# STRUCTURAL PROPERTIES OF NIOBIUM THIN FILMS DEPOSITED ON METALLIC SUBSTRATES*

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*Abstract*

Particle accelerators rely on SRF cavities to create the accelerating gradient for beam lines. Solid niobium cavities are widely employed throughout the community despite high material, fabrication, and operation cost. Energetic condensation deposition techniques for thin film technologies are being explored for the suitability of niobium coatings in accelerating cavities. Thin layers of niobium are deposited on a base material that has lower material and fabrication cost. Copper is a strong candidate for the cavity base due to availability, cost, machinability, higher thermal conductivity, and potentially improved performance characteristics of the niobium SRF surface. Preliminary results of EBSD and XRD of ECR deposited niobium thin films on copper substrates are presented to demonstrate the feasibility of the technology and establish lower limits of performance characteristics. Correlation of RRR data with the structure of niobium thin films will demonstrate the importance of thin film structural quality.

## INTRODUCTION

Selecting a suitable substrate for a given thin film is driven by its application. SRF cavities have complex organic shapes which are most easily fabricated with metals. The cavity needs to have a high thermal conductivity and heat capacity at 4K while maintaining mechanical strength. A moderately soft material is desirable to reduce machining and polishing efforts. Copper (Cu) and aluminum (Al) both meet the requirements for an SRF cavity base. Various groups have produced Nb (niobium) coated Cu cavities and samples by magnetron sputtering [1-2], LPCVD (Low Pressure Chemical Vapor Deposition) [3], HiPIMS (High Impulse Magnetron Sputtering) [4], MBE (Molecular Beam Epitaxy) [5], ALD (Atomic Layer Deposition) [6], ECR (Electron Cyclotron Resonance) [7], CED™ (Coaxial Energetic Deposition) [8] and e-beam evaporation [9]. The quality of the resultant thin film is heavily influenced by the deposition technique utilized. The energy condensation methods, ECR, HiPIMS, and CED provide ions with controllable energy, resulting in high quality films.

Understanding the theoretical arrangement of thin film atoms on a substrate is a first effort to understand if epitaxy will occur in a given thin film/substrate system. Theoretical calculations and experiments [10] predict that the bcc Nb on fcc Cu system follows the following hetero-epitaxial relationships: [110]Nb || [100]Cu, [100]Nb || [110]Cu and [110]Nb || [111]Cu. Theoretical calculations also estimate the level of lattice mismatch (or misfit) between the coating and the substrate. The degree of misfit gauges the nature of stress developed in the film and can be used to estimate the density of volume defects. Any structural defects will contribute to a reduced SRF performance. By minimizing the structural contributions to SRF characteristics, other Nb thin film properties may be investigated properly without masking from structural effects.

All metals have a passivation layer, usually a native oxide, which must be considered in epitaxial calculations. The native oxide thickness for most metals is usually on the order of nanometers, but must be removed or replaced with a well ordered surface to enable epitaxy. Without a well ordered surface the deposition will likely produce a highly textured film with an increased density of grain boundaries and other scattering centers. Cu has a native oxide layer that must be removed before epitaxy can proceed [11]. On an oxide-free Cu surface, Nb will deposit according to the reported epitaxial relationships. Deposition of Nb on native CuO will proceed in an uncoordinated manner producing close-packed plane [110] Nb fibers with a highly textured nature. The texture is developed from the random in-plane rotation of the fibers as nucleation of the thin film occurred uncoordinated and independently of the surface.

The oxide can be removed by thermal dissolution into the bulk, via in-situ chemical reactions on the surface, in-situ plasma treatments or by a combination or series of these processes. The most effective method is probably thermal and plasma treatments in cycles as utilized in Bagge-Hansen *et al.* for cleaning Cu samples [12]. If plasma treatments are chosen, the energy and anistropy of the plasma must be carefully examined to ensure that there is no sub-surface damage to the substrate, excessive roughening of the surface, process gases are not embedded and that the process is isotropic, low degree of grain or defect etching. Heating the substrate during plasma treatments will assist in point defect removal created from ion bombardment while heating alone will encourage more desorption of volatile compounds. The process chosen for this study was thermal dissolution of the oxide at temperatures just below the roughening

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temperature for the lowest energy face of Cu (111) [13].

