ON THE PROTECTION OF THE ISOLATION AT THE FABRICATION OF ALL NIOBIUM JOSEPHSON-JUNCTIONS**

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Abstract

The protection mechanism of thin gold layer for preparation of all-niobium devices is discussed. A suggestion on the electronic origin of protection is presented.

Introduction

Josephson tunnel junctions are one of the essential components of different superconducting devices. Oxide barrier junctions, using sputtered niobium for both electrodes, have several advantages: they are mechanically stable, their adhesion is good to generally used Si-based substrates and they are chemically inert. Furthermore niobium oxide is chemically stable and provides a good substrate for subsequent deposition of niobium films, the oxide makes a good tunnel barrier, and at last but not least the full niobium preparation process is easier and cheaper than the mixed processes. The mean disadvantage of these excellent methods is that the sputter deposition of niobium counter electrode onto niobium oxide normally leads to superconducting shorts in the junctions formed. On the other hand, if the all fabrication steps except for the counter electrode deposition are the same as these, only the Pb is evaporated as the top-electrode, the junction usually has good Josephson properties. Hawkins and Clarke (1976) found that a thin (0.8 nm) layer of copper on the oxide helped to prevent the destroying of Nb-oxide layer in all Nb junctions, and it has been suggested by them that the copper forms a physical barrier to niobium penetration of the oxide. Latta and Gasser (1983) found that a thin layer of gold deposited on the Nb-oxide followed by further oxidation, improved the electrical quality of all niobium junctions. Bain and Donaldson (1985) report also that a thin film (0.5 nm) of gold

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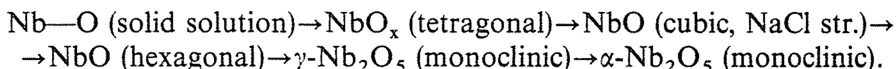
** Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

deposited before making the counter electrode prevents the insulating layer from destroying the tunnelling properties of the junction. The aim of the present investigation is to explore the mechanism of the gold protection.

The radiation damage caused by the sputtering of the second Nb layer on the top of the oxide isolation dramatically changes the oxide constitution of the isolation. This is the root of the special behaviour of them at the sputtering process of the second electrode.

Some characteristics of niobium-oxygen systems

The niobium oxide binary in nature might be ecpected to exhibit ranges of variable composition (non-stoichiometry) in a manner such as exhibited by III—V. compound semiconductors. Generally the oxides might be of the following chemical order with increasing the oxygen content (P. Kofstad, 1976):



$$\text{Nb—O (solid solution)} \rightarrow NbO_x \text{ (tetragonal)} \rightarrow \text{NbO (cubic, NaCl str.)} \rightarrow$$
$$\rightarrow \text{NbO (hexagonal)} \rightarrow \gamma\text{-}Nb_2O_5 \text{ (monoclinic)} \rightarrow \alpha\text{-}Nb_2O_5 \text{ (monoclinic)}.$$

The stoichiometric Nb_2O_5 very easily looses an oxygen and the equilibrium may be expected: $Nb_2O_5 \text{ (solid)} \rightarrow Nb_2O_{5-x} \text{ (solid)} + X \frac{1}{2} O_x$. The oxidation of Nb base-electrode is dominated by the growth of Nb_2O_5 microcrystallite and by activated oxygen diffusion, nucleating small (NbO_6) octahedral-blocks at Nb—Nb_2O_5 interface (J. Halbritter, 1985). Strains are creating defects in Nb (K. R. Lawless, 1974), helping oxygen penetration into as well as creating defects in the Nb_2O_5 counterpart (J. F. Marucco, 1978).

The transformation of the different polymorphic or microcrystalline (amorphous) niobium-oxide compounds creates extended defect states (the grain boundaries, crystalline shear planes etc.) measured by the TEM (B. Meyer, R. Gruchn, 1982; E. S. Crawford, J. S. Anderson, 1985). The more variable and easier way is the creation of the localised effects, which are the oxygen vacancies (O_{va}) first of all, which are populated by a couple of electrons and neighboured by Nb_3^+ or Nb_4^+ sites (J. F. Marucco, 1978; G. Boureau, J. F. Marucco, 1983). The enthalpy for the formation of this O_{va} defect-complexes is about $H(O_{va}) \simeq 2.8$ eV (J. F. Marucco, 1978; G. Boureau, J. F. Marucco, 1983). The excitation energy of the electrons captured by this O_{va} formation into the conduction band is only about the 1 eV, very quickly spoiling the good isolation properties of the stochiometric oxide, and pushes the properties into the metallic-like behaviour; at last into the NbO_x ($x \leq 1$) state, which is metallic (J. Halbritter, 1987). It was proposed, that the oxygen-vacancy defect complex is an $Nb^{4+}O_{va}Nb^{4+}$ cluster like in TiO_2 (W. Göpel et al., 1983), which really detectable by the XPS (R. F. Marks et al., 1983). The creation

of O_{va}-cluster, — because of their small formation enthalpy, — is the more favorable effect and the extended defects only as a second step (based on the O_{va}-states), becomes energetically more favourable (A. N. Cormack et al., 1983).

