MORPHOLOGY OF NIOBIUM FILMS SPUTTERED AT DIFFERENT TARGET – SUBSTRATE ANGLE

D. Tonini[*], C. Greggio[§], G. Keppel[◆], F. Laviano[$], M. Musiani[♌], G. Torzo[◆] and V. Palmieri[§]
[*]Università degli Studi di Padova; [§]INFN-LNL (Legnaro, PD); [◆]INFM Padua; [$]Turin Polytechnic; [♌]CNR-IENI, Padua. ITALY

Abstract

The Q-degradation versus accelerating field represents a great limitation for Niobium sputtered electron cavities. Moreover it is well-known that passing to middle beta cavities, by increasing the sputtering target-substrate angle, the Q-slope becomes more and more severe. The authors have investigated the role that such angle has onto film morphology.

INTRODUCTION

Niobium sputtered cavities have great advantages respect to bulk niobium ones because of their lower cost and better performances, but there is a big limit on their use due to the decaying of the

Q-value ($Q = \omega U/P$) when increasing accelerating field.

Studies made at CERN for medium β ($\beta = v/c$) LEP cavities [1] showed that arrival angle of niobium depositing atoms on the inner surface of the cavity seems to have an influence on film properties; those works indicate 28° as limiting arrival angle to achieve satisfactory superconducting properties of niobium film.

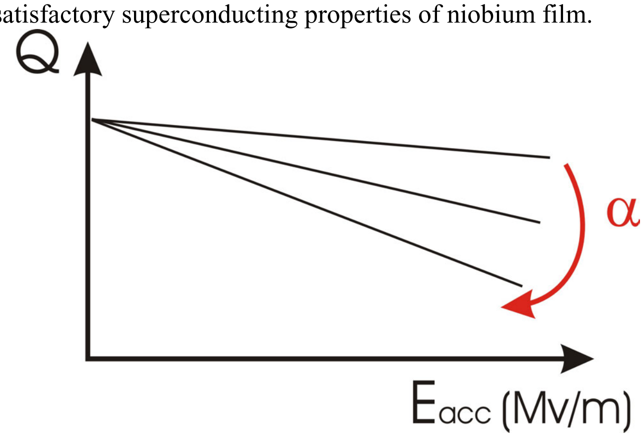

FIG. 1 Q-decaying increasing at high accelerating fields when deposition angle α increases.

Oblique incidence of depositing atoms causes a particular morphology of growing film [2] because of shadowing effects. Shadowing generates an increase in film roughness due to two combining effects:

1. There is a lower atom flux in shadowed substrate's areas.
2. Low surface mobility of niobium atoms limits diffusion in shadowed zone.

We expect an increase in film roughness when the arrival angle becomes more grazing [3].

Film morphology influences transport properties, in particular we expect an increase in residual resistivity when the film is rougher [4]; an accelerating cavity has a complex shape, so film morphology depends on the position on the inner surface of the cavity and as a consequence of this superconducting properties have great variation in different zones of the cavity itself.

There are several kinds of cavities with different shapes and region of inner surface in which the angle between target and substrate reaches 90°, so sputtering deposition of niobium films with uniform properties in all areas of cavity is a great scientific and technologic task.

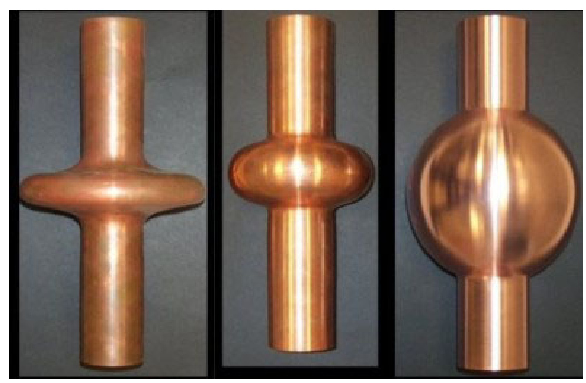

FIG. 2 Three cavities with the same resonant frequency but different beta

FIG. 2 shows three cavities with different beta, surface curvature radius influences the arrival angle of niobium atoms emitted from a cathode placed along cavities axis during sputtering process.