The structure of the thin film is a determining factor in the resultant electrical, superconducting and SRF properties. The residual resistivity ratio (RRR) is used as a screening tool to determine the cumulative superconductive quality of a thin film. The RRR is a direct measure of the mean free path and quality of the film that is affected by any present scattering center. Structural defects and features can be scattering centers. Charged impurities in the lattice are a major scattering center and affect RRR. Impurities are not easily controlled in experiments, often are influential in minute concentrations at cryogenic temperatures, and can originate from many sources proceeding during and after deposition. The efforts towards epitaxy are rationalized by providing a thin film with fewer grain boundaries and reduced defect content as compared to a fiber growth mode. To further support the structural influence on quality, ECR Nb deposited on single crystal, large, and fine grain Cu substrates will demonstrate the influence of thin film structural quality on DC resistivity.

## EXPERIMENTAL METHOD

Due to the suitability of Cu as an SRF cavity base material, 99.999% OFHC (oxide free high conductivity copper) Cu coupons were used to investigate the properties of Nb thin films produced with different ECR deposition conditions. In each run, freshly etched and passivated 2” disc and 10 X 20 mm$^2$ Cu coupons were prepared following the method presented in accompanying article [14]. To study the epitaxial relationship of Nb on Cu (Nb/Cu), single crystals of each standard Cu orientation (100), (110) and (111), were also included. The single crystals were etched for 30 seconds in 45% $H_3PO_4$ : 55% n-Butanol at room temperature at a current density of 50 mA/cm$^2$.

The substrates were mounted on a resistively heated Cu sample holder, electrically isolated to allow biasing of the substrates. Samples were heated in-situ to 360 ºC for 24 hours prior to deposition to dissolve the CuO layer into the Cu bulk, providing an epitaxial surface for Nb deposition. A single ECR run coated at -150 V bias is presented to demonstrate the epitaxial relationships of Nb on single crystal Cu and Nb on polycrystalline Cu.

The structure of the Nb films was investigated with X-ray diffraction (XRD) and electron back scatter diffraction (EBSD). XRD techniques probe the volume of the film and EBSD probes the crystallinity of the surface (~50nm). The XRD measurements were made on a Phillips X'pert powered diffractometer. Traditional $\theta$-2*$\theta$ measurements were used to screen the z-axis orientations and are complimented with pole figures of Nb (110), (200), and (211). The EBSD measurements were made on an Amray $LaB_6$ secondary electron microscope (SEM) equipped with an EDAX EBSD system. The EBSD maps were acquired with approximately 26000 points, 1.5 X 1.5 mm scan area with 10 µm steps and 0.15 mm X 0.15 mm scan area with 1 µm steps.

Transition temperature (Tc) and residual resistivity ratio (RRR) measurements were made with a four-point probe setup in a liquid helium dewar. Samples for RRR measurements were prepared by cutting a 10 X 10 mm portion of the ECR samples and dissolving the Cu substrate in an ammonium persulfate solution at room temperature.

## RESULTS

The reported Nb on Cu epitaxial relationships are confirmed with XRD pole figures and EBSD maps. The pole figures and EBSD maps for the ECR Nb thin films on single crystal Cu are presented in figures 1 and 2. The pole figures suggest that there are at least two growth variants for Nb (110) / Cu (100) and Nb (110) / Cu (111) and one variant for Nb (200) / Cu (110). The smearing effect of the center pole in the (200) pole figure is a likely result of non-planarity of the single crystals due to their fabrication method. The EBSD maps indicate the single crystal nature of the ECR Nb thin films on single crystal Cu.

