions. In our case, it is not surprising that the native oxide is thicker, as high-pressure rinsing causes a notable increase in the oxide layer thickness [23,24].

After annealing at 650 °C for 10 h, followed by HPR and air exposure, XPS reveals an altered composition of the surface. Figure 3(a) shows a decrease in Nb_2O_5 composition from 86.6% to 61.1%, along with an increase in the percentage of metallic niobium and suboxides. In particular, we witnessed the emergence of clear peaks corresponding to Nb_2O and NbO with contributions of 12%

and 8.5% to the Nb 3d signal, respectively. The HAADF imaging shown in Fig. 3(b) reveals a uniform and significant reduction in the oxide layer thickness from 6.5 to 4 nm.

The oxide layer alteration is the result of the furnace baking under HV and reoxidation after air exposure and high-pressure rinsing. Based on previous heat-treatment studies [10,14,22], niobium pentoxide becomes completely dissolved when annealed at a temperature higher than 340 °C and gives rise to other suboxides, mainly NbO . When exposed to air, the formation of NbO on the surface of Nb significantly raises the potential barrier for oxygen uptake from the air, thereby slowing the oxide's growth. While studying niobium heat treatments in the range of 250 °C–800 °C over a few hours, Yu *et al.* [22] found that the proportion of Nb_2O_5 progressively decreases after air exposure as the heat-treatment temperature rises within the range of 300–600 °C. After heat

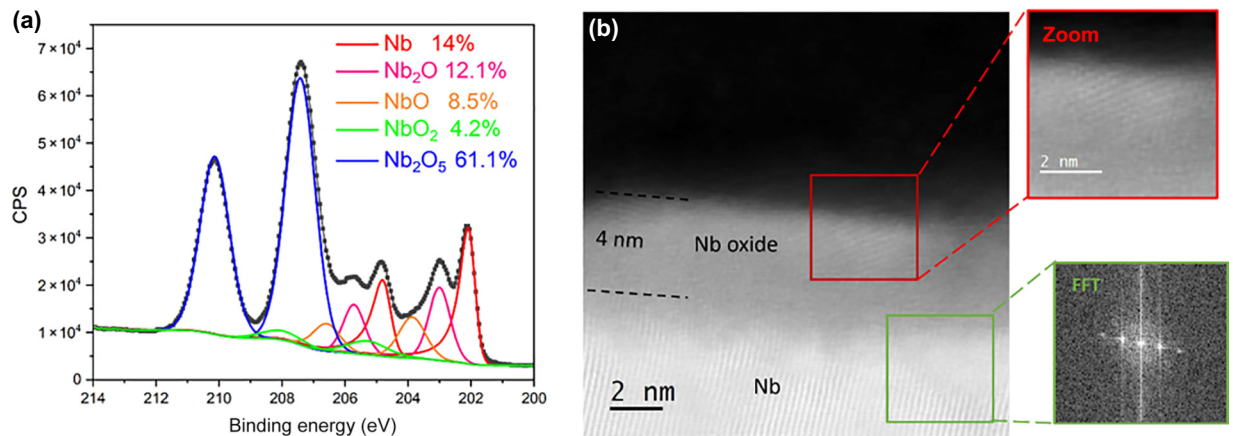


FIG. 3. (a) XPS spectrum of Nb-3d core levels of annealed niobium at 650 °C–10 h + HPR. (b) HAADF imaging and local FFT analysis on annealed niobium at 650 °C–10 h Nb + HPR.

treatment at 600 °C, their samples show the lowest concentration of Nb₂O₅ and the largest concentration of NbO, along with the emergence of peaks of Nb₂O. These results are in perfect agreement with our observations: it seems that our annealing at 650 °C for 10 h results in such a formation of a NbO- and Nb₂O-rich layer that significantly inhibits the formation of a thick Nb₂O₅ layer formation, even after the high-pressure rinsing step that is known to favor its growth. This can explain the significant difference in TLS losses at low rf fields and the associated decrease in σ_{TLS} and $\tan(\delta_{\text{TLS}})$ parameters extracted from the fits. In contrast, annealing at lower temperatures, such as 350 °C [22], does not seem to create sufficient NbO to slow the regrowth of Nb₂O₅ after exposure to air. This could explain why the reduction of the TLS observed by Romanenko *et al.* [7,10] after annealing at 340 °C does not persist upon exposure to air.

