

# PROGRESS ON ZIRCONIUM-DOPED NIOBIUM SURFACES\*

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## Abstract

The first experimental studies of zirconium-doped surfaces verified that zirconium can enhance the critical temperature of the surface, resulting in a lower BCS resistance than standard-recipe niobium. However, they also produced a disordered oxide layer, resulting in a higher residual resistance than standard-recipe niobium. Here, we show that zirconium-doped surfaces can grow well-behaved thin oxide layers, with a very thin ternary suboxide capped by a passivating  $\text{ZrO}_2$  surface. The elimination of niobium pentoxide may allow zirconium-doped surfaces to achieve low residual resistance.

## INTRODUCTION

Work on niobium-zirconium alloys as SRF materials began very recently as of this writing. Researchers in the Hennig group at the University of Florida and in the Arias group at Cornell independently identified the Nb-Zr system as a promising candidate material, which then helped motivate the development of the first niobium-zirconium surface alloy recipes at Cornell by Dr. Zeming Sun. The research quickly became even more interesting when experimental results not only showed the anticipated elimination of niobium oxide and formation of a bcc alloy, but also higher  $T_c$ 's than had previously been measured for this system. Specifically, multiple samples exhibited a  $T_c$  in the 13-16 K range, compared to the maximum of just under 11 K in reported the literature [1].

There is much still to understand about the superconductivity of zirconium-doped niobium. In particular, ongoing theory work has explored the potential effects of alloy ordering and carbon contamination on  $T_c$  in the Nb-Zr system [2, 3]. In this short proceeding, however, we will focus on the effects of zirconium doping on the oxide surface. The first zirconium-doped sample to undergo RF testing utilized an electrochemical process, which resulted in a thick, disordered surface oxide and a relatively high residual surface resistance [1]. Here we show that sputter deposition of very thin zirconium layers on niobium followed by vacuum baking can produce a thin, zirconium-rich surface oxide. Notably, we show that it is possible to completely eliminate the niobium pentoxide from the surface. The result is a niobium surface terminated by a passivating zirconium oxide

of similar thickness to the usual niobium native oxide. The usefulness of this approach was first demonstrated with a passivating  $\text{Al}_2\text{O}_3$  layer [4].

The niobium pentoxide is believed to cause significant losses that could hinder qubit and other low-field applications. Therefore, the demonstration of a practical method to eliminate this oxide from a niobium superconducting surface could be of considerable interest for low-field applications. In contrast to the niobium oxide, the zirconium oxide exists almost entirely in the inert, fully oxidized  $\text{ZrO}_2$  state which should not contribute to RF dissipation [5, 6]. Our results are in agreement with previous XPS studies of atomic-layer-deposition zirconium nitride on niobium, which also produced a  $\text{ZrO}_2$  surface with no niobium pentoxide after annealing [7].

## METHODS

We use an AJA sputter deposition tool to deposit zirconium on niobium sample coupons. Prior to deposition, coupons received a standard pre-preparation consisting of a 60-micron electropolish, a 5-hour 800 °C vacuum bake, and a 2-micron electropolish. The sputter deposition tool first removed the niobium native oxide by argon plasma sputtering, and then deposited approximately 2, 3.75, 7.5, and 10 nm of zirconium on four different samples. The deposition rate was based on the rate for similar metals and has not yet been directly calibrated. The samples then received another 800 °C vacuum bake in order to fully dissolve any remaining niobium oxide and establish a uniform interface between the niobium metal and the protective zirconium oxide layer.

XPS allows identification of various elements present near a sample surface as well as analysis of different phases or oxidation states of an element. This allows for discrimination between different oxides of niobium and zirconium, and allows for at least an approximate understanding of the relative thicknesses of different oxide layers if we assume that sensitivity decreases exponentially with depth. The XPS system used for sample analysis in this study was a Thermo Scientific Nexsa G2 X-Ray Photoelectron Spectrometer System; this paper focuses on element-specific scans for niobium and zirconium. We then use CasaXPS analysis software to fit the data to a combination of elemental and oxide phases.

## RESULTS

For increasing zirconium deposition thickness in the range of 0-3.75 nm, we find that the oxide rapidly becomes more zirconium-rich; in particular, by 3.75 nm thickness, there is no detectable niobium component in the primary oxide (Fig. 1). Additionally, the combined intensity of the

