Stable superconducting niobium ultrathin films

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ABSTRACT

We report on a combined structural and electronic analysis of niobium ultrathin films (from 2.5 to 10 nm) epitaxially grown in ultra-high vacuum on atomically flat sapphire wafers. We demonstrate a structural transition in the early stages of Nb growth, which coincides with the onset of a superconducting-metallic transition (SMT). The SMT takes place on a very narrow thickness range (1 ML). The thinnest superconducting sample (3 nm/ 9ML) has an offset critical temperature above 4.2K and allows to be processed by standard nanofabrication techniques to generate air and time stable superconducting nanostructures.

INTRODUCTION

Superconductivity has been recently shown to survive down to extremely confined nanostructures such as metal monolayers [1] or clusters made of few organic molecules [2]. While these structures are extremely interesting to probe the ultimate limits of superconductivity, their studies are limited to in-situ measurements. Preserving a superconducting state in ultrathin films that can be processed by state-of-the-art nanofabrication techniques and withstand multiple cooling cycles remains technologically challenging and is timely for quantum devices applications.

Having the highest critical temperature among elemental superconductors, niobium is an biquitous material for superconducting thin films and its performance is known to increase when epitaxy conditions can be reached. Hetero-epitaxy of niobium is best performed on sapphire substrates since both their lattice parameters and thermal dilatation coefficients match rather well [3]. Most combined structural and transport studies have involved A-plane (1000) oriented sapphire as the growing substrate. However the high step-edge roughness [4] and interfacial stress found for that crystal orientation is likely to be a probable source of rapid aging. Only few studies [5] have described Nb growth on R-plane oriented (1-102) sapphire. However, this orientation provides an ideal substrate to promote epitaxy of Nb with (001) orientation. We present here a combined structural and electronic transport analysis of the early growth stages of niobium films on that orientation with the proof of concept of the interest of these films for quantum device fabrication.

EXPERIMENT DETAILS

The niobium films are grown in ultra-high vacuum using a specific recipe: R-Plane oriented sapphire substrates that are cleaned using water-based surfactants in ultrasonics bath. The surface is then prepared by annealing during 1 hour in air at 1100°C. Wafers are transferred in the deposition chamber (base pressure $\sim 10^{-10}$ torr). Before niobium deposition, in-situ cleaning of the surface is performed during several hours using Argon milling. Then, the substrate is heated at 660°C and Niobium is deposited using electron gun at a rate of 0.02 nm/s. The vacuum is kept at

residual pressures lower than 10^{-9} Torr during niobium growth. Finally, the sample is cooled below 80°C and we covered by evaporation of 2nm thick of silicon in order to protect the film from oxidation.

DISCUSSION

Structural analysis

X-ray diffraction (XRD) measurements reveal that films thicker than 4 nm are single crystalline with a (100) niobium bulk orientation in agreement with the models. The (110) pole figure shows the diffracted intensities of the 4 diagonal (110)-plans of the body center cubic lattice of niobium (χ = 45° +/- 3°) as expected for a hetero-epitaxial growth of (001) on the R-plan sapphire. XRD patterns of samples thinner than 4nm (samples D, E, F) exhibit no trace of the body center cubic Nb lattice, suggesting that hetero-epitaxy is not achieved if the growth is interrupted in its early stages. Further investigations by grazing incidence X-ray diffraction confirm that the thinnest films (samples D, E) are indeed made of mosaic polycrystals, as the patterns are similar to the one encountered for niobium powder (Fig. 1).
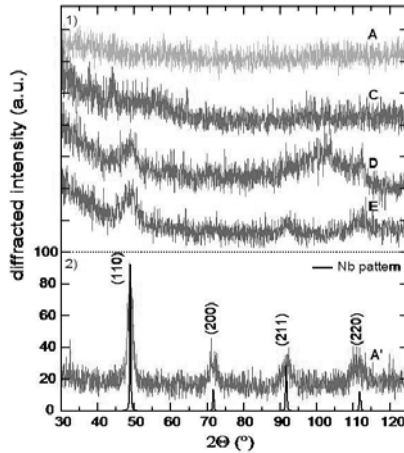

Figure 1. Grazing incidence X-ray diffraction analysis performed on a series of films with different Nb thicknesses : A=9nm, B=8nm, C=4nm, D=3.3nm, E=3nm. Curves are shifted for sake of clarity. To illustrate the difference between hetero-epitaxial (A,C) and polycrystalline films (D,E), the bottom inset show the diffraction pattern of a thicker polycrystalline niobium film (A'= 9 nm) (red curve) and compares it to a theoretical pattern of niobium powder (black curve).

The initial growth stage of niobium film on an atomically flat substrate follows the step-flow model [6] as previously predicted [5]. Niobium adatoms move on the terraces, rearrange themselves along the sapphire step edges forming patches that percolate, leading to a mosaic

polycristal film. When the layer get thicker, typically over 10 ML, volumic interactions start to dominate over the step edge 2D interaction and force the film to become single-crystalline with a (100) niobium bulk orientation.

