



Universidade do Minho
Escola de Engenharia

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Wear and degradation analysis of light management nanofabricated layers



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ABSTRACT

Wear and Degradation Analysis of Light Management Nanofabricated Layers

The growing global energy demand and crescent search for fossil fuel independence has prompted the development of sustainable energy sources. Photovoltaic technology stands out as a promising solution to meet this demand, with production costs being constantly mitigated by the development of increasingly thinner solar cells, which aim to reduce the use of raw materials and increase production. However, this thickness reduction leads to incomplete light absorption, triggering the need to implement light management strategies. One of these strategies consist of adding nanoscale texturization on the top surface of solar cells, such as a bio-inspired moth-eye pattern, which confers broadband, omnidirectional and angle-independent anti-reflection properties to the surface. This strategy involves the exposure of the nanostructures to external conditions, as they will be present at the top surface of solar modules. Thus, a tribological characterization of this layer is required to quantify the wear and degradation mechanisms. Hence, this study focuses on performing a tribological characterization of silicon moth-eye nanostructured surfaces, obtained through nanoimprint lithography, in a cleanroom environment. This study was conducted using a ball-on-plate configuration for the friction tests and a spherical 5 mm radius counterface, made of bearing steel. The surfaces were tested for two loads, 0.1 N and 0.5 N, as well as for various test cycles (from 1 to 50 cycles). The results of these experiments show that the friction curves possess a repetitive morphology for both loads, being possible to detect the pre-sliding and sliding phases. The higher load tests present an overall longer pre-sliding phase, in comparison with the lower load tests, due to the more mechanically aggressive interaction, which leads to the creation of an intermediate rough surface and delays the polishing mechanism. It is also evident from the chemical analysis of the samples that the presence of iron on the surfaces promotes adhesive mechanisms, resulting in an overall higher friction coefficient for the 0.5 N tests. This evidence only appears after 15 cycles for the surfaces tested with 0.1 N, a point from which friction values begin to rise. Through optical microscopy it was found that the width of the test track was larger for 0.5 N tests and increased with the number of cycles for both loads. Moreover, an additional study conducted on two types of moth-eye structures with similar optical performances was performed, being concluded that shorter connected pillars, which have a smaller roughness, showcase lower friction than taller individual pillars.

KEYWORDS

FRICTION COEFFICIENT, LIGHT MANAGEMENT STRATEGIES, SOLAR CELLS, TRIBOLOGICAL CHARACTERIZATION, WEAR MECHANISMS

RESUMO

Análise do Desgaste e Degradação de Camadas Nanofabricadas para Gestão de Luz

A crescente procura global por energia e pela independência dos combustíveis fósseis tem impulsionado o desenvolvimento de fontes de energia sustentáveis. A tecnologia fotovoltaica destaca-se como uma solução promissora para atender a essa procura, sendo que os custos de produção têm diminuído com o desenvolvimento de células solares mais finas, levando à redução do uso de matérias-primas. Contudo, a diminuição de espessura leva a uma absorção incompleta de luz, sendo necessário implementar estratégias de gestão de luz. Uma dessas estratégias consiste na adição de nano-estruturas na parte superior das células solares, tais como padrões inspirados nos olhos de traças (*moth-eye*), que conferem propriedades de anti-reflexão em banda larga, omnidirecionais e independentes do ângulo à superfície. Esta estratégia implica que as nano-estruturas estejam expostas a condições externas, já que estarão presentes na superfície superior. Portanto, é necessário efetuar uma caracterização tribológica, de modo a quantificar os mecanismos de desgaste e degradação. Assim, este estudo foca-se na realização de uma caracterização tribomecânica de superfícies de silício com nano-estruturas *moth-eye*, obtidas por litografia por nanoimpressão, em ambiente de sala limpa. Para os testes de atrito, utilizou-se uma configuração de esfera sobre placa e um contra-corpo esférico de aço de rolamento, com 5 mm de raio. As superfícies foram testadas para duas cargas, 0,1 N e 0,5 N, bem como para vários ciclos de teste (de 1 até 50 ciclos). Os resultados mostram que as curvas de atrito possuem uma morfologia repetitiva para ambas as cargas, sendo possível detetar as fases de pré-deslizamento e deslizamento. Os testes com carga maior apresentam uma fase de pré-deslizamento mais longa, devido a uma interação mecânica mais agressiva que forma uma superfície rugosa intermédia e atrasa o fenómeno de polimento. A análise da composição química revelou a presença do mecanismo de adesão, tendo sido detetado ferro nas superfícies, justificando os valores de atrito superiores para os testes de 0,5 N. As superfícies testadas com 0,1 N revelam a presença de ferro apenas após 15 ciclos, ponto a partir do qual os valores de atrito aumentam. Através de microscopia ótica, constatou-se que a largura da pista de teste foi maior para 0,5 N e aumentou com o número de ciclos para ambas as cargas. Foi também realizado um estudo adicional em dois tipos de estruturas *moth-eye* com desempenhos óticos semelhantes, concluindo-se que pilares conectados e mais curtos possuem menor atrito do que pilares individuais mais altos.

PALAVRAS-CHAVE

CARACTERIZAÇÃO TRIBOLÓGICA, CÉLULAS SOLARES, COEFICIENTE DE ATRITO, ESTRATÉGIAS DE GESTÃO DE LUZ, MECANISMOS DE DESGASTE

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LIST OF SYMBOLS

Latin Symbols

Symbol	Unit (SI)	Description
b	m	Position where a connection takes place
C	-	Fatigue ductility coefficient
C_a	-	Attraction parameter
d	m	Diameter of the asperity contact
f	-	Function for viscous friction
F_f	N	Frictional force
F_N	N	Normal force
H	N/mm ²	Hardness
k	-	Velocity factor of oxidation
k_i	N/m	Spring stiffness
K	-	Velocity factor of oxidation
K_w	-	Wear coefficient
L	m	Sliding distance
N	-	Number of bristles
R_a	nm	Arithmetical mean deviation
R_p	nm	Highest peak height
R_q	nm	Root mean square roughness
R_t	nm	Maximum peak-to-peak-valley height
R_v	nm	Lowest valley height
s_i	-	Steady state friction
v	m/s	Velocity
V	m ³	Volume of worn material
x_1	m	Relative position of the bristles
z	m	Average bristle deflection

Greek Symbols

Symbol	Unit (SI)	Description
η	m	Distribution of the asperity heights
γ	-	Particle size constant

ε_1	-	Strain to the failure in one loading cycle
ξ	m	Critical thickness of the reaction layer
ρ	m	Thickness of the reaction layer
θ	rad	Angle between conical asperity and surface
σ_0	N/m	Bristle stiffness
σ_1	N. s/m	Damping coefficient

NOMENCLATURE

AFM	Atomic Force Microscopy
AR	Anti-reflection
ASL	Anti-sticking Layer
CA	Contact Angle
CdTe	Cadmium Telluride
CG	Coarse-grained
CIGS	Copper Indium Gallium Selenide
CIS	Copper Indium Selenium
CVD	Chemical Vapor Deposition
EDS	Energy Dispersive X-ray Spectroscopy
GaAs	Gallium Arsenide
GNS	Gradient Nanostructured
GNG	Gradient Nanograined
HFW	Horizontal Field Width
IPS	Intermediate Polymer Stamp
ME	Moth-Eye
NG	Nanograined
NIL	Nanoimprint Lithography
NT	Nanotubes
OM	Optical Microscope
PP	Percentual Point
PV	Photovoltaic
Sccm	Standard Cubic Centimeters per Minute
SD	Standard Deviation
SEM	Scanning Electron Microscopy
UV-vis	Ultraviolet-Visible

1. INTRODUCTION

The world has been facing an escalating energy crisis, driven by not only industrialization, but also population growth. The aggravation of this crisis has become more prominent as years go by, through an exponential increase of energy consumption worldwide during the last century, in which fossil fuels have the largest share, as shown in Figure 1.1. The alignment of this constant need with the crescent search for fossil fuel independence has triggered the development of alternatives such as renewable energies. These alternatives consist of innovative approaches, based on the harvesting of energy through natural resources, such as water, sunlight, wind and biomass, which aim to not only tackle economic challenges, but also the pressing environmental issues.