The activation energy of the diffusion for the O_{va} complexes is smaller that the formation enthalpy and the conditions of the isolating Nb_2O_5 material is distorted by the easy electron hopping mechanism of conduction with a very low (0.3—0.5 eV) activation energy (J. F. Marucco, 1978; G. Boureau et al., 1983; E. H. Greener et al., 1961; R. F. Jannick, 1962; W. K. Chen et al., 1966). Consequence of these circumstances is that the oxide-layer at the top of the first Nb layer as a substrate, having a sputtered (second) Nb-layer on top is quite sensitive for radiation. During the sputtering process the dielectric or partly dielectric system becomes easily more inhomogeneous and can have more and more metallic behaviour, causing superconductive shortage in the isolating material. This short circuit is not caused by the microshorts of the Nb-channels due to the energetic penetration as was assumed, but by the reduction of the nearly proper Nb_2O_5 into the smaller stochiometric ratio with the oxygen. The damage of the oxide-layer is in fact a reduction process; consequently a "metallisation" effect; which chemically occurs on the above described processes with relatively small excitation energy.

The radiation demage can cause drastic effects on the oxide; the electrons or photons (from about the 200 eV energy and 10^{20} particle/cm^2 intensity) cause oxygen injection and precipitation on the top few layers, which can be much larger in the case of the ion-bombardment. The stresses produced are going to relay, which process cause also large damage in the oxide material.

The protection mechanism

Based on the informations described we can start to solve the question of the gold-protection mechanism. The first idea about the protection mechanism of these very thin interlayers between the isolation-oxide and the top electrode, assumed that this way is absorbed the kinetic energy of the incident Nb atoms, which otherwise would penetrate into the oxide layer (G. Hawkins et al., 1976). This idea was further developed by the practical direction. It was supposed (E. E. Latta et al., 1983), that the surface having a non-continuous metallic film islands construct itself a protection against further oxidation. The oxide-layer will be thicker only on places, where the protective islands are not screening the surface. The oxide at these non-protected regions can be so thick than the sputtered Nb-particles cannot reduce the whole layer. So the islands protected by gold have not problems by damage, the others are damaged, but because of the large thickness the

damage can not so deep, as the superconducting short could be created. Indeed both kind of the damage mechanisms can be stopped by the metal-layer, namely the electronic excitations are quickly relaxed in the metals and furthermore the metallic layer is an active defensive barrier against the collision cascades as well. This protection could work only in case of continuous and thick enough layers. The thick metallic layer destroys the Josephson tunnel junction. The essential mechanism in our real case should be more complicated, because of the non-continuous and thin layer in the actual case. The thickness of applied gold layer in our case was 3 A. This layer covers the surfaces only about 45% (S. Norrman et al., 1978), having the number of islands on one cm^2 approximately $4 \cdot 10^{+10}$ (S. Norrman et al., 1978); this far from continuous cover. Taking into account, that the applied oxide surfaces originally have a lot of defects, which with the evaporation damage of a metallic protective layer are slightly increased, the number of evaporated islands is less as was above approximated. It means that a simple physical mechanism is impossible. To solve this problem an electrochemical mechanism was suggested (R. J. P. Bain et al., 1985); protecting the oxide-surface by the large electrochemical potential of the niobium-gold couple. Unfortunately this relatively simple picture can not solve the problem because of the non protected surfaces between the islands, and there are no idea about the larger effective protecting area of islands as their real size. For the active effect the effective radius of protection should be much larger as the radius of real island and their overlapping each other for the full protection is required. For the fully isolating Nb_2O_5, the conduction band is empty, the top energy of the valence band is situated above the Fermi energy (E_f). At the reduction of the oxide by the top Nb sputtering, the difference between the conduction and valence bands become step by step smaller and smaller, the localised levels are created in the forbidden energy interval and about the

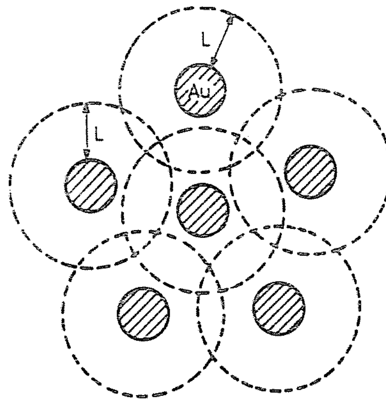


Fig. 1. The schematic diagram of band-bending in metal-semiconductor interface

$NbO_{1.8}$ composition the E_f reaches the bottom of the conduction band (J. Halbritter, 1987), and the compound becomes metallic. At the evaporation of the non-oxidative metal on the top, the metal-insulator (semiconductor) interface will increase the bottom energy of the conduction band at the near vicinity of the interface by a band-bonding (Fig. 1). This can be creating an effective area in which the behaviour of the interface is less metallic. The potential energy of the lifting the band to higher energies in the effective contact region depends on the difference of the work-functions between metal and semiconductor. The changes in the depth easily can be calculated by the Poisson equation taking into account the boudary conditions and the real charges at the touching:

