Insights into Improving Performance of Niobium Superconducting Transmon Qubit Devices through Advanced Microscopy

Akshay A. Murthy\(^1\), Paul Masih Das\(^2\), Stephanie M. Ribet\(^2,3\), Cameron Kopas\(^4\), Jaeyle Lee\(^1\), Matthew J. Reagor\(^4\), Lin Zhou\(^5\), Matthew J. Kramer\(^6,7\), Mark C. Hersam\(^2,6,7\), Mattia Checchin\(^1\), Anna Grassellino\(^1\), Roberto dos Reis\(^2,3,8\), Vinayak P. Dravid\(^2,3,8\), Alexander Romanenko\(^1\)

\(^1\)Superconducting Quantum Materials and Systems Division, Fermi National Accelerator Laboratory (FNAL), Batavia, IL 60510, USA
\(^2\)Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
\(^3\)International Institute of Nanotechnology, Northwestern University, Evanston, IL 60208, USA
\(^4\)Rigetti Computing, Berkeley, CA 94710, USA
\(^5\)Ames Laboratory, U.S. Department of Energy, Ames, IA 50011, United States
\(^6\)Department of Chemistry, Northwestern University, Evanston, IL 60208
\(^7\)Department of Electrical and Computer Engineering, Northwestern University, Evanston, IL 60208
\(^8\)The NUANCE Center, Northwestern University, Evanston, IL 60208, USA

(Dated: May 25, 2022)

Superconducting thin films of niobium have been extensively employed in transmon qubit architectures. Although these architectures have demonstrated remarkable improvements in recent years, further improvements in performance through materials engineering will aid in large-scale deployment. Here, we use information retrieved from electron microscopy to conduct a detailed assessment of defects and inhomogeneities on the atomic and nanoscale that may potentially induce quantum decoherence in transmon qubit test devices. In the niobium thin film, we observe the presence of localized strain at the metal/substrate and grain boundaries, which may amplify interactions between two-level systems and impose limits on \(T_1\) and \(T_2\) relaxation times. Additionally, we observe the presence of a surface oxide with varying stoichiometry and bond distances, which can generate a broad two-level system noise spectrum. Finally, a similarly disordered and rough interface is observed between Nb and the Si substrate. We propose that this interface can also degrade the overall superconducting properties. Based on these findings, we propose solutions to eliminate these potentially problematic imperfections in future quantum devices.

Keywords: superconducting qubits, 4D-STEM, electron diffraction, Nb thin films, interfaces, hydrides, decoherence mechanisms

Over the last two decades, many significant advances have been made towards constructing large-scale quantum computers. In particular, superconducting quantum information technology has emerged as a leading architecture to interrogate complex problems commonly deemed intractable with the most efficient classical computing platforms \(^1\)\(^4\). Nonetheless, extending this technology to large-scale devices requires continued progress to improve reliability and performance. Such improvements require higher quality materials and specifically, an increased understanding and control over imperfections including interfaces and surfaces \(^3\).

As an example, in the case of niobium (Nb)-superconducting transmon qubits, the amorphous surface oxides that form upon ambient exposure serve as major sources of electromagnetic energy dissipation. At milliKelvin (mK) operating temperatures, they also display loss tangent values that are three orders of magnitude larger compared to the Nb thin films and Si substrates \(^6\)\(^8\). This loss can be largely attributed to two-state defects in the amorphous surface oxide, i.e. two-level system (TLS) defects \(^6\). These states emerge as a result of deviations from long-range order. The system is able to transition between the two states through low energy excitations at the operating temperatures for superconducting transmon qubits \(^9\)\(^10\). Similarly, the presence of grain boundaries within the Nb film decreases mean free paths and superconducting parameters, such as the residual-resistance ratio (RRR), which can also lead to diminished \(T_1\) energy relaxation decoherence times \(^9\). As a result, it is important to understand the form-function relationships between processing parameters and structure and concentration of TLS defects in these materials.

