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Growth of Native Oxides of Niobium Thin Films for Superconducting Qubits with Etching Chemistry

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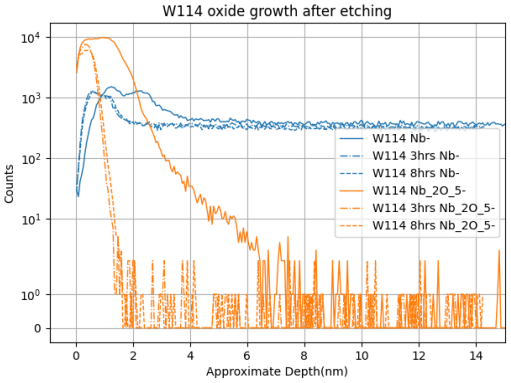
Abstract. Niobium thin films have been broadly applied in building superconducting qubits for quantum computing hardware. While improvements have been made by device engineering efforts, scaling the energy-sensitive quantum system requires materials study for further improvements. In this study, we performed XPS and ToF-SIMS analysis for Nb thin films across samples with different manufacturing techniques. By varying the air exposure time of the samples, this research comparatively investigates the chemical and depth profile of native oxides before and after the etching process. We observe a rapid logarithmic growth of oxide thickness across all samples and the dominant presence and growth of Niobium pentoxide in atomic percentage concentration on the surface. This comparative study provides insight into oxides mitigation strategies and correlation with qubits performance.

Introduction

Recent years, scientists have been aiming to establish fault-tolerant quantum computers on a large scale which is anticipated to be the optimal solution for complex problems. As a mature representation of quantum computing hardware platforms, superconducting circuits have two-level systems (TLSs) on the surface of the devices which primarily contribute to loss and dissipation that brings decoherence to the system [1]. Hence, materials science has maneuvererd to find strategies to spotlight and mitigate such sources of decoherence. In terms of material choice, Niobium thin film as a promising material selection has been broadly applied for superconducting qubits. TLSs on Nb thin film are largely contributed to Nb oxide layers at Nb-Air interfaces. This research presents a comparative study of growth of native oxides of niobium thin films with etching chemistry on three samples of different preparation techniques. Analysis in this research is implemented aiming to establish standard and reference figures for varying and iterating material engineering techniques, qubit performance and efficient loss mitigation strategies.

Result and Discussion



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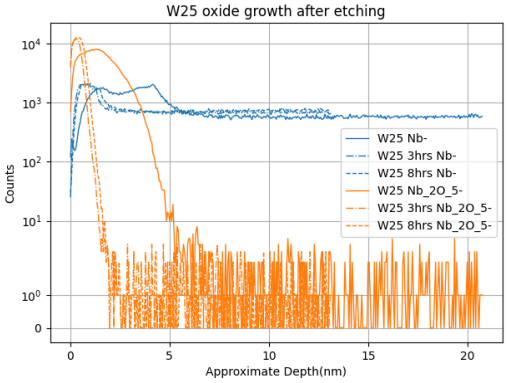

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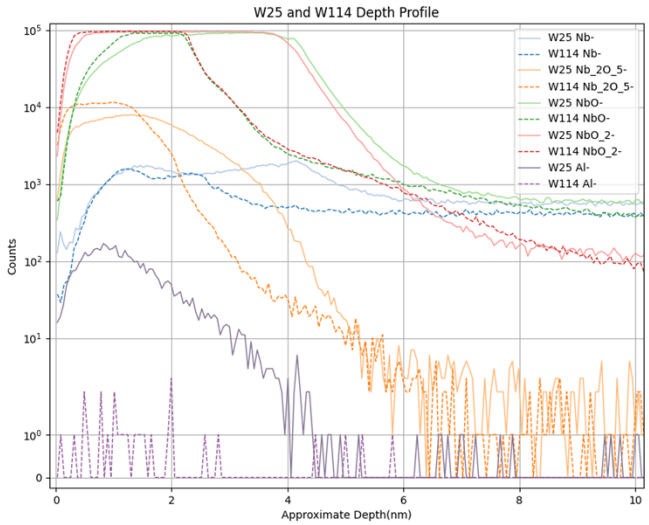

