HIPIMS: A NEW GENERATION OF FILM DEPOSITION TECHNIQUES FOR SRF APPLICATIONS*

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Abstract

Over the years, Nb/Cu technology, despite its shortcomings due to the commonly used magnetron sputtering, has positioned itself as an alternative route for the future of accelerator superconducting structures. Avenues for the production of thin films tailored for Superconducting RF (SRF) applications are showing promise with recent developments in ionized PVD coating techniques, i.e. vacuum deposition techniques using energetic ions. Among these techniques, High power impulse magnetron sputtering (HiPIMS) is a promising emerging technique which combines magnetron sputtering with a pulsed power approach. This contribution describes the benefits of energetic condensation for SRF films and the characteristics of the HiPIMS technology. It describes the on-going efforts pursued in different institutions to exploit the potential of this technology to produce bulk-like Nb films and go beyond Nb performance with the development of film systems, based on other superconducting materials and multilayer structures.

INTRODUCTION

Due to the very shallow penetration depth of RF fields (only ~40 nm for niobium [Nb]), SRF properties are inherently a surface phenomenon, involving a material thickness of less than 1 micron. One can then foresee the merits of depositing an Nb film on the inner surface of a castable cavity structure made of copper (Cu) or aluminum (Al). At the system design level, this would exploit the freedom to decouple the active SRF surface from the accelerating structure definition and its cooling, opening the possibility to dramatically change the cost framework of SRF accelerators.

CERN has conducted pioneering studies [1-3] in the field of SRF Nb films on Cu (Nb/Cu) applied to cavities and successfully implemented this technology in the LEP-2 and the LHC accelerators. Although 1.5 GHz cavities achieving gradients up around 25 MV/m [4] were produced, these cavities suffered from significant losses resulting in the significant reduction of Q at accelerating gradients above 15MV/m. Some of the defects were inherent to the magnetron sputtering technique used to produce these cavities.

In the meantime, bulk Nb cavities are approaching their intrinsic limit at $H_{max} = H_c$ (180 mT), with breakdown fields close to the de-pairing limit (50 MV/m) [5].

The challenge in developing SRF Nb thin films is to reproduce and go beyond the performance of bulk Nb. While tight correlation with the characterization of real materials has yet to be described, there exists a theoretical framework describing the relevant material parameters of surfaces as they influence SRF properties. Several material factors, highly dependent upon the surface creation conditions, contribute to degraded SRF performance with respect to ideal surfaces. These limiting factors such as intra-granular impurities and lattice defect density, inter-granular impurities and oxidation, surface topography and chemistry, may lead to the reduction of the electron mean free path, thus the reduction of the lower critical field H_{c1}.

Understanding of the film growth dynamics from nucleation to final exposed surface is therfore crucial. The defect density (which determines the electron mean free path) within the RF penetration depth is certainly affected by intragrain contaminants incorporated during the final stage film growth, but it is also strongly affected by the underlying crystal texture, which is in turn developed from the initial film nucleation process, which necessarily is strongly influenced by the substrate. The development of every stage can be expected to depend strongly on the kinetic energy distribution of the arriving Nb ions. Although the thickness corresponds to the very top 40 nm of the Nb film, this final surface is dictated from its origin, i.e. the substrate, the interface, and deposition technique (ion energy, substrate temperature…).

ENERGETIC CONDENSATION

Control over the deposition process is exercised by only three first-order vapor parameters and one first-order substrate parameter. The vapor parameters are the absolute arrival rates of film atoms, the partial pressures of background gases in the chamber and the energy of the deposition fluxes. The substrate parameter is the substrate temperature.

Without energetic atoms, only the substrate temperature influences the processes of physi- and chemisorption, thermal desorption, nucleation, nuclei dissociation, surface diffusion, and formation of specific nucleation sites. Crystalline defects, grains connectivity and grain size may be improved with a higher substrate temperature which provides higher surface mobility (the important parameter is the "homologous temperature"= $T_{substrate}/T_{melting\_of\_film}$). However practical substrates for SRF cavities (Al, Cu) may not allow heating to high temperatures.

