

# CVD DEPOSITION OF Nb BASED MATERIALS FOR SRF CAVITIES

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## Abstract

Bulk niobium cavities are widely employed in particle accelerators to create high accelerating gradient despite their high material and operation cost. Advancements in technology have taken bulk niobium close to its theoretical operational limits, pushing the research to explore novel materials, such as niobium based alloys.

Nitrides of niobium offer such an alternative, exhibiting a higher Tc compared to bulk niobium. Replacing then the niobium with a material with better thermal conductivity, such as copper, coated with thin films of nitrides in a multilayer S-I-S would lead to improved performance at reduced cost. Physical vapour deposition (PVD) is currently used to produce these coatings, but it suffers from lack of conformity. This issue can be resolved by using chemical vapour deposition (CVD), which is able to produce high quality coatings over surfaces with a high aspect ratio. This project explores the use of CVD techniques to deposit NbN thin films starting from their chlorinated precursors. The samples obtained are characterized via SEM, FIB, XRD, and EDX.

## INTRODUCTION

Superconductive niobium cavities are used in particle accelerators to provide the gradient required to accelerate the desired particles via RF energy with low losses. The physical limits of bulk niobium have been though reached, exploiting the material to its maximum potential [1]. Since the penetration depth of the SRF amounts to less than 1 micron on the inner surface of the cavities, it could theoretically be possible to obtain the same properties of niobium bulk with niobium thin films [2]. The financial gains in using thin films over bulk niobium are considerable: firstly less material is being used and secondly, high thermal conductivity materials such as copper can be used as substrate for the deposited thin film, making it easier to cool and maintain the low temperatures than with bulk superconductors, since SRF cavities operate at temperatures below 10 K [3]. Theoretical studies by A. Gurevich [4] have suggested that the use of Superconductor/Insulator/Superconductor thin films (S-I-S) can lead to an increase in the accelerating gradient, surpassing the limits of bulk niobium. CVD is a chemically driven technique [5] that can coat with high quality films large areas of complex geometry, such as cavities [6].

This technique is therefore being explored to verify the feasibility of depositing NbN and NbTiN with a homogeneous and uniform structure.

The purpose of the present study is to provide an update on the deposition system at STFC Daresbury Laboratory and discuss the early results obtained. The system previously developed to deposit pure niobium films has been upgraded, granting the possibility to deposit films based on two precursors.

## EXPERIMENTAL SETUP

The deposition system has been previously described [7]. A few major modifications were performed, regarding the number of bubblers and the number of coreagent gasses available for the depositions. A new bubbler line has been installed to allow the deposition of films made by more than one precursor, such as NbTiN. After a few experiments the new bubbler line has also been fitted with a needle valve to limit the quantity of more volatile precursors flowing in the chamber and therefore to better control the stoichiometry of the reaction.

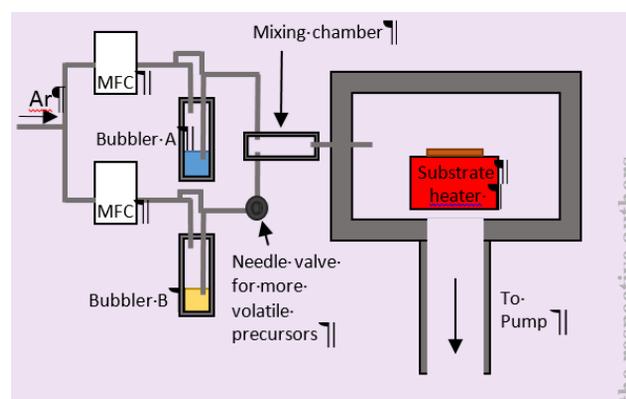


Figure 1: Schematic of deposition facility.

Two coreagent gas lines have also been installed to carry nitrogen and ammonia gas. These allow the deposition of metal nitrides, such as NbN or NbTiN. The depositions are performed on oxygen free copper substrates cleaned via in-house process (acetone – IPA- distilled water) to reduce the quantity of contaminants on the surface. Prior to the deposition, a substrate is introduced in the chamber and

kept at the chamber base pressure of  $10^{-5}$  mbar for 24 hours at 120 °C.

$\text{NbCl}_5$  is used as the niobium source for all the Nb based depositions. The  $\text{NbCl}_5$  (Sigma Aldrich, 99%) is placed under controlled atmosphere in a two-legged steel bubbler, then connected to the deposition rig and maintained at the chamber base pressure.

