Study and Characterization of Lanthanum Oxide Thin Films Grown by Pulsed Laser Deposition

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THESIS

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LIST OF ABBREVIATIONS

CA	Contact Angle
WCA	Water Contact Angle
LA	Lanthanum
LA2O3	Lanthanum Oxide
Н	Hydrogen
PLD	Pulsed Laser Deposition
TSD	Target Substrate Distance
LWD	Laser Window Distance
UHV	Ultra High Vacuum
FM	Frank-van der Merwe
VM	Vomer-Weber
SK	Stranski-Krastanov
DI	De Ionized
UV	Ultra Violet
AFM	Atomic Force Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
HT	Heat Treatment
3D	Three Dimensional

ABSTRACT

The present work investigates the surface morphology, chemistry and the wettability properties of lanthanum oxide thin films grown using a physical vapor deposition technique, the pulsed laser deposition (PLD).

A first set of sample was generated from a lanthanum target under reactive atmosphere, i.e. by introducing oxygen during the deposition. Another set of films was deposited using a lanthanum oxide target in non-reactive atmosphere. The film deposition was completed at the University of Illinois at Chicago (UIC).

The influence of two parameters on the wettability properties of the grown surfaces was analyzed. A deposition parameter, the number of laser pulses, was increased from sample to sample to investigate the role played by the coating thickness on the physical, chemical and wetting characteristics of the thin films. The second parameter under analysis was the influence of the ultra violet light (UV) irradiation, an external stimulus, on the surface properties and wettability. The samples were irradiated under UV light for different time ranges and the exposed surfaces were then analyzed.

The samples were characterized using optical microscopy, atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) to analyze respectively the surface morphology, the surface roughness and chemistry of the films. Least but not last, the surface wettability properties were studied trough surface contact angle measurements completed using an optical tensiometer.

All the analyses were completed in the laboratories of the Department of Applied Science and Technology, Politecnico of Turin and in the laboratories of surface characterization at the Politecnico of Turin, Alessandria.

1 INTRODUCTION

The wetting properties of solid material play a critical role in extensive physical, chemical, biological and engineering sciences such as micro-fluids devices design, biosensor, fabrication of self-cleaning materials and in many other fields [1][2][3].

Nowadays even if durable materials such as metals and ceramics, which are generally hydrophilic, can be made hydrophobic by polymeric modifiers, these coatings deteriorate quite easily in harsh environments. This issue clearly limits their applications as many industrial processes involve temperature gradients and abrasions that easily deteriorate the applied coatings. A family of inorganic materials, the rare earth oxides, could overcome the limitations suffered by the organic modifiers. As reported in a recent study [4], the entire lanthanide oxide series is intrinsically hydrophobic and can sustain hydrophobicity even after exposure to extreme environments. The present thesis will focus on the wettability study of silicon substrates coated with a rear earth oxide, the Lanthanum Oxide (La₂O₃).

Starting from a conceptual understanding of hydrophobic and hydrophilic principles, the wetting phenomena will be studied providing insights from literature. This introduction will be followed by an explanation of the principle characteristic of the pulsed laser deposition.

The possibility of tuning the wetting behavior both from an "in situ" perspective, i.e. varying the number of laser pulses and hence the coating thickness, and from the application of an external stimulus, i.e. the UV light, will be investigated.

A reversible switching behavior from hydrophobicity to hydrophobicity under the application of UV light followed by the storage in dark environment was already observed in photo-responsive materials such as zinc oxide, tungsten oxide and other metal oxide [5].

2 WHAT IS WETTING?

Wetting is the ability of a liquid to keep contact with a solid surface resulting from intermolecular interactions when the two media are brought together. Generally speaking, when a liquid drop is placed on a solid substrate, two main static scenarios are possible [6].

The first limit occurs when a liquid in contact with a solid surface spontaneously spread over it. When the liquid is water, the substrate material showing this behavior is called hydrophilic. Once could notice that the word 'hydrophile' derives from the Greek 'hydros' meaning water and 'philia' meaning love. Hydrophilic molecules show a great tendency in interacting with polar solvents in particular with water or with other polar groups [7]. The term "superhydrophilicity" describes an extreme situation characterized by the complete spreading of a water droplet on a solid surface making a film. It was introduced in the last years in response to the demand for surfaces and coatings with exceptionally strong affinity to water. The study of these surfaces has reached a great interest for their potential to provide antifogging and anti fouling surfaces [2].

Conversely, the second scenario presents a partial wetting where a liquid droplet tends to remain spherical on the solid surface. If the liquid is water, the solid surfaces are addressed to be hydrophobic. The extreme hydrophobicity, defined as superhydrophobicity, occurs when the water droplet maintains a spherical shape leaving the surface essentially dry [8]. Taking advantage of the etymology of the word 'hydrophobicity', it is worth noting that the Greek word 'hydros' means water, as previously stated, whereas the term 'phobos' means fear. Therefore hydrophobic molecules repel water. Generally, on these surfaces water forms round droplets that are easily removed. Common hydrophobic coating such as wax and the roughness at the micro-scale are responsible for the water repellency. This phenomenon is very common in nature not only for plant leaves, but also for many animal species like butterflies where the presence of shapes with certain sizes and geometries on the wings gives them a hydrophobic behavior [9]. Hydrophobic coatings are extremely important for wettability control. These surfaces are often demanded in many industrial application involving self-cleaning and non-wetting coatings and fabrics [10] as well as anti-icing coatings [11].

Generally speaking, hydrophobicity and hydrophilicity together fall under the description of wettability. The presence of either phenomenon is explained by the specific wetting behavior, which is classified by measuring the contact angle (CA).

2.1 <u>Contact angle, ideal surfaces</u>

The first investigations governing the wettability of ideal solid surfaces, which are assumed to be flat and chemically homogeneous, isotropic, non reactive and non deformable were expressed by Thomas Young in the early 19th century [12]. Young's equation gives the relation between the contact angle, defined as θ , and the three surface tensions under equilibrium. Indeed if we consider a liquid drop on a solid surface, three different phases are present and therefore three surface tensions need to be considered: the solid-liquid, liquid-gas, and solid-gas tension.

The balance of the surface tensions at equilibrium determines the contact angle θ :

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta \tag{1}$$

Where γ_{SG} , γ_{SL} and γ_{LG} are respectively the solid-gas, solid-liquid and liquid gas interfacial tensions. This equation is known as the Young relation. Figure 1 schematically reports a partial wetting condition outlining the three tensions and the contact angle.



Figure 1. Surface tensions and contact angle

The Young equation can be rewritten to explicit the contact angle:

$$\theta_{eq} = \cos^{-1} \left(\frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LV}} \right) \tag{2}$$

According to the magnitude of the measured contact angle a surface can be classified as superhydrophilic, hydrophilic, hydrophobic and superhydrophobic. A contact angle of 0 degrees is considered perfect wetting and characterizes a superhydrophilic state, whereas 180 degrees is perfect non-wetting and defines a superhydrophobic surface. In all the intermediate cases where the measured contact angle is in between 5 and 90 degrees, the surface is considered to have high wettability and is addressed to be hydrophilic. In contrast, a contact angle between 90 and 150 degrees describes a surface with low wettability, the wetting of the surface is unfavorable and the fluid tends to minimize its contact with the surface forming a compact liquid droplet. This is the case of hydrophobic surfaces [13].

It is worth to point out that the scale of hydrophobicity/hydrophilicity is continuous and the division between the two regimes is arbitrary. As seen previously, it is common practice to identify a macroscopic boundary between the two behaviors by the convention of a contact angle of 90°. However it has been outlined that nothing special happens at this particular value of the contact angle [13]. Table I summarizes the discussion.



TABLE I. SURFACE CLASSIFICATION BASED ON THE WATER CONTACT ANGLE (WCA)

2.2 Surface Tension

As stated in the Young relation, the contact angle defined at the liquid, solid and gas interface depends on the magnitude of the surface tensions at equilibrium. But what is the surface tension?

The surface tension is one of the most fundamental properties of liquid and solid phases and it governs a great variety of natural and technological phenomena in plant biology, washing, painting and medicine [16].

2.2.1 Liquid surface tension

Liquid is a condensed phase in which molecules interact. Ideally, in a pure liquid, bulk molecules are pulled equally in every direction by their neighboring molecules and the resultant net force is zero. For the molecules exposed at the surface, the situation is different because they do not have neighboring molecules in all direction.



Figure 2. Schematic representation of the interactions acting on bulk and surface molecules.

The growth of the liquid/vapor interface is reflected by an increase in the number of interface molecules inducing a higher surface energy. Liquids are likely to decrease the amount of interface molecules to reduce the magnitude of the surface energy. The surface energy is hence the work that should be supplied to bring the molecules from the bulk state to the surface creating a new surface of a unit area. To increase the surface area, molecules must move to the surface breaking some interactions but this require energy. The surface tension is then the energy required to increase the surface area by a unit amount [16].

For this reason the interface tension is often identified with the specific surface free energy

(mJ m⁻²) but it can also be thought as a force per unit length (mN m⁻²). The surface tension defined as force per unit length is a tensor, while specific surface free energy is a scalar thermodynamic property of an area of the surface without directional attributes. However, for liquids in equilibrium and at constant temperature and pressure, the surface tension is numerically equal and physically equivalent to the specific surface free energy [15].

In general, the stronger the forces present between the particles in a liquid, the greater is the surface tension. Water has a high surface tension $(7.3*10^{-2} \text{ J/m}^2)$ because its molecules form multiple hydrogen bonds and therefore a great amount of energy is required to increase the fluid surface area [15][16].

Due to its atomic configuration, a water molecule can establish four bonds with other molecules. A water molecule in contact with a hydrophobic surface has one hydrogen bond vector pointing toward the surface and the remaining three hydrogen bonds can form other hydrogen bonds with the water molecules in the bulk. In contrast, in the case of a hydrophilic surface, the water molecule displays three hydrogen bonds preferentially oriented towards the surface hydrophilic sites and the remaining hydrogen bond vector forms one hydrogen bond pointing preferentially from the surface to the bulk water [17].

2.2.2 Solids surface energy

It is possible to classify solids on the basis of their surface energy. According to De Gennes et al., all solid surfaces can be divided in two large groups [15]:

- High energy surfaces
- Low energy surfaces

High energy surfaces have surface energy values in the range of 200-5000 mJ/m². These surfaces are characteristics of materials with strong chemical bonds, such as ionic, metallic or covalent. Low energy surfaces present surface energy values in between 10-50 mJ/m² and are inherent for solids with relatively weak van der Waals chemical bonds, such as polymers [18].

2.3 Water adsorption on Transition Metal Oxide surfaces

The understanding of the physical and chemical reaction involving water represents a fundamental part of many biological, geological and industrial processes. In particular, many relevant reactions take place at interfaces and water is present in principle on all surfaces under ambient condition [19]. As the atom/molecule approaches the solid surface from gas-phase, the interaction with the surface starts

becoming non-negligible. Then, adsorption phenomena may occur between the different chemical species.

Adsorption is defined as the adhesion of atoms, ions, or molecules from a gas, liquid or dissolved solid to a surface [20]. There are mainly two types of adsorption:

- Physisorption
- Chemisorption

Physisorption results in a weak bonding, typically around 0.2 eV and below. It is characterized by the lack of a true chemical bond between adsorbate and surface and no electrons are shared. The energetic contribution to this mode of adsorption is the van der Waals interaction, which is the weakest form of bonding.

In contrast, chemisorption is an adsorption process that results in a stronger net chemical bonding. In this case the electronic structure of the bonding partners is strongly perturbed [21].

From a theoretical point of view, many features of the solid-liquid interface resemble those of the solid-gas interface [21]. However the understanding of the solid-liquid interface is less well developed due to the scarcity of experimental methods currently available [21]. In the present discussion, a very basic insight on the water interaction between a solid surface and atoms in the gas phase will be treated. Being the lanthanum oxide a transition metal oxide, a basic discussion will focus on the interaction between water and transition metal oxide solid surfaces.

2.3.1 Ionicity of transition metal oxide

Transition metal oxides are ionic. Qualitatively, the ionic character results in the presence of a strong electric field that points outward from the oxide surface. The separation of charges into cations and anions results in an electronic potential on the oxide surface. These effects lead to the common

phenomenon of heterolytic dissociative adsorption of molecules, i.e. the separation of a neutral molecule AB in the gas phase into A^+ and A^- species [22]. An example is shown below:



Figure 3. Dissociative adsorption of H₂ molecule on a transition metal oxide.

Figure 3 schematically shows the dissociative adsorption of a hydrogen molecule (H_2) on a transition metal oxide where M+ is the metal oxide cation and O- is the metal oxide anion. Contrary to H adsorbed on metals, the two hydrogen atoms that are dissociatively adsorbed are not equivalent and carry opposite charges. It is likely that they have different reactivities [23].

This ionic character may increase the sticking probability of polar molecules such as ammonia, water, alcohols, acids, ethers and amines. When these molecules approach the surface, their dipole moments interact with the electric field at the surface to orient the molecule, thus enhancing the probability of an attractive bonding interaction [23].

2.3.2 Surface Composition and coordinative unsaturation

The surface composition plays an important role in the adsorption process. The stoichiometry of the surface, i.e. the anion to cation ratio, may be not the same as the one present in the bulk state.

Whether the surface cation ratio is the same as the bulk ratio depends on a number of factors such as the surface tension of the component oxide, the nature of the adsorbate, the formation of a surface compound etc. [23].