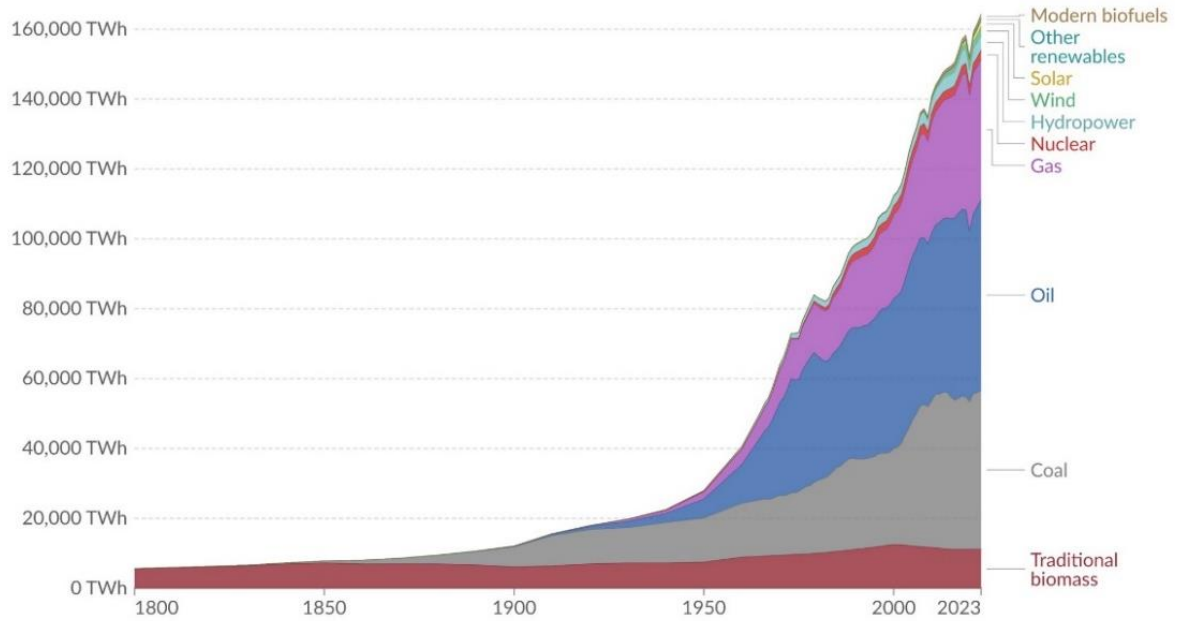


Figure 1.1 - Global primary energy consumption by source [1].

According to the Energy Institute [1], the share of total power generation by renewable energy sources increased from 29% in 2022, to more than 30% in 2023, as shown in Figure 1.2. In this scope, photovoltaic technologies have stood out, having been developed solar cells able to reach conversion efficiencies of 26.41% [2].

In order to convert solar energy into a more sustainable and economically viable option, it is imperative to reduce the use of rare materials in solar cells. This necessity has led to the development of increasingly thin technologies, which suffer from incomplete light absorption, that is, an increased reflectance.

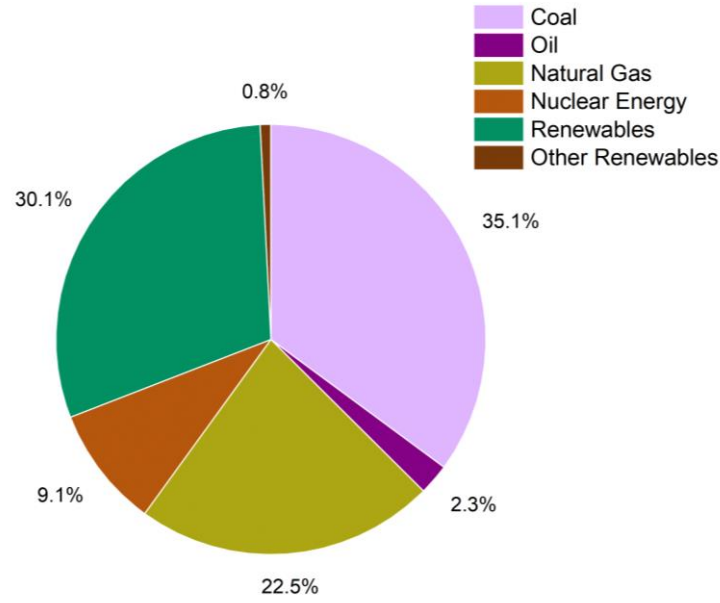


Figure 1.2 - Global electricity generation in 2023. Adapted from [1].

1.1. MOTIVATION

The decrease of the observed reflectance in these developing solar cells requires the comprehension of the optical phenomena which take place. When light passes from one medium to another, a portion of light is reflected at the interface due to the refractive index between two media, a phenomenon known as Fresnel reflection [3-4]. The mitigation of this phenomenon is fundamental to the performance of optoelectronic devices and can be achieved through the implementation of light management strategies [5-6], which are crucial to increase the number of photons absorbed in the active layer [7]. One of these strategies consists of implementing sub-wavelength surface structures, which have a graded refractive index profile. This gradual variation of spatial effective refractive index from air to a substrate significantly reduces the Fresnel reflection [3]. Henceforth, the broadband and omnidirectional anti-reflection (AR) characteristics of graded index nanostructures consist of an effective light management strategy.

Researchers have explored novel AR strategies to implement on the front contact of solar cells, having taken inspiration in nature, namely on certain moth species, which possess subwavelength structured arrays of tapered pillars on their eyes and wings. The addition of this moth-eye pattern as nanoscale texturization has been proven to promote large-angle light refraction, as opposed to a flat surface, enabling a prolonged optical path length [7-13]. In addition to moth-eye, other types of

nanostructures have also been studied, such as nanocones [14-15], nanospheres [16-17], nanowires [18-19] and so forth [20-21]. Although these structures also revealed an attractive AR performance, its fabrication has proven to be costly. Other AR strategies have also been researched previously, such as the implementation of coatings with broadband and omnidirectional characteristics. The thickness of the AR layer is typically designed to a quarter of wavelength, making the phase difference of the incident light half a wavelength. Thus, reflection is suppressed through destructive interference [22]. Chhajed et al [23] presented a study in which it is shown that the reflection losses are reduced to 5.9% by applying a three-layer graded-index AR coating to silicon, which typically reflects around 37% of incident radiation. However, the effectiveness of these coatings is dependent on not only the wavelength, but also on light's incidence angle. This indicates that if the incident light is oblique, the AR effect will also be weakened due to the change of the light's travel path [22]. Furthermore, AR coatings rely on chemical or physical deposition processes, which increase production costs [24-25]. Hence, nanostructures with broadband light trapping capabilities constitute an improved light management approach, capable of significantly suppressing the front-surface reflection [22,26]. The presence of moth-eye nanostructures at the front contact of solar cells implies its exposure to external conditions, such as environmental stresses, but also to mechanical loads, which can decrease its performance. Therefore, incorporating tribological testing into the evaluation of these architectures is a valuable approach to ensure that both optical and mechanical requirements are achieved. Tribological tests can assume various configurations, such as pin-on-disk, ball-on-disk, ball-on-plate and pin-on-plate, as seen in Figure 1.3.

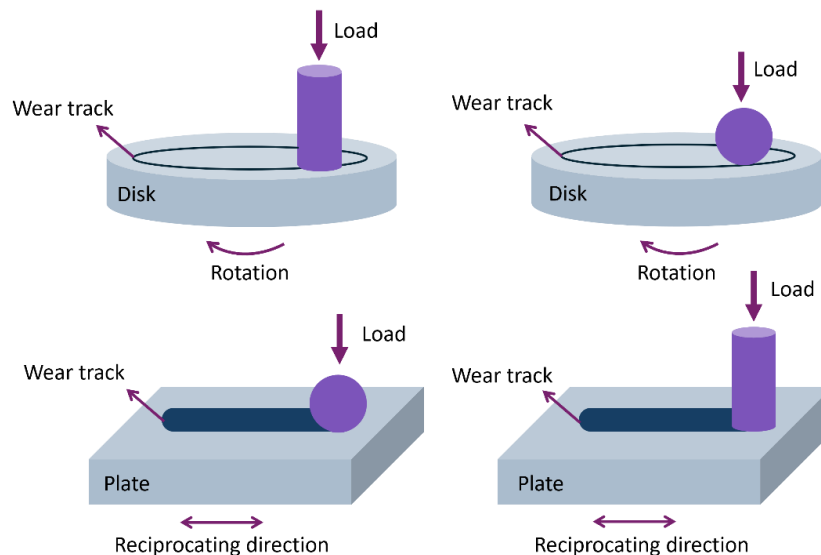


Figure 1.3 - Illustration of tribological testing configurations: pin-on-disk (on the top left), ball-on-disk (on the top right), ball-on-plate (on the bottom left) and pin-on-plate (on the bottom right).

The pin-on-disk configuration consists of a fixed pin and a rotating disk, resulting in a circular test path, with the frictional and tangential force being measured by the load cells and sensors. In this configuration, the loading force is applied on the pin, while the disk is driven by a servo motor with a certain rotational speed. The ball-on-disk configuration is similar to the previous one, with the main difference being the use of a ball instead of a pin, as the name suggests. The ball-on-plate and pin-on-plate configurations are also alike, both being designed for reciprocating sliding motion tests. Thus, the ball or pin performs an alternating linear movement back and forth over the plate.

As seen in literature, bio-inspired texturizations have also proven to be tribologically beneficial, as they exhibit a decrease in adhesion and friction forces due to the reduction of the real area of contact, as well as to their hydrophobicity [27-30]. This last feature occurs due to the fact that the nano-patterns seem to act as composite surfaces, with air being trapped between the pillars, leading to the increase of the water contact angle [29]. The tribological characterization of nanostructures has been reported in previous works. Afshar-Mohajer et al [31] has reported the effects of the employment of micro/nano-hierarchical structures, with the aim of gaining new insights regarding their mechanical behavior. This study mainly regarded the coupling between the mechanics and deformations of different lengths scales, as well as the frictional response of the structures before and after the start of sliding. This study focused on squared cross-section micro-pillars with “nano-hair” at its top base, which were obtained through a two-photon lithography process, as explained in the study of Afshar-Mohajer et al [31]. The tribological tests showed that the no-hair structures presented the highest friction, whereas the short-hair structures had the lowest friction values. The friction values of the long-hair structures were in between both previous structures. The deformation resistance of the structures has revealed that the bending was more severe for the no-hair and long-hair structures, in comparison with the short-hair structures, which only presented minor bending. These differences arise from the fact that the actual contact area at the interface depends on the nano-hair structure. The short-hair structure provides a smaller area of contact, compared to that of the no-hair structures, due to the spacing between the short hairs. The long-hair structures can undergo buckling, resulting in an increased area of contact between the buckled hairs and the counterface, in comparison with the short-hair structure.

