

Study of Nb/Al Interface Combining Spectroscopy of Reflected Electrons with Ion Sputtering

A. V. Lubenchencko ⁽¹⁾, V. P. Afanas'ev ⁽¹⁾, M. V. Lukashevsky ⁽¹⁾, M. Norell ⁽²⁾, A. B. Pavolotsky ⁽³⁾ and S. D. Fedorovich ⁽¹⁾

(1) Department of General Physics and Fusion, Moscow Power Engineering Institute, Krasnokazarmennaya 14, Moscow, 111250, Russia; e-mail: lem_a@mail.ru

(2) Department of Materials and Manufacturing Technology, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

(3) Onsala Space Observatory, Chalmers University of Technology, S 412 96, Gothenburg, Sweden; e-mail: Alexey.Pavolotsky@chalmers.se

Abstract - The study of the interface between Nb and Al thin films is motivated by the fact that electrical characteristics of Nb/Al–AlO_x/Nb superconductive tunnel junctions are very sensitive to the structure of the interfaces in the trilayer. We present a method of interpretation of energy spectra of electrons reflected from layered samples, with the help of which we can determine depth profiles and morphologies of interfaces inside Nb/Al–AlO_x/Nb structure with a nanometre resolution. Methodological specifics of the method is accounting for the whole spectrum recorded in a wide range of energy losses, rather than limited to interpretation of certain peaks as in REELS. We reconstruct depth profile data by fitting calculated spectra to recorded ones. The calculations are based on solution of boundary problem of electron transport equation in multi-layered slice-uniform media, as well as on Monte-Carlo modelling. The Nb/Al interface was found to have an intermediate layer of about 3 nm thick as-deposited which developed into about 6 nm thick layer as a result of annealing at 180°C for 20 minutes.

Received November 23, 2007; accepted February 7, 2008. Reference No. ST30; Category 2, 4.

Based on a paper accepted for Proceedings of EUCAS 2007; published in JPCS **98** (2008), paper # 012210

I. INTRODUCTION

Interest in interfaces between layers of the Nb/Al–AlO_x/Nb tri-layer persists since this superconductive tunnelling structure has been invented [1]. Already for a long time it was understood that the interfaces between the layers in the Nb/Al–AlO_x/Nb tunnel structure are responsible for the junction performance [2,3,4,5]. Chemical elements redistribution and topography in vicinity of Nb/Al interface is of the particular concern. In order to study the structure of those interface regions, an appropriate analytical method is needed that should combine high element sensitivity and non-destructive analysis. To our knowledge, neither of standard analytical methods satisfies this demand. They either use ion sputtering to build element profile (Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS)), or can hardly resolve thin light-element layer inside a thicker and heavier environment (Rutherford Backscattering Spectroscopy (RBS)), or, finally, are too local (Transmission Electron Microscopy (TEM)).

Reflected electrons energy loss spectroscopy (REELS), when measured with a high resolution in a small energy interval adjacent to probing beam energy E_0 , delivers detailed data about elementary inelastic electron energy losses in the surface layers of solids [6,7,8]. Unlike the standard implementation of REELS, the spectroscopy of reflected electrons (SRE), we deal

with in this paper, analyzes higher range of electron energy losses, typically, 300 eV and even more. The depth of REELS analysis is on the order of electron inelastic mean free path l_{in} , while SRE is able to analyze much deeper layers, up to transport length, $l_{tr}=1/(\sigma_{tr}n_0)$, where σ_{tr} is the transport cross section [12], and n_0 the concentration of atoms in solid. In the present paper, we use SRE to study interfaces in the Nb/Al–AlO_x/Nb trilayer. For the probing beam energy $E_0=3$ keV used in the present study, transport lengths are equal to 16 nm and 78 nm for Nb and Al correspondingly [11]. This implies that even for the probing beam energy as low as used in our experiments, the layers as deep as couple of tens of nm can be analyzed non-destructively. The quantitative reconstruction of the sample's depth profile is based on a procedure of fitting recorded spectrum to the theoretical one. The theoretical spectra are calculated based on the theory described in the next section of the paper and on the assumption regarding the type and the elemental composition of the structure under the study. Important is that the only fitting parameters are the layers' thickness and composition. In its traditional implementation [7], REELS recovers only the shape of bulk plasmon peak. In contrast, the present SRE method extracts electron inelastic energy losses cross-section function $\omega_n(\Delta)$. For that, homogenous targets are represented as multilayered [9], since energy losses function $\omega_n(\Delta)$ is different for surface layers and for the remaining bulk part of the target.