In most transition metal oxides, the oxygen anions in the bulk form close-packed layers and the metal cations occupy holes among the anions. According to this picture, once the oxide ions in the bulk

are densely packed and the oxide ion ligands fill the coordination sphere of the cation, the cation is then said to be coordinatively saturated [24].

Going to the surface, the discussion become more complicated. In this case the anions and cations are characterized by a reduced number of nearest neighbors with respect to the same ions in the bulk. The expression "coordinative unsaturation" (cus) was then coined to describe these ions showing a partially filled coordination sphere. The coordinative unsaturation enhances the reactivity of the unsaturated surface ions making them prone to bond with adsorbates. Although the coordinatively unsaturation results in increased reactivity of the metal oxide ions at the surface, not all the unsaturated ions are necessarily active and have a high tendency to form chemical bonds with adsorbates. Coordinated unsaturated sites may be present in a surface or can be created, for instance, by introducing defects on the surface [24].

Coordinatively unsaturated sites are responsible for chemisorption and binding of molecules to a surface. The presence of these coordinatively unsaturated sites may explain why an oxide surface becomes fully covered with adsorbed water and hydroxyl groups once it is exposed to the moisture in the atmosphere. Equation 3 reports the possible water adsorption on a general oxide metal surface [24]:

$$M^{n+}(cus) + H_2 0 \rightleftharpoons M^{n+} 0 H_2 \tag{3}$$

In the equation above, water is adsorbed molecularly to satisfy the coordinative unsaturation of the transition metal ion. These surface ions become coordinatively saturated and unable to adsorb other molecules. Heating causes removal of water and formation of surface coordinative unsaturation [24].

2.4 Contact angle, heterogeneous surfaces

The contact angle from the Young's law supposes perfectly flat, chemical homogeneous, isotropic and non-deformable solid surfaces. But as a matter of fact, most solids are naturally rough often at a micrometric scale. Indeed a surface can have induced physical or chemical heterogeneities resulting from fabrication processes or applied coatings for example [12].

Generally, for rough surfaces, the dynamic contact angle, i.e. advancing and receding contact angle, need to be measured since the static contact angle can take any value between the advancing and receding ones.

The difference between the advancing and receding contact angles is defined as the contact angle hysteresis, $\Delta \theta$ [25].

$$\Delta \theta = \theta_a - \theta_r \tag{4}$$

Where θ_a and θ_r are the advancing and receding contact angle respectively.

Hysteresis is commonly attributed to surface roughness or chemical heterogeneities on the surface of the substrate, but there is some disagreement as to the exact relationship [26]. As a matter of fact, only if the contact angle hysteresis is negligible, the wetting properties of a surface can be determined by the static contact angle.

The surface roughness impacts not only the hysteresis, but it also affects the static contact angle defined in the Young equation. For a rough surface two different wetting configurations, the Wenzel and Cassie Baxter model, were formulated to take into account the influence of surface roughness on the surface wettability properties. It must pointed out, however, that there are as yet no general guidelines regarding how smooth a solid surface must be for surface roughness not to have an obvious impact on the contact angle [25].

2.4.1 Wenzel Model

The surface roughness modifies the contact between the liquid and the solid. In the present discussion "r" defines the roughness factor, i.e. the ratio of the true surface area of a rough surface over the surface area of a comparably sized smooth surface. For a rough surface, "r" is greater than one whereas for a perfectly smooth surface this factor is equal to one. [27].

In the Wenzel's model it is assumed that the scale of the roughness is sufficiently small so that the liquid can enter inside the cavity with a complete wetting of the concave regions. The Wenzel relation is mathematically defined as:

$$\cos\theta^* = r\left(\frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}\right) = r\cos\theta \tag{5}$$

Where " θ " is a contact angle on a smooth surface and "r" is the roughness factor.

Taking into account that:

$$|\cos\theta^*| > |\cos\theta| \tag{6}$$

Since "r" is greater than one, it worths noting that the roughness factor can enhance both hydrophilicity and hydrophobicity. Indeed, if the contact angle θ is larger than 90°, the hydrophobicity of the surface is increased by the roughness factor. Conversely, for contact angles smaller than 90°, the roughness effect will enhanced the surface hydrophilicity.

In nature, one naturally occurring example of the role played by surface roughness is the lotus leaf whose superhydrophobicity is given by dense wax-coated protrusions separated at the micron (μ m) scale. This can be extended to artificial designs involving patterns of holes, spikes, or grooves. Manipulating the hydrophobic or hydrophilic behavior of a surface requires the study of the principles on a microscopic scale that affect the wetting character at a macroscopic scale [9].

2.4.2 Cassie-Baxter Model

The Cassie-Baxter model applies for chemically non-homogeneous solid surfaces. If a water droplet does not entirely wet the surface, air is trapped between the solid and the liquid phase giving rise to air pockets. Then the observed contact angle is influenced by the fraction "f" of the droplet that is in contact with the surface. In other words, the resultant surface composition will not be uniform since a fraction of the liquid will be in contact with air and the other portion will be in contact with the solid surface [28].

The original Cassie-Baxter equation is [29]:

$$\cos\theta^* = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{7}$$

With:

$$f_1 + f_2 = 1 \tag{8}$$

Where " f_1 " and " f_2 " are the fractional interfaces area of the solid and the air trapped in between respectively. " θ_1 " is the contact angle on a smooth surface of solid material and " θ_2 " is the contact angle formed by the water on an air pocket. θ_2 is assumed to be 180°.

Equation 7 then becomes:

$$\cos\theta^* = f_1 \cos\theta_1 - f_2 \tag{9}$$

And by applying equation 8:

$$\cos\theta^* = f_1(\cos\theta + 1) - 1 \tag{10}$$

It was proposed [28] that the transition between Wenzel and Cassie model depends on the degree of surface roughness. The greater the roughness, the more likely a Cassie configuration will results due to the formation of air pockets between the liquid and solid media. From these two models it comes out that the surface wettability can be tuned by controlling the surface geometrical structure, hence the roughness factor "r", independently of the chemical composition.

Figure 4 shows a schematic view of the Wenzel and Cassie-Baxter models outlining the complete wetting mode proper of the Wenzel state and the partial wetting mode with the presence of air pocket typical of the Cassie-Baxter configuration.



Figure 4. Cassie-Baxter(left) and Wenzel (right) configuration. (Not in scale)

3 PULSED LASER THIN FILM DEPOSITION

The deposition of lanthanum oxide thin films was accomplished using the pulsed laser deposition technique, whose process principles and characteristics are explained in the present section.

Pulsed laser deposition is a physical vapor deposition technique that uses pulsed laser beams as the energy source for evaporative film growth. The short pulsed beam is focused onto a target beyond the material's ablation threshold creating a plasma of the target material to expand and deposit onto a substrate [30].

This technique has been explored since the discovery of lasers whose high precision, reliability and spatial resolution has made it extremely useful in many industrial processes [31]. Initial activities with PLD began in the 1960s, but only in the late 1980s this deposition technique became more popular as a fast and reproducible oxide film growth technique. The main advantages of pulsed laser deposition with respect to other deposition methods like sputtering, and chemical vapor deposition, are the stoichiometric transfer and the simplicity in the initial setup. Thanks to its strengths, PLD has evolved in a broadly applicable technique for thin-film deposition. Indeed today it is widely used in the deposition of insulator, semiconductors, metals, polymers, and even biological materials [32] [33].

3.1 The PLD Process and Equipment

The pulsed laser deposition is a physical vapor deposition process, completed in a vacuum system. Figure 5 highlights the most important features of this technique.

In a pulsed laser deposition, both the target and the substrate are placed inside an ultra high vacuum chamber (UHV). For a deposition to occur, a laser fires a short pulse (in the range of few nanoseconds) at some rate of repetition. The laser frequency is a variable that can be set before every deposition. All the generated samples in the present work are grown with a laser frequency fixed to 5 Hz. The laser pulse has an associated value of energy per cross-sectional area, defined as fluency [units of J/cm²]. The energy density associated to each pulse is extremely high and can be more than 10⁸W cm⁻² to melt, evaporate, excite and ionize material from a bulk target [34].



Figure 5. Schematic representation of the Pulsed Laser Deposition process

3.2 Laser solid interaction

As the laser light interacts with a material, a fraction of this light radiation is absorbed into the material while the remaining part is reflected. If enough energy is absorbed by the material to break the chemical bonds holding the bulk material, then a cloud of ionized gas of target material propagates from the target towards the substrate surface. The distance at which this portion of energy penetrates the material is called the skin depth, " δ ", given by:

$$\delta = \sqrt{\frac{2}{\omega\mu\sigma}}$$
(2)

Where " σ " is the material conductivity, " μ " is the magnetic permeability of the target material and " ω " is the angular frequency of the light radiation. Within this skin depth layer the electrons absorb the radiation and are raised to higher energy states. This results in the heating, melting and vaporization of the involved regions [30].

This ejected luminous plasma is commonly called ablation plume and can occur either in vacuum or in the presence of a background gas. The luminosity comes from excited species de-exciting to lower or neutral energy states. Figure 6 shows the luminous plasma plume ejected from a zinc oxide target and a lanthanum oxide target taken during deposition.





Figure 6. Zinc oxide plume (left) and lanthanum oxide plume (right)

The area beneath the skin depth heats up to a depth known as the heat penetration depth, L_{th} , expressed as [30]:

$$L_{th} = \sqrt{\frac{2k\tau_p}{\rho c}} \tag{3}$$

Where "c" is the speed of light, " ρ " is the material density, " τ_p " is the pulse length of the laser and "k" is the material thermal conduction.

Low pressures on the order of 10^{-6} Torr are usually reached inside the chamber through turbo pumps. The pressure of the atmosphere inside the chamber plays an important role in the deposition.

By definition, the mean free path is the average distance that a molecule travels between successive collisions. In the presence of a gas in the chamber with a pressure "P", the mean free path " Λ " is given by [35]:

$$\Lambda = \frac{K_B T}{\pi \sqrt{2} P d^2} \tag{4}$$

Where " K_B " is the Boltzmann constant, "T" is the absolute temperature, "P" is the pressure and the "d" is the effective diameter of an atom or molecule. Pressure is inversely proportional to mean free path, hence the lower the pressure the higher the mean free path. The higher the mean free path, the longer is the distance travelled by a particle between two consecutive collisions. Therefore a deposition with low pressure limits the particle's interaction enhancing the growth of high quality thin films.

3.3 Lattice mismatch, Stress, Strain and Epitaxial growth

There are countless combinations of target and substrate materials that could be used in a PLD deposition. However the choice of a certain material as target/substrate deeply affects the film growth because several material characteristics such as crystal structure and orientation play an important role in the film development.

The crystalline lattice structure of the substrate is usually different from the one of the material to be deposited. This results in a mismatch between the lattices of the substrate and that of the film. The lattice is a periodic array of mathematical points that replicate the periodicity of the actual crystals [30].

Between the two materials, the percentage of lattice mismatch δ is given by [36]:

$$\delta = \frac{a_f - a_s}{a_s} * 100 \tag{5}$$

Where " a_f "and " a_s "are the lengths of the crystal unit cell for the film and substrate respectively. The presence of lattice mismatch generates lattice strains giving rise to lattice stresses. The stress is given as the amount of work applied to a surface area and strain is the dimensionless amount of deformation that a material undergoes. Usually a high lattice misfit results in relevant stresses and strains that hinder the growth of epitaxial films [37].

The epitaxial growth is a quite recurrent principle when dealing with PLD. Generally, the term epitaxy is used to describe the controlled growth of one crystalline material onto the surface of another material that eventually leads to the formation a single crystalline solid. In the 1928 Royer established

the conditions for this oriented overgrowth defining the term epitaxy. He formulated a rule according to which the epitaxial growth occurs only when it involves the parallelism of two lattice planes with identical or similar form and lattice constants. Experimental data later reported showed that epitaxial growth occurs if the lattice misfit between substrate and film is not larger than 15%. This approach introduced by Royer is still currently used to the understanding of epitaxy [37].

3.4 Thin Film Growth modes

Once a free particle generated from the target ablation reaches the surface of the substrate and adheres to it, it becomes known as an adatom. As more adatoms and molecules join the surface of the substrate, layers start to form and to grow [30].

The growth modes have been classified in three main types depending on the attractions between the different species involved in the process. These modes are:

- Frank-van der Merwe (FM) or layer by layer growth;
- Volmer-Weber (VM) or 3D island;
- Stranski-Krastanow (SK) or 3D island on layer growth.

The difference between them is mainly due to the interatomic interactions between substrate and film material. In other words, depending on whether the atoms or molecules of depositing material are more attracted to the substrate or to each other, one type of film growth will be prevailing on the other. Figure 7 shows a 3D view of the different growth modes. The drawings are not in scale.

3.4.1 Frank-van der Merwe growth mode

This mode is the simplest one where a monolayer is formed on the surface of the substrate before another one begins to grow. A smooth film is eventually obtained.

The interatomic interactions between substrate and film materials are stronger and more attractive than those between the ablated particles themselves. This results in the nucleation and growth of a thin film layer with the same stoichiometry of the target [30].

3.4.2 Volmer-Weber

In the opposite situation, if the depositing adatoms are more strongly bounded to each other, small clusters are nucleated directly on the substrate and then growth into islands. As more and more adatoms join the nucleation sites, these islands dominate the overall film growth. This is the case of the Volmer-Weber growth mode whose peculiarity lies on the nucleation and development of three dimensional islands due to the strong interaction between the depositing species [30].

