Deposition and characterization of thin MoO$_3$ films on Cu for technological applications

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Introduction

One of the most studied research area in materials science is the investigation of the surface properties. Researches involving the growth and the characterization of films and coatings represent a continuously increasing subject of study, because they can be used to improve the surface properties of any solid material. Transmission, reflection and absorption of radiation, hardness, abrasion resistance, corrosion, permeation, electrical behaviour, etc. are just some of the characteristics of a material surface that can be improved by depositing a thin layer of another material. A classic example of the use of thin films is the change of the reflection properties of a coated lens.

By nowadays, through the deposition of a thin film (from tens of nm to hundreds nm) it is possible to achieve almost any desired surface property, just by changing the coating material, the deposition technique, the annealing and pre and/or post chemical treatments. Nanotechnology also can take benefit from the knowledge of thin film properties and many applications of nanoparticles or nanostructures have been improved thanks to the deposition of thin or ultrathin layers on such nanosystems.

The recent advances in thin film growth of transition metal oxides coupled with the presence in these systems of fascinating phenomena such as superconductivity, colossal magneto-resistance, metal-to-insulator transitions, etc. have triggered an enormous interest in correlated electron effects both for technological applications and fundamental science perspectives.

In this PhD research program, we focused on transition metal (TM) oxides. These oxides are extremely interesting systems that offer a wide range of applications. However, their properties still represent an immense and still largely unexplored research area.

Among the many TM oxides, we have studied thin films of molybdenum oxides, in particular the molybdenum (VI) oxide (MoO$_3$) deposed on a metallic Cu substrate. This insulating oxide is a layered system widely used as a catalyst, in battery electrodes, as electrochromic material, etc., but many of its properties
remain unclear, e.g., the origin of its large work function or its anomalous conduction properties. Indeed, the α-MoO₃, a natural van der Walls material when deposited as a thin layer (e.g., <300 nm) exhibits quite unique properties. Recently, the team headed by Weiliang Ma et al. showed also the presence of ultra-confined infrared polaritons propagating only in specific directions along thin slabs of this molybdenum oxide.

The thesis has been dedicated to growth and to characterize the properties of thin molybdenum trioxide films deposited on copper and to the optimization of the annealing treatment. High electric field tests have been also performed on molybdenum trioxide films using a THz free electron laser in the framework of the Italian Japanese bilateral program “Spettroscopia THz lineare, non lineare e risolta in tempo con sorgenti di radiazione di ultima generazione”.

The first chapter has been devoted to the description of molybdenum oxides and their applications. The second chapter describes the original setup, the development and the optimization of the vapor deposition process on copper starting from MoO₃ powders. In the second part of this chapter we describe the characterization of these films, and the results obtained by mechanical, structural, chemical and transport measurements.

The third chapter describes the annealing procedures applied to these thin films. Different thermal treatments have been considered and applied to increase the mechanical properties, the adhesion of the film on the copper surface and to guarantee the correct stoichiometry. With scanning electron microscopy, X-ray absorption and Raman spectroscopies, we were able to demonstrate that the optimized procedure allows ordering of the film, minimize the reduction of molybdenum atoms and the oxidation of the copper substrate.

The last chapter presents an original approach we used to apply a high electric field to the sample surface to generate a reproducible damage via breakdown phenomena. The mechanism is similar to what happen in RF accelerating cavities in the presence of high electric gradients in a random way.

In our method thousands of pulses of THz radiation produced by a free electron laser source irradiates the sample surface to test in well-defined location. This approach makes possible to generate and measure the surface damage of different
films in a reproducible way. We will report the damage analysis of several annealed and non-annealed MoO$_3$ films. The results show that even 100 nm of MoO$_3$ may significantly reduce the damage produced by the high electric gradient on the uncoated copper surface. Some models foreseen the exotic coupling of light and matter via particular collective excitations named polaritons, with electronic or structural properties different along different directions. Polaritons can propagate "anisotropically" along the surface of 2D materials, e.g., along the thin slabs of the 2D molybdenum trioxide. This mechanism may appear as a form of nanoscale confinement of the radiation and may explain the large reduction of the damage observed on the exposed surface of our films.

The conclusions summarize the main results, the possible improvements and the great perspectives offered by these films, in particular in all technologies where extremely high gradient have to be applied to metallic surfaces.
Chapter 1.
Characteristic of \( \text{MoO}_3 \)
Transition Metal (TM) oxides are among the most fascinating materials, showing an incredible variety of structures and properties [1-6]. They exhibit a wide range of physical states, with different properties ranging from insulating, semiconducting, metallic, superconducting and ferromagnetic. They also show large variations of the properties as a function of temperature, pressure and stoichiometry [7]. It is possible to find metallic oxides (e.g., MoO₂, RuO₂ and ReO₃), highly insulating oxides (e.g., MoO₃, BaTiO₃), and TM oxides that show a metal to insulator transition vs. temperature, pressure or stoichiometry (e.g., VO₂, V₂O₃, etc.) [4]. Actually, cuprate superconductors containing TM oxides are among the most studied systems in condensed matter physics [6, 8-12].

The most interesting features of TM oxides are associated to the electron correlation, induced by the strong Coulomb interactions among d electrons inside d-bands. As a matter of fact, while external s and p electrons interact strongly with adjacent atoms and external f electrons are tightly bound to the nuclei, d electrons may exhibit an intermediate behaviour, as they are not screened from the adjacent atoms by external core electrons. As a consequence, d electrons display both metallic properties as well as localized electron properties in TM oxides [4].

Thousands of physical/chemical processes [13] involve TM oxides, for examples in surface charge exchange phenomena, a critical issue that strongly depends on materials electronic structure and work function. As a matter of fact due to the high work functions and conductivity, some of these oxides are intensively studied as an anode and hole transport layer OLEDs and organic photovoltaics [14].

While the work function of metallic systems ranges from the minimum of 2.14 eV for the Cs to the maximum of 5.65 eV for Pt [15], TM oxide WFs range from relatively low values, e.g., ~3 eV for the ZrO₂ to large values (~7 eV) such as in V₂O₅ [16-17].

In addition to the high WF value, some TM oxides such as MoO₃ are wide gap insulator whose transport properties can be however modified by defects [14].

During the research activity of my PhD, I worked investigating different systems, from the development of thin film organic CVD cells, to the XANES characterization of disorder in high temperature superconductors and to the deposition of molybdenum trioxide films on copper substrates, to which I
dedicated the main part of the PhD program. For this reason, this thesis is focused on the MoO$_3$ thin films deposed on copper. To better understand the motivations and the objectives beyond this work, it is necessary to summarize the structure and the main properties of the molybdenum oxides.

**Molybdenum oxides**

Molybdenum is a very hard transition metal with one of the highest melting points. It has many applications in metallurgy forming hard alloys suitable for high temperature applications [13]. It exhibits oxidation states from -II to +VI and an electronegativity of 2.16 on the Pauling scale, one of the highest in metals. Because of this, a weak oxidation of molybdenum starts at 300° C with a maximum at temperatures above 600° C [18]. Molybdenum is an interesting element also because of its peculiar oxides. Due to the wide range of valence states, from +1 to +6, Mo oxides are available in various stoichiometries, i.e., from the strong acidic MoO$_3$, to the more conducting reduced MoO$_{3-X}$ oxides, down to the metallic MoO$_2$ system.

Molybdenum based oxides are amongst the most adaptable and functional optical and electronic oxides due to their unique characteristics and tuneable properties [14,17]. The main Mo oxides are molybdenum dioxide and trioxide, which are characterized by completely different structures and properties.

The lower stable oxide is the molybdenum dioxide, a metallic opaque solid where the formal oxidation state is Mo(IV) with the electron configuration 4d$^2$. As shown in figure 1.1, the MoO$_2$ oxide has a monoclinic distorted rutile structure (space group P21/c), similar to the TiO$_2$ structure [19, 20]. In the distorted octahedra of MoO$_2$ (figure 1.2), Mo atoms are located slightly off-axis, leading to two different Mo – Mo distances and bonding.
The complex nature of these bonds involves Mo electrons. The metallic behaviour is due to the delocalization of electrons in the conduction band. [19]

Molybdenum trioxide is a higher stable oxide with three different possible phases: the orthorhombic $\alpha$-MoO$_3$ phase, the hexagonal $h$-MoO$_3$ phase, and the monoclinic $\beta$-MoO$_3$ phase. Among these phases only $\alpha$-MoO$_3$ grows with the thermodynamically stable orthorhombic crystal structure, which is formed by a series of layers oriented perpendicularly to the [010] y-axis (figure 1.3). Each layer
contains distorted MoO$_6$ octahedra characterized by three different oxygen sites [20, 21].

\[ \text{Fig. 1.3 The MoO}_3\text{ layered structure showing the Mo atoms (blue) and the oxygen atoms (red) [21].} \]

\[ \text{Fig. 1.4 The MoO}_3\text{ distorted octahedra, with the Mo site (blue) and the surrounding oxygen atoms (red). The labels identify the three different oxygens.} \]

Formally, MoO$_3$ is a 4d$^0$ Mo(VI) insulator compound with a wide indirect gap of 2.82 eV. MoO$_3$ is also characterized by one of the highest work function [14]. It originates from two contributions: the O1 terminal lying outside the layers (figure 1.4) and the additional dipole layer due to the O-Mo composition on the external layer. The latter lowers the potential inside the structure. Indeed, in this structure the dipole is poorly screened, resulting in a large potential step, i.e., a high work function [20]. Despite terminated by an anion, the MoO$_3$ layers are neutral.
Many studies pointed out that the MoO$_3$ compound, which in its pure bulk form is insulator, may become a good conductor in presence of defects and oxygen vacancies inside the structure [20-23]. Because of the high work function and of the vacancies induced conductivity mechanism we decided to focus the research on the growth of transparent metallic MoO$_3$ films. In particular, triggered by the work of Greiner et al [17], where it is analysed the band structure of the MoO$_3$-metal interface, we started to investigated the interaction between thin molybdenum trioxide films and metallic substrates, such as copper. The MoO$_3$-metal systems have found applications in solar cells, batteries and OLEDs, but the interaction mechanisms between the metallic substrate and the conductivity properties of molybdenum oxide films is still not clear [19, 20].

**Fig. 1.5** The electrostatic potential of the MoO$_3$ surface slab showing the occurrence of a work function of 6.25 eV.

**MoO$_3$ thin films on copper**

Thin film coatings are used with different purposes in a wide number of applications. Thin layers of materials allowed to develop filters or to create reflective surfaces on optical elements. They may increase the insulation or the conduction, protect the substrate or the first atomic layers below the coatings from radiation or chemical agents. Films may have different thicknesses, ranging from
few Å to several microns. There are many deposition methods and the optimal method for a given application depends on the purpose of the deposition, the surface makeup of the substrate, the adhesion requirements, the properties, the thickness desired, etc. [24].

Thin film coating is the one of the main tool used in the development of new surface devices or to respond to new technological demands. Indeed, the surface properties of a material, ranging from mechanical to electronic, can be tuned thanks to a specific coating, which can help giving rise new and unexpected surface properties [25-26].

As outlined above we focused on the MoO$_3$/Cu system. The development of a deposition technique to grow MoO$_3$ films on copper substrates, and their characterization with a wide range of mechanical, transport, spectroscopic and imaging techniques has been the main objective of the research.

Mechanical and structural methods were necessary to characterize the coating nature and the quality of both films and substrates. Annealing treatments, and the structural investigations of these films allowed to investigated and characterize adhesion and hardness before and after the annealing. Spectroscopic and transport measurements were performed to understand the different electronic structures and to monitor the conductivity as a function of the thickness and of the procedures applied to these films.

Applications

Molybdenum oxide films are widely studied and applied in many different fields [13, 14]. However, the interest on this natural van der Waals material has come very recently to the attention due to the report of anisotropic polariton propagation along its surface with elliptic and hyperbolic dispersion, and with wavelengths up to 60 times smaller than the corresponding photon wavelengths [27]. Different types of polaritons have been observed in this material tuned by electric fields or by material thickness [28].
The high work function is one of the additional extreme features of this system and the induced high conductivity observed in thin transparent films generated a large interest, due to the lack of high WF metallic surfaces [13].

The tuneable properties of non-stoichiometric MoO$_{3-X}$ point out the possibility to integrate these oxides inside 2D heterostructures and devices (figure 1.6). For example, 2D MoO$_3$ could be used to hole-dope adjacent materials, lowering the contact resistance to form 2D p–n junctions [23]. The tuneable electronic properties of sub-stoichiometric MoO$_3$ could be also used for developing a variety of novel electronic and optical devices such as mid-IR and near-IR optoelectronics [29].

![Figure 1.6](image)

**Figure 1.6** Resistance of MoO$_3$ films as a function of the electron dose. With an electron beam the conductivity increases generating oxygen vacancies inside the film [26].

One of the most stimulating applications of TM oxide films is the R&D of compact accelerating structures made in copper, to be optimized for the next generation of accelerators. This R&D is triggered by the demand to run accelerators with the highest accelerating gradients [30].
Fig 1.7 Simplified graph showing the trend of the accelerators technology as a function of the field frequency (horizontal scale) and the electrical field gradient. [30].

Thanks to the MoO$_3$ properties, copper devices coated with this oxide, could be harder, transparent and metallic and more resistant to discharge phenomena, all requirements needed by the future generations of accelerators as showed in Figure 1.7. The WF of MoO$_3$ is high and is not significantly altered by the copper substrate. This characteristic is also fundamental to optimize the properties of accelerating RF devices, since it allows to reduce the surface field emission in the presence of high electric fields.
Chapter 2.
MoO$_3$ films on copper
In this chapter, we will describe the evaporation method used to deposit ultrathin and thin films of MoO$_3$ oxides for different applications on flat and curved surfaces of dimensions from mm to few cm.

The system we assembled allows to deposit MoO$_3$ and other TM oxides on different substrates with different thickness and performing different thermal treatments in vacuum. At first, to study and optimize the preparation of MoO$_3$ coatings on large and curved surfaces, useful in many applications, we selected the vapor deposition technique, i.e., the evaporation of TM oxide powders and their deposition on a low roughness substrate. In the next we will describe the method we used to evaporate molybdenum trioxide on metallic surfaces like copper. The main goal was to evaporate in a controlled way homogenous films of MoO$_3$ on areas up to 200 mm and in a range of thickness from ~30 nm up to ~1 µm. Indeed, to deposit thicker films or coatings with an optimal adhesion with the substrate, other techniques have to be considered [31-32].

The design and the optimization of a dedicated evaporation chamber will be described in the first part of this chapter. In the following are presented the material properties and the procedure to obtain different type of molybdenum oxide samples. These films have been characterized with different techniques to probe electronic, structural and morphological properties. One section is dedicated to the description of the different experimental methods we used while at the end the chapter we will present and discuss the results obtained.

**MoO$_3$ films: physical vapour deposition**

The thermal evaporation is one of the simplest deposition techniques used to deposit ultrathin, thin and relatively thick films [33]. It is based on the sublimation in vacuum by the Joule effect, reaching a temperature superior to the evaporation temperature of the material. In this way, the vapor generated will be condensed on a substrate positioned in front of the source [34]. The evaporation must take place
in vacuum at the pressures of $10^{-4}$-$10^{-6}$ mbar, since at this vacuum pressure the free mean path of sub-nanometer particles is of the order of meters [34].

