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Il lavoro svolto in questo progetto di ricerca riguarda lo sviluppo e l’analisi di tecniche sperimentali atte alla validazione di un metodo affidabile per la qualifica spaziale di componenti ottici. In particolare è stato studiato l’effetto dell’irradiaimento di ioni accelerati (principalmente protoni e ioni di He) in coating ottici, considerando energie simili a quelle presenti nel vento solare. Lo scopo principale è stato quello di studiare sperimentalmente l’impatto del vento solare sulle performance ottiche per componenti simili a quelli che possono essere utilizzati in missioni spaziali come ad esempio Solar Orbiter o BepiColombo.

Lo studio dei molteplici fattori che influenzano e modificano le performance ottiche è stato eseguito considerando vari tipi di coating ottici, dai single layer ai multistrato. A tale scopo, diverse sessioni di irraggiamento sono state effettuate, in ognuna delle quali sono stati variati i principali parametri chiave che caratterizzano il tipo di irraggiamento, come la dose, il flusso di ioni, il tipo di ione e la sua energia. Ognuno di questi fattori è risultato essere influenante nella modifica delle performance ottiche dei dispositivi irraggiati. In particolare, si è osservato che alcuni di questi fattori producono danni comparabili fra loro su alcune tipologie di struttura, mentre su altre lo stesso comportamento non veniva mostrato.

Oltre alle analisi delle performance ottiche dei coating irraggiati sono state eseguite numerose indagini strutturali, allo scopo di chiarire quali modifiche a livello microstrutturale possono essere responsabili della modifica delle performance ottiche. Infine, è stato sviluppato un primo modello in grado di prevedere il cambiamento di riflettività prodotto su coating a single layer dall’irraggiamento con ioni.

La realizzazione di tutti i coating ottici studiati, la loro caratterizzazione ottica e strutturale prima e dopo l’irraggiamento nonché tutte le simulazioni atte alla preparazione degli esperimenti di irraggiamento sono parte del lavoro svolto in questi tre anni di dottorato.

In particolare, le attività di deposizione e caratterizzazione dei film sottili sono state realizzate utilizzando la strumentazione presente nei laboratori del CNR-IFN di Padova, nel dipartimento di fisica e di ingegneria industriale dell’Università degli Studi di Padova, e presso il sincrotrone Elettra di Trieste.

Le sessioni di irraggiamento sono state effettuate presso l’Ion Beam Center (IBC) dei laboratori Helmholtz-Zentrum Dresden-Rossendorf (HZDR) in Germania. In particolare, nell’ultimo anno ho personalmente seguito una sessione di irraggiamento della durata di un mese eseguendo le caratterizzazione ottiche e strutturali in situ.
Introduction

The objectives of the next-generation space missions lead the development of increasingly innovative instrumentation able to visit unexplored areas of the solar system, and to operate in relative increasing harsh environments. All the instrumental sub-systems, included optical components will have to be able to withstand extreme operational environments, characterized by high thermal gradients, electromagnetic irradiation, particulate and high and low energy particles/ions irradiation. In particular, recently, it was demonstrated that low energy particles could compromise the performances of optical coatings, leading a potential failure of a space instrument.

Accelerators are commonly used to reproduce the particles irradiation on components. By selecting ions energies and mission lifetime equivalent fluences it is in principle possible to replicate the effects induced by the space environment, although accelerators flux rates are higher of orders of magnitude with respect to the real space conditions. For this reason, it is arduous to be sure that ground tests are effectively representative of what occurs in space, making a crucial issue the definition of the experimental irradiation parameters like the ion flux. Moreover, the knowledge of the environmental agents of a specific space environment is still limited, and only in few cases in-situ measurements were performed. In order to overcome this lack, scaling models based on data collected at 1 A.U. can be used to estimate environment parameters of an unexplored space location.

The impact on the optical components of the space environment is the main topic of this research project. In particular, a systematic investigation devoted to define clear and reliable testing procedures for optical coatings were performed. Such systematic studies started with Monte Carlo simulations to evaluate the penetration depth of a specific ion specie or particle within an optical element, determining the energy range where the ions highly interact with the coating. After that, in order to perform a systematic investigation of the damage mechanisms that a coating can undergo, many implantation experiments were carried out by using accelerators facilities. We observed that, depending on the coating structure and the ion energy, different potential damages can occur, such as changes of the optical properties of the materials, inter-diffusion at the interfaces due to elastic scattering interactions between the incident ions and the target atoms, delamination of some layers or a full detachment of the coating or part of it.

This thesis will present a general overview of the obtained results from these 3 years of work. The exposition is organized as follow:

- Chapter 1 gives a brief introduction of the past and future solar system exploration missions, and the main aspects of the space environment that should be considered for the future space missions.
- Chapter 2 will describe how energetic ions interact with matter and in particular with thin films. An effective medium model will be presented to model the changes of the optical proprieties which can occur on irradiated materials.
- Chapter 3 will give general description of the thin film technology. As thin films are widely used in optical devices, in this chapter a complete description of how a thin film works and how its proprieties can be used to develop optical devices will be presented. Furthermore, a brief description of the main deposition processes is reported as well.
• Chapter 4 reports a detailed description of the samples, their characterizations (optical and structural), and their ground irradiation. Details of irradiation experiments on optical samples performed in these 3 years can be found here.
• Chapter 5 reports a description of the main obtained results. Different aspects of the irradiated coatings will be analysed and discussed. The presented results are only a small part of the analysed data. Future publications are needed to present all the scientific aspects emerged on this PhD work.
Introduction

This chapter’s aim is to present a general overview of the past and the future of space exploration and the impact of the space environment on a space mission. Since the beginning of solar system exploration scientists had to face the “problem” of space environment in particular with the impact of these harsh condition with all the spacecraft instrumentation. From every new mission additional details on the explored space environment are collected, in fact in every space mission dedicated instrumentations is devoted to study the visited space environment.

Every component of a spacecraft is qualified for space application and this means that all the spacecraft components can be operational for all the duration of the space mission in the relative mission environment. In a space mission, in fact, a document with a detailed description of the specific environment is draw up with the intent of giving detailed guidelines for spacecraft components space qualification.

Is clear that failure of electronic/mechanical components in the satellite instrumentation is crucial issue that can bring to the failure of the mission and the payload loss. For this reason the space qualification of these components is a well-known process that has been developed since the beginning of space exploration.

The problem of space qualification of optical components for satellite application only recently arise in the scientific panorama. Optical instrumentation is always present in a space mission with multiple instruments for different applications, and a camera to collect picture is always present in a satellite payload. A standard procedure before the mission launch is the optical calibration of a space instrument like a camera, spectrometer, etc. In this process, the efficiency and the performance of all the optical components that compose an optical space instrument is tested and measured. An example of this process can be the ground calibration of PHEBUS (Probing of Hermean Exosphere by Ultraviolet) instrument on board of BepiColombo mission [1]. In this ground calibration process is important each efficiency parameter of each single components. If during the space mission an environment agent modify the optical performances of even just one single component, in this case all the ground calibration become invalid and the collected data (during the mission) can be altered in a not predictable way. This scenario can be applied in all the space instrumentations that relies in optical ground calibrations.

After a brief introduction of the space exploration, this chapter will present two space missions with a particular focus on Solar Orbiter environment. These two space missions, BepiColombo and Solar Orbiter have in common the proximity to Sun and in particular the strong interaction of their instrumentations with the solar wind.

This thesis’ object is to study the effect of solar wind irradiation in a near-sun environment on typical optical components commonly used in satellite instruments (mirrors, optical filters ecc.).

The last chapter will introduce the near-sun space environment with a particular focus on solar wind specification. A detailed description of Solar Obiter mission environment is presented in section 1.4.1.
1.1 Solar system exploration past and future

The space exploration and the first attempts to leave the earth atmosphere starts right after the end of world war two. The first scientific exploration from space was the cosmic radiation experiment launched by the U.S. on a V-2 rocket on 10 May 1946 [2]. The first images of Earth taken from space has been collected the same year [3] and later in the 1947 the first animal (fruit fly) was send into space.

More than ten years have passed before to send the first man in the space. In 1961 the 27-year-old Russian cosmonaut Yuri Gagarin is the first men that completed one orbit around the globe, lasting about 1 hour and 48 minutes in the outer space.

The first artificial object to reach another celestial body (the moon) was Luna-2 in 1959. The first automatic landing on another celestial body was performed by Luna-9 in 1966. Luna-10 became the first artificial satellite of the Moon[4].

The 20 July 1969 is a historical data for humankind, and will be remembered as the day that a man walk for the first time on another celestial body, our satellite, the Moon.

After the moon exploration, other celestial body of our space system became object of studies and space missions. The first successful interplanetary flyby was the 1962 Mariner-2 Venus flyby. The other planets of the solar system have been reach in this order : Mars by Mariner-4 in the 1965, Jupiter by Pioneer-10 in the 1973, Mercury by Mariner-10 in the 1974, Saturn by Pioneer-11 in the 1979, Uranus by Voyager-2 in the 1986, and finally Neptune by Voyager-2 in the 1989. In 2015, the dwarf planets Ceres and Pluto were orbited by Dawn-spacecraft and passed by New Horizons spacecraft, respectively.

The first interplanetary surface mission to return at least limited surface data from another planet is the 1970 landing of Venera-7 on Venus that sent data to earth for 23 minutes before the extreme environment destroys the lander electronics. In 1975 the Venera-9 was the first to return images from the surface of another planet. In 1971 the Mars-3 mission achieved the first soft-landing on Mars returning data for almost 20 seconds. Later much longer duration surface missions were achieved, including over six years of Mars surface operation by Viking-1 from 1975 to 1982 and over two hours of transmission from the surface of Venus by Venera-13 in 1982, the longest Soviet planetary surface mission.

After these first missions, many other space missions has been lunched to explore the solar system and its celestial bodies and together with terrestrial observations, a general description of these bodies has been obtained. At this moment not all questions have been answered, in particular to the most important: is there life outside of the earth? For this reason many other space missions are scheduled in the next ten years, pushed to answer to this question and many others.

In the next decade solar system observations rely on these important space missions:

- ESA Solar Orbiter (SoLO) in 2018. SoLO is intended to perform detailed measurements of the inner heliosphere and nascent solar wind.
- ESA-ExoMars rover and NASA Mars-2020 for Mars ground exploration. The main goal is to search for signs of past life on Mars.
• ESA-RKA JUICE in 2022 for the exploration of Jupiter and its icy moons. The mission is being developed to visit the Jovian system focused on studying three of Jupiter’s Galilean moons: Ganymede, Callisto, and Europa.

• ESA-JAXA BepiColombo in 2018. The mission will perform a comprehensive study on Mercury, including its magnetic field, magnetosphere, interior structure and surface

Because their proximity to the sun, a detailed description of Solar Orbiter and BepiColombo missions is presented in the next sections in order to introduce the near-sun space environment.

1.2 Solar Orbiter mission

Solar Orbiter (also named SolO) is a Sun-observing satellite that will be probably launched in October 2018, and it will reach the Sun within a distance as never reached before. During the mission, the spacecraft and its instruments will reach a distance less than one quarter of the Earth’s distance from the Sun (as shown in Fig.1.1).

Solar Orbiter once approached the final orbit will face a harsh environment. The sunlight will be twenty times more intense then to earth distances, and the same for the solar wind ion bombardment. Solar events like flare and corona mass ejection at this distance (<0.5 AU) can be extremely dangerous for the satellite’s instrumentation since even a satellite in the earth orbit can be affected/damaged by these solar events. The technological effort required for a successful mission will be rewarded with detailed images and an unprecedented measurements of the local near-Sun phenomena.
1.2.1 Mission scientific objectives

The principal scientific goals of the Solar Orbiter are:

- determine in-situ the properties and dynamics of plasma, fields and particles in the near-Sun heliosphere;
- probe with high resolution the Sun’s magnetized atmosphere;
- identify the links between the activity on the Sun’s surface and the resulting evolution of the corona and inner heliosphere, using solar co-rotation passes;
- observe and characterize the Sun’s polar regions and equatorial corona from high latitudes.

The expected outcomes of the scientific community are to understand how the solar wind is propelled, how the magnetic fields are generated, how we can predict the solar eruptions and their intensity or if it is possible to perform long-term forecasts of solar activity.

1.2.2 Solar Orbiter payload

Into 180 kilograms of payload, scientists want to accommodate a set of in-situ and a set of remote sensing instruments [6]. A thermal shield protects the payload from the direct solar radiation, and also ensures a low operating temperature in the spacecraft’s sub-systems.

The in-situ instruments consist of detectors for observing particles and events in the immediate proximity of the spacecraft: the solar wind and its proprieties, radio and magnetic waves in the solar wind, and energetic charged particles expelled by the Sun surface. The in-situ instruments planned in Solar Orbiter are shown in fig.1.2:

- The Energetic Particle Detector (EPD) will measure the properties of suprathermal and energetic particles. Scientific topics to be addressed include the sources, acceleration mechanisms, and transport processes of these particles. An Ion Spectrograph (part of EPD) will measure energetic particles ejected from the Sun. Data will be compared to other solar and interplanetary processes to understand solar system space weather.
- The Radio and PlasmaWaves experiment (RPWE) is unique amongst the Solar Orbiter instruments in which it makes both in-situ and remote-sensing measurements. RPW will measure magnetic and electric fields at high time resolution using a number of sensors/antennas, to determine the characteristics of electromagnetic and electrostatic waves in the solar wind.
- The magnetometer (MAG) will provide measurements of the heliospheric magnetic field. This instrument will provide detailed studies into the way the Sun’s magnetic field links into space and evolves over the solar cycle; how particles are accelerated and propagate around the solar system, including to the Earth; the corona thermal dynamics and how the solar wind is accelerated.
- Solar Wind Plasma Analyser (SWA) will consist in an array of sensors that will measure the density, velocity, and temperature of solar wind ions and electrons. A complete characterization the solar wind between 0.28 and 1.4 AU will be provided. In addition to determining the bulk properties of the solar wind, SWA will provide measurements of solar wind ion composition for key elements (e.g. the C, N, O group and Fe, Si or Mg).
The remote sensing instruments will observe the Sun’s surface and atmosphere: for such Sun-close observation a thermal shied is required and this is a delicate point in the design processes. The gas of the Sun corona is characterized by its strong emissions in short-wavelength ultraviolet rays. Tuned to these wavelength a full-Sun and high-resolution imager and a high-resolution spectrometer will be developed. The outer Sun atmosphere will be revealed by ultraviolet and visible-light (VIS range is part of the radiation spectra with wavelength included from 400 to 800 nm) coronagraphs that blot out the bright disc of the Sun. To examine the surface by visible light, and measure local magnetic fields, Solar Orbiter will carry a high-resolution telescope and magnetograph. The remote sensing instruments planed for Solar Orbiter are shown in fig.1.2:

- The Extreme Ultraviolet Imager (EUI) will provide image sequences of the solar atmospheric layers above the photosphere, and will provide an indispensable link between the solar surface and outer corona that ultimately shapes the characteristics of the interplanetary medium. EUI will also provide the first-ever images of the Sun from an out-of-ecliptic viewpoint (up to 34° of solar latitude during the extended mission phase).
- Coronagraph (METIS/COR) which will simultaneously image the visible and ultraviolet emission of the solar corona and diagnose, with unprecedented temporal coverage and spatial resolution, the structure and dynamics of the full corona in the range from 1.2 to 3.0 (from 1.6 to 4.1) solar radii from Sun centre, at minimum (maximum) perihelion during the nominal mission. This is a crucial region that links the solar atmospheric phenomena and their evolution to the inner heliosphere dynamics.
- The visible imager and magnetograph (PHI) which will provide high-resolution and full-disk measurements of the photospheric vector magnetic field and line-of-sight (LOS) velocity as well as the continuum intensity in the visible wavelength range. The LOS velocity maps will have the accuracy and stability to allow detailed helioseismic investigations of the solar interior, in particular of the solar convection zone.
- The Heliospheric Imager (SoloHI) will provide measurements to pinpoint coronal mass ejections or CMEs. CMEs are violent eruptions with masses greater than a few billion tons.
They travel from 100 to more than 3000 kilometres per second. When directed to the Earth these kind of events can disturb or damage satellite orbiting around the Earth.

- The EUV Spectrometer (SPICE) will provide extreme ultraviolet spectra of light emitted from the Sun. Data will advance our understanding of the various dynamics of the Sun to better understand how these dynamics affect the Earth and the solar system.
- The X-ray Imager (STIX) will provide spectroscopic images of solar thermal and non-thermal X-ray emission. A quantitative information on the timing, location, intensity, and spectra of accelerated electrons as well as of high temperature thermal plasmas will be provided. This kind of X-ray emission is mostly connected with flares and/or microflares.

1.3 BepiColombo mission

BepiColombo is a dual spacecraft mission to Mercury developed jointly between ESA (European Space Agency) and JAXA (Japanese Aerospace Exploration Agency). The mission aim is to answer to a set of scientific questions in order to gain knowledge about Mercury planet, its evolution history and its surrounding environment. The mission will be launched in July 2016 [24]. The spacecraft is composed by the Mercury Planetary Orbiter (MPO) and the Mercury Magnetosphere Orbiter (MMO).

In additional to the two orbiters, the BepiColombo mission has two additional segments that are very important during the interplanetary journey: the Mercury Transfer Module (MTM) and the MMO Sunshield and Interface Structure (MOSIF). During the interplanetary journey, the two orbiters, the MTM and the MOSIF module are connected together, forming the Mercury Composite Spacecraft (MCS) shown in fig.1.3. The MTM module is devoted to deliver the trust needed to reach Mercury and the large amount of power required is provided by a solar electric propulsion system. The MOSIF module provides the interface structure between the MPO and the MMO and protects the MMO from the Sun radiation until it has reached its operational orbit.

Fig.1.3 Exploded view of the BepiColombo cruise configuration named Mercury Composite Spacecraft (MCS) and mission trajectory respect to the Sun distance [7].
1.3.1 Mission scientific objectives

BepiColombo is a planetary cornerstone mission of ESA’s Cosmic Vision Program, and is devoted to the thorough exploration of Mercury and its environment. The scientific objectives that BepiColombo mission will try to address with its payload can be summarized with the following points:

- Study and understand the Mercury formation and geological history, its interior structure and composition; these informations are important because they can help us to understand the composition of the primitive solar nebula and the formation of our planetary system.
- Study the actual Mercury surface to understand its composition, geology and volcanology.
- Study the magnetosphere and the intrinsic magnetic field of the planet. Bigger planets like Venus, Mars and the Moon do not have a magnetic field, the question is why Mercury has. Understand how the magnetic field interacts with the solar wind.
- The exosphere composition and dynamics.
- Research of sulphur or water ice inside the polar regions.
- Since the advance of Mercury’s perihelion was explained in terms of space-time curvature, we can take advantage of the proximity of the Sun to test general relativity with improved accuracy.

1.3.2 BepiColombo payload

The scientific goals expected from BepiColombo mission will be addressed by a highly comprehensive set of instruments and instrument suites. In the following a brief description of the MPO and MMO instruments is presented: each instrument is described in detail in many specific articles and for more details are presented the reference [8].

The MPO payload is composed by:

- The BepiColombo Laser Altimeter (BELA) will measure and characterize the topography and surface morphology of Mercury. BELA will provide absolute topographic height and position with respect to Mercury’s coordinate system. A useful digital terrain model will be obtained, and together with the data collected by others instruments, a set of information about the geology, the tectonics and the age of the planet's surface can be retrieved. The returned laser signal can be also used to measure the local surface roughness and albedo.
- The Italian Spring Accelerometer (ISA) is a three-axis high-sensitivity accelerometer. It will be devoted to study the global gravity field of Mercury, gravity time variations due to solar tides, the local gravity anomalies, the rotation state of Mercury and the motion of Mercury's center of mass. The instrument will also perform experiments devoted to testing Einstein’s theory of General Relativity reaching an unprecedented level of accuracy.
- The MPO Magnetometer (MPO/MAG) experiment consists of a dual fluxgate magnetometer system that can measure 3D magnetic fields variation from DC up to 128 Hz. The magnetic field contamination from the electronic systems of the spacecraft can be avoided performing deferential measurements from the two sensors, one inboard and one outboard of the spacecraft. The MPO/MAG will measure the planet magnetic field in order to understand the origin and the mechanism under this magnetic field production. This will help us to
understand the origin, evolution and current state of the planetary interior. These informations will be useful to understand the formation of Mercury magnetosphere.

- The MErcury Radiometer and Thermal Infrared Spectrometer (MERTIS) is an IR-imaging spectrometer that will provide detailed information about the mineralogical composition of Mercury's surface by mapping the emittance with a spatial resolution of 500 meters and a high-spectral resolution: MERTIS will cover a wavelength range from 7 to 14 m with a spectral resolution up to 90 nm. In addition, MERTIS will be able to measure thermo-physical properties of the surface like thermal inertia and surface texture.

- The Mercury Gamma-Ray and Neutron Spectrometer (MGNS) will measure the elemental surface and subsurface composition by measuring the typical nuclear γ-ray emission of major soil-composing elements, the leakage flux of neutrons and the lines of natural radioactive elements present in the Mercury surface. It will also determine the regional distribution of volatile depositions on the polar areas of Mercury, which are permanently shadowed from the Sun.

- The Mercury Imaging X-ray Spectrometer (MIXS) is a dual channel spectrometer designed to analyse the surface atomic composition using the x-ray fluorescence (XRF) analysis. The primary scientific goal of MIXS is to produce with a high spatial resolution the global elemental abundance maps of key rock-forming elements with an accuracy of 10 - 20%. The instrument can also confirm if the aurora zone, where energetic particles interact with the surface, is an intense source of x-rays. The interpretation of the MIXS measurements requires the knowledge of the solar x-ray flux that are monitored by the SIXS experiment.

- The Mercury Orbiter Radio-science Experiment (MORE) is an instrument devoted to geodesy, geophysics and fundamental physics. It will help to determine the gravity field of Mercury, the size and physical state of planet core. It will provide crucial experimental data to understand the planet's internal structure and it will test theories of gravity with unprecedented accuracy. MORE will also measure the gravitational oblateness of the Sun. Finally, MORE will also contribute to the determination of Mercury's obliquity (i.e. the obliquity of the equator with respect to the orbital plane) and the amplitude of its 88-day orbital librations in longitude: these two quantities, together with the coefficients of the second-degree harmonics of the gravity field, will indicate if the Mercury has a molten core.