A combination of various spectroscopy and microscopy techniques have led researchers to understand that deviations from crystalline range order on the nanoscale dictate quantum decoherence \(^10\). As such, scanning transmission electron microscopy (STEM) is an indispensable tool for identification of materials...
that host TLS defects in a broader effort to eliminate these sources. Namely, the ability to procure a variety of analytical and spectroscopic signals from nanometric volumes allows for detection of chemical, structural, and electromagnetic fluctuations on these relevant length scales [11, 12]. We deploy STEM imaging and diffraction methods to pinpoint specific nanoscale inhomogeneities in surfaces and interfaces associated with Nb.

Nb transmon test qubits were fabricated following the procedures detailed by Nersisyan et al. [13]. This involved preparation of a Si (001) wafer (float-zone >10,000 Ohm-cm) with an RCA surface treatment [13, 14], followed by deposition of Nb films via high-power impulse magnetron sputtering (HiPIMS) with a base pressure less than 1E-8 Torr at room temperature. TEM samples were prepared from the Nb capacitance pad indicated with the black box in Figure 1a using a 30 kV focused Ga\(^+\) ion beam. We first provide an assessment of the nanostructure and strain distribution in the Nb thin film before searching for nanoscale inhomogeneities in surfaces and interfaces associated with Nb.

**INTERFACES AND STRAIN GRADIENTS IN NIOBIUM FILM**

An annular dark field (ADF) image of the cross-section taken from the contact pad of the transmon qubit using collection angles varying between 10 mrad to 70 mrad is provided in Figure 1b. In Figure 1c, an elemental map taken from this region using energy dispersive x-ray spectroscopy (EDS) confirms the presence of a Nb film on a Si substrate. In Figures 2a and b, bright field (BF) images taken when tilted along the Nb {111} zone axis are provided. From this image, we observe that columnar grains form, which are characteristic of the HiPIMS process, and are roughly 50 nm by 170 nm. It is also apparent that many of the grains are not oriented along this zone axis. In fact, from the orientation map, the grains tend to exhibit misorientation angles between 0 and 20 degrees from the Nb {111} zone axis in the sample plane. These columnar grains are separated by grain boundaries that exist parallel to the film growth axis.

Although a variety of chemical and physical properties contribute to BF contrast, strain is the dominant mechanism in this case due to large differences in the lattice constant between the metal and underlying substrate. In order to visualize these strained areas more clearly, we performed strain analysis using the algorithm detailed by Pekin et al [15]. Strain within a crystalline sample leads to small atomic shifts in real space, which manifest in shifts to the diffraction pattern in reciprocal space. These shifts to the diffraction pattern can be measured and linked to relative in-plane strain in the sample through a transformation matrix. This approach is advantageous over direct real space mapping because it does not require the resolution and signal to noise necessary for atomic resolution imaging. The resultant maps of the strain magnitudes along various directions are provided in Figures 2c-f for a representative grain oriented perfectly along the zone axis.
Inhomogeneities in the Amorphous Niobium Surface Oxide

In addition to the Nb film, adjacent surfaces and interfaces are also known to impact the coherence properties in the system. As discussed previously, Nb surface oxides, which form spontaneously in ambient conditions, exhibit loss tangent values that are roughly three orders of magnitude larger than the surrounding film and crystalline substrate [6]. A dark field STEM image of this surface oxide and the associated thin film is provided in Figure 3a. This image was constructed by applying a virtual detector with an inner collection angle of 10 mrad and an outer collection angle of 15 mrad, which was designed specifically to match the initial diffraction ring observed in the NbO₂₅ diffraction pattern (Figure S2). Representative diffraction patterns captured from the indicated regions in the dark field image in Figure 3a are provided in Figure 3d-h. The broad diffuse rings we observe are indicative of a lack of long-range order, which is problematic because it makes this oxide prone to hosting TLS defects.

