SURFACE PREPARATION OF METALLIC SUBSTRATES FOR QUALITY SRF THIN FILMS*

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Abstract

Surface preparation is an essential prerequisite for thin film depositions. Rough or chemically impure surfaces adversely affect the nature of the thin film. Understanding the properties of the substrate and how they influence the quality of the thin film is necessary to transfer thin film deposition technologies to SRF cavity applications. A substrate that is flat, has sufficient grain size, and is chemically pure is the ideal starting point for thin film depositions. A method for copper substrate preparation is reviewed for niobium thin film deposition that provides epitaxy on large and fine grain copper as well as single crystal copper. Preliminary data on niobium substrate preparation will also be included.

INTRODUCTION

The deposition technique implemented in making a particular niobium (Nb) coated cavity in a vacuum system, as well as the specific nature of substrate, determine the resultant thin film quality. Determining the characteristics of a substrate that affect the coating process is an essential part of reliably creating a quality thin film. Characterizing what impurities may be in and on the substrate is necessary to avoid uncontrolled reactions and features. Particles, residues, and soils on the surface present alternative nucleation sites, disrupt the potential of the surface, and can be incorporated into the deposited thin film changing the film chemistry. Thin film process development must begin with substrate preparation and characterization. Inadequate substrate preparation can skew or randomly perturb process variable trending, increasing the difficulty of developing a reliable process with high yield. To be a competitive technology, the quality of Nb thin films on copper (Cu) SRF cavities needs to improve the benchmarks of bulk Nb cavities in cost structure and performance. For Nb coated SRF cavities to become practical, a suitable base cavity material must be demonstrated as a suitable thin film substrate.

Deposition of a material onto a surface is dictated by the structural and chemical aspects of the surface. The structure of the surface needs to compatible with SRF applications, dictating a surface with no protrusions or features[1] and general roughness of less than 50 nm.[2] From a thin film perspective, epitaxy requires substrates that are as smooth as economically possible, with an atomically flat surface being ideal although economically unfeasible in most applications. If a substrate is too rough, the thin film will most likely be a Zone 1 structure in the Thornton Zone Structure Model.[3] If the substrate is well prepared then the nucleation of the film can proceed in a coordinated manner yielding a high quality thin film.

METHODS AND MATERIALS

The Cu substrates prepared for this study were 99.999% OFHC (oxide free high conductivity) Cu. Fine and large grain Cu substrates were prepared for Nb depositions. The general process for preparing the fine grain substrates was mechanical polishing followed by electropolishing. Mechanical polishing was performed on a Buehler Ecomet 4 with an Automet 2 power head. The substrates were planed with 120 grit until uniformly scratched; followed by 320 grit, 400 grit, and then 600 grit SiC Carbimet 2 papers. At least two papers were used for each grit level with a thorough de-ionized (DI) water rinse and N_2 dry between every paper change. The Cu substrates were then finished with 3 micron polycrystalline diamond slurry on MicroCloths. The substrates were periodically rinsed with DI water and dried with N_2 to help reduce the embedded grit during the final polishing.

Substrates were ultrasonically cleaned for ~ 5 min then dried with filtered N_2 gun in acetone, then Micro90®, acetone, isopropyl, and finally methanol prior to electropolishing. The electropolishing setup consists of a square Cu cathode supported from the middle of a Teflon wheel. There are four positions for electropolishing with quick disconnect compression fittings to facilitate removal of the electropolished substrates. The Cu surface is very unforgiving once polished to an optical grade and can be easily damaged or contaminated. Once the substrates were mounted in the quick disconnect Teflon blocks and seated on the Teflon wheel with the cathode, the entire fixture was submersed into sulfamic acid (40 g/l) until most of the native oxide has been dissolved (~ 3 to 5 min). The samples were then rinsed in DI water and placed in the elctropolishing electrolyte, 45% H_3PO_4 / 55% n-Butynol. Fine grain Cu substrates mechanically polished were etched at a current density of 50 mA per cm^2 for approximately 1 minute. Electropolishing is utilized to remove any surface contamination, reduce the surface roughness, and remove any subsurface damage from mechanical polishing. The samples were quickly rinsed post-electropolishing and placed back into sulfamic

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acid. Samples were removed from the sulfamic bath, rinsed in DI water, followed by methanol, and then dried with filtered N_2. The Cu substrates are then immediately loaded in the coating chamber.

