

DEVELOPMENT OF A PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION SYSTEM FOR HIGH-PERFORMANCE SRF CAVITIES*

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Abstract

Next-generation, thin-film surfaces employing Nb₃Sn, NbN, NbTiN, or other compound superconductors are essential for reaching enhanced RF performance levels in SRF cavities. However, optimized, advanced deposition processes are required to enable high-quality films of such materials on large and complex-shaped cavities. For this purpose, Cornell University is developing a plasma-enhanced chemical vapor deposition (CVD) system that facilitates coating on complicated geometries with a high deposition rate. This system is based on a high-temperature tube furnace with a high-vacuum, gas, and precursor delivery system, and uses plasma to significantly reduce the required processing temperature and promote precursor decomposition. Here we present an update on the development of this system, including final system design, safety considerations, assembly, and commissioning.

INTRODUCTION

Niobium-3 tin (Nb₃Sn) is the most promising alternative material to niobium for next-generation SRF accelerator cavities. The material has the potential to double accelerating gradients and operating temperature of SRF cavities, decreasing costs and increasing efficiency of future accelerators, [1–5]. The dominant process currently used at Cornell University and elsewhere to grow Nb₃Sn films is based on vaporizing tin in a vacuum furnace and allowing the tin to diffuse to the surface of a Nb substrate cavity to form Nb₃Sn. The vapor diffusion growth process creates films of good quality, and there have been major improvements recently [4], leading to quench fields of up to 24 MV/m. Defects and surface roughness have been to hinder the performance of these films well below the ultimate potential of this material [3] and the improved vapor diffusion process in Refs. [4, 6] tries to address these concerns. Exploring alternative Nb₃Sn growth methods is important as some offer more control over the growth process and allow for more flexibility in the growth mechanism. Superconductors like Nb₃Sn, NbN, NbTiN, or depositing a thin film such as Zr in Ref. [7] could lead to superior RF performance levels in SRF cavities. Growing very thin films or compound superconductors will require advanced deposition processes to achieve high-quality, uniform films of such materials on large and complex shaped cavity surfaces. Remote Plasma-Enhanced Chemical Vapor Deposition (RPECVD) is a vacuum deposition method that allows for the deposition of a broad range

of materials with good uniformity even on complex shapes, see Fig. 1.3 in Ref. [8]. The remote part of RPECVD refers to the fact that the plasma generation region and the area of the reactor where the substrate is located are spatially separated [9]. This leads to better performance compared to having both the substrate and the plasma generation in the same region. PECVD uses various chemical precursors to deposit films and plasma reduces the temperature at which the deposition can take place. Furthermore, plasma can help with reducing contamination and with depositing a film on more temperature sensitive substrates, such as copper cavities that have a lower melting point. A broad range of chemical precursors allows for exploration of many materials under diverse growth conditions. The initial work to develop a dedicated cavity CVD system at Cornell can be found in Refs. [10, 11]. The design evolved from the initial stages and we will present here the current status.

REMOTE PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION (RPECVD) SYSTEM

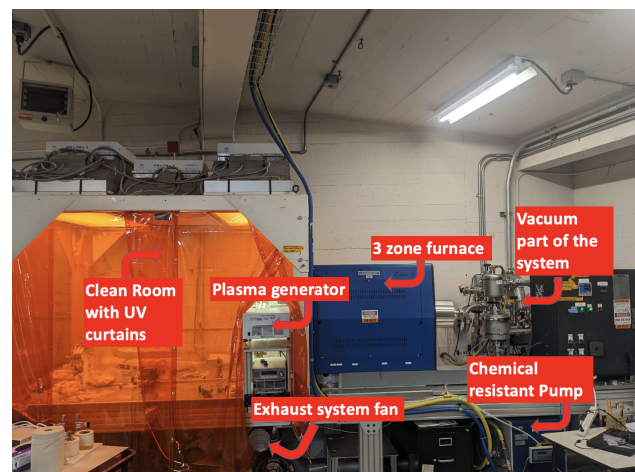


Figure 1: Overview of CVD system.

Figure 1 shows an overview for part of the CVD system and Fig. 2 shows the schematic for the whole system.

The precursor and gas delivery part of our system that are currently being installed are shown in Fig. 2. We use UHP gasses (Ar and Ar/H₂ mixtures) that carry the precursors from the bubblers to the reaction chamber. The H₂ gas plays a role in the reaction while Ar as an inert gas carries the precursors and forms the plasma. The solenoid pneumatic valves are designed to close as a protective measure in case the quartz tube breaks and the precursors are exposed to air.

