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Characterization of thick conducting molybdenum films: Enhanced conductivity via thermal annealing

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ABSTRACT

Electrical resistivity measurements vs. frequency were performed on two molybdenum coatings grown by RF magnetron sputtering technique on a sapphire substrate at room temperature and annealed at different temperatures. Data show that the surface resistivity changes with the annealing while the conductivity of these Mo coatings can be almost doubled. In agreement with other researches, the results confirm that Mo coatings with an electrical conductivity comparable to that of copper can be obtained optimizing the thickness and the post-deposition annealing process. Morphological and structural investigations on Mo coatings were performed before and after annealing by synchrotron radiation X-ray diffraction and X-ray absorption spectroscopy to identify the chemical status of Mo, to probe the presence of different oxides and to control the multiphase nature of these metallic films.

1. Introduction

Molybdenum thin films and coatings can be grown with many different techniques: electron beam evaporation, sputtering processes such as magnetron sputtering, laser ablation deposition, and electrodeposition. They are used in different technological and industrial applications as in large-scale and very large-scale integration circuits [1,2], as back contact in advanced solar cell assemblies [3,4], as electrode materials [5] and more recently using monolayers of MoS_2 for non-linear optics applications by the enhanced properties of bidimensional, atomically thick coatings [6]. Moreover, a high-conductivity metallic coating made with Mo is also an interesting option for high performance accelerator components. Although the Mo conductivity is lower compared to Cu, looking at the results of the Mo breakdown rate the application in high gradient accelerating structures is promising [6]. Indeed, the next generation of linear particle accelerators is extremely demanding in terms of the accelerating gradient. At present, using a normal copper structure only operations at a high frequency allow obtaining relatively high gradients. To reduce the length and the power consumption of any future accelerator and, in particular, to minimize costs of future high-energy linear accelerators such as X-ray Free Electron Lasers (XFEL), the design and commissioning of advanced high frequency accelerating structures are mandatory. In particular, improved technologies and new surface characterization methods are needed for the next generation of cavities that have to be characterized by performances well beyond those of the present copper based devices [7].

Several high gradient accelerating structures operating at 11.424 GHz have already been realized and commissioned with excellent performances. However, tests performed at high power still show unpredictable electrical discharge phenomena that finally induce a perforation of the inner surfaces of these structures. Actually, in terms of the accelerating gradient, cavities operating at 11.424 GHz are still worse than soft structures made with OFHC copper. The phenomenon has to be deeply investigated and this is one of the main motivations to support the R&D on innovative materials and technologies, the only route to achieve the best performance of a new accelerating structure.

R&D activities on brazing, electroforming and Electron Beam Welding (EBW) procedures to realize high-performance structures of

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hard type with OFHC Cu and Cu–Zr are in progress. However, in order to increase the accelerating electric field, while reducing the discharge phenomena other studies look with interest to harder metallic materials such as molybdenum. Belonging to the Group 6 of the chemical element, Mo is characterized by a hot strength and a large creep resistance, has a Mohs hardness of 5.5, one of the lowest coefficients of thermal expansion among commercially used metals and accounts for the sixth-highest melting point (2623 °C) of any element. Moreover, because it burns just above 600 °C, Mo is an ideal target material for sputtering that sticks/adheres well to many substrates [8].

Although the solubility of oxygen in solid Mo is extremely low, the growth of molybdenum films is strongly affected by the presence of oxygen atoms. Because of the complexity of the phase diagram of the Mo–O system with many phases corresponding to oxide compounds with both transparent and insulating phases, e.g., MoO_3, or metallic phases such as MoO_2 [9], the different molybdenum oxides are multiphase systems of high-interest for both fundamental and technological applications.

An extensive literature is available on different Mo-based films and coatings and many researches aim to clarify the role of the internal mechanical stress, the impurity concentration, the texture or the surface roughness and their correlation with deposition parameters, such as pressure, DC power or temperature of the substrate [2,10–13]. In spite of the many researches and available references on the properties of Mo films, due to the presence of different oxide compositions, amorphous phases, microstructure defects and grain size it is still not clear which is the lowest achievable resistivity value of a relatively thick films such as those necessary in high gradient accelerating structures (~μm range).