From the investigation performed by Afshar-Mohajer et al [31], it is possible to conclude that for applications where a low friction is desired, short-hair nanostructures are desirable, as they presented not only the lowest bending for the highest applied load, but also the lowest friction values, in comparison with no-hair and long-haired surfaces.

Another study which highlights the tribological advantages of the implementation of nanostructures was conducted by Singh et al [29]. In this study, a tribological characterization of bio-inspired lotus-leaf silicon surfaces is conducted. The tested surfaces underwent textural and chemical modifications, being posteriorly submitted to a normal load of 0.3 N through a ball-on-disk test configuration. This investigation has revealed that the implementation of these nanostructures is accompanied by low friction properties, as well as high wear durability, due to the reduction of the surface energy and the real contact area.

The investigation proposed in this dissertation aims to evaluate the tribological properties of silicon moth-eye nanostructures, obtained through nanoimprint lithography. The frictional characterization is performed under specific conditions in laboratorial context and is complemented by advanced characterization techniques, such as scanning electron microscopy (SEM) and ultraviolet-visible (UV-vis) spectroscopy.

1.2. STATE OF THE ART

During the last decade, the tribological characterization of nanostructures has gained particular attention. The continuous development of strategies to improve wear and confer particular frictional properties to materials and surfaces has prompted tribological investigations in various areas, such as physics, chemistry, surface engineering, nanotechnology, biomedical engineering, and so forth [32].

Considering the aim of this dissertation, a brief review of research performed in the scope of tribology is provided, with particular focus on the addition of nanoscale texturization and its influence on tribological properties. This review of academic papers was conducted through the use of search platforms such as *Scopus* and *Google Scholar*, utilizing the keywords “tribology” and “nanostructures” to search within article titles, abstracts and keywords. The results from this research are exposed in Table 1.1, which contains the main conclusions from each article, as well as the respective tribological testing parameters. The selected articles were published from 2008 to 2022 and are displayed in alphabetical order of each material’s name. Additionally, it is presented the type of nanostructure and the respective materials.

In an attempt to offer a broad overview of this research, a statistical analysis is performed. This investigation focused on the identification of trends regarding the tribological testing of nanostructured surfaces. Thus, several parameters were chosen for analysis, such as the type of test configuration and the shape of the nanostructures, as well as the material employed. This statistical analysis is presented through 2D pie charts to better illustrate and identify the trendy behaviors in tribological testing.

Table 1.1 - State of the art regarding tribological testing of nanostructures.

Material	Nanostructure	Frictional testing	Main conclusions	Year	Ref
Alumina	Nanograins Thickness: 117 - 241 μm	Equipment: Tribometer Configuration: Pin-on-disk Counterface: 0.5 mm radius silicon nitride pin Normal load: 5, 10 and 15N	Enhanced friction and wear resistance with nanograins - Lower friction coefficient (approximately 0.9 times lower) - Lower wear (up to 1.84 times lower)	2013	[33]
Alumina-titania	Nanograins (cauliflower-like agglomerates) Size: 10 - 500 nm	Equipment: Tribometer Configuration: Ball-on-disk Counterface: 3 mm radius 100Cr6 steel ball Normal load: 5 N	Enhanced friction resistance with nanograins - Lower friction coefficient (up to 0.8 times lower) - Higher wear resistance (up to 3 times higher)	2014	[34]
Carbon	Nanocrystals Size: 1-2 nm Spacing: 0.336 nm	Equipment: Tribometer Configuration: Pin-on-disk Counterface: 0.5 mm radius silicon nitride pin Normal load: 400 mN	Enhanced friction resistance with nanocrystals - Lower friction coefficient ($\mu=0.07$) and wear ($0.04 \mu\text{m}^3$) - Increased hardness	2012	[35]
Carbon / polyimide	Multiwalled nanotubes (NT)	Equipment: Tribometer Configuration: Ball-on-disk Counterface: 1.5 mm radius bearing steel (GCr15) ball Normal load: 10 N	Enhanced friction and wear resistance with NT - Higher weight percentage of NT improves tribological properties - Lower friction coefficient (2.3 to 10.8 times lower than without NT) - Improved wear resistance (smaller wear scar) - Lower wear rate (up to 18 times lower)	2020	[36]

Copper-silver alloy	Nanograins (Nanograined (NG), coarse-grained (CG) and gradient nanograined (GNG) structures) Average grain size: 20 μm	Equipment: Tribometer Configuration: Ball-on-plate Counterface: 5 mm radius WC-Co ball Normal loads: 30 to 90 N	Enhanced friction and wear resistance for GNG - Lower friction coefficient for 90 N (1.88 times lower than NG and CG) - Lower wear volume (4.8 and 10.4 times less than NG and CG, respectively) - Lower wear rate (4.7 and 10.3 times less than NG and CG, respectively) - Unaltered surface roughness after tests	2016	[37]
Silicon	Micro and nanogrooves Depth: 80 nm Width: 2.6 μm	Equipment: Tribometer Configuration: Ball-on-plate Counterface: 3 mm radius Stainless steel ball Normal load: 60 mN	- Micro and nanofriction decreased as groove area density increased - Improved wear resistance (nearly indistinguishable scratch)	2010	[38]
Silicon	Nanogroove array Width: 50 nm Periodicity: 125 nm	Equipment: Atomic force microscope (AFM) Cantilever: Flat squared (2 μm x 2 μm) tip	Enhanced friction resistance with nanopattern - Friction coefficient of patterned area is approximately half - Linear dependence of the lateral force on the applied load - Highest load provokes non-negligible wear effect	2008	[39]
Silicon	Random nanotextures	Equipment: Tribometer Configuration: Ball-on-disk Counterface: 0.8 mm radius 100Cr6 steel ball Normal load: 250 mN	Enhanced friction and wear resistance with nanotextures - Lower friction coefficient (up to 2.5 times lower than flat samples) - High dependence of friction coefficient on roughness parameters - Improved wear resistance (no wear scars detected)	2011	[40]

Silicon	Low-spatial frequency laser induced periodic nanostructures Height: 230 nm Period: 730 nm	Equipment: Nanotribometer Configuration: Ball-on-plate Counterface: 1.5 mm radius polytetrafluoroethylene balls Normal load: 5, 10 and 25 mN	Enhanced friction resistance with nanostructures - Lower friction coefficient (which decreased with increasing load) - Friction coefficient decreased with testing time	2019	[41]
Steel	Gradient nanostructured surfaces (GNS) and coarse-grained (CG) surfaces Thickness: 340 -530 nm	Equipment: Tribometer Configuration: Ball-on-plate Counterface: 5 mm radius WC-Co ball Normal load: 30 to 90 N	Enhanced friction and wear resistance for GNS - Lower friction coefficient for 50 N (1.2 times lower) - Decrease of friction with increasing load - Lower wear volume for 30 N (4 times lower than CG) - Lower wear volume for 90 N (3.4 times lower than CG) - Smooth worn surface - Accommodation of large plastic strain , due to finer grains	2018	[42]
TiMe ₁ Me ₂ -CN/TiAlSi-N	Nanostructured superlattice coatings Thickness: 6.5, 5.2, 5.5 μm	Equipment: Tribometer Configuration: Ball-on-disk Counterface: 3 mm radius 100Cr6 steel ball Normal load: 3 and 5 N	Enhanced friction and wear resistance with nanostructured coating - Lower friction coefficient (up to four times lower) - High wear resistance (up to 28 times more resistant)	2022	[43]
Titanium dioxide	Nanotubes Diameters: 30, 50, 70 and 100 nm	Equipment: Nano-indenter Counterface: 100 nm radius three-sided pyramidal tip Normal load: 500 μN	Enhanced friction resistance with nanotubes - Lower friction coefficient (for smaller nanotubes) - Higher deformation resistance for smaller-diameter nanotubes	2018	[44]

As seen in Figure 1.4, 33.3% of articles utilized a ball-on-plate configuration and 33.3% applied a ball-on-disk configuration, whereas only 16.7% employed a pin-on-disk configuration. The remaining percentage corresponding to other types of tests are associated with the use of nano-indenters and atomic force microscopes (AFM) to perform tribological tests. These lastly mentioned techniques were proven to be employed much less due to being related to the evaluation of friction and wear at a nanoscale, an area which is still not explored as much as at the micro and macroscale. As the benefits of adding nanoscale texturization to surfaces are also detected at the micro and macroscale, then the utilization of these expensive techniques is often not justified, thus the frequent use of conventional tribological testing equipment and configurations.