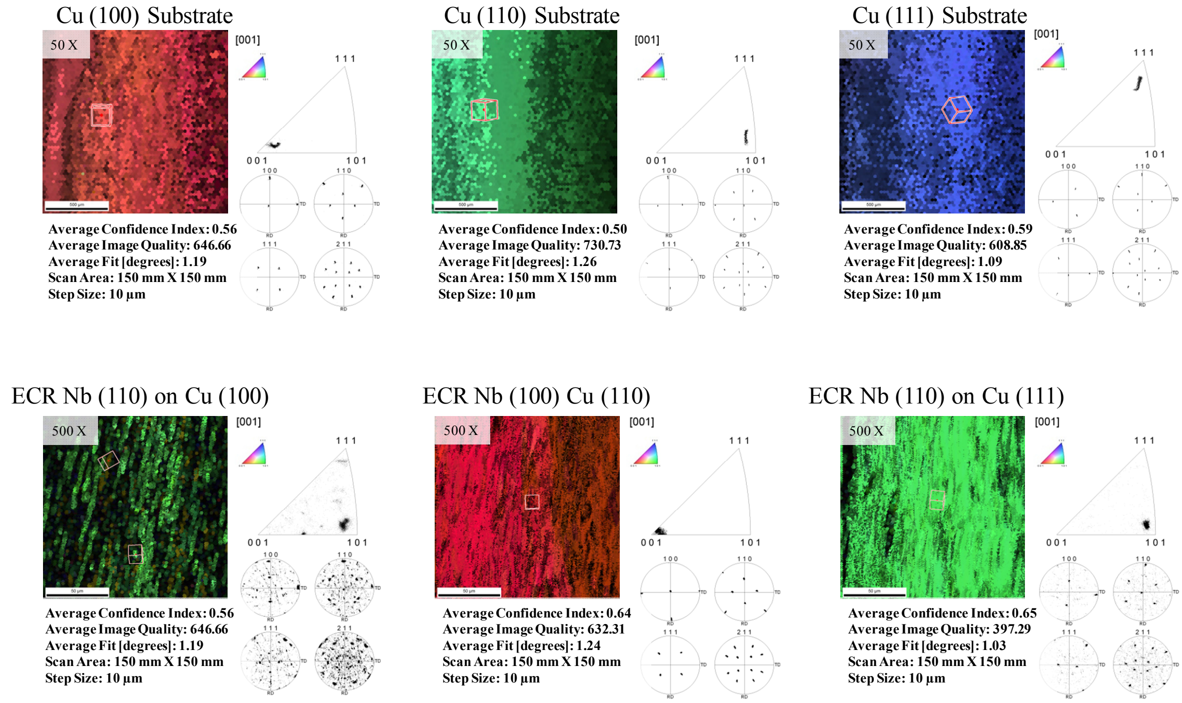


Figure 1: Top EBSD maps of Cu single crystal substrates with EBSD IPF and pole figures below. Bottom pane is EBSD for ECR Nb coatings on single crystal Cu orientations (maps post processed with neighbor confidence index (CI) of 0.2 and the EBSD map grey scale is based on a CI of 0.2%).

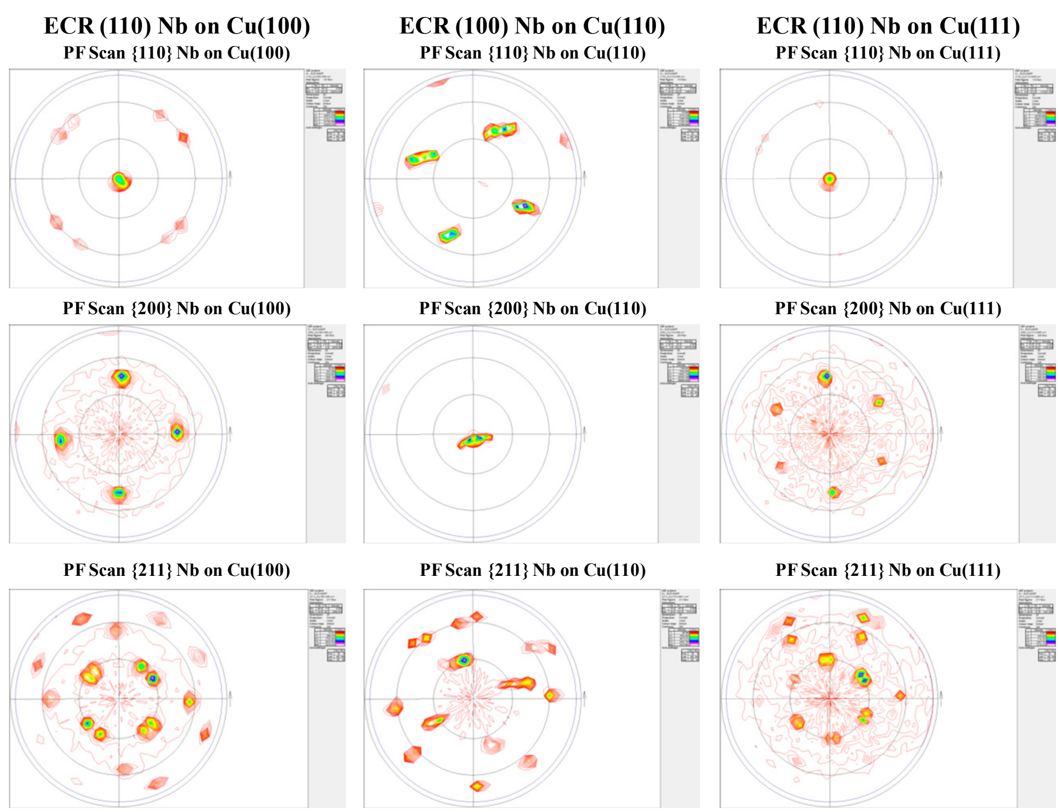


Figure 2: Pole figures for Nb(110), Nb(200), and Nb(211) are presented or each of the single crystal Cu orientations (100), (110), and (111).