In 2005, Schmidt and Seidel [14] investigated the influence of substrate properties (e.g., roughness characteristics and chemical composition) on the electrical resistivity of evaporated Mo thin films on silicon based substrates vs. film thickness (25–115 nm) and post-deposition annealing temperature up to ~900 °C. Their data showed a linear relationship between the electrical resistivity and the reciprocal film thickness with a lower resistivity limit around 80–90 μΩ cm, a higher value respect to that associated to the Fuchs–Sondheimer model (see Fig. 3 in Ref. [14]). The enhanced resistivity observed in samples annealed up to 600 °C was assigned to the increase of grain size, surface roughness, as well as to chemical compositions. More recently Rafaja et al. [15] discussed the contributions of point defects, dislocations and grain boundaries on the electron scattering in films having constant thickness of 500 nm describing the dependence of the electrical resistivity on the concentration of impurity atoms, stress-free lattice parameter, micro-strains and grains size. According to the kind of microstructure defects and to their density, this work demonstrates that different Mo films with a constant thickness of 500 nm have an electrical resistivity in the range 8–23 μΩ cm, a relatively low value, quite close to the resistivity of pure Mo (5.46 μΩ cm). This work also clearly discusses the dependence of the resistivity on electron scattering at local strain fields and from different impurity atoms, but neglects the possible presence of other phases. Conductive Mo films obtained by magnetron sputtering using highly pure Mo targets have also been reported by Glebovsky and Markaryans [16]. Using different procedures, starting from the resistivity of the Mo bulk target, they deposited films with a thickness of up to 1 μm with a resistivity in the range 7–35 μΩ cm. These experiments show the dependence of the resistivity of Mo films by the deposition rate and the presence of reactive gases in the deposition area. Significant reduction of the resistivity (up to 50%) in molybdenum films has also been obtained using a seed layer. A deposition of a few nm of a Ti–W layer allowed the Mo films to grow up to 300 nm with a resistivity of ~10 μΩ cm [17].

In the existing framework, a Mo coating characterized by these values of electrical resistivity is a possible option in RF accelerating structures working at high power and for many other technological applications. However, to optimize the performance and make it suitable for the surface of an accelerator cavity with improved characteristic and lifetime, the growth and the characterization of thick Mo films are mandatory. Here, we will present an a.c. transport characterization combined with structural, and morphological characterization of two selected thick Mo coatings deposited on a sapphire substrate and subjected to a post-deposition annealing at high temperature.

2. Material and methods

2.1. Samples preparation

Different samples of Mo films have been deposited at the Laboratori Nazionali di Frascati (LNF) using the sputtering method, in collaboration with the Istituto dei Sistemi Complessi of the National Research Council (CNR) using the RF magnetron sputtering [6,18,19]. In this contribution, we will focus on two Mo coatings grown by RF magnetron sputtering on Al_2O_3 (0001) starting from a high purity (99.995%) Mo target. The apparatus used is equipped with four targets with a diameter of 4 in., four gas inlets and two sample holders that can sputter on cold or hot samples (up to 500 °C). The sample holder can be moved during the sputtering process at a variable rate, in order to improve the uniformity of the film. Before each deposition, because the sputtered film is deposited on the shutter surface, the target was pre-sputtered for 30 min in order to remove any contamination layer. The process was performed with the substrate at the temperature of 20 °C. The base pressure in the deposition apparatus used for sputtering was ~2×10^{-7} Torr while during the sputtering process was 4 mTorr. The substrates were carefully cleaned before being put inside the chamber using ultra pure argon (23 sccm). The growth was performed in the Ar gas atmosphere with substrates positioned on a cold sample holder. The sapphire substrates were pre-cleaned in a class 10 clean room provided by the manufacturer, and housed individually. During the sputtering due to the increased temperature of the surface an oxygen migration towards the Mo coating cannot be ruled out. Information on optimized sputtering parameters and technical details of the procedure used to grow these Mo films are available in Ref. [18]. Two samples of 310 nm and 1030 nm thickness (identified in the text as BRN1 and BRN2, respectively) were deposited on substrates maintained at room temperature and selected for a tailored annealing procedure. This procedure is a standard method used to control the surface roughness, improve the structure or reduce the stress of a metallic film and control or reduce the grain size [20].

The two samples with an area of ~1 cm^2 and Mo films ~1 μm thick were sectioned in four almost identical parts. Two parts were maintained as references while the remaining two were annealed in vacuum for 1 h, the first at ~300 °C and the second at ~600 °C. The heating ramp used for both samples was ~2–3°/min. After the annealing, the samples were sealed in small plastic bags that were open before the resistivity measurements. As underlined above, the growth and the post-deposition annealing procedure are fundamental because they determine the morphological evolution of these polycrystalline multiphase films.

Among the many Mo oxide phases two are the most important: the molybdenum trioxide (MoO_3) and the molybdenum dioxide (MoO_2) [21,22]. Bulk MoO_3 is an insulating layered material, while MoO_2 is a metallic oxide, characterized by a rutile structure and an electrical resistivity ranging from ~90 to 200 μΩ cm., i.e., 16 to 40 times higher than the bulk metallic Mo (5.46 μΩ cm) [23] and at least 50 times higher than copper (~1.7 μΩ cm at RT). An assessment of the type and amount of oxides is then fundamental to interpret and possibly tune the transport properties of a thick multiphase Mo film or coating. To this purpose, in addition to the transport experiments, the samples were also characterized by X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) methods using synchrotron radiation.