- The Probing of Hermean Exosphere by Ultraviolet Spectroscopy (PHEBUS) instrument is a dual-channel EUV/FUV spectrometer devoted to characterize the structure, composition and dynamics of Mercury's exosphere and to understand the coupled surface-exosphere-magnetosphere system.

- The Search for Exospheric Refilling and Emitted Natural Abundances (SERENA) experiment will provide information about the interaction of solar wind with the global surface-exosphere-magnetosphere system. The experiment consists of four sensors that can operate individually: the Emitted Low-Energy Neutral Atoms (ELENA) measures energetic neutral particles (above 50 eV) escaping from the surface of Mercury. The STart from a ROtating Field mass spectrometer (STROFIO) that is a neutral particle spectrometer monitoring the cold exospheric gas composition with a high mass resolution. The Miniature Ion Precipitation Analyser (MIPA) that is an ion spectrometer for 10 eV-15 keV energies measuring ions that precipitate towards the surface, and the Planetary Ion Camera (PICAM) that is an ion mass spectrometer with 1 eV-3 keV energies range. SERENA and PHEBUS will jointly collect data
in the same time to produce a global mapping of the exosphere together with in situ neutrals and ions observation.

- The Spectrometer and Imagers for MPO BepiColombo Integrated Observatory System (SIMBIO-SYS) instrument suite is an integrated package for the imaging and spectroscopic investigations of the Mercury's surface. A Stereo Channel (STC) will provide the global colour coverage of the surface in full stereo at 50 m/pixel resolution, and a High spatial Resolution Imaging Channel (HRIC) will characterize special surface targets with high resolution images up to about 5 m/pixel, in four different bands, and a Visible Infrared Hyperspectral Imager Channel (VIHI). The scientific goals of SIMBIO-SYS are to characterize the surface geology, volcanism, global tectonics, surface age, surface composition and geophysics of Mercury.

- The Solar Intensity X-ray and particle Spectrometer (SIXS) experiment will monitor solar X-rays (SIXS-X) in the spectral range 1-20 keV with 300 eV of resolution and the energetic particles (SIXS-P). The x-ray data are mandatory for a fluorescence analysis of MIXS spectra. In fact, due to the high variability of the intensity and energy spectrum of both x-rays and energetic particles, simultaneous operations of SIXS and MIXS are required. Additionally, it will give important information about the physics of the Sun and, in particular, it will monitor the solar x-ray corona and solar flares.

The MMO payload is composed by:

- The main objective of the Mercury Dust Monitor (MDM) is to investigate the dust environment in the region of the solar system between 0.31 to 0.47AU. For example, the meteoroids activity on the surface may contribute significantly as one of the source processes of the planet’s tenuous atmosphere and the dust environment around the planet. This instrument is designed in order to detect impact momentum, the characteristic and the density of the dust.

- The MMO Magnetometer (MMO/MAG) instrument will collect magnetic field data in synergy with MPO/MAG. The instrument is designed to measure magnetic fields with an accuracy of about 10 pT, a dynamic range of 2048 nT and a time resolution up to 128 Hz.

- The Mercury Plasma/Particle Experiment (MPPE) is a comprehensive instrument package for plasma, high energy particle and energetic neutral atoms measurements. It is composed seven sensors: two Mercury Electron Analysers (MEA1 and MEA2), a Mercury Ion Analyser (MIA), a Mercury mass Spectrum Analyser (MSA), a High Energy Particle instrument for electrons (HEP-ele), an High Energy Particle instrument for ions (HEP-ion) and an Energetic Neutrals Analyser (ENA). Usefull information about the plasma and particle environment around the planet will be provided by MPPE.

- The Mercury Sodium Atmospheric Spectral Imager (MSASI) is a high-dispersion visible spectrometer working in the spectral range around sodium D2 emission (589 nm). A Fabry-Perot etalon is used to achieve a compact design. A one degree-of-freedom scanning mirror is employed to obtain full-disk images of the planet. This instrument will observe the Sodium in the planet exosphere and it will collect precious information about the exosphere dynamic.

- The Plasma Wave Investigation (PWI) is designed and developed in collaboration between Japanese and European scientists. The PWI will provide the first opportunity for conducting in-situ and remote-sensing observations of electric fields, plasma waves, and radio waves in
the Hermean magnetosphere and exosphere. It will give important information regarding energy exchange processes in the small magnetosphere where the role of micro-physics is more visible than anywhere else. The PWI will observe both waveforms and frequency spectra in the frequency range from DC to 10MHz for the electric field and from 0.1 Hz to 640 kHz for the magnetic field.

1.4 The solar system environment

The space environment can cause severe problems for any space system and sub-system. Proper assessment of the potential effects is an essential part of the engineering process leading to the construction of any element of the spacecraft. It is important that space environment aspects are taken into account from the earliest phases of a project when consideration is given to mass budget, protection, component selection policy, etc. In general, during the impact evaluation of the space environment on space instrumentation, the following aspects should be always considered:

- Solar and Planetary Electromagnetic Radiation;
- Neutral Atmosphere;
- Solar Wind;
- Energetic Particle Radiation;
- Particulates;
- Contamination;
- Thermal;

In some cases, depending on the space mission, part of these aspects can be neglected because their contribution is not relevant. An example can be the design of an instrument for an interplanetary mission, where it is possible to neglect Neutral Atmosphere effects. In the Solar Orbiter mission, the Planetary Electromagnetic Radiation is not present and can be neglected as well.

Specific environment documents are published and distributed to the instrumentation developers to describe the environment conditions that the spacecraft will meet. An example of this document [5] regarding Solar Orbiter mission will be used to present the relative space environment.

This environment has been studied in this PhD project as a possible source of optical degradation. In particular, we consider the solar wind irradiation impact on optical devices by selecting typical solar wind parameters like the ion type, the energy and the fluence in the ground irradiation tests.

1.4.1 A near Sun environment: Solar orbiter example

In this section, a detailed description of the Solar Orbiter environment is presented. As a near-sun interplanetary mission only few aspects of the previous list are important: the thermal issue connected to the extremely high photon flux, the solar wind interaction, and the energetic particles presence. All these parameters are evaluated using environment data collected in past space missions, or extrapolated from a model with data measured at 1 A.U. by using earth orbiting satellites.
### 1.4.1.1 Environmental parameters derivation

Many parameters of the mission’s environment can not be available for the range of heliospheric distances of Solar Orbiter but only for the distance of the earth (1 A.U.): in these cases an appropriate estimation method must be applied.

We can consider that many parameters of the environment are strongly dependent on the heliospheric distance and they propagate radially in the space, a typical example can be the solar constant. With this assumption, we can define the corrective parameter:

$$\gamma = \frac{1}{r^2}$$  \[1.1\]

Sometimes, the best analysis requires to consider the minimum distance from the Sun (e.g. thermal analysis) while other times it is more convenient to consider an average distance (e.g. total protons fluence). In tab.1.1 we have computed, for different launch dates (therefore, different orbital trajectory), the useful scaling factor. The tab.1.1 shows that also the launch data can be an important parameter for space environment considerations. In the particular case of Solar Orbiter, in fact, not only orbit parameter can be modified by the launch period, but also must be considered the Sun cyclical activity.

Unfortunately, the solar constants are difficult to estimate also at 1 A.U. because the intrinsic complexity of the measured phenomena. However, from experimental measures, we can build a statistical model and retrieve the mean values of the solar constants. ESA has released a report in which we can find the constants and models useful to estimate the environmental parameters of our interest [5].

<table>
<thead>
<tr>
<th>Launch in 2017 (cancelled)</th>
<th>Radius [AU]</th>
<th>Factor $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum perihelion</td>
<td>0,23</td>
<td>18,90</td>
</tr>
<tr>
<td>Mission average</td>
<td>0,59</td>
<td>2,87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Launch in 2018</th>
<th>Radius [AU]</th>
<th>Factor $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum perihelion</td>
<td>0,28</td>
<td>12,75</td>
</tr>
<tr>
<td>Mission average</td>
<td>0,59</td>
<td>2,87</td>
</tr>
</tbody>
</table>

Tab.1.1 Scaling factor and orbit parameters of SoIO mission for different launching data.

### 1.4.2.2 Thermal environment

In the Solar Orbiter mission, the spacecraft final orbit is very close to the Sun (<0.5 A.U.) and the expected solar irradiance will be extremely powerful. The satellite components and instruments will be protected by a proper thermal shield during the mission. However, remote sensing instruments need proper apertures through the thermal shield during the observation phases. From these holes the solar irradiance may heats dangerously the interior of the spacecraft and so a thermal analysis must be considered.

Knowing the average solar irradiance at 1 A.U. (earth orbital observation), we can estimate the irradiance at perihelion using the scaling factors as in tab.1.1: the expected flux at the perihelion will be ~$25000 \text{ W/m}^2$. At perihelion, we will have also the highest working temperature for the spacecraft. The maximum temperature reached by the internal components depends to the diameter of the aperture in the thermal shield and the geometry of the envelope. The general
specifications provided by [6] suggest, as project requirements, the maximum temperatures that each component should resist without performance degradation or permanent damage.

1.4.2.3 The solar wind

The solar wind is part of the Corona, the Sun’s external atmosphere. The expansion against the gravity of the high temperature plasma near the Sun surface create a flux of ions (and electrons) outwards the Sun, i.e the solar wind, carrying the solar magnetic field along with it. The solar wind is a hot and dense plasma near the Sun, which slowly move towards the open space, and accelerates outwards to become cool, rare and supersonic at the Solar Orbiter perihelion and beyond.

Most of the solar wind’s acceleration takes place near the Sun and so the Solar Orbiter will not observe significant difference in velocity as its distance from the Sun varies. The solar wind velocity typically lies in the range 300-1200km/s. A solar wind velocity distribution is presented in fig.1.4. As is possible to see the slow-speed component, named slow solar wind, with velocities around 400km/s is concentrated in the ecliptic area. The high-speed component, named fast solar wind, with velocities around 700km/s is concentrated in the poles area.

![Solar wind speed distribution](image)

Fig.1.4 Solar wind speed distribution. Ulysses/Swoops 2009 [10]. The ion energy of solar wind particles is double in the polar region respect to the ecliptic region.

More severe but less frequent disturbances in the solar wind can be caused by coronal mass ejections, and these kind of events are connected to the solar cyclical activity. In the solar wind, in addition to protons, we can find many ions like He++, O6+, Fe10+. Typically, the kinetic energy for protons is about 1 keV while for He++ is about 4 keV. Other heavy ions can be found in the solar wind, but as is clear from tab.1.2 that the concentration of these ions respect to proton content is very small. In order to obtain a reasonable analysis model, it is convenient consider the mean values for the solar wind and its mean composition. From [5] we have the data reported in tab.1.2:
At 1 A.U. | Mission average
--- | ---
Density (cm$^{-3}$) | 8.7 | 25
Speed (km ∙ s$^{-1}$) | 468 | 468
$N_{\alpha}/N_{\text{proton}}$ | 0.047 | 0.047
$N_{\text{O}^+}/N_{\text{proton}}$ | 0.0003 | 0.0003
$N_{\text{Fe}^{10+}}/N_{\text{proton}}$ | $8.77 \cdot 10^{-6}$ | $8.77 \cdot 10^{-6}$

Tab.1.2 Solar wind data for SoLo mission. The average energy for proton is 1 keV while for He+ ion is 4 keV.

As latter explained in chapter 5, in irradiation ground tests the important parameters are the total absorbed fluence, the irradiated ion type and its energy. For a reasonable estimation of fluence and ion energy, we consider the mean density by scaling it with the inverse square law (eq.1.1), and we assume the mean energy form the ion speed average. With these assumptions in tab.1.3 are presented irradiation parameters for one year of solar wind exposition for SoLo Mission (He++ and proton contribution).

<table>
<thead>
<tr>
<th>slow</th>
<th>Energy (avg)</th>
<th>1 year fluence (particles·cm$^{-2}$)</th>
<th>fast</th>
<th>Energy (avg)</th>
<th>1 year fluence (particles·cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>1 keV</td>
<td>$4.94 \cdot 10^{16}$</td>
<td>p</td>
<td>4 keV</td>
<td>$2.67 \cdot 10^{16}$</td>
</tr>
<tr>
<td>He</td>
<td>4 keV</td>
<td>$2.6 \cdot 10^{15}$</td>
<td>He</td>
<td>16 keV</td>
<td>$2.02 \cdot 10^{15}$</td>
</tr>
</tbody>
</table>

Tab.1.3 Solar wind slow/fast irradiation parameters for one year of SoLo mission.

### 1.4.2.4 Energetic particles

Energetic charged particles, which can penetrate external chassis of spacecraft, can be encountered throughout the Solar Orbiter mission, and the effects on the different components should to be considered. The energy for electrons is typically above 100 keV, while for protons and other ions this is above 1MeV. In addition, neutrons, γ-rays and X-rays can be considered as energetic particles in space environment considerations.

For Solar Orbiter, the main source of these particles is the Energetic Solar Eruptions (ESE). Energetic ions lose energy rapidly in materials, mainly through ionization, and this energy transfer can disrupt or damage targets. Solar particle events, due to their large variability in magnitude and frequency, must be treated statistically. However, large events are confined to a 7-year period defined as solar maximum. Although large events are absent during the remaining 4 solar minimum years of the 11-year solar cycle the occasional small event can still occur (an exception is the X9.3 solar flare in 2017/09/06 happened in a solar minimum). To investigate the effects of these particles (protons and heavy ions) on satellite instruments, it is possible to consider again the total absorbed fluence: the reference model of time-integrated effects is ESP (Emission of Solar Proton)[5] and it is also available in [9]. For example, in fig.1.5 we can see the proton fluence for different energies predicted by the EPS model for different launch dates.
Another source of high energetic particles is a continuous flux of galactic cosmic-ray ions. Although the flux is low (a few particles cm\(^{-2}\) \(\cdot\) s\(^{-1}\)), cosmic rays include about 90% protons, 9% alpha particles, and 1% of heavier ions called High Z energy (HZE) ions which can deposit significant amounts of energy in sensitive volumes and so cause problems.

In addition, also electrons irradiation contribution should be considered. The energetic electron environment encountered by the Solar Orbiter is dominated by Jovian elections (>100 keV) and solar wind electrons (~eV). The electron mass is too small to create buck damage like for the ion case. The effect of electrons is to thermalize in the material and release their energy in terms of thermal energy, for this reason they can be considered as an additional source in overall thermal analysis.
References chapter 1:


Chapter 2: Particle irradiation in solids and Thin Film

Introduction

The influence of particles irradiation on electronics devices was discovered during the first nuclear experiment connected to the nuclear bomb test in 1945. The effect of strong irradiation due to nuclear explosion in the instrumentation appeared in terms of electronics disturbances and failure. In a short period, it was clear that damage can occur as single event effect (SEEs) or as permanent modification of crucial parameters of the electronic components. Later, similar effects were observed in the components exposed to space conditions outside the atmosphere. Common electronic components exposed to space conditions became not reliable in a short period, and with a long exposure, the failure of the devices were observed. Starting from this evidence, in the last 70 years the scientific community has spent a lot of time and resources to understand the reasons and the possible solutions for this problem involving electronic devices exposed to harsh environment. Moreover, James Ziegler, while he worked for IMB, discovered that also on ground electronics were affected to problems due to energetic particles connected to cosmic rays.

Nowadays the interaction of accelerated ions with electronics and in general with solids is still under investigation. In particular, for electronics and in general for semiconductor materials, a huge amount of literature is available, while studies devoted to the investigation of the effects of radiations and particles on nanostructures materials such as coatings for optical applications has been investigated only recently. This leak of knowledge, in particular on thin films, has motivated this PhD project.

This chapter starts with a brief description of the current knowledge regarding to the damage induced in solids by particles. After, one of the most common Monte Carlo software that simulate the interaction of ions with matter will be presented. Finally, an effective medium approximation model (EMA) whose aim is to predict the optical response of a thin films irradiated by low energy ions is presented.
2.1 Damage in solids by particle irradiation

In 1940s Wigner and collaborators started a pioneering experimental and theoretical studies on the displacement damage occurring in materials irradiated by neutrons. This work was focused on the impact of irradiation of materials with technological importance [1]. Lark-Horovitz [2], Seitz [3] and Salter [4] focused these irradiation tests in semiconductor materials like silicon and germanium because of their raising importance in electronic devices. From this point of the history, the investigation of irradiated materials continued until nowadays and the importance of these studies has grown due to the coming of the nuclear era and the space exploration. In fact, it has become more common for instrumentation to face harsh environments like nuclear power plants, nuclear accelerators, space environments or future fusion power plants.

The interaction of accelerated ions with solids can be described with ionizing and not ionizing process as they lose energy inside the matter because of collisions. The result of this energy loss is the creation of electron-hole pairs (ionization) and recoiled atoms of the crystalline lattice (displacement damage). The displacement damage can occur in vacancy production and interstitial atoms. A vacancy is the absence of an atom from its normal lattice position, while a displaced atom in a nonlattice position is called interstitial. A Frenkel pair (or close pair) is the combination of a vacancy and the relative interstitial atom. Vacancies and interstitial atoms can form with the lattice impurity a new kind of defects called E-centers, which typically occur in irradiated Silicon.

These defects can be isolated or can group in cluster and this depends on irradiation parameters like energy, ion species, irradiation temperature ecc., in general incident energetic particles produce a mixture of isolated and cluster defects.

Once created, defects can evolve to more stable energetic conditions. Defects in Silicon, for example, are quite mobile at room temperature, and can move through the lattice (because thermal energy) and form more stable defects such vacancy impurities. Defect reordering is called annealing and typically the amount of damage is modified by this process and can be reduced or evolve in a more effective defect (reverse annealing).

The annealing is divided in two components, the short-term thermal annealing that is a process that complete in seconds or minutes after the irradiation damage and the long-term annealing that can continue for years after the irradiation at room temperature. In a steady condition of irradiation like in the space environment if, for example, the defects creation rate is lower than the fast-term annealing process, the result will be in quite stable damage production, and the long-term annealing effect can be observed only if the irradiation process is stopped.

The effectiveness of irradiation damage is so connected to the bombardment conditions and the time after irradiation because the reordering process is always present. The effective damage in fact depends in many factors but the most important is due to the temperature, and in general, all the thermal history of the irradiated material.

The damage displacement effect in general is due to any modification of the periodicity of the crystal lattice. The microscopic alteration of the material structure has an impact on the macroscopic electrical proprieties (modification of the conduction band) and to the optical proprieties, since the intrinsic connection between this two phenomena.
2.1.1 State of art of irradiated optical components

The aim of this PhD project is to understand how the optical proprieties of materials and devices are modified by ion irradiation, and in particular to identify each modification mechanism that can alter the optical response of an irradiated device.

Preliminary studies (2011) on multilayer mirrors demonstrated that optical devices performances can be affected by ion irradiation [5-6]. These studies showed that the optical response of a Si/Mo multilayer mirrors is strongly modified by low energy ion irradiation (calm solar wind particles).

Bulk modification like displacement damage and contamination can change the optical constants of a material but also surface alteration (like surface sputtering) can increase the surface diffusive reflectance.

In the case of a multilayer structures, the complexity of all these possible effects, included an enhanced intermixing of the layers, has moved this studies to more simpler optical devices like single coating mirrors. Studies on gold, iridium and platinum mirrors has shown that even in a single layer structure, low energy alpha particles (4 keV) have an impact on the reflectivity in the UV range[7].

Sznajder et al. studied the degradation of metallic surfaces under space condition [8] with a special consideration to hydrogen recombination process, and bubbles formation in irradiated aluminium.

High-energy proton irradiation (order of MeV) and gamma irradiation has been used to test the UV/VIS optical proprieties of different coatings for space application in Di Sarcina et al. [9].

Bi-layer structures were studied to isolate the contribution of the enhanced interlayer intermixing under 4 keV alpha particles bombardment [10].

All this studies have demonstrated that materials exposed to particles irradiation show a modified optical response but all the mechanisms under this phenomena are still not well understood, and recently the scientific community has demonstrated a particular interest on this topic with an increasing number of publications since 2002 [11-15].

2.2 Monte Carlo simulation for particle irradiation

The Monte Carlo method simulations can help to simulate the interaction of ions with solids, and in particular, for this project the aim is to simulate the interaction of solar wind with coatings. Thanks to SRIM (for software details see [16]) it is possible to simulate the interactions that a particle undergoes with a single thin film or a stack of layers. The program provides parameters such as the particle range in the material, the damage created in the crystalline lattice, and its distribution in the sample for each incident atom. For low energy ions, the interaction between the atoms of the crystalline lattice and the irradiated particles is essentially coulombian and for this reason, the energy loss is mainly due to ionization.

SRIM can perform different type of simulations, from a simple ion range calculation to a full cascade simulation where also the recoiled atoms can produce damage by subsequent collisions. Surface sputtering can be also evaluated with a dedicated optional simulation. A more detailed simulation leads to an increased usage of computational resources.
SRIM can be used to evaluate the penetration depth of an accelerated ion beam in an optical thin film or in a multilayer structure in order to understand where the damage is localized (see an example in fig.2.1). Moreover, in a multilayer structure the recoils distribution around the layers interfaces can give a rough estimation of the atom intermixing at the interface due to ion irradiation (fig.2.2).

Fig.2.1: TRIM simulations of the 4keV He+ implantation profile in SiO$_2$ (a) and TiO$_2$ (b) films.

Full cascade simulations are used to estimate the lattice damage that include vacancies distribution, recoils distribution of lattice atoms, and Frenkel pairs distribution. The full cascade simulation take into account not only primary knock on atoms (PKA) but also the secondary collisions of the recoiled atoms.

Fig.2.2: Recoiled atoms distribution in SiO$_2$(40 nm)/Al bi-layer (a) and relative Gaussian fit of the intermixed profile (b).