Since the oxide region exhibits amorphous-like character in the diffraction pattern, we employ fluctuation electron microscopy (FEM) to better understand the medium range ordering present in the sample. This analysis was conducted following the approaches detailed previously [22–24]. First, this process involves using a 1 nm probe and capturing diffraction patterns as a function of position. Following elliptical correction, the radial intensity was then calculated as a function of scattering angle. By subtracting the contribution associated with the thermal motion of atoms as well as the scattering resulting from individual atoms, we were able to calculate the scattering factor as a function of position. Finally upon performing a Fourier transform, the radial distribution function (RDF) as a function of real-space distance is accessible. An RDF profile represents the probability of finding an atom r distance away from a reference atom. As such, atomic bond distances will produce peaks in the profile.

The RDF calculated for positions 1, 3, and 5 in the dark field image are seen in Figure 3c. From these profiles, it is apparent that the intensity of the broad peak centered about roughly 1.5 Å decreases in intensity when moving in the direction away from the surface. Based on the calculated radial distribution function profile for crystalline Nb₂O₅ (Figure S1) [25], this primary feature is expected to arise from Nb-O bonding. As the experimental RDF is obtained from an amorphous area, disorder arising from local deviations in the bond length and bond angles introduce the peak broadening observed compared to the simulated profile. Nonetheless, we can monitor how this peak evolves throughout the oxide to obtain information associated with the nature of the Nb-O bonds in this region.

Specifically, the peak amplitude of this feature represents the density of Nb-O bonds whereas the peak center provides information regarding the bond distances. As the intensity of this peak corresponding to Nb-O bonds steadily decreases beginning at the top surface in the direction towards the Nb film as plotted in Figure 3b, this is suggestive of a decrease in the oxygen content in this direction. This is in agreement with previous findings suggesting that whereas Nb₂O₅ has
Figure 3. Nb/O interface (a) DF image of Nb oxide/Nb constructed using a virtual detector that matched the diffraction ring of Nb oxide seen in SI Figure 2b. (b) Evolution of normalized primary peak intensity as a function of regions labeled 1-5 in the DF image. (c) Comparison between experimental RDF as a function of position and simulated RDF for crystalline Nb$_2$O$_5$. The intensity of the primary peak at each region was plotted in (b) This simulated profile is also decomposed into a pair distribution function to understand which pairs of atoms give rise to the features observed. (d-h) Diffraction patterns taken from regions 1, 2, 3, 4, and 5, respectively. As the distinct diffraction spots indicated by the arrows fade in intensity from region 1 to region 5, it is apparent that the Nb oxide decreases in crystallinity in the direction away from the surface. 

been observed at the surface, NbO$_2$ and NbO are observed closer to the Nb film [8, 9, 26]. Based on Figure 3b, it appears that the oxygen concentration evolves continuously throughout the entire oxide. As the electronic structures of Nb$_2$O$_5$ differs greatly from NbO$_2$ and NbO, such a concentration gradient implies a spatially varying electronic structure that may thus impact the resultant superconducting properties of the film.

Additionally, the peak position of the Nb-O is plotted in Figure S1. Based on this peak position map, we observe a clear variation in the bond distance throughout the oxide. Specifically, we calculate an average bond distance of 1.39Å with a standard deviation of 0.03Å. This variation in bonding distances throughout the Nb oxide can lead to tunneling atoms or electrons imposing noise over a wide spectrum as opposed to a single frequency [27, 28].

In addition to the broad diffuse rings in the electron diffraction patterns in Figure 3d-h, we also observe a number of distinct diffraction spots. These are especially prevalent in the representative diffraction patterns taken from regions 1-3 before appearing to decay in intensity in the representative diffraction patterns taken from regions 4 and 5. This evolution in the diffraction pattern is observed throughout the film as highlighted in Figure S2. As the appearance of these distinct diffraction spots is indicative of ordering in the system, this suggests that the Nb oxide closest to the surface (Nb$_2$O$_5$) is more semi-crystalline.