(c)

FIGURE. 1. *ToF-SIMS Depth Profile for sample W25 and W114.* (a) *W25 depth profile over air exposure time after etching.* (b) *W114 depth profile over air exposure time after etching.* (c) *Comparison and reference of W114 and W25 before etching.*

ToF-SIMS depth profiles were taken at different air exposure times of 2 hours, 8 hours and 28 hours for sample W25 and W114. We mainly focused on Nb pentoxide as it is assumed to be the main contribution of the oxide layer and source of loss. Approximate depths are calculated by ToF-SIMS's sputter time and estimated sputter rate. Sputter rate for W25 is 0.032 nm/s and 0.035 nm/s for W114. Sputter rate is calculated given sample W25 sample thickness of 175 nm and sample W114 estimated oxide thickness of 5 nm. Signals below 10 counts are considered noise. Chemical components' counts are averaged values from 3-4 spots measurements.

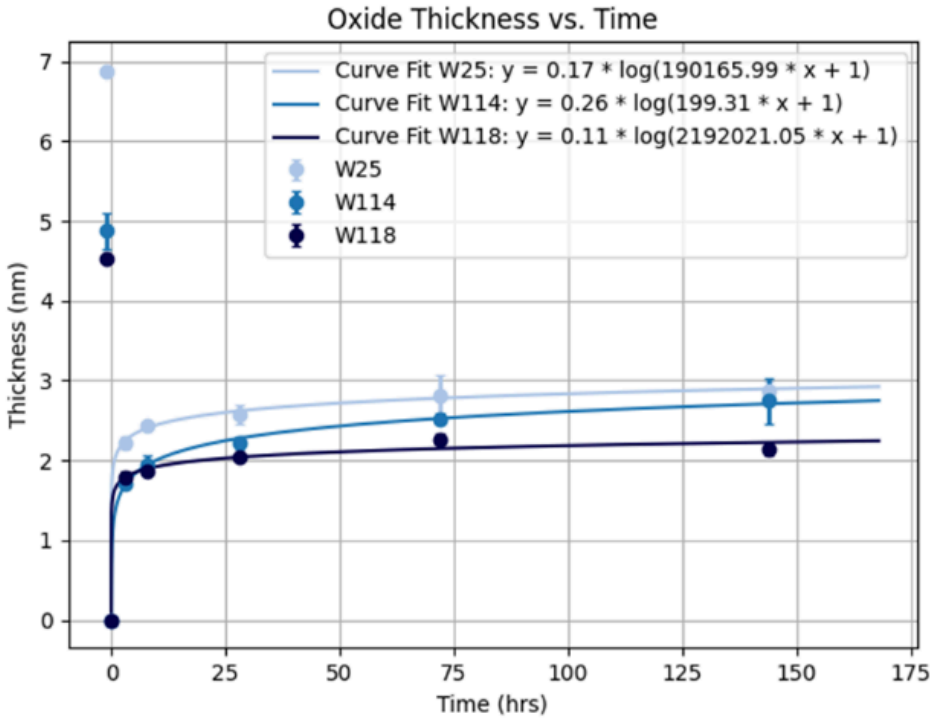

FIGURE. 2. *Oxide thickness over exposure time after etching for sample W25, W114 and W118.*