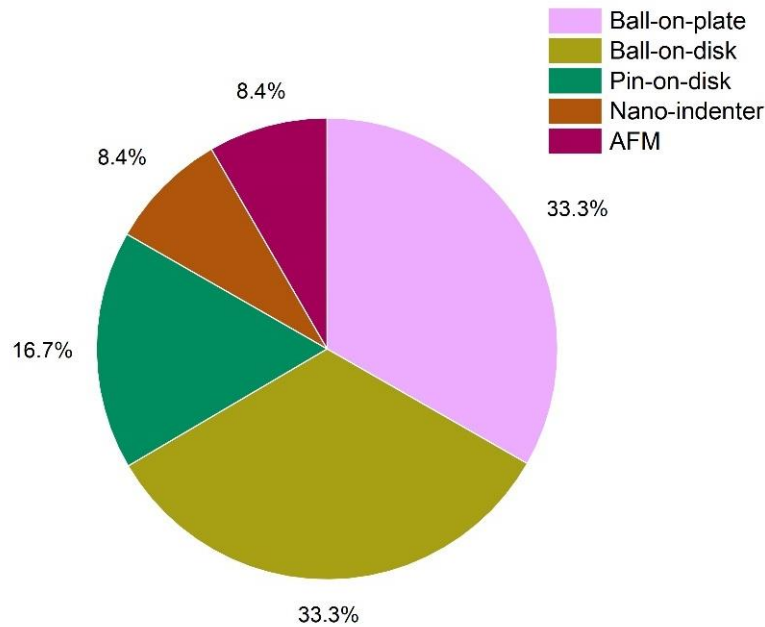


Figure 1.4 – Distribution of the type of test configuration found in literature.

Further analysis revealed a trend in the type of nanostructure which was employed. As seen in Figure 1.5, nanograins were utilized in 33.3% of studies, including agglomerates and individual nanograins. This can be justified by the simplicity of its fabrication processes, in comparison with other more intricate structures. As exposed in the main conclusions of Table 1.1, the tribological enhancements provided by these structures are as significant as the ones obtained with more complex structures, justifying their frequent use. Other similar nanostructures were also employed, such as nanogrooves and nanocrystals. All academic papers resulting from this investigation reported that the implementation of these structures resulted in a significant reduction of friction and wear, as described in Table 1.1.

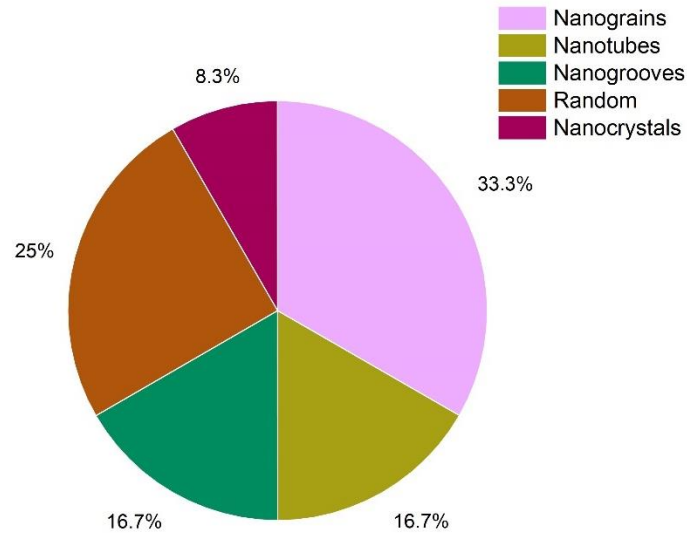


Figure 1.5 – Distribution of the type of tested nanostructures found in literature.

It was also noted that 33.3% of articles reported the tribological evaluation of nanostructures in silicon, as visually observed in Figure 1.6. The frequent use of this material can be justified by its common utilization in micro and nanoelectromechanical systems [45-48], in which a reduction of friction is often desired to reduce energy losses. Additionally, the fabrication of nanostructures has been proven to be a simpler process in this material, hence its frequent use.

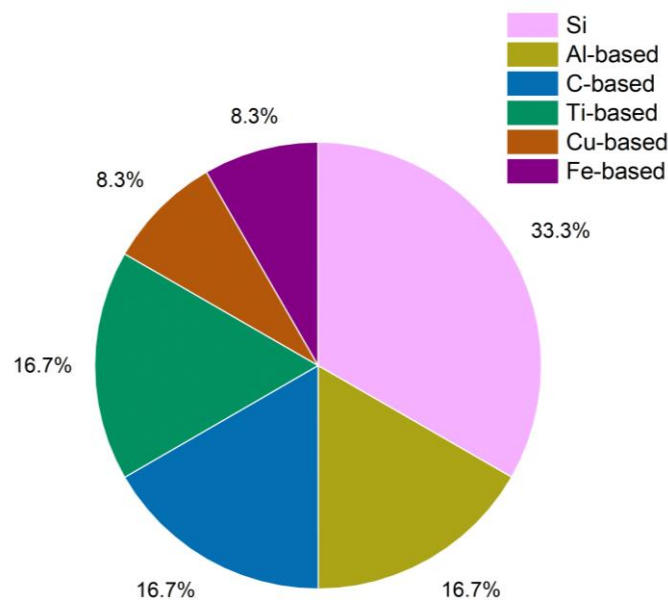


Figure 1.6 – Distribution of the tested material found in the literature.

1.3. OBJECTIVES

The purpose of the research conducted in the scope of this work is to perform a comprehensive tribological characterization of nanofabricated light management structures, which will be implemented on the top surface of solar modules. During its operational period, photovoltaic systems will be exposed to performance-deteriorating conditions, leading to the need to quantify degradational mechanisms. The wear and degradation of these systems are fundamental factors to address in order to increase its operational lifetime, as well as ensure a high standard performance. The implementation of tribological characterization provides valuable information regarding the system's behavior, as it enables the detection of critical conditions, as well as allows the evaluation of the influence held by various parameters. During this study, friction testing is employed on silicon moth-eye nanostructures, for various test cycles, with the aim of analyzing its frictional behavior when exposed to successive degradation.

The accomplishment of the main objective of this work requires the completion of secondary objectives, which are listed henceforth:

- To perform a literature review regarding the tribological characterization of nanostructures.
- To research frictional concepts and some of the existing dynamic friction models.
- To investigate various existing wear mechanisms.
- To study the types of optical and morphological characterization techniques which could be employed to nanostructures.
- To perform the nanofabrication of the moth-eye structures and the respective optical and morphological characterization.
- To conduct tribological tests for various loads and cycles.
- To analyze the resulting data.

Overall, this study includes a theoretical phase, composed of literature review regarding the tribological testing and morphological characterization of nanostructures, as well as of relevant friction and wear concepts. This work also involves an experimental phase, in which the nanofabrication and characterization of the structures is performed, as well as their tribological testing.

1.4. STRUCTURE OF DISSERTATION

This dissertation is divided into six chapters, which will be explained henceforth. In Chapter One, the project contextualization is presented, providing an overview of the objectives, as well as a brief literature review regarding AR strategies and tribological testing of nanostructured surfaces.

Chapter Two focuses on the light management strategies, namely on the implementation of nanostructures on the top contact of solar cells. Thus, concepts regarding the functioning of solar cells are introduced, being also provided a description of the fabrication process of moth-eye nanostructures. Moreover, a description of the characterization techniques employed to these structures is also provided.

Chapter Three introduces concepts related to friction, namely regarding two phases which occur during the contact between two bodies, the pre-sliding behavior and the sliding behavior. Within the sliding phase, two relevant properties are described, being those the Stribeck curve and the friction lag. Additionally, the stick-slip phenomenon is analyzed, and several theoretical friction models are briefly described.

In Chapter Four, an overview of the four basic wear mechanisms is provided, specifically regarding adhesion, abrasion, tribochemical wear and surface fatigue.

Chapter Five contains a description of the experimental characterization of the moth-eye nanostructures, presenting a description of the performed tests and its parameters, as well as a characterization of the tested samples, before and after the experimental testing. A discussion regarding the results is also provided. Moreover, an additional investigation regarding the tribomechanical performance of two distinct moth-eye patterns is provided.

Lastly, Chapter Six summarizes the conclusions drawn throughout the performed study and presents the contributions resulting from this study.

2. NANOSCALE TEXTURIZATION IN SOLAR CELLS

As the global shift to renewable energy sources occurs, various photovoltaic technologies have claimed their position in the market. Nowadays, thin-film solar cells can challenge conventional first-generation silicon technologies, not only in terms of costs, but also in terms of sustainability. The transition from thin to ultrathin absorbers in solar cells arises from the need to reduce the fabrication costs, as well as the consumption of scarce elements which constitute the absorber layers of solar cells. Some of the main second generation thin-film technologies are copper indium gallium selenide (CIGS), cadmium telluride (CdTe), gallium arsenide (GaAs) and copper indium selenium (CIS), some of which have already reached the market.

In spite of the previously mentioned advantages, the decrease in thickness also leads to incomplete light absorption, hence the need to develop light management strategies. The addition of nanoscale texturization in solar cells has proven to be a beneficial approach to this challenge [7]. This approach, when implemented on the top surface, can lead to a decrease of light reflectance, augmenting the number of photons which reach the absorber layer. Although nanoscale texturization has been developed with the intent of being implemented on ultrathin solar cells, it can also be applicable to any type of technology, including the conventional silicon solar cells.

2.1. SOLAR CELLS

Solar photovoltaic technology (PV) converts photons into electrical energy. Photovoltaic modules consist of many individual interconnected solar cells, which are made of different semiconductor materials [49,50]. When exposed to light, semiconductors absorb its energy and transfer it to the electrons in the material, allowing them to flow through it as an electric current, which is then extracted through conductive metal contacts [51]. A relevant feature of semiconductors is the bandgap, which corresponds to the minimum amount of energy required to excite an electron from the lower-level energy band, into a high-level energy band, where it can participate in electrical conduction [52]. The lower energy corresponds to the valence band, and the higher energy corresponds to the conduction band, as represented by the illustration in Figure 2.1. The excitation of an electron to the conduction band leaves an empty space with positive charge on the valence band, designated as a hole. These charge carriers, electrons and holes, are then collected on the metallic contacts of the solar cells, originating electric current.

