NB FILM GROWTH ON CRYSTALLINE AND AMORPHOUS SUBSTRATES

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Abstract

This paper describes Energetic Condensation Growth of Nb films using a cathodic arc plasma on crystalline (a- and c-sapphire, MgO) and amorphous (borosilicate) substrates. The crystal substrates were heated to 700 ºC and subsequently coated at 300, 500 and 700 ºC. Film thickness varied from ~0.25µm up to >5µm. The borosilicate substrate was preheated and coated in the 150-700 ºC range. XRD spectra (Bragg-Brentano) and pole figures show a change in crystal structure on c-sapphire from textured (with twin-symmetry) to hetero-epitaxial as the temperature is increased. RRR-43 was measured on c-sapphire which is lower than RRR-330 on a-sapphire and RRR-585 on MgO. On borosilicate, the (110) and (220) planes of Nb show sharper spectra at higher temperatures with an increase from RRR-10 to RRR-31 at 500 ºC. The growth of crystalline Nb on an amorphous substrate is driven by energetic (90-160eV) ions from the cathodic arc plasma. The observation of crystal growth on amorphous substrates has implications for future, lower-cost SRF cavities made from cast Al.

INTRODUCTION

Most RF particle accelerators worldwide utilize copper RF cavities to accelerate the particle beam. A few large research accelerators such as the Continuous Electron Beam Accelerator Facility (CEBAF) at Thomas Jefferson National Accelerator Facility (Jefferson Lab, or JLab) and the Spallation Neutron Source (SNS) at ORNL use superconducting radio frequency (SRF) accelerating cavities. SRF cavities consume less power than conventional cavities to produce a given accelerating gradient, even when the additional energy cost of the cryogenics system is taken into account. [1] Operation at higher temperature would further reduce the cryogenics costs. Niobium, the only presently accepted superconductor for SRF accelerators, has a transition temperature T_c of 9.3K, but operates at 2K, to reduce residual resistance and maximize critical magnetic field at the typically used 1.3–1.5 GHz RF frequencies. Increasing the operating temperature of the Nb cell accelerator from 2K to 4.5K could cut the cryogenics system costs in half [1] but would require use of an alternative superconductor with a transition temperature of 10K or higher. Since the RF (London) penetration depth on the cavity surface is only ~40nm, it is of interest to develop thin film coatings on the ~100nm scale for particle accelerators. One approach to reducing SRF accelerator costs is to replace the expensive, bulk Nb (~$300/lb) cavities with a Nb thin film deposited on a less expensive material, such as Cu (~$3/lb) or better yet, Al (~$1/lb). The added advantage of Al [2] over Cu is that the cavity can be cast instead of being machined, further reducing the installation cost.

Pioneering work [3-6] on Cu cavities coated with Nb thin film has been done at the European Organization for Nuclear Research, known as CERN. By 1998, 272 copper 352 MHz cavities, Nb thin film coated via magnetron sputtering, were deployed for the Large Electron-Positron Collider (LEP) project. The circular LEP collider, with a circumference of 27 kilometers, was one of the largest particle accelerators ever constructed and has recently been replaced by the Large Hadron Collider (LHC). Future accelerator facilities, such as the proposed International Linear Collider (ILC), require high accelerating field ~35 MV/m and $Q \geq 10^{10}$. It was reported [5,6] that at 1.7K the Nb thin film cavities for LEP had Q-drop to below 10^{10} at ≈15MV/m and to below 5×10^9 at ≈20 MV/m. Thus there is a motivation to better understand these limits and to improve Nb thin films' performance for future SRF accelerator cavities.