Since Nb and Al are chemically active metals, natural oxides and hydroxides a few nanometres thick readily cover their surface when exposed to air. To preserve the interface of interest from the influence of air, we prepared the samples with top layer of Al, which is sufficiently thicker than the natural oxidized layer. Later on, we used *in-situ* ion sputtering to clean the surface from natural oxidized layer and to approach the interface of interest. We would like to emphasize to the fact, that sputtering is not necessary for the analysis as such; it just makes quantitative interpretation of the results more accurate. With the help of monitoring the Nb and Al Auger peaks, we confirmed that the interface of the interest has not been touched by ion sputtering. No Auger data has been used for the SRE analysis.

II. SRE THEORY FOR MULTILAYER MULTICOMPONENT MATERIALS

The theoretical interpretation of SRE data relies on the approach presented in papers [9,10].

Let represent the 220 nm Nb / 20 nm Al sample as a set of plane-parallel layers of thickness d_i , each with its uniform relative aluminium concentration C_i . Differential scattering cross-sections in the elastic channel $\omega_{el}(\gamma)$ and in the inelastic channel $\omega_n(\Delta)$ are given by the following expressions:

$$\omega_{el}(\gamma) = C_i \omega_{el}^{Al}(\gamma) + (1 - C_i) \omega_{el}^{Nb}(\gamma) , \quad (1)$$

$$\omega_{in}(\Delta) = C_i \omega_{in}^{Al}(\Delta) + (1 - C_i) \omega_{in}^{Nb}(\Delta) , \quad (2)$$

where Δ is the electron energy loss and γ the scattering angle. We used the data from [11] for calculating values of differential elastic electron scattering cross-sections $\omega_{el}(\gamma)$. Values of differential inelastic electron scattering cross-sections $\omega_n(\Delta)$ were calculated following the approach described in [10]. Furthermore, electron energy losses due to excitation of the surface plasmons were taken into account by assigning the topmost surface layer of thickness d_s , in which differential scattering cross-sections in inelastic channel $\omega_n(\Delta)$ are defined by that type of energy losses [9].

The starting point for the calculations is the expression for reflection function for a semi-infinite niobium sample $R(\Delta, \Omega_0, \Omega)$:

$$R(\Delta, \Omega_0, \Omega) = \sum_{n=0}^{\infty} r_n(\Omega_0, \Omega) I_n(\Delta) . \quad (3)$$

Here

$$\begin{aligned} I_0(\Delta) &= \delta(\Delta) , & I_1(\Delta) &= \omega_{in}(\Delta) / \sigma_{in} , \\ I_n(\Delta) &= \int_0^{\Delta} I_{n-1}(\Delta - \varepsilon) I_1(\varepsilon) d\varepsilon , & n > 1 , \end{aligned} \quad (4)$$

where Ω_0 is the direction angle of incoming electrons measured relative to surface normal directed inward, Ω is the direction angle defining reflected electrons flow,

$$r_n(\Omega, \Omega_0) = \int_0^{\infty} A_R(u, \Omega, \Omega_0) \frac{(u/l_{in})^n}{n!} e^{u/l_{in}} du , \quad (5)$$

L_{in} is the electron mean free path between inelastic collisions; $A_R(u, \Omega_0, \Omega)$ is the electron path length and u is the distribution function.

Thereafter, appending layer after layer, we obtain the energy spectrum of electrons reflected from the multi-layer target [9,10]:

$$\begin{aligned} R(d_1, d_2, \dots, d_s, \Delta, \Omega_0, \Omega) &= R_{Nb}(\Delta, \Omega_0, \Omega) + \\ &+ \int_0^{\Delta} \int [R(d_2, \dots, d_s, \Delta - \varepsilon, \Omega_0, \Omega') - R_{Nb}(\Delta - \varepsilon, \Omega_0, \Omega')] T(d_1, \varepsilon, \Omega_0, \Omega') d\varepsilon d\Omega' , \end{aligned} \quad (6)$$

where

$$T(d, \Delta, \Omega_0, \Omega) = \sum_0^{\infty} t_n(d, \Omega_0, \Omega) I_n(\Delta) , \quad (7)$$

$$t_n(d, \Omega_0, \Omega) = \int_0^{\infty} A_T(u, d, \Omega_0, \Omega) \frac{(u/l_{in})^n}{n!} e^{u/l_{in}} du , \quad (8)$$

$A_T(u, d, \Omega, \Omega_0)$ is path length u distribution function for electrons, which passed through layer d .