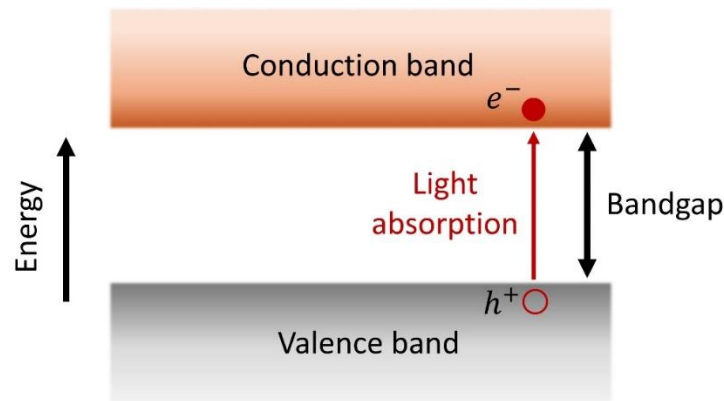


Figure 2.1 – Schematic of the energy bandgap.

There can be different types of solar cells, considering the level of maturity of the technology: first, second and third generation. First generation solar cells represent the oldest commercially available PV technology and include materials based on thick crystalline layers composed of silicon. Depending on the manufacturing process, this technology can be of two types, monocrystalline and polycrystalline. Monocrystalline solar panels are made of pure high-quality silicon, and offer high efficiency rates, having a long lifespan. On the other hand, polycrystalline solar panels have a cheaper manufacturing process, as the silicon is melted and poured into molds, having a lower efficiency. Second generation solar cells correspond to thin-film technology and are characterized by the use of alternative semiconductor materials, such as copper indium gallium selenide (CIGS) and cadmium telluride (CdTe). These modern technologies were developed as a lower-cost alternative to the previously shown technologies and offer improved mechanical properties. However, thin-film technologies suffer from a lower efficiency, mainly due to the possession of a thinner absorber layer. Hence, continuous developments are being made, in order to develop efficiency-enhancement strategies. Lastly, third generation solar cells represent a wide range of approaches, despite having poor market integration. These technologies focus on advanced materials, whether they are inexpensive with a lower efficiency, or expensive and with high efficiency, and include tandem solar cells, which are characterized by the stacking of semiconductors with different bandgap energies in the same cell [53], and also perovskite [54], organic [55], quantum dots [56], and dye-sensitized solar cells [57].

2.2. LIGHT MANAGEMENT

As previously mentioned, light management strategies are of utmost importance in solar cells, as they possess the ability to decrease the reflection of light at the top surface. In addition, these schemes are particularly valuable for ultrathin solar cells due to the incomplete light absorption, which stems from

the reduction of the absorber layer, which causes an efficiency gap in comparison to standard thin-film solar cells. Moreover, solar cells are subject to optical losses that result from shading by metallic grids and parasitic absorption in other layers which constitute the solar cells [7]. These optical losses can also be tackled with the implementation of light management schemes.

There are different approaches, which can be divided in two categories: front light management and rear light management. In summary, front light management consists of the application of an AR coating or nanoscale architectures at the top surface, to achieve broadband, omnidirectional and angle-independent AR [12]. Rear light management is implemented to increase the optical path length in the absorber by enhancing light scattering and reflectivity at the back contact interface [7]. Contrary to front light management, rear light management strategies can differ according to the type of solar cell. In this work, only front light management strategies will be considered, which can be implemented regardless of the type of solar cells. These strategies focus on minimizing the reflection at the top surface, with the most common AR strategy being the use of an AR coating. Although this strategy allows a conversion efficiency increase of 1 percentual point (PP) [7], it also has some downsides, such as being only effective in a narrow-wavelength value range, and performing optimally for certain light incidence angles [25].

These disadvantages led to the testing of nanoscale texturization, which enables an improved and broadband AR effect, due to the multiple interactions with the rough surface before being reflected [58,59]. Various patterns have been researched, namely an architecture referred to as moth-eye (ME), which consists of a bio-inspired array of closely tapered nanopillars, whose AR results from a gradually changing refractive index as light travels from air to the bottom of the structure [60], as mentioned in Chapter 1.1. These structures are considered to be a homogeneous medium, in accordance with the effective medium theory, which states that if the period of the features on a textured surface is much smaller than the incident wavelength value, the wavefront interacts with the structure as a homogeneous surface, meaning the nanopillars/air interface is perceived as one material [61]. Since the ME structure consists of tapered nanopillars, with more material being present towards the bottom, the effective refractive index increases as light travels further down the structure, reducing reflection drastically and allowing more light to enter the solar cell [62].

2.3. NANOIMPRINT LITHOGRAPHY

Nanoimprint lithography (NIL) is a contact lithography process in which a master stamp is pressed into a resist layer, conferring the stamp's reverse pattern by physical deformation, and with nanoscale resolution [63]. This method requires certain elements, such as a master stamp, containing the moth-

eye pattern, an anti-sticking layer (ASL), an intermediate polymer stamp (IPS), a photoresist, and a silicon substrate, to which the pattern will be transferred [64]. The implementation of an anti-sticking layer is justified due to the criticality of the demolding step, to ensure the pattern's quality. Since the nanoscale features increase adhesion forces between the stamp and the resist layer, it is imperative to confer anti-adhesive properties to this interface [65]. The implemented ASL in this study consists of a teflon-like C_4F_8 polymer. The IPS is implemented to avoid direct contact between the master stamp and the samples, enhancing its lifetime. Additionally, the IPS is associated to a lower cost, higher mechanical flexibility, and high resolution [64].

The fabrication of the master stamp containing the moth-eye pattern involves the use of an anisotropic silicon substrate, to which is applied a gold nanoparticles mask for a posterior etching process, as illustrated by Figure 2.2. The procedure starts with the cleansing of the silicon substrate on a microwave plasma asher (PVA TePla Gigabatch 360M system), with 500 W 2.45 GHz plasma, with 600 standard cubic centimeters per minute (sccm) O_2 and 50 sccm argon (Ar) flow, followed by the deposition of gold (step 1 in Figure 2.2) by sputtering [66] [67] on a coating system (100 W DC Kenosistec UHV PVD system), at room temperature. Then, a solid-state thermal dewetting [68-70] of the deposited gold film is performed (step 2) in an oven (Termolab Chamber Furnace Type MLM), at 800 °C for 2 h, creating the desired mask. Lastly, a reactive ion etching is performed (step 3) for 40 and 60 s, with a simultaneous C_4F_8 and SF_6 plasma. The remaining gold nanoparticles are removed utilizing a mix of hydrochloric acid with nitric acid ($HCl:HNO_3$), on a 3:1 ratio.

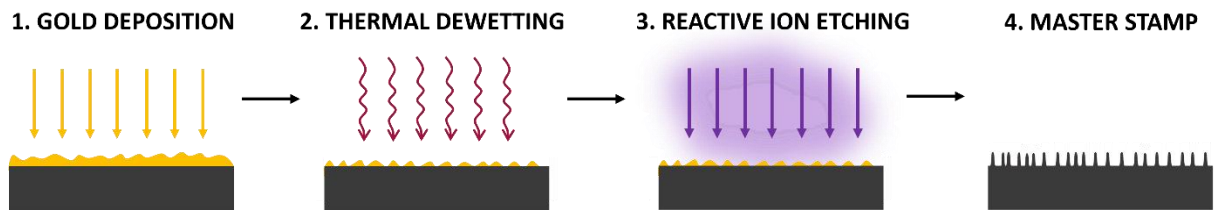


Figure 2.2 - Illustration of the master stamp fabrication process.

The pattern transferring process is described in Table 2.1 and Figure 2.3 and starts with the cleansing of the master stamp, which is achieved on the microwave plasma asher (PVA TePla Gigabatch 360M system), with 500 W 2.45 GHz plasma, with 600 sccm O_2 and 50 sccm Ar flow, followed by the deposition of a 5 nm SiO_x layer on the master stamp by plasma-enhanced chemical vapour deposition (CVD), using the SPTS MPX CVD system at 200 °C, in a 30 W 13.56 MHz plasma with 1420 sccm N_2O , 10 sccm SiH_4 , and 392 sccm N_2 . This thin layer aids the posterior demolding step, due to its anti-adhesive properties, and is considered part of the ASL. Nevertheless, the ASL is completed with a final

layer of 8 nm of the Teflon-like C_4F_8 polymer (step 1 in Figure 2.3), which is deposited on the stamp through an adapted reactive ion etching equipment (SPTS Pegasus), with a 2000 W 13.56 MHz plasma, 0 W platen power, 200 sccm C_4F_8 flow at 20 °C, and 25 mTorr.

Table 2.1 - Overview of the moth-eye nanofabrication process.