This particular feature of the simulation can be used to estimate the Nonionizing Energy Loss Rate (NIEL) that includes all the energy losses with the only exclusion of ionization process:

\[ NIEL = \frac{N}{A} \left[ \sigma_e T_e + \sigma_i T_i \right] \]  

where \( \sigma_e \) and \( \sigma_i \) are the total elastic and inelastic cross sections, respectively, \( T_e \) and \( T_i \) are the elastic and inelastic effective average recoiled energy corrected for ionization loss, \( A \) and \( N \) are the atomic weight and the Avogadro’s number.
The NEIL is particularly important because it is widely employed in electronic devices damage estimation due to ion bombardment. The last decades studies on irradiated electronic device has tried to correlate the NIEL to the device behaviour under particle irradiation, and for this reason, the NIEL can be a damage index not only in electronic devices but also in optical devices.

2.3 Effective medium model for irradiated thin film

The presence of ion implantation and lattice structure modification in irradiated materials can modify the optical response of the material itself. In fact, for example, the irradiated part can be seen as a mixture of bulk atoms and the relative implanted atoms with a consequent change of the dielectric properties. Optical response of materials, and then of thin films, strongly depends on the dielectric constant \( \varepsilon \) of the materials. In an effective medium model (EMA) the dielectric constant of a mixture, which is an effective permittivity \( \varepsilon_{\text{eff}} \), is modelled taking into account the electrical properties of each element of the mixture (inclusions), depending on its shape and to the induced dipole moment. The conditions of validity of this general model are simple: the spatial variation of the electric field has to be lesser that the variation in the structure of the medium, which means that the inclusions dimension has to be smaller than the wavelength of the incident electric field. Another condition is that the background permittivity should not be the vacuum permittivity, so this model is not valid for particles suspended in vacuum, or gas mixture.

The effective permittivity or the macroscopic permittivity \( \varepsilon_{\text{eff}} \) depends on the average displacement \( \bar{D} \) of the medium and the average electric field \( \bar{E} \):

\[
\bar{D} = \varepsilon_{\text{eff}} \bar{E}. \tag{2.2}
\]

The electric displacement depends on the polarizability of the medium:

\[
\bar{D} = \varepsilon_0 \bar{E} + \bar{P}. \tag{2.3}
\]

The macroscopic polarization moment is the sum of all microscopic polarization moments, and if each single microscopic element has the same polarizability, the sum can be written as:

\[
\bar{P} = n \bar{p} \tag{2.4}
\]

where \( n \) is the number of microscopic elements and \( \bar{p} \) is the dipole moment of a single element. If different elements of the mixture have different polarization proprieties, the sum should be weighted with effective mixture ratio of each elements (in terms of occupied volume, or volume fraction).

The dipole moment depends of the exciting electric field \( \bar{E}^e \):

\[
\bar{p} = \alpha \bar{E}^e \tag{2.5}
\]

For spherical scattering centres, the exciting field is given by the relationship [17]:

\[
\bar{E}^e = \bar{E} + \frac{\bar{p}}{3\varepsilon_0}. \tag{2.6}
\]

From equations 2.2 - 2.6 it is possible to obtain the macroscopic permittivity \( \varepsilon_{\text{eff}} \) as:

\[
\frac{(\varepsilon_{\text{eff}} \bar{E} - \varepsilon_0 \bar{E})}{n} = \alpha (\bar{E} + \frac{(\varepsilon_{\text{eff}} \bar{E} - \varepsilon_0 \bar{E})}{3\varepsilon_0}) \tag{2.7}
\]
and after some algebraic manipulations the relationship 2.7 can be rewritten as:

$$\frac{\epsilon_{\text{eff}} - \epsilon_0}{\epsilon_{\text{eff}} - 2\epsilon_0} = \frac{n\alpha}{3\epsilon_0}$$  \[2.8\]

which is the macroscopic permittivity of a random medium of $n$ spherical scattering centres. If the mixture contain scatterers with different polarizabilities, such as, in the simplest case, $N$ spheres with different permittivity, they have to be weighted with their volume fraction, and the 2.8 formula become:

$$\frac{\epsilon_{\text{eff}} - \epsilon_0}{\epsilon_{\text{eff}} - 2\epsilon_0} = \sum_{i=1}^{N} \frac{n_i\alpha_i}{3\epsilon_0}$$  \[2.9\]

The requirement for the validity of this formula is the perfect mixing of the mixture from the point of view of the incident electric field; this means that the non-uniformity of the mixture should be smaller than the incident radiation wavelength.

A very simple example of mixture can be a background medium with permittivity $\epsilon_0$, and a spherical scatterers with permittivity $\epsilon_1$ and a volume fraction $f_1$. In this case the 2.9 formula become:

$$\frac{\epsilon_{\text{eff}} - \epsilon_0}{\epsilon_{\text{eff}} - 2\epsilon_0} = f_1\frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + 2\epsilon_0}$$  \[2.10\]

and this is known as Rayleigh mixing formula. As is possible to see, the limits in eq. 2.10 of the effective permittivity are $\epsilon_{\text{eff}} = \epsilon_0$ for $f_1 = 0$ and $\epsilon_{\text{eff}} = \epsilon_1$ for $f_1 = 1$, and these values for the volume fraction correspond to the presence of only one of the two species respectively, and so the effective permittivity it the single component permittivity. Those limit conditions are two basic requirements for a good mixing formula.

A more general equation derived from 2.9 is:

$$\frac{\epsilon_{\text{eff}} - \epsilon_0}{\epsilon_{\text{eff}} - 2\epsilon_0 + \nu(\epsilon_{\text{eff}} - \epsilon_0)} = f_1\frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + 2\epsilon_0 + \nu(\epsilon_{\text{eff}} - \epsilon_0)}$$  \[2.11\]

with the $\nu$ value that can be an arbitrary positive number that takes into account the different shape and polarizability of the inclusions in the mixture. The 2.11 equation with $\nu = 0$ and solved to retrieve $\epsilon_{\text{eff}}$ is called Maxwell-Garnett mixing formula:

$$\epsilon_{\text{eff}} = \epsilon_0 \frac{2f_1(\epsilon_1 - \epsilon_0) + \epsilon_1 + 2\epsilon_0}{2\epsilon_0 + \epsilon_1 + f_1(\epsilon_0 - \epsilon_1)}$$  \[2.12\]

This formula will be latter used for the realization of an EMA model devoted to simulate the reflectance response of an irradiated single layer coating. An addition condition to the validity of this equation is that the volume fraction $f_1$ should be less than one ($f_1 \ll 1$) since it is assumed that the inclusion are spatially separated, and so they cannot overlap due to displacement $\bar{D}$ effect[18].
References chapter 2:


Chapter 3: Thin film theory and deposition technology

Introduction

In the last century, thin film technology (TFT) has revolutionized our knowledge and our life and nowadays it is largely employed in many scientific and technological fields. For example, thin films are pivotal in the development of optical components or electronic devices. In addition, TFT is largely exploited for the surfaces treatment, in art and even in food industry.

The main reason of this revolution is linked to the physical scale of the devices that can be developed by thin films. The definition of thin film or coating consists in a layer of a material having a thickness ranging from few nanometres up to hundreds of micron. The physical properties of the matter in this nano-scale dimension sometimes are different from bulk global properties, and at this scale, the physical description of the matter in this microscopic range can change from classical mechanics to the quantum world. TFT is directly linked to vacuum technology because mostly all the deposition techniques of coatings are performed in vacuum condition.

As in this thesis the TFT is used for the development of optical coatings for space applications, in different spectral range like:

- the VIS (visible) range from 400 to 800 nm of radiation wavelength;
- the EUV (extreme ultraviolet) range 10 to 124 nm, FUV (far ultraviolet) from 124 to 200 nm and NUV (near ultraviolet) from 200 to 400 nm, the vacuum ultraviolet (VUV) from 10 nm to 200 nm;
- the IR range from 800 nm up to 1 mm;
- the soft-x range from 0.2 to 10 nm.

This chapter is focused to recall the thin film general theory and to describe the fundamentals of thin film deposition. Firstly the interaction of a thin film with an electromagnetic wave is presented by using the transfer matrix formalism, also known as “admittance method”. After that, a brief description of application of the coatings and thin film structures in different spectral ranges will be presented.

The last part of this chapter will be devoted to describe the physics of the thin film deposition analysing the different properties that can be obtained on the thin film with each deposition technique. In particular, three deposition techniques that were used during the PhD will be presented.
3.1 Thin film reflectance theory

The interaction of an electromagnetic wave with a thin film is described starting from Maxwell equations [1]. The plane wave is a possible solution of the wave equation written for a medium characterized by a dielectric constant $\varepsilon$, magnetic permittivity $\mu$, and conductivity $\sigma$:

$$
\nabla^2 E = \mu \varepsilon \frac{\partial^2 E}{\partial t^2} + \mu \sigma \frac{\partial E}{\partial t} \rightarrow E = \varepsilon \exp[i\omega(t - x/v)]
$$

[3.1]

where the plane wave solution requires that:

$$
\omega^2 / v^2 = \omega^2 \varepsilon \mu - i\omega \mu \sigma.
$$

[3.2]

Considering that $c^2 = 1/\varepsilon_0 \mu_0$ and defining the dimensionless parameter $N^2 = c^2 / v^2$, the equation 3.2 becomes:

$$
N^2 = \frac{\varepsilon \mu}{\mu_0 \varepsilon_0} - i \frac{\mu \sigma}{\omega \mu_0 \varepsilon_0}.
$$

[3.3]

This implies that $N$ takes the form:

$$
N = c / v = n - ik = n = \sqrt{\varepsilon / \varepsilon_0}
$$

[3.4]

where $N$ is known as the complex refractive index, $n$ and $k$ are respectively the real part and the imaginary part of $N$. The solutions for equation 3.3 are two, one having the a positive value for the real part and the other one having a negative value for the real part; for physical reason we discard the second solution, keeping those with a positive value for $n$.

From equation 3.3 it is possible to obtain:

$$
n^2 - k^2 = \frac{\varepsilon \mu}{\mu_0 \varepsilon_0}
$$

[3.4]

$$
2kn = \frac{\mu \sigma}{\omega \mu_0 \varepsilon_0}
$$

[3.5]

The values $n$ and $k$ are generically called optical constant of the material or, alternatively, $n$ is called refractive index and $k$ is called the extinction coefficient. The wave equation can be rewritten by using $n$ and $k$ and considering $\lambda = 2\pi c / \omega$

$$
E = \varepsilon \exp \left[ (-\frac{2\pi k}{\lambda})x \right] \exp \left[ i\omega t - \left( \frac{2\pi n}{\lambda} \right)x \right].
$$

[3.6]

This equation describes the electric field $E$ of a plane wave propagating along the $z$ direction. A similar equation can be obtained from Maxwell’s equations for the magnetic field $H$, which lays along the orthogonal direction with respect to the electric field. The relationship between the two solutions is given by the pointing vector $\hat{s}$ as:

$$
\frac{N}{c\mu} (\hat{s} \times E) = H
$$

[3.7]
Optical constants are important to describe the behaviour of an electromagnetic wave propagating in a medium. In eq. 3.7 the quantity $N/c\mu$ has the dimension of an admittance, and it is known as the characteristic optical admittance of the considered medium. In the free space the optical admittance is:

$$y = \sqrt{\frac{\varepsilon_0}{\mu_0}} = 2.6544 \times 10^{-3} \text{ S.} \quad [3.8]$$

At optical frequencies we can assume that $\mu = \mu_r\mu_0 \approx \mu_0$, we can write the medium admittance by using the identity $N = \sqrt{\varepsilon_\varepsilon_0}$:

$$Y = Ny \quad [3.9]$$

Let now consider a single thin layer deposited on a semi-infinite substrate. The reflectance of this system can be calculated by using the admittance method. In particular, the presence of an interface between the thin film and the substrate produces a number of reflected and transmitted beams, as schematically reported in Fig. 3.1, that have to be considered in the calculation of the system reflectance. In the thin film theory, a film is considered thin when reflections/transmissions from multiple interfaces of the film can interfere between them, thus if the path length between those beams is less than the coherence length of the electromagnetic wave. Normally the substrate is considered thick. In figure 3.1 is reported the case in which an incident electromagnetic wave impinges on a thin film deposited on a substrate.

![Fig.3.1: A sketch of an incident plane wave on a thin film.](image)

The + or – apexes in the fields components of the electromagnetic wave describe the propagation direction respect to the z-axis in figure 3.1.

In order to compute the reflectance of the systems, we start the analysis from the interface between the substrate and the film, which is marked boundary $b$ in figure 3.1. At this interface, the continuity conditions impose the conservation of the tangential components of B and H fields Moreover, as the substrate is considered semi-infinite, there is no negative going wave in the substrate. In contrast, as at the boundary $b$ occurs a partial reflection of the impinging wave, the total wave in the film has to be expressed as the superposition of one positive-going resultant wave and one negative-going resultant wave. Consequently, at the boundary $b$ the tangential components of B and H are given by the following relationship:

$$E_b = E_{1b}^+ + E_{1b}^- \quad [3.9]$$
\[ H_b = \eta_1 E_{1b}^+ - \eta_1 E_{1b}^- \]  

where \( \eta_1 \) is the admittance of the thin film medium. In those equations the common phase factor is neglected for simplicity. Eq. 3.9 - 3.10 can be rewritten as:

\[
E_{1b}^+ = \frac{1}{2}(H_b/\eta_1 + E_b) \tag{3.11}
\]
\[
E_{1b}^- = \frac{1}{2}(-H_b/\eta_1 + E_b) \tag{3.12}
\]
\[
H_{1b}^+ = \frac{1}{2}(H_b + \eta_1 E_b) \tag{3.13}
\]
\[
H_{1b}^- = \frac{1}{2}(H_b - \eta_1 E_b) \tag{3.14}
\]

The fields at the boundary \( a \) at the same time and at the point with identical coordinates \( x \) and \( y \), can be calculated by changing the phase factor of the waves in eq. 3.11 - 3.14 in order to take into account the phase delay induced by the translation of \( -d \) along the \( z \)-axis. The phase delay induced on the positive-going waves is obtained by multiplying the fields equations with the term \( \exp(i\delta) \), where:

\[
\delta = 2\pi N_1 d \cos \vartheta_1 / \lambda \tag{3.15}
\]

and \( \vartheta_1 \) is the refracted angle from boundary \( a \), \( d \) is the film thickness, \( N_1 \) is the complex refractive index and \( \lambda \) is the wavelength. Similarly, for the negative-going waves the term is \( \exp(-i\delta) \). It is important to point out that this procedure is valid if the coherence length of the impinging wave is longer than \( \delta \). Then, the values of \( E \) and \( H \) at the boundary \( a \) are given by:

\[
E_{1a}^+ = \frac{1}{2}(H_b/\eta_1 + E_b)e^{i\delta} \tag{3.16}
\]
\[
E_{1a}^- = \frac{1}{2}(-H_b/\eta_1 + E_b) e^{-i\delta} \tag{3.17}
\]
\[
H_{1a}^+ = \frac{1}{2}(H_b + \eta_1 E_b) e^{i\delta} \tag{3.18}
\]
\[
H_{1a}^- = \frac{1}{2}(H_b - \eta_1 E_b)e^{-i\delta} \tag{3.19}
\]

obtaining, after summing the positive and negative going components of the wave, the total fields at the boundary \( a \):

\[
E_a = E_{1a}^+ + E_{1a}^- = E_b \left( \frac{e^{i\delta} + e^{-i\delta}}{2} \right) + H_b \left( \frac{e^{i\delta} - e^{-i\delta}}{2\eta_1} \right) \tag{3.20}
\]
\[
= E_b \cos \delta + H_b \frac{e^{i\delta} + e^{-i\delta}}{2\eta_1} \]

\[
H_a = H_{1a}^+ + H_{1a}^- = E_b \eta_1 \left( \frac{e^{i\delta} - e^{-i\delta}}{2} \right) + H_b \left( \frac{e^{i\delta} + e^{-i\delta}}{2} \right) \tag{3.21}
\]
\[
= E_b \cos \delta + H_b \sin \delta \]

which can be expressed in matrix notation as:

\[
\begin{bmatrix}
E_a \\
H_a
\end{bmatrix} = 
\begin{bmatrix}
\cos \delta & (\sin \delta)/\eta_1 \\
\sin \delta & \cos \delta
\end{bmatrix}
\begin{bmatrix}
E_b \\
H_b
\end{bmatrix} \tag{3.22}
\]
This relationship connects the tangential components of $\mathbf{E}$ and $\mathbf{B}$ at the incidence interface of the film with the tangential components of $\mathbf{E}$ and $\mathbf{H}$ that are transmitted through the final interface. The matrix is known as “characteristic matrix of the film”.

It is possible to define the optical admittance of the thin film/substrate system as:

$$Y = \frac{H_a}{E_a} \quad [3.23]$$

This admittance is dependent on the polarization status of the incident electromagnetic wave. In fact, the film admittance $\eta_1$ depends on the polarization status of the wave and its value can be computed for both TE and TM polarization as:

$$\eta_1 = yN_1 \cos \theta_1 \text{ for s – polarization (TE)} \quad [3.24]$$

$$\eta_1 = yN_1 / \cos \theta_1 \text{ for p – polarization (TM)} \quad [3.25]$$

The system admittance can be used to compute the Fresnel coefficient of reflection for the thin film/substrate system [see reference 2 for details] through the equation:

$$\rho = \frac{\eta_0 - Y}{\eta_0 + Y} \quad [3.26]$$

where the $\eta_0$ is the admittance of the incident medium, which still depends on the wave polarization (also when $N=1$) and the incident angle $\theta_1$ with the laws reported in eqs. 3.24 and 3.25.

Furthermore, in the near normal incident condition ($\theta_1 \cong 0$) the $\cos \theta_1 \cong 1$ in eqs. 3.24 and 3.25, and then the reflection Fresnel coefficient becomes independent to the polarization status of the impinging wave. Finally, the reflectance and the transmittance of the thin film/substrate system can be obtained from the relationships:

$$R = \left(\frac{\eta_0 - Y}{\eta_0 + Y}\right) \left(\frac{\eta_0 - Y}{\eta_0 + Y}\right)^* \quad [3.27]$$

$$T = \frac{4\eta_0 \text{Re}(Y)}{(\eta_0 + Y)(\eta_0 + Y)^*}. \quad [3.28]$$

The matrix approach is particularly suitable because it can be easily extended to the case of a stack of thin films. In particular, the reflectance of an assembly of thin films can be calculated using the same method but extended to all the interfaces of the structure. From a mathematical point of view, the problem is solved by computing the characteristic matrix of the stack which is simply the product of the characteristics matrices $(A_1, A_2, ..., A_M)$ of all M-layers taken in the correct order:

$$\begin{bmatrix} E_a \\ H_a \end{bmatrix} = [A_1][A_2] \ldots [A_M]\begin{bmatrix} E_{\text{substrate}} \\ H_{\text{substrate}} \end{bmatrix} = [A_{E_Q}]\begin{bmatrix} E_{\text{substrate}} \\ H_{\text{substrate}} \end{bmatrix}. \quad [3.29]$$
3.2 Application of the thin films as optical coatings in different spectral ranges

Metals and dielectric thin films are widely use in optical applications. For instance, metal coating can be used as mirrors in UV/VIS/IR adsorbent attenuators, filters in FUV (far ultraviolet) and edge filters in EUV (extreme ultraviolet) and soft-X. In particular, as all conductive materials are good absorbers (k>>0) in the NUV/VIS/IR range, they show an air-metal reflection Fresnel coefficient with a high module, guaranteeing a high reflectance in this spectral range. An example of the NUV/VIS/IR reflectance curves of some common metals is reported in figure 3.2.

![Figure 3.2: Reflectance of different metallic coatings in a spectral range from 0.04-10 μm.](image)

Dielectric material are commonly used in the NUV/VIS/IR for the development of narrowband mirrors with high efficiency, antireflection coating (AR), filters and narrowband filters and edge filters. The typical characteristics of a dielectric material is the low value of the extinction coefficient (k=0). Thus, the refraction index of a dielectric materials is real and it usually depends on the wavelength by following a dispersion function. In the IR/VIS/NUV range, many materials have these properties; in figure 3.3 is reported the refractive index of common dielectric material used in the IR/VIS/NUV.

![Figure 3.3: Refractive index n of typical dielectric material used in thin film deposition for optics in the VIS/IR spectral range.](image)

Thin film interference is the principle exploited in optics for manipulating the optical response of a device. Let us consider, as example, a thin film (d thickness) of dielectric material with...
refractive index \( n \). As it can be observed in figure 3.4, part of the incident light is reflected back from the point A, and part of the transmitted wave is partially reflected from point B and recombines in C.

![Interference scheme of a thin film.](image)

If the light is coherent, the optical path deference between the two beams reflected in A and B at normal incidence is 2\( d \) and the phase shift is:

\[
\delta = \frac{4\pi nd}{\lambda} - \pi \tag{3.30}
\]

where the \( \pi \) is due to the phase shift introduced in the first reflection where \( n_2 > n_1 = 1 \) (for more details see [1-2]). The beam interference occurs when:

\[
\delta = 2m\pi \quad \text{and} \quad d = (2m + 1)(\lambda/4n) \quad \text{with} \quad m = 0, 1, 2, 3...; \quad \text{constructive interference}
\]

\[
\delta = (2m + 1)\pi \quad \text{and} \quad d = (m)(\lambda/2n) \quad \text{with} \quad m = 0, 1, 2, 3...; \quad \text{destructive interference}
\]

A simple example of how to use constructive/destructive interference is reflective/anti-reflection coating.

![Quarter wave layer as anti-reflection coating for a glass substrate.](image)
From figure 3.5, an AR coating is constituted by a layer of thickness $d$ of a dielectric material with refractive index $n_1$, interposed between the medium $n_0$ (usually air), and a glass substrate $n_s$ with $n_0 < n_1 < n_s$. In this case, the AR condition, the total phase shift must be:

$$\delta = \left(\frac{4\pi n_1 d}{\lambda} + \pi\right) - \pi = \pi \rightarrow d = \frac{\lambda}{4n_1}$$

[3.31]

This thickness $d$ is called quarter wave layer (QWOT). Considering condition 3.31, an example of MgF$_2$ AR coating on a glass substrate for the wavelength $\lambda=550$ nm is then calculated:

$$d = \frac{\lambda}{4n_1} = \frac{550 \cdot 10^{-9}}{4 \cdot 1.38} \cong 100 \text{ nm}$$

[3.32]

This is the minimum thickness of MgF$_2$ that should be deposited as AR coating for a glass substrate at 550 nm. This AR coating is a very simple thin film that is used to increase transmittance of lenses and transmitting optical device.