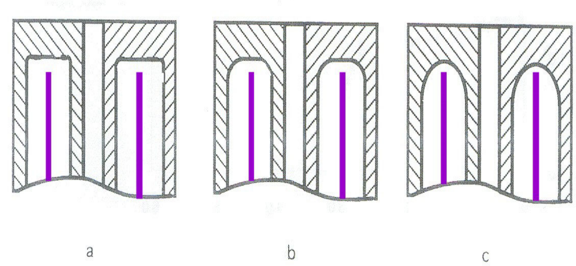

FIG. 3 section view of three QWR. The different curvature radius of the top plate modifies limiting arrival angles.

Angle problem is relevant for several kinds of cavities like Quarter Wave Resonator (QWR) showed in FIG. 3, where the top plate curvature radius modifies angular distribution of depositing atoms creating different morphologies. There is the same problem in Radio Frequency Quadrupoles (RFQ) that have a complex shape with deposition angle varying continuously from 0 to 90 degrees (see FIG. 4).

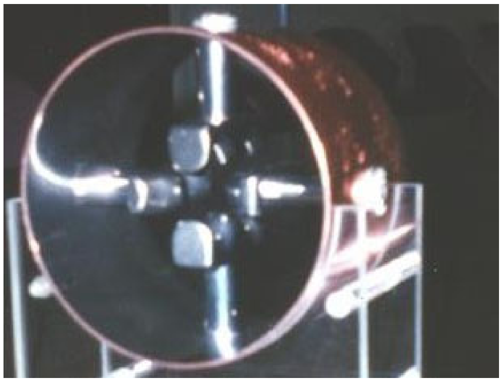

FIG. 4 Inner view of a RFQ. Deposition angle varies continuously from 0° to 90°

The main task of this work is to analyze the effect of deposition angle (defined as the angle between target and substrate surfaces) on deposited film morphology and superconducting properties. The work has been conducted systematically, depositing run of 7 samples at the same time in order to keep all process condition constant and only the angle variable. Deposited films are analyzed on the basis of superconducting properties (T_c, RRR, magneto-optical imaging), morphological aspects (Atomic Force Microscope, Electrochemical Impedance Spectroscopy) and crystal structure (X-Ray Diffraction). Depositions are performed on quartz substrate and not on a dummy cavity in order to investigate only the angle dependence of morphology, in fact in a real cavity deposition also the target substrate distance is varying.

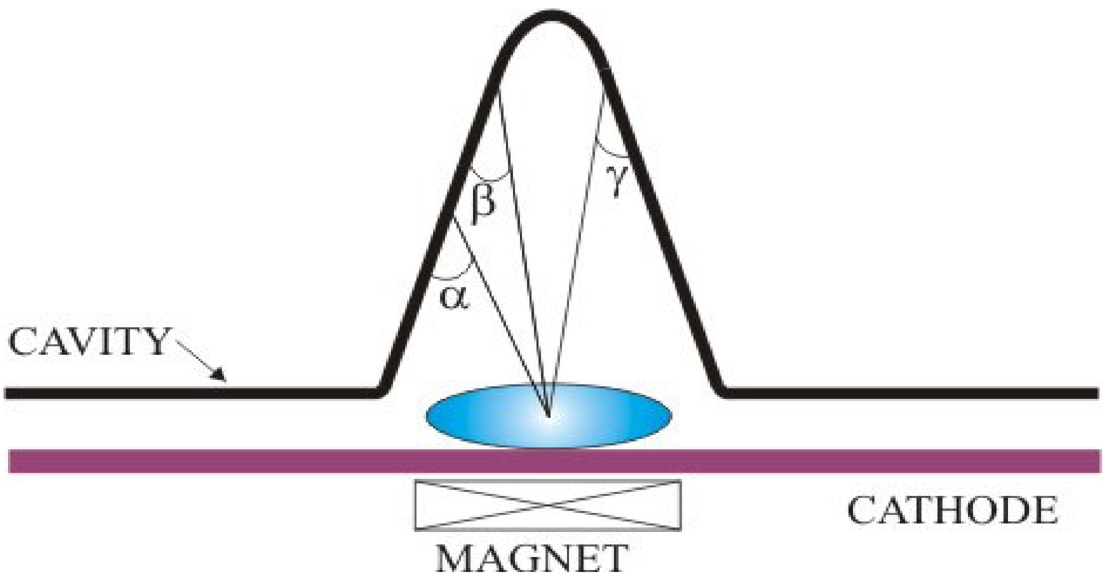

FIG. 5 Arrival angle of niobium atom in different position on the inner surface of a cavity. Also the target-substrate distance is varying.