The payoff of higher temperature SRF cavities and cavities made out of thin-film coated Cu or Al has motivated a multi-year research program at Alameda Applied Sciences Corporation (AASC). The goal is to utilize energetic condensation to produce Nb-on-Cu films of sufficient quality to determine if the thin film RF properties are adequate for high power SRF applications such as particle accelerators. Thorough characterization of the surface morphology and RF properties of Nb-on-Cu is a necessary first step toward qualifying Nb coated Cu SRF cavities. Given the high-cost (>$100M) and infrequent occurrence of large SRF accelerator upgrades and construction, it is difficult to imagine acceptance of an alternative superconductor in SRF accelerators without demonstrated performance equivalent to (or better than) that of bulk Nb (2K). Implementation of Nb-on-Cu coated cavities into commercial accelerators, our long-term goal, is likely to follow reliable operation on large accelerators.

EXPERIMENTS

The experiments were done in the CED^{TM}, a coaxial rotating vacuum arc plasma, described in detail in previous publications [7-11]. The CED apparatus allows coating of the inner surfaces of tubes and cavities, without the need of complicated structures, moving sources, bias or gas. The helical movement of the arc spot around and along the surface of the cathode allows coating of large areas at high deposition rates. For example, at the present operating current of 200A, the CED coater deposits one monolayer of Nb on a 2 foot long, 3” diameter tube in only 60 ms. Because the metallic plasma is generated in vacuum, detrimental impurities [12] are negligible. The deposition rate is linearly proportional to the arc current and the pulse duty cycle, so may be increased by increasing the current and/or the duty cycle.

The effect of the energetic deposition driven by ions from the vacuum arc, was studied on crystalline and amorphous samples, placed at 40 mm distance from the cathode surface. Several samples were placed on a 50 mm heater, thus it was possible to compare for each deposition, the influence of substrate on the Nb thin film growth.

The crystalline samples used were a-plane, c-plane, and m-plane sapphire. The amorphous substrates were borosilicate, quartz, and alumina.

The influence of thickness and deposition temperature were studied using typical characterization techniques, including XRD, Pole Figures, RRR, SIMS, EBSD and FESEM.

CRYSTALLINE SUBSTRATES

To study the effect of substrate preparation on epitaxial growth of Nb, a 3 hr pre-anneal of the substrates in the 100 ºC – 700 ºC range was performed.

Prior to the thermal treatment of the samples, the CED apparatus was baked out for 18 hours at 120 ºC. A turbomolecular pump backed by a mechanical pump, allows the chamber to reach a background pressure of 2×10^{-8} torr. The samples are supported on a 50 mm diameter Mo-heater, allowing several samples (10 mm × 20 mm) to be placed on the heater. The frequency of the discharge is 0.25 Hz, low enough to permit pump away molecules that have been desorbed from the wall by energetic ion bombardment from the previous pulse. The background pressure reaches a maximum of 1×10^{-6} torr after the first 100 pulses and decreases monotonically as new Nb is deposited on the walls of the chamber (acting like a fresh getter). The background pressure after ~10,000 pulses is $1\text{x}10^{-7}$ torr.

All the Nb thin films coated by the CED^{TM} apparatus exhibited superconducting properties: the transition temperature was ~ 9.2K, and small displacements from this value were found to depend on the substrate type and Residual Resistance Ratio (RRR). A summary of measurements is presented in Table 1. In a previous publication we observed how defects like twins can be removed during the growth of Nb thin films using a thermal treatment 10]. As the temperatures of pre-annealing and deposition increase, defects in the films are removed/annihilated, and single crystal films with low hydrogen content are produced [7]. A world record of RRR-585 has been achieved in Nb thin films grown on MgO, and RRR-330 on a-sapphire. The textures of the crystals grown at high temperature, are (110) Nb oriented for a-plane sapphire and (100) Nb oriented for MgO(100). The samples prepared at temperature below 500 ºC are {110} Nb oriented, independent of the substrate. A transition of crystal orientation occurs on MgO substrates. The synergistic effect of energetic condensation and temperature treatment drives a transition of crystal orientation from (110) to (100) Nb on MgO substrates. Details of this work can be found in a future publication [8].