The missing energy may be supplied by ion bombardment. Energetic condensation is a deposition process where a significant fraction of the condensing

species have hyper-thermal and low energies (10 eV and greater). It is characterized by a number of surface and sub-surface processes that are activated or enabled by the energy of the ions arriving at the surface [6-9].

If the incident ions have enough energy, i.e. between the surface displacement energy and bulk displacement energy, surface diffusion of atoms is promoted but no defects are created in the film bulk thus promoting epitaxial growth [10].

When the incident ion energy is increased beyond the bulk displacement energy (usually in 12–40 eV range [11]), the ions can be incorporated into the surface (sub-implantation), the collision cascades under the surface generating defects and intrinsic stress followed by re-nucleation.

A maximum of intrinsic stress exists for kinetic energies of about 100 eV; the actual value depends on the material and other factors. The existence of such maximum can be explained by insertion of atoms under the surface yet still very little annealing [12].

As the energy of these penetrating ions increases, a very short ballistic phase with displacement cascades occur followed by a thermal spike phase (atomic scale heating) with a very high mobility of atoms in the affected volume. The thermal spike can be considered as a transient liquid. As soon as atoms have found their place, i.e. the liquid "freezes", large amplitude thermal vibrations still facilitate diffusion, especially the migration of interstitials inside grains and adatoms on the surface. This favors the annihilation of defects and re-nucleation. When the majority of condensing species are ions, each of the atoms in the growing film is subject to atomic scale heating several times, namely, once when it arrived and again when neighboring atoms arrived.

As the kinetic ion energy is increased, usually by biasing, the sputtering yield is increased and the net deposition rate is reduced (re-sputtering). Film growth ceases as the average yield approaches unity (between 400 eV and 1400 eV). If the energy is further increased, the surface starts to be etched.

All energy forms brought by particles to the surface will ultimately contribute to broad, non-local heating of the film thus shift the working point of process conditions to higher homologous temperature. This could replace conventional heating and so produce dense films via enhanced surface mobility at generally low bulk temperature. At higher temperature (higher homologous temperature or temperature increase due to the process itself) the grains are enlarged because the increase of ad-atom mobility dominates over the increased ion-bombardment-induced defects and re-nucleation rates [13].

The relationship between the coating morphology, the substrate temperature, kinetic energy of the ions and the deposition rate is summarized in the revised structure zone diagram proposed by A. Anders (Fig. 1).
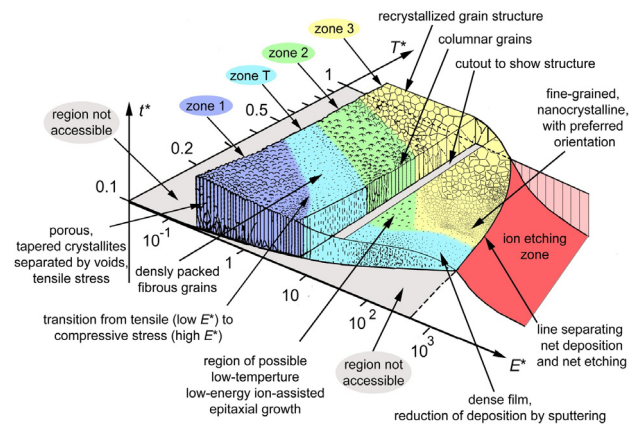

Figure 1: Generalized Structure Zone Diagram [9].

In summary, these competing processes due to the additional energy provided in energetic condensation techniques can induce the following changes to the film growth process (Fig. 2):

- residual gases are desorbed from the substrate surface
- chemical bonds may be broken and defects created thus affecting nucleation processes and film adhesion
- film morphology changes
- microstructure is altered
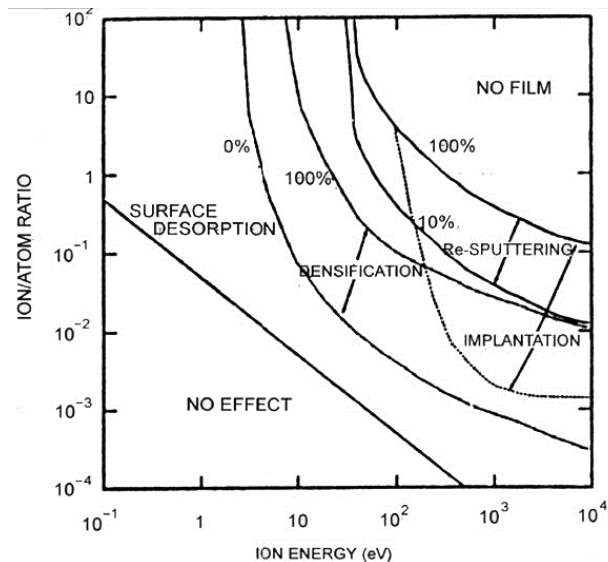- stress in the film alters

