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Degradation of Superconducting Nb/NbN Films by Atmospheric Oxidation

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***Abstract*—Niobium and niobium nitride thin films are transitioning from fundamental research toward wafer scale manufacturing with technology drivers that include superconducting circuits and electronics (SCE), optical single photon detectors (SPD), logic, and memory. Successful microfabrication requires precise control over the properties of sputtered superconducting films, including oxidation. Previous work has demonstrated the mechanism in oxidation of Nb and how film structure could have deleterious effects upon the superconducting properties. This work provides an examination of atmospheric oxidation of NbN films. By examination of the room temperature sheet resistance of NbN bulk oxidation was identified and confirmed by secondary ion mass spectrometry (SIMS). Meissner magnetic measurements confirmed the bulk oxidation not observed with simple cryogenic resistivity measurements.**

***Index Terms*—superconductivity, niobium, niobium nitride oxidation**

I. Introduction

Niobium has proven to be one of the more useful superconductors with depositions processes including sputter deposition and pulsed laser deposition (PLD)[1-3]. As a transition metal, the deposited film is highly compatible with CMOS fabrication and due to the volatility with fluorine, it is also easily etched in plasma etch systems[4]. The film has a high critical current and a reasonable transition temperature at 9.2 K, compared to other low temperature superconductors [5-7]. This material has been well studied and highly valued in its role in Nb/AlO_x/Nb Josephson junctions [8-12]. Niobium can also be reactively sputtered with nitrogen to create another useful superconductor, NbN, to achieve improved properties such as an increased transition temperature up to 17 K. Niobium nitride has also been touted as an improvement with regards to film stability[13].

This work looks at the effect of oxidation of niobium nitride and compares it with previous work of niobium. When NbN is prepared with serrations in the film's grain, bulk oxidation is observed to occur. As the oxygen approaches the interface of the film and substrate, the oxygen transmission becomes reduced. By monitoring the resistance of the film over time and comparison of the Meissner effect with electric resistance verses temperature, identification of bulk oxide can be inferred. SIMS and transmission electron microscope (TEM) electron dispersive scan (EDS) confirm the bulk oxidation of NbN.

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II. Oxidation of Niobium

Like most metals, Nb will oxidize with a final oxide which is not only not superconductive but also insulating. The oxidation process of niobium is a complex process where Nb first reduces to NbO_x and then to Nb_2O_5. Although not completely insulating, NbO_2 has a much reduced superconductive transition at approximately 1.5 K [14, 15]. As the oxidation continues it oxidize it creates a final insulating oxide of Nb_2O_5. Growth dynamics at room temperature (RT) is a rich and well investigated field [16-18]. In a simplified model, oxygen undergoes a slow, and hence shallow, diffusion where the O_2 is split and is neutralized with electrons tunneling across the oxide growth as described by Mott-Cabrera oxidation theory [16, 19]. The growth continues until electron tunneling becomes greatly reduced and the oxidation rate exponentially deaccelerates around 5-7 nm thick.

The oxide will effectively cease to grow unless the NbO_x begins to create serrations in the oxide and Nb films; achievable only if the film stress permits. When this occurs oxygen can penetrate deeper into the bulk Nb and the oxidation process continue. Similarly, if the Nb film has inherent gaps, serrations, or cracks among the film, the same oxidation process continues. The overall result is a superconductive film which is greatly diminished in transition temperature and with performance equivalent of a thinner Nb film. Although the surface oxidation, which occurs in time periods of a few days, can't be prevented without the use protective films or inert atmospheres, bulk oxide preventions has been demonstrated. Previous work has indicated that if the Nb film can be compressed adequately, the serrations which drive oxygen into the bulk film can be prevented. This was demonstrated using 200 nm Nb films with stress approximately 700 MPa in atmosphere for periods longer than 17 months with little change in RT resistivity measurements and Meissner measurements[1].