In our case, molybdenum trioxide powders placed in a tungsten crucible were heated up to 600° C [35] by a current, flowing through the crucible, ranging between 70 A and 90 A. Due to its high melting temperature (>3400° C) the crucible is not affected by this temperature.

In the vacuum chamber, the vaporized MoO$_3$ reaches almost undisturbed the substrate. In fact, oxide particles travel according to a straight path between the source and the substrate (line-of-sight). However, while the film is growing layer by layer this method does not allow to control strain. Indeed, this parameter may greatly affect mechanical and electrical properties of the evaporated film [36].

The uniformity of the deposition increases with the distance between the evaporation source and the surface, due to the anisotropic nature of thermal evaporation technique [34]. Moreover, working at a longer distance it is possible to reduce the radial heating of the source that may affect the deposition process and the film structure.

Two evaporation setups were assembled, the first with a small chamber and the second adding to the chamber a second volume, which also allow the annealing of the evaporated films.

The first high vacuum (HV) evaporation setup was based on an 8-ways stainless steel chamber with 2 DN160, 3 DN100 and 3 DN40 CF flanges. The vacuum system was equipped with a Leybold TD20 turbomolecular pump connected in series with a Trivac NT10 rotative vacuum pump. This system was connected to the HV chamber through a metal valve, which allows isolating the HV chamber. As shown in Figure 2.1a, this HV setup is made by two volumes: the bottom dedicated to the thermal evaporation and the top devoted to the deposition control and annealing. The crucible for the evaporation is in the middle of the chamber (see Figure 2.1b), as far as possible from the substrate, but still in a position easily accessible using the quick access door. The tungsten crucible was fixed between two 9 mm copper feedthroughs connected to the AC current generator. The tungsten crucible is a semispherical vessel where powders are deposed in the proper amount (see Figure 2.2a). The vacuum outlet is on the side of the HV
chamber and the quick access door allows easily to mount the substrate in the evaporation position, to fill the crucible with powders and, later to extracts the evaporated film.

![Figure 1](image1.png)

**Figure 1.** (a) Photograph of the HV chamber dedicated to the evaporation with the quick access door in the foreground; (b) the scheme of the first HV chamber with its main components.

The clean substrate to evaporate is placed inside the HV chamber upside down, with the deposition area facing the crucible (Figure 2.2b), above it and at the distance of ~130 mm. The aluminum holder with the substrate is fixed on the upper flange, and the sample is inserted through two slits.

The flow is controlled by a rotating shutter, which allows stopping or letting pass the vapor flux evaporating from the crucible. This is made by a manual actuator coupled to an aluminum mask that shields both sample and quartz balance from the deposition.

![Figure 2](image2.png)

**Figure 2.** Photographs of the main components installed inside the HV chamber. The tungsten crucible filled with MoO$_3$ powders (a) and the copper substrate on top of the holder (b).
If needed, the mask may only cover the substrate, allowing the vapor to hit the quartz balance to evaluate the evaporation rate. This layout is used to calibrate the process before starting the exposition of the substrate. The Inficon XTC quartz balance mounted near the substrate holder at about the same distance from the crucible, monitors in real time the deposition rate on the substrate.

The vacuum pressure inside the chamber is measured by the Varian BA2C ionization gauge. It monitors the vacuum pressure before, during and after the evaporation procedure. The fixed distance (~130 mm) between the crucible and the substrate holder is the main limitation of this setup that does not allow evaporating large size substrates. Moreover, in this first HV layout was not possible to perform any controlled annealing procedure after the evaporation. The second HV layout and its internal setup overcame this issue. The first HV chamber was expanded along the vertical, shifting the substrate holder and the quartz balance in a second volume on top of the first one (see Figure 2.3).

In this second layout, the crucible position is the same, but the increased distance between the substrate and the crucible allows evaporating wider areas increasing at the same time the homogeneity of the deposition [37].

![Image](image.png)

**Figure 2.3** (a) Photograph of the second HV chamber used for the evaporation; (b) the layout of the new HV chamber with its main components.
As a matter of fact, while for the first setup that allowed to evaporate areas up to ~200 mm of diameter the estimated thickness difference was ~40% between the center and the edges, with a three times longer distance as in the second layout, the difference was reduced more than six times down to ~6%.

A penning manometer Alcatel FA101 was also added to measure the internal pressure, a fundamental parameter to control the pressure during the deposition. Because of the longer distance, the shutter arm was widened and the vacuum outlet was modified with a stainless steel T-shaped connector with a gas inlet to allow evaporation and annealing procedure with different gases.

The copper substrate

The modern life and the related technologies are enabled by the use of many materials such as metals or semiconductors. Many technologies work very well, largely because the used materials match the demands. However, the technology is significantly improved in the last 2-3 decades as performances of materials and devices increased. However, many materials involved in the modern technologies have no potential substitutes for their major uses and the search for alternatives or improvements are becoming day by day more important. As an example, among the many metals used in the industry and in the technology, copper (and gold) are not yet considered critical, not certainly because of lack of importance, but because supply risks at present are considered low [38]. If shortage of these metals will occur, a better use of these materials have to seriously considered in many applications. In the case of copper, a strategic material for the R&D of RF cavities and other accelerating components [39], this is not yet happened, but all researches trying to improve the copper-based technology are of particular interest. [40-41]

As already discussed in the introduction we focused on the copper-MoO$_3$ system for many technological applications, and in particular to improve performances of high voltage RF cavities for the future accelerators.

The copper substrates considered and used in this research are the typical material used in RF cavities: polycrystalline and oxygen-free copper (OFC) or oxygen-free
high thermal conductivity (OFHC) copper, a high conductivity copper alloy that have been electrolytical refined to reduce the level of oxygen to 0.001% or below. In particular, for many experiments and characterizations we used flat substrates with typical dimensions: 10 mm x 10 mm with a thickness of 5 mm, 15 mm x 15 mm with a thickness of 1.5 mm and 30 mm x 30 mm, 5 mm thick. All copper samples were polished down to a roughness ~30 nm RMS (or better) to obtain low roughness evaporated films.

Before the deposition, two different treatments were carried out on the substrates. The first cleaning process used two different types of solvents: acetone and isopropanol to remove grease and any residual left by the lapping procedure. After, to remove surface impurities, the substrates were placed inside an ultrasonic bath with MilliQ bi-distilled water and kept for about ten minutes.

The evaporation procedure

With the substrate mounted inside the chamber, after the crucible is filled with the MoO$_3$ powder, the vacuum system is switched on, first with the rotary pump, which drives the vacuum pressure to $10^{-2}$ mbar, then the turbomolecular pump lowers the vacuum pressure inside the chamber down to $10^{-5}$ - $10^{-6}$ mbar. Once the evaporation pressure reaches $\sim 3 \cdot 10^{-5}$ the power supply that heats the crucible is turned on. After, the current is slowly increased up to 60 A, and maintained to this value for 2-3 minutes, until the temperature reaches $\sim 400^\circ$ C. The current is then increased to the steady-state value of 75 A. Since there is no control of the temperature of the crucible the method we used to evaluate the temperature of the powders is the light emitted when the crucible is heated, and the evaporation rate is measured by the quartz balance.

When the temperature of the crucible reaches $\sim 550^\circ$ C the emitted radiation falls in the visible, with a characteristic bright orange color as shown in Figure 2.4. Although this method is qualitative, it is quite effective and the comparison with the deposition rate of the material measured with the quartz balance confirms that the evaporation starts at this temperature.
Once achieved “stable” evaporation conditions, the shutter is open starting the deposition of the molybdenum trioxide vapor on the substrate. Actually, the high current (>70 A) used to heat the crucible induces a not negligible heating of the copper rods and also of the chamber wall, which may affect in particular the homogeneity of thick films that require longer evaporations times. The heating of the rods and of the wall lead to an increase of the vacuum pressure, due to the higher molecular desorption rate from the internal wall of then chamber. Then, maintain a high vacuum is an important requirement to stabilize the process. At variance, a low vacuum reduces the mean free path of the vapor molecules and enhances the probability that water molecules, carbon and other impurities can be deposited on the substrate and inside the film during its growth. To overcome this problem, we installed an external system to cool by means of an air jet the current feedthroughs. This solution allows maintaining the temperature of both contacts and chamber wall just above the room temperature. The cooling system, stabilizing the temperature of the crucible avoiding the increase of the resistance of the rods, makes the evaporation process stable and reliable. At the end of the evaporation, the power is switched off and after about ten minutes, the crucible has cooled down.
The HV chamber is brought to the atmospheric pressure and the sample is maintained in air without any further treatment after the extraction. The MoO$_3$/Cu samples are characterized by a bright colored surface. The color changes with the thickness, e.g., the coating ~100 nm thick has a gold shade while coatings 200-300 nm thick have green shades (figure 2.5) [42].

**Characterization methods**

This section is devoted to the characterization of different MoO$_3$ films deposited on copper substrates with different methods. We will present and discuss the mechanical, morphological, chemical, structural and transport properties of MoO$_3$ coatings deposited on copper without any additional treatment. The characterization of these properties is fundamental to understand how these films can be used to improve the technology in which they are used or could be involved [14].
The characterizations we performed on these films can be classified in four categories:

- morphological, in which the deposition and the homogeneity of the film are studied;
- mechanical and structural that focus on the adhesion on the substrate and the presence of ordered or disordered phases;
- spectroscopic, which return physical and chemical properties;
- transport measurements, to probe the electrical properties when these oxide films are growth on a metallic substrate like copper.

### Morphology: Profilometer, AFM, SEM and STM images

Due to the unknown nature a priori of any deposed film, we used a wide range of techniques with a spatial resolution that goes from the mm down to the Å range to explore the morphology from the meso-scale to the nano-scale.

At first we started with a profilometer to measure the real thickness of the film and the roughness and, to confirm the calibration of the deposition process. The Scanning Electron Microscope (SEM) gives us an image of the film down to the micron scale. With the Atomic Force Microscope (AFM) and the Scanning Tunneling Microscope (STM) we were able to zoom to submicron domains of the film and to better evaluate morphological parameters and the uniformity of the deposition.

The profilometer is a very simple and effective tool to measure the surface profile along selected lines. This is a wide range instrument capable of probing profiles with structures from 10 nm to 1 mm. The instrument is based on a scanning diamond tip with a radius of ~20 nm, which is placed gently on the sample surface and then moved parallel to the surface with a constant contact force. The operational modes and the technical characteristics of the profilometer KLA-Tencor Alpha-Step 500, are reported in appendix.
Practically, the height variation of the stylus having a vertical resolution of ~5 nm is transformed in an analogic signal by the gauge system.

For calibration and other characterizations, we used a more precise instrument: the atomic force microscope (AFM). This microscope working in air allows collecting morphological images of any type of film without the surface preparation.

The AFM microscope consists of a cantilever that interacts with the surface while moving. The working principle is similar to the profilometer, but an AFM has a higher precision. It can work in the contact and non-contact mode, depending on the type of measurement to be performed. It provides a “real” three-dimensional map of the surface sample and not a two-dimensional projection as for other microscope images. The working and technical characteristics of the VEECO D3100 microscope are reported in appendix. It collects maps with the Nanoscope IIIa controller operating in the Tapping® mode. As a probe we used a silicon tip with a 5 nm radius working with a constant nominal cantilever force of 40 N·m\(^{-1}\).

The electronic scanning microscope is an instrument that allows to reconstruct the image of the sample surface using an accelerated electron beam. It is able to detect secondary electrons and backscattered electrons to generate 2D images. The operational and technical characteristics are presented in appendix.

Several images both of the copper substrate and of the MoO\(_3\) films with different thicknesses have been collected at different magnifications with the MINI-SEM SNE-3200M. This microscope, operates at an accelerating voltage ranging from 5 to 30 kV, has a maximum resolution of 15 nm and a magnification factor up to 6\(\cdot10^4\).

The Scanning Tunneling Microscope (STM) is similar to the AFM, but works in vacuum measuring the current between the probing tip and the surface. The STM may reach the highest spatial resolution: a lateral resolution of the order of the Å and a vertical resolution of the order of tenths of Å. The instrument working principles and technical characteristics are reported in appendix.

STM maps of not annealed films of different thickness were collected under ultra-high vacuum conditions (7.5\(\cdot10^{11}\) mbar) at room temperature using the Omicron-STM system (Omicron) with an electro-chemically etched tungsten tip (99.9%
purity, Goodfellow GmbH). I-V resistivity measurements were collected in the constant current mode and a rigid plane subtraction was applied to all images. The morphological characterization of MoO$_3$ films deposited on copper started with the SEM microscopy. Images were analysed to distinguish the surface homogeneity of MoO$_3$ films of different thickness.

As shown in Figure 2.6, SEM images reveal a uniform coating with no crystalline domains at the micrometer scale. Areas with defects were also detected in these films, e.g., domains where the coating is no longer in contact with the substrate (figure 2.6b). This type of defect is due to the softness of not annealed films that exhibit also a weak adhesion with the substrate.

The long-term stability issue was also investigated and SEM images showed that films left in air, after ~6/8 months show numerous small damaged areas and exfoliation regions (figure 2.6c).

As written above, the deposition rate and the accumulation were measured during the evaporation with a quartz balance placed near the sample. This deposition rate has been calibrated by measuring AFM maps. As shown in figure 2.7, the calibration was performed collecting a map in the region where, due to the weak adhesion, the film was removed from the copper surface. After, we selected an area (the grey rectangular region in figure 2.7) and the software, after a slope correction of the surface, calculated the average profile. From the accurate
evaluation of the profile step, the calibration factor for the quartz balance was obtained.

Fig. 2.7 AFM map (left) of a 100 nm thick MoO$_3$ film deposited on Cu. The step profile (right) was obtained averaging all curves in the grey area of the map.

To better reconstruct the morphology, we show in Figure 2.8 an AFM map taken at high resolution on the same 100 nm MoO$_3$ film.

Fig. 2.8 AFM map (left) and 3D (right) morphology maps of a 2x2 µm$^2$ area of the 100 nm thick MoO$_3$ film deposited on Cu. In the panel (b) on the bottom left, is shown the vertical profile measured along the green line in panel (a).

The image points out a homogeneous coating with an average grain structure of ~50 nm, slightly greater than the mean free path of copper (~40 nm), a value that may be correlated with the transport properties of this film [43]. From the AFM map, we may calculate also the root mean square of the roughness ($R_q$), defined as:
\[ R_q = \sqrt{\frac{1}{L} \int |Z(x)|^2 dx} \]

where \( L \) is the length of the analyzed profile and \( Z(x) \) is the function that describes the profile [44]. This surface parameter is more sensitive to peaks and valleys than the average roughness. The analysis of the profile (figure 2.8b) corresponding to the green line on the map in figure 2.8a returns a roughness value of \( R_q = 2.9 \pm 0.1 \) nm. The profile of the section in Figure 2.8b also shows that the peak-valley excursion is <15 nm, which explains why SEM maps are not able to resolve the grain texture.

Finally, STM images were collected also on the Cu substrate and compared with the 30 nm MoO\(_3\) thick film on Cu.

**Fig. 2.9** STM topography of an area 2x2 \( \mu m^2 \) (left) and 1x1 \( \mu m^2 \) (right) on the Cu substrate showing diagonal stripes, probably due to the lapping procedure.