3.4.3 Stranski-Krastanow

Stranski-Krastanow is a combination of the layer-by-layer growth with an additional island growth mode on top. As a first step a layer-by-layer film will develop. Then a stress may build up in the developing thin film making the growth of 3D island more structurally and thermodynamically stable. From this point on, the islands will then dominate the rest of the film growth [30].



Figure 7. Thin film grow mode representation (not in scale). From top to bottom: Frank-van der Merwe, Volmer-Weber and Stranski-Krastanow grow modes.

3.5 Parameters involved in the deposition

The PLD deposition involves the interplay of several variables related to laser beam parameters, material properties and on other operating conditions [38].

The main laser parameters are:

- Pulse frequency
- Total number of pulses
- Laser wavelength
- Energy fluency

The pulse frequency and the total number of laser pulses can be adjusted allowing a partial control on the film thickness. This operation is performed before starting the deposition through a manmachine interface. The laser wavelength is depending on the type of laser generator and it is usually a fixed parameter. The laser fluency depends on the laser energy and on the laser spot size.

The material parameters include:

- Thermal conductivity
- Specific heat
- Absorption coefficient, reflectance etc.

All these material parameters influence the laser ablation process.

The quality of the thin film depends also on other factors such as:

- Substrate temperature during deposition
- Gas pressure
- Substrate to target distance.

All these parameters affect the quality and uniformity of the coating. The variation of the target to substrate distance is reflected in different degrees of crystallinity and surface roughness. Indeed, according to this distance, the energetic particles could either landing on the substrate surface or sputter

out the depositing material. Moreover, depending on the material choice, higher temperatures change the surface condition of the substrate enhancing or degrading the crystallinity of the film [38].

3.6 Advantages and disadvantages of PLD

Pulsed laser deposition has been in use from the 1980s as an effective and reliable technique for the deposition of thin films [32]. One of its most important features is the stoichiometric transfer of ablated material from target to substrate surface. This transfer is possible because a very high energy density source is absorbed by a small volume of target material in a non equilibrium process [38]. Since the energy source is placed outside the vacuum chamber, a greater flexibility in the arrangement of both system components and measurement systems can be obtained. Other advantages include the high flexibility in the material choice. PLD can work with almost any kind of materials ranging from polymers to metals. [38].

On the other hand, PLD shows some limitations that must be taken into account. First of all, the generation of thin films with high degrees of uniformity is quite a challenging issue. Indeed any inhomogeneity in flux and in the angular distribution of the generated plume reflects in non uniform thin film properties. Furthermore, any impurity in the target and the formation of droplets on the surface are issues degrading the homogeneity and the quality of the grown film. Therefore a great deal of care is necessary to reduce and in the best scenario to avoid any impurity from the starting of experiments.

For this reason the PLD depositions are limited to small areas, usually few mm². PLD is a batch process and it cannot be used for continuous deposition of thin films. This represents a strong limitation in the applicability of PLD technique for deposition of materials on extended surfaces [38].

3.7 Experimental system setup

The system set-up mainly consists of:

- Laser Generator
- Ultra high vacuum chamber (UHV)

Pumping system

The PLD equipment is schematically represented in Figure 8.

The deposition process was carried out inside the UHV chamber thanks to the laser ablation of the target material and its subsequent deposition on the substrate surface. The depositions were performed under vacuum conditions (10⁻⁶ Torr) generated using a pumping system composed of two pumps connected in series.

When the pumping system was switched off, the loading of the target and substrate in the UHV was achieved in the following way. The valve connecting the upper chamber with the lower part of the vacuum system (valve 7.1) was opened. Once the target was cleaned properly, it was mounted on a support inside the UHV chamber. The UHV chamber was then closed and the pumping system was switched on. Once the pressure inside the chamber reached a value of approximately 10⁻⁵ Torr, a pre-ablation was carried out with 4000-5000 laser pulses to see the focus of the plume.

Once the pre-ablation was completed, valve 7.1 was slowly closed. In this way the UHV chamber was isolated from the rest of the vacuum system. To place the substrate inside the chamber, the UHV had to be opened again. Hence, the pressure inside was increased up to the atmospheric pressure by opening valve 7.4. The chamber was then opened and the previously cleaned substrate was placed on the substrate holder in the middle of the plume where the deposition appeared to be more uniform. It was then fixed to the substrate holder using a clamping system of through a silver paste.

At this point, once both substrate and target were placed properly, the chamber was closed again together with valve 7.4 used to de-vacuum the chamber. An auxiliary pump was switched on and valve 7.2 was opened to decrease the pressure inside the UHV. Once the pressure reached a value of about 10^{-2} Torr, valve 7.1 was slowly opened and valve 7.2 was closed. The auxiliary pump used to reduce the pressure gap was switched off. In this way the pressure gradient between the chamber and the rest of the vacuum system was decreased avoiding the catastrophic failure of the pumping system. If this step was

skipped, the huge pressure difference between chamber and the rest of the system could lead to a catastrophic failure of the turbo-pumping system.

By detaching the chamber from the rest of the system, the loading and unloading operation could be done without a great loss of time. Indeed, once the operations were completed it was not necessary to generate the vacuum from the beginning since the vacuum system was simply detached. After setting all the laser parameters through the proper interfaces and once the pressure in the UHV chamber reached a value of about 10^{-6} Torr, the deposition was started.

Another valve connecting the UHV chamber with an oxygen reservoir was opened and closed accordingly to allow the flow of oxygen during the deposition. The flow of oxygen could be independently fixed by playing with this valve and with valve 7.1.

Oxygen flow strongly influences the film deposition process since it affects the expansion of the plasma plume and modifies the kinetic of the ablated species resulting in different surface morphologies, growth rate, orientation, etc. [34].



No.	Description	Qnt.	No.	Description	Qnt.
1	KrF Laser Generator	1	8	Gas reservoir	1
2	Ultra High Vacuum Chamber	1	9	Resistance and thermocouple	1
3	Target	1	10	UHV sensor	1
4	Substrate holder	1	11	Protection tube	1
5	DC Motor	2	12	Laser lens	1
6	Pump	3	13	Operator interface	3
7	Valve	3			

Figure 8. Schematics of the PLD equipment used for the deposition of La_2O_3 thin films.



Figure 9. PLD equipment used for the deposition of the thin films.
4 THE MATERIALS

The target materials used for the depositions are the Lanthanum and Lanthanum oxide.

4.1 Lanthanum and lanthanum Oxide

Lanthanum and lanthanum oxide belong to the family of the rare earth metal oxides. Among the family of the rare earth (RE) elements there are the fifteen elements of the periodic table (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) whose atomic numbers ranges from 57 to 71 [63].

Their outer electronic configuration presents the 6s² shell that always filled, the 5d¹ configuration appears in La, Ce, Gd and Lu, and the 4f shell is increasingly occupied as the atomic number grows [63]. For the lanthanum, the 4f shell is completely unfilled. The peculiar electronic configuration gives to the rear earth metals unique physical and chemical properties which have been extensively used in electronics, medical, biomedical and agronomic fields [40]. Rare earth thin films find numerous applications, as luminescent materials, catalysts, buffer and protecting layers, as constituents in oxide superconductors and solid oxide fuel cells [41].

Under suitable condition all the rear earth elements form sesquioxides, i.e. oxides containing three atoms of oxygen with two atoms of another element. The lanthanum oxide, La_2O_3 , is a sesquioxide because three oxygen atoms are bonded with two lanthanum atoms. There is also a general agreement that the rare earth atoms are in the trivalent, RE^{3+} configuration. All the rare earth elements have +3 as stable oxidation state, so each RE atom donates three electrons to the more electronegative oxygen ions. The remaining 4f electrons stay localized at the rare earth site [42].

Rare earth sesquioxides crystallize in three forms, A-type (hexagonal), B-type (monoclinic) and C-type (cubic) structures, according to the ionic radius of the rare earth ion. At normal condition, lanthanum oxide has a stable A-type hexagonal crystal form [43]. Figure 10 depicts a polyhedral representation of the hexagonal A-type structure of La_2O_3 . The large and small spheres represent La and O atoms respectively.



Figure 10. Polyhedral representation of the hexagonal A-type structure of La₂O₃ [43] Some properties of the lanthanum sesquioxide are summarized in the table II.

	TABLE IL L	ANTHANUM	OXIDE MATERIAL	PROPERTIES
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Material	La ₂ O ₃
Stable crystalline structure	Hexagonal
Density [kg/m ³]	6510
Lattice parameter a [Å]	3.94
Lattice parameter c [Å]	6.13
Energy gap E _G [eV]	5.5

From a wetting perspective, the work of Azimi et al. [4] has recently risen the interest in the family of the rare earth oxides. Indeed, it was observed that the oxides belonging to the entire lanthanide series are intrinsically hydrophobic and this characteristic is attributed their particular electronic configurations. In the rare earth oxides, the inner unfilled 4f orbital is shielded from interaction with the surrounding environment by an outer, full $5s^2p^6$ shell. This seems to decrease the tendency for water molecules to form hydrogen bonds with interfacial water resulting in only one hydroxyl group pointing to the substrate and the remaining three other vectors forming internal hydrogen bonds with other water molecules [4]. The recently observed hydrophobic behavior of the rare earth oxides extends their

potential applications also as hydrophobic coating that, differently from commercial hydrophobic polymeric additives, can retain their properties even after harsh treatments and damage.

4.1.1 <u>Reactivity of rare earth oxide with water</u>

The reactivity of rare earth oxide with water decreases in rare earth oxides as the ionic radius of the rare earth element decreases. In other words the lanthanum oxide, and in general the rare earth oxides, are sensitive to moisture and tend to form hydroxyl group on their surface once exposed to ambient condition [44]. The formation of hydroxide anions (OH)⁻ on the surface of rare earth oxides is attributed to their large ionic radius and low electronegativity [40].

The hygroscopicity gradually changes according to the electronegativity and the ionic radius of the lanthanide metal atom. La_2O_3 having the largest ionic radius (0.123nm) and lowest electronegativity is the most hygroscopic amongst the rare earth oxides [45]. However hydrophophilicity and hygroscopicity are not necessarly correlated. In other words, a material could adsorb moisture and being at the same time water repellent. One common example is the wool, a material that adsorbs a great amount of moisture but at the same time it is difficult to wet.

To study the wettability properties of the lanthanum oxide, lanthanum oxide thin films were deposited on silicon substrates. The lattice parameters of the target and substrate materials along with their lattice parameters are reported in table III. The values are used for the calculation of the lattice mismatch.

Material	Crystalline structure	<i>a</i> [Å]	<i>c</i> [Å]	Lattice mismatch (<i>a</i>)
La ₂ O ₃	Hexagonal	3.94	6.13	27.80/
Si	Cubic	5.43	5.43	37.870

TABLE III. LA2O3 AND SI LATTICE MISFIT

5 PHOTOINDUCED HYDROPHILICITY

Several approaches are currently used to investigate the wettability of a solid surface after the application of an external stimulus of various nature: electrical, magnetic, chemical, mechanical or optical. Indeed the control of the wetting behavior according to the applied stimulus has gained an arising interest for the development of responsive smart surfaces that respond to the external stimuli [46].

Light has been effectively used as a stimulus to tune chemical reactions, physical properties and biological evolution thanks to its noncontact mode application, and by controlling its wavelength, intensity and direction. Under light irradiation, photoresponsive materials can reversibly change their molecular geometry and electronic structure. These changes can induce modifications of physical properties such as polarity, fluorescence, refractive index and magnetism [47].

Previous studies have already shown photoinduced hydrophilicity on both polymer surfaces and on some inorganic oxide films, e.g., titanium oxide, zinc oxide, tungsten oxide, tin oxide and several other metal oxides. These materials are normally hydrophobic but the exposure to UV light makes them hydrophilic. Once kept in a dark environment for a certain period, or after heat treatment, their wetting behavior is restored [5].

For a semiconductor like zinc oxide, the reversible change of wettability character is explained by the following mechanism [5][48][49][50]. Via irradiation using UV light, the electrons in the valence band may be excited to the conduction band.

$$ZnO + 2h\nu \rightarrow 2h^+ + 2e^- \tag{6}$$

These electrons and holes can either recombine or move to the surface to react with species adsorbed on the surface. Conversely, some of the holes can also react with lattice oxygen, and are trapped by lattice oxygen (surface trapped holes); while some of the electrons react with lattice metal ions (Zn^{2+}) to form Zn^+ defective sites (surface trapped electrons).

$$0^{2^-} + h^+ \rightarrow 0^-_1$$
 (surface trapped hole) (7)

After trapping a hole, the lattice oxygen is in the form O⁻ and may be further oxidized forming a neutral O radical by a second hole. The coupling of two neutral O radicals results in the formation of a O_2 molecule. Then an oxygen molecule is ejected and an oxygen vacancy is created at the metal oxide surface.

$$O_1^- + h^+ \to \frac{1}{2}O_2 + V_0 \tag{8}$$

Where V_0 is an oxygen vacancy.

Water molecules may reach the oxygen vacancy sites, leading to dissociative adsorption of the water molecules on the film surface. It has been studied that the defective sites are kinetically more favorable for hydroxyl groups (OH–) adsorption than oxygen adsorption. This process results in an increase in the hydroxyl content on the illuminated ZnO surfaces.

