Nitrogen Plasma Passivated Niobium Resonators for Superconducting Quantum Circuits

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Microwave loss in niobium metallic structures used for superconducting quantum circuits is limited by a native surface oxide layer formed over a timescale of minutes when exposed to an ambient environment. In this work, we show that nitrogen plasma treatment forms a niobium nitride layer at the metal-air interface which prevents such oxidation. X-ray photoelectron spectroscopy confirms the doping of nitrogen more than 5 nm into the surface and a suppressed oxygen presence. This passivation remains stable after aging for 15 days in an ambient environment. Cryogenic microwave characterization shows an average filling factor adjusted two-level-system loss tangent $\tan^2\delta_{TLS}$ of $(2.9 \pm 0.5) \cdot 10^{-7}$ for resonators with $3 \mu m$ center strip and $(1.0 \pm 0.3) \cdot 10^{-7}$ for $20 \mu m$ center strip, exceeding the performance of unpassivated samples by a factor of four.

Increasing the coherence time of superconducting qubits while maintaining reasonable gate speeds enables more powerful quantum processors.  The improvement of fabrication techniques plays an important role in this effort. The fabrication process of high coherence planar superconducting quantum processors now typically involves two superconducting layers. The first layer makes up the ground plane and all the circuit elements other than the Josephson junctions (JJ) while the second layer defines the JJs. The two-layer process allows optimization of the quality factor of the superconducting capacitor pads independent from the requirements of the double-angle-evaporated aluminum JJ layer. Microwave coplanar waveguide (CPW) resonators have been demonstrated as a robust platform to characterize the microwave loss in superconducting materials and have been instrumental in the continuous improvement of film and device quality. The microwave loss of state-of-the-art superconducting materials at low excitation powers is ultimately limited by two-level-system (TLS) defects that primarily reside at the metal-air (MA), metal-substrate (MS), and substrate-air (SA) interfaces. For Nb resonators, most of the TLSs reside in the oxide layer at the MA interface and the removal of the oxide  produces CPW resonators with single-photon internal quality factor $Q_i$ up to 5 million and filling factor adjusted two-level-system loss tangent $\tan^2\delta_{TLS}$ down to $9 \cdot 10^{-8}$. However, the oxide grows back following a Cabrera-Mott behavior within several hours, reintroducing TLSs at the MA interface (Fig. 1). As the buffered oxide etch (BOE) used to etch NbO also etches the Al JJ, it is difficult to incorporate Nb resonators with a low density of TLSs at the MA interface into superconducting quantum circuits.

Nitride superconductors such as NbN and TiN are known to only have a thin native surface oxide layer at room temperature and therefore are expected to have fewer TLSs at the MA interface. However, it is suspected that the reactive sputtering process required to produce high quality nitride films forms a SiNx layer at the MS interface, which introduces additional TLSs compared to elemental superconductor. If a resonator could have the MA interface from a nitride superconductor and the MS interface from an elemental superconductor, then its microwave loss caused by TLS is expected to be extremely low. There have been attempts to deposit a thin TiN film covering Nb to prevent the growth of NbO, but the sidewalls are not covered by TiN and can still oxidize.

Nitrogen doping is a well-established technique used to create low-loss Nb 3D cavities. By baking the Nb cavity in N2 gas at a temperature above 800 °C, a conformal layer of NbN is formed at the MA interface which inhibits the growth of surface oxide. In theory, this method can be adapted to
make planar superconducting devices, however the effect of high temperature is not yet well understood. Treatment at high temperature can change the stress and grain size of the deposited metal and allow Nb to diffuse into a substitutional site inside the Si substrate, which all could potentially affect microwave loss.\footnote{\textsuperscript{22,23}} Baking at high temperature can also introduce dislocation and vacancy defects in the Si substrate, whose effects on microwave loss have not yet been systematically explored.

In this Letter, we demonstrate nitrogen doping of Nb CPW resonators without introducing potentially performance-limiting defects related to high temperature. We utilize a radio frequency (RF) plasma to satisfy the activation energy required for nitrogen doping. We show that a N\textsubscript{2} plasma at 300 °C for 10 minutes dopes the top 5 nm of the Nb surface with N which suppresses the growth of Nb oxides at the surface. Furthermore, we demonstrate that the passivation remains robust in an ambient air environment for sufficiently long periods of time to incorporate passivated Nb structures into complex, multi-layer quantum processors. Our process can be easily manifested with equipment available in typical industrial and academic facilities.

The films used in this study are fabricated by first cleaning a 2-inch intrinsic Si (111) wafer\footnote{With resistivity greater than 8000 \(\Omega\) cm in piranha solution (3:1 mixture of H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2}) at 120 °C for 10 minutes followed by a BOE clean (7:1 mixture of NH\textsubscript{4}F and HF) for 5 minutes.} with a psuedo-Voigt function and the background to a linear function.