**Fig. 2.10** STM topography of 1x1 \( \mu m^2 \), 0.5x0.5 \( \mu m^2 \) and 0.25x0.25 \( \mu m^2 \) areas on top of the 30 nm thick MoO\(_3\) film.
As shown in figure 2.9 elongated stripes ~200 nm wide, probably due to the lapping procedure can be recognized on a copper substrate having a roughness $R_q \approx 30$ nm. In the thinnest MoO$_3$ film (30 nm) the average roughness measured by the STM is ~4 nm (figure 2.10).

Indeed, in RF devices, tips and structures at the surface may be at the origin of breakdown phenomena and, for this reason RF devices require the highest surface quality and, in particular, an extremely low roughness [40, 41].

From morphological tests all MoO$_3$ films appear homogeneous with a grain-like structure of ~50 nm and a roughness of ~3 nm. Compared to other techniques as CVD or sputtering [45, 46], and considering also that we used a substrate with a ~30 nm roughness, the measured roughness of these films is lower.

**Mechanical properties: nanoindentation**

The nanoindentation, technique introduced by Oliver and Pharr in 1992, is nowadays a worldwide recognized method, widely used to characterize specific mechanical properties of a sample, such as the elastic modulus and the hardness at micro and nanoscale [47-49].

This is a mechanical test in which the indenter, whose geometry and mechanical properties are supposed perfectly known, is put in contact with the surface to probe. The NanoTest™ (Micro Materials) indenter was used to measure our films. To operate, the force was controlled by varying the intensity of the current of the electromagnetic actuator while the displacement was measured by a three plates capacitive sensor with two plates fixed and one connected to the indenter. Varying the distance of the penetrating tip, the capacity of the two plates changes and the associated displacement of the probe can be measured with a nominal spatial resolution of 0.01 nm. The instrument working and other technical characteristics are reported in appendix.

The setup we used has two probes: one diamond spherical tip with a diameter of 25 μm and a Berkovich three side diamond tip with a radius of 0.5 μm. The spherical tip was used for the softer not annealed films. In this latter case, we need
a more delicate tip with a relatively large surface and a reduced penetration. Moreover, due to the thickness of these films we always had to work at low loads, i.e., in the 0.5 - 5 mN range.

The load–displacement hysteresis (figure 2.11) were analyzed in order to measure the hardness and the elastic modulus. We measured MoO$_3$ films of thickness: 100 nm, 200 nm 300 nm and 400 nm. For these films, the indentation force was limited to 3-5 mN to indent only the coating and avoiding effects on the copper substrate.

![Load-depth hysteresis curves](image)

**Fig. 2.11** Load-depth hysteresis curves of the 100 nm thick MoO$_3$ film (red) and of the Cu substrate (black) collected with a 25 μm spherical tip. Left and right arrows show when the tip sinks into the surface and when it is pulled out.

However, this very low force causes a high noise and a large standard deviation. In figure 2.11 is compared the load-depth test of the 100 nm MoO$_3$ film on copper and of the substrate. The figure points out the two steps of the indentation process. The first step when the tip enter inside the surface (left arrow) and the second when the tip is released (right arrow) showing a clear displacement due to the plastic deformation of the sample.

In table, 1 are reported all hardness and reduced modulus parameters measured with the spherical diamond tip, on the samples and on the copper substrate. The hardness value obtained from multiple tests on these films is similar to that of the copper substrate. Indeed, within the uncertainty of the measurement both parameters of these MoO$_3$/Cu films are not distinguishable from the copper substrate.
Table I. Hardness $H$ and reduced modulus $E_r$ of the Cu substrate and of three different MoO$_3$/Cu films. Each value is the average of a set of 25 tests ($\sigma$ are the related standard deviations).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H$ [GPa]</th>
<th>$\sigma_H$ [GPa]</th>
<th>$E_r$ [GPa]</th>
<th>$\sigma_{E_r}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.43</td>
<td>0.26</td>
<td>134</td>
<td>18</td>
</tr>
<tr>
<td>100 nm MoO$_3$/Cu</td>
<td>1.32</td>
<td>0.43</td>
<td>138</td>
<td>27</td>
</tr>
<tr>
<td>300 nm MoO$_3$/Cu</td>
<td>1.47</td>
<td>0.32</td>
<td>136</td>
<td>20</td>
</tr>
<tr>
<td>400 nm MoO$_3$/Cu</td>
<td>1.47</td>
<td>0.42</td>
<td>118</td>
<td>13</td>
</tr>
</tbody>
</table>

The hardness is almost independent by thickness, while the reduced modulus slightly decreases (10-15%) increasing the thickness up to 400 nm. Actually, this film preserves the mechanical properties of copper including the hardness. To eventually increase the hardness and fix the adhesion problems detected in SEM images, we developed an annealing procedure that will be described in the next chapter.

**Structural properties: X-ray diffraction**

X-ray diffraction (XRD) technique is a perfect method to investigate the crystal structure of solids and surfaces. It is certainly the most used techniques to characterize crystalline and ordered samples. When a monochromatic X-ray beam interacts with the atomic structure of the sample, ordered atoms diffract x-rays and a constructive or destructive interference pattern is observed. The characteristic angle dependent interference pattern constitutes the X-Ray Diffraction spectrum. The Bragg’s law $2d \sin \theta = n \lambda$ is used to obtain the lattice parameter of the sample measuring the peak diffraction angle for a fixed X-Ray wavelength. The measured set of diffraction peaks allows to identify the arrangement of the atoms and the distances among reticular planes, i.e., the crystal structure and the material. The main limit of this technique is the need of a long-range order so that highly
disordered or amorphous materials and liquids do not generate diffraction patterns.

XRD experiments were performed using the Seifert MZ IV diffractometer with a Cu anode operating at 40 kV and 30 mA. A Ni filter was used during the measurements performed in the standard θ-2θ Bragg-Brentano geometry.

![Diagram of X-ray diffraction setup](image)

**Fig. 2.12** The schematic layout of the θ-2θ Bragg-Brentano geometry used for XRD measurements using a X-ray conventional source.

In this configuration showed in figure 2.12, the detector scans the angular range (θ) simultaneously with the detector (2θ), which collects the specular reflected X-ray beam from the sample. XRD patterns have been collected on not annealed films with a thickness ranging from 30 nm up to 1 μm.

![XRD Patterns](image)

**Fig. 2.13** Comparison of the XRD patterns of the 50 nm thick MoO₃ film (black) and of the 100 nm film (red). Only the two peaks associated to the diffraction from the copper substrate are detectable.
The comparison of XRD patterns of the 50 nm and 100 nm MoO$_3$ films displayed in figure 2.13 points out the lack of molybdenum trioxide peaks and only copper diffraction peaks from the substrate appear. XRD patterns of these not annealed films points out the presence of disordered oxide phases. The result will be confirmed by the characterization obtained by XAS, Auger and Raman spectroscopy.

**Spectroscopic characterizations: Raman, AES and XAS**

Spectroscopic characterizations have been performed with Raman spectroscopy, Auger Electron Spectroscopy (AES) and X-Ray Absorption Spectroscopy (XAS), different radiation probes that analyze different electronic dynamics. The results allowed to better understand structural and electronic properties of these thin films.

The Raman effect is a physical phenomenon of light diffusion discovered in 1928 by Chandrasekara Venkata Raman. It arises from the observation of the diffusion of radiation by a material. In this process we observe two components: one with the same frequency of the incident radiation (Rayleigh scattering) and one at a different frequency (Raman scattering). The difference between the frequency of the incident and the Raman scattering is related to the chemical structure of the investigated material [50]. The spectrometer and its technical characteristics are described in appendix.

Raman spectroscopy (and imaging) is now widely used in the study of materials in all phases: solid, liquid and gas. It is a fast and substantially non-damaging technique, which does not require a particular preparation of the sample to be investigated.

The coupling of a Raman spectrometer with an optical microscope extends the possibility of this technique. Indeed, with a Raman microscope is possible to select a small region, down to few $\mu$m$^2$ to be probed with the laser spot. A Raman
microscope allows investigating defined areas obtaining detailed chemical/molecular and structural information at a micrometer level (typically the size of the laser spot) [50, 51]. Portable Raman systems and handheld sized devices have also been developed. Two different Raman setups were used to characterize our films: the BW-TEK portable Raman and the high resolution JASCO 5100 Raman microscope. The BW-TEK Raman system is the BAC151B confocal microscope working with a red laser at $\lambda=784.92$ nm. Its maximum output power is 490 mW with a maximum energy resolution of $\Delta E = \pm 1.5$ cm$^{-1}$ and a laser spot of $\sim 80$ µm. The NRS-5100 is a high resolution Raman microscope that combines the flexibility of multiple detectors and multiple laser sources (figure 2.14). Its high-resolution color CCD viewing system with synchronized image capture and spectral measurement enables accurate sample identification and positioning. The maximum resolution is 0.4 cm$^{-1}$ and the measurement range from 50 cm$^{-1}$ up to 8000 cm$^{-1}$. It allows 2D mapping, z profiling and 3D mapping of the sample with a spatial resolution of 1 µm with the 100x magnifying optic.

The Auger Electron Spectroscopy (AES) is a well-know and widely used characterization technique based on the analysis of the emitted Auger electrons. The AES process can be summarized in three main steps: the ionization, the electron emission by the Auger effect and the analysis of the emitted electrons [52]. Because this technique collects low energy Auger electrons characterized by
a short mean free path it needs a UHV environment with a pressure $<10^{-8}$ mbar. The UHV avoids also the formation of adsorbates on the surface to analyze. The instrument and other technical characteristics are reported in appendix. AES and secondary electron spectroscopy were carried out on MoO$_3$ films with the Perkin-Helmer coaxial electron beam double-pass cylindrical mirror electron analyser. In order to minimize the damage of the MoO$_3$ surface due to the electron bombardment [54], the energy of the electron beam was set at $E_p=1$ keV and the filament current was tuned to a low value: $I \sim 10 \, \mu A$. In addition to the spectroscopic analysis, the secondary electron curve of the AES spectrum allows to measure the work function of the surface of the MoO$_3$ on copper, an important parameter of these films discussed in the next chapter.

XAS experiments were performed at the B18 beamline of Diamond Light Source (figure 2.15), the UK synchrotron working at the energy of 3 GeV with a current of 250 mA in the top-up mode. This bending magnet beamline covers the energy range from 2 to 35 keV with an optical configuration based on three main optical elements:

- a collimating mirror;
- a fixed-exit double crystal monochromator;
- a double toroidal focusing mirror.

**Fig. 2.15** Lateral view of the beamline B18@Diamond with its main components.
This beamline covers a wide range of energy using two sets of crystal and focusing mirrors. The monochromator can operate both in step-scan and in continuous (QuickEXAFS) scan mode. Regarding the detectors, it is equipped with different fluorescence solid-state detectors and an ionization chamber for intensity monitoring. For our experiments we used Si (111) crystals coupled to a Pt-coated mirror delivering $\sim 5 \times 10^{11}$ ph/s to the sample within a spot of 100 x 250 μm$^2$ (FWHM) nominally placed at 37.5 m from the source [55]. Investigating nanophase materials such as TM oxides, this spot does not allow to resolve single-phase domains, but simultaneously may probe thousands of small domains.

![Photograph inside the B18 experimental hutch at Diamond.](image)

The acquisition at the Mo K-edge spectra has been performed in the continuous scan mode using a nine-element Ge detector with XSPRESS-II acquisition electronics in the fluorescence detection mode. We measured in continuous scan mode samples of MoO$_3$ growth on copper with different thickness: from 50 nm to 300 nm, collecting scans at the Mo K-edge from 19800 eV to 20850 eV. XAS allowed to characterize different samples, clarifying structural and chemical properties of these films. Moreover, as already pointed out, XAS spectroscopy is a powerful technique to probe the local structure and the partial empty density of states around the photo-absorbed atom.
The near edge region of a XAS spectrum is named XANES (X-Ray Absorption Near Edge Structure) and gives information on the local structure and on the partial and local empty density of electronic states, e.g., for a K-edge the $p$-projected empty density of states (figure 2.17) [56]. The energy region that extends from 100 eV up to 1000 eV from the edge is called EXAFS (Extended X-Ray Absorption Fine Structure) and returns information about bond distances and coordination numbers of the photoabsorber in the material (figure 2.17).

![Normalized Mo K edge XAS spectra of the α-MoO$_3$ powder. XANES and EXAFS regions are outlined in the bottom.](image)

Molybdenum K edge XAS spectra were collected at the B18 Diamond beamline on MoO$_3$ coatings with thickness from 50 nm up to 300 nm. For each sample, we measured 20 different points of the surface. Each spectrum shown in figure 2.18 was aligned and summed.
Fig. 2.18 Comparison of the Mo K edge spectra collected on the 100 nm MoO\textsubscript{3} film growth on Cu. The different lines refer to different measurements.

Spectra were analyzed using the Athena package of the Demeter\textsuperscript{©} software first fitting the pre edge and then normalizing the spectrum in the XANES region. In figure 2.19 are compared XANES spectra of films of different thickness. The spectra looks very similar, and the differences between them are \sim 5\% of the signal. The observed pre-peak in Figure 2.18 and 2.19 is due to the 5p and 4d orbitals of molybdenum hybridized with the 2p orbitals of oxygen. The intensity of this structure is proportional to the distortion of the MoO\textsubscript{6} octahedra.

Fig. 2.19 Comparison of Mo K edge spectra of MoO\textsubscript{3} films on copper with different thickness from 50 nm (blue) up to 300 nm (orange).

The comparison of the XANES spectra with that of the reference MoO\textsubscript{3} measured by Kopachevska et al. [57] confirms the stoichiometry of the coating and shows
that spectra are related to disordered film. In order to highlight the variations of
the empty density of states among films with different thickness, we plotted the
difference between each normalized absorption spectrum and the 50 nm film
spectrum taken as a reference (figure 2.20). The subtle changes of the empty
density of states in the pre edge showed are a measure of the different number of
occupied electrons and of the hybridization in these films. The differences
between the 100 nm, 200 nm and 300 nm XANES spectra respect to the thinnest
50 nm film show that the local structure is the same, while increasing the thickness
an increase of the empty density of states of $d$ character occurs. It should be
correlated with the conductivity of these films growth on the metallic copper.

Looking at figure 2.20 a first change occurs for the film 100 nm thick (green line),
while for the thicker films (red and orange lines) the increase of the empty density
of states occurs near the Fermi energy. These changes probe the local and partial
empty density of states and could be correlated with the transport properties of
each film and to the charge transfer from the substrate, which is greater in the
thinner films. Cu may act as a n-type dopant for MoO$_3$ and, if Cu is oxidized to
Cu$^+$, it reduces Mo$^{6+}$ to Mo$^{5+}$, donating electrons to the MoO$_3$ conduction band.
This process generates a partially filled Mo $4d$-band, without affect the MoO$_3$
structure [57-59].
Auger electron spectroscopy (AES) investigated both the chemical composition of the copper substrate and the MoO$_3$ films deposited on copper. This technique was used first to analyze the copper substrate before deposition and later after the evaporation. As shown in figure 2.21 the Cu substrate before sputtering, presents three main features related to copper M$_{2,3}$VV (60 eV), carbon KLL (272 eV) and oxygen KVV (510 eV) [60]. Carbon atoms present on the surface are probably a residual of lapping and cleaning procedures, while the oxygen peak is due to the native oxide existing on the copper surface [60].