At the same time, the photogenerated electrons react with Zn^{2+} cations and reduce the Zn^{2+} cation to a Zn^+ state.

$$Zn^{2+} + e^- \rightarrow Zn_S^+$$
 (surface trapped electrons) (9)

The Zn^+ cations (surface trapped electrons) tend to react immediately with O_2 adsorbed on the surface forming O^{2-} or O^{2-}_2 ions.

$$Zn_s^+ + O_2(O_2^-) \to Zn_s^{2+} + O_2^-(O_2^{2-})$$
(10)

Following the proposed mechanism, the zinc oxide reaches an induced hydrophilic state after UV irradiation. This state, however, is unstable with time and the original hydrophobicity may be restored after a certain period. This instability arises at the hydrophilic state once hydroxyl adsorption has occurred. The hydroxyl adsorption results indeed in surfaces energetically unstable [64].

Furthermore, the adsorption of hydroxyl groups causes a distortion of the electronic and geometric surface structure resulting in increased instability. The exposition of the surface to ambient condition tends to revert back the original wettability property. The adsorbed OH⁻ groups can be replaced gradually by oxygen species and the surface geometric and electronic structures are reverted back to their initial states. All in all, the surface becomes hydrophobic again [48].

Heat treatment can accelerate the elimination of surface hydroxyl groups and hence the transition towards the original state [51][52].

An important purpose of the study is to investigate whether an external stimulus, the UV light, is affecting the wetting properties of the La_2O_3 surfaces. Hence, lanthanum oxide thin films were exposed to UV light and the wettability behavior was studied by measuring the contact angle. The wettability of the films before and after UV irradiation was compared.

6 SURFACE ANALYSES

The approach followed to investigate the generated films was based on both morphological and chemical analyses and it was completed with the measurement of the surface wettability. The performed analyses were the following:

- Optical microscope to observe the generated surfaces at micron-scales
- Atomic force microscopy (AFM) to quantify the degree of surface roughness
- X-ray photoelectron spectroscopy (XPS) to analyze the surface chemistry
- Optical tensiometer to determine the wetting behavior through the measurement of the static and dynamic contact angle.

This section provides a brief description of the main principles governing each technique.

All the described analyses were completed at the Politecnico of Torino and Politecnico of Torino in Alessandria, department of Applied Science and Technology.

The obtained results are discussed in chapter 8.

6.1 Optical microscopy

The optical microscope, also referred to as light microscope, is a type of microscope that uses visible light and a system of lenses to magnify images of small samples. A microscope uses a lens close to the object being viewed which focuses an image of the object inside the microscope. This image is then magnified by a second lens or group of lenses that gives, as a result, an enlarged virtual image of the object [53]. Table VI and XX report the generated surfaces at different scales.

The surface morphology was seen through the optical microscope Nikon Eclipse LV100.

6.2 Atomic force microscopy (AFM)

Although optical microscopes can easily generate two-dimensional magnified images of an object's surface, the images obtained are typically in the plane horizontal to the surface. Indeed, optical and electron microscopes do not provide the vertical dimension of a surface, i.e. the height and depth of

the surface features. Unlike optical microscope, atomic force microscopy does not rely on electromagnetic radiation, as in the case of optical microscopes.

An AFM is a mechanical imaging instrument that measures the three dimensional topography as well as physical properties of a surface with a sharpened probe. The probe is very sharp, usually less than 50 nanometers in diameter. It is positioned close enough to the surface such that it can interact with the force field associated with the surface. The probe is then scanned across the surface and an image of the surface is reconstructed by monitoring the motion of the probe as it is scanned over the surface [54].

6.3 X-ray photoelectron spectroscopy (XPS), Chemical analysis

XPS is a widely used investigation technique to study the chemical composition of a material surface. The principle at the core of XPS measurements is the photoionization. Photoionization is the interaction of electromagnetic radiation with matter resulting in the dissociation of matter into electrically charged particles. The photoelectric effect, i.e. the emission of electrons from a surface when it is exposed to electromagnetic radiation, is the simplest example of photoionization [55].

During the measurement, the sample to be analyzed is maintained in high vacuum. The working pressure of 10^{-9} mbar is required to limit the number of interactions between the emitted electrons and the molecules that are present in the chamber and to obtain samples with a low degree of surface contamination. The surface of the sample is irradiated with photons of characteristic energy; usually MgKa, 1253.6 eV, or AlKa, 1486.6 eV. These photons directly interact with core electrons, photoionization occurs and the kinetic energy of the ejected photoelectrons is measured. The equation describing the photoionization process is:

$$E_B = h\nu - E_K \tag{19}$$

Where E_B is the binding energy of a core electron, hv is the X-ray photon energy, and E_K is the kinetic energy of the ejected electrons. The measured variable is the kinetic energy. The lower the kinetic energy, the higher the binding energy will be. Once the kinetic energy of the photoemitted

electrons is measured, the resulting binding energy determines uniquely the chemical species of the atoms in the sample.

The typical output of a XPS analysis is a spectrum where the binding energy is plotted in the xaxis increasing from right to left and the intensity, i.e. the number of electrons per second (CPS) is plotted in the y axis [55].

6.4 **Optical tensiometer, contact angle measurement (WCA)**

The most widely used technique for measuring the wettability of a surface is based on the measurement of the slope of the tangent to the liquid drop at the liquid-solid-vapor (LSV) interface line [25]. The commonly used instrument is the optical tensiometer that provides video based contact angle and surface tension measurements. It consists of a horizontal stage to mount a solid or liquid sample, a micrometer pipette to form a liquid drop, an illumination source and a camera that allows to take photographs of the drop profile [25].

Contact angles are measured by fitting a mathematical expression to the shape of the liquid drop and then calculating the slope of the tangent line to the liquid drop at the interface line. Computer software gives the contact angle without operator intervention or judgment [25].

The wettability of the samples was characterized via static and dynamic contact angle measurements, performed using a CAM 200 Optical Contact Angle Meter (KSV Instruments).

6.4.1 Static contact angle measurement

For every investigated surface, 5 microliters of deionized water droplets were gently placed upon the film surface with a microliter syringe. Images were captured and the contact angle was measured using the software "Attension Theta". A single measurement was interpolated from five frames taken with a time interval of 1 second one from the other. For each frame the WCA was taken from each side of the 2D image and averaged to ensure the consistency of the results and to account for possible hysteresis. Then the five results were averaged.

6.4.2 Dynamic contact angle measurement

To take into account the eventual contact angle hysteresis, the advancing and receding contact angle were measured.

A small DI water droplet (5µl) was placed on the film surface. Then the syringe was displaced very close to the surface bringing the needle in the middle of the droplet. To measure the advancing contact angle, the volume of the droplet was increase at a rate of 0.1µl until the total solvent volume reached 8µl. Therefore a 3µl water droplet was added to the initial one for the measurement of the advancing contact angle. 0.6 frames per second were taken from the instant when the droplet volume was increased. The same rates were set for measuring the receding contact angle, but in this case the droplet volume was decreased. In the measurement of the receding contact angle, 3µl of de-ionized water were sucked away. The hysteresis was then measured as the difference between the advancing and rededing contact angle [25]. As regarding the repeatability of the obtained results, since the tool internal parameters, i.e. the syringe diameter, dispenser, acquisition camera, dispensed volume and the external factors, i.e the environmental conditions, were kept constant throughout the measurements, consistency is expected from the obtained results.

7 EXPERIMENTAL DETAILS

A rotating lanthanum oxide (La₂O₃) and lanthanum (La) target (99.9% purity, 25.4mm diameter, 6.5mm thickness) produced by SuperConductor Materials was deposited onto approximately 10mm x 10mm x 0.05 mm polished (100) n-type silicon substrates.

Pulsed laser deposition was accomplished using a 248nm KrF excimer laser, which operated approximately 1830mm away from the deposition chamber. It was programmed to pulse 2000, 3000, 4000, 5000, 7500 and 10000 times at 4.5 J/cm² energy at 5Hz with 15 ns pulse duration for every deposition.

The deposition temperature was kept constant at room temperature (~25°C). Prior to each deposition, the target was sanded and cleaned. Silicon substrates were ultrasonically cleaned for 5 minutes in solutions of acetone, methanol and isopropanol. The substrates were subsequently rinsed with de-ionized water and dried using nitrogen gas. The silicon substrates were fixed to the holder using silver paste or clamped to the substrate holder. These processes were done at room temperature.

Before starting the deposition, the chamber was pumped to a pressure of 10⁻⁶ Torr using a turbo molecular pump. The target to substrate distance was kept fixed at 70 mm for every deposition. The target was rotated and oscillated to prevent pitting by two DC motors.

Table IV reports the details of the sample deposited using the lanthanum target in the presence of oxygen. This set of samples was generated through a PLD reactive deposition.

Table V provides the details of the lanthanum oxide thin films deposited by the ablation of a lanthanum oxide target without oxygen. The latter set of samples was made to have an indication of the film characteristics and wettability. From now on, the distinction between the two sets of samples is based on whether oxygen flow was used or not during the deposition.

Laser Pulses	Deposition Temperature (°C)	Oxygen	Deposition pressure (Torr)	Laser fluency (J/cm ²)	Laser Frequency (Hz)	TSD (mm)	LWD (mm)
2000	25	YES	1.4*10 ⁻²	~4.5	5	70	20
3000	25	YES	5*10 ⁻²	~4.5	5	70	20
4000	25	YES	1.5*10 ⁻²	~4.5	5	70	20
5000	25	YES	1.7*10 ⁻²	~4.5	5	70	20
7500	25	YES	1.3*10 ⁻²	~4.5	5	70	20
10000	25	YES	1.3*10 ⁻²	~4.5	5	70	20

TABLE IV. LANTHANUM OXIDE THIN FILMS, TARGET: LANTHANUM

TABLE V. LANTHANUM OXIDE THIN FILMS, TARGET LANTHANUM OXIDE

Laser Pulses	Deposition temperature (°C)	Oxygen	Deposition pressure (Torr)	Laser fluency (J/cm ²)	Laser Frequency (Hz)	TSD (mm)	LWD (mm)
2000	25	NO	5.5*10 ⁻⁶	~4.5	5	70	20
3000	25	NO	3.5*10 ⁻⁶	~4.5	5	70	20
4000	25	NO	4*10 ⁻⁶	~4.5	5	70	20
5000	25	NO	5*10 ⁻⁶	~4.5	5	70	20
10000	25	NO	4.5*10 ⁻⁵	~4.5	5	70	20

TSD and LWD stand for target to substrate distance (TSD) and Laser window distance (LWD) respectively.

8 ANALYSES AND RESULTS

The present section reports and discusses the obtained results from the analyses whose operating principles and mechanism have already been covered previously.

The performed analyses are following a structured path and are grouped according to the target material they refer to. The films obtained by the laser ablation of the lanthanum target and of the lanthanum oxide target were investigated separately and the relative results are reported afterwards.

The first investigated set of films is the one developed by the ablation of a lanthanum target with an oxygen flow supplied during the deposition. First of all, the generated surfaces are investigated using optical microscopy, AFM and XPS to appreciate respectively the film morphology, the mean surface roughness and the film chemical composition. Afterwards, the wettability properties are quantified through the measurement of the water contact angle using an optical tensiometer. Least but not last, the films are irradiated using UV light and the contact angle measurements are repeated to investigate any change in the original wetting behavior induced by the UV light exposition.

A similar procedure is followed in the analyses of the films deposited by the ablation of the Lanthanum oxide target, with some differences though. This set of film is to be considered a preliminary study on the lanthanum oxide surface and wettability and for this reason the AFM and XPS analyses were not performed.

8.1 <u>Surface characterization of La₂O₃ thin films, target: Lanthanum</u>

8.1.1 Optical Investigation

Table VI shows the surface morphology of the thin film grown with 2000, 3000, 4000, 5000, 7500 and 10000 laser pulses from the lanthanum target ablation. The scale on the left column is 100µm and 50µm on the right column.



TABLE VI. OPTICAL INVESTIGATION: LA2O3 THIN FILMS



The deposited films seen through the optical microscope appear to be quite uniform. There are visible surface irregularities (darker regions) that may be attributed to substrate defects. Despite the increase in the laser pulses and hence in the coating thickness, there are no observable differences among the sample's surfaces.

8.1.2 <u>Atomic Force Microscopy (AFM)</u>

The films deposited using 2000, 5000 and 10000 pulses were analyzed using AFM. For each investigated film, the 3D and 2D views of the film surfaces show the detected asperities. The different colors refer to the roughness magnitude. Blue color indicates very low surface roughness while green, yellow and red colors indicate higher asperities. The scale is in nanometer.



Figure 11. 3D Surface view, 2000 laser pulses



Figure 12. Surface top view, 2000 laser pulses



Figure 13. 3D Surface view, 5000 laser pulses



Figure 14. Surface top view, 5000 laser pulses



Figure 15. 3D Surface view, 10000 laser pulses



Figure 16. Surface top view, 10000 laser pulses

Certain considerations deserve to be pointed out from the AFM analysis.

The mean surface roughness is of about 2nm for all the investigate surfaces. This is a very small value and the surface roughness is then considered negligible in every sample. As a direct consequence, it is likely that the surface wetting properties are not influenced by the very small value of surface roughness.