MULTI-ANGLE SAMPLE HOLDER

In order to investigate the morphology of films deposited at different angles, we designed a substrate holder capable to carry seven samples at the same time with seven orientation respect to the plane of target, i.e. with angles varying from 0° (parallel to the target) to 90° (normal to the target) with 15° step. This substrate holder allows depositing films with seven diverse orientations in the same run, in such a way each sample is coated keeping exactly the same process condition, therefore film morphology and superconducting properties depend only on substrate orientation. For this work three different versions of the substrate holder are realized:

1. stainless steel-made with slot for 5x10 mm wide quartz substrates (FIG. 6, bottom)
2. copper-made with chemically polished surface. Niobium film was deposited directly on the holder to analyze it with Scanning Electron Microscope (FIG. 6, top)
3. stainless steel-made with doubled dimensions and no slot on surface, used to stick on it substrates bigger than 5x10 mm.

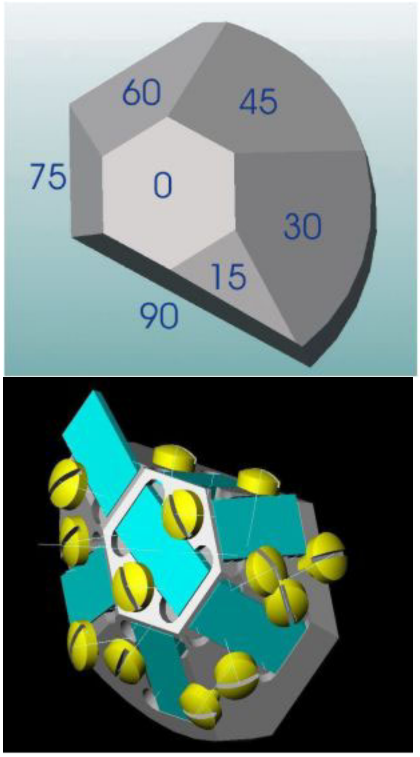

FIG. 6. Multi-angle substrate holders (faces at 0°, 15°, 30°, 45°, 60°, 75°, 90°)

Sputtering system

The depositions were performed in a cylindrical stainless steel vacuum chamber 280 mm high and with a diameter of 120 mm, equipped with a planar magnetron source with a 2 inches wide niobium target. The chamber is connected to a turbomolecular + rotary vane pumping system. The chamber was evacuated and then baked for 13 hours at 200 °C until a residual pressure $<2.0\cdot10^{-8}$ mbar was reached. We used Argon as process gas (P $=2.2\cdot10^{-3}$ mbar) and the substrate holder was placed 70 mm far from the target. No substrate heating systems were employed.

FIG. 7. Cylindrical post-magnetron (left) and 2 inches planar magnetron source (right)

SUPERCONDUCTING PROPERTIES

RF losses exponentially depend on critical temperature (***T_c***) and are proportional to the square root of residual resistivity in normal state. However both T_c and Residual Resistivity Ratio (***RRR***) are crucially affected by contamination, i.e. by the residual vacuum pressure before sputtering. The fraction f_i of impurities of the ***i***-th specie trapped during film growth is given by:

$$f_i = \frac{\alpha_i N_i}{\alpha_i N_i + R}$$

where N_i is the number of atoms of species ***i*** bombarding unit area of film in unit time; α_i is the sticking coefficient and ***R*** the deposition rate; so there are 3 ways to reduce contamination:

- reducing the background vacuum pressure i.e. decreasing N_i ;
- increasing the substrate temperature i.e. lowering α_i;
- increasing the amount of impinging Nb atoms over the impurity ions i.e. increasing ***R***.

We deposited films at different background pressure in order to vary the amount of contaminants trapped during the film growth i.e. to investigate the angle dependence of superconducting properties also in the low RRR region of the Testardi plot.

Superconducting properties was measured using a four-contact measurement probe and a custom data acquisition program. We obtained the full curve Resistance vs. Temperature and then we have calculated the RRR as the ratio between the electrical resistance at 300 K and just above the superconductive transition (10 K). The critical temperature was calculated using the formula:

$$\frac{T_{90} + T_{10}}{2}$$

where T_{90} represents the temperature at which electrical resistance is 90% of the high temperature resistance and T_{10} is the temperature at which resistance is 10% of high temperature value.