Figure 2: Regions of dominance for various ion-bombardment processes as a function of ion/atom ratio and ion energy [14].

As a result of these fundamental changes, energetic condensation allows the possibility of controlling some of the film properties. The density of the film may be modified and the crystal orientation may be controlled to give the possibility of low-temperature epitaxy.

Energetic condensation can be implemented with a variety of deposition techniques such as high power impulse magnetron sputtering (HiPIMS) [15], cathodic

energy deposition (CED[TM]) [16], vacuum arc deposition [17], electron cyclotron resonance (ECR) [18]. This contribution addresses HiPIMS and its potential for SRF applications.

HIGH POWER IMPULSE MAGNETRON SPUTTERING

HiPIMS technology is an array of ionized physical vapor deposition techniques. It is a complex variation of conventional sputtering techniques such as direct current magnetron sputtering (dcMS). It has been of great interest over the last decade, generating extensive developments especially in the field of industrial hard coatings [19].

The HiPIMS Discharge

HiPIMS uses very short pulses (Fig. 3) with power densities at the target surface (during the pulse) exceeding the typical dc power density by about two orders of magnitude (of the order of kW/ cm^2). This increases the ionization of the sputtered material creating a metal-based plasma in contrast with a gas plasma for conventional sputtering. Since the duty cycle is small (<10%) the average heating of the target is manageable. The initially high negative bias voltage used, leads to an increased kinetic energy of the charged particles bombarding the film surface, which is known to generate a denser, less columnar structure, where re-nucleation commonly takes place [20]. The energy of the ions produced is in the 20 eV - 100 eV range versus only about 2 - 10 eV in conventional sputtering. Table 1 displays typical parameters for a HiPIMS plasma by comparison to a dcMS plasma.

Table 1: Plasma Parameters for HiPIMS versus dcMS [22]

| Parameter	HiPIMS	DC Sputtering
Peak Power Density	10^3 Wcm^{-2}	1 Wcm^{-2}
Average Power Density	1^3 Wcm^{-2}	1 Wcm^{-2}
Current Density	1-10^3 Acm^{-2}	0.01-0.1 Acm^{-2}
Discharge Voltage	500-1000 V	500 V
Process Gas Pressure	10^{-3}-10^{-2} Torr	10^{-3}-10^{-2} Torr
Magnetic Field Strength	0.010-0.100 T	0.010-0.100 T
Electron Density	10^{18}-10^{19} m^{-3}	10^{16} m^{-3}
Electron Temperature	1-5 eV	1-7 eV
Degree of Metal Ionisation	30-100 %	<5 %
Ion energy (average for metal ions)	20 eV	5 eV
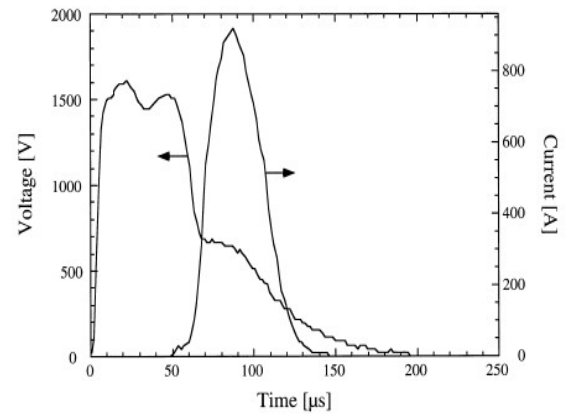
Figure 3: Typical HiPIMS pulse [21].