Step	Process	Equipment
1	Cleaning the silicon substrate	PVA TePla Gigabatch
2	Gold deposition by sputtering	Kenosistec UHV PVD system
3	Thermal dewetting	Termolab Chamber Furnace Type MLM oven
4	Reactive ion etching	SPTS Pegasus
5	Cleaning the master stamp	PVA TePla Gigabatch
6	Deposition of anti-sticking layer	SPTS MPX CVD system + SPTS Pegasus
7	Transferring of pattern to IPS	Obducat Eitre 8
8	Cleaning silicon substrate	Ultrasound bath
9	Dehydration of silicon substrate	Vapour Prime YES-310TA oven
10	Spin-coating the substrate with resist	Suss Microtec Gamma Photoresist cluster system
11	Patterning of the resist layer	Obducat Eitre 8
12	Removal of residual resist	SPTS Pegasus
13	Reactive ion etching	SPTS Pegasus
14	Removal of remaining resist	PVA TePla Gigabatch

After the deposition of the ASL, the master stamp's pattern is transferred to the IPS with the aid of a simultaneous thermal and UV (STU) NIL system on the Obducat Eitre 8 equipment (step 2), at a constant pressure of 15 bar for 60 s, at 22 °C, followed by 240 s of UV exposure to cure the IPS. Then, the patterned IPS was coated with an 8 nm ASL (step 3), and the silicon substrate was cleansed with an ultrasound bath for 15 min on acetone, and for 10 min on isopropyl alcohol and 5 min on de-ionized water. Next, the silicon substrate's surface was dehydrated in a vacuum, in an oven (Vapour Prime YES-310TA), at 150 °C, for 300 s. This was performed as a surface treatment to promote adhesion of the posterior resist layer. This step was followed by the spin-coat of a resist layer on the substrate, which consisted of 250 nm mr-Nil diluted in ma-T 1045 on a 1:2 weight ratio. This was performed in a Suss Microtec Gamma Photoresist Cluster system, at 2000 rpm for 30 s, and baked at 90 °C for 60 s.

The next step is the patterning of the resist layer through NIL (step 5), which consists of heating up the substrate and the IPS at 65 °C for 10 s, applying constant pressure of 15 bar for 100 s, and exposing to UV for 180 s, to cure the resist. This process is performed on the Obducat Eitre 8 equipment. After this, it is necessary to remove the residual resist (step 6), having been chosen to utilize an O₂ plasma, for 12 s, at 20 °C on a 85 mTorr 13.56 MHz plasma, with a coil power of 25000 W and 180 °C platen power, and an O₂ flow of 115 sccm on the SPTS Pegasus equipment. Lastly, the substrate was submitted to a Si deep reactive ion etching (step 7) on the SPTS Pegasus equipment, at 20 °C, using a 13.56 MHz plasma, at a pressure of 15 mTorr with 2000 W coil power, 45 W platen power, 160 sccm C₄F₈ and 120 sccm SF₆ flow. This process was followed by the removal of the remaining resist performed by an O₂ plasma ashing process, with 500 W 2.45 GHz plasma, 600 sccm O₂ and 50 sccm A_r flow, on the PVA TePla Gigabatch 360M system, for 8 min.

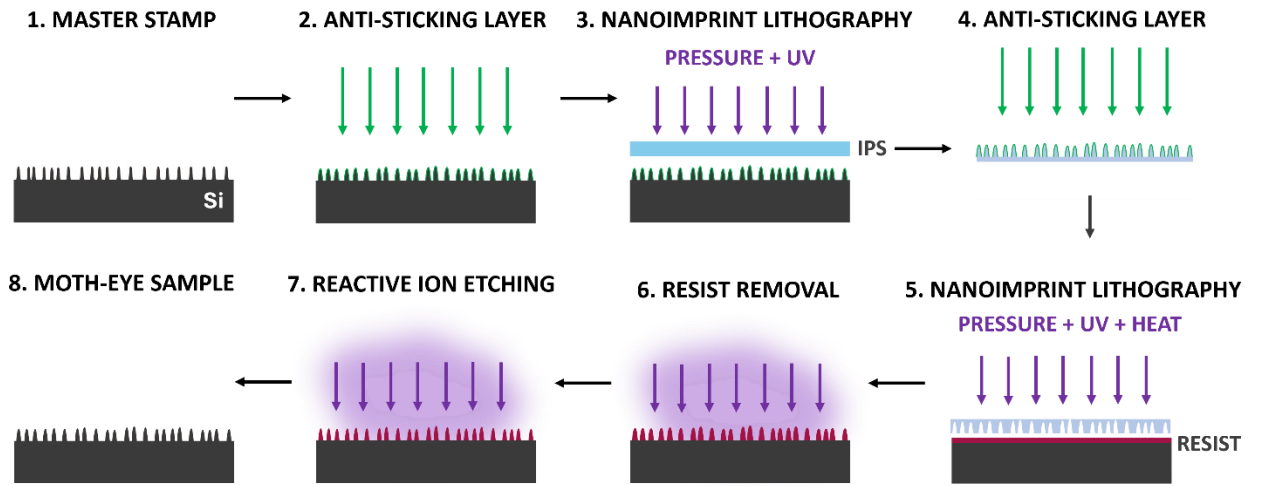


Figure 2.3 - Schematic of the fabrication process of the moth-eye nanostructures.

2.4. CHARACTERIZATION TECHNIQUES

Prior to conducting a tribological characterization, the moth-eye nanostructures must undergo a morphological and optical characterization, in order to compare the results. Hence, it is necessary to define a systematic characterization protocol which allows an accurate analysis of the obtained data.

The optical characterization is performed after the nanofabrication of the moth-eye structures, to ensure that the optical requirements are achieved. These optical measurements are performed through UV spectroscopy, which allows the study of the interaction between matter and electromagnetic radiation. During this interaction, several processes can occur, such as absorbance, reflectance, scattering, photochemical reactions, and also fluorescence [71]. Since light is a form of energy, its absorbance provokes the energy increase of matter's molecules, which can origin transitions between different

electronic energy levels, depending on the specific wavelength of the incident light [72]. As seen in Figure 2.4, the UV-vis spectrophotometer contains several components such as a light source, with the ability to generate a broadband of electromagnetic radiation across the UV-visible spectrum, a dispersion device which separates broadband radiation into wavelengths, detectors to measure the intensity of the reflected radiation, and a sample area [73]. In this investigation, the optical performance will be obtained through the reflectance measurements, performed for a wavelength range of 300 nm to 1100 nm, and a slit width of 2 nm. All measurements are in relation to a baseline and were performed on a PerkinElmer Lambda 1050+ equipment. The resulting data from this technique requires correction, which is achieved through the multiplication between a correction factor and the relative total reflectance obtained from the measurements. The correction factor consists of the division between the literature values of the reflectance for silicon, as this is the material which constitutes the samples, and the experimental data.

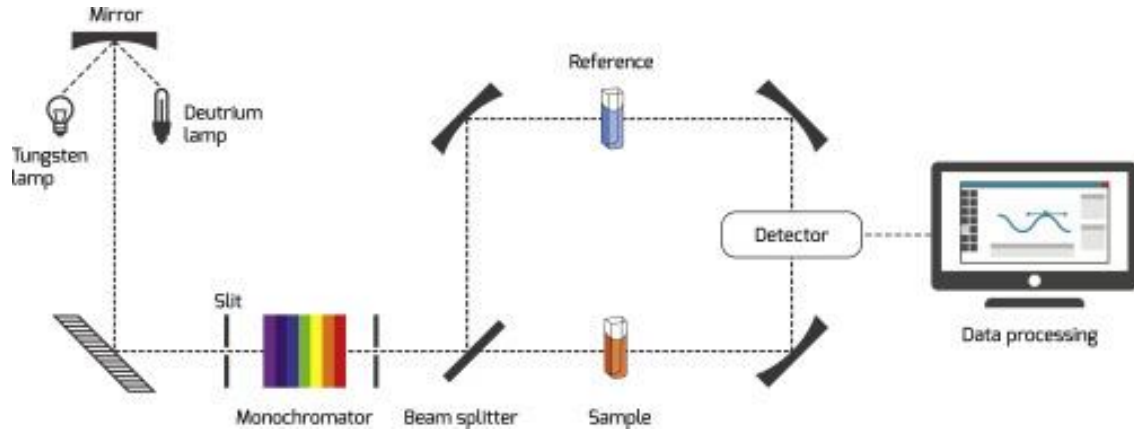


Figure 2.4 - Schematic of the UV-vis spectrophotometer [73].

The morphology of the nanostructures is analyzed through a scanning electron microscope (SEM NovaNano 650). This characterization technique allows the study of a sample's external morphology, and chemical composition, as well as its crystalline structure and orientation of the materials of which it is composed. This is possible through a focused beam of high-energy electrons which generate a variety of signals at the surface of solid specimens as a result of the electron-sample interactions [74-75]. As illustrated in Figure 2.5 (A), the SEM is composed of an electron source, electron lenses, detectors, sample stage, display, and data output devices [76]. The infrastructure requirements of this equipment are a power supply, a vibration-free floor, a vacuum system, and a room free of ambient magnetic and electric fields. When introducing the samples in the equipment, they must be attached to a support wafer with copper tape, as shown in Figure 2.5 (B), and later placed on the sample stage of the equipment. Through this technique, the moth-eye nanostructures can be analyzed before and after tribological testing.

