PHYSICAL REVIEW B VOLUME 24, NUMBER 4 15 AUGUST 1981

Modification of tunneling barriers on Nb by a few monolayers of Al

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(Received 10 June 1981)

We report that the normal-state tunneling behavior of Nb—oxide—Ag junctions is radically changed when very thin Al is deposited over the Nb before oxidation. From measurements of the oxidation rate, the conductance at high bias, the zero-bias anomaly, and observations of molecular excitations, we show that behavior generally associated with tunneling through niobium oxide disappears when the Al thickness is about two monolayers.

The tunneling characteristics of metal—oxide—metal junctions in the normal state are largely dominated by properties of the tunneling barrier (almost always an oxide), whereas it is the superconducting properties of the electrodes that determine the changes in characteristic that occur below the superconducting transition tempertature. Thus the normal-state tunneling behavior of a junction can be used to infer the properties of the barrier oxide, at least qualitatively. For example, aluminum oxide junctions are marked by a slow but asymmetrical change in conductance with voltage (say up to 0.5 V), [1] and molecular excitations[2] are easily observed at certain voltages. Lead oxide exhibits strong and distinct coupling of the tunneling electrons to phonons of the oxide,[3] whereas oxides of Nb and Ta show zero-bias anomalies (0—10 mV) and a rapid increase of conductance at higher voltages (say 10—100 mV).[4] We have made measurements of the normal-state tunneling behavior of Nb-Al—oxide—Ag (or Pb) junctions where the Al is a very thin layer, ranging in thickness from less than one monolayer up to 40 Å, which is deposited before oxidation of the composite Nb-Al film. We find that the typical characteristics associated with tunneling through niobium oxide change markedly and show some of the features expected for aluminum oxide when the Al thickness exceeds about two monolayers. Although surprising to us, this result (in hindsight) is not inconsistent with previous studies of Nb covered by very thin metallic overlayers, for example Cu (Ref. 5) and Pd,[6] of Ta (Ref. 7) and V_3Si (Ref. 8) covered by Al, and of Pt over Au and Au over Pt.[9] As difficulties encountered with Nb in tunneling spectroscopy, Josephson tunneling, and accelerator cavities have been blamed on its oxidation, such surface modification by thin overlayers is of obvious interest.

The studies reported here resulted from work in which tunnel junctions were prepared on metallic Nb-Al multilayers.[10] These multilayer samples were made by rotating substrates 8 cm from two magnetron sputtering heads with 4.5-cm-diam Nb and Al targets 120 °C apart on a 13-cm-diam circle. Films ~3000 Å thick had the individual layer thicknesses from 20 to 100 Å, and, during the same deposition, different samples had Nb or Al as the final layer of the deposit. These samples were then oxidized thermally. It was clear that the normal-state tunneling behavior was determined by the final layer of the multilayer film, suggesting that the oxide layer was primarily Nb oxide or Al oxide even down to layer thicknesses of 20 Å. We therefore decided to determine *how thin an Al layer,* when deposited over thick Nb, would cause this change in tunneling behavior. To make such Nb-Al overlayer samples the same deposition system is utilized with the substrates being held initially under the Nb target for 3 min, which results in a Nb thickness of ~3500 Å. The table supporting the substrates is then rotated, and the substrates pass once beneath the Al target to deposit a single thin film of Al, which occurs 45—60 sec after completion of the Nb film. During this time the Nb is exposed to 15 mTorr of argon. Adjusting the angular velocity and the power to the Al target allows fine control of the Al film thickness down to angstrom levels. The thickness calibration is determined in a separate deposition by passing a substrate 10^2 times (say) beneath the target under identical conditions and measuring the total film thickness. If the sticking probability of Al on Al differs significantly from Al on Nb, or if the film orientation changes, this calibration will be in error, especially for the thinnest Al films. The diffusion-pumped vacuum system (base pressure $\sim 10^{-8}$ Torr) where these films are prepared includes a large nitrogen-cooled surface surrounding the deposition volume, which acts as a getter when covered by Nb. The niobium films produced on substrates that remain <100 °C during long depositions have resistance ratios of 4 or 5 and $T_c \sim 9.2$ K. The substrates are polished silicon covered by 2000 Å of silicon oxide.