The large grain Cu substrates were processed from the fine grain electropolished Cu substrates by heat treatment and electropolishing. The heat treatment process causes recrystallization of the fine grain Cu. The fine grain substrates were vacuum heat treated at 1000 °C for 12 hours at $1x10^{-6}$ Torr in a ceramic Al_2O_3 enclosure. The recrystallization process roughens the surface and the oven deposited tungsten particles onto the substrates requiring another round of electropolishing to plane the samples and remove contamination. The last round of electropolishing occurred immediately before the samples were loaded in the ECR (electron cyclotron resonance) chamber. The goal was to minimize the time exposure to atmosphere and thickness of native oxide. The samples were pumped down to ~ $1x10^{-8}$ Torr and heated according to the ECR experimental protocol.

RESULTS

Substrates were produced as 50 mm disc and 10 × 20 mm^2 coupons. The metrology program implemented for substrate characterization included: Hirox® optical microscopy, Atomic Force Microscopy (AFM) with a Dimension 3100, and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX) and Electron Backscattered Electron Diffraction (EBSD).

The roughness of representative Cu and Nb surfaces was measured by AFM at all stages of the substrate preparation process. Scans were taken at 2×2 μm^2, 10×10 μm^2, and 50×50 μm^2 to gauge the roughness on length scales appropriate for Nb thin film epitaxy and SRF performance. Representative AFM and Hirox® images have been selected for the four stages of the process. The roughness and optical appearance for the various process steps is shown in Figure 1. The mechanically polished sample (Figure 1a) still has evident scratches from the polishing media, though it appears as a mirror by eye. After the first electropolishing (Figure 1b), Cu grains become evident with slight pitting. The thermal recrystallization process (Figure 1c) significantly roughened the surface and introduced particles that were disruptive to AFM scanning. The vertical displacement between grains and general roughness of the heat treated Cu cannot be considered for depositions. The final electropolishing removes foreign particles and leaves a smooth surface with large grains (Figure 1d). Further optimization of the electropolishing process is necessary to improve the smoothness of the substrates and reduce pitting.