In previously described work, Nb was sputter deposited on thermal silicon dioxide films, under a range of conditions[1]. Over a period of a year and a half in atmosphere, the films were periodically measured using a VersaProbe VP10 wafer level 4 –probe measurement tool and a Quantum Designs magnetic properities measurement system (MPMS) tool. The first tool, when combined with profilometer thickness measurements, measures film resistivity. The second tool injects a magnetic field with SQUID detection to measure the Meissner effect thru the film. The MPMS measurements generate an integrated

superconductive response over the entire film. The results indicated that films with stress greater than about 400 MPa, little oxidation occurred in the films and Tc's remained close to the 'dirty limit' of 8.4 K, Fig 1[7].

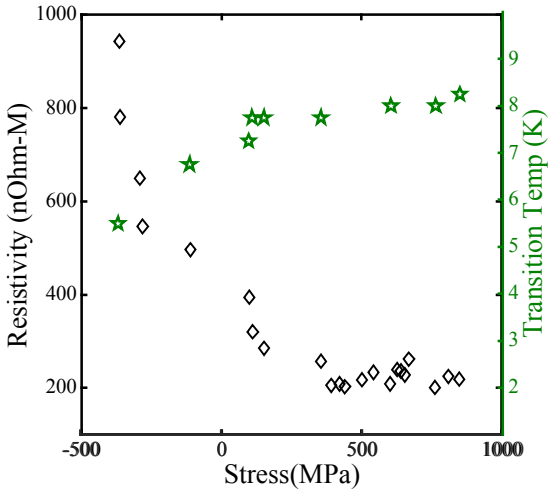

Figure 1. Effect of film stress on the resistivity (diamonds) and superconductive transition temperature (stars) of Nb after 17 months of RT oxidation.

The amount of oxidation was confirmed using SIMS and a FEI Titan S/TEM with a Cs probe corrector, operated at 200 keV by EDS comparison of the oxygen KA and niobium LA transitions, Fig 2 and 3. Overlay in figure 2 is a SIMS measurement, reporting only the atomic % of oxygen, approximately aligned with the surface of the Nb and the thermal oxide of the substrate. At the surface oxygen concentration is presumed to be due to only Nb_2O_5 oxide. In the bulk of the film, oxygen concentration decreases to below 1% at. The TEM EDS measurement confirms the surface oxide and lower concentration in the bulk of the film. The known good results of niobium were then utilized to help understand the bulk film oxidation of niobium nitride.

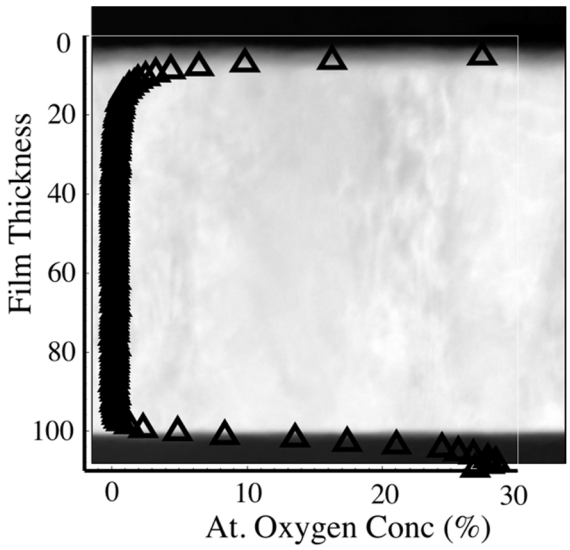

Figure 2. TEM measurement of 100 nm thick Nb with SIMS at. oxygen concentration overlaid as measured by SIMS.