In figure 2.21 are also showed the spectra of the substrate after two sputtering treatments performed with Ar at the pressure of $5 \cdot 10^{-4}$ mbar (accelerating voltage of 3 kV and 10 mA of filament current). After the first treatment of 5 minutes C and O peaks are more than halved, while after the second treatment the O peak is hardly visible and the C peak is reduced ~16 times.

In Figure 2.22 is showed the characteristic MoO$_3$ M$_{4,5}$N$_{2,3}$V spectrum composed by two peaks, one at 182 eV and one at 187 eV associated to the Mo$^{6+}$ and Mo$^{4+}$ state, respectively [54]. When the ratio between the first AES peak and the second is > 1.2 the configuration is characteristic of the MoO$_3$ [54]. In our spectrum the ratio is ~1.37 and confirms the previous chemical analysis obtained by XANES spectroscopy. On this sample was also tested a UHV annealing procedure, which will be discussed in the next chapter.
Fig. 2.22 AES spectra of the 100 nm MoO$_3$ film on copper, collected at normal incidence and using an electron beam of 1 keV. The spectrum shows the three main features characteristic of the MoO$_3$ composition.

Fig. 2.23 α-MoO$_3$ powders (left) Raman spectrum with the three main peaks above 600 cm$^{-1}$ due to the three Mo-O bonds; (right) the 3D structure of the distorted octahedron of the α-MoO$_3$: oxygen (red) and Mo (blue) atoms.

The crystal structure of the α-MoO$_3$ measured with the Raman spectroscopy, is showed in figure 2.23 (right) with its three different Mo-O bonds of the MoO$_6$ octahedron: the Mo-O terminal (defined as O1), the twofold bridged O-Mo$_2$ (O2) and the threefold bridged O-Mo$_3$ (O3).
As shown in figure 2.23 the Raman peak at 995 cm\(^{-1}\) is related to the single coordinated O1, that at 820 cm\(^{-1}\) to the O2 terminals and that at 666 cm\(^{-1}\) to the threefold O3 bridge [61, 62]. For comparison, we also measured the MoO\(_2\) bulk powder (figure 2.24a). The 205, 230, 346, 350, 364, 458, 495, 568, and 741 cm\(^{-1}\) peaks are characteristic of the MoO\(_2\) Raman spectrum [63].

![Raman spectrum of m-MoO\(_2\) and 3D structure of the octahedron of m-MoO\(_2\)](image)

**FIG. 2.24** m-MoO\(_2\) (left) Raman spectrum of the powders; (right) the 3D structure of the octahedron of the m-MoO\(_2\): oxygen (red) and Mo (blue) atoms.

As shown in figure 2.23 the Raman peak at 995 cm\(^{-1}\) is related to the single coordinated O1, that at 820 cm\(^{-1}\) to the O2 terminals and that at 666 cm\(^{-1}\) to the threefold O3 bridge [61, 62]. For comparison, we also measured the MoO\(_2\) bulk powder (figure 2.24a). The 205, 230, 346, 350, 364, 458, 495, 568, and 741 cm\(^{-1}\) peaks are characteristic of the MoO\(_2\) Raman spectrum [63].

![Broad structures of Raman spectrum of disordered 100 nm MoO\(_3\) film on copper](image)

**FIG. 2.25** The broad structures of the Raman spectrum of the disordered 100 nm thick MoO\(_3\) film on copper.
In figure 2.25 is showed the Raman spectrum of the 100 nm MoO₃ film on copper collected with the portable Raman (red laser). Compared to the narrow peaks of the α-MoO₃ standard in figure 2.23 this spectrum clearly shows a broad structure with three shoulders (red lines) in the range 600 - 1000 cm⁻¹ characteristic of a disordered/amorphous phase.

The broad peak at 829 cm⁻¹ is due to phonons of the disordered O-Mo⁶⁺-O (O2) network while the shoulder at ~ 953 cm⁻¹ can be assigned to the Mo⁶⁺ = O stretching mode of terminal oxygen atoms [61]. These oxygen terminal bonds are formed by breaking Mo₂-O bonds at the corner-shared oxygens, set between two octahedra of the α-MoO₃ phase [61]. The broad peak at 220 cm⁻¹ is also typical of an amorphous MoO₃ phase; whereas the peak at ~ 440 cm⁻¹ is due to vibrations of bonds between Mo⁵⁺ and oxygen atoms [63]. Spectra were collected also for the 200, 300, 400 and 500 nm thick films. As showed in figure 2.26, all spectra are characteristic of the same disordered/amorphous phase.

![Raman spectra of MoO₃/Cu](image)

**Fig. 2.26** Raman spectra of the 100 nm, 200 nm, 300 nm, 400 and 500 nm MoO₃ films deposited on copper. No differences are evident among these spectra.

Raman spectra shown that non-annealed coatings up to 500 nm thick, at microscale level, share the same disordered/amorphous MoO₃ phase. We measured the Raman spectra on the same films also using the JASCO Raman microscope (figure 2.27) using the green 532 nm laser with a 1 μm spot and the 100x objective.
FIG. 2.27 Raman spectra of the 100 nm MoO$_3$ films deposed on Cu, collected with the green laser and a spot of ~1 μm diameter. The spectrum confirms that no ordered phases are present at the micrometer scale.

Neglecting the different intensity, also the spectrum in figure 2.27 is characterized by a single broad structure as that observed with the red laser. The disordered nature we obtained with the evaporation technique could be correlated with the transport properties of these films that will be discussed in the next section.

**Electrical transport and surface properties**

As already underlined before, triggered by the work of Greiner et al. [17], where they were able to control the electronic properties of the films generating oxygen vacancies on the oxide layer, we measured the resistance of these thin films as a function of the thickness. The results obtained confirm the conductive nature of MoO$_3$ films grown on copper. In the next sections, we will present and discuss the transport experiments performed on different films.
The resistance of thin films

Performing I-V measurements vs. temperature by providing a voltage and measuring the current flowing in the sample, allows to obtain the current vs. voltage or the resistance characteristics. It is a basic electrical measurement and a fundamental way to study the behavior and characterize the electronic properties of a specimen and its transport dynamic.

We made electrical contacts on the surface of these films with silver paints pads. Samples were located in an optical cryostat, equipped with a cold finger using a temperature controlled liquid helium continuous flow (Figure 2.28). The measurements were performed cooling the sample from room temperature down to 20 K. The electrical resistance was recorded by the Agilent 3458A Multimeter, while the temperature was monitored by the Intelligent temperature controller of the Oxford Instruments. The error on the resistance measurement is 1% of the reading and on the temperature is ±10 mK [64].

This set of measurements covers a wide range of thickness, from 30 nm up to 750 nm with a set of seven samples for a complete analysis. Transport experiments are necessary also to establish the thickness range in which MoO₃ films exhibit a metallic behavior, an essential condition for many foreseen applications.

![Image of experimental setup](image_url)

Fig. 2.28 (left) The experimental setup: 1- the optical cryostat with the cold finger; 2- the Intelligent temperature controller of the Oxford Instruments; 3- the Agilent 3458A Multimeter; (Right) Layout of the setup with the electrodes on the MoO₃ film coated on copper.
In the next, we will show the resistance behavior as a function of temperature down to \( \sim 20^\circ C \) for the copper substrate and for MoO\(_3\) films of thickness of 30 nm, 60 nm, 100 nm, 300 nm, 500 nm and 750 nm.

![Fig. 2.29](image)

**Fig. 2.29** The normalized electrical resistance vs. temperature for the Cu substrate (left) and the 30 nm MoO\(_3\) film on copper (right). The linear behavior of the thin film confirms its resistive nature.

The linear trend of the 30 nm (figure 2.29b), 60 nm (figure 2.30a), 100 nm (figure 2.30b) and 300 nm (figure 2.31a) films point out a metallic behavior. At variance the films of 500 nm (figure 2.31b) and 750 nm (figure 2.31c) show a semiconducting behavior with an increase of the resistance at low temperature, which for the thicker films reaches hundreds of M\(\Omega\) at T<50 K. In table 2 we list the electrical resistance at 20 K and at room temperature for all the investigated films.
Fig. 2.30 Comparison of the normalized resistance vs. temperature for the 60 nm (left) and 100 nm (right) MoO$_3$ films on copper.

Fig. 2.31 Comparison of the normalized electrical resistance vs. temperature for MoO$_3$ films of 300 nm, 500 nm and 750 nm on copper. The samples >300 nm clearly show a semiconducting behavior with the resistance increasing at low temperature.

Compared to Cu, the values in Table 2 shows that the resistance may increase up to 7 times the copper value. As already discussed, the silver paste electrical contacts on the samples surfaces are similar but not identical. For this reason, a precise evaluation of the resistivity cannot be obtained, although these values are useful to understand the trend. However, we have to underline here that the resistance of the 100 nm film is smaller than that of the 60 nm.

Table 2. The electrical resistance of MoO$_3$ films at 20 K and at 290 K.

<table>
<thead>
<tr>
<th>MoO$_3$ thickness (nm)</th>
<th>Resistance @ 20 K (Ω)</th>
<th>Resistance @ 290 K (Ω)</th>
<th>Resistance variation (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu substrate</td>
<td>0.901</td>
<td>1</td>
<td>0.099</td>
</tr>
<tr>
<td>30</td>
<td>1.69</td>
<td>1.75</td>
<td>0.06</td>
</tr>
<tr>
<td>60</td>
<td>4.89</td>
<td>5.21</td>
<td>0.32</td>
</tr>
<tr>
<td>100</td>
<td>3.19</td>
<td>3.48</td>
<td>0.29</td>
</tr>
<tr>
<td>300</td>
<td>5.70</td>
<td>7</td>
<td>1.30</td>
</tr>
<tr>
<td>500</td>
<td>4.30</td>
<td>2.15</td>
<td>2.15</td>
</tr>
<tr>
<td>750</td>
<td>9·10$^7$</td>
<td>16</td>
<td>9·10$^7$</td>
</tr>
</tbody>
</table>
This anomaly could be explained by defects present on the surface that may expose the underlying copper and decrease the resistance. Moreover the maximum electrical resistance variation occurs in the thicker films (500 nm and 750 nm) supporting the observed semiconducting behavior.

Since the resistance of a semiconductive material as a function of the temperature has to follow the Arrhenius' equation. [65] We then analyzed with the Arrhenius plot resistance curves of the 500 nm and 750 nm films. This plot is made with the logarithm of the resistance vs. the inverse of the temperature [66]. A data set follows the Arrhenius' equation if a straight line is obtained. The slope is related to the activation energy in thermionic emission regime, and to the type of the conductivity.

![Arrhenius plots](image)

**FIG. 2.32** Arrhenius plots of the resistance temperature dependence of the 500 nm (left) and 750 nm (right) MoO$_3$/Cu samples.

As showed in figure 2.32 the linear behavior of the Arrhenius plot of both 500 nm and 750 nm films confirms the semiconductive nature, due to, with two different activation energy ($E_a$) related to the bandgap and to the Fermi energy [66]. However, the activation energy associated to the slope of the linear behavior of the Arrhenius equation represent the energy barrier for the thermal activation process of the materials. In the semiconducting films showed in figure 2.32 the resistance of both films increases with the decrease of the temperature, going from room temperature down to ~50 K (500 nm) or ~60 K (750 nm) with the activation energies of between 90-110 meV. This result suggests that at relatively low
temperatures both films have a similar conduction mechanism due to layered structure and to the role of the copper-molybdenum oxide interface. At lower temperatures the resistance still increases, but with a slower rate probably due only to the contribution in both of the interface with activation energies of 32-45 meV. The difference at high temperature suggests the different weight of the carrier transfer mechanisms at the interface in these films. At the same time the presence of different conduction mechanisms seems exist in this temperature range and even at higher temperatures. The difference at high temperature suggests the different weight of the carrier transfer mechanisms at the interface in these films. At the same time the presence of two conduction mechanisms seems exist in this temperature range in these films.

Infrared reflectivity of thin films

The metallic behavior based on transport experiments may be affected by systematic contributions due to both electrical contacts and inhomogeneity of the films. To confirm the observed metallic behavior in the thinner films we performed normal incidence reflectance spectroscopy in the mid-IR region. Conventional infrared (IR) spectroscopy studies the incident and transmitted light from a sample, but with samples that are difficult to analyze by the transmittance method, as in our case, the reflectance IR spectroscopy combines IR spectroscopy with reflection theories to study the interaction of radiation with matter [67]. Specular reflectance IR spectroscopy essentially involve a mirror-like reflection from the surface that occurs when the reflection angle equals the angle of incident radiation. It provides a reflection–absorption, for the surface films deposited on the substrate. We used a Hyperion 3000 Bruker FT-IR Microscope, scanning from 400 cm$^{-1}$ up to 8000 cm$^{-1}$ and a resolution of 2 cm$^{-1}$. Experiments were performed at room temperature on three samples, a copper substrate as a reference, a 100 nm and a 300 nm MoO$_3$ film deposed on Cu. The reflectance spectra were acquired on several points and analyzed, using the software OPUS, through the ratio between the reflected intensity of the MoO$_3$
film and the reflectivity spectrum of the clean copper surface. In figure 2.33, we compare spectra of two samples: one with a thickness of 30 nm (red) and a second 300 nm thick (black). The thinner film shows a reflectance value lower than one in the entire spectral region with a clear minimum around 3500 cm\(^{-1}\) associated to the plasma edge of the MoO\(_3\). This may represent an additional demonstration of the metallic nature of thin MoO\(_3\) films. The broad bump presents around 7000 cm\(^{-1}\) is possibly associated to an interband transition. Some vibrational modes due to MoO\(_3\) phonons are also present below 1000 cm\(^{-1}\). By increasing the thickness, the reflectance becomes nearly flat pointing out the insulating response of the film, which works practically as an anti-reflectance coating of the Cu substrate.

![Graph showing reflectance spectra](image)

**Fig. 2.33** Comparison of the absolute reflectance of MoO\(_3\) films of 30 and 300 nm.

At room temperature the thinner film shows a metallic behavior with the plasma edge in the mid-IR region while the 300 nm thick film exhibits an insulating behavior with a flat reflectance. The narrow peaks around 1600 and 3900 cm\(^{-1}\) are due to the water vapor absorption.
The work function

The metallic behavior opens the question about other properties of the surface such as the work function (WF). The latter is a fundamental electronic property of a metallic surface. Its determination allows to understand a wide range of surface phenomena [14]. The compilation of many WFs data, mainly derived from measurements on polycrystalline samples is due to Michaelson [68]. In Table 3 are compared the WFs of several metals.