Multilayer stacks become fundamental in the EUV/FUV spectral range where the optical proprieties of the materials are much more poorer than those in the UV/VIS/NIR. In EUV spectral range, almost all materials absorb the radiation precluding the development of optical devices working in transmission. Actually, some materials, such as MgF$_2$ or LiF, have a low extinction coefficient in the FUV range allowing their potential employment in the realization of transmission optics. Despite this, the transmission efficiency achievable with these materials is still not acceptable requiring the use of thin films stacks to improve it. The alternative approach is to work only in reflection. Multilayer mirrors are the valid solution for the low efficiency problems in the EUV/FUV spectral range.

A multilayer (ML) mirror is constituted by a stack of optical dissimilar layers, usually one with a high extinction coefficient (absorber) and the second one with a small extinction coefficient (spacers). A sketch of a ML mirror is shown in figure 3.6.

![Fig.3.6: Scheme of a periodic multilayer coating.](image)

The materials selection is performed by following different reasons. A possible choice is to select materials with a big difference in the optical constants. In the soft-x and x-ray spectral range spacers are usually materials with low Z (low atomic number) while absorbers are materials with high Z. Once selected a specific wavelength, the best candidate as spacer material is that with
an absorption edge just below the target wavelength for obtaining a small $k$. The choice of absorber materials are related to the spacers selection, and is done by selecting a material with the higher N contrast ($\Delta N = |N_{\text{spacer}} - N_{\text{absorber}}|$) and possibly a low extinction coefficient.

The multilayer optical response is defined once selected the materials, the thickness of spacers and absorber and the total number of the layers. The optical reflectivity of multilayer mirror can be calculated using the admittance method as described in chapter 3.1.

3.3 Thin film deposition techniques

Optical proprieties of a thin film and its deposition conditions are strongly connected. Real structure of a thin film and models based on an ideal thin film do not agree in the most of the cases. However, understanding the origin of such differences is pivotal for improving the quality of the design of optical coatings and, at the same time, it can help to optimize the films deposition processes.

The ideal structure of a thin film is a single oriented crystal or an amorphous structure (see fig. 3.7), but in the real case, this kind of structures almost never exit. In fact, a real structure always contains a certain number of defects which can be extrinsic, if they alter the stoichiometry of the film, or intrinsic if they don’t alter it. Those defects have an important impact on physical proprieties of thin films, highly influencing the optical or electrical behaviour.

![Fig.3.7: Ideal thin film structure on left compared with a real film structure on the right. The incoming light $I_0$ in the ideal structure is split into reflected $I_r$ and transmitted $I_t$ according to relation $I_0 = I_r + I_t$. In the real case, the incident light is split in the additional component $I_a$ and $I_s$, respectively the adsorbed and scattered intensity. The incident light, according to energy conservation, become $I_0 = I_r + I_t + I_a + I_s$.](image)

An important aspect of the thin films deposition process is the film-growing conditions. The physical-vapour deposition (PVD) is a non-equilibrium deposition process that takes place in a condition of vapour supersaturation. Normally, the PVD process occurs in a condition with a high concentration of impurities; for this reason, a great number of defects (intrinsic and extrinsic) are present in the final structure of the film. The difference between bulk material and thin film proprieties is the presence of these defects; in fact, defects concentration can be five orders of magnitude greater in thin films with respect to bulk structures.

Additional crucial parameters of an optical thin film are stoichiometry and grain size distribution, and models are required to have a control of those parameters.
Thin film formation is a process of kinetic adsorption of atom vapours by a surface (substrate), which usually take place in vacuum (in general pressures lower than 1 Pa). Three phases can be distinguished during the film growth: nucleation, coalescence and thickness grow.

Nucleation is the process occurring during the first part of the thin film growth, where the vapour atoms start to condense into the substrate, which is commonly composed by a different material. This is reason why this process is also called heterogeneous nucleation.

The vapour condensation occurs in a condition of supersaturation, which it is characterized by high values of the parameter

\[ S = \frac{p}{p_e} \]  \[\text{[3.33]}\]

where \( p \) is the vapour pressure of the deposited material and \( p_e \) is the equilibrium vapour pressure of the substrate material at \( T_{\text{sub}} \); typical values during this phase are \( S = 10^5 - 10^{50} \) making nucleation a non-equilibrium process.

During the nucleation phase, the deposition rate can be evaluated starting from \( p \) by using the relationship [3]:

\[ R = \frac{p}{\sqrt{2\pi mKT}} \]  \[\text{[3.34]}\]

where \( m \) is the molecular weight, \( K \) is the Boltzmann’s constant and \( T \) is the vapour source temperature.

Like in all transition phases, the thin film growth starts with the nuclei condensation, which progressively enlarge their dimensions. Depending on the interaction between the atoms of the vapour and the substrate, it is possible to have three kind of gowning modes (see fig.3.8):

- **Layer by layer**, or Frank-van der Merwe mode where a layer of material grows on the top of another layer. In this case, the interaction between substrate-atoms and film-atoms is stronger than between the atoms of the film.
- **Island**, or Volmer-Webber mode where the nucleation occur in separate islands upon the substrate. The interaction between atoms of the film in this case is stronger than with substrate atoms.
- **Layer plus island** or Stranski-Krastanov mode, which is a combination of the two previous modes where a layer of islands grown on a continuous layer of coalesced islands.

![Nucleation modes of a thin film initial growth. \( \Theta \) is the substrate surface coverage in atom monolayer (ML).](image)

Fig.3.8: Nucleation modes of a thin film initial growth. \( \Theta \) is the substrate surface coverage in atom monolayer (ML).
In particular, the growth mode is not only dependent on the interface energies but also by supersaturation [4], as the supersaturation $S$ increase, as the film tend to grow in layers better than in islands.

Coalescence is the growth process occurring after nucleation; during this phase, the islands grow until they touch one another, reaching the formation of a continuous layer. During this process, the grains are formed by means of the fusion of different islands. A specific threshold, called percolation thickness, can characterize the transition from isolated island to a continuous macroscopic layer. The percolation thickness is the specific thickness where an ensemble of coalesced islands start to merge, and the macroscopic conductivity of the film (metallic) increases of several order of magnitude. It is clear that also the optical properties drastically change after the percolation thickness; in fact this phenomenon is exploited to create semi-transparent metallic films.

The percolation thickness usually lays between $1 – 20 \text{ nm}$; once passed this thickness value the thin film start to grow and real structure of the film arise from the following process:

- **Shadowing** is the name of the effect due to the geometrical interaction between the roughness of the film and the arriving atoms. The trajectories of vapour atoms are ballistic and usually follow a common direction, for this reason dendritic surface can occur especially if the substrate temperature is low (low atom mobility at surface).
- **Surface diffusion.** Mobility of admolecules (adsorbed molecules) at the surface and grain interfaces; dominant at $T_{\text{sub}}$ medium.
- **Bulk diffusion.** Mobility of admolecules inside the volume of the grains; dominant at high $T_{\text{sub}}$.
- **Recrystallization.** A phase transition can occur in the whole thin film, the film change its crystalline orientation. Dominant at large film thickness and high $T_{\text{sub}}$.

For most metal and dielectric, activation energies for diffusion are related to the melting point temperature of the material $T_m$. The four process just described are strongly related to a parameter called homologous temperature:

$$T_H = \frac{T_{\text{sub}}(K)}{T_m(K)}$$

where $T_m$ is the melting point of the deposited material. If one of this process dominate during the deposition, the real structure of the film exhibit different proprieties.

Fig. 3.9: Typical example of the zone diagram by Thornton [5] and Movchan [6].
Those proprieties are described in the so-called structure zone diagram (see an example in fig. 3.9), diagram that is composed by three zones:

- The zone I, where $T_H < 0.3$, the low mobility of the deposited atoms tend to stop them where they land forming fine-grained pours structure.
- The zone II, $0.3 < T_H < 0.5$, the surface diffusion of the deposited atoms tend to form a columnar structure.
- The zone III, $T_H > 0.5$, bulk diffusion tend to form equiaxed grain.

Pressure and $T_H$ are not the only one parameters that govern the real structure of a thin film. Thin film deposition in supersaturation condition as mentioned before is a not clean process, and contamination is always present. In fact the residual gas in a high vacuum deposition chamber always contain traces of water vapour, hydrocarbon, air residual ($N_2$, $O_2$, $CO_2$) that act as contaminants during the film grown. Chemical adsorption or physical adsorption of these unwanted elements during the film grown change the dynamics described in the zone diagram. Impurities that are not soluble in the film lattice are segregated in the grain boundary and in the surface/interfaces; while impurities that chemically react with the deposited atoms change the material proprieties, and not only the film structure.

High impurity concentrations act as low $T_H$ and for this reason all the zone diagram is shifted to a fine grain crystalline structure (zone I) [7].

### 3.3.1 Dielectric and metallic film proprieties

Dielectric films are commonly used in the fabrication of mirrors for laser application and optical filters. Often dielectric films are transparent to NUV/VIS/NIR spectral range and the light absorption in this spectral range is caused by defects included in a pours structure. Effective medium theories can be used to connect the real-contaminated structure of the thin film and its optical proprieties [8].

A simple model can estimate the number of inclusions, as the attenuation coefficient $\alpha$ is proportional to the defects concentration in a not-absorbing material:

$$\alpha = \frac{2\pi}{\lambda} k = \sigma N_d$$  \[3.36\]

Where the $N_d$ is the defects concentration and $\sigma$ is the scattering cross section for an incident photon (with wavelength $\lambda$), cross section that can be estimated as the area of an atom ($10^{-16}$ cm$^2$)[9].

Table 3.1 are reported typical value of $\alpha$ for and $\alpha^{-1}$ in dielectric film:

<table>
<thead>
<tr>
<th>Type of film</th>
<th>$N_d$</th>
<th>$\alpha$(cm$^{-1}$)</th>
<th>$\alpha^{-1}$(m)</th>
<th>$k(@250\text{ nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td>$10^{13}$</td>
<td>$10^{-3}$</td>
<td>10</td>
<td>$2*10^{-9}$</td>
</tr>
<tr>
<td>Thin film</td>
<td>$10^{16}$</td>
<td>$10^2$</td>
<td>$10^{-4}$</td>
<td>$2*10^{-4}$</td>
</tr>
</tbody>
</table>

Tab.3.1: The attenuation coefficient and the extinction coefficient in a dielectric thin film vs defects concentration.
Radiation losses are also present due to scattering effect in the real structure (see fig.3.7) and are connected to grains boundary, pores, rough interfaces and surfaces.

Metallic coating nucleation in most of cases is Volmer-Weber, island growth. Island are transparent to visible and infrared radiation due to the small size (few nm) and the low conductivity of the film. Once reached the percolation thickness the film is continuous so the infrared is reflected but the visible light still not. At larger thickness (>20 nm) all the radiation is reflected or adsorbed by the film.

This behaviour distinguish three type or metallic coating: metal island film, transparent metallic film and non-transparent metallic film. These type of metallic films can be use in multiple application like self-assembled quantum dot Ge island on Si substrate [10], visible beam splitter and transparent electrodes for transparent metallic film, and finally mirrors and multilayer mirrors [11] for continuous metal film. An important fact, that latter will be cited for this thesis’ samples production, is that a fine-grained polycrystalline metal structure can be obtained using the “quick-and-cold rule”. It has been proved that this particular deposition technique maximize the thin film reflectivity by using high deposition rate (quick) and low substrate temperature (cold $T_{sub} < 300^\circ$ C). Furthermore a high deposition rate (fast film grown) in a fixed residual gas environment (base vacuum), insure a lower contaminants density inside the film than at low deposition rate (slow film grown). In fact, the total number of contaminants present in a thin film is directly proportional to the deposition time, and for this reason, a short deposition time is necessary to minimize the number of contaminants included in the coating.

3.4 Thin film deposition methods

Physical vapour deposition (PDV) is a category of thin film deposition method that concern a variety of process where a thin film is deposited by the condensation of a vaporized solid material onto specific surfaces. PVD processes include physical ejection of material as atom or molecules and the condensation of these atoms on a substrate. The material vapour can react in the process with gas present in the vapour forming a new compound before arriving to the substrate, and this process is called reactive deposition. PVD process are various, here follow the most used:

- Thermal evaporation;
- Electron beam (e-beam) evaporation (reactive and not-reactive);
- Sputtering reactive and not reactive(magnetron sputtering with its variant, diode sputtering, ion beam sputtering);
- Cathodic arc deposition (reactive and not-reactive);
- Pulsed laser deposition (PLD);
- Ion planting.

The most used PVD techniques are evaporation, sputtering and ion planting.

Every PVD process can be described in three basic step:

1. Creation of vapour-phase atom or molecules. In this step, a material (target) is converted to a vapour phase using a physical process like evaporation, sputtering etc.
2. “Transport” the vapour-phase atom from the source to the substrate. The created vapour must travel from the target to the substrate, and this process can occur, for example, in vacuum chamber only if the mean free path of the vapour particle is bigger than the distance target-substrate.

3. Film grown on the substrate. Once the vapour is condensed (nucleation) on the substrate, the film increase its thickness and various surface process can be applied while the film is growing to control the coating microstructure.

In this thesis three PVD methods has been used to produce optical coating (RF magnetron sputtering, E-beam evaporation and thermal evaporation), and here follows a brief description of the used techniques.

3.4.1 Magnetron sputtering deposition system

The simplest sputtering system is a diode discharge chamber. In a diode discharge system a voltage is applied between an anode and a cathode in a vacuum chamber. By using an appropriate gas (working gas) and under specific conditions of gas pressure and voltage, a current between anode and cathode start to flow. Different type of discharge regime can be obtained changing the working gas pressure at fixed voltage or vice versa, but in all cases a flux of positive charged ions strike the cathode (any conductive material) surface creating an erosion effect called surface sputtering. Diode sputtering is low efficiency process resulting in a low deposition rate and low film adhesion on substrate.

The evolution of diode sputtering method is the DC magnetron sputtering method. In a DC magnetron system a specific magnetic field is applied on the cathode using permanent magnet (or electromagnet). A DC planar magnetron deposition system is presented in figure 3.10.

![DC planar magnetron deposition system](image)

Fig.3.10: DC planar magnetron deposition system.

The particular combination of magnetic and electric field confine the free electron of the discharge (plasma) near the cathode, while the trajectory of ions are almost not perturbed due to their big mass. The $E \times B$ drift force create a ring current and the plasma appear as a horizontal cut donut. The magnetic confinement of the free electrons create a high efficiency ionization area near the cathode. Electrons are no more dispersed in the vacuum chamber walls,
and, in this case, a great number of working gas ions are created near the target if compared with diode discharge. The sputtering effect, as mentioned before, is caused by working gas ion bombardment on cathode surface; more ions are created more atoms are ejected from the target (high deposition rate, high process efficiency).

The particular toroidal shape of the discharge can be notice in the erosion profile of the target. This means that not all the part of the target are equally eroded, and this can be a drawback if the target material is precious.

Particular gas can be introduced during the discharge in a process called reactive sputtering. In this process the ionizing proprieties of plasma are used to sustain a chemical reaction between the sputtered atoms and the reactive gas (typical gas used are oxygen and nitrogen). The result of this process is the deposition of a film composed by the produced reactants.

Different magnetic configuration and different cathode shape (electric field) has been used since the creation of this deposition technique. Particular shape of the plasma discharge can in fact modify the thin film proprieties. For example, in an unbalanced magnetron configuration the plasma area is extended and can interact with the substrate and so with the growing film. In this case the ion bombardment due to the discharge involve not only the target but also the thin film, and by using this effect is possible to control many properties of the growing film.

Although the use of DC power is commonly use in magnetron sputtering, RF (radio frequency) or pulsed power source are also used. In the RF magnetron system an electromagnetic wave in the radio frequency spectral range (13.56 MHz) is used to transfer power to the target and so creating a RF discharge. The main advance of this technique is the possibility to use not-conductive and conductive target material, but a limited use of power is introduced due to the physical limits of high power electronic devices working at high frequency.

High-power impulse magnetron sputtering (HIPIMS) is a particular novel approach to the use of magnetron [12]. Ultrashort high-voltage pulses (~10 µs) are delivered to the magnetron surface producing a transient plasma with a high current and plasma density. The main advantage of this technique is to create not only gas ions but also sputtered atom ions, condition that can be very useful in certain application.

3.4.2 E-beam and thermal evaporator deposition system

A schematic scheme of an evaporation system is show in fig. 3.11. The evaporation source is a thermally heated (or resistive heated) crucible or e-beam heated source, which contains the desired material. Once the material is melted, the pressure vapour of the material increase until the supersaturation condition are satisfied and the thin film start to grown in all the deposition chamber and so on the substrate. The substrate is placed at an appropriate distance facing the evaporation source.

Evaporation process is usually performed in a vacuum range from $10^{-5}$ to $10^{-8}$ mbar. In this pressure range the mean free path (MFP) of the evaporated vapour is large, orders of the meters, if compared with the typical distance source-substrate ($<1$ meter). For this reason the evaporated atoms undergo to an essentially collisionless motion (straight line) before the condensation on the substrate. Particular motorized stages of the substrate holder are need to
create uniform film since the deposition profile in the chamber follows the geometric feature of the source (typically a parabola shape with higher deposition rate in the center).

Substrate holder can be heated or biased using a DC/RF power supply (diode discharge surface modification on the thin film) in order to control/modify the structure of the growing film. Ion bombardment of the substrate can be produced alternatively in an ion-assisted evaporation process, where an ion gun deliver a constant flux of low energetic ions (typically Ar ions) to the film surface.

![Resistence heating evaporation and electron beam evaporation](image)

Fig.3.11: Thermal evaporation system on the left. E-beam evaporation system on the right.

In some cases an inert gas like argon can be fluxed inside the chamber to reduce the particle MFP. Multiple collisions of the vapour with the inert gas can in fact remove the geometric shape of the deposition rate resulting in an increased thin film uniformity. This technique is called gas scattering evaporation planting [13].

Reactive gas can be introduced in the chamber as for the reactive sputtering process previously described. This technique is called reactive evaporation and is used to deposit oxide/nitride films. Recently the reactive evaporation has been improved by introducing a plasma environment in the deposition chamber; the chemical processes in this case are activated by the plasma resulting in a more efficient deposition of reactants [14].
References chapter 3:


Chapter 4: Experiment description

Introduction
Many papers in literature report that optical devices’ performances can be heavily affected when exposed to the space environment. High and low energy particles and ions are among the most common environmental agents that can be encountered during the operation of an instrument [1]. For this reason, it is important to study the effects induced by such particles in order to predict the changes of optical components behaviour under ion bombardment, and develop a procedure able to validate such components for a specific space environment.

Ground irradiation tests are commonly performed by employing ion accelerators. In fact, by selecting ions energies and mission lifetime equivalent fluences it is in principle possible to simulate the effects induced in space, although flux rates in laboratory are always higher of orders of magnitude with respect to the real space conditions.

Ground irradiation tests on optical devices is the main part of my PhD program and consist in these different steps:
- Optical samples preparation;
- Optical/structural characterization of the samples;
- Selection of irradiation parameters and accelerator facilities;
- Samples irradiation;
- Optical/structural characterization of the irradiated samples.

The first section of this chapter is devoted to describe the techniques that were used to characterize the coatings proprieties (optical and not) during my PhD project.

The second section of this chapter is devoted to describe the two techniques that I used for the physical realization of the samples. The samples were deposited at the CNR-IFN Padova laboratory, by using or the e-beam/thermal evaporation technique either the magnetron sputtering deposition system, and the full preparation process is presented. Finally, in the last section a detailed description of the irradiation experiments performed during my PhD is reported. Irradiation tests were carried out at the Ion beam center (IBC) located in the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) center.
4.1 Coatings characterization

Thin films optical properties are strongly connected to the surface morphology and the internal structure as it was already described in chapter 3. Several methods are available to characterize thin film properties and in this section, a brief description of all the techniques used during my PhD project is reported.

4.1.1 Stylus profilometer and atomic force microscope (AFM) for surface analysis

Surface properties of a thin film are important not only from the optical point of view, but also for understanding the film microstructure and the growth dynamics. In general, surface morphology can be described using two parameters: waviness and roughness (see fig.4.1). The roughness is quantified by the deviations in the direction of the normal vector of a real surface from its ideal form in a microscopic scale (few microns)[2]. If these deviations are large, the surface is said “rough”; if they are small, the surface is said “smooth”. Waviness is the measurement of the more widely spaced component of surface texture, and it is a broader view of roughness (scale of hundreds of microns).

Fig.4.1: An example of waviness and roughness of a surface profile. Specific analysis tool can extract from a scan trace the desired profile.

A Park Systems XE-70 atomic force microscope (fig.4.2) were used to measure surface roughness of the deposited thin films. Atomic-force microscopy (AFM) is a very high-resolution scanning probe microscopy (SPM), a branch of microscopy that forms images of surfaces using a physical probe that scans the specimen surface. The image of the surface is obtained by mechanically moving the tip of the probe on the surface of the sample, with a line-by-line scan type, and recording the probe-surface interaction as a function of position, reconstructing the 3D topography of the sample.
AFM calculates the distance probe-sample by measuring the force between them, the Van der Waals attraction, in non-contact mode or the Coulomb repulsion in contact mode, which is a function of the distance.

In contact mode, repulsive forces present sharp variations providing a better resolution of the instruments, higher scan speeds and easier scans in samples with high roughness. In some cases, the contact of the tip with the sample might produce distort images, and can produce damages in soft samples (scratch).

In non-contact mode forces are very weak and to improve the system sensitivity and the signal/noise ratio a lock-in technique is needed: the cantilever (the structure on which the tip is attached) is forced to vibrate at its resonant frequency. Changes in the force gradient lead a modification of the resonance frequency, reducing the oscillation amplitude. This modification in the oscillation is transduced into an electric signal and converted in topographical information. Moreover, the signal is usually used also as feedback in order to keep constant the tip-sample distance. The oscillations of the cantilever, and so to the tip, are mechanically provided by a piezoelectric bimorph, and at the same time a laser monitors the tip distance using a laser triangulation configuration [3].