The HiPIMS plasma breaks down in isolated ionization zones (IZs) [23] that rotate in the direction given by the ExB drift, with velocities around 10^4 ms-1 and frequencies in the range of about 100 kHz. The positive feedback loop between electron mean free path and ionization leads to "bunching" of plasma ionization zones. These IZs move in ExB direction because ions are "evacuated" from ionization zones by electric field, exposing new neutrals to ionization by drifting electrons Electrons drift according to the local E and B fields, perpendicular to both, and produce electron jets related to the azimuthal electric field of the plasma zone. From the target point of view, a HiPIMS discharge represents therefore a situation of continuous temporal and spatial change in local sputtering conditions. The physically relevant power density of HIPIMS is much higher than the typically reported average power density. IZs explain how HIPIMS can offer "energetic condensation" in the context of sputtering.

Some of the shortcomings of HIPIMS are the reduction of deposition rate and the potential transition to an arc discharge. The deposition rate for the HIPIMS discharge is expected to be in the range 30-80 % compared to a conventional magnetron discharge, with the same average power. The other problem with HIPIMS is the generation of arcs on the cathode surface, especially for target materials with low melting point.
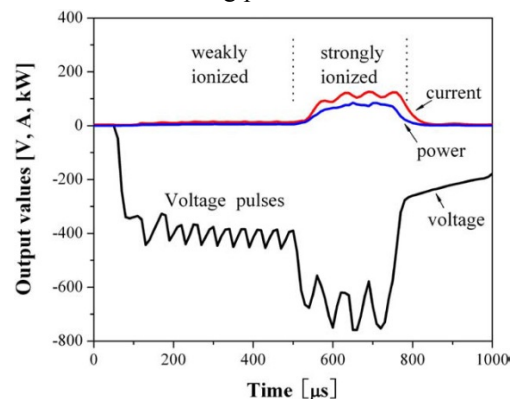

Figure 4: Modulated pulsed power discharge [24].

An alternative approach to HiPIMS, referred to as modulated pulse power (MPP), consists in modulating the pulse such that in the initial stages of the pulse the power level is moderate (typical for dcMS) followed by a high power pulse. The MPP technique uses longer pulse lengths (up to 3 ms) than classic HiPIMS and utilizes multiple steps and micro pulses in one pulse period. One typical MPP pulse consisting of two stages in one pulse is shown in Fig. 4. The first step is the weakly ionized period, in which low voltage current and power are loaded on the target to ignite the plasma. Then the pulse goes to the strongly ionized period with high voltage, current and power. There can be multiple steps in one MPP pulse to reach the strong ionization period. By varying the pulsing width, frequency, the width and the distance between micro pulses, MPP can generate controllable peak power, a maximum average target power, and a maximum peak current on the target during the strong ionization segment. The micro pulses within the pulse segments offer the flexibility to stabilize the plasma and control the voltage, current and power. A combination of reduced gas rarefaction effects, prevention of sustained self-sputtering, and a relaxation of ion trapping leads to an increase of the deposition rate.

HiPIMS Potential for SRF Applications

HiPIMS plasma and the resulting films have been found to display the following characteristics:

- High level of ionization
- High energy ions, tunable with bias voltages
- Possibility to control the film structure
- Phase-tailoring [25] leading to improved performance
- Allow lower temperature process
- Proven improved coverage of complex-shaped surfaces (even for high aspect ratio objects and rough substrate surfaces) [26]
- Enhanced adhesion to substrate
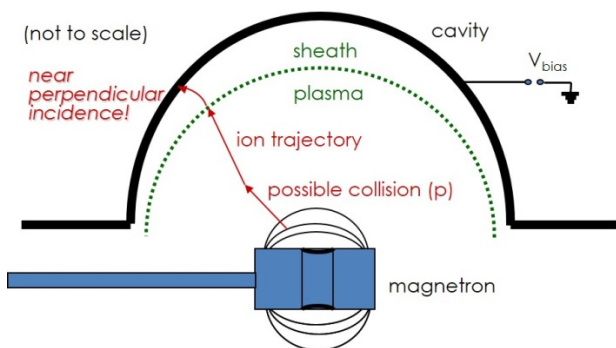- Film smoothness
- Film densification

Figure 5: Possible configuration for the HiPIMS setup for cavity deposition [27].