We attempted to measure how the high work function of the insulating phase of the MoO$_3$ is modified at the surface of films with a metallic behavior. As described previously, the Auger Electron spectroscopy can be used to measure the work function of a surface. Actually, the WF is determined by the measure of the “tail” of the secondary electron cut-off of the AES spectrum.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Phi_m$ [eV]</th>
<th>Element</th>
<th>$\Phi_m$ [eV]</th>
<th>Element</th>
<th>$\Phi_m$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>3.5 ± 0.15</td>
<td>Ni</td>
<td>5.15 ± 0.1</td>
<td>Ag</td>
<td>4.0 ± 0.15</td>
</tr>
<tr>
<td>Ti</td>
<td>4.3 ± 0.1</td>
<td>Cu</td>
<td>4.7 ± 0.05</td>
<td>La</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>V</td>
<td>4.3 ± 0.1</td>
<td>Y</td>
<td>3.1 ± 0.15</td>
<td>Ce</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>Cr</td>
<td>4.5 ± 0.15</td>
<td>Zr</td>
<td>4.05 ± 0.1</td>
<td>Sm</td>
<td>2.7 ± 0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>4.1 ± 0.2</td>
<td>Nb</td>
<td>4.3 ± 0.15</td>
<td>Gd</td>
<td>3.1 ± 0.15</td>
</tr>
<tr>
<td>Fe</td>
<td>4.5 ± 0.15</td>
<td>Mo</td>
<td>4.6 ± 0.15</td>
<td>Pt</td>
<td>5.65 ± 0.1</td>
</tr>
<tr>
<td>Co</td>
<td>5.0 ± 0.1</td>
<td>Pd</td>
<td>5.55 ± 0.1</td>
<td>Au</td>
<td>5.4 ± 0.1</td>
</tr>
</tbody>
</table>

The simplified model of the MoO$_3$/Cu system showed in figure 2.34 can be used to evaluate the work function of these films. After aligning the Fermi energy level of the metal with the conduction band of the oxide, we obtain the ideal description of the electronic structure of our system. This layout shows the Cu and the MoO$_3$ electronic levels and the difference between the two WFs, which is expected to be ~2 eV. From the comparison of the AES secondary electrons cut-off of the 100
nm MoO$_3$ film and of the copper substrate, we obtain the WF difference between the two surfaces.

![Diagram showing the band structure of MoO$_3$/Cu system with predicted energy gap and measured WFs.](image)

**Fig. 2.34** Simplified description of the band structure of the MoO$_3$/Cu system with the predicted energy gap and the measured WF of both MoO$_3$ and Cu surfaces.

In figure 2.35 is showed the secondary electron curve of Cu (orange) and of MoO$_3$ (brown). From the experimental spectra, we obtain the difference $\Delta\Phi_{\text{exp}} = (1.8 \pm 1)$ eV, a value in excellent agreement with the theoretical evaluation.

![Comparison of secondary electron tails of AES spectra of Cu and MoO$_3$/Cu.](image)

**Fig. 2.35** Comparison of the secondary electron tails of AES spectra of Cu (orange) and of the 100 nm MoO$_3$ film (brown). The energy difference between the tails is the difference between the work function of the two surfaces.
Summarizing, the 100 nm MoO₃ films deposited on copper have a WF at room temperature of ~ 6.7 eV, a value from ~1 eV up to ~ 4 eV higher than any WF of bulk metals, as shown in the table 3. This result is very important for all applications where a metallic surface with a reduced electron yield is required [70].

The results obtained in the transport measurements complete the analysis performed on the MoO₃/Cu system. The morphology and the structure of these films, discussed above are associated to conductive films up to 300 nm thick and with a high WF. The results confirm that is possible to achieve a high conductive MoO₃ coating on a copper substrate, without the need to induce oxygen vacancies or applying external voltage.
Chapter 3.
Annealing of MoO$_3$ films on copper
The growth of metallic films is a complex phenomenon, which is affected by many parameters. To control and enhance the properties of metallic films a thermal annealing is typically performed to favor the release of intrinsic stress, enhance the order, improve the structure and control the surface roughness. In a qualitative way, we should say that a proper combination of temperature, time and atmospheric condition might control the adhesion, tune the “consistency”, drive the formation of a specific “phase” and affect the surface morphology and the roughness of the film. Since the not annealed MoO$_3$ films we growth with the PVD evaporation setup are metallic disordered phases with a limited hardness and a weak adhesion to the substrate, we had to optimize the film properties via a thermal treatment. Most of the studies on MoO$_3$ films performed the annealing process, in some cases during the deposition process as in sputtering or laser ablation [31], in other after the deposition as for evaporation or CVD techniques [32, 33]. In these studies, the annealing temperature is in the range between 400° C and 600° C in air or in an oxygen rich atmosphere. In our case the copper substrate, which easily form a thick oxide layer at high temperature represents a limitation for the annealing in air or in an oxygen rich atmosphere. The MoO$_3$, on the other side, needs oxygen to avoid the reduction to MoO$_2$. 

![Figure 3.1](image1.png)

**Figure 3.1** (left) Photographs of an amorphous 100 nm MoO$_3$ film deposed on copper; (right) Molybdenum oxide film deposed on Cu and annealed in air up to ~500° C.

Attempts to anneal the MoO$_3$/Cu system in air were performed and resulted unsuccessful. As expected, at temperatures above 300° C required to trigger the crystallization [63], the oxidation of the copper substrate strongly affect the
morphology of the film as shown in figure 3.1. As a consequence, we had to develop and test a different annealing procedure in vacuum. The characterization of the annealed samples has been the key issue to optimize this annealing process described in the next sections.

Annealing in UHV: AES data

As already introduced in the previous chapter a first annealing treatment was performed on a 100 nm MoO$_3$ film deposited on copper, inside the Auger chamber, which allows performing both measurements and heat the sample in UHV conditions.

We performed the annealing process using the sample holder shown in Figure 3.2 equipped with a heater made by a silicon wafer. The latter, because of its semiconductive nature, to start heating needs a high voltage to overcome the voltage threshold [71]. When the heater reaches the proper temperature, its resistance decreases. A Chromel/Alumel K thermocouple is positioned on the surface of the sample and the temperature of the film is monitored with a HANNA® HI93531R thermometer with a 0.1°C resolution.

![Fig. 3.2 Photographs of the UHV sample holder with the silicon heater (left); the 100 nm MoO$_3$ film and the Cu substrate mounted on the holder after the annealing procedure (right).](image)

For the annealing procedure the sample is introduced in the pre-chamber where the pressure is lowered to ~10$^{-8}$ mbar with a vacuum system composed by a
rotative, a turbomolecular and an ionic pump. The sample is then introduced in the UHV chamber at the working pressure of \( \sim 10^{-10} \) mbar.

The surface was heated up to 400° C with an annealing ramp of 0.5° C/min. We collected an AES spectrum at RT and after at the temperature of 150° C, 230° C, 330° C and 400° C. As described in the previous chapter, Auger spectra have been collected and analyzed, and the secondary electron cut-off used for the evaluation of the work function of the films[72-73].

As shown in figure 3.3 and 4 the evolution of the M_{4,5}N_{2,3}VV peaks describes the dynamic of this film vs. temperature. As pointed out by Lin et al. [54], from the ratio between the 183 eV peak, associated to the Mo\(^{6+}\) state, and the 187 eV peak related to the Mo\(^{4+}\) state, it is possible to monitor the chemical composition of the Mo oxide film. In the left panel in figure 3.4 we plot the peaks ratio as a function of temperature. At \(~150^\circ\) C the ratio is < 1, indicating the partial reduction of the coating to MoO\(_2\), i.e., Mo atoms in the +4 valence state. From 230° C and above the peak ratio is < 0.7, which can be associated to a fully reduced MoO\(_2\) film.

![Diagram](image-url)
In order to study the WF evolution during the annealing we have to consider a model also for the MoO\textsubscript{2}/Cu system (figure 3.5). Because of the similar WF between these two metallic materials, we predict a WF difference $\Delta \Phi_{\text{th}} \sim 0$ between them. Therefore a reduction of the WF of $\sim 1.8$ eV is expected during the annealing of the film because of the transition from MoO\textsubscript{3} to MoO\textsubscript{2} [17].

![Figure 3.5](image)

**Figure 3.5** A simplified band structure model for the MoO\textsubscript{2}/Cu system with the predicted energy gap and the measured WF of both MoO\textsubscript{2} and Cu.
In figure 3.6, we show the evolution of the secondary electron cut-off of the AES spectra as a function of the temperature. While the MoO$_3$ cut-off is steeper and the tail exhibit a bump, the MoO$_2$-like film is characterized by a smother edge and its shape is associated to a lower work function surface with a partially filled $d$-band electronic structure [74].

The measured WF reduction is $\Delta \Phi_{exp} = (1.2 \pm 0.1)eV$, a value lower than the predicted one of 1.8 eV, probably due to an incomplete transition of the film to MoO$_2$.

The discrepancy among AES results, which show a complete transition to MoO$_2$, and WF experiments described above, can be understood considering also the different probing depth of the techniques. The Auger spectroscopy has a probing depth in the range 1-5 nm, while the characteristic probing depth of the secondary electron spectroscopy is ~100 nm [75]. The first technique is then extremely sensitive to the chemical state of the first layers, more affected by the Mo reduction than the deeper layers of the films.

The Auger data clearly point out that the annealing process at UHV conditions is not suitable for the crystallization of thin MoO$_3$ films. The MoO$_2$ formation due to the oxygen loss is certainly due the absence of air and then to the lack of the
oxygen rich atmosphere required by the annealing process [76]. We have to consider also that the long annealing procedures trigger the reduction dynamic, especially at the lower temperatures (150° C - 300° C).

**Annealing in a low vacuum regime**

Since we ruled out the use of the annealing procedure in UHV, a different annealing procedure to preserve the stoichiometry of the films has to be identified. To this purpose we setup a heating system in a low vacuum environment, i.e., from the pressure of 0.1 up to 1 mbar. We considered also a fast procedure to minimize the Mo reduction process, and to avoid also the possible oxidization of copper ions.

The vacuum chamber we used to assembly the heating system was the same HV chamber used for the sample preparation. The system is composed by a ceramic rod filled with a tungsten coil. A current flowing inside the coil heats the rod, which is inserted in the copper support shown in figure 3.7. The sample placed on the support shown in the right panel of figure 3.7 can reach temperatures over 600° C in a short time. The K-thermocouple positioned on the surface of the sample allows the precise control of the temperature.

![Figure 3.7](image1.png) The heating setup for the annealing process at low vacuum. On the left is visible the rod inserted in the drilled copper support. On the right, the sample placed on top with the thermocouple fixed on the surface.
The annealing procedure is managed by a PID controller with a feedback mechanism. With the sample placed on the support, the annealing procedure starts at the vacuum pressure of ~0.5 mbar and the heating system is turned on with the set point temperature. Once the sample surface reaches the maximum temperature, the controller turn off the heater. The PID controls the surface temperature and power on or off the ceramic heater during the procedure to maintain the temperature constant. As showed in figure 3.8, the temperature oscillates within ~20° C around the maximum in the annealing process running at the temperature of ~350° C, due to the thermal inertia of the copper support and of the substrate. In the annealing process described in figure 3.8, the film is maintained around 350° C for 5 minutes before starting to cool down. The cooling procedure is not assisted and the temperature slowly decreases in a non-linear way. The final and fundamental step on this procedure is the exposition of the film to air at the atmospheric pressure.

![Graph showing temperature vs. time](image)

**FIG. 3.8** The behavior of the temperature vs. time measured on the sample surface of the film during the annealing procedure.

In the next section, we will show also the results obtained with a different procedure characterized by a different inlet temperatures, i.e., changing the temperature of the sample when it is exposed at the atmosphere. All parameters
of the annealing treatment were analyzed and the different results will be presented and discussed.

Raman characterization

To understand the results of the annealing process on these films we used the Raman microscopy. The JASCO microscope allowed to collect Raman images and maps that allows to visualize and recognize the different results of the annealing procedures. This characterization it is fundamental to identify the chemistry and the structural phase of these films annealed at low vacuum, with different annealing temperatures and different air inlet temperatures.

In figure 3.9 are compared five different spectra of the 300 nm MoO$_3$ films on copper, collected with a green laser and with a spot of 1 μm of diameter. The spectra refer to samples annealed with different maximum temperatures, but with the same air inlet temperature of 200° C. The comparison clearly point out that the crystallization of the $\alpha$-MoO$_3$ can be associated to the appearance well above 300° C of the three peaks related to the O1, O2 and O3 features of the MoO$_3$ phase [77].

![Raman spectra comparison](image)

Fig. 3.9 Comparison of the Raman spectra of 300 nm MoO$_3$ films annealed with different temperatures. The characteristic peaks of the $\alpha$-MoO$_3$ phase appears above 300° C.
At 200° C the broad peak of the disordered phase is still visible but the peak at \( \sim 950 \text{ cm}^{-1} \) associated to the Mo=O terminal (O1) start to appear. At 300° C the main feature at 820 cm\(^{-1} \) (O2) and the two side peaks at 720 cm\(^{-1} \) and 920 cm\(^{-1} \) also appear while the broad peak starts to disappear [61]. The 400° C and 500° C spectra are almost identical, and the three main features have the same peak ratio. While the most intense central peak (O2) exhibits the same position as the \( \alpha \)-MoO\(_3\) the two side peaks are slightly shifted (\( \sim 60 \text{ cm}^{-1} \)) respect to the positions of the contributions associated to O1 and O3 of the \( \alpha \)-MoO\(_3\). The O1 peak is blue shifted of \( \sim 70 \text{ cm}^{-1} \), pointing to an increase of the terminal bond length probably due to a tensile stress, while the O3 peak is red shifted of \( \sim 60 \text{ cm}^{-1} \), with a decrease of the threefold O3 lengths associated to a compressive stress [78-79]. The strains due to the mismatch with the copper substrate and also those induced by the fast heating and the cooling procedures are probably at the origin of these Raman shifts.

The air exposition temperature is another critical parameter to drive the ordering of the originally amorphous MoO\(_3\) films. This study has been performed measuring films annealed at the same maximum temperature, but exposed to air at different temperature. We define here the air inlet temperature the value measured at the surface of the sample when it is first exposed at the air pressure of 1 atm after the annealing, i.e., when it is extracted from the vacuum chamber. In figure 3.10 we show spectra of two molybdenum oxide samples with the same thickness, annealed at the same temperature and at the pressure of 0.2 mbar, cooled down but then exposed to air with different extraction temperatures. Since they differ only in the extraction condition, this temperature appears to be a fundamental parameter for the phase ordering of these films.
Fig. 3.10 Raman spectra of two 300 nm MoO$_3$ films annealed at the same temperature, but with two different air inlet temperatures. The sample extracted at 110° C (black) shows the features of the MoO$_2$ phase and only a weak MoO$_3$ peak at 922 cm$^{-1}$. At variance, the second film extracted at 200° C exhibits the features of the α-MoO$_3$ phase and weak and broad peaks of the MoO$_2$ phase.

As it will be shown by SEM images, the crystallization of these films exhibit on the surface a classical 'arborization' pattern (figure 3.11) that has been chemically characterized by Raman with a green laser using a spot of ~5 μm.

Fig. 3.11 On the left the optical image (20x) of the annealed 300 nm thick MoO$_3$ film on copper (inlet temperature 200°C). On the right the Raman map of size 200 x 200 μm$^2$ taken in the central region of the SEM image on the left. The map shows the integrated area of the 820 cm$^{-1}$ peak of the α-MoO$_3$ phase.
Fig. 3.12 (left) Optical image (100x) of the annealed 300 nm thick MoO$_3$ film on copper (inlet temperature 200°C); two Raman maps of the same area obtained integrating the 820 cm$^{-1}$ peak of the $\alpha$-MoO$_3$ phase (center); and of the 360 cm$^{-1}$ peak, characteristic of the MoO$_2$ phase (right).