* This work was supported by the U.S. National Science Foundation under Award PHY-1549132, the Center for Bright Beams.

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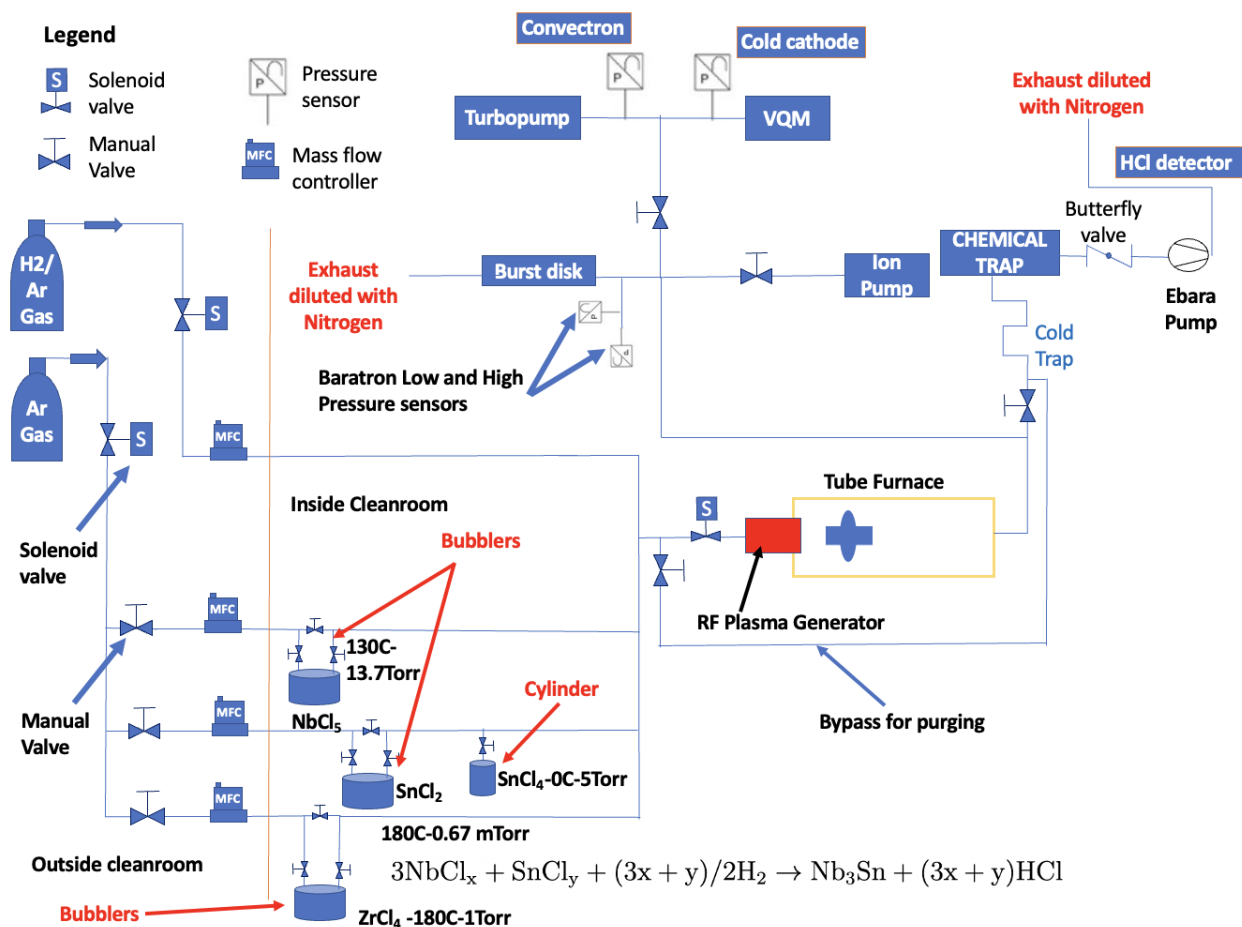


Figure 2: Schematic for CVD system including gas delivery and vacuum parts. The precursor species and their vapor pressure at a specific temperature as shown in the picture. A chemical reaction is shown for using both Nb and Sn precursors to deposit Nb₃Sn.