RRR	Substrate	Nb Orientation	Texture	Tc (K)	Thickness (µm)	Temp.Anne(C)/. Temp.Dep(C)	Method
3-27	Quartz	(110)	Fiber structure		2	150	Magnetron Sputtering [3-6]
12	Oxidized Cu	(110)	Fiber structure	9.5	2	300	
30	Ox Free Cu	(110), (200), (211)	Fiber structure	9.4	2	300	
35-40	Cu	?	Fiber structure	?	4	550	
10	a-pl. sapp.	(110)	110 w/twins	9.23	2	700/150	Vacuum Arc
330	a-pl. sapp	(110)	**Single Crystal**	9.34	2	700/500	Vacuum Arc
16	c-pl. sapp	(110)	110 w/twins	8.95	2	700/150	Vacuum Arc
43	c-pl. sapp	(110)	**Single Crystal**	9.15	2	700/700	Vacuum Arc
266	m-pl. sapp	(110)	**Single Crystal**	9.33		700/500	Vacuum Arc
7	MgO(100)	(110)	Fiber structure	9.25	2	150/150	Vacuum Arc
196	MgO(100)	(110), (200)	Polycrystalline	9.25	2	500/500	Vacuum Arc
316	MgO(100)	(200)	**Single Crystal**	9.24	2	700/700	Vacuum Arc
585	MgO(100)	(200)	**Single Crystal**	9.24	6	700/500	Vacuum Arc
10	Borosilicate	(110), (211)	Fiber structure	9.19	2	20-150/150	Vacuum Arc
21	Borosilicate	(110)	Fiber structure	9.25	2	400/400	Vacuum Arc
31	Borosilicate	(110)	Fiber structure	9.24	2	700/500	Vacuum Arc
24	Quartz			9.33	2	700/500	Vacuum Arc
25	Alumina			9.26	2	700/500	Vacuum Arc

RRR and Texture for Nb on c-plane Sapphire

To investigate cryogenic performance, a four-point-probe was used at JLab to measure the thin film materials' residual resistivity ratio RRR [1]. The RRR is defined as the ratio of resistivity at 300 K to that at 10 K. Details on the measurement can be found in a previous publication [11].

A parameter scan of RRR versus temperature of pre-annealing and temperature of deposition of Nb on c-sapphire is shown in Figure 1. In what follows, for example, a substrate-anneal temperature $T_{substrate-anneal}$=700 ºC followed by a coating at $T_{deposition}$=150 ºC is denoted by 700/150, etc. As the temperature increases, the RRR reaches a maximum value of 41 for 700/700.

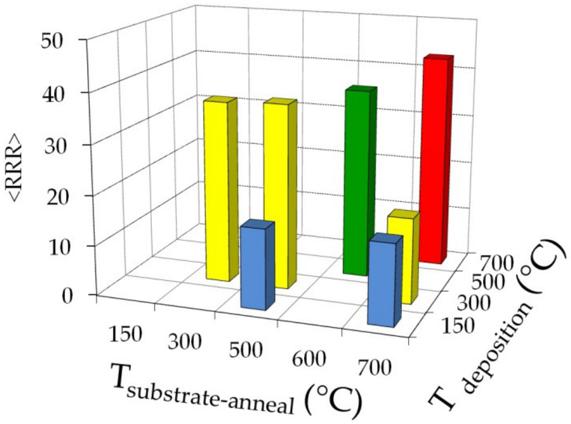

Figure 1: RRR vs. substrate-anneal temperature ($T_{substrate-anneal}$, horiz. axis) and deposition temperature ($T_{deposition}$, depth axis) for Nb films on c-plane sapphire. Note that all films were of the same thickness of ≈ 2 µm.

X-ray diffraction (XRD) studies revealed the crystal structure and texture via θ/2θ scan and pole figure by a four-circle PANalytical X'Pert PRO-MRD diffractometer.

Figure 2a show the Pole Figures of Nb thin films with RRR=16, prepared at low temperature of deposition, 700/150. The orientation of the films is Nb(110), with broad peaks and twins, indicating disorder and defects. However for films prepared at higher temperatures, the Pole Figures show no twins and very narrow peaks that are almost not identifiable in the figure. The RRR increases by almost a factor of three to 41. This correlation between higher RRR and higher crystallinity is present in all the Nb thin films coated using energetic condensation, independent of the substrate.