Residual Resistivity Ratio

As shown in FIG. 8 Residual Resistivity Ratio decreases monotonically increasing the target-substrate angle. We performed depositions increasing the amount of contamination in the growing film obtaining, as expected, lower RRR at higher level of impurities, but the plots still show the same dependency on deposition angle.

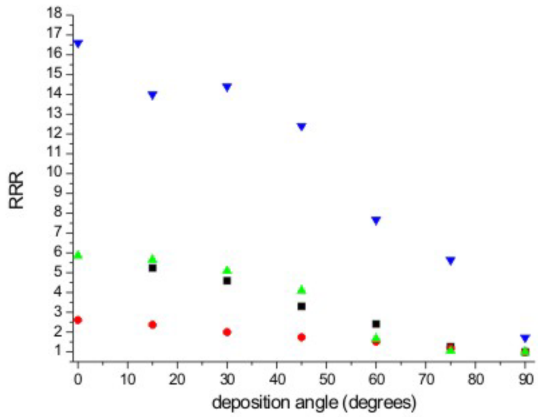

FIG. 8. RRR vs. deposition angle for samples at different level of contamination

Critical Temperature

As for RRR, the transition temperature has been found decreasing with deposition angle. Angular dependencies of T_c are plotted in FIG. 9 for the same process conditions of Fig. 3; the amount of impurities in the film play an important role in depressing the transition temperature of niobium film, as is clearly shown for experimental run performed at higher contamination level in which transition temperature does not reach 9K.

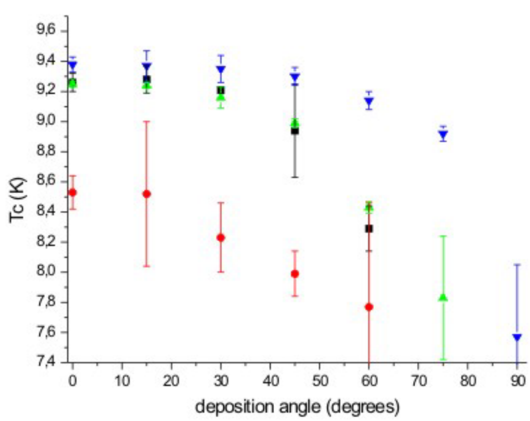

FIG. 9. T_c vs. deposition angle for samples at different level of contamination

X-RAY DIFFRACTION

FIG. 10 shows two important features in the crystal structure of deposited films:

- there is a change in the preferential orientation of crystallographic planes varying the deposition angle, in particular films deposited at lower angle shows high orientation along the (110) plane. This alignment is lost increasing the angle between target and substrate;
- Great deposition angle causes an amorphization of the coating: over 60 degrees almost all but the higher (110) peak vanishes.

The latter feature can explain the decay of superconducting properties, especially of RRR: as crystallites became smaller, i.e. the film tends to be amorphous, the number of grain boundaries and lattice imperfections increases and so the residual term of resistivity that strongly depend on them.

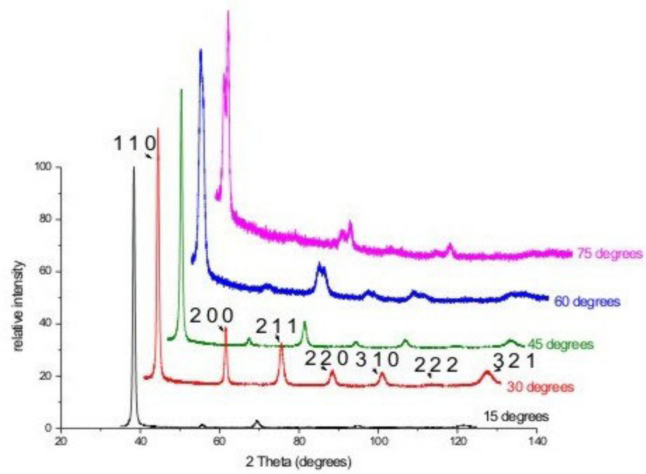

FIG. 10. Normalized X-ray diffraction spectra at various deposition angles

AFM IMAGING

The appearance of film surface at submicrometer scale is clearly seen by using Atomic Force Microscope (AFM) imaging. FIG. 11 shows the evolution of surface roughness increasing the deposition angle, and FIG. 12 is a plot of calculated average roughness vs. the deposition angle. Roughness is peaked at 75° and doesn't increase monotonically. We explain the lower roughness at 90 degrees since the mechanism of nucleation of perfectly perpendicular films should give rise to a kind of long and thin anisotropic fibres morphology, like long chains with high conductivity and small diameter. The T_c of such samples is of course depressed if the grain size is smaller than the coherence length.