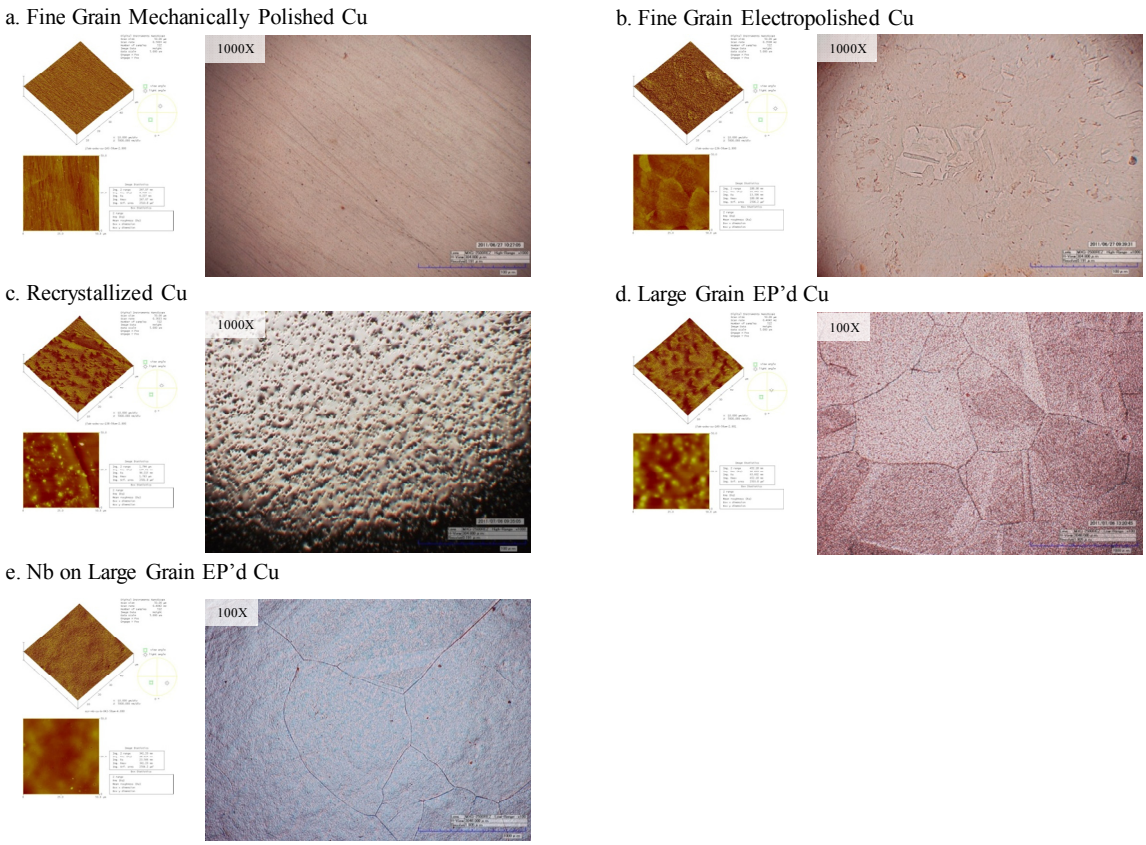

Figure 1: Representative AFM and Hirox images for the substrate preparation steps and ECR Nb on large grain Cu.