Oxide thicknesses are derived from the SIMS depth profiles based on the Nb_2O_5 signal. Data points before t = 0hr represent thickness before etching. Oxide thickness of all samples is assumed to be 0 nm immediately after etching, and native oxides start forming on the surface immediately after air exposure. Data points represent the average oxide thickness across 3-4 spots' ToF-SIMS measurements and error bars indicate standard deviation across different spots on samples. Curve fitting is implemented using Python. Curving fitting is done based on the assumption of monotonic growth trend, seeing that the ToF-SIMS data (FIG. 1) suggests a monotonic change for oxides counts over exposure time. In this FIG. 2, we observe that all three samples' oxide thickness behave logarithmic growth and are almost saturated within the first 24 hours. W25 and W114 have thicker layers at the end and relatively slower growth rate initially, while W118 appears to saturate rapidly and remain thinner overall. It's also worth noticing that W25 has much higher initial oxide thickness than W114 and W118. Also, all three samples do not appear to restore the same amount of native oxides thickness prior to etching within the first week, with more than 50% thinner saturation layer. This implies the etching chemistry process might prevent or control oxides growth on Niobium thin films compared to native oxides growth.

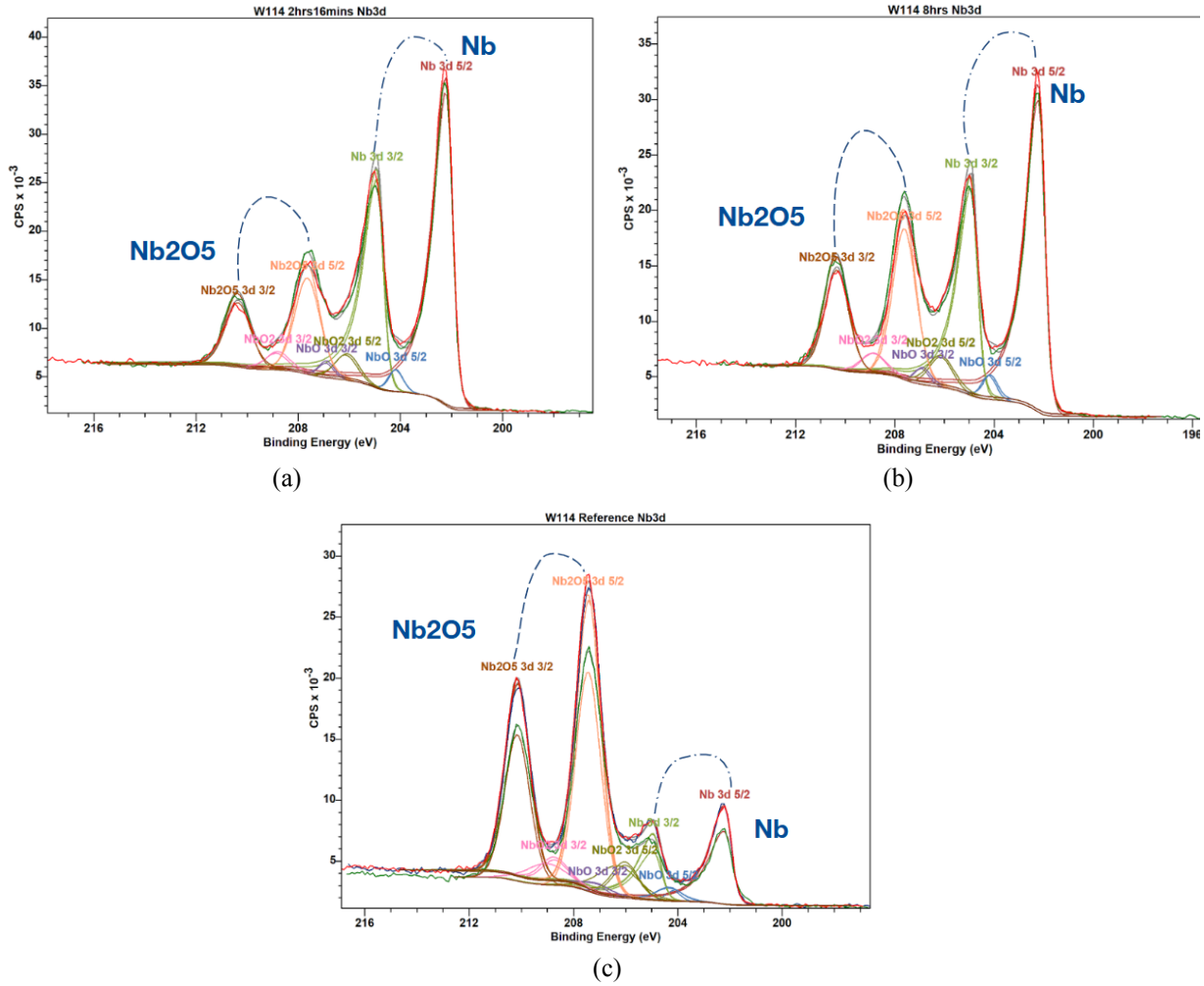

FIGURE. 3. *High resolution XPS spectra and peak fitting for Nb 3d of sample W114 over exposure time.* (a) *2 hrs and 16 mins,* (b) *8 hrs,* (c) *Reference of oxides over 3 months.*