The map in figure 3.11 shows the integrated area of the O$_2$ Raman peak of the $\alpha$-MoO$_3$. The comparison of map and optical image shows that the substrate is covered by a pattern of a crystalline molybdenum trioxide. As showed in figure 3.12, among the branches of this structure Raman spectra pointed out the coexistence of both MoO$_2$ and MoO$_3$ phases [61].

Fig. 3.13 Raman spectra of three MoO$_3$ annealed films with thickness 100 nm, 300 nm and 450 nm annealed and cooled with the same conditions. The same process occurs with similar patterns also at different thickness as shown in figure 3.13 where we compared the Raman spectra of the 100 nm, 300 nm and
450 nm films annealed at 400° C and with the air inlet temperature of 200° C. All spectra present the three main MoO$_3$ peaks at 920, 820 and 720 cm$^{-1}$.

The optical images showed the presence of an inhomogeneity that we attempted to analyze with a SEM characterization presented and discussed in the next section.

**SEM characterization**

As showed in the next images, the thickness is another fundamental parameter to achieve a homogeneous crystallization process. Actually, MoO$_3$ films on copper with thickness smaller than 200 nm, exhibit an inhomogeneity after the annealing and the substrate is not completely covered by the film as showed in figure 3.14 where appear SEM images of films treated at different annealing temperatures.

![SEM images of 100 nm MoO$_3$ film on Cu annealed at 400° C](image)

**Fig. 3.14 Optical and SEM images of the 100 nm MoO$_3$ film on Cu annealed at 400° C in a low vacuum (inlet temperature 200°C).** The optical images of the sample show two different zones: quite coated regions as in (a) and large uncovered substrate areas as in (d). SEM images of the region (a) taken at 1500x (b) and 6000x (c) magnifications show an ordered phase with crystalline structures ~500 nm wide. Images of the (d) area taken at 3000x (e) and 15000x (f) magnifications point a copper substrate mostly uncovered with small MoO$_3$ crystals of dimensions up to ~1 μm.
In figure 3.15 are showed two spectra collected in different regions of the 100 nm MoO$_3$ film deposed on Cu in vacuum and annealed at 400° C at the pressure of 0.2 mbar. The previous SEM images showed that films may crystallize leaving wide regions of the substrate uncovered (see panels 14d, 14e and 14f) with MoO$_3$ crystals up to ~1 μm distributed irregularly on the surface. On the contrary, areas almost fully covered by an ordered crystalline film with structures with dimensions of ~500 nm are visible in the panels a, b and c always in figure 3.14. Raman spectra collected with a green laser and a spot of ~5 μm diameter recognize on the surface of these films the presence of the MoO$_2$ phase (Figure 3.15).

Summarizing, these results show that the 100 nm film is too thin to form, after the annealing, a homogeneous ordered MoO$_3$ film. When the deposed material starts
to crystallize the film leaves the copper substrate uncovered. Images of film with thickness of 500 nm and 300 nm annealed respectively at 400° C and 500° C are showed in figure 3.16 and 3.17.

![Image](image.jpg)

**Fig. 3.17** Optical (left) and SEM (right) images of the 300 nm MoO$_3$ film on Cu annealed at 500° C in a low vacuum (inlet temperature 250°C).

The samples with thickness higher than 100 nm and annealed at 400° C in low vacuum and exposed to air at 250° C exhibit a coating, which cover the entire surface of the substrate homogeneously. Raman spectroscopy characterized the composition of the sample surface, and thanks to SEM images we were able to evaluate the homogeneity of these films. However, to confirm the quality of these films with a less surface sensitive probe we performed also XAS experiments.

**XAS characterization**

As introduced in chapter 2 XAS experiments were also performed at the B08 beamline at ESRF, the European synchrotron radiation in Grenoble, working at the energy of 6 GeV with a current of 200 mA in the top-up mode. The B08 beamline is the Italian CRG optimized for x-ray absorption measurements. Its optical layout showed in figure 3.18 covers a wide range of energies from 5 to 40 keV and delivers a flux to the sample of ~$10^{11}$ ph/s within a spot of ~200 μm.
Fig. 3.18 Layout of the LISA B08 optical hutch. From right to left: the cylindrical collimating mirror (M1), the double crystal monochromator (DCM) and the toroidal focusing mirror (M2). Mirrors operate at the incidence angle of 2 mrad and have a Si and a Pt coating to cover a wide range of energy.

Fig. 3.19 Comparison of XAS spectra of the MoO$_3$ standard and three amorphous MoO$_3$ films with a different thickness growth on Cu.

The acquisition at the Mo K-edge spectra was performed with the monochromator working in the step scan mode collecting the fluorescence signal with a 10-elements Ge detector. We measured samples of MoO$_3$/Cu with different thickness and different annealing treatments. In figure 3.19 are compared three amorphous MoO$_3$ films growth on Cu with the spectrum of the α-MoO$_3$ powders (Sigma-Aldrich - 99.97% trace metals basis). The intense pre-edge associated to the Mo$^{6+}$ valence is evident in all spectra. Moreover, while the α-MoO$_3$ crystalline spectrum presents three pronounced peaks in the XANES region, due to their disorder phase
all films exhibit only quite weak and smooth structures. We measured also samples with different annealing temperatures, but the same air inlet temperature of 250° C shown in figure 3.20. The comparison of these spectra point out important differences among these films both in the pre-edge and in the XANES region. Figure 3.20 clearly shows that in addition to the ordered α-MoO₃ phase a MoO₂ contribution is present in the thicker films, in particular those treated at the higher temperatures.

![Comparison of XAS spectra among the MoO₃ standard (black) and four MoO₃ films with different thickness and different annealing temperature.](image)

Analyzing in more detail the figure 3.20, we may recognize that the intensity of the pre-edge decreases from the standard molybdenum trioxide to the 300° C annealed sample, down to a weak shoulder in the 400° C annealed sample. The decrease of the intensity is clearly related to the decrease in the empty density of state of the Mo 4d band, i.e., to the reduction of the Mo valence state from 6+ to 4+ as expected in the MoO₂ phase. The XANES structure of the 300° C annealed sample is very similar to the spectrum of the α-MoO₃ standard although this film exhibits smoother structures justified by the partial ordering of these films as outlined by Raman and SEM images. The samples at 350° C shows also a shift of the first two peaks and a shape
similar to the m-Mo$_{11}$O$_4$ structure [80]. At variance, the spectrum of the 400° C annealed sample has the typical XANES shape of the MoO$_2$ phase [80]. From the XAS results of annealed films, we obtained important information to combine with the other spectroscopic and imaging characterizations. As a matter of fact, the film annealed at 400° C, which Raman assign to a MoO$_3$ phase, contains also a not negligible MoO$_2$ contribution as pointed out from the XANES spectrum. This is certainly due to the different probing depth of the techniques and the different surface sensitivity of X-rays at these energies.

These results point out that all experiments performed on these films are fundamental to characterize the complex annealing process and the role of the different parameters to achieve the right metallic ordered phase. Combining the different analysis an optimal annealing procedure to achieve metallic MoO$_3$/Cu films can be outlined. Basically, after evaporation we need working to a vacuum pressure of 0.5 mbar heating the film in the temperature range 300° C - 350° C for about 10 minutes. After the film has to be cooled gently for other ~10 min and brought to air at the inlet temperature between 200°C and 250° C. This procedure allows obtaining α-MoO$_3$ films greater than 100 nm with crystalline and metallic characters coupled to a high work function. A small amount of the Mo dioxide phase can be still present inside the film but the oxidation of the copper substrate is avoided. As clearly seen in SEM and optical images, the thickness is an issue for the annealing treatment. The best results in term also of homogeneity can be obtained for films in the 200-500 nm range. Films with a lower thickness led to a partial coverage of the substrate, especially for annealing temperatures above 400° C.
Chapter 4.
Breakdown phenomena
induced by high electric fields
In addition to have metallic surfaces with high work function, another main motivation of this study is to find the way to enhance the resistance of metals to breakdown phenomena. In particular, we focused on the possible improvement of copper based devices used in accelerator technologies that experience high accelerating gradients. The latter is one of the main parameters that affect the cost of an accelerator project, such as high brilliance photon sources know as free electron lasers (FELs) [81, 82]. The main limitation of using high accelerating gradients inside RF cavities is the breakdown in vacuum, i.e., the discharge that occurs inside these RF cavities damaging surfaces and reducing performances [28]. Existing accelerators work at gradients of 15/20 MV/m, but tests have been done with an X-band accelerator at 65 MV/m [83]. About future initiatives, the CERN based Compact Linear Collider (CLIC) design requires RF cavities with a gradient of ~100 MV/m at 12 GHz [84].

Although the breakdown phenomenon is still poorly understood, the current consensus is that vacuum RF breakdowns are enhanced by movements of crystal defects induced by the periodic mechanical stress. The latter may be caused by the pulsed surface heating and by the presence of large electric fields [85-86]. Theoretical models predict that at low temperatures the cavity gradient performances increase respect to room temperature. Actually, the breakdown statistics depend on pulsed surface heating [85], the peak electric field, the peak magnetic field [86], the peak Poynting vector [87], and the hardness of the material with which the cavity is manufactured [88]. Therefore, decreasing the crystal mobility and reducing the thermally induced stress, should lower breakdown rates. Since the RF surface resistance and the coefficient of thermal expansion decrease decreasing the temperature, this can be obtained by operating RF accelerating structures at cryogenic temperatures, where both the yield strength correlated with the hardness and the thermal conductivity increase [89-90]. However to test a real RF device we have to operate continuously for many days and measure the breakdown at different gradients. This is a long and certainly costly procedure.

Since at present the possibility to improve properties of copper structures is only associated to cryogenic operation, exploit the possibility to minimize the damage of copper testing new coatings is a practical and much less expensive route.
In the presence of a high electric field, the catastrophic discharges called breakdowns generate on copper local surface melting, craters, bubbles and even holes. In last decades, numerous studies tried to understand the dynamics that occurs during this phenomenon, the role of the type and structure of the material and the surface roughness [91-93].

Films can be used to protect copper substrates from damage and wear and probably also to reduce the effects of the catastrophic discharges induced by breakdowns. In this chapter, we will show how to generate breakdown phenomena and how to characterize the damage associated to these highly destructive phenomena first on copper and later on copper coated by different MoO$_3$ films.

There are different ways to generate breakdowns. Typically, a DC high electric gradient is applied between two metal surfaces until the discharge occurs, or, as in the case of RF accelerating cavities, an AC high electric field is applied for long time [93]. These methods are effective, but the breakdown dynamic in vacuum is not predictable and reproducible. In addition, using real RF structures the effects can be studied only performing the autopsy on the investigated structure at the end of the long test procedure.

In this chapter, we present a new method suitable to generate high field gradient on any surface (flat or bent) based on the THz radiation emitted by a free electron laser. In this work, in the framework of a bilateral project of the Italian Minister of Foreign Affairs and International Cooperation with Japan, we used the ISIR Free Electron Laser of the Osaka University [94]. This FEL generates a coherent EM radiation at ~3 THz (~ 100 μm). In our breakdown experiments, the beam was focused on the sample surface to generate in a controlled and repetitive way the electric field up to several GV/m.

Characterizing the damage with the spectroscopic non-destructive technique we proposed it is possible to investigate in a repetitive way the damage induced after the THz irradiation.
The ISIR Free Electron Laser

The Free Electron Laser called ISIR, is a coherent THz source where the electron beam is accelerated up to 15 MeV (figure 4.1 left). The pulsed electron beam is travelling inside the undulator (figure 4.1 right) where, accelerated and deflected by the magnetic field, it emits synchrotron radiation in the THz range [81, 94]. A series of optics extract the highly coherent THz beam outside the hutch, focusing it on the sample position for the experiments (figure 4.2).

**FIG. 4.1** Photographs of the LINAC electron beam accelerator of the Osaka university (left) and of the undulator that is used to generate the THz radiation (right).

**FIG. 4.2** (Left) The sample holder with the stage of the off-axis parabolic mirror used for focusing. The diamond window that allows extracting both the THz beam and the He-Ne laser used as the optical guide (red light) is visible in the background. The red spot of the laser is used for the alignment (right); image of the off-axis parabolic mirror (on the left) and of the sample holder in the center.
The sample is attached to the holder with an x-y stage that can translate it also along the z-axis. A red He-Ne laser paraxial to the THz beam is focused to the same position of the THz spot (figure 4.2b). It is used to visualize the focal position of the THz beam on the sample.

The focal spot of the THz beam generated by the undulator and by the optical system is a “circular” region with Gaussian intensity distribution with a radius $2\sigma \approx 130 \, \mu m$ (Figure 4.3), where 95.5\% of the signal inside this radius [95].

![Fig. 4.3 The minimum dimension of the THz spot obtained by the measure of the integrated transmittance by a knife-edge scan. From the derivative is obtained the measure of the radius (~130 μm).](image)

The electron beam structure of the ISIR FEL. In the top panel is showed the macro pulse structure, in the middle the micro pulse (20 ps long) and in the bottom the THz oscillating wave at 3 THz inside the micro pulse.

![Fig. 4.4 The electron beam structure of the ISIR FEL.](image)
The time-structure of the THz beam is related to the electron beam structure of the LINAC, and it is characterized by “macro” and “micro” pulses. The macro pulse, 4 μs long, has a frequency of 5 Hz and each macro pulse contains 108 micro pulses (27 MHz) each one 20 ps long (figure 4.4).

Inside the micro pulse, the THz EM wave oscillates for 60 cycles [94-95]. In order to evaluate the electric field intensity on the surface we measured the energy of the macro pulse and calculated the power density of both a macro and a micro pulse. The energy of a single macro pulse 4 μs long measured with the calibrated Coherent® energy meter is:

\[ E_{\text{macro}} = (10 \pm 0.1) \text{ mJ} \]

and considering its duration of 4 μs, the associated macro pulse power is

\[ P_{\text{macro}} = \frac{E_{\text{macro}}}{t_{\text{macro}}} = 2.5 \text{ kW} \]

The energy of a single micro pulse is obtained from the energy \( E_{\text{macro}} \):

\[ E_{\text{micro}} = \frac{E_{\text{macro}}}{\# \text{ pulses}} = \frac{10 \text{ mJ}}{108} = 92.6 \text{ µJ} \]

and considering the length of 20 ps, the power of a single micro impulse is:

\[ P_{\text{micro}} = \frac{E_{\text{micro}}}{t_{\text{micro}}} = 46.3 \text{ MW} \]

To calculate the electric field generated by the THz beam in the focal spot, we need to calculate the power density (also known as irradiance) of the single micro pulse, defined as the power divided by the spot area:

\[ I_{\text{micro}} = \frac{P_{\text{micro}}}{\text{area} (r = 130\mu m)} = 0.15 \text{ TW/cm}^2 \]

In order to obtain the electric field intensity generated by the THz pulses we need to apply the far field approximation to the above equations.

