Influence of TMAH development on niobium nitride films

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The use of electron beam lithography to pattern niobium nitride (NbN) films has facilitated devices of critical importance to the fields of communication and computation, such as superconducting nanowire single photon detectors (SNSPDs) and comparator-like nanocryotrons[1]. Hydrogen silsesquioxane (HSQ) is a popular electron beam resist for such processes due to its high resolution and superior line-edge roughness. Development of HSQ patterns is often done with a 1-4 min dip in 25% tetramethylammonium hydroxide (TMAH); TMAH is also used to pre-treat the substrate in order to promote HSQ adhesion. Despite the overall importance of TMAH in this process, a complete study of its impact on NbN films has yet to be reported.

In this work, we show that TMAH exposure increases the etch resistance of NbN in CF_4 due to a modification of the surface chemistry. As observed experimentally, this negatively impacts pattern transfer for thick NbN films by threatening to etch away the HSQ mask before the surrounding NbN is removed. Figure 1 compares the sheet resistance of ~30 nm thick NbN films after reactive ion etching as a function of development time in 25% TMAH. The difference in resistance between the developed substrates and the undeveloped control increases with longer etch time, indicating that a type of etch barrier has been created by the interaction of NbN with TMAH. Complete removal of the developed films required nearly twice the etch time as the control. To test if this barrier was resistant against dilution, we performed these measurements on films that had been rinsed in deionized water for the typical 30 s after development, and on films that had been rinsed vigorously under running DI water for 3 min. Comparison of the results shows that while a vigorous 3 min rinse can help reduce the etch barrier, the alteration of NbN by TMAH is still present. The increase in resistance with development time indicates that the superconducting film reacts with TMAH to form the etch barrier, thinning the pure NbN. This has been alluded to in past literature by an observed increase in sheet resistance and decrease in critical temperature after prolonged exposure (~ 4 min) to TMAH[2].

Recent studies on aqueous polyoxometalates have demonstrated that clusters can form from interactions between Group V metal oxides and TMAH salts[3]. As shown in Figure 2, an NbN film that is submerged in 25% TMAH for 4 hours has noticeably enhanced surface roughness in comparison to a bare NbN film. This is an initial indication that the interaction of TMAH with NbN forms an etch barrier comprised of niobium-based clusters. Further material investigations (*e.g.* IR spectroscopy) are needed to confirm the identity of the clustered species.

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[1] McCaughan, A. N., Berggren, K. K. *Nano Letters*, **2015**
[2] Najafi, F. *et al*. *IEEE Journal of Selected Topics in Quantum Electronics*, **2015**
[3] Fullmer, L. *et al*. *Cryst. Growth Des.*, **2015**

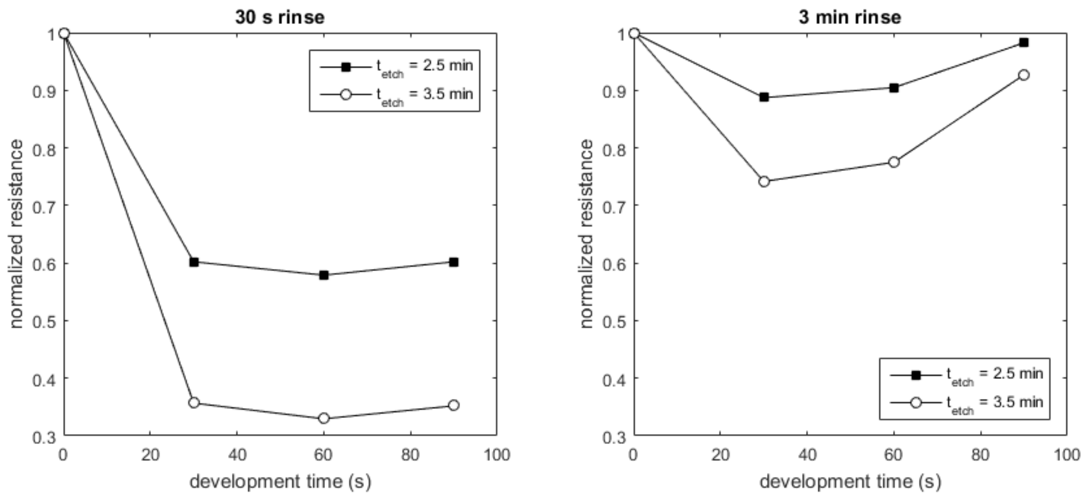

Figure 1: Impact of TMAH development on the reactive ion etching of NbN. Plots show the resistance versus development time in 25% TMAH, where resistance has been normalized as a fraction of the resistance of the bare NbN film. Resistances were measured after 2.5 min and 3.5 min of reactive ion etching (RIE) in CF_4. (Left) Samples were rinsed for 30 s in DI water after TMAH development. The slight difference between the three developed films in comparison to the bare film indicates that the etch barrier is still very present after a 30 s rinse. (Right) Samples were vigorously rinsed under running DI water for 3 min after TMAH development. The data suggests that vigorous washing leads to roughly the same etch barrier thickness for each of the developed samples; however, the remaining NbN film thickness depends on the total time it has been developed. As a result, the resistance follows a directly proportional relationship with development time, since longer exposure to TMAH reduces the film thickness and increases the sheet resistance.

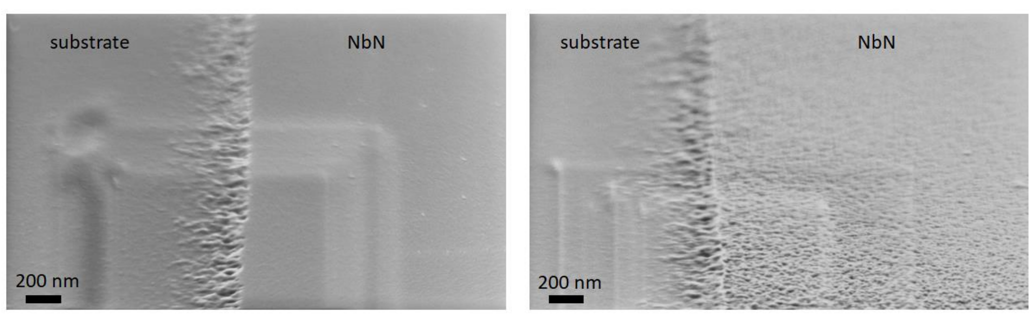

Figure 2: Effect of TMAH on the surface of NbN. SEMs reveal the difference in surface features between a bare NbN structure (left) and one that has been submerged in 25% TMAH for 4 hours (right). The edge was created on a single NbN film using direct write laser lithography. After cleaving the chip and stripping the resist, half of the sample was submerged in 25% TMAH and the other was left bare. Rectangular features in the SEMs are caused by residue from previous imaging.