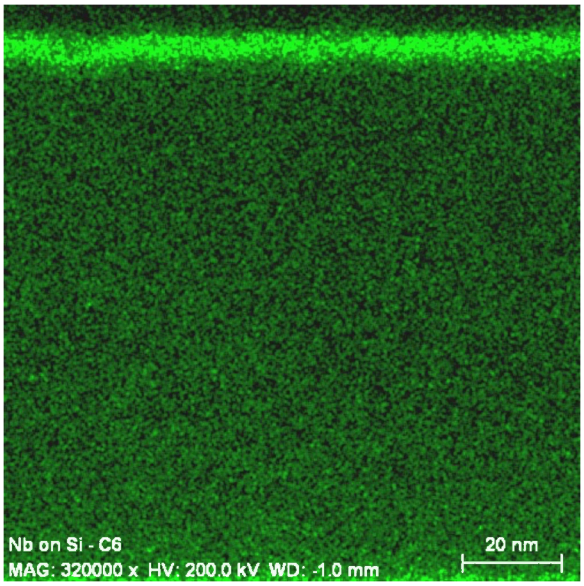

Figure 3. TEM EDS measurement oxygen concentration in the 100 nm Nb film.

III. Oxidation of Niobium Nitride

The niobium nitride was sputter deposited using a Denton Discovery 550 reactive sputter deposition tool using 15 sccm of Ar on 150 mm (100) silicon wafers with 500 nm of thermal silicon dioxide. From over 15 different films deposited under varying N_2 and DC power conditions, the two highest Tc NbN films are reported here. Film A was deposited with 1 sccm of N_2 at 125 W approximately 150 nm thick and film B was deposited with 0.4 sccm of N_2 at 75 W. Using the same tooling as the Nb films, measurements performed on the two nitride films after 17 days in atmosphere included RT resistivity 4 probe, MPMS and 4 probe electrical vs. temperature, TEM and EDS, and SIMS.

Using the VersaProbe, RT measures demonstrated a rapid oxidation growth of the film by plotting a normalized resistivity measurement verses time, Fig 4. For comparison, RT oxidation of a 100 nm thick Nb film is also presented. Where the Nb terminates oxide growth, as noted by a limiting 1% change in total resistivity, the NbN continues to oxidize well past 4%. This data is re-plotted, as suggested by Ghez [19], to demonstrate Mott-Cabrera growth, Fig 5. When oxide thickness is plotted in the $1/t_{ox}$ vs log $(time/t_{ox}^2)$ format, negative linear slopes have been shown to follow terminal surface Mott-Cabrera oxidation. This slope is seen with Nb. However, NbN is seen to have exactly opposite characteristics with a positive linear slope clearly indicating that the oxidation is not stopping at the surface of the nitride.

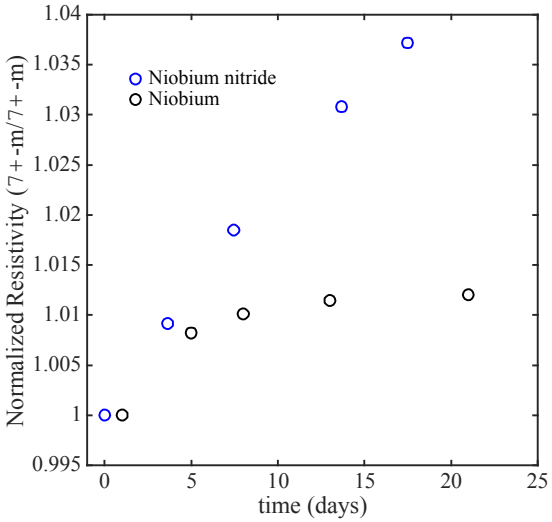

Figure 5. Resistivity measurement of Nb and NbN films over time and normalized. Nb develops a terminal surface oxide while NbN continues to oxidize.

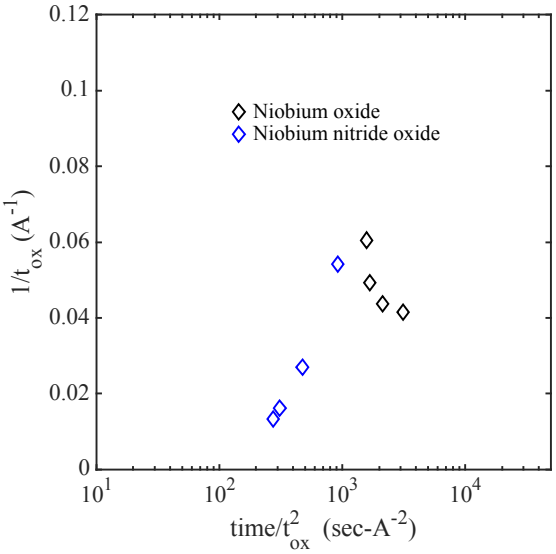

Figure 6. Resistivity measurement of Nb and NbN films over time plotted to confirm Mott-Cabrera oxidation. Nb develops a terminal surface oxide while NbN continues to oxidize.

