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TAILORING THE PRODUCTION OF Nb SUPERCONDUCTING FILMS FOR SRF CAVITIES: MASS/ENERGY SPECTROSCOPY AND FILM CHARACTERISATION*

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Abstract

SRF cavities are commonly coated with superconducting materials (e.g., niobium) using magnetron sputtering. In this process, various power supplies are employed such as DC, pulsed DC or HiPIMS. The sputtered ions are ejected from the target to the cavity or sample surface with an energy dependent on the power conditions and pressure range. In this study, we investigated the efficiency of such deposition by tracking the mass and energy of the main ions produced (e.g., Kr^+, Kr^{2+}, Nb^+, Nb^{2+}) using mass spectroscopy. We report the optimal conditions suitable to enhance both ions energy and film growth by comparing to power supplies (DC and HiPIMS), for different pressure conditions ranging from 10^{-3} mbar to 10^{-1} mbar. To support the gas phase analysis, niobium films were produced on copper substrate and the film structured was analysed by SEM.

INTRODUCTION

Bulk niobium (Nb) cavity has been the material of choice for superconducting RF (SRF) applications. This comes primarily to its high critical temperature (T_c = 9.2 K) and critical magnetic field (H_c) compared to other pure metals. Over the years, RF performance of bulk Nb cavities has improved and is approaching the intrinsic limit of the material ($H_c \approx 200$ mT) [1]. To further improve the RF performance of the cavity, two routes can be explored such as the replacement of bulk Nb into Nb thin films on copper substrate, leading to consequent cost reduction in cryomodule production. Alternatively, other materials can be investigated (NbN, NTiN, Nb_3N, etc.), known to possess a higher T_c and H_c than Nb, which could potentially reduce operational costs by working at temperature higher than 4.2 K [2].

When looking at SRF properties, most of phenomenon are surfacing and confined within few micrometers of the material thickness [3]. Similar to bulk Nb, most properties of the thin film are inherently linked with the deposition process. Most Nb/Cu cavities have been produced using DC sputtering technique like DC magnetron sputtering (DCMS) or diode sputtering [4, 5]. In these process, the deposited species are mainly metal neutrals originated from the target material. The flux of ionic species is mainly dominated by inert gas ions (i.e., Ar^+ or Kr^+), with only a small fraction of sputtered ions arriving at the substrate surface [6]. Thus, the deposition rate is dictated by the flux of neutral sputtered atoms. The ion-assisted growth process can be changed when transitioning to High Power Impulse Magnetron Sputtering (HiPIMS); where the sputtered species composition is dominated by metal ions (high bombarding energies) rather than metal neutrals (low bombarding energies). Compared to DCMS, the bombarding energy of the deposited species can be controlled and guided with a reduction in gas incorporation within the thin film [7]. Thus, improving the final properties and characteristic of the thin films.

In this work, DCMS and HiPIMS process were investigated for the production of Nb thin films. To highlight the effect of the pressure conditions, analysis of the plasma phase were achieved by mass spectrometry at different pressure ranging from 10^{-3} to 10^{-1} mbar. Ion energy distribution function (IEDF) for the main ions are plotted and compared. Lastly, Nb thin films were grown on Cu substrate and analyzed by SEM.

EXPERIMENTAL PROCEDURE

The experiments were carried out in a ultra high vacuum system in which a magnetically balanced magnetron was mounted. The base pressure of the system was 1×10^{-8} mbar. A Nb rod was used as sputtering material (45 cm long, 4.4 cm diameter, 99.999% purity) inserted over a copper tube containing a set of magnets forming a total length of 9.5 cm.

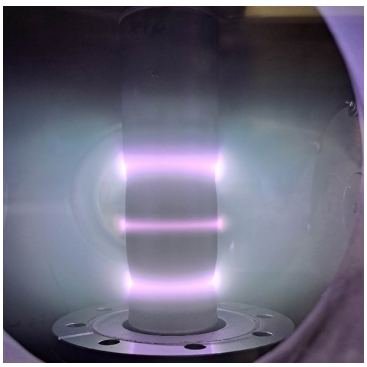

Figure 1: Picture of the discharge achieved in the chamber.