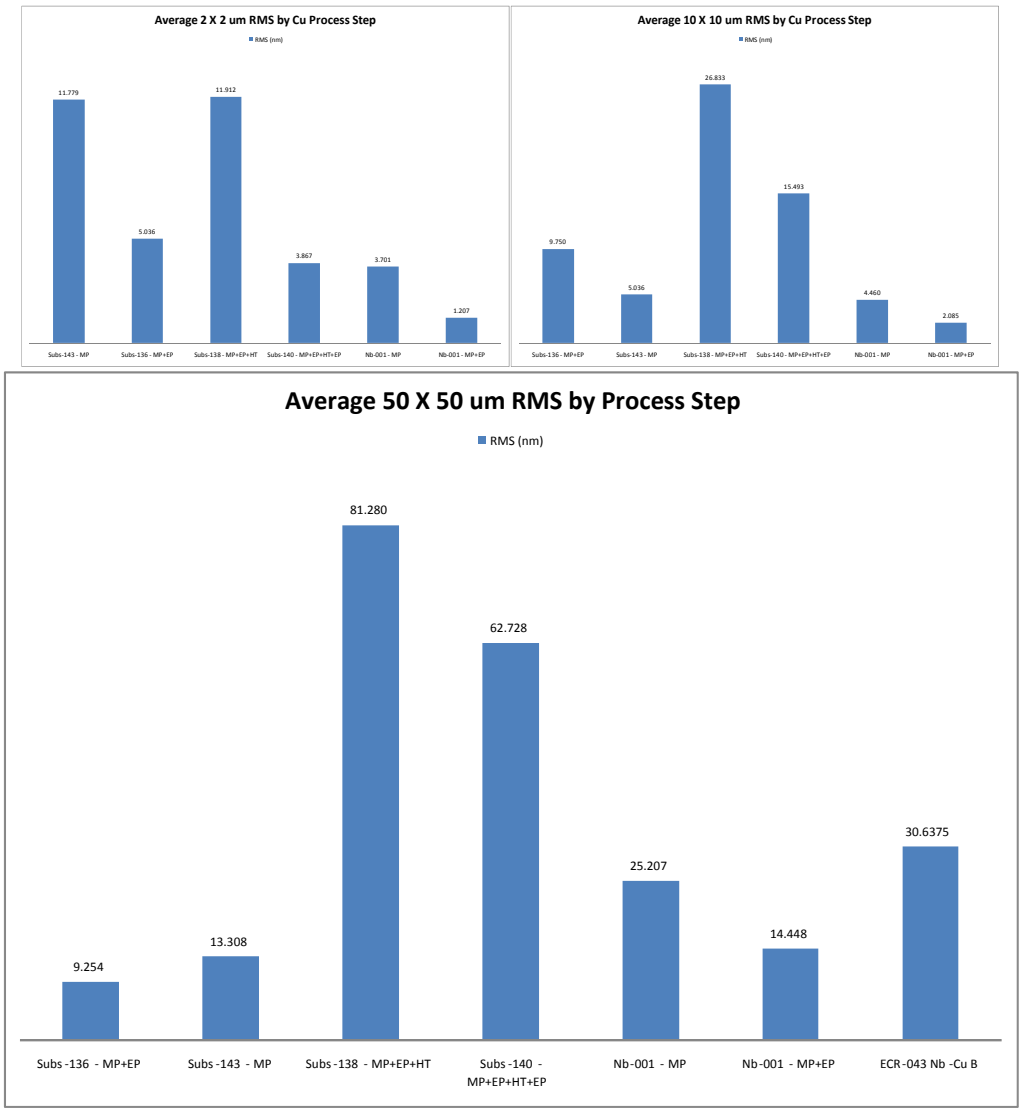

Figure 2: Average AFM RMS (nm) for Substrate Preparation Steps by Scan Area.

SEM investigation of the surface for non-conforming features, such as: pitting, particulates, and structural defects, revealed expected blemishes in the mechanically polished and thermally recrystallized surface. In the mechanically polished sample, a small amount of material was found that could be embedded 3 micron grit but most of the particulates examined by EDX were organic in nature. The thermal treatment of the Cu substrates decorated the surface with alumina and tungsten particles. The alumina particulates are speculated to arise from the alumina shields protecting the samples during thermal vacuum annealing. The tungsten likely originated from the heater elements or residual particulates in the oven. The average RMS per scan length size per process step is included in Figure 2. Although the mechanically polished sample has a very low RMS, it is an unsuitable substrate due to a lack of good long range crystallinity and roughness on a very fine length scale that would be deleterious to epitaxy.

The crystallinity of the surface is as important as the roughness when considering thin film epitaxy. Poor crystallization will lead to an incoherent condensation and poor resultant film quality. The substrates were also investigated with EBSD (Figure 3) to determine the crystalline quality of the surface. The mechanically polished surface had insufficient crystalline quality to be imaged by EBSD possibly due to the small grain size of the stock material and the structural damage induced during polishing. The mechanically polished then electropolished sample had marginal crystallinity. Heat treating the Cu had a large improvement in K-pattern quality and the final electropolish produced the best EBSD patterns of all presented process steps.