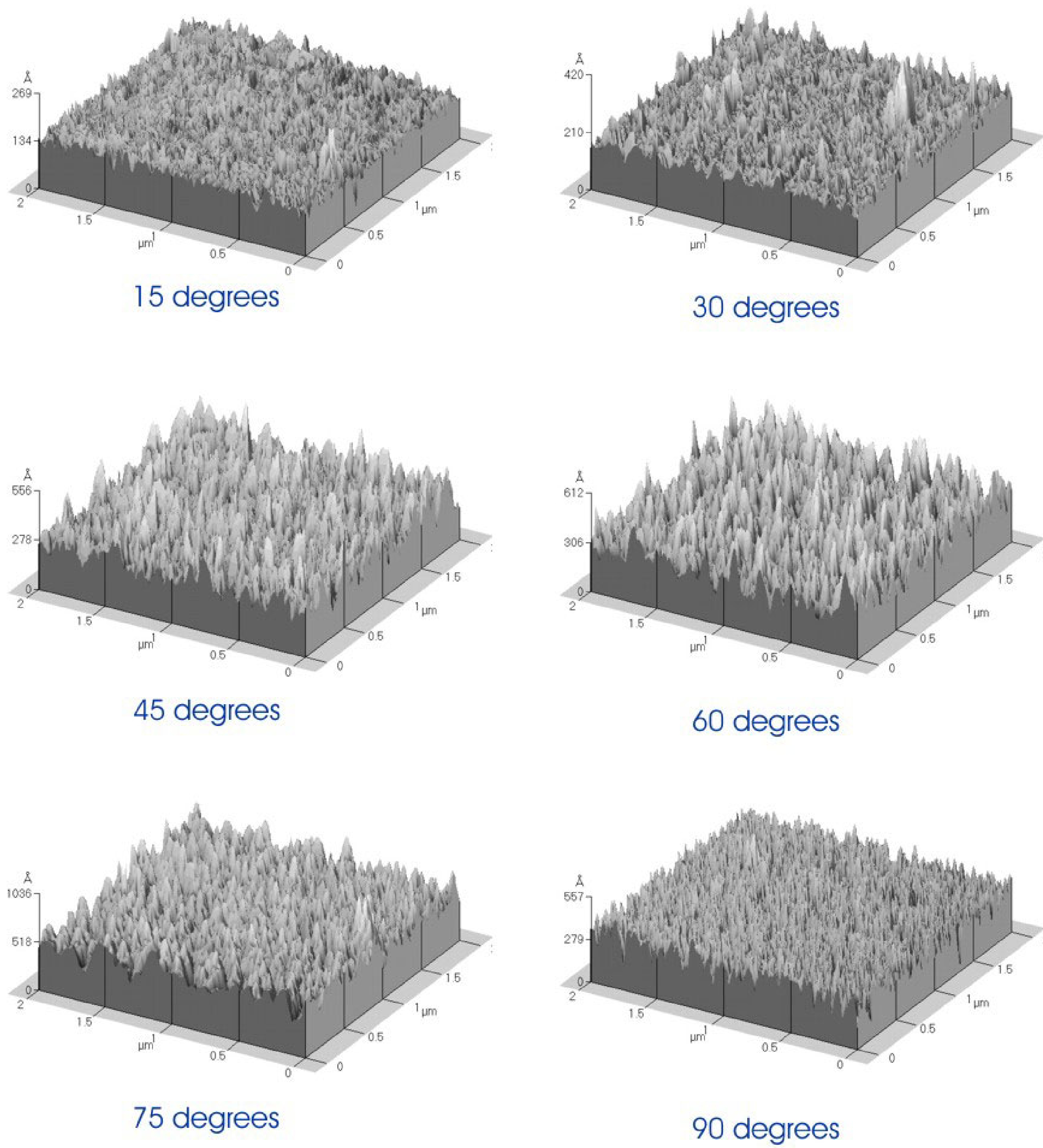

FIG. 11. AFM topographic images of niobium films deposited at different target-substrate angle

