# Examining the effects of the surface oxide layer on Nb and Ta superconducting films for quantum devices

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## Abstract

After performing angle-resolved x-ray photoelectron spectroscopy, we observed a significant amount of Nb oxide and Ta oxide on the surface of the superconducting thin films. Using x-ray photoelectron spectroscopy (XPS) with an Al K-alpha x-ray source of 1486.6 eV, we were able to examine the surface oxide layers and using angle-resolved x-ray photoelectron spectroscopy (AR-XPS) we could estimate the oxide layer thickness. We rinsed the Ta thin film with $H_2SO_4$:HF and we suspect that the Ta oxide layer will be significantly reduced. The formation of oxide layers on superconducting thin films is a known source of decoherence and two-level system losses in quantum devices; ways to mitigate these the formation of oxide layer and metallic hydrides are also discussed.

## Introduction

Superconducting thin films are necessary components of many quantum devices and the formation of oxide layers on these films causes decoherence or two-level system (TLS) loss. Decoherence occurs when the entangled particles collapse into the classical components, which is not ideal for quantum bits or quantum devices.[3] TLS loss is the loss that occurs at the junction of two interfaces; for this experiment, the metal-air interface.[1] The interaction of the air with the surface of the metal causes oxygen to bond with the metal atoms; these metal oxides are amorphous structures. When the superconducting thin film is cooled down to cryogenic temperatures, the coupled electrons (cooper pairs) cannot travel through the amorphous structure like it can with a metallic lattice. The electrons will be pulled towards the metal oxide atoms, generating heat within the quantum device, causing the wave function to collapse into its classical components.

The wet-etching process can introduce hydrogen to the surface thin film, creating metallic hydrides. Wet-etching is a process in which the thin film is placed into an acidic or basic solution to dissolve the native oxide layer. Or the thin film can be coated in a photoresist and etched to have a specific pattern, then placed into the solution. The solution will dissolve the areas that are not covered with the photoresist, hence creating a pattern on the film. Metallic hydrides, like metallic oxides, are amorphous structures that contribute to decoherence in superconducting thin films for quantum devices. Unlike other elements, hydrogen cannot be detected using XPS, because of its small cross section. So, we must observe the hydrides via a different method.

We used x-ray photoelectron spectroscopy to study the oxide layers on Nb and Ta superconducting thin films. XPS is a non-destructive technique that implements the photoelectric effect. The photoelectric effect is the emission of electrons when electromagnetic radiation hits the surface of a sample. The XPS machine detects the emitted electron of a certain energy; the energy of each electron corresponds to a particular orbital of a specific element.[5] The detector uses the binding energy, the energy it takes for the electron to be liberated from the atom, or the kinetic energy, the energy of the electron in motion; to relate it back to a certain element. Angle-resolved XPS is a surface sensitive technique of the XPS. The sample stage will be tilted to pre-set angles. The higher the angle of the sample stage, the more surface sensitive the data collected is. Because the x-ray does not penetrate the sample to the depth it does at 0º, we can estimate the thickness of the oxide layer on the film.

**Experimental Procedure**

The first sample was 155 nm Nb deposited onto a Si substrate; the second, Ta deposited onto an $Al_2O_3$ (sapphire) substrate.

To examine the oxide layer, we used the XPS with an Al K-alpha x-ray source at 1486.6 eV. To obtain an estimate of the oxide layer thickness, we used AR-XPS, a technique of the XPS. We tilted the sample from 0º to 30º in increments of five, taking data from each. All data was taken under vacuum conditions at room temperature. We used CasaXPS software to analyze the data by fitting peaks to the curves of the data. A Shirley background was used to peak fit all the data.

After analyzing the Ta/$Al_2O_3$ sample, we soak it in a solution of $H_2SO_4$:HF with a molar ratio of 9:1 for one minute. Then, it was taken out of the solution and rinsed with water for less than 5 minutes. It was exposed to air for 1 to 2 minutes before being placed into a plastic bag that was then pumped with nitrogen.