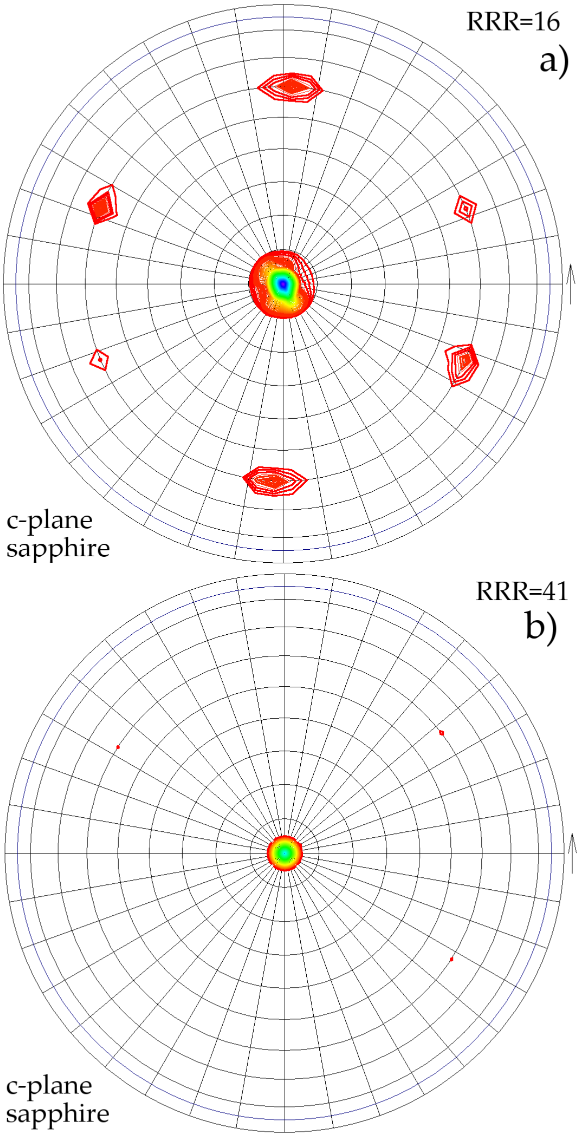

Figure 2: XRD {110}Nb Pole Figures for RRR=16 and 41 of Nb on c-plane sapphire.

AMORPHOUS SUBSTRATES

Borosilicate glass, quartz and alumina ceramic were coated with Nb using the CED^{TM} apparatus. All films presented superconductivity properties. However, we will focus here on the borosilicate results. These substrates were purchased from McMaster Carr, and originally were used as witness plates for other experiments. They have provided interesting information on the growth of Nb films on amorphous surfaces that have no epitaxial relationships with Nb.

Figure 3 shows the RRR-map of thin films of Nb coated on borosilicate samples vs temperature of pre-annealing and temperature of deposition. Like all the other RRR-maps, i.e. a-plane and MgO substrates, RRR values present a strong correlation with temperature treatment.

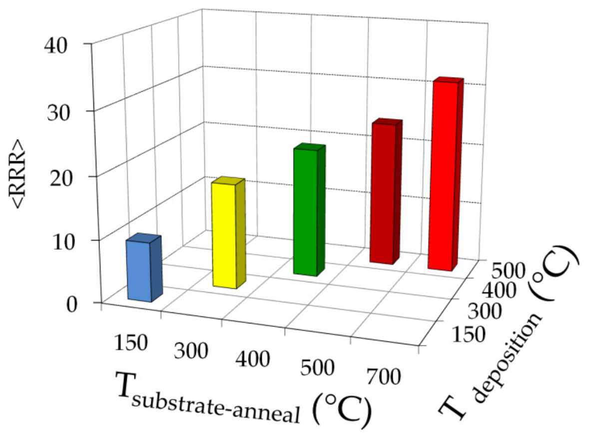

Figure 3: RRR vs. substrate-anneal temperature ($T_{substrate-anneal}$, horiz. axis) and deposition temperature ($T_{deposition}$, depth axis) for Nb films on borosilicate. Note that all films were of the same thickness of ≈ 2 μm.