The valves automatically shut if they detect pressure close to atmosphere to prevent any release of corrosive gasses. The mass flow controllers control the amount of precursors delivered to the coating chamber and are controlled using a cDAQ system. The bubblers are made of hastelloy that is resistant to corrosion from the precursor materials. Each bubbler will be brought to a temperature that ensures a high enough vapor pressure for an effective deposition. There is a bypass valve that allows for purging the gas and precursor part of the system while avoiding the main deposition chamber.

The tube furnace/deposition chamber part of the setup is seen clearly in Fig. 1. A loading system will be installed in the clean room to allow for clean loading and unloading of the furnace. Since the last update, a plasma generator was installed alongside UV and RF protection. UV protection curtains were added to the clean room and metal meshes were added to protect from RF radiation. The 3 zone furnace contains a quartz tube that can be heated up to 1070 °C without risking Si contamination [12].

The flow regime in the system is important in determining the uniformity of the deposited film on a complex cavity shape. The Knusenden number is a measure used to deter-

mine the flow regime inside a CVD reactor $K_n = \frac{\lambda}{D}$, where D is a typical dimension of the reaction chamber, and λ is the mean free path for the molecules inside. If we run the CVD system at $T=500\text{ }^\circ\text{C}$ and $p=1\text{ Torr}$ we obtain a $K_n = 0.0006$. A small Knudsen number $K_n < 0.01$ means that the system is described well by the Navier–Stokes equations and that the flow will be continuous [9]. We are currently working on creating a simulation in Ansys to model the deposition and the diffusion of precursors in the system. The goal of this is to determine the parameter space for growing a uniform film on a 2.6 GHz cavity. On the right side of the furnace, Figs. 1 and 3 show the turbopump and the ionpump used for high vacuum annealing. The Vacuum Quality Monitor (VQM) and turbopump/ionpump are used for high temperature annealing in good vacuum ($\approx 10^{-7}\text{ Torr}$), for leak checking the system and for monitoring residual contamination. The chemical resistant pump is used to obtain a low vacuum during CVD. A butterfly valve is used to control the pressure inside the deposition chamber. A cold trap and a chemical trap have been added to capture the corrosive products and protect the chemical resistant pump. The exhaust of the pump is diluted with air and a HCl gas detector is used in the exhaust to monitor the safety of the gases exhausted outside.

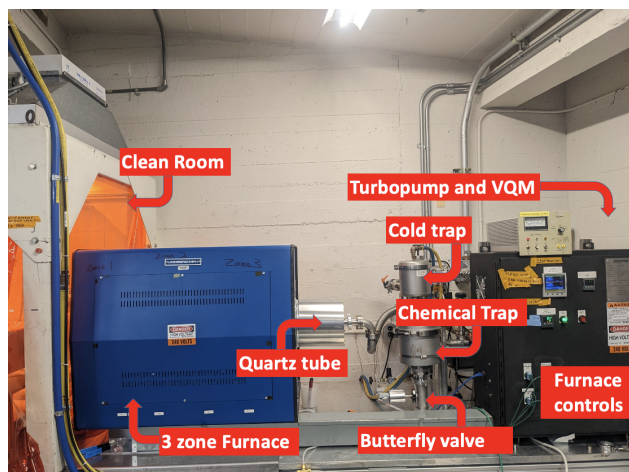


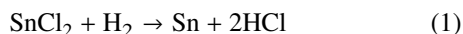
Figure 3: Pumpside section of tube furnace system and furnace controls.

PRECURSOR SELECTION

There are different methods for growing Nb₃Sn films using CVD. One way is to deposit Sn on a Nb substrate using a Sn precursor. Annealing the Sn layer at temperatures above 950 °C [3] can lead to Nb₃Sn with the desired 3 to 1 ratio. This is similar to the electrochemical Nb₃Sn coating process that was recently developed at Cornell [13].

Another way is to deposit Nb₃Sn layer by layer on a substrate as is detailed in Ref. [14], where both Sn and Nb precursors are used at a high temperature (825-850 °C). Deposition of Sn followed by annealing at high temperatures has the advantage that the high temperature bake can be done at a high vacuum $\approx 10^{-7}$ Torr, also ensured correct stoichiometry, and promotes grain crystallization and growth.

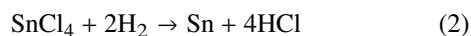
For the deposition of Sn on a Nb surface we are interested in halides and organometallic precursors. SnCl₂ and SnCl₄ are two halides that could be used in depositing Sn. For a less volatile precursor like SnCl₂ [15], at 200 °C, the vapor pressure is around 1.16 Pa \approx 9 mTorr. The deposition reaction in broad terms is described in Ref. [16] and a modified version is:



This reaction may not produce a good film due to the low vapor pressure of the precursor. There is evidence as described in Ref. [4] that growing a thin uniform film might require a high vapor pressure for the precursor. This seems to help with reducing the formation of anomalously large thin grains.