During this work, the instrument was mainly used in non-contact mode, with the tip scanning small portions of the samples (5 µm x 5 µm). The tip, a PPP-NCHR non-contact cantilever with a radius of less than 10 nm, can obtain tridimensional images with vertical resolution of a few Ångström and a lateral resolution limited only by the x-y piezoelectric actuator precision. The scanned area ranges from less than 1 x 1 µm up to 100 x 100 µm in the x-y plane, with a maximum vertical range of 12 µm. Piezoelectric scanners ensure maximum accuracy of tip and sample movements, along the z-axis for the tip and along the x-y plane for the sample.

An optical microscope helps for a rough alignment of the samples under the tip. Insulation from ground vibrations and air streams is mandatory to reduce the noise of the measure. We adopted a passive pneumatic table (BM-10 bench top vibration isolation platform, by Minus K Technology) and an acoustic isolator (a 510 x 655 x 720 mm cage provided by Park Systems).
A second instrument, a KLA-Tencor P-16+ profilometer, was used to measure waviness and thin film thickness. The instrument, shown in fig. 4.3, is a contact profilometer, that exploits a diamond stylus pressed on the sample and moved along a direction for a specified distance and a specified contact force, to scan the surface morphology of a specimen. It can measure small variations of the stylus along the vertical direction which are directly correlated to the surface morphology of the sample. The height position of the diamond stylus chances due to the surface morphology and it is converted to an analogic signal by means of a piezoelectric transducer; finally, this signal is converted into a digital signal. Profilometer scans can be 200 mm long with a vertical resolution of few nanometres and a vertical range up to 1 mm (greater than AFM vertical range).

In the case of stylus profilometer, the tip is pressed against the surface by a spring, applying on the sample a force between 0.5-50 mg. In particular, high applied forces can means high fidelity of the scan trace with the surface morphology, but also high possibility to damage the surface during the scan. This instrument, even if less precise than AFM, is able to quickly produce images and profiles because of the simplicity of measurement method, and for this reason it was used to measure coating thickness.

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**Fig.4.3: KLA-Tencor P-16+ stylus profilometer.**

### 4.1.2 Secondary ion mass spectrometry SIMS analysis

Secondary-ion mass spectrometry (SIMS) is a technique used to analyse the composition of solids and thin films by sputtering the surface of the specimen with a focused primary ion beam (FIB) and collecting and analysing ejected secondary ions. The mass/charge ratios of these secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the sputtered materials. Due to the large variation in ionization probabilities among different materials, SIMS is generally considered a qualitative technique, although quantitative analysis are possible with the use of calibrated standards. SIMS is the most sensitive surface analysis technique, with elemental detection limits ranging from parts per million to parts per billion.

A secondary ion mass spectrometer consists of a primary ion gun generating the primary ion beam (see fig.4.4), a primary ion column, accelerating and focusing the ion beam onto the sample. A high vacuum chamber host the sample and a set of secondary lenses extract ions from the sample.
chamber. Finally a mass analyser separate the ions according to their mass-to-charge ratio, and a
detector observe the filtered ions.

SIMS requires a high vacuum with pressures below $10^{-4}$ Pa ($10^{-6}$ mbar). This is needed to ensure
that secondary ions do not collide with background gases on their way to the detector (i.e. the mean
free path of gas molecules within the detector must be large compared to the size of the
instrument), and it prevents surface contamination by adsorption of residual gas particles during
measurement.

![Diagram of a typical dynamic SIMS instrument.](image)

Three types of ion guns are employed. In the first one, ions of gaseous elements are usually
generated with duoplasmatron or by electron ionization, for instance noble gases (Ar+, Xe+), oxygen
($^{16}$O−, $^{16}$O$_2$+, $^{16}$O$_2$−), or even ionized molecules. This type of ion gun is easy to operate and generates
roughly focused high current ion beam. In a second source type, the surface ionization source
generates $^{133}$Cs+ primary ions. Cesium atoms vaporize through a porous tungsten plug and they are
ionized during evaporation. Depending on the gun design, fine focus or high current can be
obtained. In the third type of source type, the liquid metal ion gun (LMIG) operates with metals or
metallic alloys, which are liquid at room temperature or slightly above. The liquid metal covers a
tungsten tip and emits ions under influence of an intense electric field. While a gallium source is
able to operate with elemental gallium, recently has been used as sources gold, indium and bismuth
alloys (lower melting point than the single element m.p., eutectic).

The choice of the ion species and ion guns respectively depends on the required current (pulsed or
continuous), the required beam dimensions of the primary ion beam and on the sample that has to
be analysed. Oxygen primary ions are often used to investigate electropositive elements due to an
increase of the generation probability of positive secondary ions, while Cesium primary ions often
are used when electronegative elements are being investigated.

Depending on the SIMS type, there are three different analysers available: sector, quadrupole, and
time-of-flight. A sector field mass spectrometer employs a combination of an electrostatic analyser
and a magnetic analyser to separate the secondary ions by their mass-to-charge ratio. A quadrupole mass analyser separates the masses by resonant electric fields, which allows only the selected masses to pass through it. The time of flight mass analyser separates the ions in a field-free drift path according to their velocity. Since all ions possess the same kinetic energy, the velocity and therefore time of flight (TOF) varies according to mass. It requires pulsed secondary ion generation using either a pulsed primary ion gun or a pulsed secondary ion extraction. It is the only analyser type able to detect all generated secondary ions simultaneously, and is the standard analyser for static SIMS instruments.

A Faraday cup measures the ion current hitting a metal cup, and it is sometimes used for high current secondary ion signals. Alternatively, an electron multiplier can be used to detect single incident ions increasing the detection sensitivity.

A typical SIMS scan is reported in figure 4.5. In our measurements, the used ion gun was a Cs+.

![Graph](image)

Fig.4.5 A typical SIMS image. The penetration depth is calibrated with the erosion rate of the focus ion beam. The different ion signals on the y-axis represent the number of ions collected in the mass spectrometer. In this example a gold sample of 150 nm.

SIMS analysis were carried out in the Physic Department of the University of Padua (Italy).

4.1.3 Electron imaging technology (SEM/TEM) and Energy dispersive spectroscopy (EDS)

Electron imaging is one of the most versatile technique for the examination and microstructure analysis of solids with sub-nanometric resolution. Electrons can be used to scan surfaces (scanning electron microscope) or to analyse the bulk structure by using electron transmission (transmission electron microscope). In fig.4.6 an electron microscope principle scheme.
In an electron microscope an electron beam is produced by an electron gun, usually composed by a tungsten filament, then a system of accelerating stages and magnetic lenses are designed in order to focus the electron beam on the specimen. Two detectors collect the scattered electrons (secondary electrons and backscattered electrons for SEM, transmitted electron for TEM) form the sample and create the image.

Secondary electrons are originated in the first nanometres from the surface and provide topographic information. Back scattered electron are high-energetic electrons, that are scattered out of the sample and loose only a small part of their energy (see fig.4.6). These electrons interact with the part of the sample under the surface and for this reason, the given image has a lower resolution. On the other hand, back scattered electrons can provide information about sample composition.

SEM and TEM images presented in this thesis were collected in the ion beam canter (IBC) located in the HZDR center. The used SEM/TEM microscopes are now described.

The Hitachi S-4800 (fig.4.7) is a cold-cathode field-emission scanning electron microscope (FE-SEM). This device is a very advanced imaging system that can provide resolution of approximately ~1 nm at 15 keV of beam energy. This FE-SEM allows the imaging of metallic, inorganic, organic and biological specimens with the minimum damage in soft samples. The energy dispersive x-ray spectrometer (EDS technique is described in the following) coupled to this FE-SEM provides the capability to analyse materials by determining the elemental composition and mapping specimen surfaces. A YAG backscattered electron (BSE) detector is available to capture contrast-enhanced images of multi-phase materials. Silicon wafer and other substrate materials up to 4” in diameter can be imaged.
The FEI Titan 80-300 (fig.4.7) scanning transmission electron microscope (STEM) was used to obtain cross-section images of thin film structures. This scanning transmission electron microscope is able to perform the imaging at atomic-level on a wide range of materials and nanostructures. The Titan is equipped with an electron energy loss spectrometer and an x-ray energy dispersive spectrometer for elemental and chemical analysis of materials at high spatial resolution. The microscope system includes a scanning module and a high angle annular dark field detector for scanning transmission electron microscopy (STEM) and for chemical analysis of very small volumes. The acceleration voltage can range from 80 kV up to 300 kV with a maximum STEM resolution of 0.136 nm at 300 kV. Besides classical TEM specimen preparation (sawing, grinding, polishing, dimpling, and Ar ion milling), target preparation can be done using a focused ion beam device (FIB, Zeiss NVision 40).

Energy-dispersive X-ray spectroscopy (EDS, EDX) is a technique used for the elemental analysis of a sample. As a spectroscopic technique, this analysis is based on detection of characteristic emission line in the electromagnetic spectrum of exited atoms. In particular, the internal core levels have a typical emission spectrum in the x-ray and this phenomenon is similar to x-ray fluorescence.

To stimulate the emission of characteristic x-rays from a specimen, a high-energy beam of charged particles such as electrons (in electron microscope) or protons (see PIXE), or a beam of x-rays or γ-rays (x-ray fluorescence), is focused onto the sample under investigation. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. If an electron in an inner shell is somehow exited and ejected from the shell, an electron hole is created. An electron from the near energy levels then fills the hole, and the difference in energy between the two shells may be released in the form of an x-ray.

The number and energy of the x-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. The energy of the x-rays is characteristic of the difference in energy between the two shells, and it is specific for each element atomic structure. This allows measuring the elemental composition of the sample.
Often, instead of x-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. This ejected species are called Auger electrons, and the method that analyse these electrons is known as Auger electron spectroscopy (AES). Auger electrons to be detected must be created only on the sample surface, while EDS signal is created deeper in the sample bulk (see fig.4.6 right).

In the Hitachi S-4800 FE-SEM the EDS analysis is provided by a Si(Li) x-ray detector with S-UTW-window (INCA, Oxford Instruments), for elemental detection with Z ≥ 5. The EDS cross-section analysis was used to evaluate the intermixing between interfaces in multilayer samples, and to detect an eventual important presence of contaminants in the deposited films.

4.2 Optical characterizations

Optical performances in different spectral range are a crucial aspect in this PhD project, and the modification of parameters such as the optical reflectance or transmittance was used to evaluate the impact of ion irradiation on coatings. Different facilities were used to perform such optical analysis as described in the following.

4.2.1 Cary 5000 UV/VIS/NIR spectrophotometer

A spectrophotometer is a device that can be used to measure the reflectivity and the transmission proprieties of a specimen in a specific spectral range. A typical spectrometer exploits a monochromator for obtaining a monochromatic test beam at a specific wavelength which is used to measure the transmittance or reflectance of a sample. In particular, the monochromator is designed to sweep a specific range of wavelengths, allowing to measure the optical response as a function of the wavelength. The Varian Cary 5000 spectrophotometer is a double out-of-plane Littrow monochromator (see fig.4.8 left). This instrument has been used in this thesis on several occasions and for different purposes.

The Littrow monochromator optical scheme is reported in fig.4.8, on the right. The double Littrow monochromator is simply a cascade of two of such monochromators; in this way, the band selected by the slit in the first of two Littrow monochromators is further diffracted and selected in the second monochromator with a consequent increase of the resolving power of the instrument.

The use of blazed gratings implies that they are optimized for a specific wavelength range. As this instrument is designed to work is a wide spectral band, two gratings are available in each monochromator and they are interchanged in order to cover the full band.
The Cary 5000 is designed as a double-beam, zeroing spectrophotometer. After the monochromator the full beam is split into two parts by an optical chopper, and the light is alternatively (with a frequency of 30 Hz) directed in two different directions. One of these parts, called test beam or sample beam, probes the sample to investigate the optical properties whereas the other one is used as reference beam. In this way the reflectance \( R \) (or transmittance \( T \)) is continuously calculated from the ratio between the test beam intensity and the reference beam intensity, and the apparatus response becomes insensitive to the eventual variations occurring on the source intensity or other mechanisms that can change the test beam intensity along the time. After the measurement, the collected data must be corrected with a baseline in order to compute the absolute reflectance/transmittance. In particular, for reflectance measurements the baseline signal is collected by measuring a reference sample (a calibrated reference mirror) while for transmittance measurements the baseline is taken by removing the sample from the test beam. Once the baseline is collected, the output signal \( S \) is computed as:

\[
S = \frac{I_{\text{sample}}}{I_{\text{baseline}}} \cdot 100
\]

In this way the response of the components constituting the sampling light path (through the sampling accessory) is also rejected and an absolute measure of reflectance and transmittance can be obtained.

The wavelength range of the Cary 5000 is 175-3300 nm. The light in this spectral range is provided by a halogen lamp for the VIS/NIR spectral range, and a deuterium lamp for the UV.

The UV+VIS sensing element of Cary 5000 is a R928 photomultiplier tube manufactured by Hamamatsu Photonics K.K. [4]. Its spectral sensitivity extends from 185 to 900nm. This sensor is made by a photocathode followed by an electron multiplier. From 900 to 3300 nm the detector is a cooled PbS photocell.

This spectrometer can use different accessories to increase the measure capabilities and in particular for this thesis an integrating sphere were used. This accessory is devoted to measure the diffuse reflectance that is the amount of energy not directed towards the specular reflection angle.
This energy is collected with an integrating sphere that is a 110mm hollow sphere [5] internally coated with Polytetrafluoroethylene (PTFE); this sphere exhibits NIR diffuse reflectance that is superior to traditional coatings, whilst maintaining good UV-VIS performance.

![Integrating sphere optical scheme.](image)

Fig. 4.9: Integrating sphere optical scheme.

As it is possible to see in fig. 4.9, both the sample beam and the reference beam enter in the integrating sphere and after multiple reflection, the light is collected by the detector. The first reflection of sample beam is on the sample mounted at 3.5° of normal incidence with respect to the sample beam. In this way, the only difference between the reference and the sample beam signal is the total reflectance (specular + diffused) of the sample. The contribution of multiple reflection inside the sphere by the entrance holes and the sample are neglected. To measure only the diffuse contribution of the sample, the sample holder can be arranged in order to set a 0° normal incidence. In this configuration, the specular reflected part of the test beam is back-reflected toward the source, allowing the detection of the single diffused component. The Cary 5000’s statistical error on a single measurement is about 1% of the registered value (reflectance, transmittance, absorbance etc.)

### 4.2.2 Normal incidence EUV/FUV facility

The EUV/FUV normal incidence facility located in the CNR-IFN laboratory is designed to perform reflectivity measurements in the 30-160 nm wavelength range. In the lower part of this range, called Vacuum-UltraViolet (VUV), the light absorption due to the air is very high and the measurements can be only performed in high vacuum (~10^-6 mbar) conditions. The overall structure of the facility is similar to a spectrophotometer: a beam coming from a chosen light source is spectrally dispersed by a monochromator and directed to the sample. The reflected intensity is then measured with a channel electron-multiplier (CEM). In this application, the needed performance of the optical components allowed their use in nearly normal incidence configuration.
In order to improve the efficiency of the monochromator, a design with a minimum reflections has been implemented in this facility. In fact, although plane grating monochromators (PGMs) have often a large scanning range and good resolutions, the cascade of many reflective components such as in Czerny-Turner configurations, leads to high losses at short wavelengths. In contrast, concave gratings are able to disperse and directly focus the image of the input slit onto the output slit, without the use of additional optical components. By using such kind of grating, a single reflection is present, and thus the efficiency of the monochromator can be strongly increased. Moreover, toroidal (even holographic) gratings can be used to minimize the astigmatism aberrations [6], that critically affect resolution and efficiency of the device.

The main component of the EUV reflectometer facility is a Johnson-Onaka monochromator [7]. The grating used is toroidal, with a horizontal curvature radius of \( R = 0.5 \, \text{m} \), ruled with 600 grooves/mm and coated with Platinum. This grating has the property that an input image is diffracted and refocused on the output slit.

The components of the EUV facility, with reference to fig.4.10, are:

- light source: several types of light sources can be connected to an aluminium flange that contains also the entrance slit. For these measurements, deuterium and hollow cathode lamp were used.
- entrance slit: the width of this slit controls the size of input image (and then the extended source effects) and the input power. The slit width can be adjusted between 0 – 650 \( \mu \text{m} \) whereas its height is fixed to 3mm. It is located at the right distance on the Rowland circle.
- grating: the toroidal grating in the Johnson-Onaka configuration is enclosed in a circular steel chamber connected with the entrance and exit slit with two steel pipes. A stepping servo mechanism moves the grating on the right trajectory. The first order diffraction (\( m = 1 \)) is used.
- exit slit: a slit identical to the one at the entrance is located at the same distance onto the Rowland circle.
- focusing mirror: a Pt-coated toroidal mirror working at 45° of incidence is located in a hexagonal chamber and it refocus the diffracted beam exiting from the monochromator in the centre of the experimental chamber.
• experimental chamber: another circular steel chamber is designed to contain the samples under investigation. A sample holder maintains the sample in a vertical position, and allows it to move in polar coordinates. The tilt angle \( \theta \) is controlled manually by a rotating graduated stage, whereas an endless-screw motorized guide alters the distance from the chamber centre. On the cover, a rotating arm can hold a detector that can be aligned with the reflected beam. The flange connecting this chamber to the previous one can be untightened to reconnect the chamber tilted at 90° to take measurements with different orientation.

The cascade of optical components induce a certain degree of polarization on the output radiation, which is normally absent in the source light. A method based on up/down-orientation measurements was used to eliminate the influence of this factor [8]. This is a single beam instrument, as only the reflected beam is measured. Zero correction is done measuring direct light two times for each measure. In this facility it is possible to measure reflectance from 8° to about 70° form the normal incidence.

4.3 Samples preparation for irradiation tests

Part of the work on this PhD project consist in the production of optical samples, based on thin film deposition, and the subsequent ground irradiation tests. The available deposition facility at CNR-IFN laboratory are two: a RF magnetron sputtering and an e-beam/thermal deposition system. After a general description of these deposition techniques in chapter 3, a detailed description of these deposition facilities is presented.

4.3.1 Ionvac Magnetron sputtering SP400

This facility is equipped with two balanced magnetron source of 4” of diameter (see fig. 4.1b), and a 300-Watt RF generator and the relative matching unit. The matching unit is devoted to couple the impedance (capacitive coupling) of the RF generator and the magnetron source. In this way, the 13.56 MHz radiofrequency power is totally transferred to the magnetron source and can create the plasma. The RF power source allows to use both insulating and conductive targets.

The process can start once reached a base vacuum of \( 10^{-6} \) mbar. This pressure is achieved using a tubomolecular pump Pfeiffer Hi pace 700 and an Edwards coolstar 800 cryo-pump both in series of a scroll primary pump. Afterwards, a mass flow controller start to inject the gas (working gas) needed to sustain the discharge. For an efficient sputtering process, the atomic mass of the working gas should be similar to the atomic mass of the target; for instance, for sputtering light elements neon is preferable, while for heavy elements krypton or xenon are required. Argon is a good compromise to sputter light and heavy elements. In this facility the discharge starts at \( 8 \cdot 10^{-3} \) mbar and the plasma is stable for a pressure ranging in \( 3 \cdot 10^{-3} < p < 5 \cdot 10^{-2} \) mbar interval. Outside this pressure range the discharge can disappear (low value of pressure) or electric discharges can occur on target surface (high value pressure); for this reasons all the samples were produced within this pressure interval.

During the deposition process, the pressure is kept constant while the substrate temperature is not controlled and it can increase by the presence of plasma. An Inficon XTM/2 thickness monitor microbalance is used to control the growing film thickness during the process; more details about this measure are presented in section 4.4.1.
In this facility the target material available are Silicon, Molybdenum, Aluminium and Titanium. Reactive sputtering can be performed to deposit the relative oxide or nitride of these elements.

A system of shutter on targets and on substrates allows the deposition of different thin films for the realization of multiple layer stacks (see fig. 4.1b).

![Magnetron sputtering vacuum chamber](image1)
![Internal part of magnetron chamber](image2)

**Fig.4.11:** Magnetron sputtering system on the left (a). An internal view (b) shows the shutter system, the magnetron source and the quartz microbalance.

The deposition process can be easily stopped by turning off the RF generator once the desired thickness is obtained.

### 4.3.2 Ionvac E-beam/thermal evaporator

The evaporator facility (fig.4.2) is a vacuum chamber with a dual deposition system. The vacuum chamber is a cylinder 52 cm high and with a 35 cm diameter. A Varian Turbo-V 550 turbomolecular pump in series with a scroll pump provides a base vacuum of \(~10^{-7}\) mbar. At this pressure, the mean free path of an evaporated atom is around 60 meters, and for this reason in this system the motion of atomic vapour can be considered collision-less.

A Temescal systems apparatus generates the electron beam; the main supply CV-6SL generates currents up to 30 mA, that heat a tungsten filament, causing the thermal emission of electrons, reaching currents of hundreds of mA. The tungsten filament potential is - 9 kV with respect to all the other elements of the system. This potential accelerates the thermo-emitted electrons and a system of magnetic lenses allows to obtain a collimated electron beam. The motion of the beam in both longitudinal and latitudinal direction is controlled by an array of electrostatic lenses which allow to set the swiping amplitudes and frequencies. The e-beam system can contain up to four different evaporation sources, positioned in crucibles of 1.167" diameter and 0.563" height. Different materials can be placed in the relative crucible and Kurt J. Lesker Company provides the evaporation materials and crucible with a minimum purity > 99.95 % (as well for magnetron target). A list of materials that were used is present in tab.4.1.
Intensity of the beam can be tuned to provide the desired heating of the target and consequently the desired evaporation and deposition rates.

![Evaporator vacuum chamber](image1.png)  ![Internal part evaporator system, the thermal source and the e-beam source](image2.png)

Fig.4.12: Evaporator chamber in figure (a). An internal view (b) shows the e-beam crucible in center and the boat of the thermal source on the left side.

Substrates are mounted hanging from the top of the chamber and they can rotate in order to improve uniformity of the final thin film. Substrates can be thermally controlled by an array of quartz lamps coupled with a thermocouple type-K in a closed loop feedback. The substrate temperature can vary from room temperature up to 300 °C.