This is reasonable as oxygen diffusion is responsible for growth of the surface oxide. In this process, the oxygen concentration is expected to decay as a function of position in the direction from the top surface of the NbO$_2$ to the Nb film. As such, regions closest to the surface have a higher likelihood of approaching an ordered and stoichiometric Nb$_2$O$_5$ state. Meanwhile, this mechanism for oxygen transport may cause regions closest to the Nb film to be amorphous and sub-stoichiometric as suggested by these findings. Due to the amorphous nature of the sub-oxide, as well as the fact that sub-oxides of niobium may give rise to magnetic dipoles [29], it is likely that in addition to the large loss tangent value of Nb$_2$O$_5$, regions 4 and 5 in Figure 3a play a critical role in introducing decoherence in the transmon qubit [30, 31].

NONUNIFORM NIOBIUM/SILICON INTERFACE

The metal/substrate interface between Nb and Si may serve as a source of decoherence as well. In Figure 4, a phase map of this interface is provided. This map was constructed using virtual annular detectors with collection angles of 40-45 mrad as well as 20-25 mrad for Nb and Si, respectively (Figure S3). The former were used to capture signal diffracted from the Nb{110} family of planes and the latter were used to capture signal diffracted from the Si{200} family of planes. The two resultant maps were overlaid upon one another to obtain a qualitative understanding of chemical distribution. Based on the slowly varying intensity gradients in the phase map, we observe that an Nb and Si form an alloy phase that exists between the metal and the...
substrate. Additionally, we also observe that the underlying Si substrate is very rough and has likely been altered by the buffered oxide etchant, which is used to remove Si oxide prior to Nb deposition.

Based on electron diffraction patterns taken across this interface, we define 3 distinct regions that exist between the crystalline Nb metal and Si substrate. Representative diffraction patterns taken from each of these indicated regions are provided in Figure 4b-d and representative diffraction patterns taken from the Nb film and the Si substrate are provided in Figure S3. Each of these regions display diffuse rings which are again indicative of a lack of long-range order. Based on the presence of intense diffraction spots associated with Nb along with weak diffraction spots associated with Si, we hypothesize that region 1 is an amorphous niobium silicide region that is niobium rich in nature. Conversely through this analysis, region 2 is an amorphous niobium silicide region that appears to be silicon rich. Finally, although the diffraction pattern taken from region 3 also exhibits a diffuse ring, the consistency between this diffraction pattern and the reference pattern taken from the Si substrate suggests that this region likely represents a semi-crystalline region of Si that has been roughened during various steps in the deposition and lithography process.

We hypothesize that structural properties in each of these regions should be investigated and improved for potential coherence benefits. For instance, regions 1 and 2 are amorphous regions, which may house TLS defects. Additionally, we would expect these niobium silicide regions to be non-superconducting, which would impact \( T_1 \) coherence times. Because region 3 exhibits significant surface roughness and disorder, we expect charge carriers in these regions to exhibit very low mean free paths, which may impact the superconductivity properties.

CONCLUSIONS

In this study, we applied STEM imaging and diffraction methods to identify structural inhomogeneities and defects on the atomic and nanoscale in Nb films and associated interfaces within a test transmon device. Based on an understanding of loss mechanisms in superconducting qubits, we hypothesize that many of these features may be linked to decoherence. In the Nb film, we observed grain sizes with the minimum dimension on the order of tens of nanometers and localized strain at grain boundary interfaces. In the disordered niobium surface oxide layer, we observed a significant variation in the bond distances and in the diffuse metal/substrate interface, we detected significant atomic disorder and surface roughness. These local structural and atomic features can lead to broad TLS frequency spectra, charge noise, and impact the superconducting parameters of the film. As such identification of synthesis and processing parameters focused on achieving larger grains, eliminating the entire surface oxide, and obtaining an epitaxial metal/substrate interface offer routes to obtaining improved qubit performance.