More interestingly, we notice the formation of clear crystalline regions in the oxide layer. Unlike the native oxide on top of the unannealed sample, which is thick and amorphous, the annealing at 650 °C during a period of 10 h results in the formation of nanoscale crystallites inside the overall amorphous matrix of the oxide. Figure 4 shows different HAADF images of the Nb sample annealed at 650 °C for 10 h and high-pressure rinsed, along with a local FFT analysis. It can be seen that, in some regions (such as zone A), the crystallite is located near the interface with the metallic niobium. An FFT analysis in this region shows a d-spacing of 2.1 Å, which can be associated with NbO (200) planes [25]. In zones B and C, we observe another configuration where crystallite is formed at the surface on top of an amorphous layer of oxide. The FFT analysis in

these zones shows d-spacings of 1.5 Å, 2.4 Å, and 2.9 Å, which can be associated with the (220), (111), and (110) planes of NbO, respectively [25]. In other regions, such as zone D, the crystal grows starting from the interface with the metal and continues to the surface. In this zone, we measure a d-spacing of 2.4 Å, which can be associated with the (111) planes of NbO [25]. Based on these observations, a plausible scenario is that, during the 10 h annealing at 650 °C, the original amorphous Nb₂O₅ decomposes to a nanocrystalline layer of NbO and possibly Nb₂O (although there is no reported crystalline structure of Nb₂O in literature). Upon exposure to air and high-pressure rinsing, Nb₂O₅ regrows surrounding the crystallites of NbO and sometimes underneath it (zones B and C). In other cases, the crystalline-NbO layer formed during the annealing is already passivating and, thus, no Nb₂O₅ is formed after the exposure to air. Similar observations have been reported by Hellwig *et al.* [26], who witnessed the formation of a crystalline and passivating layer of NbO-(111) on top of a Nb-(110) film. Our discovery of these nanocrystalline regions is in perfect agreement with the surprisingly low TLS losses of the Nb 1.3 GHz cavity.

Shortly after the discovery that qubit energy relaxation and decoherence were linked to TLS in amorphous materials, several efforts were made to create fully crystalline tunnel-junction barriers. Despite the technological difficulties of this approach, Seongshik *et al.* [27] showed the benefit of integrating single crystal epitaxial Al₂O₃ tunnel barriers into Josephson phase qubits and presented measurements showing a correlation between the crystallinity of the tunnel barrier and the density of TLSs in the qubit. In another study, Patel *et al.* [28] incorporated a single crystal

