The influence of aging and annealing on the properties of Nb/Al-AlO\textsubscript{x}/Nb tunnel junctions

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Abstract. This paper presents results of our studies on aging and annealing properties of Nb/Al-AlO\textsubscript{x}/Nb junctions. We performed a long room temperature aging with subsequent annealing at different temperatures up to 250\degree C. A distinct change of the junctions’ normal-state resistance has been observed. Aging at room temperature results in a slight decrease of the normal-state resistance combined with improved junction quality, characterised by a better subgap-to-normal resistance ratio. Annealing at moderate temperatures in air increases the normal-state resistance and leads to improvement of the junction quality followed by degradation at higher annealing temperatures. The increase in the junction quality after long-term aging at room temperature is attributed to relaxation of the internal junction structure and interfaces, thus, resulting in a lower density of interface traps. The deterioration at higher annealing temperatures could be a consequence of diffusion processes at the Al/Nb interface. We observe a sufficiently clear difference between the behaviour of preliminary aged and newly fabricated junctions after annealing: for the aged high-quality junction, the degradation was negligible up to temperatures of 200\degree C, while non-aged junctions show a much faster and abrupt degradation at lower annealing temperatures.

1. Introduction
Superconducting Nb/Al-AlO\textsubscript{x}/Nb tunnel junctions have been used widely for instrumentation in millimeter and submillimeter-wave astronomy [1] as well as in many other applications such as voltage standards [2], SQUIDs [3, 4], particle detectors [5], temperature sensors [6], and ultra-high speed logics [7, 8]. The aging properties of the active components are of high importance for all these applications. Long-term storage at room temperature, repeated thermal cycling and annealing at moderate temperatures could lead to degradation of Nb/Al-AlO\textsubscript{x}/Nb junction [9] and large spreads in the critical parameters such as the normal-state resistance, $R_N$, the critical current, $I_c$, and the subgap-to-normal resistance ratio, $R_J/R_N$.

There are few mechanisms, which may cause a change in the junction properties: i. a slow glass-like relaxation of disordered Al-AlO\textsubscript{x} interfaces [10]; ii. an interdiffusion between Nb and Al and iii. absorbing of hydroxyl groups [11, 12]. The first mechanism manifested itself most clearly during aging by storage at room temperature, where a neutralisation of interface traps take place [10]. However, the latter two processes can be observed after annealing treatments.

In this work, we analyze the properties and behaviour of more than 100 high-quality Nb/Al-AlO\textsubscript{x}/Nb tunnel junctions subjected to a long-term aging at room temperature. It was found
that the long natural aging affects the $R_N$ value by decreasing it with a few percent. This result is in principle consistent with previously reported data on aging and annealing of Al/AlO$_x$/Al junctions [13, 14]. Additionally, we show that changes in the resistance are most pronounced at early stages of aging, as earlier observed in Al/AlO$_x$/Al junctions [10]. It is also discussed that the tunnel junctions’ quality parameter, namely the subgap-to-normal resistance ratio $R_J/R_N$, could be controllably improved by means of annealing under certain conditions. In general, our results on annealing of the Nb/Al-AlO$_x$/Nb junctions are in line with the earlier studies of Nb/Al-AlO$_x$/Nb [9, 15], where the $R_N$ increase at moderate annealing temperature was also observed.

2. Experimental

2.1. Fabrication process

The tunnel junctions used in this study were produced at different stages of the development of a SIS mixer chip to be used for the Band 3 (385 – 500 GHz) receiver at the APEX telescope [16, 17]. The Nb/Al-AlO$_x$/Nb tunnel junctions were fabricated on a 1 x 1” polished z-cut crystal quartz substrates by means of a DC magnetron sputtering. The base Nb electrode was deposited at $8 \times 10^{-3}$ mbar at 1 A resulting in a 200 nm thick film. The subsequent Al layer was placed at 60 W DC power thus producing about 7 nm thick layer. The fresh Al surface was exposed to a pure oxygen at room temperature at a pressure of $1.7 \times 10^{-2}$ mbar for 15 minutes to form the AlO$_x$ tunnel barrier. The trilayer is completed by deposition of a 100 nm thick Nb top electrode under the same conditions as the base electrode. The junctions had an area of $3 \mu m^2$, which was defined by standard photolithography and reactive ion etching (RIE) processes. The etching process is followed by an anodisation up to a voltage of 13 V, using the same resist mask in order to protect the edges of the junction pillar. Then a 250 nm thick SiO$_2$ insulation layer was coated and lifted-off. A 400 nm thick Nb wiring layer was coated at $1.2 \times 10^{-2}$ mbar by DC sputtering at 1 A and patterned by RIE, thus, connecting the open areas of the top Nb electrode. Finally, a contact pad layer of a sputter-deposited Nb(100 nm)/Pd(150 nm) was patterned onto the upper Nb wiring. The inset in figure 1 illustrates the schematic cross-sectional structure of the fabricated SIS mixer chip.