For functions $A_R(u, \Omega, \Omega_0)$ and $A_T(u, d, \Omega, \Omega_0)$ we employed formulas derived in [9,10].

The depth profile of the interface region in 220 nm Nb/ 20 nm Al structure can be recovered by varying of the layer thicknesses d_i and relative concentrations of aluminium in them C_i , so that the calculated theoretical energy spectrum of electrons reflected from the sample fits best with the experimentally recorded one. In other words, we vary d_i and C_i so that the functional

$$\int_0^{\Delta_{max}} [R_{theor}(d_1, d_2, \dots, C_1, C_2, \dots, \Delta, \Omega_0, \Omega) - R_{exp}(\Delta, \Omega_0, \Omega)] d\Delta \text{ is minimized.}$$

III. EXPERIMENT: SAMPLES AND MEASURING SETUP

Samples for the study have been prepared by vacuum magnetron sputter deposition of sequence of 220 nm Nb/ 20 nm Al layers on a substrate of polished silicon with a deposition rate of 1 nm/s for Nb and 0.3 nm/s for Al. The full sequence of layers has been deposited in the single run without breaking of vacuum between the layers; residual vacuum level was $< 2 \cdot 10^{-6}$ Pa. Annealing of the samples has been performed by placing them onto hot-plate set to 180°C in room air of 42%±2% relative humidity.

Measurements have been carried out with a scanning Auger microscope *PHI660* [13]; its cylindrical mirror analyzer was set at energy resolution $\Delta E/E_0 = 0.3\%$. Probing beam energy has been chosen equal to $E_0 = 3$ keV at normal incidence to the target; electron current on the sample

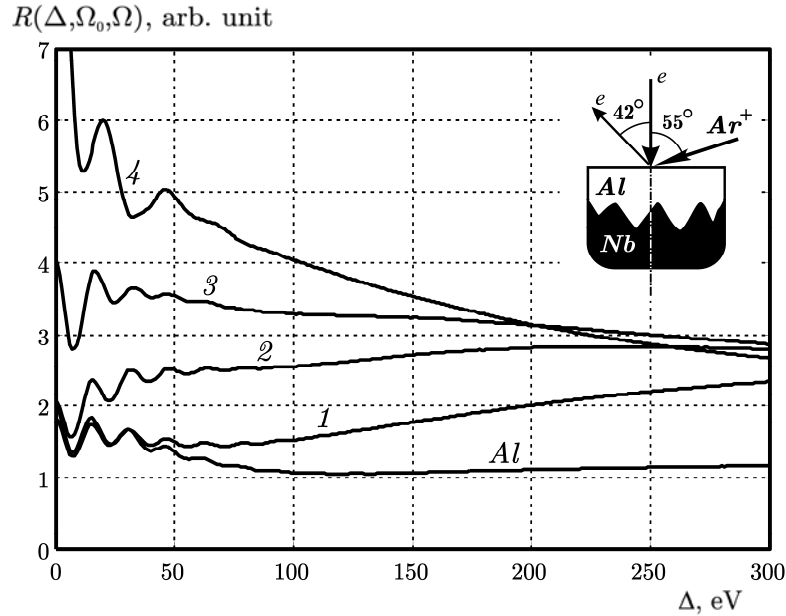


Fig. 1. Energy spectra of electrons reflected from Nb/Al target after different sputtering time. (1) - After first cleaning of the surface (Auger peaks of C and O disappeared); (2) - about 12 nm of Al is removed, as estimated from sputtering time (Auger peak of Nb is not yet present); (3) - Sputtered to the proximity of the Nb/Al interface (Auger peaks of Al and Nb were comparable); (4) - all Al sputtered away, only Nb left (Auger peak of Al disappeared; only Nb peak is observed).

was in the range of 250...260 nA. Electron spectra were taken in the reflected electron energy range 0 to E_0 . Base vacuum level during the measurements was about $2.5 \cdot 10^{-7}$ Pa. The 1.5 keV Ar ions at 55° angle to the sample normal were used for sputter profiling. The Auger-analysis did not detect any traces of argon in the studied samples. The Auger peaks of Nb, Al, O and C were monitored for every sputter depth.