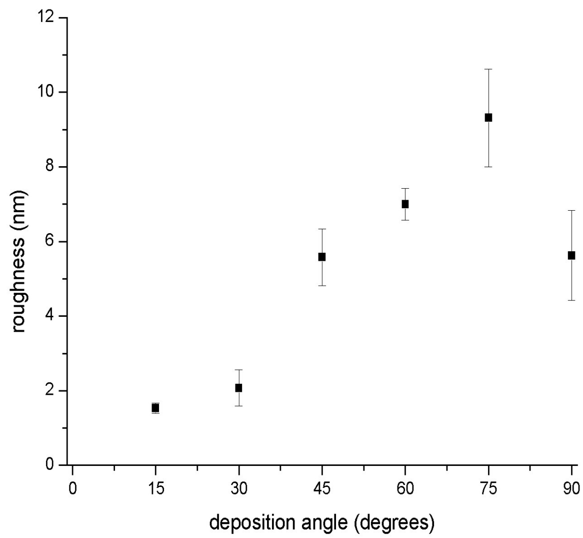

FIG. 12. Calculated average roughness vs. deposition angle

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Impedance spectroscopy is a powerful method to investigate properties of electrochemical systems and separate the contributions of different phenomena, like double layer charging, electron transfer and mass transport. An electrochemical interface is commonly represented by an equivalent circuit made of capacities and resistances (see FIG. 14): the double layer capacity (C_{dl}) is in parallel with interface resistance (R_{ct}) and diffusion impedance (Z_W); this parallel circuit is in series with solution resistance (R_s). An applied *dc* current can flow only through the resistive branch of the circuit, whereas an *ac* current can flow also through the capacitor that contributes to total impedance with $1/(2\pi f C_{dl})$, where f is the frequency of applied signal. If the case of rough or porous electrodes the apparent C_{dl} depends on the frequency of the applied signal because the field penetration in the pores increases as the frequency decreases. At a sufficiently low frequency the whole electrode/electrolyte interface within the pores is sampled and the measured C_{dl} becomes identical to that of an ideally flat electrode with a surface area as large as the developed area of the porous electrode. Therefore the surface roughness of Nb samples deposited at different angles can be estimated as the ratio between its C_{dl} (measured at low frequency) and the C_{dl} of an ideally flat Nb sample of the same geometric area.

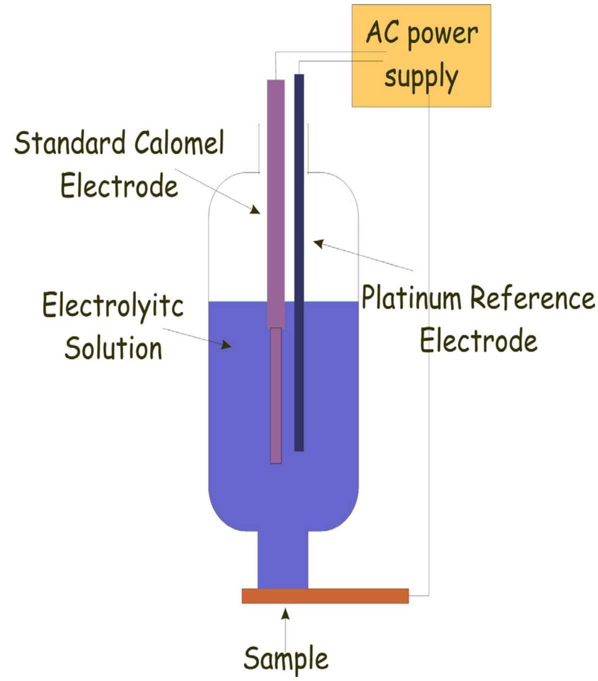

FIG. 13. Schematic view of experimental apparatus for impedance spectroscopy measurement

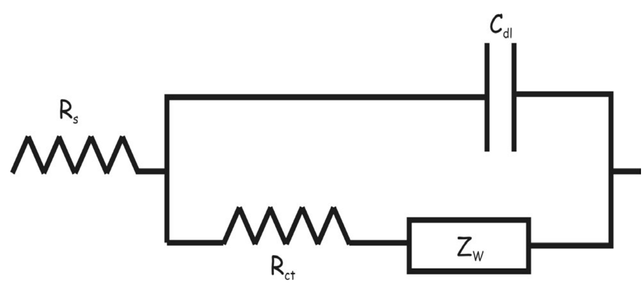

FIG. 14. Equivalent circuit for a porous electrode

The calculated roughness (FIG. 15)is in fairly good agreement with AFM data, with a shift in the maximum toward smaller deposition angle. Correlating the results of both measurement (AFM and impedance spectroscopy) we can conclude that deposition angle between 60 and 75 degrees generates film with the roughest surface.