For the deposition of Nb films, the carrier gas (argon) and the reducing gas (hydrogen) used are purified through a heated filter system to ensure that the presence of residual contaminants in the gas delivery system is kept as low as possible.

Common to all the depositions, the  $\text{NbCl}_5$  precursor is heated up to 130 °C, the temperature at which a vapour pressure is suitable for the deposition [8] and the substrate is heated to 700 °C. The carrier gas is then bled into the bubbler where it forces the evaporated precursor in the reaction chamber, where the reducing gas is also introduced. For the Nb film, the same flow of 100 sccm of Ar and  $\text{H}_2$  grants a sufficient transport of precursor and a sufficient amount of reducing gas in the chamber.

For the deposition of NbN films, the coreagent used is  $\text{NH}_3$  instead of  $\text{H}_2$ , since the ammonia supplies the atomic hydrogen (H) needed as well as the atomic nitrogen (N). The gas flows are varied while leaving the other parameters constant.

For the depositions of NbTiN films, a second precursor is introduced in the chamber through the recently installed line. The chosen precursor is  $\text{TiCl}_4$  (Sigma Aldrich, 99%), which compared to the Nb precursor is liquid and more volatile. This precursor doesn't require heating to develop a suitable vapour pressure, so the quantity that enters the chamber is regulated via a calibrated needle valve.

Once reached the desired deposition time, the coated substrate (sample) is cooled down to room temperature while kept at the chamber base pressure. Once the sample has cooled down, it is then extracted and analysed.

NbN and NbTiN samples are presented in this work as some of the new superconductive materials that have been deposited with our system.

Microstructural analyses were performed by SEM, FIB, XRD and EDAX. SEM and EDAX analyses were performed to determine the thickness of the films, their uniformity and their composition. FIB was performed to study the samples section and in conjunction with XRD they were used to verify the crystalline structure of the films.

## RESULTS AND DISCUSSION

Contamination can be a concern when depositing CVD thin films, since due to the nature of the chemical processes small quantities of impurities can remain in the deposited layer and reduce the layer properties. Superconductive thin films are even more sensitive to this issue, since these contaminants can cause flux pinning and an overall reduction of the film performances [9].

The use of halogen based precursors has led to successful deposition of the films, which have been studied to verify their contamination level.

The EDX results show that the films have a very low percentage of contaminants, especially chlorine that is undetectable which is attributed to the deposition temperatures in excess of 400 °C. Carbon was measured at < 1 weight %, which is important for superconductivity properties, while oxygen seems to be present, however the exact level can't be determined since the surface oxide is always present. Due to the difficulty for EDX to detect accurately light elements (i.e. oxygen), further studies (via XPS) are planned to confirm the level of contamination.

Pure niobium films were deposited on copper substrates, using  $\text{H}_2$  as a coreagent, with and without the use of an ECR plasma source. Their morphology has been previously discussed [7], so further magnetic characterisation have been conducted.

SQUID magnetometer measurements were performed on the films after the removal of the copper substrate via chemical etching, the film deposited with PECVD has 10 times lower thickness than the one deposited with CVD, the results reported in Fig.2 are normalised to the film thickness.

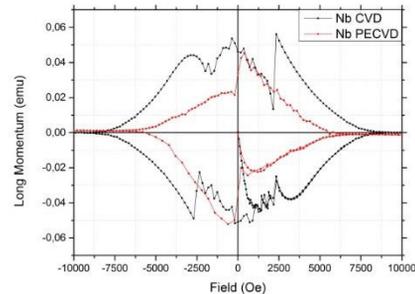


Figure 2: SQUID measurement of CVD and PECVD Nb samples.

The sample deposited via CVD shows flux pinning between 1200 and 2500 Oe, suggesting the presence of defects (grain boundaries and point/dislocation defects) in the film. The field of first flux penetration has a value of 350 Oe, while the  $H_{c2}$  value is 8000 Oe.

The sample deposited via PECVD if compared to the CVD sample shows less flux pinning. This could be an indication of less defects in the film, although the number of points taken and the different thickness of the samples don't allow us to speculate in absence of more in depth data. The field of first flux penetration also seems to have a value of <350 Oe, while the  $H_{c2}$  value is 7000 Oe, which is about a 1000 Oe less than the CVD sample. Further studies are being conducted on the pure Nb films.

The gas delivery system and the position of the samples in the chamber has been tweaked to produce a uniform coating of the surface. The lack of visible thickness gradients confirmed afterwards by FIB pictures proves that the thickness uniformity is satisfactory for the Nb, NbN and NbTiN films.