As mentioned before, in this system a thermal source can be also used to produce thin films. Materials (in the form of wire, pellets, shots) are placed onto heated semimetal (ceramic) evaporators called “boats”. A current that can vary from 0 to 900 A is used to heat up the boat by using the Joule effect. Alternatively, a W wire is wrapped around a crucible, and a current flowing through the tungsten wire heat up this system (crucible + wire). The materials which are placed in the crucible start to evaporates when the specific temperature is reached. There are different evaporation approaches that can be used with the thermal evaporation. One of these is the flash evaporation, where the material is directly in contact with the W wire, without the use of crucibles. In this case, the direct contact of the material combined with high current in the W wire allows a huge exchange of heat, achieving a conversion of almost all material in atomic vapour within few seconds; with this approach an extremely high (although not controlled) deposition rate is achievable (see fig.4.13).
Fig. 4.13: Thermal evaporation sources. From the top an oven + alumina crucible, an alumina-coated boat, a W wire with Al pellet for flash evaporation and a BN crucible + W wire.

As in the magnetron system, a microbalance is used as thickness monitor for both thermal and e-beam evaporation process.

In this facility the material available are in tab. 4.1. Reactive evaporation cannot be performed in this facility.

<table>
<thead>
<tr>
<th>Material name</th>
<th>Symbol</th>
<th>E-beam suitability</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Al</td>
<td>Excellent</td>
<td>Alloys and wet W. Surface passivation</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>Good</td>
<td>Sublimes. Adherent film</td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td>Excellent</td>
<td>Soft film. Not very adherent</td>
</tr>
<tr>
<td>Iridium</td>
<td>Ir</td>
<td>Fair</td>
<td>--</td>
</tr>
<tr>
<td>Magnesium Fluoride</td>
<td>MgF₂</td>
<td>Excellent</td>
<td>Rate control &amp; substrate heat required</td>
</tr>
<tr>
<td>Palladium</td>
<td>Pd</td>
<td>Excellent</td>
<td>Rapid evap. Suggested, spits in E-beam</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt</td>
<td>Excellent</td>
<td>Poor adhesion, film soft</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>Fair</td>
<td>Surface passivation</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>SiC</td>
<td>Poor</td>
<td>Sputtering preferred</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>SiO₂</td>
<td>Excellent</td>
<td>Quartz excellent in e-beam</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>Excellent</td>
<td>Evolves gas on first heating</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>Fair</td>
<td>Reactive evaporation suggested</td>
</tr>
</tbody>
</table>

Tab. 4.1 Material list of evaporation materials available. Remark from [9].

4.4 Thin films deposition method

The investigated optical samples in this PhD work are mainly mirrors for different spectral range applications. Mirrors can be composed by a single layer of metal, by a multilayer structure where a metal layer is protected with one or more dielectric layers or with a multilayer of dielectric materials. Hereafter, only mirrors composed by single metal layers or protected metal layers will be considered. As shown in fig. 3.2 metals are commonly used in different spectral range as reflective coatings. The single layer mirror must be enough thick to reflect all the incident electromagnetic wave with the wavelength ranging in a specific spectral range: a film with this thickness is said, from the optical point of view, a “bulk material”.

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4.4.1 Samples deposition method

The thin film production starts with the calibration process. The aim of this process is to control all the parameters of the deposition facility in order to obtain specific features of the film such as film thickness, surface roughness ($R_q$), stoichiometry (multi elemental materials), purity, and internal structure (see section 3.3).

Film thickness control is the first part of the calibration of a deposition facility. Quartz microbalance is commonly used for thickness monitoring during a deposition process. This device can measure the growing film depending on the film density, but it must be calibrated. Since the monitoring point cannot be in the same point as the deposited sample, and so the deposition rate, a spatial calibration of the deposition rate must be performed, to obtain the corrective scale factor. In fig.4.14 is possible to see an example of this calibration process. Different single layer thin films have been deposited in different deposition sessions. The measured thickness obtained with a profilometer scan is plotted versus the microbalance thickness value and a linear behaviour is expected. A linear fit is used to obtain the calibration line, and now a sample with a specific thickness can be deposited by calculating the relative microbalance value. The difference between the profilometer measurement and the microbalance value is connected to a geometric factor, and to the material density. In fact, different points in the deposition chamber have different growing factor due to the different distance from the target/evaporated material. Moreover, the film density might be different from tabulated one and it should be corrected with a specific density calibration, or a direct density measurement (for example X-ray reflectometry).

![Graph showing profilometer and linear fit of profilometer](image)

**Fig.4.14:** E-beam evaporated aluminium calibration line. Microbalance values vs profilometer measurements.

In this calibration process is essential the evaluation of the real film thickness of the deposited sample. Profilometer scan can measure the film thickness only if the film is not present in a portion of the substrate, producing a step whose amplitude is the film thickness. This step can be obtained with different techniques; one of the most simple techniques is to apply a Kapton® tape on the sample and remove it after the deposition process. However, the aim is not only to produce a step, but for a precise profilometer measurement the step must be sharp (see fig.4.15a). For this reason is important that no shadowing/edge effect appears along the step (see fig.4.15b). Furthermore,
good features for a good mask are: easy to remove, small thickness (<10 µm) and resistant to ion bombardment (and temperature if the substrate is heated) during the film growth. A method that I used for this purpose consists of applying on the sample a marker line. The marker ink forms a sort of non-adherent coating, that can be easily removed after the deposition process with a solvent like 2-propanol alcohol or acetone. All step production techniques have advantages and disadvantages but after some tests, I decided that the marker solution was the best.

![Diagram of step profile and deposition process](image)

**Fig.4.15:** Typical step profile for coating thickness measurement (left picture) obtained with stylus profilometer. The red profile is obtained with Kapton® mask, and the black profile is obtained with marker mask. On the right figure is possible to see possible the shadow/edge problem when the deposition has a preferred direction. The shadow/edge problem is more evident when the mask thickness is bigger than the film thickness.

Optimum optical performances for coating can be obtained only if the surface roughness is reduced as much as possible. For this reason, AFM measurements were performed to evaluate the surface roughness during the calibration process. Many factors can modify the roughness of the thin films, including substrate temperature, mean free path of the deposited vapors and the deposition rate. For example, for aluminum deposited via e-beam it is important that the substrate temperature is as low as possible, as shown in fig. 4.16. In general, for each material the deposition process must be studied in order to find the best deposition conditions that minimize the surface roughness, or at least to find a good compromise with the deposition conditions that the facility allow to change.

Moreover, different deposition conditions can produce thin films with different optical properties, as explained in section 3.2. Reflectance or transmittance measurements can be used to evaluate the quality of the coating by comparing the experimental data with the simulations. In particular, in order to simulate the optical response of a coating or a thin films structure I have developed a software based on the admittance method presented in section 3.1. This software can be used to simulate the reflectivity of an irradiated and not irradiated coating or a thin films structure and it will be described in details in section 5.3. In alternative, for the same purpose, the IMD software can be used [10].

Optical responses and their comparison with the theoretical simulations were used as important feedback for the optimization of the deposition parameters. Once the deposition parameters are determined, the samples production can start. A set of identical samples are required for the ground
irradiation tests. I usually deposited a single big substrate (Ø 100 mm) and then I cut it in order to obtain samples of about 1 x 1 cm.

Fig. 4.16: No contact AFM surface images of e-beam deposited Al calibration thin film. The surface roughness is $R_q = 1.2$ nm for the sample deposited at $t_{sub} = 25^\circ$ while the sample deposited at $t_{sub} = 70^\circ$ has a $R_q = 12.6$ nm.

In some cases, the optical constants of a single layer were measured by using a depolarization method with a V-VASE spectroscopic ellipsometer (J.A. Woollam) [11]. An example of this measurement is reported in fig. 4.17.

A multilayer sample can be deposited by following the just described calibration method, with the accuracy of using a substrate coated of the same material where the thin film will actually grow during the sample production. For example, in a bilayer of Al/SiO$_2$ on Si wafer the calibration of aluminum must be done on the Si wafer substrate, while the calibration of silicon dioxide on Al has to be performed with Al substrates. This because the substrate has a great influence on the film growing, especially in the nucleation process as explained in section 3.3.

Fig. 4.17: UV/VIS optical constants of a 40 nm gold thin film on a Bk7 glass substrate measured with J.A. Woollam ellipsometer.
4.5 Irradiation tests description

Since the beginning of this PhD project, several irradiation tests on optical components were performed. Here a list of the proposals presented for accessing to the accelerator facilities:

- May 2013: Proposal U13599989688582 for ion implantation/irradiation Title: “Impact of low energy alpha particles on optical components for space application”;
- March 2015: Proposal 15100274-ST for Ion Implantation/Irradiation Title: “Ions bombardment of optical components in space”;
- February 2016: Proposal 15000503-ST for Ion Implantation/Irradiation Title: “He+ ions bombardment in gold and platinum coatings”;
- July 2017: Proposal 17001046-ST for ion implantation/irradiation Title: “He+ and protons bombardment in bi-layer and multilayer coatings for space instrumentation”.

All the experimental data presented in chapter 5 concern samples irradiated in these experimental campaigns.

4.5.1 Proposal U1359989688582 specification

This was the first experiment that involve irradiation test of single layer thin films.

The aim of this experiment was to study the effect of different fluences of He ions at 4 keV in gold and iridium thin films. Optical analysis of irradiated and not-irradiated samples were performed in the VIS and VUV spectral range. The thickness of the thin films was big enough to ensure the implantation of the He ions within the films and to appear as a bulk in the optical measurements (thickness > 150 nm).

The irradiation energy and the fluences were selected to simulate He+ ion irradiation due to the calm solar wind in an environment that was compatible with the SolO space mission. The ground irradiations simulate exposition to solar wind for different years of mission (1, 2, and 4 years).

Irradiation specs:

<table>
<thead>
<tr>
<th>Ir or Au Sample name</th>
<th>Fluence (#Alpha particles·cm⁻²)</th>
<th>Flux (#Alpha particles·s⁻¹·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A=2.6·10¹⁵</td>
<td>1.5·10¹¹</td>
</tr>
<tr>
<td>2</td>
<td>B=5.2·10¹⁵</td>
<td>1.5·10¹¹</td>
</tr>
<tr>
<td>4</td>
<td>C=10.4·10¹⁵</td>
<td>1.5·10¹¹</td>
</tr>
<tr>
<td>Ref</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab.4.2: Irradiation specs for proposal U1359989688582.

Deposition specs:

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition method</th>
<th>Pressure(mbar)</th>
<th>Deposition rate(Å·s⁻¹)</th>
<th>T substrate(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>E-beam</td>
<td>~10⁻⁶</td>
<td>~0.2</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Iridium*</td>
<td>Magnetron sput.</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Tab.4.3: Deposition specs for proposal U1359989688582. * The iridium samples where purchases and deposition parameters are unknown.
4.5.2 Proposal 15100274-ST specification

The aim of this experiment was to study the effect of different fluences of He+ ions at 4 keV in gold and palladium thin films like for the experiment U1359989688582. Optical analysis of irradiated and not-irradiated samples were performed in the VIS spectral range and around Lyman-α line. The thickness of the thin films was big enough to ensure the implantation of the ions in the films (see SRIM simulation in fig.4.18), and to appear as a bulk in the optical measurements (thickness > 150 nm). The ion flux used in this experiment was 20 time bigger than the flux used in Proposal U1359989688582, while the fluences were the same except for the addition of 6 years of equivalent SoI0 mission.

![Fig.4.18 SRIM distribution of implanted He ions at 4 keV in a gold thin film.](image)

Irradiation specs:

<table>
<thead>
<tr>
<th>Pd or Au Sample name</th>
<th>Fluence (#Alpha particles·cm⁻²)</th>
<th>Flux (#Alpha particles·s⁻¹·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A=2.6·10¹⁵</td>
<td>3·10¹²</td>
</tr>
<tr>
<td>B</td>
<td>B=5.2·10¹⁵</td>
<td>3·10¹²</td>
</tr>
<tr>
<td>C</td>
<td>C=10.4·10¹⁵</td>
<td>3·10¹²</td>
</tr>
<tr>
<td>D</td>
<td>D=15.6·10¹⁵</td>
<td>3·10¹²</td>
</tr>
<tr>
<td>Ref</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab.4.4: Irradiation specs for proposal 15100274-ST, fluence error < 5%, flux error < 20%.

Deposition specs:

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition</th>
<th>Pressure(mbar)</th>
<th>Deposition rate(Å·s⁻¹)</th>
<th>T substrate(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>E-beam</td>
<td>~10⁻⁶</td>
<td>~1</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Palladium</td>
<td>E-beam</td>
<td>~10⁻⁶</td>
<td>~1</td>
<td>Room temp.</td>
</tr>
</tbody>
</table>

Tab.4.5: Deposition specs for proposal 15100274-ST.
4.5.3 Proposal 15000503-ST specification

The aim of this experiment was to study the effect of different fluences and fluxes of He+ ions at 4 keV in gold and platinum thin films. In fact, the experimental outcomes form proposal 15100274-ST have confirmed that the flux parameter has an impact on optical performances of irradiated coatings.

Optical analysis of irradiated and not-irradiated samples were performed in the VIS spectral range and around Lyman-\(\alpha\) line. The thickness of the thin films was big enough to ensure the implantation of all ions in the film, and to appear as a bulk in optical measurements (thickness > 150 nm).

Irradiation specs:

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Fluence</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#Alpha particles·cm(^{-2})</td>
<td>#Alpha particles·s(^{-1})·cm(^{-2})</td>
</tr>
<tr>
<td>1</td>
<td>A=2.6·10(^{15})</td>
<td>F1=1.5·10(^{11})</td>
</tr>
<tr>
<td>2</td>
<td>A=2.6·10(^{15})</td>
<td>F2=3.0·10(^{12})</td>
</tr>
<tr>
<td>3</td>
<td>A=2.6·10(^{15})</td>
<td>F3=8.8·10(^{12})</td>
</tr>
<tr>
<td>4</td>
<td>B=5.2·10(^{15})</td>
<td>F1=1.5·10(^{11})</td>
</tr>
<tr>
<td>5</td>
<td>B=5.2·10(^{15})</td>
<td>F2=3.0·10(^{12})</td>
</tr>
<tr>
<td>6</td>
<td>B=5.2·10(^{15})</td>
<td>F3=8.8·10(^{12})</td>
</tr>
<tr>
<td>7</td>
<td>C=10.4·10(^{15})</td>
<td>F1=1.5·10(^{11})</td>
</tr>
<tr>
<td>8</td>
<td>C=10.4·10(^{15})</td>
<td>F2=3.0·10(^{12})</td>
</tr>
<tr>
<td>9</td>
<td>C=10.4·10(^{15})</td>
<td>F3=8.8·10(^{12})</td>
</tr>
<tr>
<td>10</td>
<td>D=15.6·10(^{15})</td>
<td>F1=1.5·10(^{11})</td>
</tr>
<tr>
<td>11</td>
<td>D=15.6·10(^{15})</td>
<td>F2=3.0·10(^{12})</td>
</tr>
<tr>
<td>12</td>
<td>D=15.6·10(^{15})</td>
<td>F3=8.8·10(^{12})</td>
</tr>
<tr>
<td>Ref</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab.4.6: Samples specification for irradiation test n. 15000503-ST “He+ ions bombardment in gold and platinum coatings”. He+ ion energy is 4 keV. These samples have been optically investigated around Lyman-\(\alpha\) and in the visible (VIS) spectral range. Samples are gold and platinum single layer of 200 nm with an adhesion layer of titanium. Fluence error < 5%, flux error < 20%

Deposition specs:

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition</th>
<th>Pressure(mbar)</th>
<th>Deposition rate(Å·s(^{-1}))</th>
<th>T substrate(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>E-beam</td>
<td>~10(^{-6})</td>
<td>~1</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Platinum</td>
<td>E-beam</td>
<td>~10(^{-6})</td>
<td>~1</td>
<td>Room temp.</td>
</tr>
</tbody>
</table>

Tab.4.7: Deposition specs for proposal 15000503-ST.
4.5.4 Proposal 17001046-ST specification

The aim of this experiment was not only to study the interaction of low energy particles, typical of the calm solar wind (proton or He ions), with bilayer structures and single layer (SL) films, but also to study the effect of fast solar wind components. Selected energies are presented in tab 4.8. Energies greater than 16 keV were selected to compare the damage difference between low-energy irradiation tests (1, 4, 16 keV) with high-energy irradiation tests (50, 100 keV) on the same samples.

Bilayer samples are protected mirrors of aluminium with typical capping layer SiO$_2$ and TiO$_2$. Samples are designed to maximize the interaction of the irradiated ions with thin films interfaces, and also to maximize the reflectivity of the sample in a particular spectral range (see optimization in tab.4.10). SRIM simulations were used to evaluate the ion range of low-energy proton and He$^+$ ions inside the two different capping layers (see an example in fig.2.1).

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Energy (keV)</th>
<th>Range in SiO$_2$ (nm)</th>
<th>Range in TiO$_2$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (proton)</td>
<td>1</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>H (proton)</td>
<td>4</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>He$^+$</td>
<td>4</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>He$^+$</td>
<td>16</td>
<td>140</td>
<td>95</td>
</tr>
</tbody>
</table>

Tab.4.8 Range calculation with SRIM software. Ion range in SiO$_2$ and TiO$_2$ thin film for fast and slow solar wind components.

An evaluation of the intermixing width induced by ion irradiation has been simulated with SRIM software. Recoiled atoms distribution in the bilayer interface was calculated and an example is presented in fig.2.2. This parameter can be useful to simulate the optical behaviour of the irradiated samples by introducing a graded interface in the optical model.

<table>
<thead>
<tr>
<th>SiO$_2$ Thickness (nm)</th>
<th>Energy (keV)</th>
<th>Intermix width (nm)</th>
<th>SiO$_2$ Thickness (nm)</th>
<th>Energy (keV)</th>
<th>Intermix width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>He @ 4 keV</td>
<td>0,87</td>
<td>20</td>
<td>He @ 50 keV</td>
<td>0,71</td>
</tr>
<tr>
<td></td>
<td>He @ 4 keV</td>
<td>0,88</td>
<td>130</td>
<td>He @ 16 KeV</td>
<td>0,82</td>
</tr>
<tr>
<td></td>
<td>He @ 4 keV</td>
<td>0,80</td>
<td>200</td>
<td>He @ 50 keV</td>
<td>0,76</td>
</tr>
</tbody>
</table>

Tab.4.9 Calculated intermixing width for different energy of He$^+$ ion and different bilayer structures SiO$_2$/Al. The intermixing width is the FWHM of the Gaussian fit (see fig.2.2).

As it is possible to see from tab.4.9, the intermixing width do not change irradiation parameters or capping layer thickness. The reason is linked to the type of collision between the irradiated ion and a lattice atom. In fact the recoils distribution and collisions are due to ionization collisions, and the transferred energy to the recoiled atoms is low, and almost constant with the irradiated ion energy.

If the intermix width does not change with irradiation parameters, the damage entity does. In fact the total number of recoiled atoms increases in the proximity of the implantation peak, and for this reason to maximise the irradiation damage we selected the capping layer thickness with a value near to the ion range as in tab.4.8.
The thickness of the capping layer is specified in the parenthesis near the material name. Optical analysis of irradiated and not irradiated samples were performed only in the VIS/NUV spectral range. Irradiation fluxes were compatible with previous experiments in order to compare the obtained results.

Fluences and energies higher (one order of magnitude) than previous experiments were also chosen in order to maximize the damage effects of particle irradiation. The aim of this choice was to test optics to extreme irradiation conditions, and enlarge the structural damage of the samples. In fact, only in this way it is possible to understand with cross-section analysis how and where the internal structure is modified, since the ion damage belongs to sub-nanometric phenomena.

Sample specs:

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mirror Type</th>
<th>Protective Capping layer</th>
<th>Capping layer thickness (nm)</th>
<th>Optimized spectral range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au200 (SL)</td>
<td>Au</td>
<td>--</td>
<td>No</td>
<td>--</td>
</tr>
<tr>
<td>TiO₂125 (SL)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>500-800</td>
</tr>
<tr>
<td>Al200 (SL)</td>
<td>Al</td>
<td>--</td>
<td>No</td>
<td>--</td>
</tr>
<tr>
<td>SiO₂(20)/Al</td>
<td>Al</td>
<td>SiO₂</td>
<td>20</td>
<td>200-800</td>
</tr>
<tr>
<td>SiO₂(40)/Al</td>
<td>Al</td>
<td>SiO₂</td>
<td>40</td>
<td>150-200</td>
</tr>
<tr>
<td>SiO₂(140)/Al</td>
<td>Al</td>
<td>SiO₂</td>
<td>140</td>
<td>400-600</td>
</tr>
<tr>
<td>TiO₂(15)/Al</td>
<td>Al</td>
<td>TiO₂</td>
<td>15</td>
<td>500-800</td>
</tr>
<tr>
<td>TiO₂(30)/Al</td>
<td>Al</td>
<td>TiO₂</td>
<td>30</td>
<td>380-500</td>
</tr>
<tr>
<td>TiO₂(95)/Al</td>
<td>Al</td>
<td>TiO₂</td>
<td>95</td>
<td>550-750</td>
</tr>
<tr>
<td>SiO₂(125)/TiO₂(75)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>QWL @ 550 nm</td>
</tr>
</tbody>
</table>

Tab.4.10: Samples specification for irradiation test n. 17001046-ST “He+ and protons bombardment in bi-layer and multilayer coatings for space instrumentation”. These samples have been optically investigated in the UV/VIS spectral range. Single layer samples are labeled with SL. SiO₂(125)/TiO₂(75) is a quarter wave layer at 550 nm.

