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1 Aim of the experiment

In order to determine the maximum sustainable gradients in normal conducting RF powered particle beam accelerators operating at 11.424 GHz with extremely low probability of RF breakdown, the HCPAF group investigated the possibility of using the Mo coating method. Molybdenum films were grown by RF magnetron sputtering technique on glass and sapphire substrates at room temperature. The sputtering parameters were optimized specifically addressing the growth of oxygen free Mo layers. The characterization of the chemical properties of the coated film has been carried out at Diamond Light Source (UK) with the XANES (X-ray Absorption Near Edge Structure) technique.

2 Introduction

Technological advancements are strongly required to fulfill the demands of new accelerators devices with highest accelerating gradients reliability for the future collider [1)] and [2)]. An intense technological activity is therefore committed to making X-band accelerating structures, using different materials and methods.

In the frame of the collaboration with INFN-LNF/SLAC/KEK concerning breakdown studies about RF high gradient accelerating structures working at 11.424 GHz, an extensive R&D activity concerning molybdenum coatings is also in progress.

Materials with a higher fusion point seem to be good candidates to fabricate the accelerating structures working at 11.424 GHz with a higher accelerating gradient. A sintered Mo bulk brazed RF structure has been realized at LNF and tested at SLAC [3)].

The breakdown rate of the brazed Mo structure is higher than that of copper structures for the same RF parameters. From the investigation of the sintered molybdenum bulk brazed section some technological problems have been detected: the main issue is for sintered molybdenum bulk is the long time for machining the cavity, a maximum of 300 nm surface roughness using tungsten carbide tools, the gas contamination and an uneven loading stress in the brazed region [3)]. For these reasons we are investigating the possibility to grow Mo films on copper.

3 Sputtering technique procedure at the Thin film Laboratory of CNR (Institute of Complex Systems, ISC)

Mo thin films were grown by rf magnetron sputtering technique on different insulating substrates, such as Corning 7059 glass, Al2O3 (0001) and Al2O3(11-20), starting from a high purity (99.995%) Mo target [4)]. The sputtering system is a custom apparatus equipped with a turbo molecular pump backed by a dry scroll pump: the primary pump is used to rough out the chamber to a pressure low enough for use of a secondary turbo molecular pump. The use of a dry mechanical pump instead of an oil sealed mechanical pump avoids the oil back-streaming, thus improving the sputtered films quality, controlling the gas contamination. The apparatus is equipped with four targets (4" in diameters), four gas inlets and two sample holders; the films can be sputtered on cold samples or on hot samples (up to 500C). The sample holders move during the sputtering process at a

Background pressure	2 10^{-7} Torr
Substrate type	Corning glass; sapphire (0001) and (11-20); silicon (001)
Substrate temperature	20 C
Pre-sputtering pressure	4mTorr
Pre-sputtering power	100 W
Pre-sputtering gas	ultra pure Argon (23 sccm)
Sputtering pressure	4mTorr
Sputtering power	60 W (150W)
Sputtering gas	ultra pure Argon (23 sccm)
Film thickness	3000 $\AA$; 6000 $\AA$; 9000 $\AA$.

Table 1: *Mo film optimized sputtering parameters*

variable rate, in order to improve the film uniformity. Before each deposition, the target was pre-sputtered for 30 minutes in order to remove any surface contamination layer, being the sputtered film deposited on the shutter surface. The sputtering process was performed in ultrapure Ar gas atmosphere and the substrates were positioned on a cold sample holder. In order to optimize the sputtering parameters, two different sputtering powers were tested: 60 and 150 W.

A series of preliminary runs was made in order to select the sputtering parameters suitable for low oxygen Mo films. The optimized sputtering parameters are listed in the Table 1. The glass substrates were carefully cleaned before being put inside the chamber in an ultrasonic bath containing an hot aqueous alkaline solution and then were carefully rinsed by ultra-pure deionized water; finally the samples were dried by an Ar flux. Cautions were also used to clean the sapphire substrates which were housed individually and pre-cleaned in a class 10 room provided by the manufacturer. Two different sputtering RF power values, 60 and 150 Watt, were applied, corresponding to two different deposition rates (and obviously deposition time): the Mo films grown on glass were sputtered at 60 Watt, while the Mo films grown on Al2O3 (11-20) and Al2O3 (0001) were sputtered at 150 Watt. At present, preliminary investigations on the Mo films grown on glass reveal that the films have a quite low oxygen content and Mo films grown on sapphire substrates show an oxygen content lower than 5%. The different oxygen content may be due to a possible surface contamination from the glass substrates: although the high quality of the Corning 7059 glass substrates, an oxygen migration from the slide to the Mo film may be induced by the sputtering process, as a consequence of the locally increased temperature of the slide surface. Moreover, the lower Mo sputtering power used for the glass substrates and hence the longer layer deposition time increases the probability of film contamination from the residual gasses.