ACKNOWLEDGEMENTS

This material is based upon work supported by the U.S. Department of Energy, Office of Science, National Quantum Information Science Research Centers, Superconducting Quantum Materials and Systems Center (SQMS) under the contract No. DE-AC02-07CH11359. This work made use of the EPIC facility of Northwestern University’s NUANCE Center, which received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR-1720139) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. The authors thank members of the Superconducting Quantum Materials and Systems (SQMS) Center for valuable discussion. S. M. R. gratefully acknowledges support from IIN and 3M. The authors thank Dr. Anahita Pakzad from Ametek/Gatan, Inc, Pleasanton, CA, for the valuable feedback on the usage of the Stela pixelated detector.
[1] M. Kjaergaard, M. E. Schwartz, J. Braumüller, P. Krantz, J. I.-J. Wang, S. Gustavsson, and W. D. Oliver, Annual Review of Condensed Matter Physics 11, 369 (2020). https://doi.org/10.1146/annurev-conmatphys-031119-050605.

[2] G. Wendin, Reports on Progress in Physics 80, 106001 (2017).

[3] N. P. de Leon, K. M. Itoh, D. Kim, K. K. Mehta, T. E. Northup, H. Paik, B. S. Palmer, N. Samarth, S. Sangtawesin, and D. W. Steuerman, Science 372 (2017).

[4] C. E. Murray, “Material matters in superconducting qubits,” (2021). arXiv:2106.05919 [quant-ph].

[5] A. A. Murthy, J. Lee, C. Kopas, M. J. Reagor, A. P. McFadden, D. P. Pappas, M. Checchin, A. Grassellino, and A. Romanenko, Applied Physics Letters 120, 044002 (2022). https://doi.org/10.1063/5.0079321.

[6] A. Romanenko, R. Pilipenko, S. Zorzetti, D. Frolov, M. Avida, S. Belomestnykh, S. Posen, and A. Grassellino, Phys. Rev. Applied 13, 034032 (2020).

[7] C. R. H. McHae, H. Wang, J. Gao, M. R. Vissers, T. Brecht, A. Dunsworth, D. P. Pappas, and J. Mutus, Review of Scientific Instruments 91, 091101 (2020). https://doi.org/10.1063/5.0017378.

[8] J. Verjauw, A. Potoczniak, M. Mongillo, R. Acharya, F. Mohiyaddin, G. Simion, A. Pacco, T. Ivanov, D. Wan, A. Vanleenhove, L. Souriau, J. Jussot, A. Thiam, J. Piao, S. Couet, M. Heyns, B. Govoreanu, and I. Radu, Phys. Rev. Applied 16, 014018 (2021).

[9] A. Premkumar, C. Weiland, S. Hwang, B. Jaeck, A. P. M. Place, I. Waluyo, A. Hunt, V. Bisogni, J. Pelliciari, A. Barbour, M. S. Miller, P. Russo, F. Camino, K. Kisslinger, X. Tong, M. S. Hybertsen, A. A. Houck, and I. Jarrige, arXiv (2020), 2004.02908 [physics.app-ph].

[10] C. Müller, J. H. Cole, and J. Lisenfeld, Reports on Progress in Physics 82, 124501 (2019).

[11] C. Ophus, Microscopy and Microanalysis 25, 563-582 (2019).

[12] S. M. Ribet, A. A. Murthy, E. W. Roth, R. dos Reis, and V. P. Dravid, Materials Today (2021). https://doi.org/10.1016/j.mattod.2021.05.006.

[13] A. Nersisyan, S. Poletto, N. Ailodoust, R. Manenti, R. Renzas, C.-V. Bui, K. Vu, T. Whyland, Y. Mohan, E. A. Sete, S. Stanwyck, A. Bestwick, and M. Reagor, in 2019 IEEE International Electron Devices Meeting (IEDM) (2019) pp. 31.11.1-31.11.4.