Irradiation specs:

<table>
<thead>
<tr>
<th>Particles and energies</th>
<th>Flux=8,3·10^{11} particles·s^{-1}·cm^{-2}</th>
<th>Flux=8,3·10^{12} particles·s^{-1}·cm^{-2}</th>
<th>Fluence =2,68·10^{16} particles·cm^{-2}</th>
<th>Fluence = 2,68·10^{17} particles·cm^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>p 1 keV</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>p 4 keV</td>
<td>L</td>
<td>H</td>
<td>L</td>
<td>H</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particles and energies</th>
<th>Flux=1.6·10^{12} particles·s^{-1}·cm^{-2}</th>
<th>Flux=1.6·10^{13} particles·s^{-1}·cm^{-2}</th>
<th>Fluence =4·10^{16} particles·cm^{-2}</th>
<th>Fluence = 4·10^{17} particles·cm^{-2}</th>
<th>Fluence = 24·10^{16} particles·cm^{-2}</th>
</tr>
</thead>
</table>
Tab.4.11: Irradiation specs for proposal 17001046-ST. Letters stand as L= low H= high M=middle and indicate the values of flux and fluence. Fluence error < 5%, flux error < 20%

Irradiation session parameters and samples:

<table>
<thead>
<tr>
<th>Name of implantation Session</th>
<th>Combined name (see tab.4.11)</th>
<th>Implantation duration (h)</th>
<th>Samples (considering the holder with 4 spots)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMP1-1</td>
<td>1pLL</td>
<td>1,39</td>
<td>SiO$_2$(20)/Al, SiO$_2$(40)/Al</td>
</tr>
<tr>
<td>IMP1-2</td>
<td>1pLL</td>
<td>1,39</td>
<td>Au200, TiO$_2$(15)/Al</td>
</tr>
<tr>
<td>IMP2-1</td>
<td>1pHL</td>
<td>0,139</td>
<td>SiO$_2$(20)/Al, SiO$_2$(40)/Al</td>
</tr>
<tr>
<td>IMP2-2</td>
<td>1pHL</td>
<td>0,139</td>
<td>Au200, TiO$_2$(15)/Al</td>
</tr>
<tr>
<td>IMP3</td>
<td>1pHH</td>
<td>1,39</td>
<td>Au200, TiO$_2$(125), Al200</td>
</tr>
<tr>
<td>IMP4-1</td>
<td>4HeLL</td>
<td>1,39</td>
<td>SiO$_2$(20)/Al, SiO$_2$(40)/Al, Al200</td>
</tr>
<tr>
<td>IMP4-2</td>
<td>4HeLL</td>
<td>1,39</td>
<td>Au200, TiO$_2$(30)/Al</td>
</tr>
<tr>
<td>IMP5-1</td>
<td>4HeHL</td>
<td>0,139</td>
<td>SiO$_2$(20)/Al, SiO$_2$(40)/Al</td>
</tr>
<tr>
<td>IMP5-2</td>
<td>4HeHL</td>
<td>0,139</td>
<td>Au200, TiO$_2$(30)/Al</td>
</tr>
<tr>
<td>IMP6-1</td>
<td>4HeHH</td>
<td>1,39</td>
<td>Au200, TiO$_2$(125)</td>
</tr>
<tr>
<td>IMP6-2</td>
<td>4HeHH</td>
<td>1,39</td>
<td>Al200, SiO$_2$(125)/TiO$_2$(75)</td>
</tr>
<tr>
<td>IMP7-1</td>
<td>100HeHH</td>
<td>1,39</td>
<td>SiO$_2$(125)/TiO$_2$(75)</td>
</tr>
<tr>
<td>IMP7-2</td>
<td>100HeHH</td>
<td>1,39</td>
<td>TiO$_2$(30)/Al, TiO$_2$(95)/Al</td>
</tr>
<tr>
<td>IMP7-3</td>
<td>100HeHH</td>
<td>1,39</td>
<td>SiO$_2$(40)/Al, SiO$_2$(140)/Al</td>
</tr>
<tr>
<td>IMP8</td>
<td>4pHH</td>
<td>1,39</td>
<td>SiO$_2$(20)/Al, TiO$_2$(15)/Al</td>
</tr>
<tr>
<td>IMP9</td>
<td>50HeHM</td>
<td>0,833</td>
<td>SiO$_2$(40)/Al, TiO$_2$(30)/Al</td>
</tr>
<tr>
<td>IMP10</td>
<td>16HeHH</td>
<td>1,39</td>
<td>SiO$_2$(140)/Al, TiO$_2$(95)/Al</td>
</tr>
<tr>
<td>IMP11</td>
<td>4pHH</td>
<td>1,39</td>
<td>SiO$_2$(40)/Al, TiO$_2$(30)/Al</td>
</tr>
<tr>
<td>IMP12</td>
<td>50HeHM</td>
<td>0,833</td>
<td>SiO$_2$(140)/Al, TiO$_2$(95)/Al</td>
</tr>
<tr>
<td>IMP13</td>
<td>16HeHH</td>
<td>1,39</td>
<td>SiO$_2$(20)/Al, TiO$_2$(15)/Al</td>
</tr>
</tbody>
</table>

Tab.4.12: Irradiation session name for proposal 17001046-ST. For each particle two fluences and two flux has been used. The combined name is composed as xxyyzz, where the xx is the energy in keV, yy is the particle type (p for proton, He for Helium), and zz is the flux and the fluence relative to used particle (HL for example stand for High flux, low fluence). Fluences and fluxes for proton and He irradiation are slightly different.
Deposition specs:

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition</th>
<th>Pressure(mbar)</th>
<th>Deposition rate(Å·s⁻¹)</th>
<th>T substrate(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>E-beam</td>
<td>~10⁻⁶</td>
<td>~2</td>
<td>80</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Thermal Flash</td>
<td>~10⁻⁶</td>
<td>~350</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>E-beam</td>
<td>~10⁻⁶</td>
<td>~0.9</td>
<td>Room temp.</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>E-beam</td>
<td>~10⁻⁶</td>
<td>~5</td>
<td>Room temp.</td>
</tr>
</tbody>
</table>

Tab.4.13: Deposition specs for proposal 17001046-ST.

4.5.5 Description of the 40keV low energy implanter (LEI) and the 200 keV ion implanter

Ground irradiation of optical samples were performed in the Ion beam center (IBC) in the HZDR laboratories. The selected ion energies, for irradiation test presented in this thesis, vary from 1 keV up to 100 keV. In this energy range, two facilities of the IBC were used: the 40 kV ion implanter and the 200 kV ion implanter (see fig.4.14). These accelerators are static charged accelerators and the ions are produced at the maximum bias available and then decelerated along the beam line. The difference of voltage between the line front end and the ion source determines the ion energy. The ion beam pass also through a Wien filter for ensuring a good energy precision and avoiding ion beam contamination. The beam spot area is about 1 cm² and a rastering movement (1 kHz x-y triangle waveform) of the beam spot insures a high level of irradiation uniformity over an area that can vary from 5 cm² to 15 cm² (see chamber specs in tab.4.15). In order to monitor the total fluence and the flux, the irradiation area lays between four-faraday cups, which monitor the ions current by integrating it over irradiation time.

Here follows a table with different specifications of these two accelerators.

Fig.4.19: The 40 kV Ion Implanter on the left and the 200 kV Ion Implanter on the right @ HZDR laboratories.
<table>
<thead>
<tr>
<th>Accelerator specs</th>
<th>40 kV Ion Implanter</th>
<th>200 kV Ion Implanter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Danfysik A/S, Denmark, Model 1050</td>
<td>Danfysik A/S, Denmark, Model 1090</td>
</tr>
<tr>
<td>Ion source</td>
<td>Chordis, gaseous and solid source feed</td>
<td>Hot filament, gaseous and solid source feed</td>
</tr>
<tr>
<td>Energy range</td>
<td>100 eV - 40 keV (for singly charged ions)</td>
<td>20 - 200 keV (for singly charged ions)</td>
</tr>
<tr>
<td>Scanning principle</td>
<td>Twofold electrostatic</td>
<td>Twofold magnetic / electrostatic</td>
</tr>
<tr>
<td>Implantation chamber</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Tab.4.14 Table of general specifications of 40 kV Ion Implanter and 200 kV Ion Implanter.

<table>
<thead>
<tr>
<th>Chamber specs</th>
<th>40 kV Ion Implanter</th>
<th>200 kV Ion Implanter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrates</td>
<td>Wafers or smaller samples</td>
<td>Wafers and smaller samples</td>
</tr>
<tr>
<td>Substrate size</td>
<td>0.3x0.3 cm² to 6&quot; wafers</td>
<td>3&quot; and 4&quot; wafers and smaller samples</td>
</tr>
<tr>
<td>Implantation area</td>
<td>max. 150 x 150 mm</td>
<td>max. Ø 100 mm</td>
</tr>
<tr>
<td>Implantation angle</td>
<td>0° and 7°, other angles upon request</td>
<td>0° and 7°, other angles upon request</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Nitrogen cooling for 2&quot; wafers upon request</td>
<td>up to 1100 °C temperature controlled</td>
</tr>
<tr>
<td>Fluence range</td>
<td>$10^{12}$ to $10^{17}$ cm⁻² (higher fluences upon request)</td>
<td>$10^{13}$ to $10^{17}$ cm⁻² (higher fluences upon request)</td>
</tr>
</tbody>
</table>

Tab.4.15: Irradiation chamber specifications of 40 kV Ion Implanter and 200 kV Ion Implanter.

4.5.6 Irradiation procedure details

Since the beginning of this PhD project, many irradiation sessions were performed at HZDR laboratory. I personally followed the irradiation session performed in July 2017 after the proposal entitled "He+ and protons bombardment in bi-layer and multilayer coatings for space instrumentation" (proposal no.: 17001046-ST).

In the following, a brief description of the irradiation process is reported:

1. Irradiation session plan: Each irradiation session is characterized by the following parameters: irradiated ion specie, ion energy, fluence and ion flux (current). A sample holder can host a maximum of four samples for each irradiation session.
2. Samples preparation: samples were mounted in a circular wheel sample holder (see fig.4.20). Different samples were mounted in a single irradiation session and for this reason, samples were marked to avoid mistake and exchanges after the irradiation session. A carbon tape was used to fix the sample to the sample holder. It is important that the ion beam do not irradiate the carbon tape because sputtering effect can contaminate the implantation
chamber and so the samples. During the high energetic irradiation sessions (ion energy < 16 keV) the substrate temperature can increase causing a brazing effect of the carbon tape and the sample, to avoid this problem a metallic clip was used instead of carbon tape (see fig.4.20). In some irradiation sessions a Tantalum metallic mask was placed upon the sample to mask it partially from the ion irradiation. This mask was applied to evaluate sputtering effect of the ion beam and to have a direct comparison between the irradiated and not irradiated portion of the sample. Before closing the irradiation chamber, samples were fluxed with N₂ gas to remove the eventual presence atmospheric dust on samples surface. All these procedures were performed in a class 100 clean room.

3. Irradiation chamber pumping: a pumping system composed of a turbomolecular pump and a cryo-pump produce the vacuum. Before starting the irradiation process, the pressure must be less than 10⁻⁷ mbar in order to limit the contamination of the samples due to residual gas presence (contaminants are always present in a vacuum chamber).

4. Irradiation: the irradiation started once the beam stop valve was open. During the irradiation session a HZDR operator monitors the stability of the ion beam by means of the beam current value (the ion flux is manually stabilized during the irradiation and the final flux error is less then 20% of the flux value). Irradiation sessions can take several hours and in some cases, the irradiation sessions were suspended and restarted the day after. This might have an impact on the irradiation process but it cannot be avoided in HZDR facilities.

5. Sample extraction: after the irradiation, samples were removed from the chamber and inserted in specific labelled box.

Fig.4.20 Gold samples mounted in the circular wheel sample holder with the Tantalum mask in left figure. Different aluminium bilayer samples (undistinguishable among them) with identification marks (cross scratch) mounted with metallic clips for high energy irradiation sessions are visible in the right figure. The carbon tape is visible under the transparent sample (Bk7 substrates) in left figure.
References chapter 4:


Chapter 5: Data analysis and modelling

Introduction

In this chapter the experimental results obtained in the four different irradiation sessions described in the section 4.5 are reported and discussed.

Section 5.1 is devoted to present the optical behaviour changes undergo in irradiated optics (single layer and bilayer thin film), with a particular focus on the effects induced by the total fluences and the fluxes adopted during the 4 keV He+ ions irradiations. In section 5.2 a detailed description of the structural modifications observed after the ion irradiation of thin films is reported. Different analysis will be used for addressing this aim, including SEM/TEM, AFM and SIMS. The comparison between irradiated and not irradiated structures can help to understand the mechanisms which lead the change of the optical performance, giving a connection between the ion damage and the optical damage. This passage is pivotal for the development of numeric models that can simulate the optical degradation induced by ion irradiation on coatings.

Finally, in section 5.3 an EMA model developed to simulate the reflectance changes occurring on irradiated single layer coatings in different spectral range is presented. The approximation that a simple effective medium model is valid in a large spectral range is too demanding; in fact, the model has shown a good approximation to experimental data only in specific spectral ranges. Only a full comprehension of all the mechanisms under the optical degradation due to ion irradiation can allow to build a more reliable model.
5.1 Optical behaviour of irradiated optics

In this section the optical analysis in different spectral ranges (from the VUV to VIS) of irradiated coatings are presented. Reflectance and transmittance measurements of irradiated samples are compared with those of the un-irradiated samples in order to study the effect of irradiation parameters like fluence, ion flux, ion energy and ion specie. Irradiation parameters were chosen to simulate not only the impact of the solar wind on optical devices in a space mission like SOLAR ORBITER, but also to test the resistance of these coatings to extreme doping (high fluences), different type of ions and energies. Harsh space environments are characterized by the presence of a limited number of ions (protons, He ions and electrons and a fair amount of heavier ions), with energies that go from keV (solar wind) to GeV (cosmic ray), and low values of ion flux (in a near sun environment ~$10^7$ ions$\cdot$s$^{-1}\cdot$cm$^2$). All these parameters except the ion flux are easy to reproduce in standard accelerators, while ion flux values below $10^{11}$ ions$\cdot$s$^{-1}\cdot$cm$^{-2}$ are very problematic for several technical reasons. Another reason, that is not technical limit, to use higher ion flux value is the irradiation test time. In fact, commonly an irradiation facility cannot be used for a long-term period and irradiation tests must be performed in maximum some weeks.

As expected from previous works on irradiated EUV multilayer mirrors [1-2], the type of irradiated ions and its energy are parameters that modify the optical behaviour of coatings and thin film structures, but also the ion flux must be considered. In fact, during this PhD work, it was observed that the ion flux is a crucial parameters as the fluence or energy, and for this reason a specific experiment was dedicated to study this aspect.

This PhD project started with the studies on simple optical devices like single layer thin film, and moved to more complex structures (bilayer coating). As expected, more complex is the irradiated optical structure and more complex is the experimental outcome.

Reflectance measurements here presented were taken in the VIS/NUV range with the Cary 5000 spectrometer (see subsection 4.2.1) and in the EUV by using the BEAR(Bending magnet for Emission, Absorption and Reflectivity beamline) beamline at ELETTRA synchrotron located in Trieste (Italy)[4]. The EUV NUV/VIS reflectance measurements were all performed at 5° of incidence. All the optical measurements (reflectance, diffusion, transmittance etc.) are affected by a statistical error of 1%. Moreover, all the presented curves refer to unpolarized radiation.

5.1.1 Effect of ion fluence and flux of 4keV He in single layer samples and bilayer samples

A preliminary work on iridium and gold single layer mirrors has shown a reflectance drop due to irradiation of He ions at 4 keV [3].

As shown in fig.5.1, an overall reflectance decrease in both coatings type with the increase of the ion fluence was observed (fluence calculated on years of SoO space mission, see details in 4.5.1); furthermore, at these fluences the effect is more pronounced in the EUV and VUV spectral range than in VIS range. In particular, the degradation effect in the VIS range is not clear, but a clear reflectivity variations is connected to different irradiation fluences.
Fig.5.1 Reflectance in the VUV and VIS/NUV range of Au and Ir samples irradiated with increasing fluences (for fluence values see subsection 4.5.1 and tab.4.2) and a flux of $1.5 \times 10^{11}$ ions·s$^{-1}$·cm$^{-2}$ (image published in [3] from data collected in proposal n. U1359989688582, reflectance error ± 1%).

In fig.5.1 the irradiation flux was $1.5 \times 10^{11}$ ions·s$^{-1}$·cm$^{-2}$ and is the lowest flux value that the irradiation facility at HZDR can achieve.

As mentioned in subsection 4.5.3, the flux variation in irradiated gold mirrors can produce different results. For this reason, a similar experiment has been repeated (as before with 4 keV He ions) including a study of ion flux variation on platinum and gold mirrors. As is possible to see from fig.5.2a, irradiation with low fluxes in Pt mirrors show a similar behaviour already seen in irradiated gold mirrors, confirming a modification of reflectance also in Pt mirrors due to fluence (like in gold samples), but with high fluxes the reflectance modification starts to disappear.
F1 = 1.5 \times 10^{11} \text{ ions s}^{-1} \text{ cm}^{-2}

F2 = 3.0 \times 10^{12} \text{ ions s}^{-1} \text{ cm}^{-2}

F3 = 8.8 \times 10^{12} \text{ ions s}^{-1} \text{ cm}^{-2}

Fig. 5.2a Reflectance of Pt sample irradiated with different flux and fluence values in the VUV range (data collected from proposal n. 15000503-ST see section 4.5.3 for details, reflectance error ± 1%).

In fig. 5.2b is shown the relative reflectance modification defined as $R_{rel} = R_{sample}/R_{ref}$ in the VIS/NUV range for irradiated gold mirrors with different fluxes and fluences; the un-irradiated gold is taken as reference. The reflectance modification shows a clear drop in the NUV range (from 400 to 200 nm) while the R drop is more limited in the VIS range (400 to 800 nm). In particular, the reflectance drop for fluxes F2 and F3 is limited (max 5%). Irradiation of 4 keV He ions has been performed also in bilayer structures, as described in the experiment presented in subsection 4.5.4. The aim of this experiment was to see if the fluence and flux effects occur also in a more complex structure, and in particular how the ion irradiation interacts with the bilayer interface. The selected fluences for bilayer irradiation are higher of a factor ten with respect to the single layer experiment, while fluxes are similar. Since the fluence effect is limited in the visible ranges, as we observed in single layer experiments, we decided to increase the fluences to maximize the degradation effect. Optical measurements on bilayer sample were performed in the VIS range since this optical devices are developed for this spectral range (see optimized spectral range in tab. 4.10).

Is useful to define the relative reflectance difference $\Delta R$ as:

$$\Delta R = \frac{(R_{ref} - R_{irradiated})}{R_{ref}}$$  \hspace{1cm} [5.1]\

where $R_{irradiated}$ and $R_{ref}$ are respectively the reflectivity of the irradiated sample and the un-irradiated one. The $\Delta R$ index is a parameter that describe how intense is the optical performance modification due to ion irradiation in a sample with respect to the reference sample. By using this parameter, it is possible to compare the optical damage of irradiated optics also between different sample types in the same spectral range.
In fig.5.4 the reflectance of SiO$_2$(20)/Al and SiO$_2$(40)/Al bilayer with the same fluence and different fluxes is presented. He ions implantation range in silicon dioxide is 40 nm, and the distribution of lattice damage due to ion collisions follows the ion implantation distribution like in fig.2.1. The structural damage in the two different capping layer (20 and 40 nm) of the bilayer samples SiO$_2$(20)/Al and SiO$_2$(40)/Al is expected to be similar because SRIM simulations show a similar recoils distribution concentrations in the interlayer area (see fig.5.3).

![Fig.5.3 Comparison between 4 keV He bombardment in SiO$_2$(20)/Al and SiO$_2$(40)/Al bilayer samples. The atom recoil distributions show similar concentration values of the recoiled atoms at the sample interface for both the samples.](image)

In fact, the relative reflectance modifications presented in fig.5.4c are similar. The same fluences produce different damage if a different ion flux is used; in particular, as seen in the single layer coatings case, low fluxes induce a major modification of the optical response.
The effects of fluence and flux were studied in single layer and thin film structures irradiated with He ions at 4 keV. The ion flux seems to modify the damage effects that an ion beam induces in the thin film structure. Low fluxes seem to modify more the optical response of irradiated thin films and the same effect is present in thin film structures.

Another evidence is that the fluence seems to modify the optical response in all the spectral ranges but the effect seems to be more pronounced in the EUV and NUV spectral range, and in general near the absorption edges of the involved materials (see fig. 5.6). The relative damage ($\Delta R$ index) in an irradiated structures (see fig. 5.4c) seems the same if the same irradiation damage is expected (from SRIM simulation).

A similar analysis was carried out for bilayer samples with titanium dioxide capping layers. The results are presented in fig. 5.5, where a comparison between the two capping layers is shown. Unlike the samples protected with silicon dioxide, the flux dependence of the reflectivity modification is not present in the TiO$_2$-protected samples.

Fig. 5.4 A comparison between irradiated SiO$_2$(20)/Al sample and SiO$_2$(40)/Al sample in the VIS/UV range. Same fluence and two different fluxes are presented (data from proposal n. 17001046-ST, see tab. 4.12 for label description of all the samples irradiated in this proposal, reflectance error ± 1%).
For a selected fluence, a different flux value changes the irradiated power on the sample, and this might be connected with a thermal variation and heat dissipation during the irradiation process. Higher fluxes can promote the natural annealing process on irradiated samples, and partially restore the induced irradiation damage on the thin film structure. The absence of this flux effect in sample TiO\(_2\)(30)/Al can be connected to a different behavior of the capping-layer material to heat exchange during the irradiation process respect to SiO\(_2\)(40)/Al sample. The understanding of the resistance difference to ion irradiation for a capping layer is a key point for future selection of protective layer of mirrors for space applications.

The ΔR index in fig.5.5 for the TiO\(_2\)(30)/Al sample has a maximum near 344 nm wavelength. For this reason, we decided to compare the refractive index \(n\) of the titanium dioxide [5] with ΔR index.

Fig.5.6 shows in the same plot the \(n\) value of TiO\(_2\) and the ΔR index of irradiated TiO\(_2\)(30)/Al sample, evidencing a correlation between these two parameters. A similar behavior might be supposed for the SiO\(_2\)(40)/Al, but in the VUV range close to 150 nm wavelength, where the SiO\(_2\) refractive index has a typical resonance shape (near absorption edge). Unfortunately reflectance measurement
below 200 nm of radiation wavelength require a spectrophotometer that work in the vacuum UV, and this is a pending measurement.

5.1.2 Effect of ion type and energy in single layer samples and bilayer samples

Similar studies of previous subsection have been carried out on single layers and thin film structures when irradiated with different ion species and energies. The solar wind is mainly composed of two type of ions, protons and He ions, with two average energy values respectively (see details in chapter 1.4.2.3). Here are presented data that compare, as before, the induced damage of these type of ions (and the relative energies) in single layer and bilayer structures. Energies higher than 16 keV were considered for He irradiation in order to have an overview of the ion energy dependence on the optical performance modifications in bilayer structures.