2.2. Characterisation

Each wafer layout contained 34 contact pads that allowed for DC characterisation of the SIS tunnel junctions before dicing the mixer chips. Typical current-voltage (I-V) characteristics of the Nb/Al-AlO$_x$/Nb junctions are shown in figure 1, obtained using four-probe DC measurements at 4.2 K. To study the effects of aging and annealing on the Nb/Al-AlO$_x$/Nb junctions, we have chosen to track the changes in the normal-state resistance $R_N$ and the $R_J/R_N$ ratio, where the subgap resistance value $R_J$ is taken at 2.0 mV.

Cross-sectional imaging of as-deposited and annealed Nb/Al-AlO$_x$/Nb trilayers, figure 2, was done by High Resolution Transmission Electron Microscopy (HRTEM). The specimens were prepared with the help of a FEI Strata235 DualBeam work, whereas the high-resolution imaging was made in a Philips CM200 transmission electron microscope operated at 175 kV. The trilayers for the HRTEM characterisation were deposited with the same deposition parameters and layer thicknesses as those used for the SIS mixer chip fabrication.

3. Aging effects

Room temperature aging data was collected from three wafers, which were stored for more than one year at standard conditions (air-conditioned laboratory room with controlled humidity and temperature). No additional protection was used to keep the wafers from atmospheric exposure during the storage period.
Figure 1. Typical I-V curves at 4.2 K of Nb/Al-AlOx/Nb junctions (1) before and after annealing at (2) 150°C, (3) 200°C and (4) 250°C.

Figure 2. A cross-sectional HRTEM micrograph of an Nb/Al-AlOx/Nb trilayer deposited on a quartz substrate with a close-up view of the tunnel barrier.

Histograms of the measured normal-state resistance, \(R_N\), and the \(R_J/R_N\) ratio for the three different wafers fabricated at different time are shown in figure 3. During the aging the mean \(R_N\) changed noticeably, by a few percent, as viewed in figure 3(a), figure 3(c) and figure 3(e). Moreover, the aging does not have just a simple effect of reducing the normal-state resistance. In fact, the quality factor, the \(R_J/R_N\) ratio, either remains unchanged, figure 3(b) and figure 3(f), or improves as shown in the histogram in figure 3(d). To our knowledge, this interesting effect has not yet been observed for Nb/Al-AlOx/Nb tunnel junctions or received an adequate attention, although the junction quality is always quite important for practical applications. The observed decrease of \(R_N\) is in conjunction with the studies done by Nesbitt et al. [10], who looked at the physical processes related to interface phenomena in in-situ aged Al-AlOx-Al tunnel junctions. We believe that the same mechanism of relaxation of interface traps works for longer aging interval as well as at higher temperatures although it might be weak or shaded by some other stronger effects. Besides, we suggest that the observed effect of lower \(R_N\) and improved \(R_J/R_N\) ratio in our Nb/Al-AlOx/Nb tunnel junctions might be attributed to eventual removal of trap-related conduction paths in the barrier. This removal of trap-related conduction paths changes the interface morphology due to stress relaxation processes inside the layers. Tunnel barriers usually fabricated by thermal oxidation, e.g. in this study, result in an oxide layer where atoms are not in their global equilibrium positions [18]. It is likely that a relaxation from this state could take months at room temperature. The result of such a long and slow relaxation process is an improved quality of the tunnel barrier, i.e., a better junction quality, as supported by our study.

4. Annealing effects
After performing the long-term room temperature aging, the same junctions were subjected to a thermal annealing. Annealing of the samples has been performed by placing them onto a hot plate with the temperature set at 120°C for 1 hour in the atmosphere of 42% ± 2% RH room air. After the annealing, the junction \(I - V\) characteristics were measured in a dipstick in LHe at 4.2 K. The same procedure was repeated several times with a temperature increment of 10°C up to a temperature as high as 250°C keeping the same annealing time. Since the temperature
range of the hotplate was limited to 200°C, the annealing at higher temperatures was done in
an oven by placing the wafer onto a preheated massive metal wafer holder in order to have
temperature ramping conditions similar to that of the hotplate.

