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A NEW METHOD FOR GRAIN TEXTURE MANIPULATION IN POST-DEPOSITION NIOBIUM FILMS

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Abstract

Niobium films are frequently grown using forms of energetic condensation, with modest substrate temperatures to control grain structure. As an alternative, energetic deposition onto a cold substrate results in a dense amorphous film, with a much larger energy density than the re-crystallized state. Re-crystallization is then performed using a pulsed UV (HIPPO) laser, with minimal heating to the substrate. In addition, a graded interface between the substrate and Nb film can be created during the early stages of energetic deposition. Experimental approach and apparatus are described, and preliminary surface analyses are presented..

INTRODUCTION

As a result of the increased interest of high-energy particle accelerators, extensive research has been performed on the creation of superconducting (SC) accelerator cavity designs which exploit the application of thin films. Typical penetration depths of ~28 nm have encouraged decades of institutions to perfect the thin film formula, but have been met with disappointment with respect to cavities fabricated from bulk niobium [1,2].

The primary methods used to grow niobium films have been hetero-epitaxial growth, and fibrer growth, encouraged by careful elevated substrate temperature manipulation. In this work, a third method is explored, utilizing re-crystallization of an amorphous film. Specifically, niobium is sputtered onto a 77 K substrate as a thick (~1 um) amorphous layer. While not in the desired form, it is subsequently re-crystallized, using a localized thermal source (eg. 5 W UV laser), producing a bulk-like structure with larger grain size. The propensity of copper substrate diffusion into the Nb film is of concern, and mitigated by the 77 K substrate, as well as the short pulse and raster control of the laser. The objectives of this method include minimization of the substrate surface energy by cooling to 77 K (LN_2), maximizing the internal energy of the condensate (by minimizing diffusivity), carefully controlling film thickness during deposition, and precisely controlling temperature conditions during re-crystallization. Protecting the substrate from high temperatures during re-crystallization is important in order to preserve the graded interface, as well as to eventually minimize the diffusion of copper into the SC Nb film. Anticipated benefits of re-crystallization include simplistic deposition for manufacturability, grain texture*

manipulation (per precise heat source) for detailed studies, and maximizing the film-substrate adhesion by *ion stitching*.

ENERGETIC CONDENSATION

This process, known as energetic condensation, begins with a niobium plasma source, such as a cathodic arc, or high-power pulse power magnetron sputtering (HiPPMS), which provides a combination of neutral metal atoms, as well as ions [3]. While the kinetic energy of neutral metal atoms and ions is relatively low (~5-10 eV), the ionization potential energy of the Nb+ ions (~60 eV) is added to the kinetic energy, and deposited in the first few monolayers of the film. This results in large thermal spikes, and atomic displacement, characterized as *subplantation.* [4,5,6]. In addition, electron cyclotron resonance (ECR) has been used with good results, as well as a process known as coaxial energetic deposition (CED) [7]. Most recently, a technique known as modulated pulse-power magnetron sputtering (MPPMS) was introduced, which is similar to HiPPMS, but utilizes a train of shaped pulses, but with a lower operating voltage, to produce the ionic content [8].

MPPMS

The success of HiPPMS is, in part, due to the availability of high voltage/current insulated gate bipolar transistors (IGBT), which are capable of > 2000 V at 1000 A with a < 1% duty factor. However, this still represents sate of the art, and the modulators tend to be expensive ($100k), and rather inflexible. Alternately, MPPMS delivers a modest ~600 V pulse train, with up to 10% duty cycle, using moderately priced IGBTs ($1k), and also increasing the deposition rate. In the case of niobium, MPPMS has been compared to HiPPMS and DCMS, with respect to voltage, current, average power, and relative ion content [8]; while HiPPMS still retains the highest ion/neutral ratio, MPPMS is attractive for low-cost, extreme flexibility, and ability to be produced in most laboratories. Films exhibiting high density (especially during first monolayers), minimal fiber

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growth, and good uniformity are typical for MPPMS-produced films.