In our case, the incident THz beam can be considered as a plane wave because it extends in the region farther than ~2 wavelengths from the source [96]. In this far field approximation the irradiance, is defined as:
\[ I_{\text{micro}} = E \cdot H = \frac{E^2}{\mu_0} \]

where \( E \) is the electric field modulus and \( H \) the magnetic field intensity. The electric field intensity is:

\[ E = \sqrt{I \cdot Z_0} ; \quad Z_0 = c\mu_0 \]

where \( Z_0 = 377 \, \Omega \) is defined as the impedance of the free space [96]. Accordingly, for a spot of radius \( \sim 130 \, \mu\text{m} \) we have an average electric field \( E_{\text{micro}} = 0.56 \, \text{GV/m} \).

Because the distribution of the electric field intensity is Gaussian, within a smaller region inside the focus, the electric field is higher than the average. Accordingly, the relative intensity on a central region of radius \( \sigma/32 = 2 \, \mu\text{m} \), the value of the electric field is 5.8 \, \text{GV/m}, as showed in figure 4.5b.

Fig. 4.5 (left) The normal distribution of the E.F. intensity in which in the center we have a higher power density than at the sides; (right) the electric field calculated for areas with different radius \( (2\sigma = 130 \, \mu\text{m}) \).

An alternative calculation, based on the work of Agranat et al. [97] returns a very similar result, with an average electric field of \( E_{\text{micro}} = 0.58 \, \text{GV/m} \) and electric field at the center up to \( \sim 5.9 \, \text{GV/m} \).

With different calculations, we obtained the same value of an extremely high electric field. To give an idea, this value is more than 50 times higher than the working gradient field proposed by the X-band devices of the CLIC project of \( \sim 100 \, \text{MV/m} \) [84].
This high electric field is able to generate local discharge in almost any surface and as we will present in the next chapter, the damage generated by the irradiations has an angular dependence with the angle of incidence of the beam.

![Diagram](image1)

**Fig. 4.6** Schematic representation of the EM wave irradiating the sample. At angles $90^\circ < \Theta < 0^\circ$ the beam transfers a momentum $k_\parallel$, parallel to the surface, coupled with an electric field parallel to the surface (left). On the right is shown the solid angle of the irradiation process and the illuminated area (right).

This angular dependence is related to the horizontal polarization of the radiation. When the THz beam hits the surface with a pulse of 20 ps in the angular range $0^\circ < \Theta < 90^\circ$, it transfers a momentum $k_\parallel$ with an electric field parallel to the surface (figure 4.6). By coupling the electric field and the momentum is possible to excite surface collective excitations, transferring energy and momentum to the system. As said above, this dynamic is the preliminary possible explanation to the angular dependence of the damage that will be discussed in the next section. A more complex analysis based on the peculiar properties exhibited by these van der Walls materials is in progress [98]

**Irradiation with THz radiation at high electric field**

The possibility to expose in a controlled way different regions of a surface with a defined number of high electric field pulses represents a useful and practical method to investigate the effects of breakdowns on different materials.
To test the resistance to breakdowns of molybdenum oxide films, we irradiated with THz radiation Cu substrates and MoO$_3$ films on Cu with different thickness, annealing treatments and different angles of incidence. We also prepared and tested a film made by a sandwich of MoO$_3$ and carbon nanotubes on copper, to test a more exotic and complex coating trying to identify the role of the molybdenum oxides.

As we will see the THz irradiation damage exhibits a strong angular dependence. While at normal incidence ($\theta = 90^\circ$) the damage is almost negligible and in most cases no differences are detectable, decreasing the angle an evident damage occurs.

Irradiation tests were performed first on copper substrates used for the growth of the films. In figure 4.7 are shown optical images of the irradiation on the copper surface at different angles of incidence. Decreasing the angle the irradiated area increases, but the damage increases, so, in a non-intuitive way, the overall damaged area increases, with a maximum in the $20^\circ$ - $50^\circ$ range.

![Fig. 4.7 From left to right, the image of the irradiated copper surfaces after 5000 shots of THz radiation ($\lambda \sim 100\mu$m) at the angles of incidence of $20^\circ$, $40^\circ$, $50^\circ$ and $70^\circ$.](image)

Looking at the photographs, the irradiated region shows two different damage areas, the central one where the THz beam is focused and the energy is transferred to the surface, and the external “corona” where heat is conveyed from the central area. As shown before the electric field of this source may reach several GV/m in the central irradiation region. This area is exposed to an extreme heat with a melting of the upper layers and the removal of the copper oxide layer. This is the
reason why, after 5000 pulses, the central zone appears cleaner than the corona. Indeed, after each shot part of the oxide layer is vaporized and removed. SEM images allowed to identify the small structures formed during the irradiation and visible in figure 4.8 (right panel) and 4.9 (right panel).

![Fig. 4.8 Optical (left) and SEM images (center and right) of the irradiated copper surface after 5000 shots of THz radiation at the incidence angle of 40°. On the right image are visible small copper oxide crystals formed by the breakdowns.](image)

Indeed, in the central region of irradiation small structures of melted copper are visible. The copper melting temperature is ~1080° C and the formation of these structures confirms the high temperature reached in this region.

![Fig. 4.9 Optical (left) and SEM image (right) of the central zone of the irradiated copper surface showed in figure 4.8.](image)

To recognize the chemistry of these structures we performed a spectroscopic analysis. Raman spectroscopy with its high spatial resolution is the perfect technique to analyze the surface damage studying the chemical composition point by point, still mapping quite large areas in a short time. These measures,
performed with a green laser (532 nm) with 5 μm spot, was used to recognize differences on the surface of this MoO$_3$ film and the presence of copper oxides on the substrate.

In figure 4.10, we show the Raman characterization performed on the copper surface irradiated at 40°. On the right is displayed the Raman spectrum associated to the copper oxides measured in the external corona. Here are visible contributions of both copper (II) oxide (CuO) and copper (I) oxide (Cu$_2$O). The central map obtained integrating the peak of the Cu$_2$O at 430 cm$^{-1}$ shows that this copper oxide is mainly present in the corona recognized in the optical images.

![Figure 4.10](image)

**Fig. 4.10** Optical image (left) of the copper region irradiated by 5000 THz shots at the incidence angle of 40°. Raman spectra (right) and map (center) of the Cu$_2$O in the damaged area.

After the copper, we irradiated MoO$_3$ thin films coated on copper to measure the damage on the oxide films and the effect on the copper substrate. In figure 4.11 we showed the damage observed at the incidence angle of 40° for the 100 nm MoO$_3$ film.

The shape of the damaged area is similar to that observed on copper with a clear central region of ~150 μm diameter. Using the Raman characterization we recognize in the damaged area the presence of MoO$_3$, including in the central zone (figure 4.11, right), where the highest temperatures are reached. Inside the map, signal variations of the MoO$_3$ peak are less than 10%.
Fig. 4.11 Optical (left) and SEM image (center) of the irradiation of the 100 nm MoO$_3$ film not annealed, with 5000 shots at incidence angle of 40°. On the right the Raman map of the amorphous MoO$_3$ peak.

In figure 4.12 we compare the damage of the central zone of the 100 nm MoO$_3$ (left) and the copper substrate (right). Also with a relatively thin film (100 nm) is evident a strong reduction of the damage and the absence of tips formations.

Fig. 4.12 (a) SEM images of the irradiation with 5000 shots at the incidence angle of 40° on the 100 nm MoO$_3$ film not annealed. On the right, the SEM image of the central damaged region on the copper substrate showed in figure 4.8.

We tested also films with different annealing treatments and at different angles of incidence. In figure 4.13 are compared two optical images of the irradiation with 5000 THz shots of the annealed oxide films at 400° C, measured at the angle of incidence of 40° (left) and 50° (right). The damage shape is the same as in the previous film, with a central bright zone and a dark corona.
In figure 4.14 is shown the damage pattern obtained at the incidence angle of 40° and two Raman maps, one associated to the peak at 820 cm$^{-1}$ characteristics of the MoO$_3$ and the other relative to the peak at 430 cm$^{-1}$ characteristics of the copper(I) oxide. The distributions point out that the MoO$_3$ film survived to the irradiation and except few small spots, no copper oxide is detected at the surface.

Images and spectroscopic analysis point out that MoO$_3$ thin films, from 200 nm up to 500 nm, survive to the irradiation and the underlying copper substrate also remains undamaged to the multiple breakdowns induced by an electric field up to $\sim$6 GV/m. Ordered films as well as not annealed amorphous films of MoO$_3$ inhibits the formation of copper oxide and also no structures of melted copper were observed, as in the case of the irradiation of the uncoated substrates.
Since as shown by the work of Esconjauregui et al. [99] the coating of MoO$_3$ on carbon nanotubes make them highly conductive, we attempted to test with the same irradiation procedure a particular coating composed by a sandwich of 50 nm of MoO$_3$ and a layer of 50 nm of single wall carbon nanotubes (SWCNT).

The carbon nanotubes film on copper was prepared (Figure 4.15) by a simple, rapid and inexpensive vacuum filtration process of a SWCNT aqueous dispersion. The SWCN film formed on a cellulose filter was cut and deposited by wet-transfer printing on the low roughness (<30 nm) copper substrate (figure 4.15) [100].

Fig. 4.15 (left) A single wall carbon nanotubes film deposed on the cellulose filter; (center) the 50 nm MoO$_3$ film coated on the low roughness Cu substrate; (right) the Cu substrate covered in the center region by the carbon nanotubes film 50 nm thick and half covered by the 50 nm MoO$_3$ film as the purple color demonstrates.

Fig. 4.16 Optical (left) and SEM images of the irradiation at the incidence angle of 40° of the MoO$_3$-carbon nanotubes sandwich coated on the Cu substrate. After exposition of 5000 macro-pulses, a central damaged area of ~200 µm of diameter appears on the film.
After the carbon nanotubes deposition the sample was half covered with a 50 nm MoO$_3$ film using the evaporation technique described in the second chapter. This sample was exposed to the THz focused radiation with the same irradiation procedure performed in the previous cases. As shown in figure 4.16 and 4.17 this coating is more damaged than the oxide film alone. In the SEM images in figure 4.16, it is clearly visible the damaged region at the incidence angle of 40°. Moreover, in the highly damaged central region, the coating has been removed and the substrate is partially exposed. The right panel in figure 4.16 shows that in the region of major damage the carbon nanotubes film is still present, but also few copper tips can be detected. The Raman maps in figure 4.17 show the integration of the Raman D and G band of the SWCNT film [100], and from these maps is evident that in the central zone the signal is reduced 10 times. This proves that the coating was partially removed and the substrate in the central region is exposed, although no copper oxide is formed.

FIG. 4.17 Raman maps of the D-G carbon nanotubes peaks (left) and the fluorescence generated by the underlying copper (center). No visible copper oxide peaks are detected. On the right, the comparison of the Raman spectra collected on the undamaged film (orange), on the corona (green) and in the central region (blue) showing the decrease of the nanotube film in the irradiated region.

Compared to Cu substrates without coating, also the MoO$_3$/C-nanotubes film shows the reduction of the damage of the copper surface, and of the formation of tips as clearly observed in the uncoated Cu substrate.

The characterization of the irradiation of different coatings show the incredible opportunities offered by a controlled discharge process made by the THz radiation
at extremely high electric fields (~6 GV/m). The mechanisms of the observed angular dependence damage has still to be understood, but these results point out a possible correlation with the excitation of surface plasmons on the surface of these metallic surfaces. As a matter of fact, at normal incidence the radiation is totally reflected, due to the high copper reflectivity in the THz range [101]. At lower incidence angles, the coupled momentum and electric field could generate a Sommerfeld–Zenneck surface plasmon wave [98], which propagates parallel to the interface and decays exponentially vertical to it. This type of excitation exists below the plasma frequency of the copper, i.e. at THz regime. The energy absorbed by the substrate through this dynamic could be the main cause of the copper surface damage. 

Both SEM and Raman characterizations demonstrated that these coatings made by molybdenum oxides might reduce the damage, limiting the energy transferred on the copper surface. This damage reduction is still to be understood, but could be related to the polaritons propagation on the MoO$_3$ film. In fact, W. Ma et al. [102] showed that the electromagnetic wave travels along certain directions at the MoO$_3$ surface with almost no obstacles, with an ultra-low energy transfer [102]. This mechanism in addition to minimize the damage of the surface, does not allow the transfer of the thermal energy on the underlying copper substrate. The best results were obtained with annealed films with a thickness between 200 nm and 500 nm, annealed at 350° C - 400° C.
Conclusions

Molybdenum trioxide is a unique material, which similarly to many transition metal oxides exhibits different properties depending on the crystalline structure, stoichiometry, strain and dimensionality that can be tuned for different applications. As an example, the large separation between adjacent layers and the large distorted octahedron unit, allows tailoring the electronic band structure and phonon modes of the $\alpha$-MoO$_3$ phase. This tunability makes this material useful in optoelectronics [14]. The $\alpha$-MoO$_3$ can exhibit also a negative permittivity and polaritons can be observed in this material tuned by electric fields or by material thickness. For example, MoO$_3$ flakes with the appropriate stoichiometry can sustain the anisotropic polariton propagation, an effect observed in artificial hyperbolic metamaterials [102]. In fact, due to its layered crystal structure the $\alpha$-MoO$_3$ surface exhibit natural anisotropic optical phenomena.

In the last years, this material has been the subject of many researches, which focused mainly on the local variations in the oxygen content and internal defects, which are considered the main cause of the different electronic properties that this compound exhibits [24]. In this research, we attempted to understand the origin of the metallic behavior of MoO$_3$ thin films that we produced while growing MoO$_3$ layers on copper substrates.

The research was focused on MoO$_3$ films growth on copper, because this hard and transparent material exhibits a metallic behavior only on metallic surfaces and because of the possible applications in many fields, from accelerating devices such as cavities or metallic cathodes to the spatial technology and in microelectronics. Using spectroscopic techniques combined with transport measurements on MoO$_3$ films deposed on Cu, with thickness ranging from 30 nm up to hundreds of nanometers, we characterized the structural, chemical and electric properties of this material.

From Raman and XAS measurements we demonstrated the amorphous nature of these films and identified a correlation between film thickness and empty density of states of the molybdenum $d$ band. From transport measurements, the metallic
behavior has been observed for films with a thickness less than 300 nm. These results have allowed to explain the relationship between thickness, copper n-doping and conductivity of the films, demonstrating that for a thickness lower than 300 nm the film is conductivity because a charge transfer occurs between the copper and the interface with the MoO$_3$ film. The occupation of the molybdenum $d$ band obviously decreases the local empty density of states of the molybdenum atoms. In spite the metallic behavior, MoO$_3$ thin films are characterized by a high work function ($\sim$6.5 eV) as the insulating counterpart.

We also investigated and optimized the annealing treatment of the disordered nanophased MoO$_3$ films in the ordered $\alpha$-MoO$_3$ phase. The annealing optimization improves mechanical properties such as hardness and the adhesion to the copper substrate. XAS and Raman techniques have been applied to identify the optimal annealing parameters, such as the vacuum pressure during the evaporation, the maximum temperature and the inlet temperature, i.e., the temperature at which the film is exposed to the atmosphere after the annealing. The results demonstrate that also the exposure to air at temperatures higher than the room temperature is important in the annealing procedure to minimize the formation of this metallic non-transparent MoO$_2$ phase.