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The sputtering was achieved using Kr (BOC, 99.999% purity) introduced using a variable leak valve allowing working pressure ranging from 10^{-3} up to 10^{-1} mbar. The cathode was connected to either a classic DC power supply (Pinnacle Plus, Advance Energy) or a pulsing unit (HiPSTER 1, Ionautics AB) fed by a DC power supply delivering a negative potential. The unit was controlled by computer at a frequency of 1000 Hz with negative pulses of 100 µs (duty cycle of 10%). Figure 1 shows picture of the discharge.

In-situ mass- and energy-dependent analyses of the positive ions was carried using a Hiden Analytical mass spectrometer (EQP-9 system, Hiden Analytical) allowing the measurements of ion energies up to 100 eV. The spectrometer was placed facing the discharge at a distance of 8.5 cm. In a second time, Cu samples were coated for a period of 4 hours by either DCMS or HiPIMS. Prior deposition, the substrates were cleaned in an ultrasonic baths of acetone, then isopropanol, and rinsed with deionized water. The samples were loaded and the whole system was baked at 140 °C over 48 hours. The resulting films were observed by SEM.

RESULTS AND DISCUSSIONS

Figure 2 reports the mass scan of the positive ions obtained in both DCMS and HiPIMS for an identical input of power of 300 W. From the top figure, DCMS is significantly shadowed by the HiPIMS process with higher ion intensities up to 10^6 c/s for both Kr^+ and Nb^+, whereas DCMS reaches up to 10^5 c/s for Nb^+ and few hundreds for Kr^+. Aside from the single charge ions of Nb and Kr, double charged (resp. 46 and 42 amu) and triple charged (resp. 31 and 28 amu) ions can also be found in HiPIMS whereas only Nb^{2+} and Kr^{2+} were observed in DCMS.

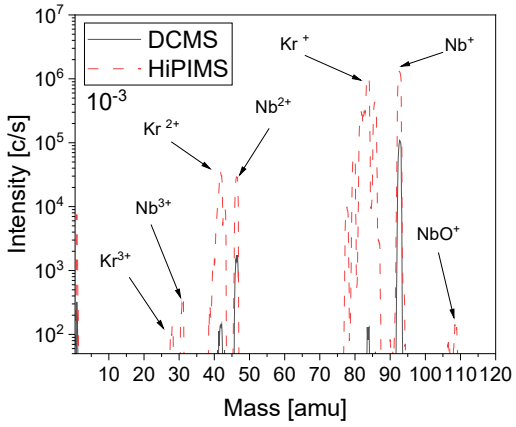

Figure 2: Mass scan obtained for the positive ions produced by either DCMS or HiPIMS at 10^{-3} mbar.

Additionally, a peak at 109 amu was observed in the HiPIMS scenario corresponding to NbO, due by the recombination between Nb and oxygen from the residual water molecule present in the chamber. Due to a high current peak from the HiPIMS process (≈ 13 A) and inefficient baking of the chamber, the residual water could participate in the overall chemistry. Measures were taken to minimise this effect by performing an residual gas analysis and tracking water molecule prior deposition on Cu substrates.

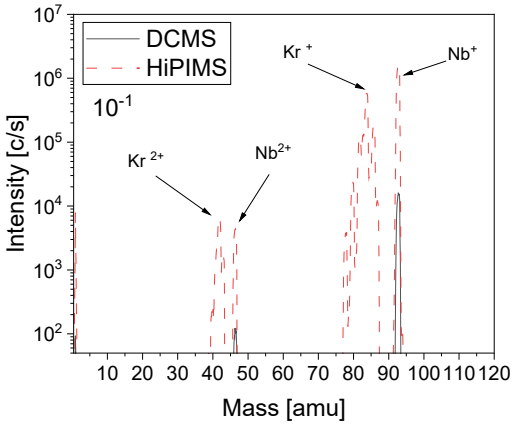

Figure 3: Mass scan obtained for the positive ions produced by either DCMS or HiPIMS at 10^{-1} mbar.

A higher deposition pressure result in a decrease of the overall peak intensity at the exception of Nb^+ and Kr^+ for the HiPIMS scenario as reported in Fig. 3.

Figure 4 reports the IEDF of Nb^+ in both process. The trends reported here are commonly found in literature [8, 9]. At 10^{-3} mbar, both ion peak energy and intensity are favored in HiPIMS. Similar peak energy is observed (≈ 5 eV), however in the HiPIMS scenario the ions energy possess a tail with energy up to 100 eV. In DCMS, the maximum peak energy is followed by a fast decay of the signal intensity with a maximum of 55-60 eV for less than 100 c/s.

