Aging of Ultra-Thin Niobium Films

Daniel F. Santavicca and Daniel E. Prober

***Abstract*—We characterize the evolution of the electrical properties of ultra-thin niobium films stored in ambient conditions over a period of approximately seven months. Patterned films with thicknesses between 8 and 16 nm were fabricated via electron-beam deposition on unheated silicon substrates using a lift-off process. The film quality is similar to previous results obtained with sputter deposition onto unheated silicon substrates. The increase of the resistance and the decrease of the superconducting critical temperature are well described by an exponential function with a time constant of approximately 37 days.**

***Index Terms*—Nanofabrication, niobium, superconducting devices, superconducting thin films.**

I. Introduction

NIOBIUM (Nb), with the highest critical temperature of any elemental superconductor, is widely used in superconductive electronics. In detector applications—such as bolometers [1]–[3], superconducting nanowire single-photon detectors [4], [5], and kinetic inductance detectors [6], [7]—it is advantageous to minimize the volume of the active superconducting element, and so very thin films are commonly used. Decreasing the cross-sectional area of a superconducting nanowire increases its kinetic inductance, so ultra-thin films are also useful for applications based on kinetic inductance [8]–[10].

While it is possible to achieve critical temperatures above 4.2 K with Nb film thicknesses below 10 nm [11]–[16], we have observed that devices made with such ultra-thin films exhibit a significant reduction in critical temperature after being stored in ambient conditions for an extended period of time. Aging effects can be minimized by employing a capping layer to prevent oxidation [11], [12], but this is not always practical, e.g. due to fabrication limitations or because the additional material alters the electromagnetic or thermal properties of the device. To understand the aging of devices that do not employ a capping layer, we have characterized the electrical properties of patterned Nb films of different thicknesses over a period of approximately 7 months.

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II. Sample Fabrication and Experimental Procedure

High-resistivity ($> 20\,\mathrm{k}\Omega\mathrm{cm}$) silicon substrates with a native oxide were spin-coated with a monolayer of PMMA A3 and patterned with electron beam lithography. Development was performed in a 1:3 mixture of IPA and water with sonication. Nb was deposited via electron-beam evaporation in a system with a base pressure of 1×10^{-7} torr. During deposition, the pressure increased to $\approx 4 \times 10^{-7}$ torr. Prior to deposition, the substrate was subjected to a 30 s ion beam cleaning. Nb was deposited on the unheated substrate at a nominal rate of 0.5 nm/s.

Electron-beam deposition of Nb onto unheated substrates produces granular, polycrystalline films [15]. High-resistivity silicon was chosen as the substrate because it is compatible with far-infrared detector applications [16]. The films studied have thicknesses of 8, 12, and 16 nm. The Nb thickness as a function of deposition time was calibrated with spectroscopic ellipsometry, and the run-to-run variation in film thickness is expected to be less than ± 0.5 nm. Samples were allowed to cool for 10 minutes after deposition prior to removal from the vacuum system.

Previous work by Delacour *et al.* found that electron-beam deposition of Nb in ultra-high vacuum on heated R-plane sapphire substrates (660 °C) produced crystalline films that exhibited superconductivity at thicknesses down to approximately 3 nm [11]. These films were capped with 2 nm of silicon to minimize oxidation. In contrast, our deposition on unheated silicon produces granular films that exhibit lower critical temperatures for the same thickness. Deposition on an unheated substrate has the advantage that it is compatible with lift-off and multi-step fabrication processes and hence it is often more convenient for device fabrication.

Films were patterned in strips 500 nm wide and 50 μm long with large contact pads at either end, as shown in Fig. 1. The samples were connected to a sample holder in a four-wire configuration. The resistance of each sample was measured as a function of temperature using a lock-in amplifier with an rms excitation current of 100 nA. Radio-frequency low-pass filters at room temperature were used on all measurement lines. Measurements were performed in a dipper-style helium-4 insert. Pumping on the helium bath enabled temperatures down to 1.4 K. Each sample was initially measured the day after deposition. Multiple subsequent measurements were made over a period of approximately 7 months. After each measurement, samples were brought up to room temperature before being removed from the vacuum can to prevent water from condensing on the sample. When not being measured, samples were stored in ambient conditions in the laboratory. The period of study extended from mid-winter, with lower average

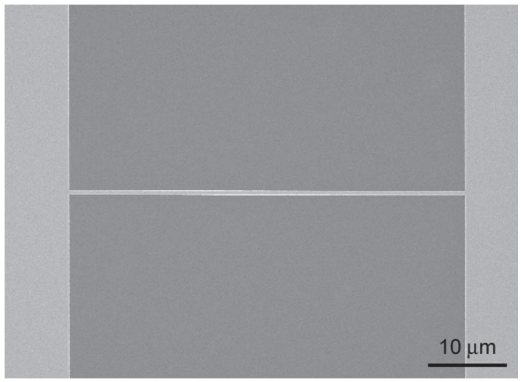

Fig. 1. Scanning electron micrograph of Nb film patterned into a 500 nm wide, 50 μm long strip between contact pads.

