HIGH-PERFORMANCE THIN-FILM NIOBIUM PRODUCED VIA CHEMICAL VAPOR DEPOSITION (CVD)*

R. Porter†, D. L. Hall, M. Liepe, and J. T. Maniscalco
Cornell Laboratory for Accelerator-Based Sciences and Education (CLASSE), Ithaca, NY, USA
V. Arrieta, S. McNeal, and B. Williams, Ultramet, Pacoima, CA, USA

Abstract

Bulk niobium cavities have been the standard for superconducting particle accelerators for many years. However, the cost of high RRR niobium start materials makes them expensive. The use of Chemical Vapor Deposition (CVD) processing technologies to produce thin Nb films on low-cost substrates (e.g. copper) offers a method to significantly reduce the cost of accelerator cavity fabrication while increasing cavity performance capabilities. Recent optimization of CVD niobium processes for high RRR Nb films has led to RF performance approaching that of bulk Nb. In collaboration with Ultramet, Cornell continues to explore the potential of CVD techniques. This paper presents results from a detailed study of CVD thin film Nb materials produced by Ultramet on 5-inch diameter copper and molybdenum substrates, including RF performance results with T-mapping and detailed surface analysis of performance limiting regions. Our work shows that CVD-based cavity fabrication methods are a promising alternative to sheet-formed bulk cavities, and to other thin Nb film techniques, warranting further development. Additional results from the field will be discussed.

INTRODUCTION

High RRR bulk niobium cavities have been used in accelerators for decades and are nearing their theoretical performance limits [1, 2]. The superconducting penetration depth is significantly less than 1 μm making it feasible to create a superconducting surface on accelerator cavities made from copper or other low-cost substrates via the application of a thin niobium film. A thin-film approach offers several advantages over traditional bulk niobium: Materials having thermal conductivities much higher than niobium, such as copper (75 W/m · K for niobium vs. $300 - 2000$ W/mv · K for copper), increase the thermal stability fo the cavity and decreases the sensitivity of the cavity to surface defects; copper is roughly one tenth the price of high RRR niobium sheet start materials, reducing the cost of manufacturing; thin films have been shown to have reduced flux trapping sensitivity (reduced by as much as 1%), reducing magnetic shielding requirements [3]; the techniques can avoid or substantially reduce the need for electron beam welding and mechanical manipulations such as pressing and rolling, re-

ducing cost and likelihood of inclusions; and if the produced thin film is of sufficient quality, mechanical and chemical polishing may be avoidable, though some techniques still require mechanical or chemical treatments.

Chemical Vapor Deposition is used in industry to produce free-standing niobium components, and thin and thick films of niobium on substrates. The CVD-based technique has advantages over other thin-film niobium techniques. CVD techniques can rapidly grow niobium films. Ultramet, through several decades of CVD process development routinely achieves deposition rates exceeding 300 μm/hr. The CVD process forms a robust metallurgical diffusion bond between the niobium coating and the substrate for optimal thermal contact and is compatible with high pressure rinsing and mechanical polishing (e.g. centrifugal barrel polish).

In this paper we will summarize previous work towards the adaption of CVD niobium processing for SRF applications, with particular focus on work done in the past year by Cornell University in collaboration with industry partner Ultramet. Much of the work discussed here has been previously published by Cornell University [4–6], Ultramet [7], and P. Pizzol et al. [8–10]. Although a CVD technique, we will not discuss Atomic Layer Deposition (ALD) in this work.

CHEMICAL VAPOR DEPOSITION

In the CVD process one or more precursor and reactant gasses/vapors are exposed to the substrate (in a chamber called the reactor) and either react or (thermally) decompose, leaving behind the coating material. A diagram of a reactor used can be seen in Fig. 1. There are a variety of compounds, temperatures, pressures, and configurations for coating various materials. A common process for coating niobium is to vaporize $NbCl_5$ (the precursor) in a bubbler, carry it into the reactor using a gas (such as argon) while simultaneously pumping in hydrogen gas (the reactant gas). The reaction: $2 NbCl_5 + 5 H_2 \rightarrow 2 Nb + 10 HCl$ takes place, leaving niobium on the substrate while the remaining gasses are pumped out of the reactor. The substrate is heated (to, say, 700 C) so that the reaction primarily takes place on the substrate. This technique is used by P. Pizzol et al. to produce niobium thin films [8].