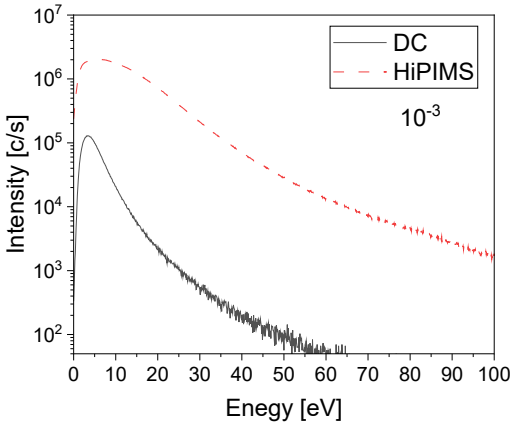

Figure 4: IEDF of Nb^+ for DCMS and HiPIMS at 10^{-3}.

Increasing the pressure lead to an increase of collisions within the vicinity of the target between Kr gas and ions sputtered from the target. Thus, leading to a drastic modification of the ions kinetic energy as shown in Fig. 5.

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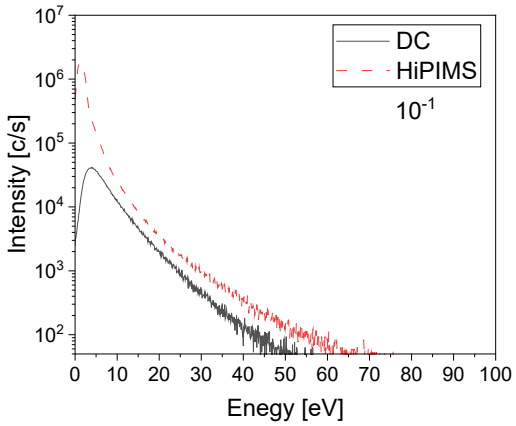

Figure 5: IEDF of Nb^+ for DCMS and HiPIMS at 10^{-1}.

At 10^{-1} mbar, the IEDF of Nb^+ for both HiPIMS and DCMS follows a similar trend with a higher maximum peak energy in DCMS (4 eV in DCMS vs 2.5 eV in HiPIMS). Although, the origin of the high-energy tails remain complex and under active investigation. Some studies reported that this trend could be associated to ion acceleration in plasma instabilities or related to spokes in electric potential structures [10, 11].

Figure 6 reports the surface analysis obtained from two samples deposited by DCMS and HiPIMS at identical pressure/power conditions.

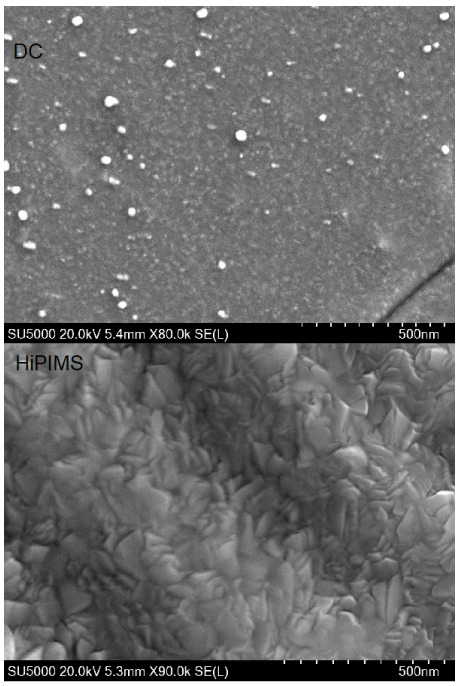

Figure 6: Surface analysis of Nb thin film deposited on Cu substrate at 10^{-3} mbar and 300W: DCMS on top and HiPIMS at the bottom.

Comparatively, the film deposited by HiPIMS present a denser structure associated by a denser plasma with higher ionisation degree. The flux of ionic species at the substrate shifts from being dominated by gas ions (i.e., Kr) to metal ions, leading to a denser film with higher hardness and uniformity.