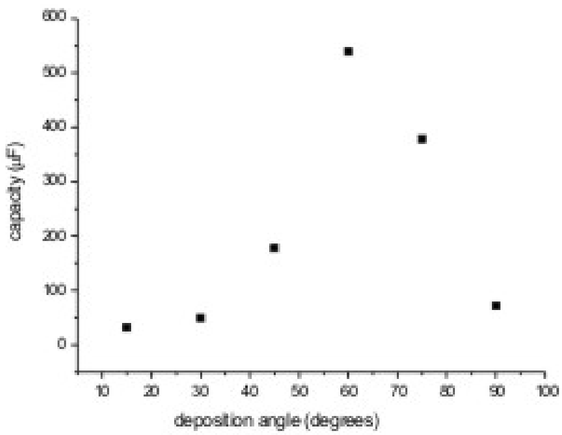

FIG. 15 Roughness vs. deposition angle measured by electrochemical impedance spectroscopy

MAGNETO-OPTICAL IMAGING

The magneto-optical measurement is based on the Faraday effect and on the use of a ferromagnetic indicator as the magnetic probe The indicator locally rotates the polarization plane of an incident light beam and the amount of rotation is proportional to the local magnetic field.

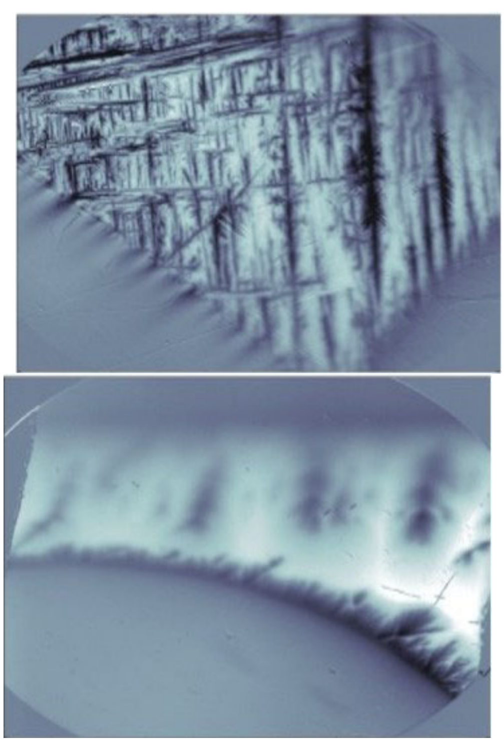

FIG. 16. Magneto-optical images of film deposited at target - substrate angle of 0 (top) and 45 (bottom) degrees. depositions are performed onto copper substrate. External applied field is 176 mT at T = 5K.

A microscope and a light polarization analyser directly show the magnetic field distribution over the sample as an image with bright and dark tones. Higher local field values are displayed as bright

colours, negative values (field line directed from the reader to the image) are dark, e.g., stray field outside the film edges.

FIG. 16 shows magneto-optical images of two film deposited onto copper substrate at 0 and 45 degrees target – substrate angle. In the 0 degrees film, vortex trapped at pinning sites are displayed as bright areas, the coating shows a good connectivity in the central part with little substrate effect. As concerns 45 degrees film, substrate morphology plays an important role, in fact macroscopic defects (represented as dark lines), following the trace left on copper surface by mechanical polishing, are clearly visible. Sample stray field is closed inside defects and the whole film has poor connectivity.

Substrate effect increases with deposition angle, because of three combining factors:

1. Shadowing by substrate roughness is enhanced for atoms arriving at low angle respect to the surface plane, so Nb atoms deposit preferentially on the surface asperities generating a film that follow the pattern of substrate superficial defects.
2. Deposition on samples at low target – substrate angle is mainly in “line of sight”, at the pressure used for our experiments the mean free path of arriving Nb atoms is long enough to permit a significant part of sputtered atoms to be deposit with almost no gas-phase scattering. When target – substrate angle increases, greater percentage of atoms must arrive to the sample surface with a direction different from the one they have when they left the target; i.e. atoms arrive to high angle substrates after performing more collisions with gas atoms, so mean arrival energy is lower at high deposition. The low arrival energy doesn’t allow great surface diffusion of deposited adatoms that stop preferentially on energetically favourite sites, i.e. on surface defects.
3. Deposition rate decreases with increasing target – substrate angle and consequentially film thickness decreases. The influence of substrate roughness on film morphology is obviously greater for thinner coatings, i.e. for higher angle samples.