SAMPLE STUDIES

Initial work between Cornell and Ultramet began in the early 2000's [4]. In 2005 Cornell tested a CVD niobium coating on a molybdenum puck provided by Ultramet (with no coating process information provided). This sample had a slightly suppressed T_c of 8.88 K versus 9.26 K for bulk
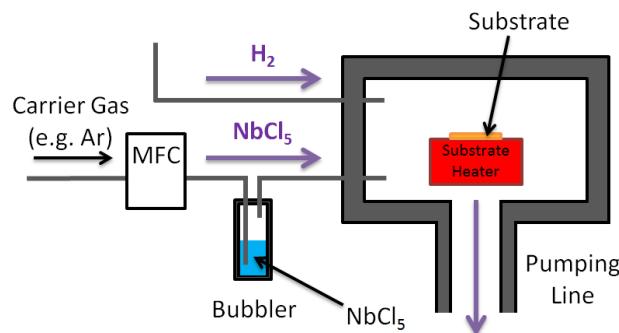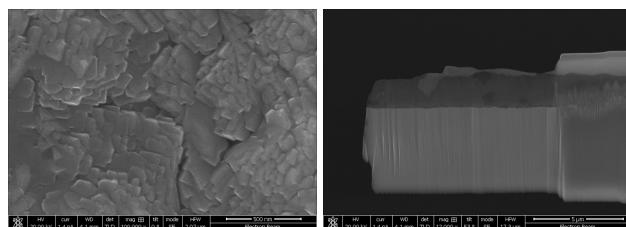
Figure 1: Diagram of the reactor utilizing $NbCl_5$ and H_2.

niobium, however, H_{c1} at 1.9 K was found to be identical to bulk niobium. The sample had significantly amounts of dissolved gasses, including 3 at. % hydrogen.

In 2012 Cornell measured the RRR and T_c of several CVD niobium samples created by Ultramet using different parameters in the CVD process (temperature, pressure, coating length, reactor design, etc.). Cornell's RRR tests and additional RRR measurements done at Oak Ridge National Laboratory found one sample with a RRR of 283 and several other high RRR samples [5, 7]. Critical temperature measurements at Cornell were also found to be in agreement with bulk niobium [5]. This showed that the CVD process can produce niobium with properties comparable to bulk niobium.

Chemical Vapor Deposition and Plasma Enhanced Chemical Vapor Deposition (PECVD) of niobium on copper has also been produce by P. Pizzol et al. [8, 9]. They have managed to produce uniform niobium layers (see Fig. 2) with low levels of contamination (< 1 at. % oxygen and carbon). They have found the x-ray diffraction pattern to be that of bulk niobium, achieved T_c consistent with niobium, and achieved RRR as high as 31.

(a) SEM of niobium film surface. (b) TEM section of niobium film.

Figure 2: Niobium CVD films produced by P. Pizzol et al. [8, 9].

FULL CAVITY

The success in creating high RRR CVD niobium, prompted Ultramet and Cornell University to create a 3 GHz elliptical cavity using only CVD niobium [5]. The cavity was formed on a low-cost graphite mandrel (see Fig. 3 A) treated with a sacrificial carbon-diffusion boundary layer developed by Ultramet. A two layer approach was used to