Following Al deposition the films are oxidized at room temperature by exposure to air for 16 h, except for pure Nb and for Al thicknesses < 4 Å in which

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case the oxidation is as long as three days. After insulating the edges of the Nb-Al film the Ag or Pb counterelectrodes are prepared by evaporation in separate systems.

We will now describe the changes in tunneling behavior that occur with increase in Al thickness (t). The first of these is the oxidation rate itself. For our pure Nb films the oxidation rate is so slow that no useful tunneling resistance is produced after 16 h of thermal oxidation at room temperature. The tunnel resistance, increasing with t, reaches a very convenient value $\sim 10^{-2}$ Ω cm^2 for $t \sim 20$ Å, and appears to be comparable to that of pure Al for $t \gtrsim 60$ Å.

The conductance change of a tunnel junction from $V=0$ to relatively high voltages (say 0.5 V) is determined by the barrier height and thickness.[1] We show in Fig. 1 measurements of dynamic resistance for a series of functions with increasing t. It is clear that the behavior changes from the rapid fairly symmetrical change of resistance that is typical of Nb to the slow asymmetrical change more typical of Al and that this change occurs with 1–4 monolayers of Al. The limited voltage range shown for some of the junctions is because they had low resistances and became unstable at high current densities.

Although the slow resistance change of the junctions with larger t is similar to junctions on pure Al, there is one major difference, which is the asymmetry of the tunnel barrier. To our knowledge all Al–oxide–metal junctions show a more rapid decrease in resistance for the Al positive bias than for Al negative, and this is independent of counterelectrode. For the Nb-Al–oxide–Ag (or Pb) junctions we find the asymmetry is reversed with the rapid change being for Nb-Al negative. This asymmetry of resistance results from asymmetry of the barrier[11] and in some cases a very distorted barrier shape has to be invoked. It has been suggested[11,12] that organic molecules trapped on one side of the oxide give this distortion, but it is not clear why, if this is the cause, it should be reversed for junctions on Nb-Al compared with Al.

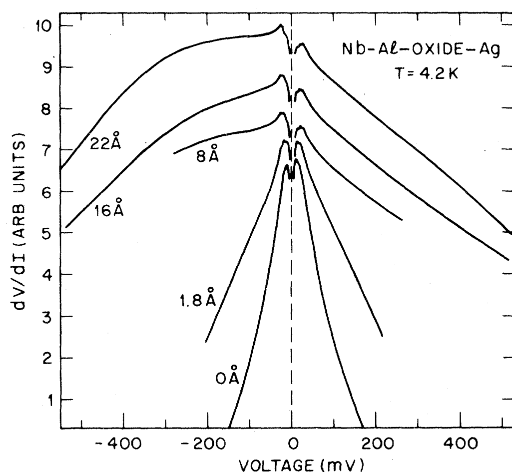

FIG. 1. Resistance (dV/dI) vs voltage for Nb-Al–oxide–Ag junctions at 4.2 K with various Al thicknesses from 0 to 22 Å. The structure near $V=0$ is from superconductivity in the Nb. The curves have been offset vertically, the maximum resistance is 10 (arb. units) for all the junctions. Positive voltage is for the Ag electrode positive.

A simple way to parametrize the junctions of Fig. 1 is to ignore the asymmetry and assume a square tunnel barrier. Then, from the resistance at zero voltage and the mean voltage required to reduce this resistance to half its value, the barrier height (ϕ) and thickness (s) can be calculated.[1] Although far from realistic, such a model gives the following interesting trends. The pure Nb junction has a low thick barrier ($\phi = 0.31$ V, $s = 26.0$ Å) which, for even 1.8 Å of Al, is made thinner and higher ($\phi = 0.55$ V, $s = 18.2$ Å). Note that we change the oxidation time to maintain the resistance in a useful range, say 10^{-3} to 5×10^{-1} Ω cm^2. For $16 < t < 42$ Å the barrier thickness changes little with t ($\phi = 2.0 \pm 0.2$ V, $s = 13.5 \pm 1.0$ Å), and is comparable to that in a pure Al–oxide–Ag junction ($\phi = 2.65$ V, $s = 12.7$ Å), but the barrier height is somewhat lower. The effect of Pb counterelectrodes is to give higher barriers, previously associated with the presence of organic molecules,[11,12] expecially on pure Al ($\phi = 3.60$ V, $t = 11.0$ Å).