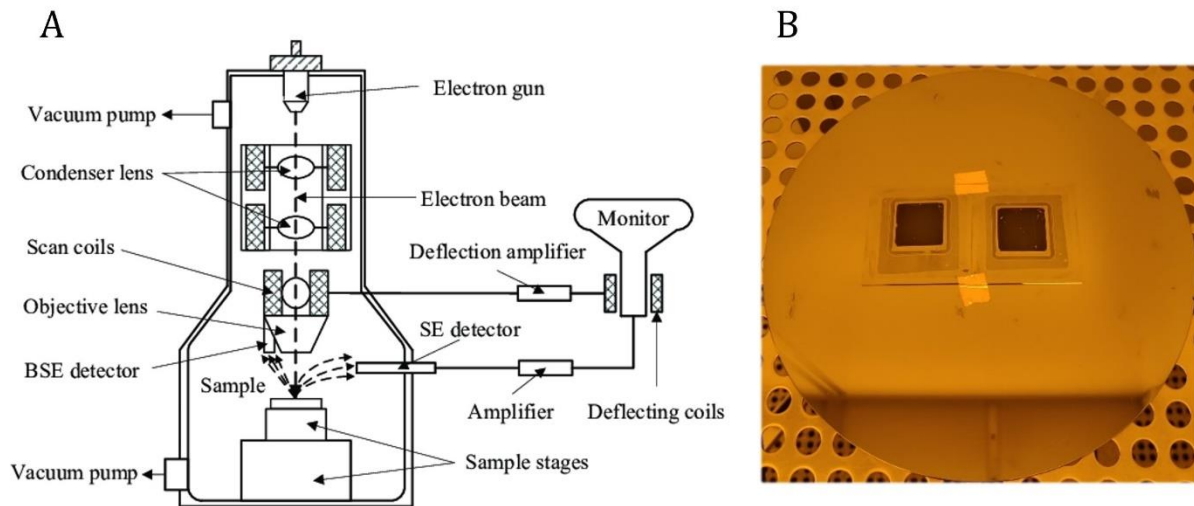


Figure 2.5 - (A) Illustration of the SEM constituents [76] and (B) Samples attached to a wafer prior to SEM analysis.

The SEM allows for an additional method, denominated energy dispersive X-ray spectroscopy (EDS), which enables the analysis of the chemical composition of the samples. EDS is a technique based on the measurement of the energy and intensity of the X-rays which are emitted by a sample when exposed to the electron beam of the SEM. The energy of the emitted X-rays is unique for each element, thus enabling the assessment of the sample's chemical composition [77].

In addition to SEM and SEM-EDS, the tested sample surface was also analyzed through optical microscopy (OM) using a Leica DM8000 M microscope for inspection of the tested area, enabling the measurement of the track widths.

Another technique which can be utilized to analyze the morphology of samples is the atomic force microscopy (AFM) (Bruker AFM Dimension Icon Atomic Force Scanning Probe Microscope). This technique is a high-resolution form of scanning probe microscopy that is frequently used to visualize small-scale structures, at a scale ranging from below a nanometer, up to one micrometer [78-79]. Additionally, AFM can also measure electromechanical strain, chemical structure, adhesion, and electrical conductivity. This method scans a 3D profile of the surface by measuring any type of force detected by a sharp tip, due to its proximity to the surface of the sample [80-81], provoking a deflection of an elastic cantilever, which is connected to the sharp tip. Through the measurement of this deflection, it is possible to estimate the interactive forces between the tip and the surface of the sample, such as the interatomic and electromagnetic forces. A simplified illustration of the AFM constituents is presented in Figure 2.6.

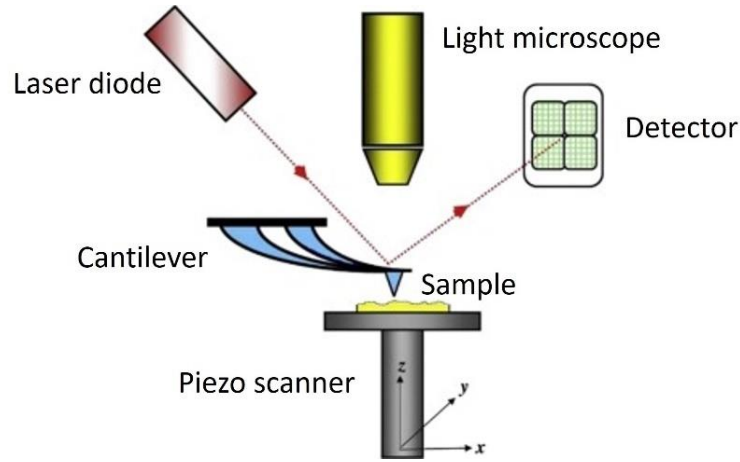


Figure 2.6 - Simplified illustration of the AFM constituents [81].

For the investigation performed in this study, the AFM could not be utilized to characterize the moth-eye-patterned surface, due to the reduced space between the nanostructures, which causes the tip to detect repulsive forces upon approach and, consequently, its retraction, obtaining an inaccurate profile. To employ this characterization technique, it would be necessary to utilize a reduced-size tip. Nevertheless, this method constitutes a valuable characterization tool for nanostructured profiles, with various applications.

As a part of the surface characterization, contact angle (CA) measurements have also been performed. This characterization technique provides information regarding surface characteristics, such as wettability, hydrophilicity, surface charge and tension, as well as interaction energy [82]. The CA is known as the angle between a solid/liquid/gas interface on a surface, as illustrated by Figure 2.7, and can be defined as the ability of a liquid to wet the surface of a solid. If the measured angle is between 0° and 90° , then the surface is considered hydrophilic. For angles between 90° and 180° , the surface is considered hydrophobic. Any angle which is close to 180° can be considered ultrahydrophobic.

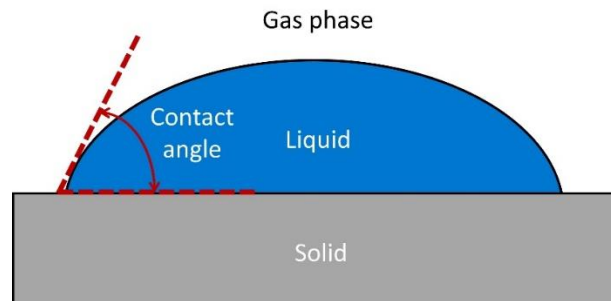


Figure 2.7 - Representation of the contact angle.

In this work, the CA measurements are performed with the aim of assessing the hydrophobic features of the moth-eye nanostructures. These measurements are performed on a Drop Shape Analyzer

(Kruss DSA100), shown in Figure 2.8, in which a drop is located at the tip of a needle. The measurements are obtained through the recording of an image of the drop on the sample's surface, which is then transferred to the drop shape analysis software, calculating the CA through a grey-scale analysis of the image, as well as a geometrical model of the drop shape.

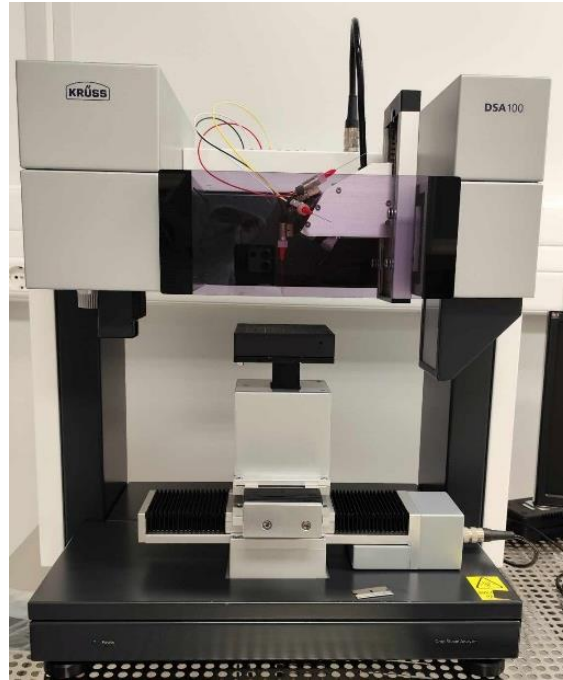


Figure 2.8 - Drop Shape Analyzer (Kruss DSA100).

3. FRICTIONAL CHARACTERIZATION

Friction is considered a complex non-linear phenomenon, resulting from the contact and sliding of two surfaces against each other. This phenomenon is dependent on several parameters, such as the surface topography, the contacting materials, the presence and type of lubrication and the relative motion [83]. At the contact interface, a frictional force acts to oppose the sliding motion. All solid surfaces have various irregular asperities, which interlock during the contact between the two surfaces. Based on this phenomenon, it was proposed that the real contact area changes according to the normal load, although the apparent contact area remains the same. This asperity interlocking phenomenon was considered the main cause of friction by earlier researchers, such as Leonardo da Vinci, Amonton and Coulomb [84]. Coulomb presented one of the first friction models, stating that the magnitude of friction is proportional to the normal contact force [85]. This early model depends on the direction of the relative velocity but does not specify a friction force at zero velocity, which can lead to perturbations upon the analysis of a dynamic system's response. However, this model is still employed to simulate friction behavior, due to its simplicity, as it only requires the coefficient of friction.

Various relevant friction models and concepts have been developed in the following years, being presented in the succeeding sub-sections.

3.1. FRICTION COEFFICIENT

The friction coefficient, μ , is a dimensionless scalar value that can be described as the ratio of the tangential force between two contacting surfaces and the normal force pressing them together, as defined by the following equation:

$$\mu = \frac{F_f}{F_N} \quad (1)$$

where, F_f is the frictional force, and F_N corresponds to the normal force. Two types of friction coefficients can be distinguished: static and kinetic. The static friction coefficient represents the friction opposing the start of relative motion, whereas the kinetic friction coefficient represents the friction opposing the continuance of relative motion once it has started. As a result, the static friction coefficient is larger than the kinetic, with its values depending on the pair of surfaces in contacts. As illustrated in Figure 3.1 friction can be considered as a mechanical system. Upon a close examination of the sliding process, it is

verified the occurrence of two friction regimes, a pre-sliding regime and a sliding regime, which will both be explained in the following sub-sections.