IV. RESULTS AND DISCUSSION

Figure 1 represents spectra of electrons reflected from Si 220 nm Nb/ 20 nm Al target after different sputtering times. The SRE spectra from homogeneous Nb and Al samples contain characteristic peaks due to excitation of bulk and surface plasmons, as well as due to energy losses for ionization of $4p_{1/2}$ and $4p_{3/2}$ electron shells in Nb and $2p_{1/2}$ and $2p_{3/2}$ in Al. Curve 1 corresponds to the sample after minimal ion etching providing appropriate cleaning of the surface: Auger peaks of carbon and oxygen became much smaller than aluminium peak. Curve 2 shows the SRE spectrum of the sample, when about 12 nm of aluminium was removed, as estimated from the sputtering time: Auger peak of niobium was not yet present. Curve 3 shows the spectrum from the sample etched to the proximity of the Nb/Al interface: Auger peaks of aluminium and niobium were of comparable intensity. Curve 4 represents the spectrum from the sample with all aluminium sputtered away and only niobium left: Auger peak of aluminium disappeared; only niobium peak was observed. For the probing beam energy $E_0 = 3$ keV the transport path lengths are equal to $l_{tr}^{Nb} = 16$ nm and $l_{tr}^{Al} = 78$ nm [12]. Since the niobium layer thickness exceeds more than twice the transport path length ($d_{Nb} > 2 l_{tr}^{Nb}$), the spectrum of electrons reflected from such layer should coincide with a spectrum of electrons reflected from semi-infinite Nb target.

We modelled the Nb/Al interface as a sequence of six layers with different Al/Nb content in each layer, placed on top of semi-infinite Nb sample. Following equation (6), we calculated

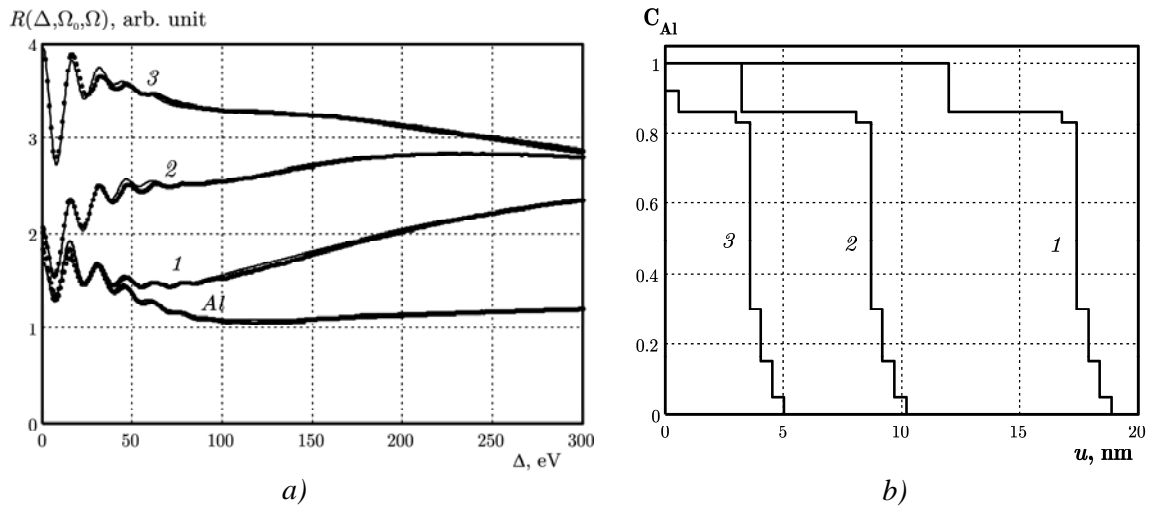


Fig. 2. (a) - Comparison of experimental spectra with theoretical ones with assumption of the rough Nb/Al interface surface (two-phase structure). Dots - experiment, solid lines - theoretical spectra for different upper Al layer thickness: (1) - 12 nm, (2) - 3.2 nm and (3) - 0 nm. (b) - Aluminium depth profiles, corresponding to the best fit of experimental spectra by theoretical ones, showed at (a).

the theoretical spectrum of reflected electrons for the six-layer. We calculated the spectrum with an assumption of roughness of Nb/Al interface, in terms of formula (9) from [10] (two different phases, Al and Nb). We varied the layers' thicknesses d_i in the six-layer together with Al/Nb content C_i in each layer to achieve the best fit (Figure 2). The set of $(d_i; C_i)$, corresponding to the best fit of experimentally recorded spectra by the theoretically calculated gives the depth profile of Al/Nb sample. We would like to emphasize that the depth profiles of Nb/Al interface have been found to be the same for different Al upper layer thicknesses, 12 nm, 3.2 nm and 0 nm, corresponding to the lines 1, 2 and 3 on Figure 2. This proves that the sputtering did not change the interface and confirms the reliability of the analysis.