Thus, using a more volatile precursor like SnCl₄ might be preferable. SnCl₄ has a vapor pressure of 5 Torr at 0 °C [17].

The precursor combination of SnCl₄ and H₂ is mentioned in literature, [8], and a modified version of the equation found in Ref. [14] is:



Another option is to use an Organo-metallic precursor like ((C₂H₅)₄Sn) as detailed in Ref. [18]. Organometallics have

the advantage of allowing for deposition at low temperatures, T=350 °C as detailed in the paper, but present the additional problem of carbon incorporation. Some organometallic precursors bring additional safety concerns, e.g., high toxicity and ignition on contact with air.

IMPORTANT CONSIDERATIONS

Contamination Discussion

A fundamental problems we will have to address is silicon contamination from the quartz tube, as this was observed when initially trying to grow Nb₃Sn films [12] by Siemens. These contamination issues lead to using a Nb furnace insert for the vapor diffusion based Nb₃Sn growth process.

The main problem seems to be the devitrification of quartz and silica glass [19] in the presence of some impurities on the quartz, like Sn. Other reducing or oxidizing agents can speed up this devitrification process. This represents a transition from a metastable (vitrified) state to a stable crystallized state of cristobalite. A solution has been found for other high temperature CVD systems as described in Ref. [19]. The use of a quartz tube with an internal coaxial alumina screen tube and a tantalum sample holder (or other refractory materials) eliminates silicone contamination. In our system, we use a molybdenum boat to hold the cavity and samples. Using a loading system is important in preventing the Mo boat from scratching the quartz surface and leading to Si contamination.

Corrosion Mitigation

The hallides we plan to use as precursors are corrosive so the system needs to be robust for corrosion. The bubblers are made of corrosive resistant hastelloy and the rest of the delivery system is made of stainless steel and designed to keep humidity out of the system and prevent corrosion.

GOAL FOR NIOBIUM-3 Sn GROWTH ON COUPONS

We will use methods similar to the ones used by Zeming Sun in Ref. [13, 20] to determine the quality of Sn films. SEM and EDS can be used to check for SiO₂ impurities and to ensure Sn was deposited and there are no major impurities. XPS and EDS can give information about the initial Sn film. For the Sn film uniformity and roughness AFM measurements will be used to guide the recipe.

For the annealing stage we will heat up the substrate to temperatures higher than 950 °C to form stoichiometric Nb₃Sn. We can also do bakes at high temperatures and good vacuum to modify the oxide on the Nb substrate before Sn deposition.

PLANS FOR SCALING TO CAVITY

We are using Ansys to understand the flow to the surface of the cavity and the conditions for obtaining a uniform coating. More accurate results can be obtained by using a dummy 2.6 GHz cavity. We can cut holes and attach samples to the surface of the cavity to measure coating uniformity

and the levels of contamination using SIMS/EDX as done in Ref. [4].

Our plan is to start out with samples to optimize the CVD process. Then we will use the cavity with samples attached to it to ensure uniform coating on the inside surface of a cavity and adjust the CVD process as needed. The final step will be to coat 2.6 GHz cavities with a Nb substrate and test their RF performance.

CONCLUSION

Chemical vapor deposition is a very versatile method of depositing high quality films that has had great success in the semiconductor industry and in material science. Developing the same technique in the field of superconductors is the next technological and scientific step for obtaining better materials for SRF applications. It requires an understanding of the recent efforts towards improved material growth for vapor diffused Nb₃Sn and the many advances in the broader field of Chemical Vapor Deposition. CVD allows for much more controlled material growth and a broader range of precursors and growth conditions compared to vapor diffusion. Careful and thorough imaging of the produced Nb₃Sn film coupons will allow for fine-tuning of the growth parameter space. The next challenge after good sample results is scaling the process to 2.6 GHz cavities and obtaining a good uniform film. This can lead to a much better understanding of the growth process of Nb₃Sn and ultimately improved SRF cavity performance.

ACKNOWLEDGEMENTS

G.G. would like to thank Z. S. for the initial conceptual design of the CVD system, for ordering much of the initial equipment, supervising its installation and initial runs and helping G.G. understand the challenges and possibilities for this system when he started working on the project.

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