As shown in Figure 3, the RRR values increase almost monotonically as the temperature of the pre-annealing and temperature of deposition increase.

Figure 4a shows the Bragg Brentano spectra for low RRR films deposited at low temperature. The thin film is polycrystalline, and peaks Nb(110), Nb(211) and Nb(220) can be identified. A strong [110] Nb fiber structure perpendicular to the substrate is observed (Figure 5a), while twin grains oriented with (110) and (211) planes are shown in the diffraction intensity as a function of rotation (phi-scan) and tilt (psi-scan).

Figure 4b shows the Bragg Brentano spectra of a Nb sample prepared at 400 ºC, The Nb(110) is sharper and almost 3 times higher than the Nb(110) peak prepared at room temperature, at the same time the Nb(211) peak has disappeared. The fiber texture of the film changes from polycrystalline to monocrystalline. Figure 5b shows how the (211) lobes disappear.

This is a result that is very different from epitaxial growth, where the Nb film tries to mold its orientation and grain size to that of the substrate underneath. On amorphous substrates an extra degree of freedom is provided (in terms of surface energy) [13] and the energetic condensation plus thermal treatment help the Nb define its preferred orientation. The Nb ions with ~ 100-200eV and substrate temperature >400 ºC define the Nb(110) orientation.

I.G. Brown and P.K. Chu [14] reported a change of orientation as the energy and the temperature of deposition are increased, suggesting a control of the orientation of the films by this synergetic process, also S. Mandl [15] observed how the texture of the film is changed by the energy and angle of the ions with respect to the surface normal. Brice et al develop a model using experimental data and TRIM calculations to understand this synergetic process [16]. Vacancies created by substrate atom displacement due to the energetic ions can migrate to the surface and be annihilated. Then the incoming Nb interstitial atoms that have been subplanted can be reorganized. This result reveals an interesting new approach, where no epitaxial relations need to exist on the surface to be coated. The substrate does not need to have large grains, or a preferred orientation, as long as it is clean with low surface roughness, a crystalline film can be deposited. A new spectrum of possibility is now available; for example, a thin film of Nb can be coated on the inner surface of a cast aluminium cavity, on amorphous copper, or may be used to repair existing Nb cavities that have defects such as pits.

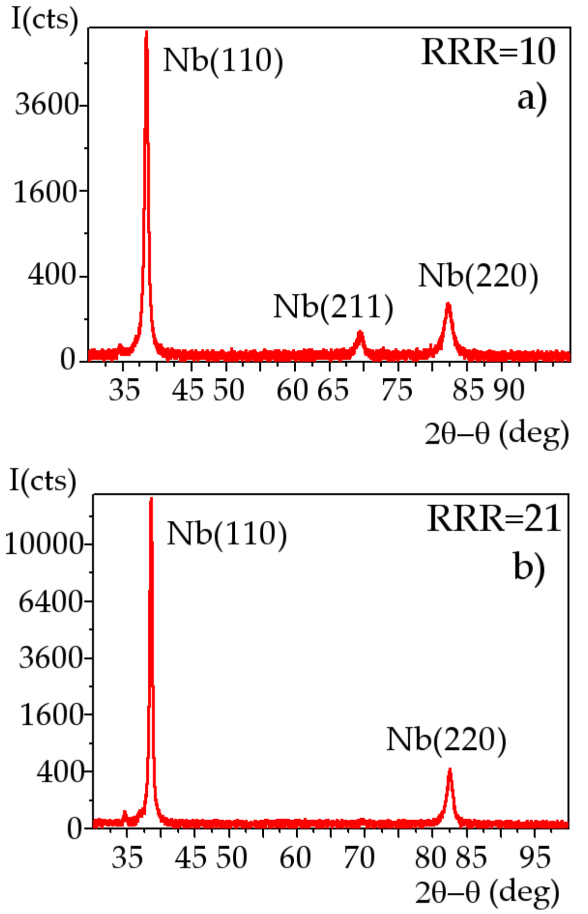

Figure 4a: XRD Bragg Brentano Spectra for low RRR(a) and high RRR(b) of Nb films on borosilicate substrates.