The EBSD maps and representative Hirox images are presented in figure 3a for ECR Nb on large grain Cu and figure 3b for ECR Nb on fine grain Cu. The mm size large grain Cu EBSD map, and representative Hirox image correlate in figure 3a with those for the ECR deposited Nb. The large grain crystalline nature of the Cu substrate induces a long range ordering in the ECR Nb. The fine grain Cu substrate and corresponding ECR deposited Nb (figure 3b) demonstrate the substrate's influence on the film texture. The fine grain Cu produces an ECR Nb thin film with more grain boundaries and a higher degree of anisotropy. Attempts at XRD pole figures of ECR Nb thin films on polycrystalline Cu were unsuccessful due to the lack of z-axis orientation in the large and fine grain Cu. In the large grain ECR Nb, very strong peaks of many facets can be found in the Bragg-Brentano scans but there was no reference plane that can reduce the projections of other facets in pole figures to resolve a single orientation or grain.

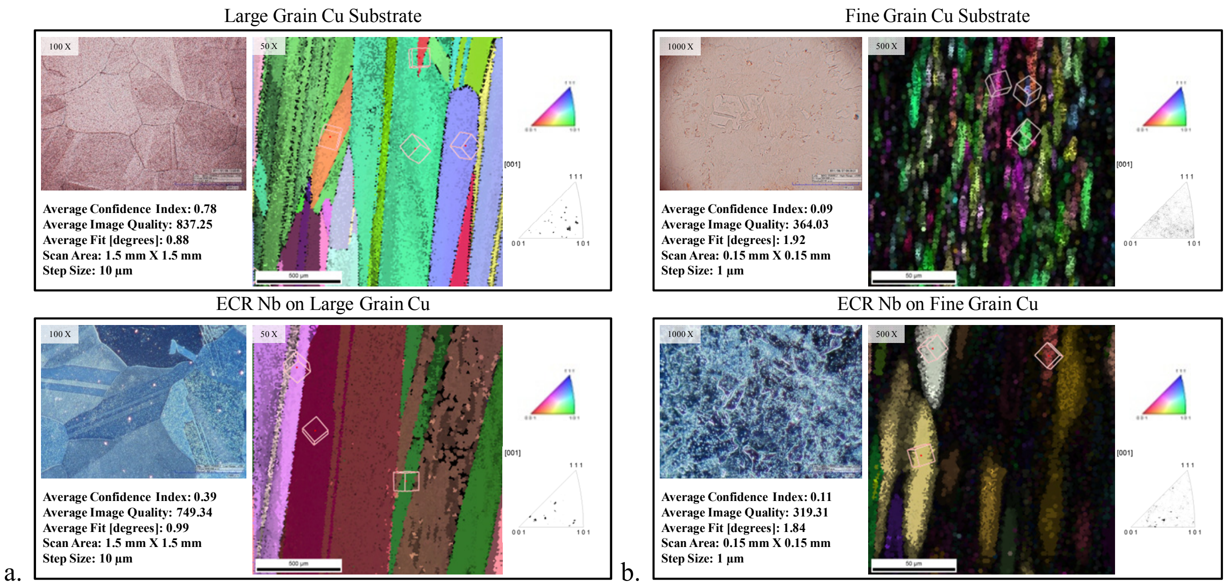


Figure 3: Hirox images and EBSD maps of large and fine grain Cu substrates and ECR deposited Nb thin films.

a. Upper left: Hirox image of large grain Cu substrate, upper right: EBSD map of large grain Cu substrate. Lower left: Hirox image of ECR deposited Nb on large grain Cu, lower right: EBSD map of ECR deposited Nb on large grain Cu.

b. Upper left: Hirox image of fine grain Cu substrate, upper right: EBSD map of fine grain Cu substrate. Lower left: Hirox image of ECR deposited Nb on fine grain Cu, lower right: EBSD map of ECR deposited Nb on fine grain Cu.