RBS (Rutherford Back Scattering) measurements were performed on Mo films sputtered on glass and sapphire and compared with simulations of a pure Mo film of equal thickness: the acquired spectra show only a 0.5% O_2 concentration on the films surface assessing the optimization of the sputtering parameters [5]. Structural and electronic properties were estimated by XAS spectroscopy. Data will be discussed in the next section. Moreover, samples resistivity measurements at room temperature as function of the frequency up to 20 GHz have been also completed.

4 Structural and morphological characterization of molybdenum coatings

Different methods are typically used to characterize the properties and the structure of metallic thin films or coatings [6]. To characterize our Mo coatings we used non-conventional methods. The first is an imaging technique with a high spatial resolution recently introduced, that involves

the use of a Focused Ion Beam (FIB) microscope [7)] to obtain morphological and dimensional information, the second is a spectroscopic technique: the X-ray Absorption Spectroscopy (XAS), used to investigate the Mo structure at the local level.

4.1 Focused Ion Beam (FIB) microscope

A FIB microscope can be usefully considered to characterize metallic coatings. This non-conventional microscopy technique now available has imaging and micromachining capabilities at the nm-μm scale, two characteristics extremely important and nowadays widely used in materials science. Actually, in addition to imaging, a FIB can be also used to prepare extremely thin and oriented crystal sections. Thanks to its versatility and spatial resolution, FIB was employed here to visualize with high spatial resolution the coating morphologies and the cross sections of these films, to measure the thickness of the Mo coatings. A typical FIB image of one of the Mo films grown on Al_2O_3 (sample B5) is shown in Fig.1. It refers to a film with a thickness of $\sim$ 615 nm. The Mo coatings investigated are reported in Table 2. The FIB characterization has been performed at the LIME laboratory of the Roma Tre University.

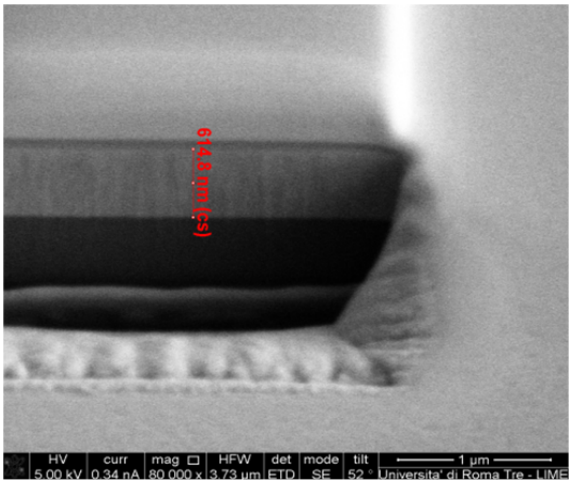

Figure 1: Figure 1 The FIB image of one Mo/Al2O3 coating (sample B5)

5 XAS (X-ray Absorption Spectroscopy)

The XAS (X-ray Absorption Spectroscopy) technique is a well-established method capable to perform a quantitative analysis of local structural properties such as geometry and coordination numbers in ordered and disorder systems such as coatings or interfaces. To characterize the chemical status of Mo atoms in our samples (see Table2), we performed X-ray Absorption Spectroscopy experiments at the Mo K edge. XAS experiments were carried out at B18, the Core XAS beamline of the Diamond Light Source (UK). This synchrotron radiation source operates at the electron energy of 3 GeV with $\sim$250 mA current, in the top-up mode. Data were collected using a double crystal monochromator equipped with two Si(111) crystals and coupled to a Pt coated mirror focusing radiation in a spot of $\sim$200x200 μm. Acquisition of Mo K-edge spectra has been performed in the continuous scan mode using a 9-element Ge detector with XSPRESS-II acquisition electronics in the fluorescence detection mode. Experiments have been performed both at normal incidence and at grazing incidence to enhance the signal associated to thin surface layers, and in different areas of the Mo coatings to probe the homogeneity of the investigated samples

Sample	Mo coatings	Thickness /nm[a]
A1	Mo/ Cu	630
A2	Mo/Cu	1300
B1	Mo/Al_2O_3	70-75
B2	Mo/Al_2O_3	130-140
B3	Mo/Al_2O_3	205-225
B4	Mo/Al_2O_3	310
B5	Mo/Al_2O_3	615
B6	Mo/Al_2O_3	1030

Table 2: Measured thickness of all investigated Mo coatings. a)measured with a Focused Ion Beam (FIB)

6 Results and discussions of XAS (X-ray Absorption Spectroscopy)

In Fig.2 we compared XAS spectra of different Mo coatings with a Mo metallic film. Spectra were normalized by fitting linear polynomials in the pre- and post-edge regions. Looking at the comparison of X-Ray Absorption Near Edge Spectroscopy (XANES) data between Mo coatings and Mo metallic film measured in the transmission geometry we may claim that all coatings have a slightly disordered structure. An observed energy shift comparing with the metallic Mo film indicates that all Mo coatings are negligibly contributed by oxygen. Furthermore, spectra are similar except for the sample with a thickness of 1300 nm, which shows a significant Mo oxide contribution, e.g., MoO_2 and/or MoO_3 [8].