The JLAB MPPMS modulator design was based on a bipolar half-bridge, and, while capable of pulses of 1200 V at 1500 A (500 J), it was optimized for a 2-1/2" Aja DC magnetron, rated for 400 W of average power. Following the prescription of prior researchers, an initial 100 us pulse was followed by 750 us pulses, delivering ~6.4 kW (3 J) of peak macropulse power, with a 100 Hz repetition rate. Figure 1 is a photo of the modulator, and an oscillograph demonstrating the V-I characteristic of the magnetron, during deposition.
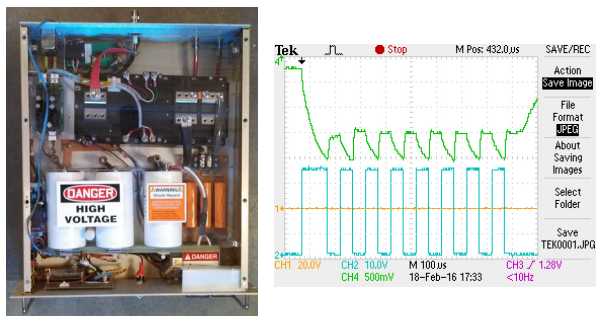

Figure 1: MPPMS modulator (left), and oscilloscope trace of a single MPPMS macropulse, for voltage (green, Volts) and gate drive (blue).

Deposition Chamber with LN₂ Substrate Holder

The chamber used for deposition is mostly constructed with off-the shelf components, except for the substrate holder and LN$_2$ container, which was completely customized. The container assembly contains a manual manipulator, to which is affixed a stainless steel crucible. LN$_2$ is put in to the crucible, externally, which provides the thermal ballast for the substrate (and subsequent laser processing). The manipulator allows the substrate to be rotated 90 degrees, thus facing a quartz window for laser access. Ceramic breaks in the manipulator/crucible assembly facilitate application of bias voltages, in the event additional charge is required to extract the plasma from the guide coil. It is also possible to create limited energetic ion bombardment, allowing the Nb atoms to bury themselves into the copper substrate. Presently, the base pressure for the system is ~10^{-9} Torr, and utilizes krypton as the sputtering gas, to optimize niobium ion yield.

LASER RE-CRYSTALLIZATION

While many options are available for obtaining re-crystallization temperatures (~1500 K for Nb), an industrial Nd-YAG laser, with 12 ns pulse period, 50 kHz repetition rate, and 355 nm wavelength (optimal absorbtivity for Nb) was employed, primarily due to availability, and, that it was used in prior annealing and surface-melt experiments (λ = 1064 nm), which provided a good starting point for sub-melt parameter determination [9]. As an expedient, the samples were processed on the laser table, with the output focused to a 100 um spot diameter, and raster-scanned over the film surface for a period of 15 minutes, ensuring full coverage. Educated trial and error provided convergence of ~300 mJ/cm^2 of fluence for inducing observable effects within the film, while fluences in excess of 500 mJ/cm^2 resulted in evaporation of he Nb. Analytical and static thermal models were consulted, which indicated a 90% spot overlap for the 12 ns pulses, or a scan rate of ~50 cm/s.

FILM ANALYSIS

Studies of the physical film properties were performed on the raw, as-deposited films, as well as laser processed films. Morphological analysis included X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron beam back-scatter diffraction (EBSD). Electrical residual resistance testing was also performed, mostly for the purpose of demonstrating SC transition, before and after heating.

XRD

XRD was used with good utility during the parametric search for optimal laser fluence. As more energy was applied to the samples, peak narrowing was observed, until a decrease in signal-to-noise was seen, indicating film destruction (and ultimately ablation). The raw film displayed a double-peak, which also seemed to converge at ~300 mJ/cm^2, strongly suggesting a significant change in film morphology. Nominal grain size (Scherrer method) for 300 mJ/cm^2 films was ~9 nm, compared to 4 nm for that of the raw film. Figure 2 compares several samples, processed with different fluences; as a comparison, XRD data for bulk Nb foil is also shown.
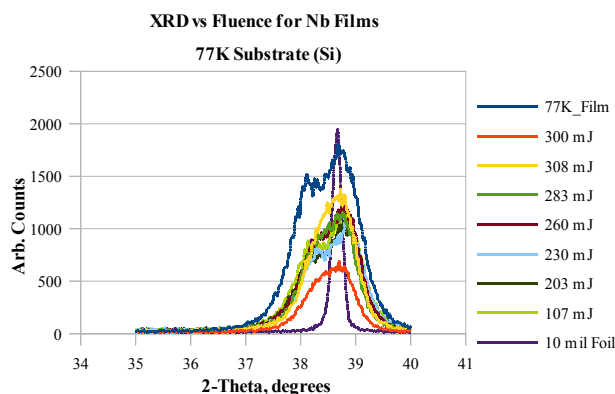

Figure 2: Bragg angle XRD data for raw and processed films, for various fluences. Double peaks resolve, and narrowing is seen for ~300 mJ/cm^2 films. Scherrer grain size doubled from 4 nm to 9 nm during processing. Bulk Nb foil is included as a comparison, as well as a fiducial.