reduce the cost of manufacturing and resulted in a cavity that looked like typical bulk niobium cavities (see Fig. 3 D). First, a thin high RRR CVD niobium layer was deposited on the prepared mandrel. This surface was then smoothed using a CNC grinding operation, followed by a final, less costly and lower-grade RRR CVD niobium layer added for structural support. The final outer surface was then machined for wall uniformity and average wall thickness of 3 mm prior to removal of the mandrel.
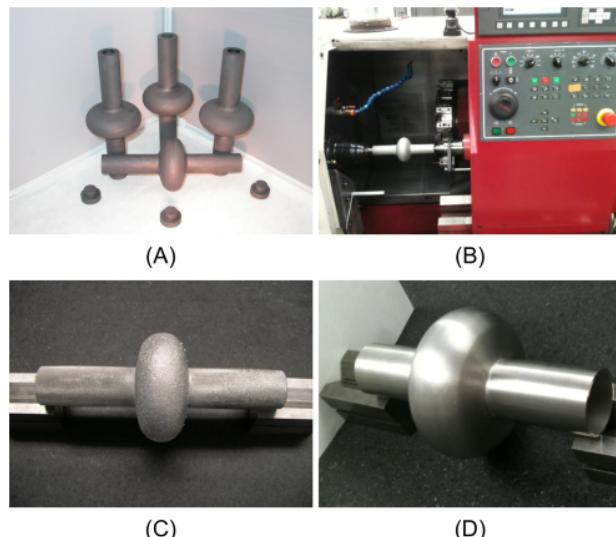

Figure 3: A. Graphite mandrel prototype machined using CNC methods. B. The mandrel immediately following application of the sacrificial interlayer metal. C. The cavity immediately after CVD. D. The completed cavity after removal of the mandrel and exterior finish. Figure originally from [5].

Cornell electron beam welded two reactor grade niobium flanges to the cavity. The cavity received a 4 day Ultra-High Vacuum bake at 700 C, a 3 hour UHV bake at 210 C, a total of 25 μm of buffered chemical polish (Ultramet expected all contaminants to be confined within 20 μm of the mandrel based on previous work), and a high pressure rinse.

RF Measurements

Initial RF testing can be seen in Fig. 4. The quality factor was around $2 \cdot 10^7$ and the surface resistance was dominated by a residual resistance of 14 μΩ, much higher than the <10 nΩ expected for bulk niobium. The high residual resistance suggests the presence of surface defects, poor superconductivity, or normal conducting defects.

In order to remove surface contaminants a 100 μm buffered chemical polish was performed and the cavity was tested again. This lowered the residual resistance to 650 nΩ and improved cavity performance, reaching a Q of $4.45 \cdot 10^8$ at 1.5 K (see Fig. 5).The BCS-resistance at 4.2 K was found to be 2.9 μΩ, in good agreement with the expected BCS-resistance of 2.5 μΩ for bulk niobium at 4.2 K and 3 GHz.
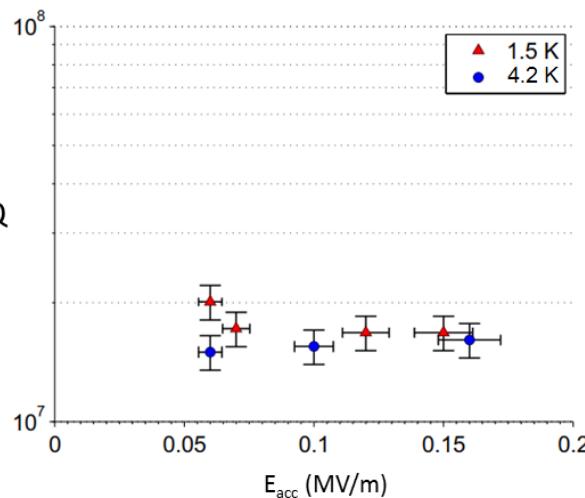
Figure 4: Initial RF testing results of a CVD 3 GHz. The test was limited to 0.2 MV/m due to poor coupling to the cavity.
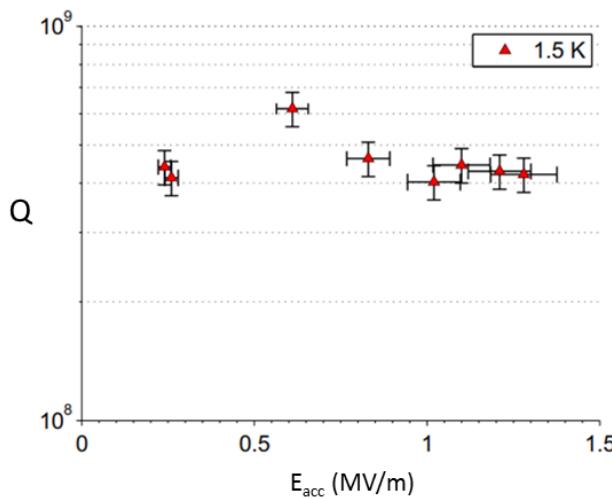

Figure 5: RF testing results of a CVD 3 GHz after a 100 μΩ buffered chemical polish. The test was limited to 1.3 MV/m by cavity quench.