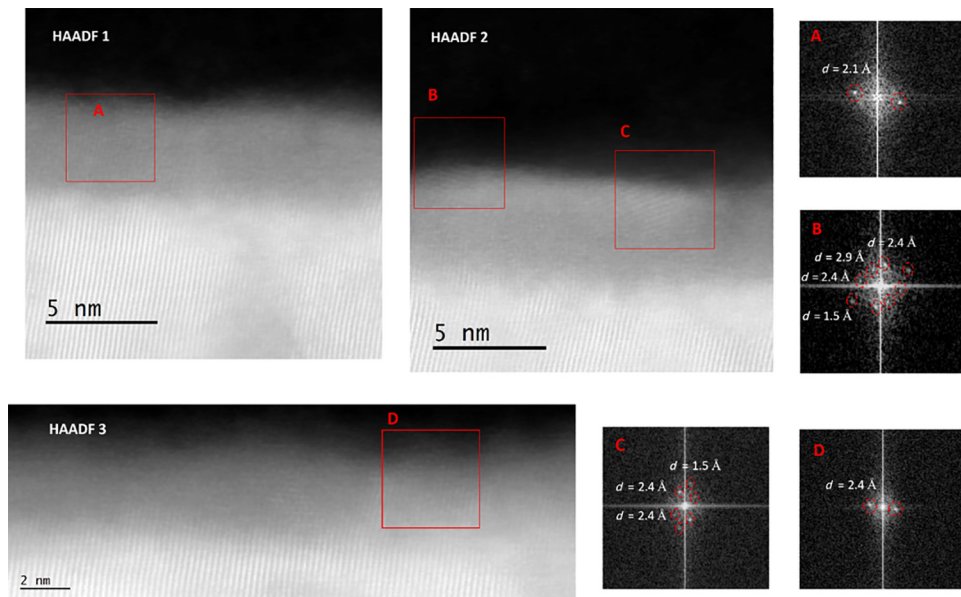


FIG. 4. HAADF imaging on three different locations on the annealed niobium samples at 650 °C–10 h + HPR and corresponding local FFT analysis.

silicon shunt capacitor into a Josephson phase qubit and showed that the superior dielectric loss of the crystalline silicon leads to a more than doubling of the qubit energy relaxation times compared with those seen in amorphous phase qubits. Our findings confirm the dominant participation of the niobium pentoxide Nb_2O_5 in TLS losses of Nb-based quantum devices and provide evidence that crystalline NbO can be a much less dissipative alternative for passivating Nb-based devices.

C. Tunneling spectroscopy

We measured the surface superconducting properties by means of point contact tunneling (PCT) spectroscopy, as described in Ref. [19]. In our setup, the junctions were formed by approaching the sample surface with an Au tip, creating a superconductor-insulator-normal (SIN) junction where the insulator is the oxide layer on the sample surface.

The PCT data were analyzed using the expression for the differential tunneling conductance, i.e.,

$$\frac{dI}{dV} \propto \int N_S(E) \left[-\frac{\partial f(E + eV)}{\partial (eV)} \right] dE, \quad (1)$$

where I is the current flowing through the SIN junction under a difference of potential V , $N_S(E)$ is the superconducting density of states (DOS), and $f(E)$ is the Fermi function.

We considered two models to describe $N_S(E)$. The first is the widely known Dynes model given by the formula [29]

$$N_S(E) = N_S \text{Re} \left[\frac{E + i\Gamma}{\sqrt{(E + i\Gamma)^2 - \Delta^2}} \right], \quad (2)$$

where N_S is the DOS at the Fermi surface in the normal state, Δ is the superconducting gap, and Γ is the phenomenological quasiparticle lifetime broadening parameter.

The second model is based on the Usadel equations for a proximity-coupled, dirty, and thin normal layer (N) on the surface of a bulk superconductor (S) [30]. The resulting DOS is controlled by four parameters: the Dynes broadening parameter Γ , the bulk pair potential Δ , and two dimensionless parameters α and β . These are determined via the N-layer thickness and the N-S interface transparency, i.e.,

$$\alpha = \frac{d}{\xi_S} \frac{N_N}{N_S}, \beta = \frac{4e}{\hbar} R_B N_N \Delta d. \quad (3)$$

Here, ξ_S is the bulk coherence length, d is the N-layer thickness, N_N and N_S are the DOS at the Fermi surface in the normal state of the N-layer and S-layer, respectively, and R_B is the contact resistance of the N-S interface.

We performed PCT measurements on the same samples used for the TEM cross-section measurements, as described previously. For the reference sample that received an EP and an HPR, we could not gather sufficient statistics because the tunnel-junction resistances were too high ($>2\text{--}5\text{ G}\Omega$) to be measured by our experimental PCT setup. Such high tunnel-junction resistances are most likely due to the thick native niobium oxide layer (6.5–7 nm) measured by the TEM in Fig. 2. We, therefore, decided to use as a reference sample an electropolished Nb coupon rinsed in water but without the HPR step. As far as we know, the main effect of HPR is to increase the surface oxide thickness, so it is reasonable to assume that it does not significantly alter the DOS. For each sample, about ~ 100 junctions were measured over an area of $\sim 100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ at $T = 1.8\text{ K}$.