**Results**

**Figure 1** shows Nb 3d spectra from the Nb/Si thin film taken at 0º, 5º, 10º, 15º, and 20º. After fitting the curve, there was a large amount of $Nb_2O_5$ present, as well as Nb sub-oxides of NbO and $NbO_2$. Metallic Nb was also detected and is less abundant when compared to $Nb_2O_5$. The concentration of the Nb oxides increases with increasing angle. The amount of metallic Nb decreases with increasing angle.

**Figure 2** is the O 1s spectra from the Nb/Si sample, also taken at 0º to 20º in increments of five. There was a signal from the $Nb_2O_5$, oxygen double bonded to carbon is also detected on the surface of the thin film.

**Figure 3** shows the Ta 4f orbital from the Ta/$Al_2O_3$ sample taken at 0º to 20º. $Ta_2O_5$ and metallic Ta were detected on the surface of the film. Ta sub-oxides exist on the sample, but they did not show in the curve to a significant degree, so we could not accurately peak fit them. Like the Nb, as the angle increases, so does the concentration of $Ta_2O_5$ and the concentration metallic Ta decreases.

**Figure 4a** and **4b** show the thickness of the oxide layers on Ta and Nb thin film samples. The thickness of the Nb oxide layer was 3.9 nm and the thickness of the Ta oxide layer was 3.0 nm. To calculate the thicknesses of each, the following equation was used:

$$d_{ox} = L_{ox} cos\Theta(1 + \frac{I_{ox}}{R_{ox} I_{ele}})$$

$d_{ox}$ being the thickness of the oxide layer, $L_{ox}$ and $R_{ox}$ are the values of linear interpolation of the metallic oxide and the metal as it relates to the amount of oxygen bonded to the metal. $I_{ox}$ is the sum of the area underneath the metallic oxide peaks. $I_{ele}$ is the sum of the area under the curve of metal spin-orbit pair.[2] Using AR-XPS we could obtain the area under the peak-fitted curve for each Nb oxide, then we summed them together to get an estimate of the total oxide layer thickness. For the Ta sample, we could only fit $Ta_2O_5$, so summing the oxides was unnecessary. The XPS machine was down at the time the $Ta/Al_2O_3$ was rinsed, so we could not analyze the resultant Ta oxide layer thickness or potential contaminants introduced. Even so, suspected results are discussed.

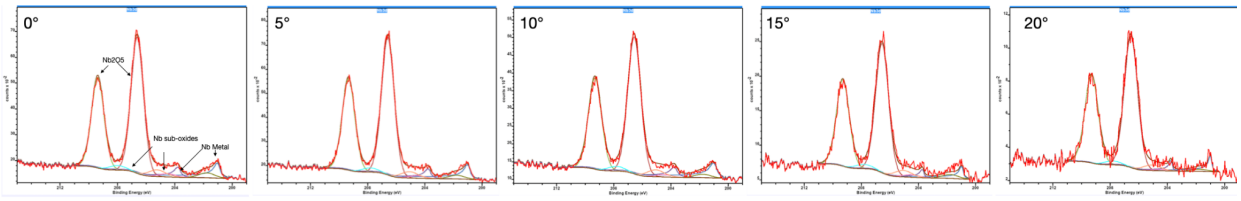



**Figure 1** - The peak fitting of Nb 3d spectra obtained from the Nb/Si thin film sample as Nb metal and oxides relate to increasing surface sensitivity.