There are some visible asperities on every sample surface but they may be due to external contaminations since the surfaces were not cleaned before the analysis. The films were not cleaned because conventional cleaning processes containing water species within the cleaning solutions are not appropriate in the case of La_2O_3 thin films [57]. Indeed it is well known that rare earth oxides are degraded by the adsorption of moisture and hydration reaction [58].

8.1.3 X-ray photoelectron spectroscopy (XPS)

The following figures report the XPS spectra obtained from the XPS analyses. The films are investigated in the following order: 2000 laser pulses, 5000 laser pulses and then 10000 laser pulses. For each sample the survey spectrum the O1s, La3d, La4d, La4p3/2 and the spectrum showing the valence band region are reported. The uncertainty in the position of the detected peak is less than 0.4 eV calculated through the calibration on the peak Ag 3d5/2.

8.1.3.1 XPS spectra, target: Lanthanum, 2000 laser pulses



Figure 17 shows the survey spectrum of the film deposited with 2000 pulses.

Figure 17. XPS spectra. Target: Lanthanum, 2000 pulses

The XPS spectra for the O1s is reported in Figure 18.



Figure 18. XPS Spectrum O_{1s}

The XPS spectra for the La3d is reported in Figure 19.



Figure 19. XPS Spectrum: La_{3d}

The XPS spectra for the La4d is reported in Figure 20.



Figure 20. XPS Spectrum: La_{4d}.

The XPS spectra for the 4p3/2 is reported in Figure 21.



Figure 21. XPS Spectrum: La_{4p3/2}

The XPS spectrum showing the valence band is reported in Figure 22.



Figure 22. XPS spectrum: valence band.

Table 7 shows the binding energy values associated to the relevant peaks.

	Peak (eV)	%
O _{1s}	529.2	19.0
	531.4	81.0
	834.6	51.8
La 3d5/2	836.8	9.4
	838.6	38.8
La 4d5/2	102.6	44.5
	104.3	4.5
	105.2	3.8
	105.9	35.4
La 4d3/2	108.0	8.7
	109.5	3.1
La 4p3/2	196.0	72.3
	198.5	9.2
	199.9	18.5

TABLE VII.	XPS BINDING	ENERGIES,	2000 PULSES

8.1.3.2 XPS spectra, target: Lanthanum, 5000 laser pulses

Figure 23 shows the survey spectrum of the film deposited with 5000 pulses.



Figure 23. XPS spectra. Target: Lanthanum, 5000 pulses

The O1s, the La3d5/2, the La4d, the La4p3/2 electron levels and the valence band spectrum are reported in the following pages. Table VIII collects the binding energy values of the detected peaks for each electron level.

It is possible to anticipate that there are not appreciable differences in the spectra of the films grown with 2000 and 5000 laser pulses.

The XPS spectra for the O1s is reported in Figure 24.



Figure 24. XPS Spectrum O_{1s}

The XPS spectra for the La_{3d} is reported in Figure 25.



Figure 25. XPS Spectrum: La_{3d}

The XPS spectra for the 4d is reported in Figure 26.



Figure 26. XPS Spectrum: La_{4d}

The XPS spectra for the 4p3/2 is reported in Figure 27.



Figure 27. XPS Spectrum: La_{4p3/2}

The XPS spectrum showing the valence band is reported in Figure 28.



Figure 28. XPS spectrum: valence band.

Once again the valence band spectrum is showing the presence of a double peak in the lower binding energy region. The significance of these peaks will be discussed later by comparing the XPS spectrum of lanthanum and lanthanum oxide. Table 8 shows the binding energy values associated to the relevant peaks.

	Peak (eV)	%
O _{1s}	529.1	20.4
	531.3	79.6
	834.4	51.8
La _{3d5/2}	836.6	9.1
	838.4	39.1
La 4d5/2	102.2	41.3
	104.8	3.5
	105.6	3.6
	105.4	44.4
La 4d3/2	108.2	4.5
	109.5	2.7
La 4p3/2	195.8	75.3
	198.4	8.4
	199.7	16.3

TABLE VIII. XPS BINDING ENERGIES, 5000 PULSES

A negligible difference exists between the films deposited using 2000 and 5000 laser pulses from a chemical perspective. The results obtained in terms of binding energies values were compared and both intensity and binding energy remain practically constant.

8.1.3.3 XPS Spectra, target: Lanthanum, 10000 pulses

Figure 29 shows the survey spectrum of the film deposited with 10000 pulses.



Figure 29. XPS spectra. Target: Lanthanum, 10000 pulses

The O1s, the La3d5/2, the La4d, the La4p3/2 electron levels and the valence band spectrum are reported in the following pages. Table IX collects the binding energy values of the detected peaks for each electron level.

It is possible to anticipate that there are not appreciable differences in the spectra of the films grown with 2000 and 5000 and 10000 laser pulses. These films will be compared in Figure 35.

The XPS spectra for the O1s electron level is reported in Figure 30.



Figure 30. XPS Spectrum O_{1s}

The XPS spectra for the La3d5/2 is reported in Figure 31.



Figure 31. XPS Spectrum: La_{3d5/2}

The XPS spectra for the 4d is reported in Figure 32.



Figure 32. XPS Spectrum: La_{4d}

The XPS spectra for the 4p3/2 is reported in Figure 33.



Figure 33. XPS Spectrum: La_{4p3/2}

The XPS spectrum showing the valence band is reported in Figure 34.



Figure 34. XPS spectrum: valence band.

Once again the valence band spectrum is showing the presence of a double peak in the lower binding energy region. The significance of these peaks will be discussed later by comparing the XPS spectrum of lanthanum and lanthanum oxide. Table 9 shows the binding energy values associated to the relevant peaks.

	Peak (eV)	%
O _{1s}	529.2	19.2
	531.2	80.8
	834.6	52.1
La _{3d5/2}	836.9	13.1
	838.7	34.8
La 4d5/2	102.2	37.3
	104.5	4.9
	105.3	5.1
	105.4	44.7
La 4d3/2	107.9	3.7
	109.1	4.3
	195.7	75.4
La _{4p3/2}	198.4	10.1
	199.7	14.5

Figure 35 reports the 3d3/2 and 3d5/2 spectra for all the investigated surfaces.

The black spectra refers to the film grown with 2000 laser pulses, the red spectra was detected for the film developed using 5000 pulses and the blue spectra was observed in the case of the film deposited with 10000 laser pulses.



Figure 35. XPS spectra. 2000, 5000 and 10000 pulses. Target: Lanthanum.

Since the XPS analyses on the films deposited with 2000, 5000 and 10000 laser pulses present the same results, only the film grown with 2000 pulses will be compared to the XPS spectra reported by Sundinga et al. [56].

The binding energy values of the detected peaks reported were compared to the XPS analyses of lanthanum oxide and lanthanum hydroxide powder reported by Sundinga et al. [56].
The O1s, the La3d and the valence band spectra are compared. Figure 36 reports the O1s electron level from the XPS analysis completed at the Politecnico of Torino and Figure 37 reports the XPS spectra of the O1s electron level from literature [56].



Figure 36. O1s XPS spectrum.



Figure 37. O1s XPS spectrum of lanthanum oxide (left) and lanthanum hydroxide (right) [56].

The spectrum reported in Figure 36 presents two peaks. This means that oxygen atoms are distributed onto two different sites resulting in different La-O bonds [56]. The most intense peak is detected at the binding energy value of 531.4 eV and the second weaker peak has a corresponding binding energy value of 529.2 eV.

In Figure 37 two peaks are detected in the O1s spectrum of lanthanum oxide. The strongest peak at 530.5 eV is inside the notably wide range of energies reported for oxygen in lanthanum oxide. The second peak at higher binding energy has been attributed to either adsorbed water, hydroxyl groups of O^{1-} surface atoms [56].

Also in the XPS spectrum of the lanthanum hydroxide reported in Figure 37 two peaks are clearly present. The most intense peak at 531.4 eV is close to literature values reported for this compound. The second weaker peak can be attributed to oxidic bonds. This peak is thought to result from a partial dehydration of $La(OH)_3$ in the analysis chamber of the instrument caused by the combined effect of high vacuum and X-ray irradiation [56].

The comparison of the O1s spectra of Figure 36 and Figure 37 is suggesting that the films under investigation are mainly composed of lanthanum hydroxide. The results obtained at the Politecnico of Torino show the presence of two peaks whose corresponding energy values coincide with the energy values reported in literature for lanthanum hydroxide.

The next electron level under analysis is the La3d. Also in this case the XPS spectrum of the film deposited using 2000 laser pulses reported in Figure 38 is compared to the La3d XPS spectra from Sundinga et al [56].

In Figure 39 the same tendency are observed for all core electron peaks. The most intense peaks for the lanthanum oxide and lanthanum hydroxide show almost the same binding energy values. In this case the comparison between the different spectra is not providing a clear indication on the chemical composition of the investigated film.



Figure 38. La3d XPS spectrum.



Figure 39. La3d spectrum of lanthanum oxide (top) and lanthanum hydroxide (bottom) [56].

The last comparison relates the valence band spectrum of the sample under investigation reported in Figure 40 and the spectra reported from a reference source in Figure 41 [56].



Figure 40. XPS valence band spectrum.



Figure 41. Valence band spectrum of lanthanum oxide (top) and lanthanum hydroxide (bottom) [56].

Differences in peak position and width are observed between the $La(OH)_3$ and the La_2O_3 in the valence band region as reported in Figure 41. In the valence band spectrum of the lanthanum hydroxide a clear double peak is present while a single peak is concentrated in the spectrum of the lanthanum oxide. The higher binding energy part of the valence band, contains contributions from O s and H s orbitals can be related to the O-H bond [57]. This region is only present in the lanthanum hydroxide XPS spectrum.

The valence band spectrum of the investigated film, reported in Figure 40, clearly shows a second peak in the binding energy region 8-11 eV, a peak associated to the O-H bond that is absent from the XPS spectrum of lanthanum oxide.

From the obtained results and from the comparison with previous studies, the chemical composition of the investigated film mostly presents lanthanum hydroxide with a smaller amount of lanthanum oxide. This is not an odd result since several previous studies [56][57][60] report the high reactivity of lanthanum oxide when it is exposed to water. When La_2O_3 contacts H_2O , a hydration reaction changes La_2O_3 into $La(OH)_3$ [59].

8.1.4 Optical tensiometer, contact angle measurement (WCA)

Both the static contact angle and the dynamic contact angle were measured using the optical tensiomer KSV CAM 200. The used solvent was ultra pure DI water. The dynamic contact angle, i.e. the advancing and receding contact angle, was measured to quantify the contact angle hysteresis. The results are reported in the following discussion.

8.1.4.1 Static Contact angle

Figure 42 collects the static WCA measurements for every surface classified also in this case according to the number of laser pulses.



WCA vs. Number of laser pulses

Figure 42. Static contact angle measurements, target: Lanthanum

Each contact angle value, reported in Figure 42, has been calculated as the average value between three contact angle measurements performed in three consecutive days. The wettability properties of the films are quite unstable and the two films generated with 2000 and 3000 laser pulses are hydrophilic.

A clear relationship between the films wetting behavior and the number of laser pulses is missing. Apparently, the increase in the coating thickness is slightly increasing the surface hydrophobicity as can be seen by comparing the two extreme films. For all the intermediate surfaces, the wettability is not changing with the increase in the number of laser pulses. The only exception is the film developed with 3000 pulses, the most hydrophilic one among all surfaces.

Table X relates the film surfaces with the corresponding WCA measurement.

TABLE X. SURFACE MORPHOLOGY AND WCA MEASUREMENT





8.1.4.2 Contact angle Hysteresis

The modulus of the contact angle hysteresis ($|\Delta \theta|$) is calculated according to equation 4. Table XI reports the values for the advancing contact angle, receding contact angle and the contact angle hysteresis.

Laser pulses	Advancing WCA (deg)	Receding WCA (deg)	Hysteresis Δθ (deg)
2000	76.1	73.2	2.9
3000	82.78	80.4	2.4
4000	83.5	74.8	8.7
5000	92.1	94.2	2.1
7500	92.2	89.8	2.4
10000	101.2	104.3	3.1

TABLE XI. CONTACT ANGLE HYSTERESIS

As suggested by the instrument guidelines [60], the WCA measurements accuracy should account for +/- 2 degrees of accuracy. The measured hysteresis is very small (~2/3deg) for every tested sample. This result suggests a high surface uniformity as confirmed by the AFM analysis.

Since the hysteresis can be considered negligible, the wetting behavior of the generated film will be characterized by the static contact angle only.

8.1.5 Evolution of the WCA with time

The evolution of the WCA was monitored by placing a 5µl water droplet on the lanthanum oxide film generated with 2000, 5000 and 10000 laser pulses. The water contact angle was measured from the time when water and film became in contact (t=0 min) and then after 1 min, 2 min, 3 min and 10 min. Figure 43 and Table XII show the obtained results comparing the WCA measurements.



Figure 43. Static contact angle evolution, target: Lanthanum

|--|

	0min	1min	2min	3min	10min	WCA reduction (0min – 10min)
2000	98	96.6	93.6	91.6	63.8	-34.9%
5000	94.9	95	88	84.7	51.4	-45.84%
10000	102.3	95.9	94.7	93.7	63.1	-38.32%

The analysis on the contact angle evolution with time shows a considerable reduction of the contact angle itself for every tested sample.

8.1.6 Optical microscopy after WCA

After the water contact angle measurements, the film surfaces were investigated again using the optical microscope. Table XIII compares the film surfaces before and after the contact angle measurements using ultra pure DI water.