The high residual resistance has two likely causes. The mandrel may not have been sufficient outgassed before the coating process, resulting in gasses migrating into the surface layer. This is supported by the final cavity RF surface having a short electron mean free path (low RRR). In addition to this, the CNC grinding step that was applied to the high RRR niobium may have imbedded contaminants into the surface. In this case, etching the surface would have revealed more hidden defects. In future cavity build efforts it will be critical to minimize both of these issues.

Optical Inspection

The cavity test was limited to 1.3 MV/m by cavity quench. Optical inspection revealed numerous pits and defects on a narrow band of the surface. These were as large as 200 μm

across and 50 – 100 μm deep. It was surmised that these defects formed due to locating errors during the machining of the first high RRR layer deposited on the mandrel causing thin or bare areas in the high RRR niobium film prior to the final coating. Additional etching could have then exaggerated these pits. This is supported by the defects being localized to a narrow band on the cavity wall, and likely all produced during the same machining step.

SAMPLE PLATES

In 2016, under DOE funding, further testing of Ultramet CVD niobium was conducted by Cornell to validate the high RRR CVD niobium process and to develop a lower temperature CVD niobium process compatible with copper substrates. 5-inch diameter test plates were produced for testing in the Cornell Sample Host Cavity (see Fig. 6) [11–15], a TE mode 3.9 GHz mushroom type cavity featuring a 5-inch removable "sample plate." This cavity attains fairly uniform magnetic fields over the sample plate and can achieve a quality factor of 1×10^{10} at 2 K with a good niobium plate. The cavity is equipped with a temperature mapping system attached to the back of the sample plate to locate areas of increased heating. Increased heating suggests areas with increased surface resistance, typical for chemical or morphological defects.

Figure 6: The Cornell Sample Host Cavity. The sample plate is at the top of the cavity with a temperature mapping system attached to it.

The plates tested (see Fig. 7) included a mix of copper and molybdenum substrates, coated using a mix of low (< 500 C) and high (> 500 C) temperature CVD processes, some including a niobium diffusion step before CVD (see Table 1). The specifics of the coating process were not provided (temperatures, chemicals, pressures, etc.). Some plates also received mechanical polishing.

RF Measurements

Figure 8 shows the compiled results of RF testing at 2 K for the Ultramet specimens. Two plates underwent testing

Table 1: Summary of CVD Niobium Sample Plates

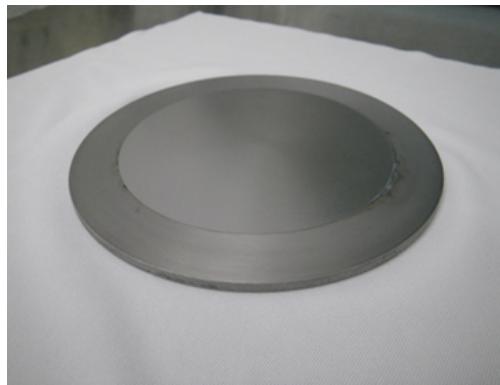| Sample	Substrate	Treatment
PN2	Molybdenum	High-temperature CVD, mechanical polishing
PN4	Molybdenum	Low-temperature CVD 5 µm EP for second test
PN6-Cu	Copper	Low-temperature CVD, mechanical polishing, 5 µm EP
PN7-Cu	Copper	Nb diffusion coating, Low-temperature CVD, 5 µm EP
PN11-Cu	Copper	Low-temperature CVD, mechanical polishing, 5 µm EP
PN4-Cu	Copper	Nb diffusion coating, Low-temperature CVD, coating removed by EP
PN8-Cu	Copper	Nb diffusion coating, Low-temperature CVD, coating removed by EP

Figure 7: A picture of a CVD Niobium plate after receiving an electropolish.

at 1.6 K and showed that the BCS resistance at 2 K in the 100 nΩ to 300 nΩ range, and each were flat with respect to field strength (within statistical errors).