At low voltages (<10 mV) a zero-bias anomaly is commonly observed in niobium oxide junctions, being a conductance peak centered at zero bias having a logarithmic dependence of conductance with voltage and of conductance at zero voltage with temperature.[4] It has been explained in terms of magnetic scattering in the barrier analogous to the Kondo effect in bulk materials.[13] This feature is not observed in aluminum oxide junctions unless they are deliberately doped with magnetic impurities. In Fig. 2 we show how this zero-bias anomaly becomes weakened by as little as 1.8 Å of Al and is small once more than two monolayers of Al are deposited over the Nb.

The evidence of the data of Figs. 1 and 2 is that the tunneling behavior of junctions grown on a niobium surface change from being "niobium oxide-like" when the niobium surface is covered by as little as two monolayers of Al, and even one monolayer has an appreciable effect. This result raises interesting questions concerning the nature of the oxide, especially when we consider the two limits of Al thickness. In the thin limit, one or two monolayers of Al are not sufficient to form a thick enough layer of aluminum oxide to account for the whole of the barrier; hence niobium oxide must also be involved. In the thick limit, say $t > 15$ Å, there is sufficient Al (if uniform) for the junction resistance to then be in-

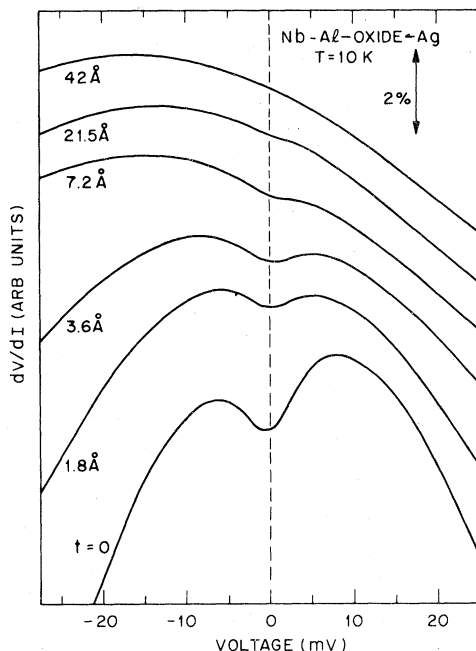

FIG. 2. Resistance (dV/dI) vs voltage for Nb-Al–oxide–Ag junctions as the Al thickness is increased from 0 to 42 Å. The curves have been offset vertically, a 2% change in resistance is as shown.

dependent of increasing Al thickness, but we observe a slowly increasing resistance up to about 60 Å. Identification of the tunnel barrier as a function of oxide thickness clearly will require a study utilizing surface physics techniques. We did attempt to see whether the tunneling characteristic itself yields any information concerning the nature of the barrier material, from direct coupling of barrier excitations to the tunneling electrons. In Fig. 3 we show second derivatives $(d^2I/dV^2$ vs $V)$ for both Nb-Al–oxide–Pb and Al–oxide–Pb junctions (the counterelectrode was changed from Ag to Pb because Pb junctions have less noise at high voltages), which are dominated by the excitation of characteristic vibrations of organic molecules trapped in the barrier, particularly C–H stretching and bending modes near 360 and 180 mV.[2] These are a well-known feature of Al oxide junctions but have not previously been seen in Nb oxide barriers. Once again, they appear in Nb-Al–oxide–Pb once the Al thickness is >2 monolayers. The double-peaked feature at 110–116 mV in Al–oxide–Pb has been ascribed[14] to O–H modes in hydrated aluminum oxide, and there are peaks at the same energies in Nb-Al–oxide–Pb. In fact, on closer examination of the region below 100 mV, there are only three small features that do not occur in both the Al–oxide–Pb and Nb-Al–oxide–Pb junctions, and these occur at 71, 86, and 97 mV in the latter. Although these energies are close to some of the modes of Nb_2O_5 appearing in Raman spectra,[15] they could also arise from different organic impurities, as is clear when Fig. 3 is compared with previous inelastic tunneling spectroscopy.[16] Thus, unless the organic content of the junctions is greatly reduced, such spectroscopy does not appear as a viable way of characterizing the barrier.