TABLE XIII. SURFACE MORPHOLOGY BEFORE AND AFTER WCA, Target: Lanthanum





No visible differences are detected from the optical surface investigations before and after the WCA measurements.

8.1.7 UV light irradiation

To investigate if the wetting properties of the lanthanum oxide thin films are changing after exposure to UV light, the generated surfaces were placed in a closed chamber and were uniformly irradiated with UV light for certain time intervals. UV light irradiation was performed in ambient air by the middle pressure mercury vapor lamp "Helios Italquartz". The provided intensity was set to 20mW/cm². The intensity was measured using the uvmetro power puck II. The UV spectrum generated by the lamp had a wide peak at a wavelength of 300nm.

The film grown with 2000, 3000, 4000 and 5000 laser pulses were exposed to UV light for respectively 15min, 30min, 60min and 120min. The film grown using 7500 and 10000 laser pulses was exposed to a complete irradiation cycle, in other words they were irradiated consecutively for 15, 30, 60 and 120 minutes.

After the UV irradiation, a 5μ l de-ionized water droplet was gently placed on the film surface and the static contact angle was measured from the time the droplet reached the surface (t=0min) and then after one minute (t=1min), two minutes (t=2min), three minutes (t=3min) and ten minutes (t=10min).

Figure 44 and table XV compare the WCA of the films grown using 2000, 3000, 4000 and 5000 laser pulses before and after exposition to UV light as a function of the irradiation intervals. In Figure 44 the lighter colors refer to the WCA before UV treatment while the darker colors denote the measurements taken after UV irradiation.



Figure 44. WCA before and after UV irradiation, target: lanthanum.

Laser pulses	WCA before UV (deg)	Exposition time	WCA after UV (deg)	WCA change
2000	85.2	15 min	85.8	+0.70%
3000	76.5	30 min	77.1	+0.78%
4000	89.6	60 min	89.5	-0.11%
5000	89.5	120 min	86.9	-2.91%

TABLE XIV. WCA MEASUREMENTS BEFORE AND AFTER UV EXPOSITION, target: lanthanum

From the measurements of the WCA reported in table XV, the UV light plays a negligible influence on the wettability of the exposed surfaces. After each exposition cycle, the contact changes less than 1% with respect to the original state. An exception is detected after irradiating the film for 120 minutes. In this case the WCA reduction is slightly more relevant.

The films grown with 7500 and 10000 laser pulses were irradiated for 15 minutes, 30 minutes, 60 minutes and 120 minutes. The contact angle was measured after each irradiation cycle and the obtained results are reported in Figure 45 and Figure 46 for the film grown with 7500 and 10000 pulses respectively.



Figure 45. WCA before and after UV irradiation, 7500 pulses, target: lanthanum.



WCA before & after UV irradiation

Figure 46. WCA before and after UV irradiation, 10000 pulses, target: lanthanum.

Table XVI collects all the WCA measurements before and after UV irradiation.

Laser pulses	WCA before UV (deg)	Exposition time	WCA after UV (deg)	WCA change
2000	85.2	15 min	85.8	+0.70%
3000	76.5	30 min	77.1	+0.78%
4000	89.6	60 min	89.5	-0.11%
5000	89.5	120 min	86.9	-2.91%
		15 min	89.5	-0.78%
7500	90.2	30 min	86.9	-3.66%
		60 min	88.7	-1.66%
		120 min	91.3	+1.22%
		15 min	92.8	-3.73%
10000	06.4	30 min	92.5	-4.05%
	90.4	60 min	85.3	-11.51%
		120 min	90.9	-5.71%

TABLE XV. WCA MEASUREMENTS BEFORE AND AFTER UV EXPOSITION

From the contact angle measurements reported in table XVI, the wettability of the investigated surfaces after UV irradiation is practically not affected by the exposition to UV light. It can be noted that the increase in the irradiation time results in a general reduction of the contact angle but this trend is not always confirmed.

The thickest film appears to be the most influenced by UV light among all the films. The same experiment should be repeated on a new sample with the same characteristics to ensure the consistency of the obtained result.

8.1.8 Evolution in time of the contact angle with time after UV exposition

The contact angle evolution of the irradiated samples was also monitored with respect to time. The WCA was measured immediately after the contact between the water droplet and the solid surface and

then after 1min, 2min, 3min and 10min leaving the droplet on the surface. Figure 47 and table XVII collect the WCA measurements for the films grown with 2000, 3000, 4000 and 5000 laser pulses



Evolution of the contact angle with time

Figure 47. WCA evolution after UV irradiation, target: lanthanum.

TABLE XVI. WCA EVOLUTION AFTER UV IRRADIATION

Laser pulses	Irradiation time	0min	1min	2min	3min	10min	WCA reduction (0min – 10min)
2000	15 min	85.76	84.94	81.66	81.4	51.05	40.47 %
3000	30 min	77.05	75.23	73.08	67.17	40.82	47.02 %
4000	60 min	89.48	88.01	86.58	82.65	54.28	39.34 %
5000	120 min	86.94	85.29	82.82	81.64	52.9	39.15 %

The WCA evolution of the thinner films (2000 and 3000 pulses) exposed to shorter irradiation cycles results to be more influenced. They experience a greater WCA reduction in time.

Figure 48 and Figure 49 report the WCA evolutions of the sample generated using 7500 and 10000 laser pulses respectively. Table XVIII collects all the results.



Figure 48. WCA evolution after UV irradiation. 7500 laser pulses



Figure 49. WCA evolution after UV irradiation. 10000 laser pulses.

Laser pulses	UV exposition	WCA 0min	WCA 1min	WCA 2min	WCA 3min	WCA 10min	WCA reduction (0min – 10min)
2000	UV 15 min	85.76	84.94	81.66	81.4	51.05	40.47 %
3000	UV 30 min	77.05	75.23	73.08	67.17	40.82	47.02 %
4000	UV 60 min	89.48	88.01	86.58	82.65	54.28	39.34 %
5000	UV 120 min	86.94	85.29	82.82	81.64	52.9	39.15 %
	UV 15 min	89.5	87.7	87.6	86.4	65.1	27.26%
	UV 30 min	86.9	85.6	83.1	81.4	57.7	33.60%
/500	UV 60 min	88.7	87.1	84.9	80.6	59.7	32.69%
	UV 120 min	91.3	90.9	88.7	87.8	67.7	25.96%
	UV 15 min	94.7	92.8	91.4	86.3	73.2	22.7%
10000	UV 30 min	93.1	92.5	90.9	89.4	69.7	25.13%
	UV 60 min	87.2	85.3	82.6	80.5	55.3	36.58%
	UV 120 min	91.3	90.9	88.7	87.8	67.7	25.96%

TABLE XVII. WCA EVOLUTION AFTER UV IRRADIATION

The wettability evolution in time after UV irradiation is presenting a trend. By considering the same irradiation cycle, the WCA reduction from 0min to 10min is remarkably higher for the thinner films. In other words, the contact angle evolution of the films generated with a greater number of laser pulses seems to be less influenced by the exposition to UV light.

Also in this case, few exceptions should be outlined. After 60min of UV irradiation, the film with the highest number of laser pulses presents the greatest WCA reduction in time. After 120 minutes of UV irradiation, the films grown with 7500 and 10000 pulses present the same WCA reduction.

8.1.9 Dark storage to restore the initial wetting behavior

Previous studies have confirmed that the original wetting properties are restored after dark storage or upon annealing [59][60]. The WCA measurements of the irradiated surfaces were repeated after three days by keeping the samples in a dark environment. Table XIX reports the WCA measurements.

Laser pulses	WCA Before UV (deg)	UV exposition	WCA After UV (deg)	WCA After 3 days (deg)	Difference
2000	85.2	15 min	85.8	83.4	-2.11%
3000	76.5	30 min	77.1	79.1	+3.40%
4000	89.6	60 min	89.5	88.1	-1.67%
5000	89.5	120 min	86.3	94.5	+5.59%
7500	90.2	120 min	91.3	89	-1.33%
10000	96.4	120 min	90.9	86.3	-10.48%

TABLE XVIII. TRANSITION TOWARDS ORIGINAL WETTABILITY

The difference has been calculated between the WCA before UV irradiation and the WCA repeated three days after irradiation. All the samples were stored in a dark environment under ambient pressure and temperature.

The general scattering of the results may be explained by the dependency of the surface on the atmospheric conditions. As previously stated, lanthanum oxide is the most hygroscopic among all the rare earth oxides and therefore even a small change in the atmospheric humidity can influence its surface wettability.

In conclusions, the contact angles measured three days after UV irradiation are not thought to be related on any UV irradiation effect since the changes induced by the UV light were measured to be practically negligible.

8.2 Surface characterization of La2O3 thin films, target: Lanthanum oxide

8.2.1 Optical Investigation

Table XX shows the surface morphology of the thin film grown with 2000, 3000, 4000, 5000, and 10000 laser pulses from the lanthanum oxide target ablation. The scale on the left column is $100\mu m$, on the right column is $50\mu m$.

Magnification: 10x, Scale: 100 µm Magnification: 50x, Scale: 50 µm 2000 pulses 3000 pulses

TABLE XIX. OPTICAL INVESTIGATION La2O3 THIN FILMS





5000 pulses



10000 pulses





From the surface morphologies reported in table XX it is possible to see that an increase in the number of laser pulses, from 2000 to 4000, results in the increase in both density and dimension of the observed clusters. Their maximum size is reached at 4000 pulses and a further increase in the number of laser pulses, i.e. 5000 and 10000, results in the creation of a more homogeneous film.

8.2.2 Optical tensiometer, contact angle measurement (WCA)

The static contact angle was measured using the optical tensiometer KSV CAM 200. Ultra pure DI water was used to measure every contact angle.

Figure 50 collects the WCA measurements relative to the respective surface. Also in this case the films are identified by the number of laser pulses used during the deposition.





Figure 50. Static water contact angle measurement. Target: La₂O₃

From the results reported in Figure 50, a positive trend regarding the surface hydrophobicity can be easily detected. As the number of pulses increases, the contact angle increases as can be seen from the samples grown at 3000, 4000 and 5000 pulses respectively. As reported in table XX, the surfaces of

these films are characterized by an increase in both size and density of the so defined "islands". Once the film reaches a more uniform surface morphology, the WCA tends to a more stable value.

Our results suggest that the film thickness may play a role in the wettability of the generated surfaces. At a certain number of laser pulses or in other words at a certain thickness value, the film surface becomes practically uniform and no clusters are observable any more. The observed relation between film thickness and resulting film morphology could influence the surface wettability as the WCA measurements are suggesting. The WCA is higher than 90 degree for all the samples with the only exception of the film grown with 2000 pulses that is hydrophilic (84.7°).

Table XXI relates the images taken from the WCA measurements with the corresponding film morphology.



TABLE XX. SURFACE MORPHOLOGY AND WCA MEASUREMENT



8.2.3 WCA evolution with time, target: Lanthanum oxide

The contact angle was monitored also in this case with respect to time. The experiment was performed by placing a 5μ l water droplet on the lanthanum oxide film generated with 10000 pulses and on the silicon substrate. The water contact angle was measured from the time when water and film became in contact (t=0min) and then after 1 minute, 2 minutes, 3 minutes and 10 minutes. Figure 51 and table XXII report the obtained results comparing the WCA evolution for the two different materials.

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Evolution of the contact angle with time

Figure 51. La₂O₃ and Si surface contact angle evolution

TABLE XXI.	WCA EVOLUTION	IN TIME, Si AND	LA2O3 SURFACES

	0min	1 min	2min	3min	10min	WCA reduction (0min – 10min)
La ₂ O ₃	99.54	98.59	96.84	96.05	85.89	13.71%
Si	52.14	47.66	46.48	45.25	33.63	35.50%

As comes out from the obtained measurements, a great reduction of the contact angle as time increases is observable in either hydrophobic (La_2O_3) and hydrophilic surfaces (Si). It is expected that water evaporation and water molecular adsorption are the two main phenomena involved in the observed WCA reduction. The higher reduction observed in the case of the silicon substrate may be due to its hydrophilicity.

Table XXIII provides a visual insight on the observed WCA reduction.



TABLE XXII. SI AND LA2O3 CONTACT ANGLE EVOLUTION

8.2.4 Optical microscopy after WCA

After the water contact angle measurements, the film surfaces were investigated again using the optical microscope. Table XXIV compares the film surfaces before and after the WCA measurement. While no detectable changes were observed in the case of the films deposited using a Lanthanum target, some surface changes are clearly seen on the films deposited from the lanthanum oxide target. Even if ultrapure de-ionized water was used for the contact angle measurements, the contact between water and the film left some traces on the surfaces.

TABLE XXIII. SURFACE MORPHOLOGY BEFORE AND AFTER WCA





A possible explanation may be found on the high reactivity of the lanthanum oxide with water. Indeed the hydration of lanthanum oxide films exposed to water has already been investigated in several studies [57][59]. It was proposed that the principal interaction of water with the oxide films leads to the formation of surface hydroxyl groups.

In the case of the lanthanum oxide thin films, the formation of lanthanum hydroxides is explained by the dissociative adsorption of the incident water molecule with the resultant formation of hydroxyl groups. The mechanism is schematically shown in Figure 52 [60].