The plate that performed the best was PN2, a high temperature CVD Nb on Mo plate, achieving an R_{BCS} of ≈330 nΩ at 2 K and low magnetic fields–somewhat above the expectation for the BCS resistance (≈110 nΩ). At low magnetic fields the residual resistance is ≈20 nΩ, approaching the residual resistance range of good bulk niobium plates (<10 nΩ), but rises to ≈500 nΩ at 50 mT where it quenches.

The rest of the plates tested had significantly higher residual resistance, ranging from 200 nΩ up to 50 µΩ. To try to improve performance, some of the plates received electropolishing intended to remove 5 µm of material. Unfortunately, this completely removed the niobium film from two of the samples, showing that the coating thickness was substantially less than the nominal thickness. For the surviving sample plate the resistance was not statistically significantly reduced (see Fig. 8).

Microscopy

Thermometry used during RF testing revealed general global heating of the plates, as well as "hot spots". This indicates a high surface resistance, and some localized defects. We cut coupons out of one of the plates at these "hot spots" and performed surface analysis using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

(a) Total surface resistance.
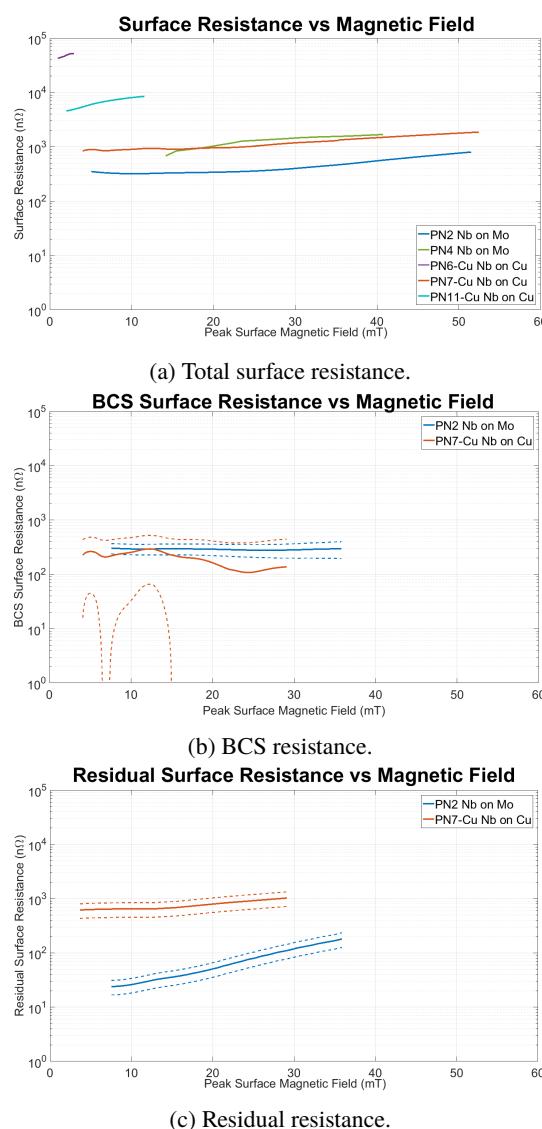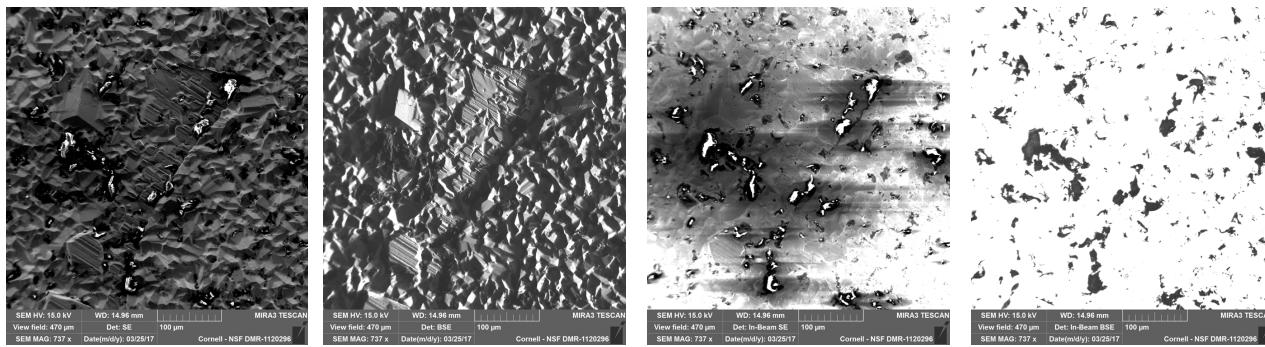

(b) BCS resistance.

