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2013 J. Phys.: Conf. Ser. 430 012091

(http://iopscience.iop.org/1742-6596/430/1/012091)

Journal of Physics: Conference Series **430** (2013) 012091 doi:10.1088/1742-6596/430/1/012091

Structural and morphological characterization of Mo coatings for high gradient accelerating structures

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Abstract. A series of Mo coatings grown on Al_2O_3 and Cu were prepared via sputtering method. XAS experiments were performed at the Mo K edge to characterize the coating structure and the chemical status of Mo atoms. From the XANES analysis we recognized that all Mo coatings on Al_2O_3 have a slightly disordered structure with a negligible Mo oxide contribution. Moreover, the chemical state is that of the Mo metal with a negligible oxygen contribution. Compared with Cu based materials, molybdenum is an attractive material for accelerator components and a reliable option for RF linear accelerating structures to achieve high accelerating gradients and low breakdown rates, two fundamental parameters for the next generation of linear accelerators.

Introduction

The next generation of linear accelerators is highly demanding in terms of accelerating gradients, one of the main parameter of linear accelerators since it limits the accelerator length and affects the power consumption. The experience shows that obtaining high gradients with a normal conducting structure requires operation at a relatively high frequency. As a consequence to make possible the construction of the future high-energy linear accelerators and X-ray Free Electron Lasers (XFEL) and minimize costs, advanced high frequency accelerating structures are required. Significantly improved manufacture technologies and surface characterization methods are fundamental issues to achieve advanced cavities with performances well beyond the existing copper based device now in operation [1]. Molybdenum is a Group 6 chemical element with the atomic weight of 42 g/mole. Pure molybdenum is characterized by a high melting point, a hot strength and a creep resistance. The pure element has a *Mohs* hardness of 5.5, accounts for the sixth-highest melting point (2623 °C) of any element and easily forms hard, stable carbides. Although it has one of the lowest coefficients of thermal expansion among commercially used metals, molybdenum burns just above 600°C [2]. As a consequence, molybdenum appears as an interesting material for accelerator components and a possible option for RF linear accelerating structures with low breakdowns at high RF power. In particular, if compared with Cu for applications in high gradient accelerating structures, the results of Mo breakdown rate are very promising [1]. A series of Mo coatings grown on Al_2O_3 with different thickness were prepared via the sputtering method at the Laboratori Nazionali di Frascati (LNF) and at ISC-CNR at Monterotondo (Rome). The deposited films are thick metallic disordered layers with different resistivity values. In this contribution, in order to investigate materials for future devices with improved RF performances, we will describe a characterization method of these different molybdenum coatings.

Experiment

Different methods are typically used to characterize the properties and the structure of metallic thin films or coatings. 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 [3] 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 atomic level.

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 nowadays extremely important and 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 evaluate the thickness of the investigated Mo coatings. A typical FIB image of one of the Mo films grown on Al_2O_3 (sample B5) is shown in Figure 1. It refers to a film with a thickness of ~ 615 nm. The thickness of the investigated coatings is reported in Table 1. The FIB characterization has been performed at the LIME laboratory of the *Roma Tre* University.

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 liquids, glasses, coatings or interfaces [4]. To characterize the chemical status of Mo atoms in our samples (see Table 1), 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 ~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 ~200x200 μm [2]. 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.

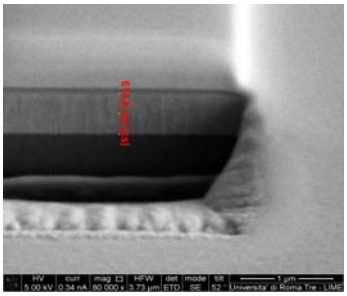

Figure 1 FIB image of the Mo/Al_2O_3 coating (B5).

Table 1 Measured thickness of all investigated Mo coatings.

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

[a]measured with a Focused Ion Beam (FIB)

Results and discussions

XAS (X-ray Absorption Spectroscopy)

In figure 2a 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 [5]. 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. From the comparison with the metallic Mo film, the observed energy shift indicates that all coatings have a negligible oxygen contribution. 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 [6]. To better analyze XANES spectra we plot the edge energy shift relative to the metallic Mo film absorption edge vs. thickness. 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 Figure 2b, for samples grown on Al_2O_3 (B1-B6), the position of the edge shifts 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 occurs. For samples grown on Cu (A1-A2), XANES spectra are slightly different (in particular for the 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. We explain this behaviour with an expansion of the nest-nearest distance around Mo atoms due to oxygen atoms [6].

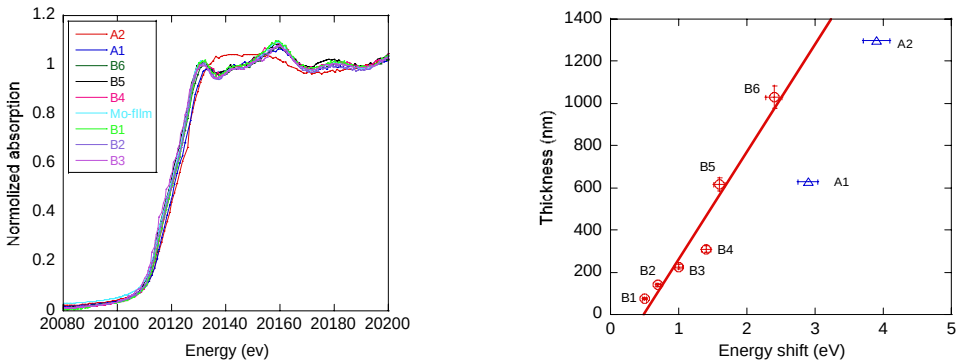

Figure 2 (a) Normalized Mo K-edge XANES spectra of coated samples (Table 1); (b) behaviour of the edge shift vs. thickness of Mo films on Al_2O_3. Cu samples are well outside the linear behaviour.

Conclusions

Large efforts to grow and characterize Mo coatings on Al_2O_3 have been done to optimize performance of coating materials required by the extremely demanding next generation of accelerating structures. In particular, in this contribution we present a XAS characterization of a series of Mo coatings obtained via the sputtering method. As shown by the experimental results we presented, the sputtering method is really a promising approach to obtain homogenous 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. 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. 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 [7]. 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. Because dedicated RF devices with such coatings have to be manufactured and tested at high power, work is still in progress to improve both quality and performances of Mo coatings. A full characterization of conductivity properties and of the behaviour 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 of the next generation of accelerating devices.

Acknowledgments

We thank the Diamond Light Source for access to beamline B18 (Proposal nt1984-1). One of us (X.Y.) gratefully acknowledges the *Joint PhD program* of the *Chinese Scholarship Council*. Thanks are also due to S. Bini and P. Chimenti for technical support.

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