The general trend after several annealing steps is the $R_N$ value increase. Figure 4 shows the
change on the $R_N$ and $R_J/R_N$ ratio normalized to their initial, i.e., as-fabricated value, after
repeated annealing steps for wafer R8. The data is also representative for wafers R5, R6, R7
and D1. When annealing at temperatures up to 150°C, we observed a noticeable increase in the

![Figure 3. Distribution of the normal-state resistance and $R_J/R_N$ ratio for as-fabricated and aged Nb/Al-AlO$_x$/Nb tunnel junctions from three different wafers, R5, R6 and R7, aged for 20, 18 and 13 months, respectively.](image-url)
junction quality followed by a quick drop of the $R_J/R_N$ ratio for higher annealing temperatures. This result is valid for junctions having different sizes. However, depending on the method used for the junction fabrication, reduced values for $R_N$ are also possible at the same annealing temperatures as discussed in [13].

As mentioned in section 3, during the moderate temperature annealing of the studied Nb/Al-AlO$_x$/Nb trilayers the improvement of the tunnel barrier quality might be attributed to the removal of trap-related conduction paths in the barrier. This might be considered as a consequence of a changed interface morphology due to stress relaxation processes inside the layers. Furthermore, despite the noticeable increase in the $R_N$ values of the tunnel junctions, we were not able to distinguish by HRTEM any visible increase of the tunnel barrier thickness after annealing at these temperatures. For comparison, at slightly higher temperatures, about 180°C, by using spectroscopy of reflected electrons (SRE) method, it was possible to identify clearly the interdiffusion processes at the Nb-Al interface [19]. We believe, the observed rise of $R_N$ ($R_J/R_N$) might be explained in terms of glass-like relaxation processes of the surface traps [10].

Whereas wafers R5, R6, R7 and R8 were stored for more than a year at room temperature before being exposed to annealing, wafer D1 was taken for annealing almost right after fabrication. In general, it followed the trend of the rest of the wafers but a larger number of the junctions could not survive the annealing at temperatures higher than 160°C. Along with the annealing, we exposed wafer D1 to aging at room temperature up to two weeks between the annealing steps while the junctions were measured at three different stages – right after fabrication/annealing, after one week of aging and after two weeks of aging. The results of this experiment are presented in figure 5, showing that the most dramatic change in the junction parameters occurs during the first ten days after fabrication. This is followed by a stabilisation of the junction parameters after certain aging and annealing, which is in agreement with Nesbitt’s observations [10].

Despite having nominally the same device processing, a difference of the junction-to-junction lifetime variation during the annealing process could be found for each wafer. Tunnel junctions from wafers, which have been subjected to the long-term storage, have comparatively longer median lifetimes than the junctions from wafer D1, which was annealed shortly after its fabrication.

![Figure 4](image1.png)  **Figure 4.** Normalized normal-state resistance and $R_J/R_N$ ratio as a function of the annealing temperature. Data points are representative for wafers R5, R6, R7, R8 and D1.

![Figure 5](image2.png)  **Figure 5.** Quality evolution/stabilisation of the newly fabricated tunnel junctions subjected to a short room temperature aging and subsequent annealing.
fabrication. It is important to mention that the tunnel junctions from wafer D1 originally had higher $R_J/R_N$ figures compared to other wafers. The only factor that might possibly attribute to the shorter lifetime during annealing is the considerably shorter aging time of this wafer.

5. Conclusion
In this work, we focused our attention on the effects of long-term room temperature aging of Nb/Al-AlO$_x$/Nb tunnel junctions as well as their response to high temperature annealing in air. We found a noticeable decrease in the normal-state resistance as well as improved junction quality after storing the tunnel junction for more than one year in standard conditions. We believe that this effect might be attributed to an eventual removal of trap-related conduction paths in the tunnel barrier. This is ascribed to changes of the interface morphology due to stress relaxation processes inside the layers. Furthermore, this assumption is supported by the higher quality factor, $R_J/R_N$ ratio, of the tunnel junctions, reached after a long-term storage in standard conditions, which fail considerably less often during the annealing process compared to newly fabricated junctions.

In addition, the tunnel junctions were subjected to a high-temperature annealing in air and an observable improvement in the quality factor $R_J/R_N$ was found at annealing temperatures of up to 150°C, however, followed by a rapid quality degradation after annealing at higher temperatures. The reproducible effects from the aging and annealing on the $R_N$ and $R_J/R_N$ figures of Nb/Al-AlO$_x$/Nb junctions can be used for a post-fabrication fine-tuning of those parameters for practical applications.

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