Such characteristics can be of great benefit in the development of Nb film coating for SRF applications. One can imagine a magnetron configuration as shown in Fig. 5 [27] where the magnetron travels along the inner

axis of the cavity. A bias voltage can be applied to the cavity to tune the energy and favor the normal incidence of the incident ions.

Other opportunities in the use of HiPIMS present themselves beyond just the film growth. The substrate can be treated in-situ to clean the surface or remove native oxides, typically with plasma etching (high voltage applied to the substrate), thus generating an optimum surface for film nucleation. By using very high energy incident ions, film forming species can be implanted in the substrate, forming a gradient towards the surface allowing interface engineering for the creation of an adequate template for the SRF film subsequent growth.
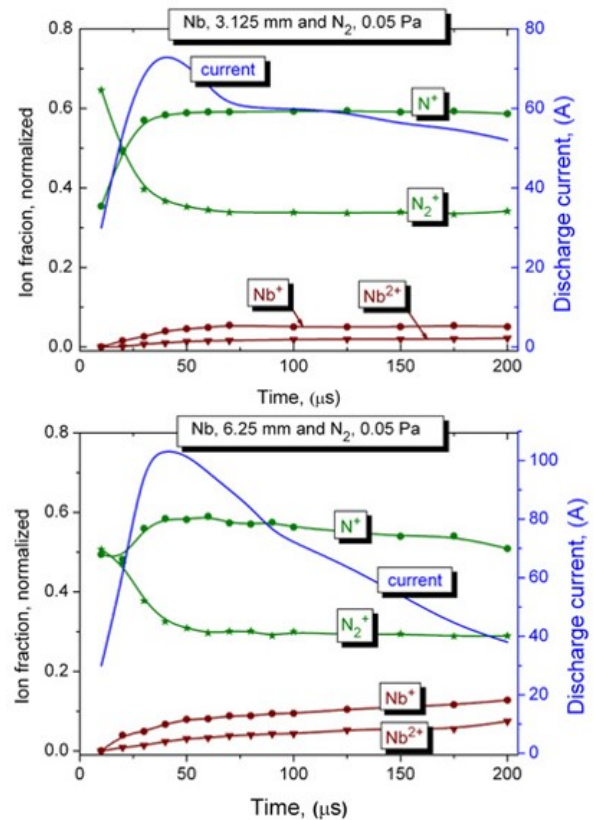

Figure 6: Time-Of-Flight study of Nb HIPIMS with N_2 gas [28].

The HiPIMS technology could also be easily extended to the development of alternative SRF materials [5]. NbN, or NbTiN film deposition is relatively straightforward by using the HiPIMS discharge in a reactive gas (N_2) atmosphere. The ion species measured in the studies reported in [28] (Fig. 6) suggest the formation of dense, textured NbN films.

HIPIMS AT LBNL

The HiPIMS process has been the object of extensive plasma studies applied to a variety of materials at Lawrence Berkley National Lab (LBNL) in the group of Andre Anders [29-30].

Various experiments are carried out in a general-use chamber to explore the plasma physics and characteristics

of the HiPIMS process, especially applied to Nb and other SRF materials. The possibility of "gasless" self-sputtering [31] of Nb, i.e. a HIPIMS mode in which the sputtered atoms satisfy the need for a process gas was explored. Thus no argon (Ar), krypton (Kr) or any other gas is needed, eliminating the issues related to noble gas inclusion. Such "gasless" self-sputtering has been demonstrated for HIPIMS using high sputter yield materials such as copper [32]. In the case of Nb [27], the sputter yield is not sufficient to produce enough "niobium gas". Rather, noble process gas is always needed to obtain HIPIMS pulses. This leaded into the exploration of the minimum pressure needed to obtain a HIPIMS Nb discharge [28]. It was found that, due to some "residual plasma" of the previous pulse, the pulse repetition rate is an important parameter that allows pressure reduction while still maintaining a stable and reproducible operation.

Another recent development of the HiPIMS process consists in superimposing a Mid Frequency (MF) discharge in between the HiPIMS pulses to lower the frequency pulses of the HiPIMS pulses. Though they do not depend on MF pulse pattern, the HiPIMS pulses can be spaced as far (or close) in time as desired as long as the MF discharge is present. Conditions are found where the species in the plasma are largely dominated by Nb^+ [33].