(c) Residual resistance.

Figure 8: BCS, residual, and total surface resistances at 3.9 GHz and 2 K versus magnetic field for various sample plates and treatments. 50 mT corresponds to 12 MV/m in a TESLA style cavity. The error bars were calculated by assuming the error in the total surface resistance after removing the effect of the host cavity was 20%; actual errors may be higher.

(a) Secondary electron image.

(b) Back-scattered electron image.

(c) In-beam secondary electron image.

(d) In-beam back-scattered electron image.

Figure 9: Scanning electron microscope mages of samples cut from plate PN11-Cu, a niobium on copper plate that received mechanical polishing. In-beam images highlight chemical defects, while off-beam images highlight morphological defects. The SEM in-beam back-scattered image (d) highlights niobium in white and chemical defects in black, showing numerous chemical defects.

Figure 9 shows SEM scans of both morphological and chemical defects found on plate PN11-Cu, a low temperature CVD niobium on copper plate that received mechanical polishing. These are typical of the defects that were found at various "hot spots" on the plate, with numerous chemical defects located across the plates.

EDX of the chemical defects revealed they were comprised primarily of carbon, oxygen, niobium (≈ 2 at.%), as well as traces of several alkalis and alkaline earth metals. Ultramet suspects these chemical defects are caused by CVD reactor condensates forming on cold surfaces overhanging the plate, then falling onto the sample during deposition. Fortunately, this would not be a concern when coating cavity geometries as the shape will prevent any condensates from dripping onto the RF surface.

The milled coupons showed that the niobium films had very strong adhesion to the substrate. Figure 10 shows a cross-section of a CVD niobium on copper sample milled out of one of the test plates. Milling lines are present on the side of the sample, but the niobium has remained strongly bonded to the copper substrate. Also shown is an EDX line scan showing copper and niobium signals. This scan shows that there is a fast transition from the copper substrate to the niobium film (5 - 10 μm), indicating little diffusion of copper into the niobium.

Sources of High Residual Resistance

Surface defects are among several potential factors contributing to the high residual resistance observed in the tested samples. An electropolishing intended to remove 5 μm of surface material did not significantly improve the measured performance of the plate, but it is possible that the defects were thicker than 5 μm (there is no information on the thickness of the defects, but many were on the order of 10 μm wide) and electropolishing was ineffective for removing the surface defects remaining, or the etching could have revealed additional defects.

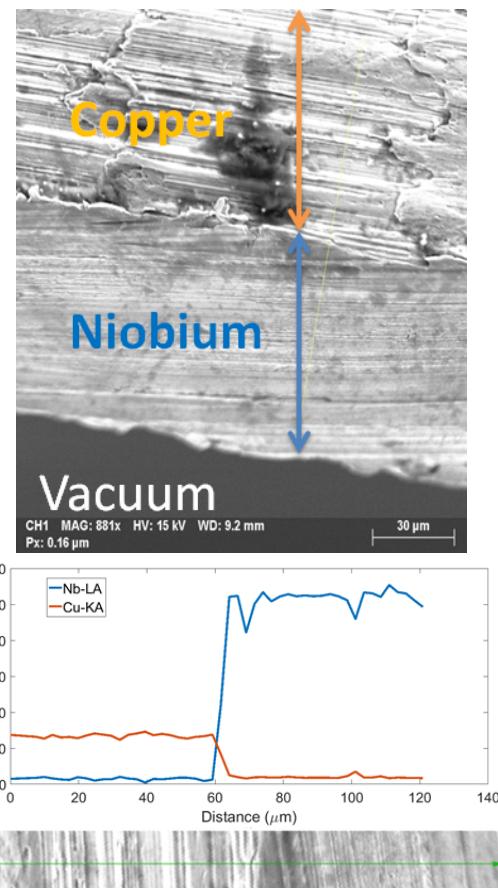Additionally, Glow Discharge Mass Spectrometry (GDMS) of some CVD niobium on copper plates has found

Figure 10: Top: Scanning electron microscope image of cross-section of a 60 μm CVD niobium film on a copper substrate. Bottom: An EDX line through the cross-section showing both niobium and copper content. The magnitudes of the two line should be considered separately.