DISCUSSION

A distinguishing feature of these cathodic arc plasma coaters is that the metallic ions that impinge upon the substrate to grow the film have energy in the range of ~100-200 eV. This is to be contrasted with much lower incident energy in evaporation sources, MBE or e-beam sputter sources. Electron Cyclotron Resonance (ECR) and High-Impulse Pulsed Magnetron Sources (HIPIMS) also have high ion energy and in that respect fall into the same class as our sources. The high ion

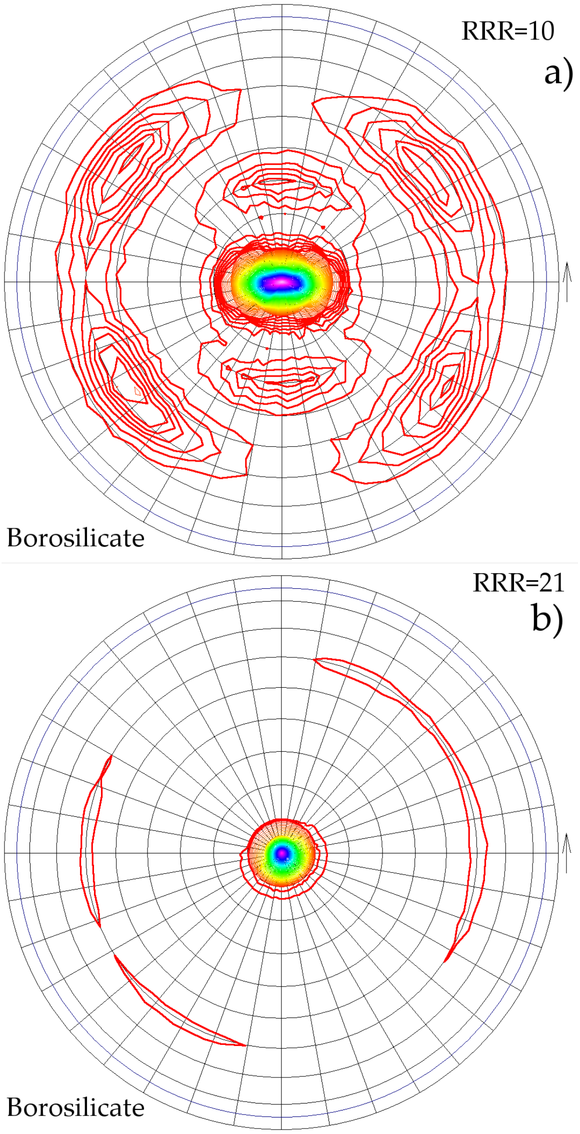

Figure 5: XRD {110}Nb Pole Figures for RRR=10(a) and 41(b) of Nb on borosilicate substrates.

energy alters the surface of the substrate (creates defects and vacancies within the first few atomic layers) and hence enables epitaxial crystal growth under the right conditions. A heated substrate allows these shallow defects to migrate to the surface and be annihilated, leading to low-defect crystal growth. The CED (or CAD/FCAD) process delivers ions to the substrate that maximize surface interactions (within a few mono-layers) while minimizing bulk defect creation. Thus we have demonstrated hetero-epitaxial films of Nb on various substrates, with good superconducting properties and crystal size (10mm × 20mm) limited only by substrate size.

The RRR of Nb thin films on crystalline substrates, increases as the defects of Nb thin film are reduced [7-10]. The grain sized is increased, then the number of grains is reduced. A dense film results, with fewer places where impurities can diffuse and be trapped. The total effect is a minimization of inter-grain resistivity, which minimizes the total resistivity of the films [1,6].