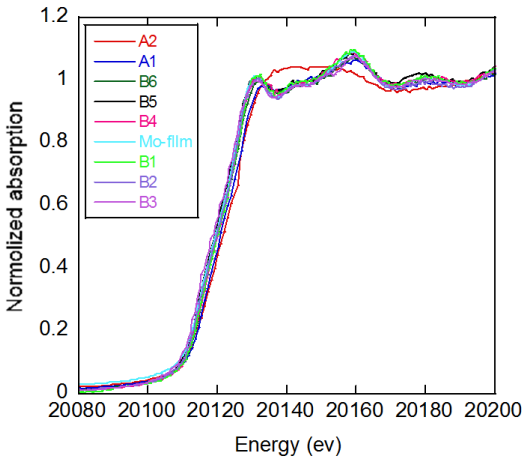

Figure 2: Mo K edge XAS spectra (info in Table 1)

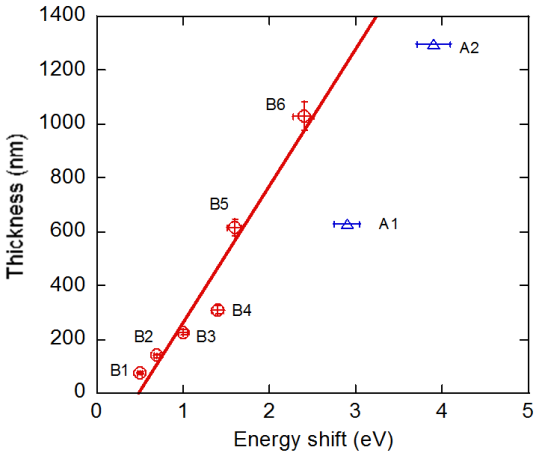

Figure 3: The linear behavior of the edge shift vs. thickness of Mo films on Al_2O_3. Coatings on Cu substrates are well outside the observed linear behavior.

To better analyze XANES spectra, we plot the edge energy shift relative to the metallic Mo film absorption edge versus the thickness of Mo coatings. For all samples the edge has been determined from the normalized absorption at the height corresponding to the value of 0.8. As shown in Fig.3, for samples grown on Al_2O_3 (B1-B6), the position of the edge moves linearly towards higher energies. The mechanism is possibly associated to a shift of the Fermi level increasing the

film thickness, while EXAFS data (not shown here) point out that the Mo-Mo distance of the main contribution decreases with thickness. Samples have not been annealed and for the thinner samples a clear distortion of the unit cell with the presence of a lower distance component occur.

For samples grown on Cu (A1-A2), the XANES spectra are slightly different (in particular for thicker samples) and the measured energy shift position shows that those samples are well outside the trend associated to the samples grown on Al_2O_3. This can be attributed to the expansion of the nest-nearest distance around Mo atoms caused by oxygen contributions [9].

7 Summary and future work

As shown by the experimental results we presented, the sputtering method is really a promising approach to obtain homogeneous Mo coatings increasing the performances of RF cavities working at high frequencies. Structural properties of these sputtered coatings have been determined by a combined analysis of FIB imaging and XAS spectroscopy [10]. We used a FIB microscope to visualize at high spatial resolution the morphology of these films and to accurately measure their thickness. XAS spectra were used to characterize the chemical state of Mo coatings, their local structure and the possible presence of Mo oxides. Data show that all coatings are made by metallic molybdenum with negligible oxygen contributions. The measurements have shown that modifying the thickness of the films both structural and electronics changes occur. While the Mo bcc structure close to the Mo/substrate boundary is naturally deformed, the Fermi level shifts to higher values. This has direct consequences on the transport properties of the coating material [11].

XAS spectroscopy is really a powerful method for coatings characterization not only because allows to identify the oxidation state but also because it may easily probe order/disorder composition in metallic coatings of different thickness. Other experiments have been planned at Diamond and a more detailed analysis of XAS data is in progress.

Because dedicated RF devices with such coatings have to be manufactured and tested at high power, a lot of work is in progress to improve both quality and performances of Mo coatings. A full characterization of conductivity properties and of the behavior under high fields is under way for these systems and will the subject of a forthcoming publication Moreover, to optimize coatings performances on film grown on copper, deposition with other metals, different manufacturing and characterization methods are in progress. This extensive characterization is required to improve the RF breakdown performance and a lot of work is really necessary to identify reliable procedures for the components of the next generation accelerating devices.

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