Typical tunneling conductance spectra for both samples with the corresponding fits are shown in Fig. 5. For the Nb + HPR + 650 °C–10 h + HPR sample [Fig. 5(a)], the fits obtained from the Usadel proximity model are in very good agreement with the data, whereas the fits extracted from the Dynes model fail to accurately reproduce the spectra. This indicates the presence of a normal metal layer on the niobium surface, which is in agreement with the TEM observations in section B that reveal the presence of metallic NbO nanocrystals. In contrast, the Dynes model essentially fits with the reference sample spectra shown in Fig. 5(b) with no indication of a proximity effect, which is also consistent with the TEM cross sections of the referenced sample shown in section B that show an abrupt transition from an amorphous Nb_2O_5 to the metallic Nb. In the Usadel theory, the gap induced in the normal metal layer, referred to as ε_0 [31] and sometimes called the minigap, is given by the following equation:

$$\beta = \frac{1}{(\varepsilon_0/\Delta)} \left(\frac{1 - (\varepsilon_0/\Delta)}{1 + (\varepsilon_0/\Delta)} \right)^{1/2}. \quad (4)$$

The effective superconducting gap ε_0 is the one measured on the conductance spectra in Fig. 5(a) and is approximately given by half the energy separation between the quasiparticle peaks. The gap Δ in the superconductor underneath the normal metal layer is inferred from the fits but not directly probed by tunneling spectroscopy. In the Dynes model, there is only one superconducting gap Δ .

The statistics of the superconducting gaps Δ extracted from the fits on the Dynes and Usadel models and the corresponding cartographies are represented in Fig. 6. The histogram [Fig. 6(a)] shows, for the annealed sample, a large distribution of Δ values centered around $0.9 \pm 0.2\text{ meV}$, significantly lower than the well-established bulk Nb gap value around 1.5 meV [31]. In contrast, the histogram distribution for the reference sample peaks around the bulk Nb gap value of 1.45 meV with a smaller spread of $\pm 0.17\text{ meV}$. The cartography represented in

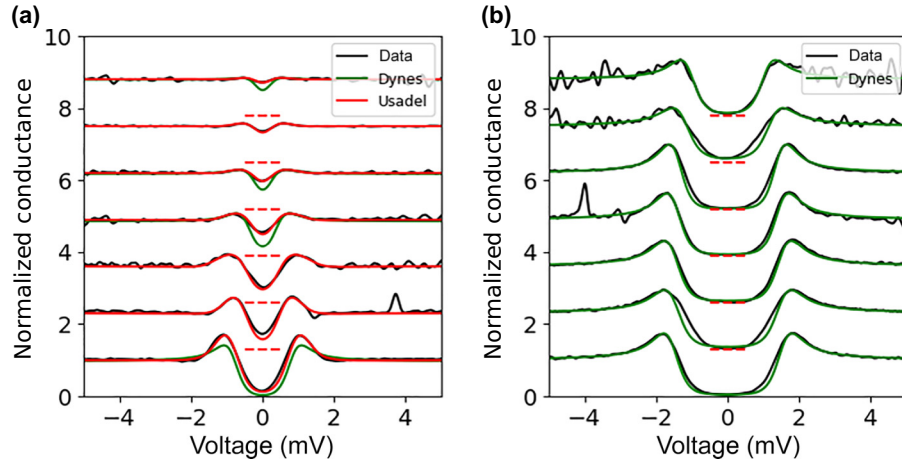


FIG. 5. (a) Selected tunneling conductance curves from Nb + HPR + 650 °C - 10 h + HPR sample measured at $T = 1.8$ K and the corresponding fits using the Usadel and Dynes models. The parameters Δ , Γ , α , and β , extracted from the proximity fits are from top to bottom: 0.64, 0.09, 0.094, 3.18\0.8, 0.07, 0.15, 2.9\1.01, 0.09, 0.2, 3.1\1.13, 0.1, 0.2, 2\1.35, 0.09, 0.15, 1.44\1.05, 0.045, 0.13, 0.93\1.28, 0.045, 0.15, and 0.47. The parameters Δ and Γ , extracted from Dynes fits, are from top to bottom: 0.19, 0.001\0.32, 0.02\0.46, 0.01\0.83, and 0.001. (b) Selected tunneling conductance curves from Nb + EP sample measured at $T = 1.8$ K and the corresponding fits using the Dynes model. The parameters Δ and Γ , extracted from the Dynes fits, are from top to bottom: 1.08, 0.06\1.26, 0.12\1.42, 0.02\1.47, 0.05\1.51, 0.1\1.55, 0.07\1.53, and 0.07.