Sample studies are in progress for Nb films deposited on Cu and Al. The characteristics such as crystal structure, adhesion to the substrate, T_c, RRR are investigated [27].

In parallel to the exploration of HiPIMS process for the development of SRF materials, a cavity dedicated deposition chamber was designed and built (Fig. 7). The system is composed of a set of two, movable cylindrical magnetrons, sized for 1.3 GHz cavity deposition. The two magnetrons are mounted on movable arms, as shown in Fig. 7, to uniformly coat the inside of the cavity while slowly traveling through it. Their travel is synchronized by computer-controlled stepper motors. The use of two magnetrons allows the option of biasing the cavity, where the bias is one of the main parameters for film optimization. The concept is to use one target as the cathode, and the other as the anode. The polarity of the targets is alternated at a frequency typical for HIPIMS. As a result, the cavity does not participate in the discharge process and can be biased using another, independent power supply. Additionally, the deposition rate can be doubled each by using each of the magnetrons at its maximum power rating. This leads to a shorter process time and a reduced incorporation of residual gas contaminants.
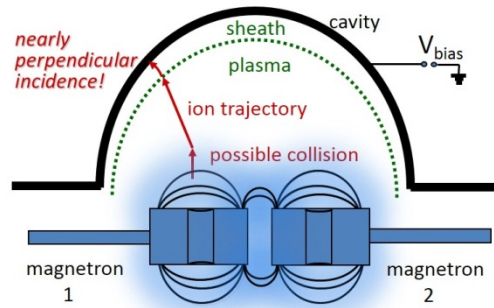
Figure 7: LBNL dual magnetron HiPIMS deposition chamber dedicated to the coating of 1.3 GHz cavities with niobium [27].

HIPIMS AT CERN

CERN in collaboration with Sheffield Hallam University is conducting studies on HiPIMS plasma with Nb [34] and developing the technique for the coating of 1.5GHz Nb/Cu cavities.
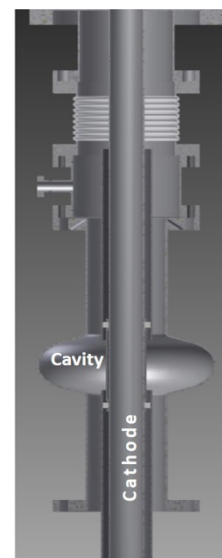

Figure 8: HiPIMS cavity deposition system used at CERN.

The HiPIMS coating system described in details in [35] has a vertical cylindrical magnetron configuration (Fig. 6). It is built on the basis of the DC cylindrical magnetron coating system for 1.5 GHz Nb/Cu cavities used in previous studies [36]. It is an all-metal UHV system with the cavity being part of the vacuum system. The base pressure of the system is in the 10^{-10} - 10^{-11} mbar range. The cavity beam pipes are coated in sequential steps by DC magnetron sputtering (dcMS), while the cell is coated either by HIPIMS or by dcMS. The coatings are performed in a 10^{-3} mbar range Kr atmosphere.

Some 1.5 GHz Cu cavities have been coated with both HiPIMS and dcMS. Figure 9 represent the quality factor curves at 4.2 K and 2.1 K for a dcMS cavity and HiPIMS cavity, both coated with Kr. These preliminary results show an improvement in the performance of Nb films coated by HiPIMS compared to dcMS.
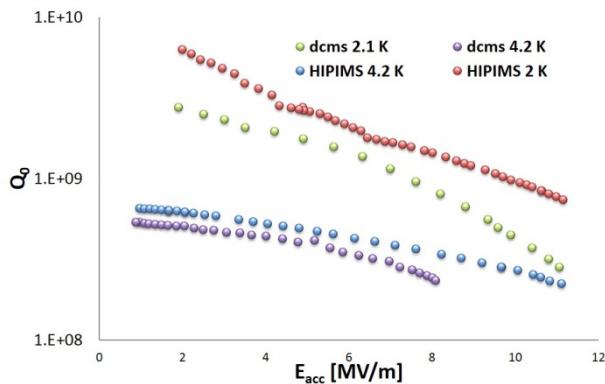
Figure 9: Quality factor of two elliptical single cell cavities, produced by dcMS and HIPIMS sputtering.