FIG. 2. XPS depth profile of N and O on Nb surfaces with different treatments. (a) The observed N 1s peak for a passivated Nb film at 1 nm depth. (b, c) The N 1s peak (b) and the O 1s peak (c) for different film treatments as a function of etch depth by in-situ Ar ion milling.

F in the chamber which reacts with the Nb films. To mitigate contamination from F, we deposit \(\sim 1 \mu\text{m}\) of SiO\textsubscript{x} on a dummy wafer and the chamber wall immediately before passivating our sample.

We characterize the surface atomic species of passivated and unpassivated Nb films using X-ray Photoelectron Spectroscopy (XPS). The XPS system (Physical Electronics 5000 VersaProbe II Scanning ESCA Microprobe) uses an Al K\textsubscript{\alpha} line source and in-situ Ar ion milling to facilitate analysis of material at depth. Figure 2(a) shows the XPS scan of a passivated Nb film with its top 1 nm removed. The observed peak corresponds to N 1s electrons. We fit the N 1s peak to a pseudo-Voigt function and the background to a linear func-
The study of N and O 1s electrons confirms a suppressed oxygen concentration near the surface for passivated samples. We now examine the Nb 3d electrons to investigate the oxides present near the surface of the films. Figure 2(b) shows the raw XPS spectrum of the different chemical states of the Nb 3d peaks from the same samples shown in Fig. 2. As the stoichiometry of the oxide layer is complex and we have also introduced a nitride with unknown stoichiometry, we expect the spectrum to contain at least 10 individual peaks that overlap with each other. We examine the trend of two sets of easily defined peaks. At zero depth, we observe clear Nb 3d doublet peaks corresponding to Nb₂O₅ for the unpassivated films. The passivated films do not exhibit these clear peaks (corresponding to O-rich oxides), rather there is a larger weight at smaller binding energy, corresponding to Nb of lower valency states. As shown in Fig. 3(b), at 1 nm depth the unpassivated samples still exhibit significant intensity at the Nb₂O₅ doublet energies. In contrast, the passivated sample shows intensity primarily at the Nb 3d doublet peaks. We also observe that the passivated sample does not accumulate more oxide at the surface after being aged for 15 days.

To study the effect of the passivation process on the quality of the Nb films, we measure the direct-current (DC) resistance of the passivated and the untreated films as a function of temperature using a 4-point technique inside a Quantum Design physical property measurement system (PPMS). Both samples are diced from the same Nb film deposited on the same Si (111) wafer allowing us to attribute the change in film properties to the passivation process alone. We extract the residual resistivity ratio (RRR) by taking the ratio between the resistance value at 297 K and 10 K. We find that the untreated sample has a RRR of 4.86, which is similar to our previous result on Si (100). The plasma passivated sample has a reduced RRR value of 2.96. Figure 4(a) shows the resistance near the superconducting transition of both samples. We observe a superconducting critical temperature $T_c$ of 9.28 ± 0.05 K for the untreated sample, and a suppressed $T_c$ of 8.49 ± 0.05 K for the plasma passivated sample. Both samples are diced from the same Nb film deposited on a single Si (111) wafer, allowing us to attribute the change in film properties to the passivation process alone. Both the resistance and the XRD measurements show that our passivation process produces a more disordered superconductor.

We utilize cryogenic microwave measurements to extract the power-dependent quality factor of CPW resonator structures, and to study the effect of passivation on the TLS-induced loss in the devices. We apply the passivation process to the resonators after the CPW structures are defined with RIE so that the sidewalls of the resonators are also passivated. The resonators are capacitively coupled to a transmission line.
with coupling quality factor $Q_s \simeq 0.5 \times 10^6$. Hanger-style resonators with two types of geometries are fabricated. The first geometry has a center strip width of 3 $\mu$m, gap width of 2 $\mu$m, and has a continuous ground plane. This design allows us to clearly observe the effect of TLSs by maximizing capacitive dielectric loss\(^{19}\) and minimizing inductive\(^{21}\) and radiative losses. The second geometry has center strip width of 20 $\mu$m, gap width of 12 $\mu$m, and has holes ($5 \times 5 \mu m^2$ squares) periodically (every 15 $\mu$m) etched into the ground plane\(^{34}\). This design minimizes the capacitive loss but is more susceptible to radiative loss\(^{33}\) and loss caused by trapped magnetic flux\(^{31}\). We use GE varnish to attach each resonator sample to a microstrip-style microwave launch with Pd-coated Cu metallization and Rogers Duroid 6010LM dielectric. We make 3 wirebonds to each port with 1 mil Al-1%Si bonding wire. The microstrip launch is enclosed inside a Pd-coated Cu sample package. The package is cooled inside a Rainier Model 103 adiabatic demagnetization refrigerator (ADR) down to 50 mK. We add $\sim 100$ dB of attenuation distributed among different temperature stages to the input line\(^{10}\). We shield the sample from stray magnetic fields with a high permeability can (Amuneal Cryoperm) surrounding the sample package. The output of the sample passes through one circulator to a high electron mobility transistor (HEMT) amplifier at the 4 K stage. Further amplification is used at room temperature.