Figure 52. Water reaction with Lanthanum Oxide

8.2.5 UV light irradiation

To investigate if the wetting properties of the lanthanum oxide thin films deposited from the lanthanum oxide surface are changing after exposure to UV light, the coated films were placed in a closed chamber and were uniformly irradiated with UV light for certain time intervals. UV light irradiation was performed in ambient air by the middle pressure mercury vapor lamp "Helios Italquartz". The provided intensity was set to 20mW/cm². The intensity was measured using the uvmetro power puck II. The UV spectrum generated by the lamp had a wide peak at a wavelength of 300nm.

The films grown with 2000, 3000, 4000 and 5000 laser pulses were exposed to UV light for respectively 15min, 30min, 60min and 120min. The film grown using 10000 laser pulses was exposed to a complete irradiation cycle, in other words it was irradiated consecutively for 15min, 30min, 60min and 120min.

A 5µl ultrapure de-ionized water droplet was gently placed on the film surface and the contact angle was measured from the time the droplet reached the surface (t=0min) and then after one minute (t=1min), two minutes (t=2min), three minutes (t=3min) and ten minutes (t=10min). Figure 53 and table XXV compare the water contact angles of each sample before and after exposition to UV light as a function of the exposition time. In Figure 53 the lighter colors indicates the WCA before UV exposure while the darker colors denote the measurements taken after UV irradiation.



Figure 53. WCA measurements before and after UV irradiation, target: La₂O₃

Laser pulses	WCA before UV	Exposition time	WCA after UV	WCA change
2000	84.7	15 min	81	-4.37%
3000	92.3	30 min	90	-2.49%
4000	101	60 min	95	-5.49%
5000	98.7	120 min	76.5	-22.49%

TABLE XXIV. WCA MEASUREMENTS BEFORE AND AFTER UV EXPOSITION

From the WCA measurements, the UV irradiation is lowering the water contact angle for all the irradiated samples. Moreover, as can be seen from table XXV, an increase in the UV irradiation cycle is resulting in a decrease of the water contact angle. This trend has only one exception represented by the film irradiated for 30 minutes whose WCA reduction presents a smaller value.

A complete cycle of UV irradiation was completed in the case of the film generated using 10000 laser pulses. The surface was irradiated for 15, 30, 60 and 120 minutes. The contact angle and the contact angle evolution in time were measured after each irradiation interval.

Figure 54 collects the WCA measurements before and after UV irradiation for the film deposited using 10000 laser pulses.



WCA before & after UV irradiation

Figure 54. WCA before and after UV irradiation, 10000 laser pulses

Laser pulses	WCA before UV (deg)	Exposition time	WCA after UV (deg)	WCA reduction
2000	84.7	15 min	81	4.37%
3000	92.3	30 min	90	2.49%
4000	101	60 min	95	5.49%
5000	98.7	120 min	76.5	22.49%
10000		15 min	99.48	0.06%
	99.54	30 min	94.89	4.67%
		60 min	97.18	2.37%
		120 min	97.83	1.72%

TABLE XXV. WCA BEFORE AND AFTER UV IRRADIATION

From the obtained results, the film grown with the highest number of laser pulses is less influenced by the UV irradiation. There is only one exception detected after 30 minutes of UV exposition. Indeed this is the only case where the thickest film shows a greater WCA reduction. In all the other cases, the wettability of the thinner films is more influenced from UV exposition.

As the results are suggesting, the UV influence on the contact angle seems to be inversely related to the coating thickness. In other words, the thicker films are less affected by UV light at least from a wetting perspective.

8.2.6 Evolution of the contact angle in time after UV exposition

The contact angle evolution of the irradiated samples was monitored with respect to time. Thanks to the optical tensiometer, the wettability was measured immediately after the contact between the water droplet and the solid surface and then after 1min, 2min, 3min and 10min leaving the droplet on the surface. Figure 55 and table XXVII collect all the measurements.



Evolution of the contact angle with time after UV irradiation

Figure 55. WCA evolution in time after UV irradiation, target: La₂O₃

To gain a visual insight of the wetting evolution in time, the frames used for the WCA measurements were collected accordingly in table XXVII where for each UV exposition interval the WCA evolution in time follows a top-down direction.



TABLE XXVI. WETTABILITY EVOLUTION AFTER UV IRRADIATION
Also the WCA evolution of the film grown with 10000 pulses was measured after each irradiation interval and the results are reported in Figure 56 and table XXVIII.



Evolution of the contact angle with time after UV irradiation

Figure 56. WCA evolution in time after UV irradiation, target: La₂O₃, 10000 pulses

Laser pulses	UV exposition	WCA 0min	WCA 1min	WCA 2min	WCA 3min	WCA 10min	WCA reduction (0min – 10min)
2000	UV 15 min	81	79.3	78.1	76	56.3	-30.49%
3000	UV 30 min	90	87.4	86.8	82.8	66	-26.67%
4000	UV 60 min	95	92.5	90.7	89.6	71.5	-24.74%
5000	UV 120 min	76.5	72.6	70.5	67.8	49.1	-37.12%
	UV 15 min	99.48	97.33	96.27	94.1	76.35	23.25%
	UV 30 min	94.89	91.3	89.95	88.65	71.54	24.61%
10000	UV 60 min	97.17	96.72	96.18	97.18	76.08	21.7%
	UV 120 min	97.83	97.01	94.41	91.98	64.91	33.65%
	Before UV	99.54	98.59	96.84	96.05	85.89	13.71%

TABLE XXVII. WCA EVOLUTION AFTER UV IRRADIATION

As regarding the evolution of the contact angle in the time, a notable difference is present between the irradiated and non-irradiated surfaces. The measured WCA reductions for the irradiated lanthanum oxide exceed the 21%, while the WCA evolution before UV exposition resulted in a contact angle decrease of about 14% (table XXII).

A second consideration comes from the WCA evolution of the films grown with different laser pulses. Indeed, the 10000 pulses film, i.e. the thickest film, presents a smaller decrease in the contact angle if compared to the one observed in the thinner films.

Summing up, for the lanthanum oxide films deposited from the ablation of the lanthanum oxide target, the wettability of the thickest film appears to be less influenced by the UV exposition.

8.2.7 Heat treatment (HT) to restore the initial wetting behavior

To restore the original wetting properties, the films grown with 2000, 3000, 4000 and 5000 laser pulses were annealed in a furnace for two hours at 200°C in ambient atmosphere and pressure. The samples were then cooled outside the furnace in ambient air and pressure. Table XXIX shows the contact angle measured after the heat treatment.

Laser pulses	WCA before UV (deg)	UV Exposition	WCA after UV (deg)	WCA after HT (deg)
2000	84.7	15 min	81 (0min) – 56.3 (10min)	64.1
3000	92.3	30 min	90 (0min) – 66 (10min)	80.1
4000	101	60 min	95 (0min) – 71.5 (10min)	70.2
5000	98.7	120 min	76.5 (0min) – 48.1 (10min)	87.5

TABLE XXVIII. WCA AFTER HEAT TREATMENT

It is possible to notice that after annealing the wettability of the irradiated samples tends to revert back to its original value. The contact angle is increased but the transition towards the initial wetting behavior is not fully completed. Moreover it must be noted that the WCA of film grown with 5000 laser pulses is remarkably increased after the heat treatment. The irradiated films were also investigated with the optical microscope after annealing. Table XXX compares the surfaces before and after heat treatment. From the optical microscope investigation, it is possible to notice that the film generated using 5000 pulses and irradiated with UV light for 120 minutes, presents a clear change in the surface morphology after UV irradiation and heat treatment. Also the film grown with 2000 pulses is showing a change in the surface morphology presenting an increased cluster density after annealing.



TABLE XXIX. SURFACE INVESTIGATON BEFORE AND AFTER HEAT TREATMENT (HT)



To monitor the transition towards the original wetting behavior, the contact angle measurement was regularly repeated after UV irradiation. The results, reported in table XXXI, show that 7 days after the UV irradiation only in one case the initial wetting behavior was restored almost completely with a difference less than 0.5%. In this case, the initial wettability can be considered as fully restored.

Laser pulses	WCA Before UV (deg)	WCA After UV (deg)	WCA After HT (deg)	WCA After 7 days (deg)	Difference
2000	84.7	56.3	64.1	84.6	-0.12%
3000	92.3	66	80.1	89	-3.58%
4000	101	71.5	70.2	95.1	-5.84%
5000	98.7	48.1	87.5	90.2	-8.61%

TABLE XXX. TRANSITION TOWARDS ORIGINAL WETTABILITY

The measurements repeated after 30 days show that the original wetting properties are not fully restored in the case of the samples generated with 3000 and 4000 pulses and irradiated for 30 and 60 min respectively. Table XXXII collects the measurements repeated after 30 days.

TADIE VVVI	TDANSITION	TOWADDS	ODIGINIAL	WETTADILITY
IADLE AAAI.	TRAINSTITION	TOWARDS	UKIGINAL	WEITADILITY

Laser pulses	WCA Before UV (deg)	WCA After UV (deg)	WCA After HT (deg)	WCA After 30 days (deg)	Difference
2000	84.7	56.3	64.1	-	-
3000	92.3	66	80.1	96.3	+4.33%
4000	101	71.5	70.2	95.1	-5.84%
5000	98.7	48.1	87.5	98.7	-0.51%

8.2.8 Dark storage to restore the initial wetting behavior

For the film grown with 10000 laser pulses a different approach was followed. To avoid the formation of a new interfacial layer, the irradiated film was simply stored in a dark environment, under ambient temperature and pressure. Contact angle measurements were repeated to monitor the time needed to complete the backward transition to the initial properties. Table XXXIII collects the WCA measurements.

WCA before UV WCA after UV WCA after 3 days Laser pulses UV exposition (deg) (deg) 15 min 99.48 (0min) - 76.35 (10min) 30 min 94.89 (0min) - 71.54 (10min) 10000 99.54

60 min

120 min

TABLE XXXII. TRANSITION TOWARDS INITIAL WETTABILITY

Just 3 days after UV irradiation, the initial wetting behavior of the film was reverted back almost completely. Only a negligible difference of 0.66% was measured before and after UV exposition.

97.17 (0min) - 76.08 (10min)

97.83 (0min) - 64.91 (10min)

(deg)

100.2

9 CONCLUSIONS

The recently discovered hydrophobic properties of the rare earth oxides have sparked a great interest among the scientific community for their potential application in several industrial fields where self-cleaning and de-icing surfaces are demanded.

For this reason, surfaces coated with a rare earth oxide, the lanthanum oxide, has been generated and investigated. Indeed, thin films of lanthanum oxide were deposited on a silicon substrate by the laser ablation of a lanthanum oxide target and by the ablation of a lanthanum target providing oxygen flow during the deposition.

As outlined in the preliminary theoretical study, the wettability of a surface is influenced by two main factors: the surface roughness and its chemical composition. To investigate these properties, the films generated from the lanthanum target using 2000, 5000 and 10000 laser pulses were analyzed using AFM and XPS. The AFM analysis revealed a very low mean roughness value of ~2nm regardless of the number of laser pulses used during the deposition. The surface roughness was then considered to be negligible.

The XPS spectra reported that the films chemical composition was that of the lanthanum hydroxide and lanthanum oxide and no appreciable differences were detected among the investigated samples.

The so far mentioned analyses were performed at the Politecnico of Turin, (Italy) and provided useful insights regarding the generated solid surfaces. But, unfortunately, they are not sufficient to fully evaluate and explain the wettability property of the solid material surface itself.

This is because the solid-liquid interface is a very complex topic and still today the interface interactions at a molecular scale between solid and liquid media are not completely understood [62]. Most of the powerful experimental techniques used to study solid-vacuum and solid-solid interfaces in UHV cannot be applied to solid-liquid interface and the scarcity of experimental methods is resulting in a less well developed understanding of the solid-liquid interface [21]. Even the commonly used

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distinction between hydrophobic and hydrophilic surface is merely based on the conventional contact angle value of 90°, but nothing really special happens at this value.

The analyses done on the films generated from the ablation of a lanthanum oxide target are reporting interesting results. First of all, it was observed trough optical microscopy that an increase in the number of laser pulses and hence in the coating thickness is resulting in different surface morphologies. Notably, some clusters are detected and their size and density are increased when the number of pulses is increased as well up to a certain thickness value at which the surfaces morphology becomes uniform.

The relation between the number of laser pulses and the obtained surfaces morphology resulted in a defined wettability trend. That is, the contact angle increases when the surface thickness increases up to a certain value where an additional increment in the number of laser pulses is not influencing the wettability any more. The highest WCA value was measured to be 101° in correspondence of the film with highest cluster size and density. As previously stated, and additional increase in the number of laser pulses results in the development of more uniform surfaces. The WCA measurements revealed that once a more uniform surface is achieved, the contact angle stabilizes as well.

When the generated lanthanum oxide films (target: La₂O₃) were irradiated with UV light different behaviors were observed. For the films generated using 2000, 3000, 4000 and 5000 laser pulses, the water contact angle decreased when the UV irradiation time was extended. In other words, the increase in the UV irradiation time was lowering the water contact angle making the surfaces more hydrophilic. Repeated contact angle measurements in the days following the UV exposition revealed that a long time was needed to revert back the original wetting properties.

By considering the same irradiation cycle, the wettability of the thickest coating (10000 laser pulses) was less influenced by the UV irradiation. After every UV exposition cycle the film maintained its hydrophobic behavior. In this case after few day the surface wettability was restored to its original value. Further investigations may support the hypothesis according to which the coating thickness plays a role in the wettability of the surface itself. To this aim, several other films deposited from the ablation of a lanthanum oxide target are needed to ensure the repeatability of the obtained results.