Data is bounded by Shirley background. Fit peak indicates the presence of Nb metal and oxides. Nb metal doublet peaks are fitted using line shape LA(1.2, 5, 12) and GL(30) for Nb oxides doublet peaks. Binding Energy spectra are calibrated based on Nb Metal binding energy at 202.2 eV. Doublet separations are set to be 2.72 eV. Calibration and Fitting are implemented with CasaXPS. We observe dynamics between Nb metal and Nb_2O_5 metal over exposure time where pentoxide is growing and metal is shrinking. In these three figures, Nb pentoxides signals grows from around 15, 20 to 30 $\times$ 10^{-3} counts per second, while Nb metal signals shrinks from around 35, 30, to 10 $\times$ 10^{-3} counts per second. The ratio of Nb/Nb_2O_5 goes from ⅓, ½, to 3. Given that XPS information depth for Nb is around 7 nm, it is reasonable to assume that pentoxides continue to grow on the surface and thicken the oxide layer over exposure time, resulting in Nb_2O_5 slowly overwhelming the Nb metal signals for the first few nanometres of surface. Meanwhile, though counts of NbO and NbO_2 slightly change, they are unremarkable compared to the significant shift between Nb and Nb_2O_5.

TABLE 1. *Nb Oxide Atomic Percentage Concentration (%At conc) and Oxides ratio of Sample 114 before etching.*

Time	Nb 3d 5/2	NbO 3d	NbO2 3d	Nb2O5 3d	NbO ratio	NbO2 ratio	Nb2O5 ratio
2 hrs 16 mins	69.2%	2.8%	4.9%	22.5%	9.2%	16.2%	74.6%
8 hrs	60.6%	2.6%	5.5%	29.3%	7.0%	14.8%	78.3%
3 months	22.9%	2.3%	10.5%	60.6%	3.1%	14.3%	82.5%

Atomic percentage concentrations are quantified using the Scofield Sensitivity Factor (SF) of Nb 3d at an excitation energy of 1487 eV for XPS source Aluminum 400 W. By dividing the factor, we derived the corrected area below the oxides and metal peak from XPS data (FIG. 3) and atomic percentage concentration. And ratios of each oxide (NbO, NbO2, Nb2O5) are calculated by oxide %At conc over total oxide %At conc.