Figs. 6(b)–6(d) illustrates these differences with a significant inhomogeneity observed across different locations for the annealed sample, with some areas showing a strong suppression of Δ , reaching values as low as ~ 0.4 meV. The low values of the superconducting gap Δ for the annealed sample indicate that the superconductor underneath the normal metal layer is systematically strongly reduced in comparison with the bulk Nb gap.

The histograms for the other parameters extracted from the Usadel fits of the annealed sample spectra, namely the minigap ε_0 , β , and α and their associated spatial variations, are represented in Fig. 7. It is notable that the interface transparency β varies significantly between a nearly transparent N–S interface ($\beta \ll 1$) and a weak N–S coupling ($\beta \gg 1$) [30]. These variations can be explained by considering that the transparency of the N–S interface

strongly depends on the proximity of the NbO nanocrystals to the Nb. For crystals directly above the Nb, as observed in regions A and D of Fig. 4, we expect a better interface contact and, therefore, a small β . On the other hand, for crystals formed at the surface on top of the amorphous layer of oxide, as seen in regions B and C of Fig. 4, we would expect weak coupling since the N and S layers are separated by an insulating barrier, which increases the contact resistance R_B .

Despite the complexity of the nanocrystal distribution within the amorphous oxide matrix, we can perform a simple calculation to estimate the thickness of the N-layer on top of the Nb. From α statistics, we obtained a peaked value at $\alpha = 0.15 \pm 0.05$. Assuming $N_N \sim N_S$ in Eq. (3), we have $\alpha \sim d/\xi_S$. If we take $\xi_S \sim 40$ nm for bulk Nb, the estimated thickness of the N-layer on top of the Nb is

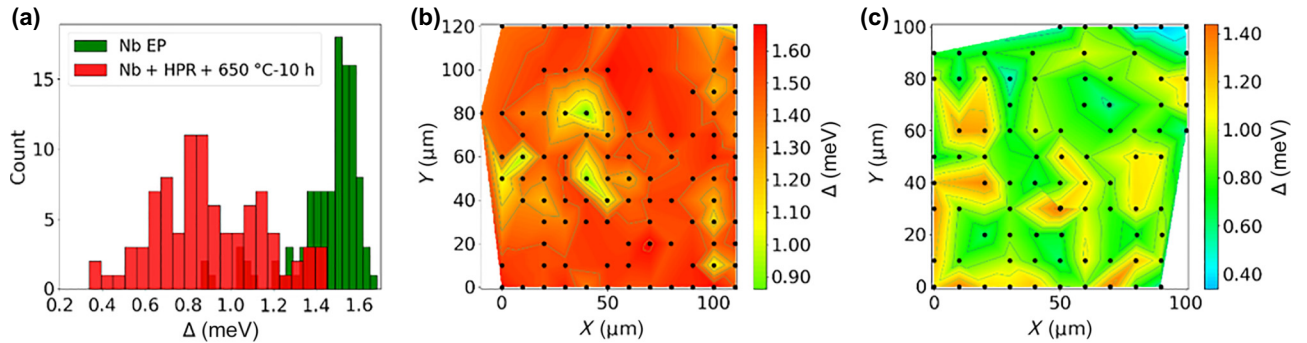


FIG. 6. (a) Histograms of the superconducting gap Δ extracted from the fits of the measured conductance curves of Nb + HPR + 650 °C - 10 hr (red – Usadel fits) and Nb + EP (green – Dynes fits) samples respectively over an area of $\sim 100 \mu\text{m} \times 100 \mu\text{m}$ at $T = 1.8$ K. Contour maps of the superconducting gap Δ extracted from the fits of the (b) reference sample and (c) annealed sample. The black points represent the location of the tunnel junctions.