The same study on fluence and flux variations (presented in the previous section for He ions) for a thin film of gold has been carried out also for proton irradiation at 1 keV. For instance, in fig.5.7a the reflectance measurements show a dependence with fluences with a clear reflectance drop; but in this case the high fluxes seem to damage more than the low fluxes.

In fig.5.7b a comparison between proton irradiation at 1 keV and He irradiation at 4 keV of a gold thin film is presented. The ion implantation range of these two ions is of the same order (~15 nm) and for this reason the irradiated area can be considered the same. It is clear that in this condition where the flux and fluence is the same, the He ion irradiation modifies the reflectance much more than the proton irradiation.

Fig.5.7 The left plot shows the flux and fluence effect of 1 keV proton irradiation on gold thin film reflectivity. On the right the damage comparison between 1 keV proton irradiation and 4 keV helium irradiation on gold thin film in the VIS/UV range. Fluences and fluxes for the two type of ions are similar but not the same due to accelerator limitations (see details in chapter 4.5.5 and in tab.4.11, data collected in proposal n. 17001046-ST, reflectance error ± 1%).

Fig.5.8 shows the same comparison of fig.5.7 but for the sample SiO$_2$(20)/Al. The SiO$_2$ capping layer is selected to maximize the implantation of both ions, He and proton in the interlayer area. The range of 4 keV He in SiO$_2$ is of course bigger than 1 keV proton in SiO$_2$; but as it seen in the fig.5.4c the damage effect of 4 keV He on SiO$_2$(20)/Al and SiO$_2$(40)/Al samples can be considered equal. This allows a reasonable parallelism of the irradiation effect of these two ions on the same sample.
Fig. 5.8 Damage comparison between 1 keV proton irradiation and 4 keV helium irradiation on the same bilayer structure (SiO₂(20)/Al) in the VIS/UV range. Fluences and fluxes for the two type of ions are similar but not the same due to accelerator limitations (see details in chapter 4.5.5 and in tab.4.11, data collected in proposal n. 17001046-ST, reflectance error ± 1%).

In fig.5.8 is clear that the flux differently affects the sample reflectance for proton and He irradiation. Even if fluences and fluxes are not exactly the same the difference is clear. In fact, high fluxes for proton irradiation damage more than low fluxes and the opposite effect occurs with He+ irradiation in almost all the VIS/NUV spectral range.

Higher He energies (>4 keV) has been chosen to test bilayer sample SiO₂(140)/Al and TiO₂(95)/Al. Again, for both samples the capping layer thickness is selected to implant the 16keV ions in the interlayer area. The 50 keV He ion irradiation is used to compare the damage effect if the particle range overcome the capping layer thickness and the maximum of the implantation profile falls after the capping-layer.

Fig. 5.9 The comparison between different energy irradiation of He+ ions in bilayer samples, 16 keV and 50 keV. Samples are designed to maximize the interaction of the impinging ion to the bilayer interface SiO₂/Aluminum and TiO₂/Aluminum. The thickness of the TiO₂/SiO₂ capping layer is equal to the ion range of the irradiated He ion at 16 keV in the relative material. The 50 keV He+ ion range in these samples is bigger than the capping layer thickness and the maximum damage is not localized in the interlayer but more deeper in the structure (data collected in proposal n. 17001046-ST, reflectance error ± 1%).
As expected, the damage effect is more evident when the implantation peak lays in the interface of the bilayer sample in both cases (SiO$_2$(140)/Al and TiO$_2$(95)/Al). This means that interface modifications are a crucial aspect when the irradiated sample is a multilayer. The reflectance drop in the case of high energy is dramatic, with deeply modifications of the surface and the internal structure. These aspects will be discussed in section 5.2. The reflectance drop in the case presented in fig.5.8 is also due to sample light diffusion (see fig.5.10) while for previous reflectance measurements the diffusion contribution of irradiate samples was negligible with respect to the reflectance drop.

![Graph showing diffusion reflectance measurements](image.png)

**Fig.5.10** Diffusion reflectance measurements in VIS/NUV of irradiated sample SiO$_2$(140)/Al and TiO$_2$(95)/Al (data collected in proposal n. 17001046-ST, diffusion error ± 1%).

The energy of the irradiating particles is an important parameter since the damage can be localized in parts of the sample that are more sensitive to optical variations (e.g. interfaces).

Protons and He ions damage thin films in a different way and further investigations are required to understand the different mechanisms occurring. The chemical behavior of these two ion species can have a role in this aspect in fact the He ion after the implantation becomes an inert species, while hydrogen can chemically bond with the irradiated material atoms.

### 5.2 Surface and structural modification of irradiated optics

Structural and surface proprieties of a thin film lead the optical behaviour of the film itself. Optical constants of thin films are connected to structural parameters like: material density, contamination, stoichiometry in case of composite, crystallinity, crystals size and their orientation, internal stress.

Thin film roughness is another crucial parameter that control not only the light scattering on the surface but also intermixing effects in case of layer stack.

This chapter is devoted to present different structural analysis used in this PhD project to identify the modifications of structure and surface due to the ion irradiation.

AFM images were used to evaluate roughness modifications, sputtering effects which can occur with high fluences and formation of nanobubbles.
Electron imaging techniques were used to analyse the surface changes (SEM) and the cross section structure (TEM). High magnification images of the sample can be used to observe the nanostructure modifications of the irradiated sample. The TEM-EDX combined image was used to identify the intermixing width in bilayer samples, and to retrieve a rough stoichiometry estimation of compounds.

SIMS analysis have been carried out to confirm the ion implantation profile on irradiated sample.

### 5.2.1 Surface modification

Atomic force microscopy was used to analyse the eventual surface modification due to ion irradiation.

Fig.5.10 shows the comparison between gold irradiated samples with 4 keV He+ ions (Au4) and the reference sample (Au0). The reflectance measurements of these two samples are those presented in fig.5.1. AFM analysis of all the others irradiated samples was carried out as well but, as in this case, no significant modifications of the surface roughness ($R_q$) were observed. The same analysis was performed on the irradiated bilayer samples and the same results were confirmed.

![AFM image of irradiated gold with 4 keV He ions.](image)

**Fig.5.11** AFM image of irradiated gold with 4 keV He ions. The reference sample Au0 and the irradiated sample Au4 (see fig.5.1 for reflectance data) do not show a clear difference in the surface roughness (samples irradiated in proposal n. U1359989688582).
In fact, it was observed that irradiation with low energy particles (He or proton with energy below 4 keV) and fluencies lower than $4 \times 10^{15}$ ions cm$^{-2}$ do not modify the surface proprieties of the coatings. For this reason, the contribution of surface light diffusion in this case is limited and the specular reflection can be considered the total sample reflection.

Sputtering effect on surface and deep modifications of the internal structure of the coatings can modify the surface roughness as well. When the fluence is above $10^{16}$ ions cm$^{-2}$ the sputtering effect starts to be significant and it can partially remove some layers of the thin film. If this erosion is not uniform, a surface roughness modification occurs. In fig. 5.13 the damage induced from 16 keV He ions on a SiO$_2$(140)/Al bilayer structure is presented. In this case, a Tantalum mask of 0.5 mm was used to stop the irradiated ions and partially protect the sample surface. The result is a sample in which the irradiated area and the un-irradiated area can be investigated directly compared with AFM analysis (see fig. 5.13). The surface modification observed was notable, with a roughness increase from 2 nm up to 41 nm and a film thickness expansion up to 20 nm. The diffusive reflectance contribution in this case is an important part of the total reflectance drop already reported in fig.5.9, while the spectral modification can be due to the capping layer expansion.

The effect of fluence and energy is now clear; the damage increase with both fluence and the ions energy and at a certain point the thin film structure modifications are no longer in the sub-nanometric scale but they start to be evident even if observed by eyes. In fact if the surface roughness of an optical coating, for example a mirror, is approximately greater than 50 nm, the surface diffusion of light starts to be eyes-evident and the surface appears slightly opaque. For example, in fig.5.14 a picture of how the SiO$_2$(140)/Al and TiO$_2$(95)/Al irradiated with 16 keV and the relative reference samples look (see fig.5.8 for the relative diffusion measurement in VIS/NUV range), is presented.
Fig. 5.13 AFM image of SiO2(140)/Al irradiate with He ions at 16 keV. The irradiated area (green) is obtained by using a tantalum mask on the sample. The histograms on the right show the difference of surface roughness of the two surfaces. Irradiated $R_q = 41 \pm 1\%$ nm and not-irradiated $R_q = 2 \pm 1\%$ nm (samples irradiated in proposal n. 17001046-ST).

Fig. 5.14 Image of irradiated SiO2(140)/Al and TiO2(95)/Al and the relative reference samples. Implantation session imp10. The reference sample is a mirror like surface and eyes can see no light diffusion. In the irradiated sample the opacity of the surface is evident.
5.2.2 SEM/TEM investigation on irradiated gold thin film

One of the objective of this PhD project is to relate optical performance modifications with structural modifications occurring in thin films irradiated by ions. For this reason, several SEM/TEM analyses were carried out. In fact nanoscale modifications of a thin film structures can be seen only using electron imaging. The first attempt to detect structural modifications in irradiated thin films was performed on gold samples. In particular, the sample Au4 whose reflection in the VUV range was extremely reduced after the 4 keV He+ ion irradiation (see fig.5.1), was deeply investigated. As shown in fig.5.15, no surface modifications were detected in the SEM images and no evident grain structure modifications are visible between the irradiated sample and the relative reference sample. In contrast, TEM cross section images revealed a tiny modification of the topmost nanometres of the irradiated sample, although this change is not evident.

These images suggest that at these fluencies the internal structure of the films is slightly damaged by the ion irradiation.

Considering such results, a second experiment devoted to highlight this damage was recently performed always on irradiated gold thin films by increasing the fluence of He+ ions. The
investigated sample is the 4HeHH Au film irradiated in the imp6-1 session. The reflectance measurements of this sample are presented in fig.5.7 (on the right). The evident reflectance drop in the NUV/VIS range is connected to surface modifications of the sample. Surface and cross section electron images of this sample are presented in fig.5.16.

Fig.5.16 SEM images of irradiated gold with 4 keV He ions on the top and TEM images on the bottom. The left part of the figure show a reference gold sample while on the right side the gold sample implanted in the imp6-1 session (see tab.4.11). A clear surface modification is visible, the not irradiated image show a crystalline structure with boundary grains while in the irradiated sample grains are disappears and the surface show the presence of nano-holes (samples irradiated in proposal n. 17001046-ST).

The surface modification of the irradiated sample is confirmed also by SEM surface image. The grain boundary are not defined in the irradiated sample and a porous structure of the first nanometres of the material is supposed. TEM cross section images confirm the internal pours structure that is limited only the He+ ion range area (see 4 keV SRIM simulation on Au fig.4.18). This particular behaviour of irradiated materials has been already seen in [6], and is confirmed in our measurements.

However, further investigations are required to connect the optical performance changes to structural modifications. On the other hand, the evident density modification occurring on the irradiated materials can be the starting point of a model that can predict optical constants changes after the implantation of accelerated ions. Moreover, the bubble structures formed in the films can
be a source of optical scattering which will be more efficient at wavelengths that are of the same spatial dimension to the bubble size (~10 nm).

5.2.3 SIMS implantation profile

SIMS analysis were carried out to investigate the implantation profile of the implanted ions inside the films. The implantation profiles obtained were then compared with SRIM simulations, as reported in fig.4.18, in order to confirm the structure damage profile. For instance, in fig.5.17 the SIMS analysis of the implantation profile performed on a gold sample (Au4) irradiated with He+ ions at 4 keV is presented. In this image, the ion selected in the SIMS analysis is the He atoms.

![SIMS Distribution of Implanted He Ions at 4 keV](image)

Fig.5.17 SIMS distribution of implanted He ions at 4 keV in a gold sample and the comparison with SRIM simulation with different Au density: bulk density 19.3 gr/cm$^3$ (left figure) and an estimation of the thin film density 18 gr/cm$^3$ (image published in [3]).

In this figure, the He implantation profiles calculated with SRIM are also reported for comparison. In order to match the SIMS profile, the density of the film material was varied, achieving a better match with the density of 18 gr/cm$^3$, lower with respect to the normal density of Au (i.e. 19.3 gr/cm$^3$). However, it is important to point out that the density of a thin film is usually different from the relative material bulk density; in fact, in the thin film growing process void sectors are often included in the material and then pours structure are common. Moreover, as shown in fig.5.16, the film density can be also modified by the ion irradiation at high fluences; this irradiation density variation cannot be take into account by SRIM software.

SIMS analysis were also performed in Au samples irradiated with the same He ion fluence but different fluxes. The results are presented in fig.5.18. As it is possible to see from this figure, the flux variation does not affect the implanted ions distribution, confirming that the ion flux does not affect the implanted ions profile inside a specific material.
SIMS analysis can also be used to investigate the intermixing effect in a bilayer structure and to analyse if the ion irradiation can modify the natural intermixing width of two adjacent layers. Together with TEM cross-section images, this can be a powerful tool to understand the optical behaviour of the irradiated bilayer. Unfortunately, at this moment no any SIMS analyses are available on bilayer samples, but are scheduled for future investigation on bilayer or multilayer structure.

5.3 Effective medium approximation on irradiated thin film

Optical reflectance of a thin film (a single layer or multi-layers) can be simulated considering the film structure and its optical constants (n, k) by using the optical admittance method (see chapter 3). Furthermore, optical constants are strictly related to the dielectric constant $\varepsilon$ of the material, which describes its electric and absorption properties with the relationship:

$$N = \sqrt{\varepsilon}$$  \[5.2\]

A simple model to describe coatings optical performance changes due ion irradiation were developed. This model is based on the effective medium approximation (EMA model) by using Maxwell-Garnet equation, which was described in section 2.3.

Maxwell Garnett’s formula estimates the variation of $\varepsilon$ using an EMA model if the bulk structure of the material has been somehow modified. From this formula it is possible to compute the new values of n and k, and then the new optical reflectance.

In general, the damage induced in materials by ions irradiation can be drastically summarized into two contributions: ions implantation and lattice damage. The irradiated ions lose their energy into material due to scattering with the atoms of the lattice. When the ion’s energy is completely transferred to the material and stops inside the material lattice, the ion is said “implanted”. On the other hand, the ions passing inside the material collide with the lattice atoms and they can create vacancy sites with the related interstitial atoms (Frenkel pair). This lattice damage is localized inside the range of the irradiated particles and the distribution is well reproduced by a Landau distribution (see an implantation distribution in fig.4.18).
Maxwell-Garnett formula takes into account the presence of this irradiation damage in the material bulk, and it modifies the dielectric constant as:

\[
\varepsilon_{\text{new}} = \frac{2(1 - v_f)\varepsilon_{\text{bulk}} + (1 + 2v_f)\varepsilon_X}{2 + v_f}\frac{\varepsilon_{\text{bulk}} + (1 - v_f)\varepsilon_X}{\varepsilon_{\text{bulk}} + (1 - v_f)\varepsilon_X}
\]  \[5.3\]

\[
v_f = \frac{N_{\text{bulk atom}}}{N_{\text{inclusion}}}
\]  \[5.4\]

where \(v_f\) is the inclusion abundance related to bulk atoms, \(\varepsilon_X\) is the dielectric constant of inclusions, \(\varepsilon_{\text{bulk}}\) is the dielectric constant of the bulk material. Once the dielectric constant is computed, the modified optical constant can be retrieved by using the following relationships:

\[N = \sqrt{\varepsilon_r}\text{ with }\varepsilon = \varepsilon_r\varepsilon_0\]  \[5.5\]

\[N = n - ik\quad n = Re(N)\quad k = Img(N)\]  \[5.6\]

\(V_f\) can be calculated by using different distributions. The simplest choice is a uniform distribution of the total irradiated particles inside the portion of the material that interacts with the particles (thickness equal to the range of the irradiated ions).

A better model can be obtained by using the real distribution of the implanted ions inside the irradiated layer. To simulate the real damage distribution, we used the software SRIM [8]. The EMA model discussed here take as input the atoms vacancies (lattice damage) or the implanted ions distributions (inclusion).

An example of these two distributions is reported in fig.5.19, where a thin film of gold irradiated with a fixed fluence of He+ ions at 4 keV has been considered. The \(V_f\) is already calculated for a thin film of gold with density 19.32 g/cm\(^3\) and considering an irradiation with a He+ fluence of \(1.1 \times 10^{16}\) He+/cm\(^2\). The number of gold atoms inside the irradiated layer can be easily estimated, while the distribution of the inclusions (and their number) inside the irradiated layer is simulated by SRIM software. Using the total fluence and SRIM results, it is possible to have an estimation of the inclusions density and its variation through the irradiated layer. The ratio between these two quantities is exactly the \(V_f\).

![Fig.5.19 V_f distribution for two different models. On the left the implanted ions distribution is used to calculate the V_f, whereas on the right the vacancy distribution is used. The distributions used in EMA simulation are compared with the SRIM’s distributions.](image)
After the evaluation of $V_f$, the modified dielectric constant (and then the optical constants of irradiated material) can be estimated using the Maxwell-Garnett equation (see eq.5.3), where to the inclusions and vacancies is assigned the vacuum dielectric constant ($\varepsilon = 1$).

In the following, the reflectance simulations carried out on a gold sample with a thickness of 200 nm are presented. From SRIM simulations we found that the ions beam interacts with the first 40 nm of material; previously, those results were also experimentally determined using secondary ion mass spectroscopy (SIMS) analysis (fig.5.17).

The irradiated portion of the material is split into at least 20 layers, and to each sub-layer a different value of $V_f$ (the corresponding value of the Landau distribution calculated by SRIM) is assigned. In this way, the simulation computes the reflectance of a multilayer structure, where the irradiated part consist in a stack of layers with modified optical constant due to the different value of $V_f$.

The selected two different profiles in fig.5.20 show different optical behaviour in the reflectance simulations. Here follows their comparison with a fixed fluence ($1.1 \cdot 10^{16}$ He+/cm$^2$) that in this example correspond to 4 years of He+ slow solar wind exposition.

![Ions distribution](image1)

Fig.5.20 Reflectance loss due to irradiation. On the left, ions distribution model shows a not good agreement between experimental data (blue triangle, reflectance error ± 1%) and simulation (black solid line). The $V_f$ in the figure legend indicates the presence or not of the irradiation. A better agreement is obtained with the vacancies distribution model on the right. The not irradiated samples ($V_f = 0$) are presented to give an idea of the reflectivity loss. This example is for a 4 years fluence.

The fig.5.20 shows the reflectance from 100 to 160 nm at 5° of normal incidence. In the figure both experimental data (see fig.5.1) and simulations of the irradiated thin films (experimental data are dot lines while simulations are continuous lines) are compared with the performance of a non-irradiated films ($V_f = 0$ means not irradiated sample).

Au vacancy distribution model shows a better agreement with experimental data, and it is clearly visible with the reflectivity loss% ($\Delta R$ index is defined in eq.5.1). Gold reference simulations and experimental data are slightly different due to optical constants available in the database for the simulations.
Fig. 5.21 $\Delta R$ index calculated for the two different methods.

The $\Delta R$ index decrease at longer wavelengths, and this means that shorter wavelengths interact with more efficiency inside the damaged zone (see also fig. 5.23 right, no effect in the VIS range).

Next figures show the dependency of reflectivity loss due to an increasing irradiation fluence, and the calculation use the Au vacancy distribution to evaluate the $V_i$ distribution.

Fig. 5.22 reflectivity loss for Au vacancy distribution method. One year fluence on left and two years fluence on right. $\Delta R$ index for Au vacancy distribution method. One year fluence on left and two years fluence on right.
The fluences are calculated to simulate the equivalent fluence for different years of He+ (5% of solar wind composition with an average energy of 4 keV) irradiation in a near sun environment (~0.3 A.U.)

The fluence is $2.6 \cdot 10^{15}$ He+/cm$^2$ for one year of mission, so is twice for two years and so on.

The graphs of four years fluence for Au vacancy distribution has been previously presented in fig.5.20 and fig.5.21b.

More important than reflectance simulations is the $\Delta R$ index, because optical constants always change even if the coating structure is the identical. In fact, small changes in deposition conditions can produce big differences in optical constant of a thin film due to its porosity, grain size, surface roughness and percolation thickness (see chapter 3.3).

![Graph showing reflectivity loss for Au irradiated thin film induced by different years of irradiation. UV and far UV on left and Visible range on right. Au vacancy distribution method.](image1)

![Graph showing $\Delta R$ index for six years fluence in a large spectral range.](image2)

From fig.5.23 and fig 5.24 it is possible to see the different behaviour of reflectivity loss in a different spectral range. As mentioned above, the reflectance loss in the visible range seems to be reduced and probably this evidence is due to the big difference in the size of the radiation wavelength (hundreds of nanometres) and the irradiated layer (tens of nanometres).
References chapter 5:


Conclusions

The degradation of optical coatings induced by accelerated ions with characteristics similar to those encountered in a near-Sun environment was investigated. In particular, the objective of this project was:

- Study the solar wind and the impact of ion irradiation on optical components;
- Identify the mechanisms which drive the thin film optical performance modification after the ion irradiation;
- Identify guidelines for the space qualification tests of optical coatings.

Experimental evidences have confirmed that ion irradiation modifies optical coatings performances. In particular, our results show that low energy particles (proton and He⁺ ions) can damage the optical coatings in different ways, depending on the irradiation parameters such as ion fluence, ion flux, ion specie or ion energy.

It was demonstrated that in addition to the optical response changes, the irradiated films underwent deeply superficial and structural modifications. Although many of such modifications can be directly connected to the change of the optical proprieties of the films, some aspects are still unclear and further investigations are ongoing.

Moreover, a model based on an effective medium approximation was proposed to predict the behaviour of irradiated optics. The proposed model is simple and cannot take into account all the phenomena occurring on a thin film upon ion irradiation, and then not all the experimental results can be predicted at this moment. On the other hand, this model demonstrated to be able to estimate the changes of reflectance or transmittance occurring on simple coating structures when irradiated with fluences and fluxes not too high. Based on this thesis’ outcomes, further irradiation experiments are scheduled in future in order to pursue a systematic investigation of the effects occurring on ion irradiated coatings. In particular, these activities will allow to select the most promising candidate materials for hard coatings development, and/or to adopt appropriate countermeasures to avoid potential degradation of the components.
List of publications:


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