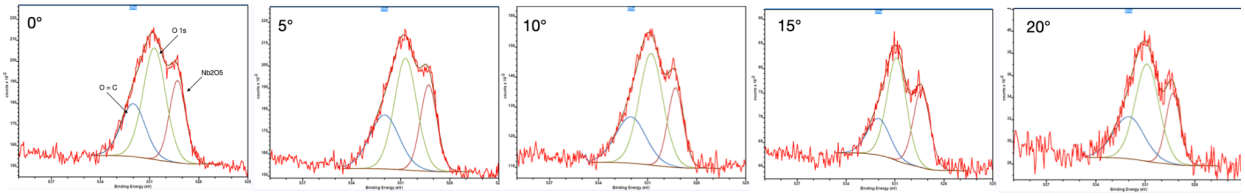



**Figure 2** - Peak fitting of the O ls spectra from the Nb/Si sample as it relates to increasing surface sensitivity.

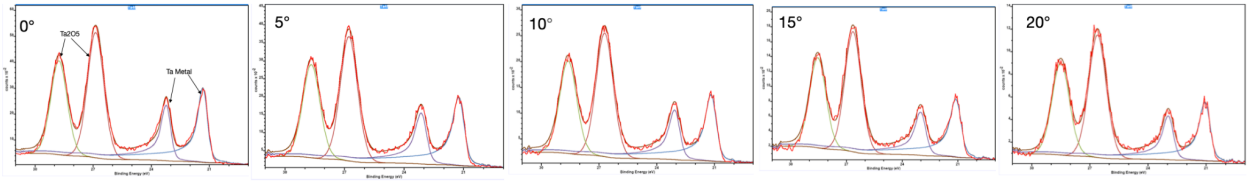
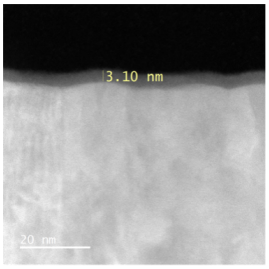



**Figure 3** - Peak fittings of the $Ta_2O_5$ and Ta metal from the Ta 4f spectra as they relate to increasing surface sensitivity. From the $Ta/Al_2O_3$ sample.

a. 

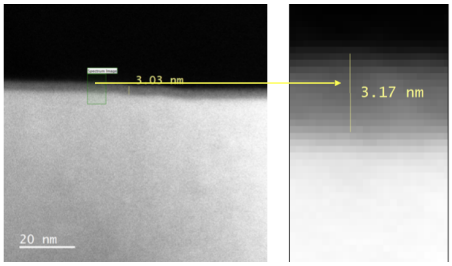
b. 


**Figure 4** - a. An image of the Nb oxide layer of the Nb/Si thin film sample. b. An image of the Ta oxide layer of the Ta/$Al_2O_3$ sample and a zoomed in image of the Ta oxide layer. Data provided by Jae-Yel Lee.

**Discussion**

The data suggests that there is a significant amount of metal oxides on the surface of the Nb and Ta thin films. For both the Ta and Nb films, the amount of metal oxides increases with the increasing surface sensitivity; while the elemental Ta and Nb decreases with increasing surface sensitivity. Because of the unordered nature of oxides, it is essential to reduce their concentration as much as possible, so decoherence in quantum devices does not occur.

Ways to reduce the oxide layer include optimizing the wet-etching process and baking the thin film to dissolve the oxide layer. Using an acidic etchant, like Hydrofluoric acid (HF) will dissolve the Nb and Ta oxides, but can introduce hydrogen which will bond with Nb and Ta to create metallic hydrides, an amorphous, non-superconducting material.[6] We rinsed the sample with a 9:1 $H_2SO_4$:HF ratio for one minute. Suspected results would be a decrease in the thickness of the oxide layer, but perhaps the introduction of metallic hydrides. The use of a basic solution in the wet-etching process such as sodium hydroxide (NaOH) can, potentially, reduce the formation of metallic hydrides.[4,7] Baking a thin film requires the sample to be heated to high temperatures to dissolve the oxide layer on the surface.

**Conclusion**

On the surface of Ta and Nb superconducting thin films, a significant amount of metallic oxides exist. Using XPS we were able to study these oxide layers, and using AR-XPS we could estimate the thickness of the oxide layers on the two samples. The rinsing of the Ta/$Al_2O_3$ sample with $H_2SO_4$:HF can, possibly, reduce the oxide layer thickness on the surface of the thin film.

Future steps to reduce the amount of metallic oxide and the formation of metallic hydrides would be to optimize the wet-etching process, possibly, by implementing the use of a base instead of an acid. And, baking the film can reduce the oxide layer by dissolving it at high temperatures.

**References**

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