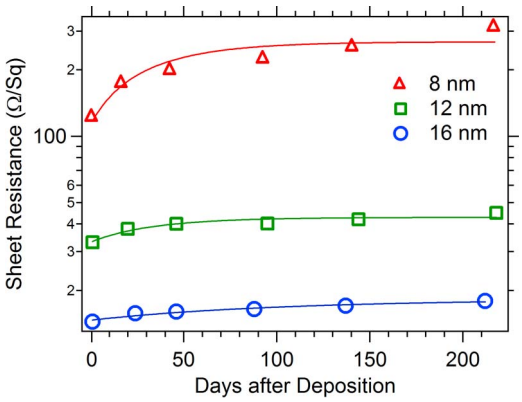

Fig. 2. Sheet resistance as a function of time elapsed since deposition. Data are fit to a constant plus an exponential function with a time constant of 37 days.

ambient humidity, to late summer, with higher average ambient humidity.

III. Results and Discussion

Each high aspect-ratio sample consists of 100 squares. This structure was designed to facilitate measurement of the sheet resistance. The sheet resistance was determined at approximately 10 K. The sheet resistance as a function of time since deposition for the three film thicknesses is shown in Fig. 2. The data for each of the three thicknesses are fit to a constant plus an exponential function with a time constant of 37 days.

The measured resistance versus temperature data are shown in Fig. 3. We define the superconducting critical temperature (T_c) of each film as the temperature at which the sample exhibits half the resistance in the normal state. The transition width, defined as the temperature over which the resistance changes from 90% to 10% of its normal state value, remained approximately constant for the 12 nm and 16 nm films, with a value of ≈0.2 K. After a sufficient period of time, the 8 nm films developed a small residual resistance that did not disappear at the lowest temperature measured (1.4 K). For these films, it may be that the grain size is comparable to the film thickness

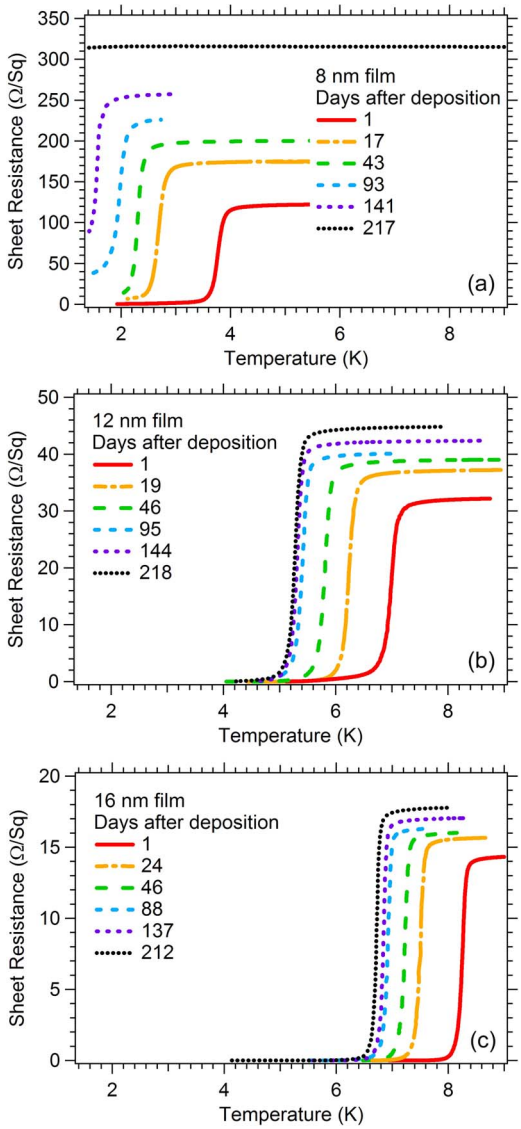

Fig. 3. Sheet resistance as a function of temperature for film thicknesses of (a) 8 nm, (b) 12 nm, and (c) 16 nm.

and oxidation along larger grain boundaries produces localized regions of suppressed superconductivity. These films eventually reach a state in which T_c is no longer measurable at our base temperature of 1.4 K.