Finally we presented and discussed the first results obtained with a new technique we introduced to study, in a controlled and reproducible way, the breakdown phenomenon and the induced surface damages on different metallic surfaces. Using the powerful coherent THz source of the FEL at the Osaka University, and tuning the intensity and the repletion rate of the electron beam we induced thousands of breakdown events on the surface of MoO$_3$ films, with and without annealing treatments.

To explain the damage observed in the irradiated zone we applied two models the electric field generated on the surface. The analysis shows that the setup allows irradiating a sample surface in air with a power density up to 0.15 TW/cm$^2$ and with an electric field up to $\sim$6 GV/m generating disruptive discharge phenomena similar to natural breakdowns.

Although preliminary, this study performed also at different angles of incidence clearly shows an angular dependence of the damage, with a maximum in the
angular range 40°-50°. From the analysis of the surface, we may hypothesize that
the angular dependence is probably due to the excitation of surface collective
excitations, which can be excited via coupling of the electric field with a
momentum parallel to the surface. This may happen only for angle of incidence
out of the normal.
To evaluate and calibrate the method, we carried out in particular breakdown tests
on films previously characterized by spectroscopy (Raman) and imaging (Raman
and SEM) on areas illuminated by the THz radiation. In spite of the low thickness
of these films (~100-200 nm) metallic-like MoO₃ films on copper exhibit an
unexpected thermal and mechanical resistance to breakdowns with a dramatic
reduction of the damage observed on the underlying copper surface.
In particular SEM images at high spatial resolution show that while in the
uncoated copper substrate the irradiation induces the formation of an oxide phase
and melted tips, in the coated samples, none of these process has been detected on
the film surface. In addition, Raman maps of the damaged areas of the 100 nm
non-annealed MoO₃ film show a variation less than 10 % of the MoO₃ peak, while
no signal variation occurs in the annealed MoO₃ film of ~500 nm. In any case,
both annealed or not annealed MoO₃ films survive to electric field up to ~6 GV/m.
Therefore, this film is an promising candidate for conductive and protective
coatings against discharge phenomena.
This research offers many new perspectives and the next steps will be devoted to
the application of these films to coat curved surfaces, at first to manufacture a
compact coated RF accelerating cavity made in copper. The annealing procedure
will be also modified to take care of more complex surfaces. The deposition and
technique, developed in this work, will be extended to other transition metal
oxides, also for multiple coatings depositions with different materials.
The study of the irradiation will continue to understand the angular dependence
of the damage, the role of the surface collective excitations in this dynamic and,
from the fundamental point of view to unravel the mechanism of thermal
dynamics in these materials where due to the long-range van der Walls interaction
between layers, the electronic and photonic properties are strongly dependent on
the film thickness.
Appendix
Profilometer

A profilometer is an instrument used to measure a surface's profile, in order to measure height variation and quantifying roughness. The resolution of this technique is quite low compared to other morphology techniques but the measure is collected in about a minute.

In this instrument a diamond tip is brought in contact with the sample and then moved laterally across the sample for a defined distance and contact force.

The electronics acquire the height variations as an analogic signal, which is transformed in digital data.

The stylus arm–gauge configuration shown in figure 6.1 is the classical spring-mass system that controls the tracking force exerted between the stylus tip and the surface in contact with it [103]. The characteristic resonant frequency of this gauge is few hundred Hz, and an automatic system controls the stylus speed and maintains the measurement frequency below this value.

![Diagram of profilometer](image)

**Fig. 6.1** The simplified measuring system of the profilometer with the diamond tip scanning the surface. The spring and damping mass allow the tip following the surface variations while the arm-gauge system converts them in a digital signal.
AFM

Atomic force microscopy is a technique similar to the profilometer, which scanning probe and has a resolution on the order of fractions of a nanometer. The information is gathered by "feeling" or "touching" the surface with a mechanical probe.

As showed in figure 6.2 the AFM is composed by the cantilever, the tip position measurement system and the sample stage. The cantilever is a springy lever with a tip of ~1 nm radius at the end. During the scan it may remain fixed or may oscillate, depending to the selected measuring mode. The tip interacting with the surface is made usually in silicon or silicon nitride. Probing the Van der Waals forces of the interface, the tip is attracted or repelled, deflecting the supporting lever. The deflection angle of the cantilever, both in static or oscillating mode, can be correlated to the surface morphology. A laser beam is used to measure the cantilever position via the reflection of the radiation from the lever terminal. This acquisition system may detect extremely small variations of the tip position thanks to a photodiode matrix.

Fig. 6.2 The simplified layout of the AFM system showing its main components.

The sample stage system allows to control the distance between the surface and the tip (along the z direction) and simultaneously to scan the surface along the x-
y axis. The microscope has a high spatial resolution especially along the z axis, with a resolution of 0.1 nm ($10^{-10}$ m) possible thanks to a combined piezoelectric and interferometer feedback system.

An AFM microscope allows three type of surface probing modes: the contact, the tapping and the non-contact mode. In the first, the tip is pressed against the sample with a fixed force and the sample z position is measured during the scan, returning the lever to the initial position when the system detects a height/depth variation. In this mode, associating the vertical variations with the relative x-y positions, we obtain a “real” morphological map of the surface.

The second mode is called the Tapping® mode and is based on the measure of the oscillation of the tip while scanning the surface. The cantilever oscillates with fixed characteristic frequency and amplitude, a fundamental condition for measuring the minimum variations associated to the interaction between tip and surface. In this mode the height/depth variations of the lever in the z direction needed to adjust the sample to restore the initial oscillating parameters, generate the morphological map. This procedure is more precise than the previous one, but at the same time more “soft” probing the surface, since avoids scratching.

The third method is similar and also avoids the contact with the surface. Here, the tip “floats” at a defined distance from the surface, while oscillating. During the scan when a height/depth variation occurs, the tip feels the Van der Wall attraction or repulsion. This force is measured as a variation in frequency and amplitude. Although more delicate and difficult to run, this last mode offers the highest resolution because is not affected by tip defects.

The main advantages of the AFM technique are

- it can run under atmospheric pressure conditions;
- can work on any type of surface, even on liquid surfaces;
- measurements does not need any sample preparation.

At variance, the main disadvantages of this instrument are:

- it is quite slow. To collect a map requires several minutes;
- the continuous wear of the tip, which can lead to artifacts;
- a fixed xyz scale with the measurable area limited to ~100x100 μm$^2$. 
While due to the diffraction limit optical microscopes cannot resolve structures smaller than ~1 μm, the scanning electron microscope, working with an electron beam this instrument, allows to beat the diffraction limit. Actually, considering that the electron De Broglie wavelength is in the picometer range, the ultimate limit of an electron microscope is determined by its optics.

The electron microscope is composed by three components: the electron source, the optics and the detection system. Electrons are thermoionically produced by an electron gun typically based on a tungsten filament. The filament heated by the current emits electrons via the thermionic effect. A system of electromagnetic lenses made by a toroidal electromagnet focus electrons, reducing the beam diameter (figure 6.3). Slits between lenses filter electrons also reducing the beam size. The last lens is a system of coils that allows to deflect the electron beam to scan the sample surface. After focusing, a conventional SEM with a thermionic source, as in our system, can be focused down to ~10 nm, a value that can be considered the ultimate spatial resolution of this microscope.

![Diagram of Scanning Electron Microscope](image)

**FIG. 6.3** Layout of the Scanning Electron Microscope with its main optical components.
The primary electron beam hits the sample and the interaction induces different mechanisms: secondary electron, backscattered electrons, and Auger electrons emission. The region of interaction of the beam with the sample, which has the shape of a drop (figure 6.4), broadens according to the different phenomena. The emission of secondary electrons, the most used in SEM topography, involves a region of about tens of nanometers, depending on the energy of the beam. The backscattered electrons region is even deeper and can even reach a depth in the micrometer range.

![Fig. 6.4 Schematic representation the electron beam interaction with the sample surface (left); the secondary electron detection system (right).](image)

The magnification in a scanning electron microscope can range from 10x up to 30000x. Unlike the optical microscope, the magnification does not depend on the optics, but on the solid angle of the incident beam and on the solid angle of the detected beam. The detection of secondary electrons allows high-resolution observations of the sample while the small volume of interaction allows to detect details with a spatial resolution up to 15 nm. The depth of field of the observation with the secondary electrons is very high, allowing to analyze a surface in three-dimensions. The secondary electron detector is composed by a scintillator and a photomultiplier. Secondary electrons emitted from the sample are attracted by a high positively charged grid and subsequently accelerated by a potential difference up to the scintillator (figure 6.4). The scintillator is excited by emitting cathodoluminescence, which is then detected by a photomultiplier and converted...
into an electrical signal. This dynamic is related to every single point of the image. In fact, once the signal in one position has been collected, the scanning coil shifts the electron beam and the signal in the new position is collected. The scan proceeds until the entire surface is mapped and a morphological image is obtained.

**STM**

The STM microscope is based on the tunnel effect: a potential difference is applied between the tip and the surface and the tunneling current is measured when the tip approaches the surface without touching it. The current value associated to different points on the surface and to the surface electronic states allows to generate a high-resolution 3D map probing at the same time the morphology and the surface local density of states of the sample.

The instrument is characterized by the scanning tip, the mechanics of the tip and the acquisition system. The quality of the image and the spatial/electronic states resolution mainly depend by the shape and the size of the tip. It is made in tungsten and the modern manufactures are capable to produce a tip-end with a single atom.

If the tip scans the sample surface the current measures the changes in the surface height/depth and in the density of states. The sample is first approached with a high voltage bias. The tip fine piezoelectric movement achieves a tip-sample separation in the 0.4 - 0.7 nm range, which is the typical equilibrium position between attractive and repulsive interactions. In this condition, the voltage bias will cause electrons to tunnel between the tip and the sample, generating a measurable current. To operate, the tip and the sample are then polarized by a voltage that allows tunneling of electrons which depends by:

- the distance tip-surface;
- the Fermi energy of the tip;
- the work function of the surface;
- the density of the states of the sample.
For this reason STM maps contain additional morphological and electronic information than the two microscopy techniques described before.

**Fig. 6.5** Schematic representation of the STM setup (left); and of the constant current mode acquisition. In this mode the tip changes the trajectory to maintain constant the current value (right).

For simple morphological maps, the instrument is used in the constant current mode, in which the system stores the current during the scan and in the presence of a height/depth variation, the tip-sample distance is corrected to return back to the initial value of the current (figure 6.5). From these corrections a morphological map can be obtained.

Since this technique uses the tunnel effect phenomenon, which is high sensitive to the distance due to the exponential relation between current and inverse of the distance, it may produce high-resolution images (resolution down to tenths of Å) of the investigated surface. The current generated between the tip and the surface can be also used to obtain I-V characteristic of the sample, i.e., a highly local measure of the conductivity. Advantages and disadvantages of this technique are very similar to those of the AFM, although due to its high sensitivity it may investigated extremely smooth surfaces and needs to remove as much as possible noise and vibrations.
Nanoindenter

The characteristic geometry of the contact is identified and classified within two classes: a contact area measurement independent by the applied load, as for cylindrical shaped tip, or a load-dependent contact area, as for spherically or diamond shaped tips.

The hardness of the material is related to the maximum penetration of the tip at a certain force, defined as:

\[ H(\text{GPa}) = \frac{P_{\text{max}}}{A_r} \]

where \( P_{\text{max}} \) is the maximum load impressed during the measure and \( A_r \) is the residual area left by the indentation, which is obtained assuming the shape of the diamond tip measuring the maximum depth is perfectly known \[47\]. The reduced modulus is defined by the equation:

\[ E_r = \frac{\sqrt{\pi} S}{2\beta \sqrt{A_p}} \]

where \( S \) is the slope of the “extraction” part of the curve (figure 6.6), also defined as Young modulus, and \( A_p \) is the projected area of the tip at a certainty depth \( d \) \[47\]. It is calculated using the polynomial function of \( d \):

\[ A_p(d) = \alpha_0 \ d^2 + \alpha_1 \ d + \alpha_2 \ d^{1/2} + \alpha_3 \ d^{1/4} + \ldots \]

where \( \alpha \) coefficients are known.

The difference from the reduced modulus \( E_r \) and \( S \) is the first to take into account to evaluate the deformation and the displacement induced by the penetrating tip. Higher is \( E_r \) and stronger is the force needed to induce a deformation inside the material \[47\].
In the figure 6.6 the tip touches the sample surface and the load-displacement hysteresis curve describes the loading/unloading behavior of the tip. The unloading is different from the loading curve due to “plastic” deformations of the material.

**Raman**

In a Raman experiment the sample is illuminated by a monochromatic radiation emitted by a laser source. By analyzing the diffuse radiation we can distinguish components at different energies. The Rayleigh component, which represents almost all diffused radiation, comes from the elastic diffusion process that does not involve the exchange of energy with the system. It has the same energy of the incident radiation. The lines observed at lower and higher energy of the incident radiation are the Stokes and the anti-Stokes components and originate from inelastic diffusion processes.
The Raman scattering phenomenon is due to the polarization induced in a molecular system by the interaction with the monochromatic electromagnetic field. When the laser beam hits the sample, the oscillating electric field interacts with the system and generates a collective movement of atoms inducing a variation of the electronic polarizability $\alpha$. Vibrations involving bonds where electrons are delocalized produce large variations of the polarizability and are characterized by an intense Raman response.

**AES**

Auger electron spectroscopy (AES) is a common analytical technique based on the Auger effect. When an electron (or another particle) hits an atom with an energy between 2 and 50 keV, a core electron can be removed, leaving a hole in an internal orbital. The excited atom relaxes when the core hole is filled by one of the electrons of the external orbitals. In this process the excess energy of the atom can be released via X-ray emission (radiative process) or via emission of an electron from the external orbitals. This non-radiative process is called Auger and is dominant for the light elements and its probability decreases for high Z.
elements. The Auger electrons are emitted with a kinetic energy related to the orbital of origin and by the chemical state of the sample.

![Double pass CMA](image)

**Fig. 6.8** Scheme of electron detection based on a double pass Cylindrical Mirror Analyzer (CMA) typically used in the Auger spectroscopy.

All elements of the periodic table, except hydrogen and helium, can be detected and this technique probes a surface layer 1 to 3 nm thick. Moreover, since the kinetic energy of the Auger electrons depends on the chemical bond of the excited atom with the neighboring atoms, it is possible to obtain information also on the chemical state of the excited atom. By cleaning and/or removing the top surface atomic layers using Ar⁺ ions of different energies (0.5-5 keV), the Auger analysis can be performed also to clean surfaces or to layers below the surface. When the surface to be analyzed is irradiated with an electron beam the emission of Auger, secondary and backscattered electrons may occur and have to be collected and analyzed with a high-resolution electron detector. In figure 6.8 is shown a typical double pass cylindrical mirror analyzer (CMA), a detector that collects and analyze the energy of emitted electrons from the surface. Since the intensity of the Auger electrons is typically small compared to background, inside the CMA detector Auger electrons are multiplied and this enhanced signal is sent the electronics. Moreover, by modulating the CMA voltage with a small applied AC signal, AES is often performed in a derivative mode, a procedure that enhances the presence of small peaks. In this mode the detected signal is related to the current derivative dN/dE. Before the experiments of samples exposed to the atmosphere it is always necessary to clean the surface.
removing the contamination presents at the surface. This operation is commonly performed with a sputtering procedure as described above.
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