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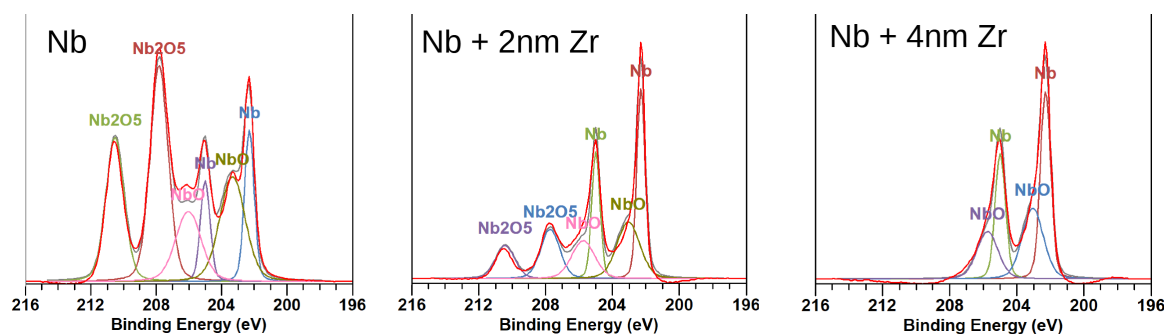


Figure 1: Peak fitting of niobium XPS data. The overall niobium oxide intensity decreases monotonically with increasing zirconium deposition thickness, and the pentoxide intensity in particular becomes undetectable by 3.75 nm zirconium deposition thickness.

niobium and zirconium suboxide peaks (Fig. 2) decreases slightly relative to the intensity of the niobium metal peak, suggesting that the suboxide layer in the 2 nm and 3.75 nm samples is very thin (Fig. 3). For increasing zirconium deposition thickness in the range 3.75-10 nm, however, both the primary  $\text{ZrO}_2$  oxide and the suboxide (which is now zirconium-rich) become thicker.

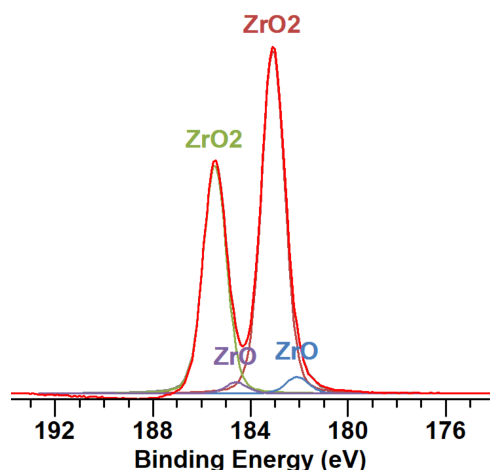


Figure 2: Peak fitting of zirconium XPS data. All samples were very similar in this regard, showing a small but significant suboxide shoulder and no detectable elemental zirconium component.

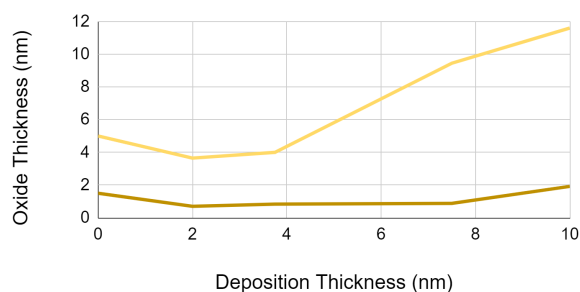


Figure 3: Preliminary estimates of oxide layer thickness as a function of zirconium sputter deposition thickness.

## DISCUSSION

Our results can be explained by the energetic favorability of the zirconium oxide compared to the niobium oxide, and by the absence of ternary oxide phases involving niobium and zirconium. In contrast to other capping layers that have previously been explored, in particular  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$ , it is apparent that  $\text{ZrO}_2$  on niobium resists decomposition to high temperatures [7]. This can be explained by the fact that  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$  will react with niobium to form ternary oxides such as  $\text{MgNb}_2\text{O}_6$  [8],  $\text{NbAlO}_4$  [9],  $\text{YNbO}_4$  [10] respectively, but no ternary oxide exists for the Nb-Zr-O system. The Nb-Zr- $\text{O}_2$  interface is therefore highly stable, and  $\text{ZrO}_2$  is a particularly effective passivating oxide for niobium.

In general, the zirconium-doped niobium surface consists of a primary oxide layer, a suboxide layer, and the metal substrate layer. Increasing zirconium deposition thickness first affects the composition of the primary oxide, then affects the composition of the suboxide, and eventually (for thicknesses beyond what was considered in this study) will begin to affect the composition of the metal substrate. It is clear that within the current methodology of sputter deposition with post annealing it will not be possible to achieve alloying without also forming a very thick (compared to the niobium native oxide) zirconium oxide layer (Fig. 3). Concerningly, the normal-conducting suboxide layer also appears to become thicker with increasing zirconium deposition thickness, which we infer from an increasing magnitude of the zirconium suboxide XPS peak relative to the niobium metal peak. This motivates us to move toward a chemical vapor deposition system to apply this method to RF cavities, which would allow for *in situ* deposition of zirconium at high temperatures, potentially allowing for alloying without the formation of a very thick zirconium oxide.

## CONCLUSIONS

We have demonstrated a method to eliminate the niobium pentoxide from a niobium superconducting surface. We expect that this method may be applicable to niobium superconducting devices and niobium-zirconium alloy surfaces,

as well as possibly other niobium-based superconducting surfaces which typically form a niobium-rich oxide.

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