The plots in Figure 3 represent the depth profiles of Nb/Al before and after annealing at 180°C, 20 minutes, corresponding to the best fit of spectra. The Nb/Al interface, as-deposited, has been found to have a 2 nm thick intermediate region, associated with interface roughness.

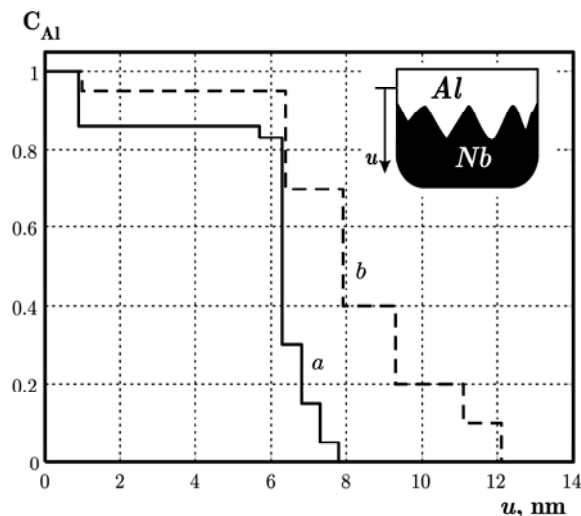


Fig. 3. Depth profile of the Nb/Al interface before (solid line) and after annealing at 180°C, 20 minutes (dashed line).

After annealing, the intermediate layer developed into about 6 nm thick region. Depth profiles of both as-deposited and annealed samples had about 5 nm thick low Al concentration tail, apparently due to diffusion. Our measurements of Nb/Al border interface are in good agreement with transmission electron microscopy studies of a similar border [4].

V. CONCLUSION

We have determined the depth profile of an interface of sputter-deposited 220 nm Nb/ 20 nm Al double-layer. It has an intermediate layer of about 2 nm thick for as-deposited sample and about 6 nm thick for one annealed at 180°C, 20 minutes. Depth profiles of both, as-deposited and annealed, samples had about 5 nm thick low Al concentration tail, apparently due to diffusion.

In this paper, we have demonstrated the possibility of quantitative and nondestructive depth profile study of multi-layered targets by means of SRE. We would like to point out that combination of Auger spectroscopy with SRE offers an encouraging possibility of analysis matching Auger power of element identification with convincing accuracy and nondestructive nature of SRE depth profiling.

ACKNOWLEDGEMENTS

This work was supported by a grant from the Swedish Royal Academy of Science. Authors are thankful to Dr. V. Belitsky for many useful discussions and reading the manuscript.

REFERENCES

- [1] Rowell J M, Gurvitch M and Geerk J, *Phys. Rev.* **B24(4)** 2278 (1981).
- [2] Chang C C, Gurvitch M, Hwang D M and Blonder C W, *J. Appl. Phys.* **61(11)** 5089 (1987).
- [3] Morohashi S and Hasuo S, *J. Appl. Phys.* **61(10)** 4835 (1987).
- [4] Imamura T and Hasuo S, *IEEE Trans. Magnetics* **27(2)** 3172 (1991).
- [5] Shiota S, Imamura T and Hasuo S, *IEEE Trans. Appl. Supercond.* **2(4)** 222 (1992).
- [6] Gomoyunova M V, *Sov. Phys. - Uspekhi* **25(1)** 58 (1982).
- [7] Tougaard S and Chorkendorff I; *Phys. Rev.* **B35** 6570 (1987).
- [8] Gergely G, *Surf. Interface Anal.* **3** 201 (1981).
- [9] Afanas`ev V, Lubenchenko A and Gubkin M, *Eur. Phys. J. B* **37**, 117 (2004).
- [10] Afanas`ev V, Lubenchenko A, Lukashevsky M, Norell M and Pavolotsky A, *J. Appl. Phys.* **101** 064912 (2007).
- [11] Jablonski A, Salvat F and Powell C J, *NIST Electron Elastic-Scattering Cross-Sections Database - Version 3.0, 2002* (Gaithersburg, MD: National Institute of Standards and Technology)
- [12] Powell C Í and Jablonski A *NIST Electron Inelastic-Mean-Free-Path Database - Version 1.1, 2000* (Gaithersburg, MD: National Institute of Standards and Technology)
- [13] Physical Electronics USA, 18725 Lake Drive East, Chanhassen, MN 55317