Electronic properties

The square resistance of samples have been measured on strip lines etched from the films using 4 probes techniques from room temperature down to 0.1 K using a dilution refrigerator.

Resistance-temperature curves (Fig. 2) shows superconducting transitions for all films thicker than 3 nm. Critical temperature T_c is found to be inversely proportional with d and the transition widen notably for polycrystalline films (samples D, E). This widening mostly occurs on the onset of the transition as a result of an increase of the superconducting fluctuations. However there is no trace of residual resistance below T_c that would have revealed the existence of phase fluctuations.

The thinnest films (samples F,G) do not show superconducting transition at the lowest temperature (0.1K). For sample F, high resolution measurements have shown a drop at 0.5K towards a partially resistive state which equals 70% of the resistance measured at 10K, suggesting the transition towards an intermediate metallic state. For sample G, this decrease clearly follows a logarithmic dependence with temperature, which is a signature of a 2D weak localization.
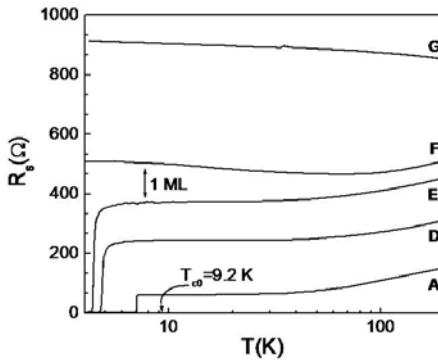

Figure 2. Sheet resistance R_S as a function of temperature. As thickness is reduced (from A=9nm, D=3.3nm, E=3nm, F=2.8nm, G=2.5nm), R_S (10K) increases and the superconducting transition temperature T_C vanishes. An electronic transition occurs for a critical Nb thickness of 2.98 nm (F) on a very narrow thickness range (1 ML).

The suppression of superconductivity has been studied before in several configurations, for granular or amorphous films and with different elemental materials and alloys. Its origins could be multiple as they range from transition to a localized state due to disorder [7] to quantum confinement [8,9] or to inverse proximity effect with the surrounding materials [10]. In a disorder induced superconducting to insulator transition [11], R_s was believed to be of the order of the resistance quantum $h/(4e^2)=6.5$ kΩ In our system however the transition is observed for a

well lower resistance per square (Fig. 2) suggesting that the localization is not the dominant factor that leads to the suppression of the superconducting state.

Application to quantum devices

The reported single crystalline niobium films are stable in time over months even exposed to the ambient atmosphere, as demonstrated by the 4 nm Nb-thick with Tc= 5 K that is still preserved after multiples thermal cycling and even 3 years after its growth. The thinnest samples are also resistant to micro and nano-fabrication processes, with a superconducting transition temperature preserved above 4.2K for nanostructures made from sample C. This 3-nm-Nb-thick sample has been patterned using conventional Deep-UV photolithography followed and AFM nanolithography leading to nanometer scaled superconducting quantum interferometer devices (fig.3) [12].
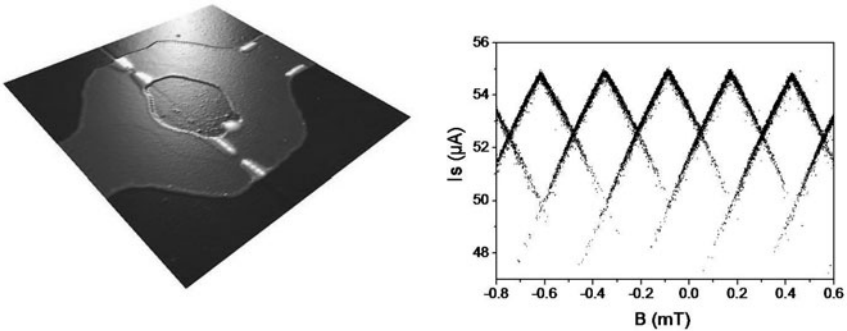

Figure 3. Left: Atomic force micrograph of a nanosized superconducting quantum interference device (SQUID) AFM-made by using the 3-nm-thick niobium film described in the main text. Right: variations of the maximum supercurrent of the device as a function of the applied magnetic field. The measurement temperature is 50mK.

CONCLUSIONS

We have presented a combined analysis of structural and electron transport properties of sub-10 nm niobium films evaporated on R-plane sapphire. The films undergo a sharp non-universal superconducting-metalic transition at 3nm which follow a structural transition from poly to single crystal occurring occurs at thickness slightly above that value. The Tc cut-off occurs over a narrow thickness range (1ML) obtained for a non-universal critical resistance which is more than 10 times below the quantum of resistance $h/(4e2)$. Resistance temperature measurements show a transition toward a metallic state with 2D weak localization features. Above that critical thickness, the overall stability demonstrated by both structural and electronic

measurements of the ultrathin films offers a reliable starting material for the realization of quantum superconducting devices.

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