SIMS measurements were made showing very high atomic oxygen content for both films; well over 8% at O, Fig 6 and 7. Instead of the decaying oxygen gradient seen in Nb and suggestive of a diffusion limited process, a very different profile was observed for the NbN films. Very high concentrations of oxygen were observed well over 50 nm deep in the bulk and only decayed below 1% at. for the final 20 nm. TEMs with the SIMS measurements overlaid, show very deep serrations into the bulk of the film and suggest that once the film became compacted to a stress level sufficient to prevent oxygen diffusion, the oxidation of NbN could be slowed.

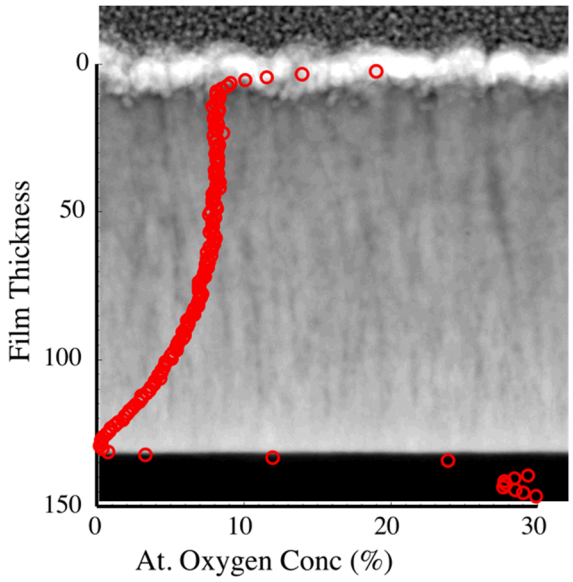

Figure 7. TEM measurement of NbN film A with SIMS at. oxygen concentration overlaid as measured by SIMS.

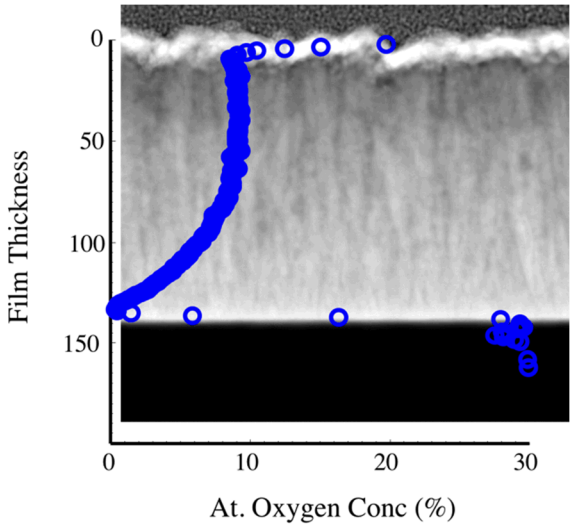

Figure 8. TEM measurement of NbN film B with SIMS at. oxygen concentration overlaid as measured by SIMS.

EDS measurements of oxygen confirm the SIMS results, Fig 8. To understand the impact of the oxidation on the superconductive properties of the NbN, both electrical and MPMS cryogenic measurements were performed. Both films demonstrated electrical transition temperatures close over 13 K, Fig 9 and 10. However, MPMS results indicated a much lower bulk Tc closer to 10 K. This suggests that although filaments exist in the films with good superconductive properties, the majority of the film has been negatively altered with the bulk oxidation.