The top surface of the films will have less defects than the layers closest to the substrate, hence the RRR should increase with thickness [6,8]. This is a important difference when compared with bulk Nb. The best region of the film (top layer) will block penetration of the magnetic field. The cooper pairs will move on the top surface of the film, where the number of defects is much lower than the substrate portion of the film. For a-plane sapphire we measured an increase from RRR=100 to RRR=200, as we increased the thickness from 1 µm to 2 µm. The same trend was observed for all other films. Based on this observation, If we make the films 3 times thicker on amorphous substrates, we hope to reach RRR>100. Then too, such an average RRR implies a still higher RRR in the topmost layers of the film [6,8].

In a recent study by P. Kneisel et al. [17] of the performance of Nb single crystal cavities with different orientations, they report that a cavity with Nb(110) did not improve its Q-slope and quench limit after 12 hours of baking. By contrast, a cavity with mostly Nb(100) orientation, after 12 hours of mild baking at 120 ºC, exhibited an increase in quench field from 31 MV/m to 39 MV/m, with a $Q_0 = 1.8 \times 10^{-10}$, more than 2 times higher than the cavity with Nb(110) orientation. Also the cavity with Nb(100) orientation presented a shiny and smooth surface, whereas the NB(110) surface was scaly and rough. The authors point out that the performance of a cavity can be influenced by crystal orientation and further investigation is needed.

The results on borosilicate open the possibility for superconducting coatings on amorphous surfaces. An Al cavity would be such a surface. Alternatively, a Cu cavity surface might first be bombarded with high energy ions (simple bias of ~1-2kV of the substrates would boost the native energy of the CED generated ions from ~100eV to ~1100-2100eV, causing implantation and rendering the Cu cavity surface amorphous. After the dense amorphous layer is created, the energy of the ions can be reduced (by reducing the bias) to change from sputtering mode to sub-surface implantation of Nb atoms. When accompanied by adequate heating, the energetic condensation will promote thin film growth with a gradual change from initially fibrous texture to epitaxial crystal growth, as shown in Fig. 5. When no a priori epitaxial relation exists between the atoms deposited and the substrate, there is no constraint (lattice match condition) and hence the Nb film could grow differently than on crystal or polycrystalline substrates.

On MgO substrates for lower temperature of deposition, the orientation was primarily Nb(110), but as the temperature is increased a switch of orientation occurs as both Nb(110) and Nb(100) are present in the medium RRR-196, 500/500 film, evolving to a unique Nb(100) orientation at RRR-585, 700/500, where a single crystal is present across the whole 10x10mmm substrate surface.

This suggests growing a (100) thin film directly on a Nb cavity cell.

Our films are denser and with presumably lower density of defects, given the growth of single crystal Nb on a-sapphire, c-sapphire and MgO. The acid test of our energetic condensation grown films must be a coating of ~few µm thick films on a multi-cell cavity, followed by high field Q-slope tests.

Future work will be performed on borosilicate, bulk Nb, amorphous copper and aluminum, where the roughness of the substrate will be a parameter to study under the metric presented in this work. We hope to be able to produce denser with minimum defect niobium films. Coat a cavity after this learning will be our next milestone.

SUMMARY

High RRR Nb thin films were grown on a-plane sapphire, MgO(100) and borosilicate substrates, using a UHV cathodic arc source called CED^{TM}. RRR up to 585 was measured in hetero-epitaxial Nb(100) films grown on MgO substrates, and RRR up to 330 for Nb(110) on a-plane sapphire was achieved. Proper substrate annealing and heating during deposition, combined with sub-plantation dynamics driven by the ~100 eV ions impinging upon the substrate, has allowed us to achieve these high RRR values. Of note is the achievement of RRR=31 in Nb on amorphous borosilicate. This result suggests that energetic condensation modifies the substrate surface and when combined with substrate heating and sufficiently thick films, would promote homo-epitaxial growth of Nb. Optimization of this process could lead to SRF cavity coatings on lower-cost Al cavities.

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