[14] M. R. Vissers, J. Gao, D. S. Wisbey, D. A. Hite, C. C. Tsuei, A. D. Corcoles, M. Steffen, and D. P. Pappas, Applied Physics Letters 97, 232509 (2010). https://doi.org/10.1063/1.3517252.

[15] T. C. Pekin, C. Gammer, J. Ciston, A. M. Minor, and C. Ophus, Ultramicroscopy 176, 170 (2017). 70th Birthday of Robert Sinclair and 65th Birthday of Nestor J. Zaluzec PICO 2017 – Fourth Conference on Frontiers of Aberration Corrected Electron Microscopy.

[16] R. C. Cammarata, Progress in Surface Science 46, 1 (1994).

[17] C. Wu, Thin Solid Films 64, 103 (1979). international Conference on Metallurgical Coatings, San Diego, 1979-Part III.

[18] L. R. Nivedita, A. Haubert, A. K. Battu, and C. V. Ramana, Nanomaterials 10 (2020). 10.3390/nano10071287.

[19] L. Faoro and L. B. Ioffe, Phys. Rev. Lett. 109, 157005 (2012).

[20] M. David Henry, S. Wolflyte, T. Monson, B. G. Clark, E. Shaner, and R. Jarecki, Journal of Applied Physics 115, 083903 (2014). https://doi.org/10.1063/1.4866554.

[21] S. E. de Graaf, L. Faoro, L. B. Ioffe, S. Mahashabde, J. J. Burnett, T. Lindström, S. E. Kubatkin, A. V. Danilov, and A. Y. Tzalechuk, Science Advances 6, eabc5055 (2020). https://www.science.org/doi/pdf/10.1126/sciadv.abc5055.

[22] E. Kennedy, N. Reynolds, L. Rangel DaCosta, F. Hellman, C. Ophus, and M. C. Scott, Applied Physics Letters 117, 091903 (2020). https://doi.org/10.1063/5.0015532.

[23] T. F. Harrellson, E. Sheridan, E. Kennedy, J. Vinson, A. T. N’Diaye, M. V. P. Altoé, A. Schwartzberg, I. Siddiqi, D. F. Ogletree, M. C. Scott, and S. M. Griffin, Applied Physics Letters 119, 244004 (2021). https://doi.org/10.1063/5.0069549.

[24] X. Mu, D. Wang, T. Feng, and C. Kübel, Ultramicroscopy 168, 1 (2016).

[25] C. L. Farrow, P. Julhas, J. W. Liu, D. Bryndin, E. S. Božin, J. Bloch, T. Proffen, and S. J. L. Billinge, Journal of Physics: Condensed Matter 19, 335219 (2007).

[26] I. Lindau and W. E. Spicer, Journal of Applied Physics 45, 3720 (1974). https://doi.org/10.1063/1.1663849.

[27] J. M. Martinis, K. B. Cooper, R. McDermott, M. Steffen, M. Ansmann, K. D. Osborn, K. Cicak, S. Oh, D. P. Pappas, R. W. Simmonds, and C. C. Yu, Phys. Rev. Lett. 95, 210503 (2005).

[28] A. P. Paz, I. V. Lebedeva, I. V. Totakli, and A. Rubio, Phys. Rev. B 90, 224202 (2014).

[29] E. Sheridan, T. F. Harrellson, E. Sivonxay, K. A. Persson, M. V. P. Altoé, I. Siddiqi, D. F. Ogletree, D. I. Santiago, and S. M. Griffin, “Microscopic theory of magnetic disorder-induced decoherence in superconducting nb films,” (2021). arXiv:2111.11684 [cond-mat.supr-con].

[30] A. Sundaresan, R. Bhargavi, N. Rangarajan, U. Siddesh, and C. N. R. Rao, Phys. Rev. B 74, 161306(R) (2006).

[31] R. J. Čava, B. Batlogg, J. J. Krajewski, H. F. Poulsen, P. Gammel, W. F. Peck, and L. W. Rupp, Phys. Rev. B 44, 6973 (1991).