SEM

Cross-sectional microscopy was performed on the samples, guided by the XRD data. Initial evaluation of the

raw film confirmed the expected density and amorphous composition of the cold Nb film. Minimal columnar growth is observed, and no voids were detected in any of the measured samples. No visible effects were present until ~300 mJ/cm^2 was delivered, at which point two distinct layers within the film emerge. An apparent thickening is also present, but not yet confirmed by other means. While possible grain coarsening is depicted in XRD, and possibly visibly apparent, EBSD analysis was unable to distinguish crystals > 100 nm, due to the resolving power of the SEM. Figure 3 shows a film before and after processing at 300 mJ/cm^2/pulse of fluence.
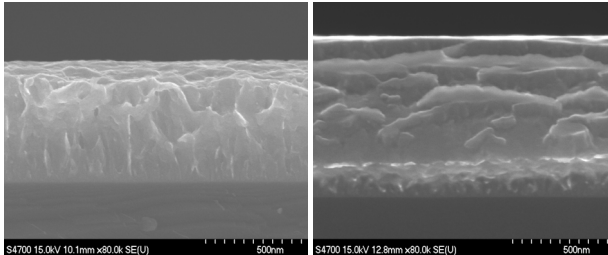

Figure 3: SEM comparison of raw film (left), processed with 300 mJ/cm2 of 355 nm laser light (right). XRD data indicates an increase from 4 nm to 9 nm average bulk grain size. Distinct layers and possible thickening suggest coarsening/recrystallization.

TEM

Transmission microscopy of the processed film also confirmed the high density with no voids, and extremely small grain size. Examination of the Si-Nb interface shows amorphous growth initiating from what is likely the oxide layer, forming crystallites. Polymorphic crystal structure also appears in the electron diffraction pattern, while retaining some preference to orientation, as shown in Figure 4.
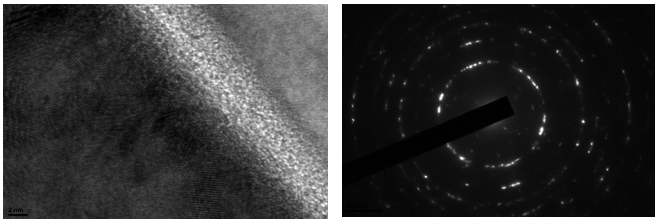

Figure 4: TEM of Nb-Si interface, showing high density with no voids. Electron diffraction pattern (right) has polymorphic features, indicating small grains.

SC Transition

Accurate prediction of RF performance under SC conditions remains elusive. However, the presence of a SC transition at DC is essential as a starting point for evaluation. Nevertheless, RRR provides an economical method for evaluating the basic electrical conductivity of the bulk. Here, it was used to validate the deposition process, and also verify that the SC properties of the films had not been destroyed by the laser heat processing. Narrow transitions were observed on all raw film

samples, as well as all processed samples < 500 mJ/cm^2. Average T_c before treatment was 9.4 K, while post-processed films showed 9.3 K average T_c. Figure 5 compares before and after transitions for a film receiving the 300 mJ/cm^2 dose.
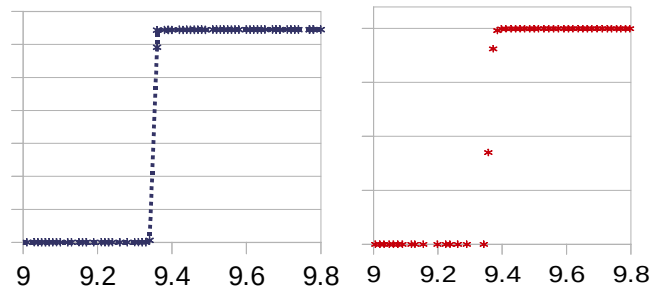

Figure 5: Electrical test data for raw (left) and processed (right) films, depicting the SC transition. T_c = 9.3 K is preserved, with a sharp transition. Units are degrees, Kelvin, and arbitrary resistance.

CONCLUSION

While much of this study is still in it's infancy, the results are very encouraging, and demonstrate the ability to increase grain size by re-crystallizing an amorphous film, containing internal energy. The reduced number of control parameters results in a simplistic process, adaptable to industrial process. MPPMS was successfully demonstrated as a method to produce dense, amorphous films, while the cold substrate results in a film with energy far from equilibrium, and able to drive subsequent grain growth. Finally, in situ heat treatment avoids the formation of oxide layers and provides a heat sink to protect the substrate from excessive heating. While it was hoped to obtain > 100 nm crystals, more parametric studies of fluence delivery are needed to promote the production of larger grains.

ACKNOWLEDGEMENT

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