A vector network analyzer (VNA) is used to measure the transmission through the sample. The $Q_i$ of each resonator is extracted at different average circulating photon numbers $\langle n \rangle$ ranging from $-1$ to $10^7$ using the diameter correction method\(^{25}\) (DCM). $F_{\delta TLS}$ and the high-power internal quality factor $Q_i^{HP}$ are calculated from\(^{8}\)

$$F_{\delta TLS} \frac{\tan(\frac{hf}{k_B T})}{\sqrt{1 + \frac{\langle n \rangle}{n_c}}} = \frac{1}{Q_i^{HP}} - \frac{1}{Q_i},$$

where $h$ is the Planck constant, $f$ is the resonant frequency of the resonator, $k_B$ is the Boltzmann constant, $T$ is the temperature of the resonator, and $n_c$ is the critical photon number that differentiates the high and low power regions. When $\langle n \rangle$ is large, the contribution to microwave loss from saturable TLSs approaches zero, so $Q_i^{HP}$ gives a good estimate of the other sources of loss which mainly result from quasiparticles, trapped magnetic flux, radiation, and unsaturable TLSs.

Figure 5(a) shows a comparison of the $F_{\delta TLS}$ value among plasma passivated and untreated samples of both designs. Untreated resonators with the 3 $\mu$m center strip geometry have an average $F_{\delta TLS}$ of $(12.5 \pm 1.5) \cdot 10^{-7}$. This agrees with the result for untreated samples obtained in our previous study\(^{29}\) which uses the same design but intrinsic Si (100) wafers instead of Si (111). In comparison, the passivated resonators have an average $F_{\delta TLS}$ of $(2.9 \pm 0.5) \cdot 10^{-7}$, which is $\sim 4$ times lower than the untreated value. Resonators with the 20 $\mu$m center strip geometry have an average $F_{\delta TLS}$ of $(4.6 \pm 1.0) \cdot 10^{-7}$ for untreated samples and $F_{\delta TLS}$ of $(1.0 \pm 0.3) \cdot 10^{-7}$ for passivated samples. Figure 5(b) shows the extracted $Q_i^{HP}$ of the same resonators shown in Fig 5(a). Resonators with the 3 $\mu$m center strip geometry show an increased $Q_i^{HP}$ compared to untreated devices. We attribute this to a reduced TLS density in the regions of the sample that are too far from the resonators to be effectively saturated at high power. The $Q_i^{HP}$ values of the resonators with the 20 $\mu$m center strip geometry are less uniform. We suspect that this could be due to their susceptibility to trapped vortices and radiation to lossy regions inside the package. The $Q_i^{HP}$ values of our resonators are lower compared to other similar studies, for which we attribute to specific details of the sample package\(^{13,35}\) and measurement setup.

To test the stability of the passivated samples over time, we allow some of the samples to age in an ambient environment for 45 days. Figure 5(a) indicates the change in $F_{\delta TLS}$ after this aging duration. We observe negligible change in $F_{\delta TLS}$ for the untreated devices, indicating that the oxide had already reached self-limited thickness before the first measurement. The passivated resonators exhibit increased $F_{\delta TLS}$ of varying degrees. In particular, two of the five passivated resonators maintained a significantly lower $F_{\delta TLS}$ compared to the untreated resonators, validating the stability of the passivated samples. Three of the passivated resonators, however, exhibited a significant increase in $F_{\delta TLS}$, which could be due to additional contamination of the resonators during storage. Visual inspection reveals significant residue and debris in the gap regions of CPWs for the resonators with significantly increased $F_{\delta TLS}$, indicating that the reduced performance could
be due to contamination during storage. In Fig. 5(b) we indicate the change in $Q_{\text{HP}}$ for the aged devices. For all samples we observe a reduction in $Q_{\text{HP}}$ after aging.

Our study demonstrates a recipe for passivation of Nb structures with nitrogen plasma which dopes the top 5 nm of the Nb surface with N atoms. These N atoms suppress the O concentration and therefore reduce the amount of TLS defects that induce microwave loss. The N and O populations are stable after 15 days of aging in ambient air according to XPS measurements. Cryogenic microwave measurements confirm that our passivation process reduces the microwave loss of CPW resonators of two different design geometries. Our process removes the stringent time sensitivity associated with the regrowth of NbO$_x$ and allows for the incorporation of low microwave loss Nb structures into state-of-the-art quantum processors. Our process also creates a platform on which other microwave loss Nb structures into state-of-the-art quantum processors. Our process also creates a platform on which other microwave loss Nb structures into state-of-the-art quantum processors.