The dependence of T_c on film thickness is plotted in Fig. 4. The critical temperatures obtained the day after deposition are similar to those obtained previously with films that were sputter-deposited onto unheated substrates [16]. For comparison, we also plot the thickness dependence approximately 140 days after deposition. The thickness dependence of the critical temperature is fit to theory for the suppression of T_c in disordered homogeneous two-dimensional films due to the Coulomb interaction [17], [18]. In this theory, the dependence of T_c on the normal-state sheet resistance R_{sq} is given by

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \frac{1}{|\gamma|} - \frac{1}{\sqrt{2t}} \ln \frac{|\gamma| + \sqrt{\frac{t}{2}}}{|\gamma| - \sqrt{\frac{t}{2}}} \tag{1}$$

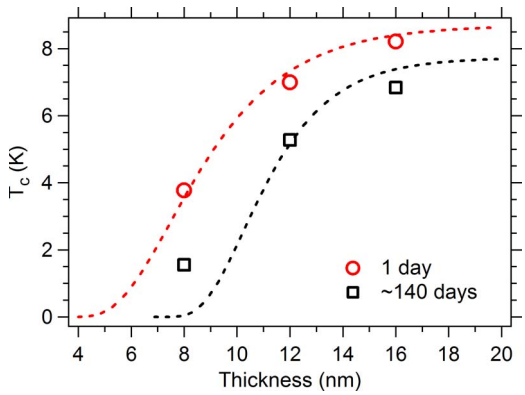

Fig. 4. Critical temperature versus thickness measured 1 day and ≈140 days after deposition. Dashed lines are fits to (1).

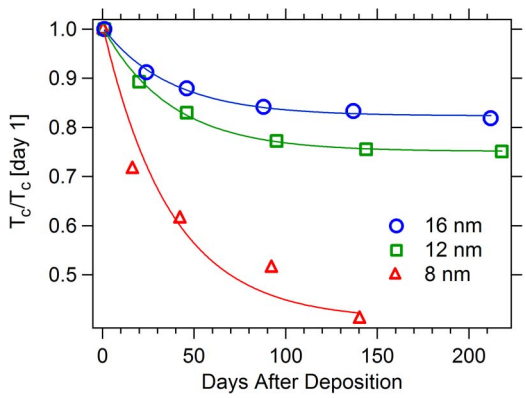

Fig. 5. Normalized critical temperature as a function of time since deposition for the three different film thicknesses. Data are fit to a constant plus an exponential function with a time constant of 37 days.

where T_{c0} is the bulk critical temperature, $t = (e^2/\pi h)R_{sq}$, and $\gamma^{-1} = \ln((k_B T_{c0}\tau)/h)$ with τ the elastic scattering time ($\gamma < 0$). It is suggested to treat γ as a fitting parameter, as it may not correspond to a correct value of the scattering time for very disordered samples in which τ^{-1} is greater than the Debye frequency ω_D [18], [19].

First we fit the measured sheet resistance as a function of film thickness to an exponential function for each of the two times (1 day and ≈140 days). This exponential function is then used in (1) to fit the data in Fig. 3. For the fits shown in Fig. 4, T_{c0} is taken as 9.3 K, the bulk value for Nb. This yields $|\gamma| = 0.067$ for the data at 1 day and $|\gamma| = 0.055$ for the data at ≈140 days. The fit exhibits better agreement with the data at ≈140 days if we take $T_{c0} = 8.0$ K instead of 9.3 K, which yields $|\gamma| = 0.068$ (not shown). We note that aging does not result in a simple decrease in the effective film thickness. In comparison, Delacour *et al.* found $|\gamma| \approx 0.105$ for crystalline Nb films [11]. Our value of $\gamma = -0.067$ corresponds to $\tau \sim 10^{-18}$ s. Since $\tau^{-1} \gg \omega_D$, this extremely small value of τ should not be taken as the actual scattering time.

T_c as a function of the time since deposition is shown in Fig. 5 for the three different film thicknesses. To facilitate comparison, each T_c is normalized by its value at the first measurement. The data are fit to a constant plus an exponential function with a time constant of 37 days, the same time constant seen in the resistance data of Fig. 2. Beyond 140 days, the T_c of the 8 nm thick sample was too low to measure in our experimental system.

IV. Conclusion

Because of their convenience for device fabrication, we have studied films prepared by electron-beam deposition onto unheated substrates. As a result of oxidation, the electrical properties of these ultra-thin films change significantly over time. The evolution of the normal-state resistance and superconducting critical temperature are both well described by an exponential function with a time constant of approximately 37 days.

The effect of oxidation is expected to depend on the granularity of the film and hence on the deposition conditions. Previous work on Nb films sputter-deposited onto unheated silicon substrates found similar properties to the present work, but the effect of aging in those samples was not studied [16]. Electron-beam deposition has the advantages that it is directional and it produces no plasma radiation damage. It is anticipated that epitaxial Nb films, which have higher critical temperatures than granular films for the same thickness [11], will show decreased but still significant aging behavior. The results presented here should provide quantitative guidance for the development of superconductive devices based on Nb films deposited under similar conditions and at least qualitative guidance for films deposited under different conditions.

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