HIPIMS AT JEFFERSON LAB

In the framework of a project dedicated to the development of SRF films via energetic deposition, JLab is implementing the HiPIMS process in the ultra-high vacuum (UHV) multi-technique deposition system [37] and a cylindrical cavity system [38].

The UHV system is equipped with several magnetrons and described elsewhere [37]. A sample center stage, equipped with shutters, heaters and bias voltage connections, is in development to optimize the sample-target relative positions. One of the objectives is to apply energetic condensation through the HiPIMS process to the development of alternate SRF materials and S-I-S multilayer structures and improve the results achieved with dcMS [39]. A concept for coating cavities with multilayer structures is also under development for this system. Another objective is to bridge the HiPIMS study for Nb/Cu cavity deposition with the newly built cylindrical HiPIMS magnetron sputtering system with the ongoing studies on Nb films produced by energetic condensation via ECR (which produces 64 eV Nb^+ ions in UHV [40]).

The cylindrical HiPIMS magnetron sputtering is dedicated to the coating of 1.5/1.3 GHz Nb/Cu cavities and is under commissioning. In this system, the cavity is part of the vacuum system, as shown in Fig.10. The magnetron is mounted on a bellow at the opposite end of the system. The cathode and internal rare earth magnets are cooled by water. The field from these magnets extends the entire length of the cavity (Fig.10). The intermediate chamber between the cavity and the cathode chamber will also be used to produce Nb films on small samples for material characterization.
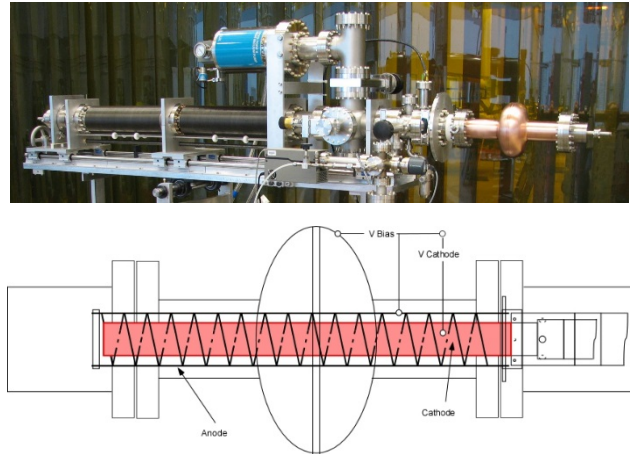
Figure 10: JLab cylindrical HiPIMS deposition system dedicated to cavities (top) and schematic of it cathode setup (bottom) [38].

The system parameter space and film properties (initially T_c & RRR) will be first investigated. The ion flux, ion energy spectrum and Nb ions-to-neutral ratio are to be characterized under various pulse conditions.

The substrate cavity preparation will consist of mechanical polishing by central barrel polishing (CBP) followed by electropolishing to mimic the substrate preparation done for small samples studies [41]. To minimize particulate contamination prior to coating, the cavity will be assembled in an ISO 4 clean room. The system will be baked at adequate temperature to achieve the lowest vacuum pressure. Kr will be used as a working gas to minimize gas trapping in the Nb film [4]. The other coating parameters will be derived from the extensive studies of Nb films deposited with ECR plasma [42-44].

SUMMARY

HiPIMS is an emerging array of energetic condensation techniques. Due to the interest in industry, extensive studies in plasma physics and materials have been and are conducted. HiPIMS offers a variety of features to produce improved film deposition.

Plasma studies focused on Nb are being conducted at LBNL and at CERN in collaboration with Sheffield Hallam University. Nb has a relatively low self-sputtering yield and "gasless" self-sputtering in vacuum could not be demonstrated. Low pressure operation works well with

optimized pulse frequency thus preventing significant trapping of sputtering gas in the films.

HiPIMS systems dedicated to cavity deposition are ready at LBNL, CERN and JLab. The first HiPIMS Nb/Cu cavities have already been coated at CERN with modest but encouraging results. This technique is directly applicable to the deposition of SRF materials beyond Nb both in single layer or S-I-S multilayer structures.

ACKNOWLEDGMENT

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