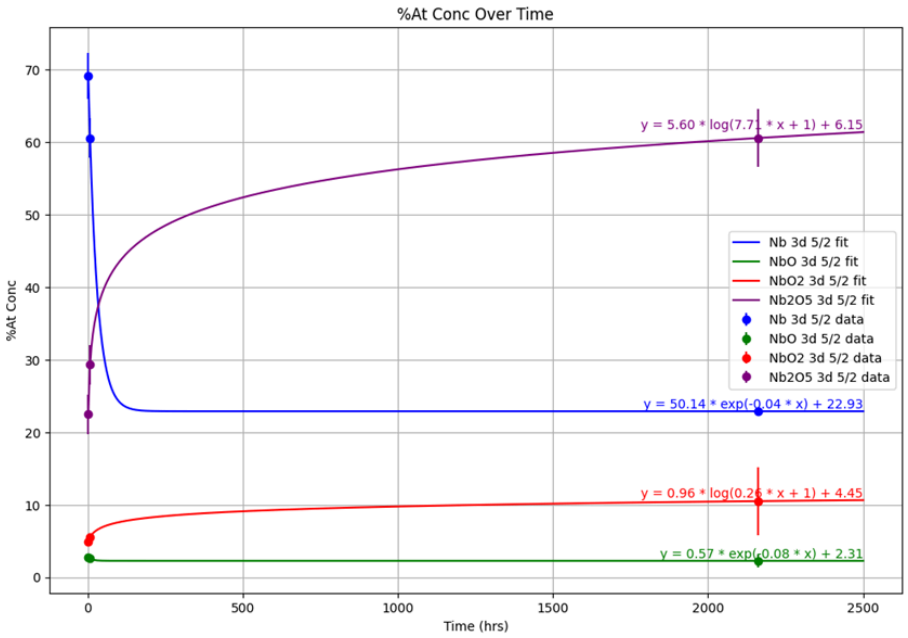

FIGURE. 4. *Nb oxide %At conc growth of Sample 114 before etching.*

Assuming the Nb oxide %At conc growth follows a monotonic growth or decay and continues to behave similarly at our reference point, we derived FIG. 4 from Table 1. Error bars indicate standard deviation from spots at the same exposure time. We observe a similar pattern between Nb oxides and metal follows FIG. 3. Nb_2O_5 follows a logarithmic growth and Nb has a sharp exponential decay. Though NbO and NbO_2 remains relatively unremarkable, we found interesting that NbO is decaying exponentially along with Nb metal while other oxides are growing. This might mean that NbO does not participate majorly or is independent of the oxide thickness growth. And we can make assumptions that as the oxides layer continues to grow, the thin film surface's chemical composition will be majorly occupied by Nb_2O_5, Nb and NbO_2 with little or no NbO.

The behavior of native oxides growth on Nb thin films has been cross-researched using XPS and ToF-SIMS measurements. In particular, the rapid formation and dominance of Nb_2O_5 on the surface is observed. Both XPS and ToF-SIMS data and analysis suggest that Nb oxides grow rapidly and overwhelm Nb metal within the first 24 hours following a logarithmic growth. Nb_2O_5 growth is dominant out of all types of Nb oxide with reaching 80% At conc within 80 days. NbO_2 is quickly saturated, maintaining 10% At conc over time with a logarithmic growth. NbO on

the opposite follows an exponential decay. Oxide thickness growth also implies sample preparation techniques impact oxide saturation and growth rate.

METHOD

Native oxides growth is investigated across samples that are with Nb thin films on Sapphire (Al_2O_3) as comparative studies. Samples' exposure time are controlled by high vacuum prior to and after the etching process. Instruments involved are Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and SPECS Custom-built x-ray photoelectron spectroscopy (XPS). They are complementary to each other to establish a depth and chemical profile for the samples' oxides.

CONCLUSION

We investigated growth of native oxides on Nb thin films after etching employing XPS and TOF-SIMS analyses. According to the XPS and TOF-SIMS analyses, we find that Nb oxides grow rapidly within 24 hrs and they saturate gradually following logarithmic equations. Detailed XPS analyses reveal changes in relative amount of NbO, NbO2, and Nb2O5 during the growth of native oxides on Nb thin films. It provides valuable insights on the evolution of native oxides after the etching process and helps improve the fabrication process of superconducting qubits to mitigate decoherence due to the surface oxides on Nb thin films.

FUTURE WORK

More data can be collected to clarify and establish stronger correlation, further investigation within the first few hours is helpful for understanding the rapid growth and saturation. In addition, comparison with other promising materials such as Tantalum which has thinner oxides thickness and less loss are worth investigation [1].

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