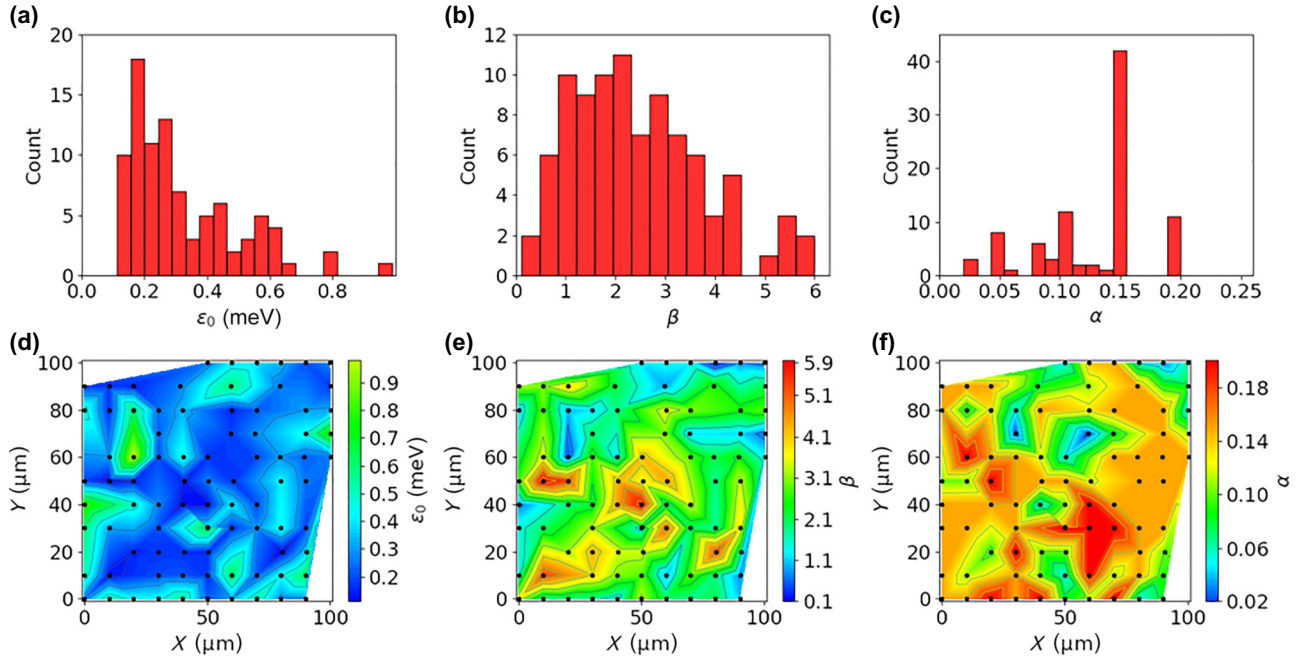


FIG. 7. (a),(b),(c) Histograms and (d),(e),(f) contour maps of ε_0 , α , and β , extracted from the Usadel fits on the measured conductance curves of Nb + HPR+650 °C–10 h + HPR sample over an area of $\sim 100 \mu\text{m} \times 100 \mu\text{m}$ at $T = 1.8 \text{ K}$. The black points represent the location of the tunnel junctions.

$d \sim 5 \text{ nm}$, which is close to the $\sim 4 \text{ nm}$ observed in the TEM images for the nanocrystallites.

IV. CONCLUSIONS

In conclusion, we have investigated the effect of high-temperature annealing on the rf performances of Nb 1.3-GHz resonators in the TLS-dominated regime at rf field intensities below 10^{-2} MV/m . An annealing in vacuum at 650 °C for 10 h resulted in a tenfold enhancement of the low-field quality factor after air exposure and high-pressure rinsing, which is caused by an alteration of the chemical composition of the niobium native oxide and its partial crystallization, as probed by STEM, XPS, and PCT. Our findings provide a new route for suppressing TLS defects in superconducting Nb-based resonators, which consists of promoting the niobium oxide crystallization instead of uniquely dissolving the Nb_2O_5 . Our findings on the chemical composition and structural evolution mechanism of Nb surface oxides can also be used to guide the thermal treatments of other superconducting quantum devices.

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