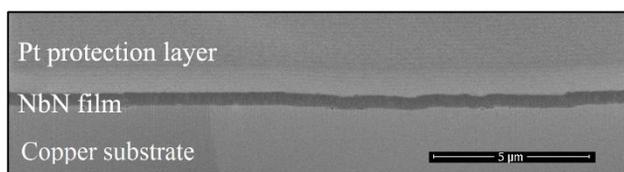


Figure 3: High magnification SEM of section of thin NbN film.

The HRSEM (Fig. 3) obtained via FIB shows a homogenous coverage of the copper substrate. The thickness of the deposited films has been measured and varied according to deposition temperature and precursor dosage. The films were grown with thickness varying from 50 nm to 1 μm (Fig. 4).



Figure 4: High magnification SEM of section of thin NbTiN film.

FIB analysis was used to investigate the film microstructure: due to time constraints only NbN samples were analysed. The results show a polycrystalline structure with columnar growth (see Fig. 5).

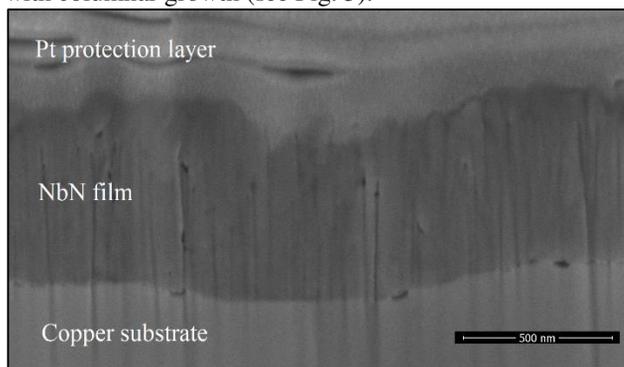


Figure 5: FIB of section of thin NbN film.

X-ray Diffraction (XRD) for nitrides was performed on the samples to confirm the crystalline structure. Removal of the substrate via chemical etching has proved to be challenging, since the method developed for pure niobium films is not suitable. Therefore, the spectra obtained all showed copper diffraction peaks. For better clarity, the copper peaks have been removed from the presented plots, to better show the film peaks. The spectrum for NbN is reported in Fig. 6. The pattern matches the standard XRD pattern of a cubic phase niobium nitride (JCPDS card no. 03-065-5011), which allows the identification of the preferred lattice orientation. This corresponds to the (200) orientation. The grain size has been calculate to an average value of 25 nm, with a lattice parameter of 4.4 angstrom.

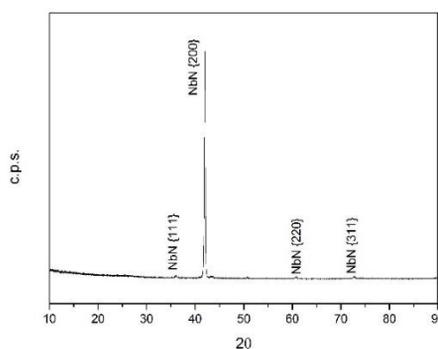


Figure 6: XRD of NbN on copper.

NbTiN samples were also studied via XRD; one of the obtained spectra is reported in Fig. 7.

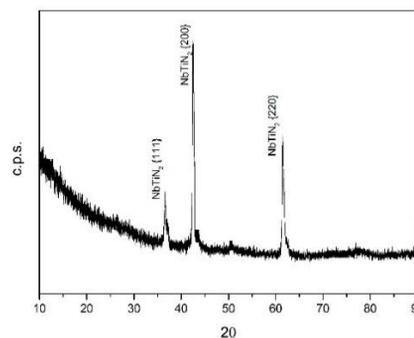


Figure 7: XRD of NbTiN on copper.

The spectrum shows the diffraction peaks of NbTiN2 (JCPDS card no. 01-071-9837), a cubic phase with a preferred orientation along the 200 orientation. The grain size has also been calculated to an average value of 21 nm, with a lattice parameter of 4.3 angstrom.

## CONCLUSIONS

We have improved our deposition system to allow us to deposit multi-precursor thin films by using CVD and some of the new materials microstructural properties have been investigated. SQUID measurements have been performed on pure Nb films, showing that PECVD seems to produce a film with less defects. Further studies will be done to verify this assumption.

RRR measurements and SQUID will be performed to relate the deposition parameters and the superconductive properties. A future upgrade for the deposition system is the addition of atomic layer deposition valves, which will allow to deposit multi-layered films at lower temperatures.

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