CONCLUSION

In this work, DCMS and HiPIMS were investigated for the production of Nb thin films on Cu substrate. From the mass scan of the positive ions, it was found that generating a plasma a lower pressure favoured the production of single and double charged positive ions, with higher ions energy due to a higher mean free path. Following the initial results from the plasma phase, production of Nb thin films at 10^{-3} mbar was achived and analysed showing a denser film in HiPIMS compared to DCMS. This work highlight the importance of characterising the plasma phase prior deposition to optimise the deposition parameters, similar preparation could be applied for the deposition of Nb thin film cavities.

FUTURE WORK

Characterization of the plasma phase plays a paramount role in understanding the behaviour of the ions formed in sputtering process. Combination of various diagnostic techniques such as optical emission spectroscopy and mass spectrometry could provide a better view of the ion/neutral ratio; IV plasma properties could be compared using a retarding field analyser or Langmuir probe could provide. These techniques are currently investigated and extended to the study of other materials at Daresbury Laboratories.

REFERENCES

[1] A. Gurevich, "Enhancement of rf breakdown field of superconductors by multilayer coating," *Applied Physics Letters*, vol. 88, no. 1, 2006. doi:10.1063/1.2162264

[2] R. Valizadeh *et al.*, "Synthesis of Nb and Alternative Superconducting Film to Nb for SRF Cavity as Single Layer," in *Proc. SRF'21*, East Lansing, MI, USA, 2021, p. 893. doi:10.18429/JACoW-SRF2021-FROFDV06

[3] C. James *et al.*, "Superconducting nb thin films on cu for applications in srf accelerators," *IEEE Transactions on Applied Superconductivity*, vol. 23, no. 3, pp. 3 500 205–3 500 205, 2013. doi:10.1109/TASC.2012.2235503

[4] A. Miyazaki and W. V. Delsolaro, "Two different origins of the q-slope problem in superconducting niobium film cavities for a heavy ion accelerator at cern," *Physical Review Accelerators and Beams*, vol. 22, no. 7, p. 073 101, 2019. doi:10.1103/PhysRevAccelBeams.22.073101

[5] R. E. Laxdal *et al.*, "Superconducting Sputtered Nb/Cu QWR for the HIE-ISOLDE Project at CERN," in *Proc. LINAC'10*, Tsukuba, Japan, Sep. 2010, pp. 827–829. https://jacow.org/LINAC2010/papers/THP033.pdf

ISBN: 978-3-95450-247-9 ISSN: 2673-5490 doi: 10.18429/JACoW-IPAC2024-WEPS49

[6] U. Helmersson, M. Lattemann, J. Bohlmark, A. P. Ehiasarian, and J. T. Gudmundsson, "Ionized physical vapor deposition (ipvd): A review of technology and applications," *Thin solid films*, vol. 513, no. 1-2, pp. 1–24, 2006. doi:10.1016/j.tsf.2006.03.033

[7] G. Greczynski, I. Zhirkov, I. Petrov, J. E. Greene, and J. Rosén, "Control of the metal/gas ion ratio incident at the substrate plane during high-power impulse magnetron sputtering of transition metals in ar," *Thin Solid Films*, vol. 642, pp. 36–40, 2017. doi:10.1016/j.tsf.2017.09.027

[8] G. Terenziani, I. A. Santillana, S. Calatroni, T. Junginger, and A. P. Ehiasarian, "Nb Coating Developments with HIP-IMS for SRF Applications," in *Proc. SRF'13*, Paris, France, Sep. 2013, pp. 627–630. https://jacow.org/SRF2013/papers/TUP078.pdf

[9] M. Mišina, L. R. Shaginyan, M. Maček, and P. Panjan, "Energy resolved ion mass spectroscopy of the plasma during reactive magnetron sputtering," *Surface and Coatings Technology*, vol. 142, pp. 348–354, 2001. doi:10.1016/S0257-8972(01)01071-4

[10] D. Lundin, P. Larsson, E. Wallin, M. Lattemann, N. Brenning, and U. Helmersson, "Cross-field ion transport during high power impulse magnetron sputtering," *Plasma Sources Science and Technology*, vol. 17, no. 3, p. 035 021, 2008. doi:10.1088/0963-0252/17/3/035021

[11] C. Maszl, W. Breilmann, J. Benedikt, and A. von Keudell, "Origin of the energetic ions at the substrate generated during high power pulsed magnetron sputtering of titanium," *Journal of Physics D: Applied Physics*, vol. 47, no. 22, p. 224 002, 2014. doi:10.1088/0022-3727/47/22/224002