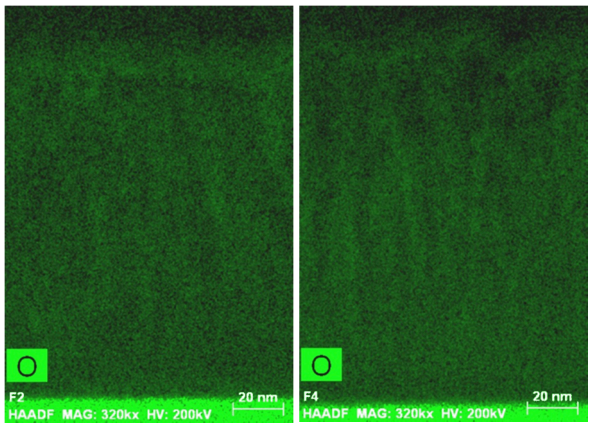

Figure 9. TEM EDS measurement oxygen concentration in the NbN films. (left) is film A and (right) is film B measurements.

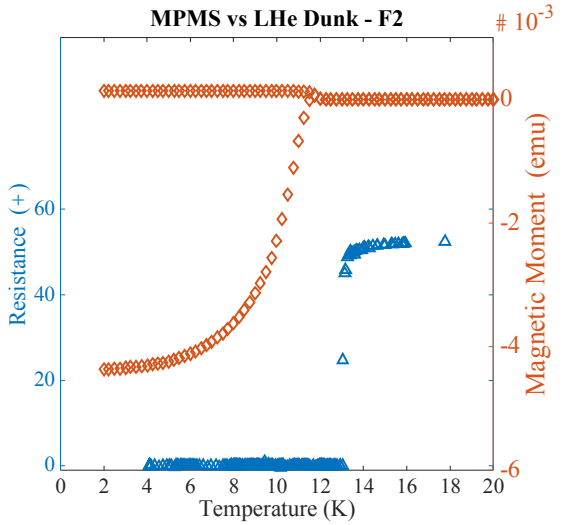

Figure 10. Superconductive measurements of NbN film A using MPMS (diamonds) and electrical resistivity (triangles).

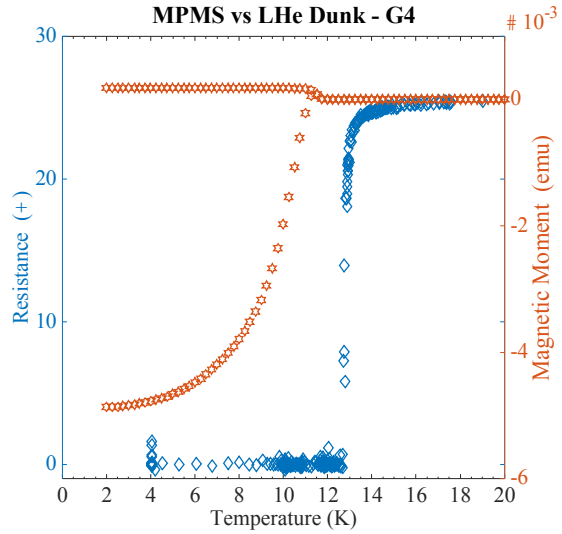

Figure 11. Superconductive measurements of NbN film A using MPMS (diamonds) and electrical resistivity (triangles).

IV. Conclusion

This work has demonstrated the oxidation effects of NbN into the bulk of the films. Due to serrations in the film, oxygen was able to diffuse and react deep into the bulk. SIMS and TEM EDS measurements indicated oxygen transport along the grains but simple RT resistivity measurements also suggested that a terminal surface oxidation and bulk oxidation effect could be differentiated when plotted over time. Although good superconductive electrical transitions could be observed, likely due to filament conduction paths, bulk film superconductive properties measured using Meissner measurements suggests that the NbN films were severely degraded. This work indicates that RT surface resistance measurements combined with MPMS could be useful as a screening method for identification of bulk film oxidation of NbN and Nb.

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