SIMULATION OF FILM GROWTH

The results obtained simulating film growth with different arrival angle of depositing atoms on the substrate are in good agreement with morphological features shown by the analysis performed on real niobium films, in particular – as shown in FIG. 17 and FIG. 18 – films became more and more rough increasing deposition angle.

Film grown with simulated target – substrate angle of 0 degrees has a more compact and ordered morphology respect to the one grown with an angle of 45 degrees that shows an porous morphology and poorer order in atoms piling.

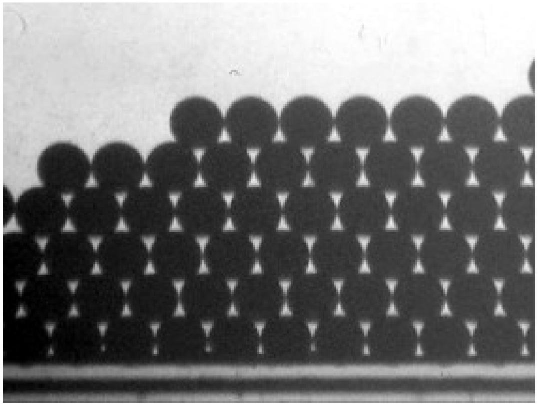

FIG. 17. simulation of film growth at target – substrate angle of 0 degrees

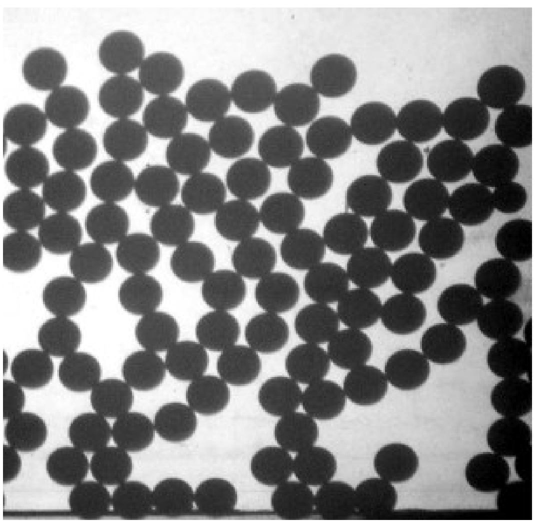

FIG. 18 simulation of film growth at target – substrate angle of 45 degrees

CONCLUSION

A decreasing in superconducting properties of niobium films has been observed when increasing the deposition angle between target and substrate, this effect is clearly due to change in the coating morphology. Films with different level of contaminants show the same angle dependence of residual resistivity ratio and transition temperature. In order to investigate how the morphology varies, we performed several kinds of physical and chemical analysis: X-ray Diffraction, Atomic Force Microscopy, Electrochemical Impedance Spectroscopy and Magneto-Optical Imaging.

XRD spectra show a change in preferential orientation of crystallographic planes as the deposition angle varies and a tendency towards amorphization for samples deposited at larger angles. Crystal structure influences superconducting properties, so XRD results give an explanation of the decay of RRR and T_c at high angle. Noteworthy, film roughness doesn't follow the same monotonically decreasing trend of superconducting properties, but seems to have a peak at deposition angle between 60 and 75 degrees as shown by AFM and EIS measurements. Both this two analysis indicate that film roughness decreases abruptly for film deposited at 90 degrees, this phenomenon apparently contrast with depression of T_c and RRR in perfectly perpendicular films can be explained with the nucleation and growth of long and thin anisotropic fibres morphology, like long chains with high conductivity and small diameter. Film of such morphology has low roughness but T_c is depressed because grain size is smaller than the coherence length.

At last we performed Magneto-Optical measurements of films deposited onto copper substrate that agree with RRR data (higher deposition angles led to poorer superconducting properties) and also underline the importance of substrate surface treatment, in fact substrate defect largely influences film morphology, especially at higher angles.

Looking at the work done we can state that the angle between target and substrate is a critical parameter for deposition inside accelerating cavities and that the reduction of the dramatic dependence of superconducting properties on deposition angle is a fundamental objective for overcoming of actual sputtered cavities limitation.

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