The resistivity versus temperature curves for large grain ECR Nb on Cu, dashed line with filled square, and fine grain ECR Nb on Cu, solid line with filled circles, are presented in figure 4. The RRR of ECR Nb on large grain Cu was measured to be ~ 170 and the ECR Nb on fine grain Cu was measured to be ~ 82. The difference in RRR observed for large and fine grain substrates is due to the structural purity of the materials including the grain boundaries density. Impurities resulting from all in-situ and ex-situ sources should be equal as the samples were electropolished, cleaned, deposited, and characterized simultaneously. By coating and handling substrates in parallel, most sources of impurities and other uncontrolled variables should be considerably reduced. The resistivity values should be treated as a lower bound due to the Cu substrate removal for the RRR measured samples. The electrical properties were likely degraded during the substrate removal and manipulation of the free standing Nb films.

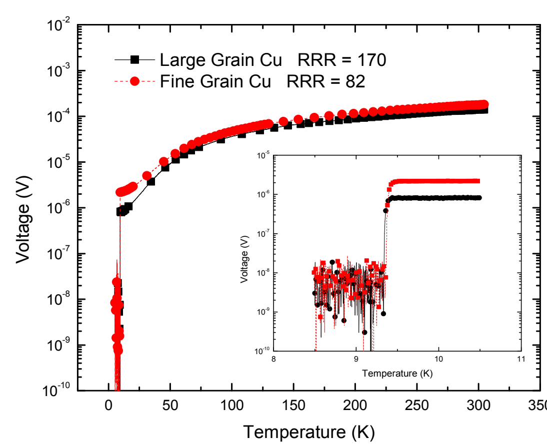


Figure 4: Resistivity versus temperature curves for ECR Nb on large and fine grain Cu. Large grain Cu substrate is the red dashed line with filled circles and fine grain substrate is the solid black line with filled squares.

The resistivity versus temperature curves for the ECR

Nb films on single crystal Cu are presented in figure 5. The highest RRR was 249 for Nb(110) / Cu(111), followed by ~ 89 for Nb(100) / Cu(110), and then ~ 77 for Nb(110) / (100). The qualitative nature of the EBSD maps are confirmed by the quantitative EBSD data ranking the surface crystal quality in the same order. The EBSD structural ranking is ECR Nb(110) / Cu(111) as the highest quality crystal followed by Nb(100) / Cu(110) and finally Nb(110) / Cu(100).

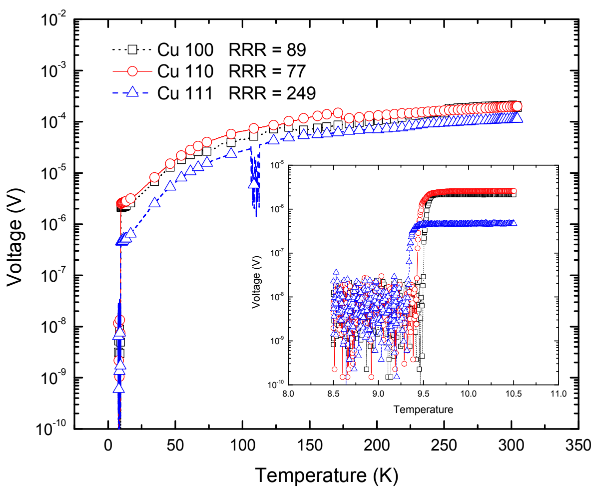


Figure 5: Resistivity versus temperature curves for ECR Nb on single crystal Cu orientations (100), (110), and (111). ECR Nb on (100) Cu is the dotted black line with open squares, ECR Nb on (110) Cu is the red solid line with open circles, and ECR Nb on (111) Cu is dashed blue line with open triangles.

## CONCLUSIONS

The structural quality of ECR single crystal Nb thin films on single crystal Cu correlates well with RRR. The structural properties of the thin film undoubtedly contribute greatly to RRR values but they are only some of the many factors determining a given film's RRR.

Comparing the structural quality of the fine and large grain ECR Nb on corresponding fine and large grain Cu substrates, it seems that there is ~ 10:1 ratio in grain size and feature density with the large grain Nb inheriting some features from annealing twins in the large grain Cu substrates. Further structural investigations via focused ion beam and transmission electron microscopy (FIB/TEM) are underway.

Epitaxy of high quality Nb on polycrystalline Cu by ECR can be achieved at deposition temperatures low enough to maintain the Cu cavity integrity. RRR values over 250 and 150 for ECR Nb on single crystal and polycrystalline Cu, respectively have been measured. Further optimization of the deposition parameters and refinement of related processes will further improve the RRR values observed for ECR Nb films deposited on Cu. RF measurement for corresponding Nb/Cu disk samples are also in progress.

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