From the evidence of the tunneling results alone, as presented above, it seems more reasonable to assume that the presence of the Al overlayer modifies the oxidation behavior of Nb oxide rather than claim the barrier is only Al oxide. It has been shown that during the exposure of pure Nb to oxygen there is appreciable diffusion of oxygen into the bulk, then formation of the suboxide NbO (which is metallic), and finally growth of the insulating Nb_2O_5. If the Al suppressed the oxygen diffusion and growth of NbO and as a result the barrier is a mixed oxide of Nb_2O_5 and Al_2O_3, then this may have the properties observed in Figs. 1–3.

One further important note should be made. There is, in fact, no *proof* of tunneling above ~30 mV in Nb oxide junctions as conventionally prepared, although we have analyzed Fig. 1 as if this were the case. The rapid conductance change with voltage may result from a multistep transport[17] rather than a low barrier. It has also been noted that the

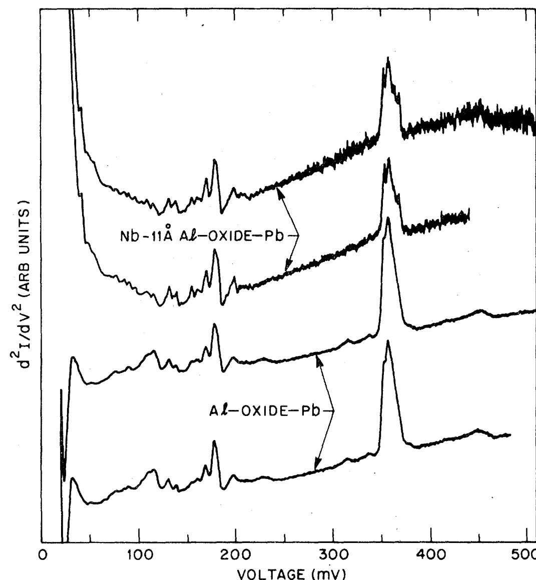

FIG. 3. Second derivative (d^2I/dV^2) vs voltage for two Al–oxide–Pb junctions (lower two traces) and for two Nb-Al–oxide–Pb junctions with 11 Å of Al (upper traces). Two junctions of each type have been shown to demonstrate reproducibility of the tunneling excitations. The traces have been offset vertically.

superconducting Nb density of states loses intensity with increasing voltage. This has been interpreted as a superconducting effect due to contamination of the Nb electrode, but it can equally well be due to the fact that tunneling does not account for the whole transport current through the oxide as the voltage increases. Another test for tunneling, namely, observation of molecular excitations at ~180 and 360 mV, is also negative for Nb oxide junctions.

Finally, we should ask whether it is reasonable that two monolayers of Al should affect the whole Nb surface. If it did not, then the very slow oxidation of Nb pinholes would mean that tunneling would occur preferentially into these regions. There is related work that suggests that such thin layers are fairly uniform. Hauser *et al.*[8] made junctions on V_3Si with as little as 30 Å of Al. Hawkins and Clarke[5] showed that Nb–oxide–Nb junctions could be made if thin Cu was evaporated over the oxidized first electrode. Wolf and co-workers[7] have covered single crystal Nb, Ta, and V with thin Al layers for proximity-effect tunneling studies. Pick *et al.*[6] demonstrated that two monolayers of Pd on Nb were sufficient to make Nb absorb hydrogen, much as bulk Pd. The activity of bulk Pt for a certain catalytic reaction, as reported by Sachtler *et al.*, was enhanced by a monolayer of Au, and that of bulk Au covered by two monolayers of Pt was greater than bulk Pt.[9] Thus the marked modification of the oxidation properties of Nb by two monolayers of Al should not be too surprising.

This surface modification is not unique to Al, as we have observed some of the same effects with Zr, although the junctions were not of the same quality. We do not as yet know whether the deposition method used for the overlayer is important; in our case the rotating substrate receives Al from a broad solid angle, and this may assist in covering any roughness on the Nb surface.

We would like to thank D. B. McWhan for valuable discussions concerning the structrue of the Nb-Al multilayers. The assistance of H. A. Huggins is much appreciated.

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