200-400 ppm copper on the surface. This may be negatively impacting the performance of the copper substrate plates, which performed worse than the molybdenum substrate plates overall. However, it is not clear how low levels of copper would impact the performance.

It is also possible that these CVD niobium plates were suffering from Q-disease. Some CVD techniques, including the common $NbCl_5$ process, use or produce hydrogen gas. In these processes the newly formed niobium is essentially baked in hydrogen at a high temperature. Ultramet samples previously tested by Cornell in 2005 showed high concentrations of hydrogen (3 at. %) [4]. The current sample plates were not analyzed for hydrogen content or degassed in a vacuum furnace.

The samples here were tested as provided to see if additional post treatment is required after the CVD process. In the future, further precautions will need to be taken with CVD production to avoid contaminants and more post treatments may be necessary (e.g. chemical polishing, ultrahigh vacuum furnace degassing).

BEYOND NIOBIUM

In addition to niobium, there is research into CVD processing of other niobium based materials. P. Pizzol et al. have produced CVD NbN and NbTiN [9, 10]. The niobium nitride was produced by replacing hydrogen in the $NbCl_5$ process with NH_3, and NbTiN by further adding a second precursor, $TiCl_4$, to the reaction and carefully controlling the flow rates. Uniform layers of both materials were observed (see Fig. 11 and 12), as were the correct x-ray diffraction peaks for cubic phase NbN and NbTiN2.
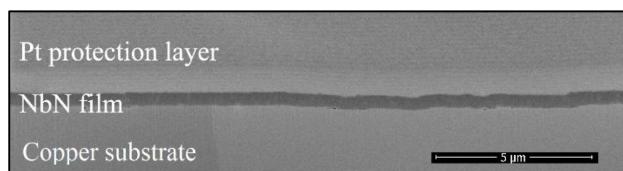

Figure 11: SEM of a section of a CVD NbN film produced by P. Pizzol et al. [10].
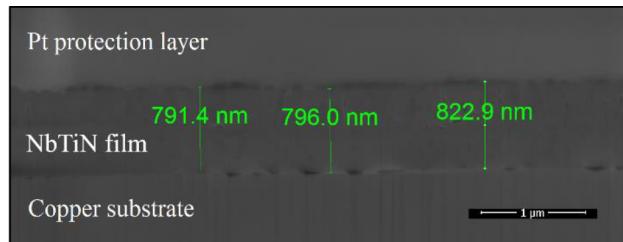

Figure 12: SEM of a section of a CVD NbTiN film produced by P. Pizzol et al. [10].

In this conference P. Pizzol et al. will also present results on CVD of Nb_3Sn and Nb_3Ge [16].

CONCLUSION

Chemical vapor deposition processing has been demonstrated to produce high RRR niobium, similar to what has been achieved with current sputtered niobium techniques. The CVD coating process forms strong coating-to-substrate bonds with good thermal contact on both copper and molybdenum and can be applied to complex structures such as cavity geometry. Furthermore, CVD techniques show promise in being extended to other SRF-relevant material coatings.

Recent CVD niobium samples have performed well and results suggest current high residual resistances are an effect of process rather than a fundamental limitation. Further CVD process and reactor design optimization are needed to reduce the risk of in-process niobium contamination necessary to reduce the residual resistance of the final niobium surface. Even with the current residual resistances observed, the best performing sample plate tested would achieve a Q of $4.5 \cdot 10^9$ at 2 K (and low field) for a 1.3 GHz TESLA cavity (ignoring any frequency dependence of the residual resistance), a similar quality factor to some employed sputtered niobium cavities.

Current results are very promising and we strongly encourage further research and development efforts.

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