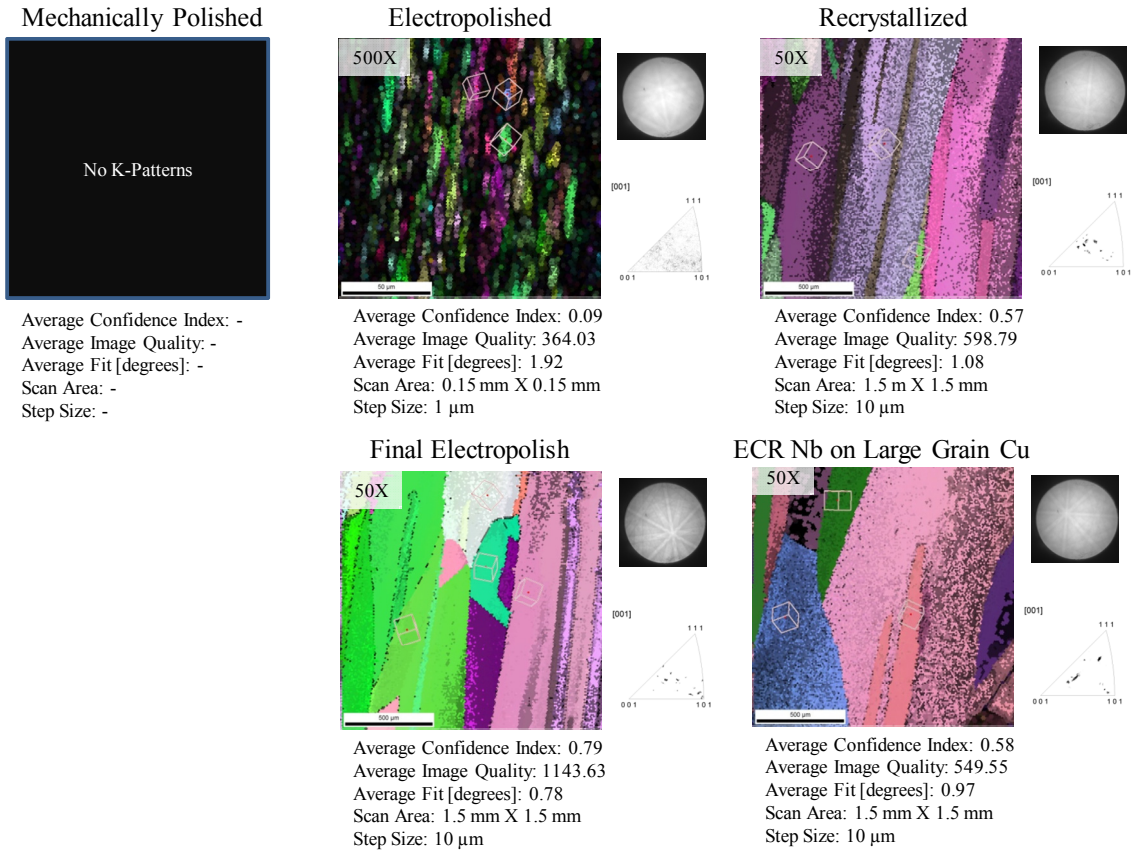

Figure 3: EBSD characterization of Cu substrates at each processing step and a typical ECR Nb deposition on the final electropolished surface (Maps cleaned up with neighbour CI correlation of 0.2%, represented by the dark pixels).

CONCLUSIONS

A method for producing high quality Cu substrates is presented. The final surface roughness is less than ideal but still supports epitaxy from ECR Nb depositions. Further refinement of the mechanical and electropolishing steps should produce lower RMS substrates. Potentiodynamic studies of Cu need to be investigated as a function of surface preparation, electrolyte, bath temperature, and degree of agitation during electropolishing. To further improve the reliability of the substrate's surface, a quartz box is being designed to better shield the samples during the recrystallization heat treatment. It will have baffles that will allow gas exchange between the oven and substrates local environment but condense low volatility species. Extensive work needs to be done on optimizing the Nb mechanical polishing method to produce substrates for homo-epitaxy.

Despite non-optimal features, the Cu substrates presented allow epitaxy of Nb. The suitability of the surface roughness and defect concentration in the context of SRF requirements needs to be investigated when the substrate optimization is established. The high degree of crystallinity in the final electropolished substrates seems to be the determining factor for good epitaxy. For other soft low melting temperature substrate materials, such as Al, the method presented for Cu should produce similar or better results. State of the art RRR values can be obtained on ECR deposited Nb films on Cu substrates prepared by reported method. [4]

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