$$\frac{d^2V}{dx^2}=\frac{4\pi e^2}{\varepsilon}[c_2(x)-c_1(x)] \tag{1}$$

where c_1 is the electron concentration in the conduction band, c_2 the concentration of the ionised donor centers at the distance x from the metal semiconductor interface. After a simple calculation we get

$$\frac{d^2V}{dx^2}=\frac{4\pi e^2 c_1(\infty)}{\varepsilon}\left[\exp\left(\frac{v(x)}{kT}\right)-\exp\left(\frac{-v(x)}{kT}\right)\right] \tag{2}$$

with the boundary condition

$$V(0)=V_b; \qquad V(\infty)=0.$$

After a further calculation we got an special spatial of the energy of the band into their equilibrium state by the

$$\frac{dV}{dx}=2\frac{kT}{L}\,\mathrm{sh}\,(V(x)/kT) \tag{3}$$

$$L=\sqrt{\varepsilon kT/8\pi^2 e^2 c_1(\infty)} \tag{4}$$

characteristic distance (where ε is the dielectric permeability, k is the Boltzmann constant, T is the temperature and $c(\infty)$ is the density of electronic states in the conduction band of the semiconductor in equilibrium). ε can be widely varying by the preparation (M. L. A. Robinson et al., 1968; V. E. Henrick, 1983; T. W. Hickmott, 1966; F. P. Emmenegger et al., 1968; J. M. Gallego et al., 1983; G. C. Vezzoli et al., 1983; D. Stützle et al., 1969; K. Sasaki et al., 1980; M. Pollack et al., 1961; S. Basavaich et al., 1976; J. H. Magerlein, 1981) as well as can be considerably enhanced by the easy polarisability of $Nb^{4+}O_{va}Nb^{4+}$ complexes, populating densely the Nb_2O_5—NbO_x interface (R. F. Marks et al., 1983).

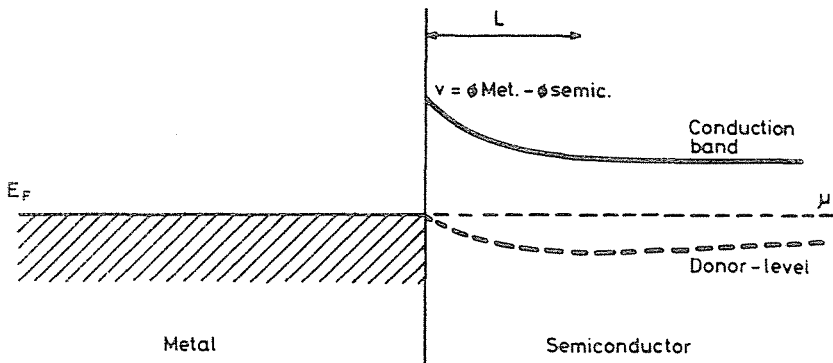


Fig. 2. The overlap of protected areas of gold-islands

Due to the relatively large permeability and a small density of conduction electrons (G. Aeppli et al., 1981), the effective distance of the band-bending (L) becomes large. Supposed that the band-bending effect of the contact is isotropic, so approximately the same in the lateral and vertical directions, we have a relatively large effective protected area (Fig. 2), which is not so metallic-like as would have been in the equilibrium state. For a simple estimation using

$$\varepsilon_r = 30 \quad c_1(\infty) = 10^{20} \frac{1}{\text{cm}^3} \qquad \text{and} \quad kT = 0.025 \text{ eV}$$

values, we obtain:

$$L \simeq 2.4 \text{ Å}.$$

This effective protection length around the metallic islands is in excellent agreement with the real situation: because the estimated average distance between the gold islands (S. Norrman et al., 1978) is about 5 Å. It means, that the spatial requirements for the protection around one island is about 2.5 Å.

In the case of using a protective metal, which can react with the oxygen, we have not so sharp a metal-semiconductor interface, because of the non-metallic behaviour the new metal oxide. In this case the protecting possibility is smashed.

There are some additional effects for the real situation of this phenomenon. The protecting of islands using the high electrochemical contact potential of the Nb—Au-couple is effective in the near vicinity of island regions (R. J. P. Bain et al., 1985). The evaporated gold has large internal stresses (J. Woltersdorf et al., 1981) which together with the small-cluster structure is considerably lowering the melting temperature of the protecting metal; consequently the alloying with the arriving Nb metal is very likely. This means, that the effective area of the protective islands is growing by this

process. Moreover a further support to the effective protection, that the Au—Nb alloy has good superconducting properties. The other non-negligible effect is caused by the presence of the fractions of the pumping oil. The H and OH species promote the oxidation process (J. Halbritter, 1987) and the Si and/or C atoms are binding with d-electrons of Nb, reducing the metallic behaviour of the surface. The band-bending, as was published just recently (C. Laubschat et al., 1989), could have a dominant role in nonreactive metal-semiconductor interfaces.

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