CITED LITERATURE

- 1. de Gennes, P., G.: Wetting: statics and dynamics. *Review of Modern Physics*, 1985, Vol. 57. No.3. Part I.
- 2. Drelich, J., Chibowski, E., Meng, D., and Terpilowski K.: Hydrophilic and superhydrophilic surfaces and materials. *Soft Matter*, 2011, 7, 9804-9828.
- 3. Bonn, D., Eggers, J., Indekeu, J., Meunier, J., and Rolley, E.: Wetting and spreading. *Review of Modern Physics*, 2009, Vol. 81.
- 4. Azimi, G., Dhiman, R., Kwon, H., Paxson, A.T., and Varanasi, K.K.: Hydrophobicity of rare-earth oxide ceramics. *Nature Materials*, 2013, NMAT3545.
- 5. Miyauchi, M., Nakajima, A., Watanabe, T., and Hashimoto, K.: Photocatalysis and Photoinduced Hydrophilicity of Various Metal Oxide Thin Films. *Chemistry of Materials*, 2002, 14, 2812-2816.
- 6. Bormashenko, E.Y.: Wetting of real surfaces. *De Gruyter Studies in Mathematical Physics*, 2013, Vol. 19, Ch. 2, ISBN 978-3-11-025853-0.
- 7. "Hydrophilic." Compendium of Chemical Terminology, Gold Book. *International Union of Pure and Applied Chemistry*, 2012, p. 699.
- 8. Bico, J., Marzolin C., and Quéré, D.: Pearl Drops. *Europhysics Letters*, 1999, 47 2.
- 9. Bocquet, L., and Lauga, E.: A smooth future?. *Nature Materials*, 2011, Vol. 10.
- 10. Zimmermann, J., Reifler, F.A., Fortunato, G., Gerhardt, L.C., and Seeger, S.: A Simple, One-Step Approach to Durable and Robust Superhydrophobic Textiles. *Advanced Functional Materials*, 2008, 18, 3662-3669.
- 11. Cao, L., Jones, A.K., Sikka, V. K., Wu, J. and Gao, D.: Anti-Icing Superhydrophobic Coatings. *Langmuir*, 2009, 25, 12444-12448.
- 12. Quéré, D.: Wetting and Roughness, Annu. Rev. Mater. Res, 2008, 38:71-99.
- 13. Giovambattista, N., Debenedetti, P.G., and Rossky, P.J.: Enhanced surface hydrophobicity by coupling of surface polarity and topography. *Proc. Natl Acad. Sci.*, 2009, 106, 15181-15185.
- 14. Antonini, C., Innocenti, M., Horn, T., Marengo, M., and Amirfazli, A.: Understanding the effects of superhydrophobic coatings on energy reduction in anti-icing systems. *Elsevier, Cold regions science and technology*, 2011, 67, 58-67.
- 15. Bormashenko, E.Y.: Wetting of real surfaces. *De Gruyter Studies in Mathematical Physics*, 2013, Vol. 19, Ch. 1. ISBN 978-3-11-025853-0.
- 16. Silberberg, M.S.: Chemistry, the Molecular Nature of Matter and Change. *McGraw-Hill*, 2009, Ch. 12. ISBN 978-0-07-128354-0.

- 17. Giovambattista N., Debenedetti P.G., and Rossky P.J.: Effect of Surface Polarity on Water Contact Angle and Interfacial Hydration Structure. J. Phys. Chem, 2007, 111, 9581-9587.
- 18. Verplanck, N., Coffinier, Y., Thomy V., and Boukherroub, R.: Wettability Switching Techniques on Superhydrophobic Surfaces. *Nanoscale Res. Lett.*, 2007, 2:577-596.
- 19. Klas A.: Structure, Bonding and Chemistry of Water and Hydroxyl on Transition Metal Surfaces. Dissertation for Doctorate Degree in Chemical Physics, Stockholm University, 2006.
- 20. "Adsorption." Compendium of Chemical Terminology, Gold Book. International Union of Pure and Applied Chemistry, 2012, p. 41.
- 21. Lüth, H.: Solid Surfaces, Interfaces and Thin Films. *Graduate Texts in Physics*, 2010, Chapter 10. ISBN 978-3-642-13591-O.
- 22. "Heterolytic dissociative adsorption." Compendium of Chemical Terminology, Gold Book. *International Union of Pure and Applied Chemistry*, 2012, p. 675.
- 23. Kung, H.H.: Transition Metal Oxides: Surface Chemistry and Catalysis. *Elsevier, Studies in Surface Science and Catalysis,* 1989, Ch. 3. ISBN: 0-444-87394-5.
- 24. Kung, H.H.: Transition Metal Oxides: Surface Chemistry and Catalysis. Elsevier, *Studies in Surface Science and Catalysis*, 1989, Ch. 4. ISBN: 0-444-87394-5.
- 25. Yuan Y., and T.R. Lee: Contact angle and Wetting Properties. Springer Series in Surface Sciences, 2013, Vol. 51, Ch. 1.
- 26. Smyth, K.M.: Wetting Hysteresis and Droplet Roll Off Behavior on Superhydrophobic Surfaces. Bachelor Degree thesis in Mechanical Engineering, Massachussetts Institute of Technology, 2010.
- 27. Wenzel, R.N.: Resistance of Solid Surfaces to Wetting by Water. *Ind. Eng. Chem.*, 1936, Vol. 28, No. 8.
- 28. Barthier, J., and Braake, K.A.: The Physics of Microdroplets. *Wiley*, 2012, Ch. 4. ISBN: 978-0-470-93880-5.
- 29. Milne, A.J.B., and Amirfazli A.: The Cassie equation: How it is meant to be used. *Advances in Colloid and Interface Science*, 2012, 170 48–55.
- 30. O'Haire, R.J.: Growth by Pulsed Laser Deposition and Characterization of Zinc Oxide Thin Films and Nanostructures. Dissertation for Doctoral Degree in Physical Sciences, Dublin City University, 2009.
- 31. Bertolotti, M.: The history of the Laser, Bollati Boringhieri, 1999, Ch. 6. ISBN: 0 7503 0911 3.
- 32. Eason, R.: Pulsed Laser Deposition of Thin Films, *Wiley*, 2007, Ch. 1. ISBN: 0-471-44709-9.

- 33. Miotello, A., Ossi, P.M.: Laser-Surface Interactions for New Materials Production, *Springer Series in Materials Science*, 2010, Ch. 7. ISBN: 978-3-642-03306-3.
- 34. Ellmer, K., Klein, A., and Rech, B.: Transparent Conductive Zinc Oxide, *Springer Series in Materials Science*, 2008, Ch. 7. ISBN: 978-3-540-73611-0.
- 35. Chen, G.: Nanoscale Energy Transport and Conversion, *Oxford University Press*, 2005, Ch. 1. ISBN: 0-19-515942-X.
- 36. Vlassak J.: Thin Film Mechanics. DEAS Harvard University, 2004.
- 37. Herman, M.A., Richter, W., and Sitter H.: Epitaxy, Physical Principles and Technical Implementation. *Springer-Verlag*, 2004, Ch. 1. ISBN: 3-540-67821-2.
- 38. Nagar, S.: Multifunctional magnetic materials prepared by Pulsed Laser Deposition. Doctoral dissertation, Royal Institute of Technology, Stockholm, 2012.
- Wang, C., Cheng, B.L., Wang, S.Y., Lu, Y.L., Zhou, Z.H. and Yang, G.Z.: Effects of oxygen pressure on lattice parameter, orientation, surface morphology and deposition rate of (Ba_{0.02}Sr_{0.98})TiO₃ thin films grown on MgO substrate by pulsed laser deposition. *Thin Solid Films*, 2005, 485 82 89.
- 40. Fanciulli, M., Scarel, G.: Rare Earth Oxide Thin Films. *Springer, Topics in Applied Physics*, 2007, Ch. 1. ISBN: 978-3-540-35796-4.
- 41. Adachi, G., Imanaka, N. and Kang, Z.C.: Binary Rare Earth Oxides. *Springer Science*, 2005, Ch. 1. ISBN: 978-1-4020-2568-6.
- 42. Petit, L., Svane, A., Szotek, Z. and Temmerman, W.M.: First-principle study of rare-earth oxides. *The American Physical Society*, 2005, 72 205118.
- 43. Zinkevich, M.: Thermodynamics of rare earth sesquioxides. *Progress in Materials Science*, 2007, 52 597–647.
- 44. Jun, J.H., and Choi, D.J.: Effects of the wet air on the properties of the lanthanum oxide and lanthanum aluminate thin films. *Thin Solid Films*, 2006, 504 205 208.
- 45. Frohlich K., Luptak R., Dobrocka E., Husekova K., Cico K., Rosova A., Lukosius M., Abrutis A., Pisecny P., and Espinos, J.P.: Characterization of rare earth oxides based MOSFET gate stacks prepared by metal-organic chemical vapour deposition. *Materials Science in Semiconductor Processing*, 2006, 9 1065–1072.
- Yan B., Tao J., Pang C., Zheng Z., Shen Z., Cheng H.A.H., and Yu, T.: Reversible UV-Light-Induced Ultrahydrophobic-to-Ultrahydrophilic Transition in an α-Fe2O3 Nanoflakes Film. Langmuir 2008, 24, 10569-10571.

- 47. Wang S., Song Y., and Jiang L.: Photoresponsive surfaces with controllable wettability. *Journal* of photochemistry and photobiology, 2007, 8 18-19.
- 48. Sun, R.D., Nakajima, A., Fujishima, A., Watanabe, T., and Hashimoto, K.: Photoinduced Surface Wettability Conversion of ZnO and TiO2 Thin Films. *J. Phys. Chem.*, 2001, 105, 1984-1990.
- 49. Khranovskyy, V., Ekblad, T., Yakimova, R., and Hultman, L.: Surface morphology effects on the light-controlled wettability of ZnO nanostructures. *Applied Surface Science*, 2012, 258 8146-8152.
- 50. Watanabe, T.: Wettability of ceramic surfaces a wide range control of surface wettability from super hydrophilicity to super hydrophobicity, from static wettability to dynamic wettability. *Journal of the ceramic society of Japan*, 2009, 117 12 1285-1292.
- Pant R., Singha S., Bandyopadhyay A., and Khare K.: Investigation of static and dynamic wetting transitions of UV responsive tunable wetting surfaces. *Applied Surface Science*, 2014, 292 777– 781.
- 52. Papadopoulou, E.L., Zorba, V., Pagkozidis, A., Barberoglou, M., Stratakis, E., and Fotakis, C.: Reversible wettability of ZnO nanostructured thin films prepared by pulsed laser deposition. *Thin Solid Films*, 2009, 518 1267–1270.
- 53. Brune, D., Hellborg, R., Whitlow H.J., and Hunderi O.: Surface Characterization. *Wiley-VCH*, 1997, Ch. 1. ISBN: 3-527-28843-0.
- 54. Brune, D., Hellborg, R., Whitlow H.J., and Hunderi O.: Surface Characterization. *Wiley-VCH*, 1997, Ch. 3. ISBN: 3-527-28843-0.
- 55. Hofmann, S., Auger- and X-Ray Photoelectron Spectroscopy in Materials Science. *Springer series in Surface Sciences*, 2013, Ch. 1. ISBN: 978-3-642-27380-3.
- 56. Sundinga, M.F., Hadidia, K., Diplasb, S., Løvvika, O.M., Norbyb, T.E., Gunnæs, A.E.: XPS characterisation of in situ treated lanthanum oxide and hydroxide using tailored charge referencing and peak fitting procedures. *Journal of Electron Spectroscopy and Related Phenomena*, 2011, 184 399–409.
- 57. Jun, J.H., Kim, H.J., and Choi, D.J.: Effect of hydration on the properties of lanthanum oxide and lanthanum aluminate thin films. *Ceramics International*, 2008, 34 957–960.
- 58. Kikuchi, A., Akama, S., Tonotani, J., Ohmi, S., and Iwai, H.: Stability of high-k thin films for wet process. *Journal of the Electrochemical Society*, 2006.
- 59. De Asha, A.M., Critchley, J.T.S., Nix, R.M., Molecular adsorption characteristics of lanthanum oxide surfaces: the interaction of water with oxide overlayers grown on Cu(111). *Surface Science*, 1998, 405 201–214.

- 60. Paulidou, A., and Nix, R.M.: IR studies of the interaction of water with lanthanum oxide surfaces. *Surface Science*, 2000, 470 L104-L108.
- 61. Jun, J.H., and Choi, D.J.: Effects of the wet air on the properties of the lanthanum oxide and lanthanum aluminate thin films. *Thin Solid Films*, 2006, 504 205 208.
- 62. Kung, H.H.: Transition Metal Oxides: Surface Chemistry and Catalysis. *Elsevier, Studies in Surface Science and Catalysis,* 1989, Ch. 3, pp. 35-36. ISBN: 0-444-87394-5.
- 63. Scarel, G.: Scientific and Technological Issues Related to Rare Earth Oxides: An Introduction, *Topics in Applied Physics*, 2006.
- 64. Khranovskyy, V., Ekbald, T., Yakimova, R. and Hultman, L.: Surface morphology effects on the light-controlled wettability of ZnO nanostructures, *Applied Surface Science*, 2012.

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