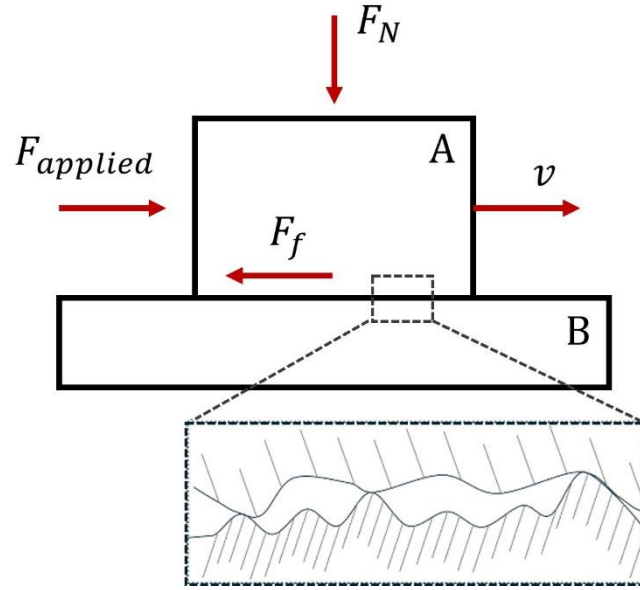


Figure 3.1 - Representation of the mechanical system formed during the sliding process.

3.2. STICK-SLIP PHENOMENON

The stick-slip phenomenon concerns the dynamic interaction between two surfaces and is characterized by the alternation of the friction force of the contact spots between adhesion and slip during the sliding movement [86-87], as illustrated by Figure 3.2. In other words, the sliding surface will remain stationary until the external tangential force reaches a magnitude sufficient to overcome the static friction force. This is an unstable effect which is repeated in rapid succession, being able to cause noticeable low frequency vibration of the slide [88]. For this phenomenon to occur, the system must be flexible enough in order to enable a change in the speed of the sliding body, and also the friction coefficient must be variable [89].

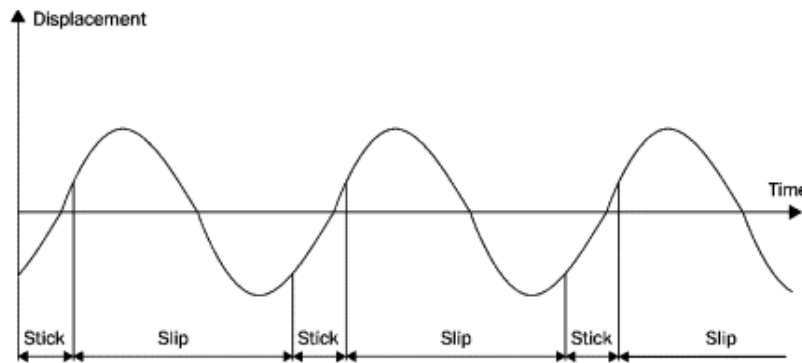


Figure 3.2 - Representation of the stick-slip phenomenon, showcasing the transitions between adhesion and sliding [52].

3.3. PRE-SLIDING AND SLIDING BEHAVIOR

The pre-sliding regime occurs at very small displacements and corresponds to the static friction phase. This phase is characterized by the dominance of adhesive forces, due to the asperity contacts. The shear stress between two contacting surfaces is not big enough to break the contacting linkage [90], being the friction force primarily a function of displacement, rather than velocity, as suggested by Figure 3.3. That is, in this regime, a hysteretic displacement-dependent friction force was identified [91,93]. The shape of the hysteresis function is determined by the distribution of the asperity heights, the tangential stiffness and the normal stiffness [94]. This hysteresis behavior is justified by the breaking of the adhesive contacts, that is, the elasto-plastic deformation of the asperity junctions. With the increase of displacement, there is an increasingly higher number of junction breakage, which eventually results in sliding [95]. This transition between the two regimes is a result of a buildup in micro-slip and must not be considered as a sudden discontinuity in the sliding process [91].

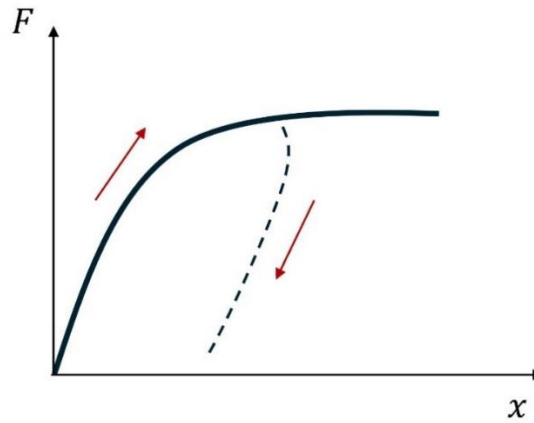


Figure 3.3 - Pre-sliding displacement behavior

The sliding regime of the frictional interface, or kinetic friction phase, can be characterized as a process of continuous formation and breaking of asperity junctions, such that the friction force becomes predominantly a function of the velocity. The transition from pre-sliding to gross sliding is dependent on not only the relative velocity, which corresponds to the displacement rate, but also the acceleration of the sliding objects. Within this phase, there are two properties: the Stribeck effect, which corresponds to the steady-state friction force behavior with increasing steady-state sliding velocities, and the frictional lag, or friction memory phenomenon, which consists of the change of friction force with the velocity variation.

The Stribeck effect is a phenomenon associated with the continuous passage from static to kinetic friction [96], being characterized by the initial decrease of friction force for increasing velocities, which is a consequence of the rising adhesion coefficient for dry friction, as a function of the contact time. Thus,

this functional relationship resulting from the measurement of the friction force at constant velocity has a characteristic shape, as demonstrated in Figure 3.4. The actual friction-velocity curve depends on parameters such as the time evolution of adhesion and the surface topography, as well as the asperity parameters, such as the tangential stiffness and inertia [94,97]. In lubricated sliding, the velocity decrease arises from the initial buildup of hydrodynamic pressure (hydrodynamic: condition in which the surfaces are separated by a lubricant film with thickness greater than their asperity heights and the pressure of the film causes negligible surface elastic distortion [98]), while the velocity increase is attributed to the viscous shear of the lubricating film.

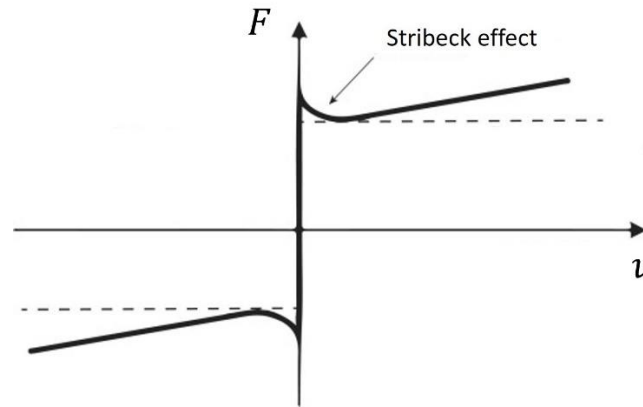


Figure 3.4 - Representation of the Stribeck characteristic curve (Adapted from [50]).

One of the parameters which is often assumed to be negligible is the asperity mass. However, when analyzing its influence, it was detected that friction increases with the velocity, for high velocities [94], a phenomenon known as velocity strengthening. Hence, the influence of other parameters has been analyzed, with the results being presented in Figure 3.5, showing the splitting of a steady-state friction curve (A) in different components, such as the deformation of the asperities (B), the adhesion forces (C) and the asperity masses (D).

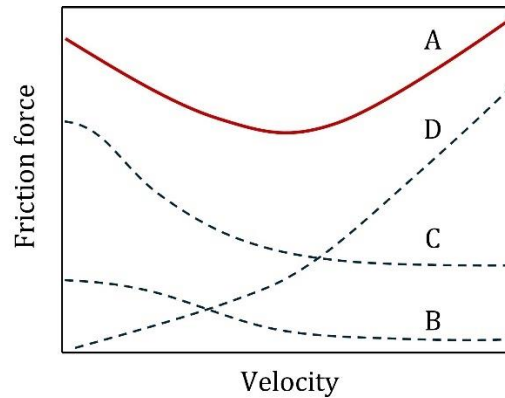


Figure 3.5 - Steady-state friction curve (A) split in different components: influence due to (B) deformation of the asperities, (C) the adhesion forces and (D) the asperity masses.

This analysis showed that both the deformation of the asperities and the adhesion forces components are decreasing functions of the velocity, with only the mass of the asperities being an increasing function of the velocity. However, from solely the investigation of the original curve (A), it is not possible to distinguish the different components and their influence.

Another important property is the frictional lag, which is characterized by a delay in the friction force relative to the sliding velocity [99-100]. This phenomenon is represented in Figure 3.6, in which it is shown that the friction force does not instantaneously respond to the velocity variation, and results in lower friction forces for decreasing velocities, and higher friction forces for increasing velocities. This frictional lag is well recognized in lubricated friction, where this characteristic derives from the time required to modify the lubricant film thickness, known as the *squeeze effect*. This mechanism is similarly observed in dry friction experiments, as the local adhesion coefficient increases with the time of contact of two opposing asperities, due to normal creep, which is caused by the sinking of the surfaces into each other. Thus, the friction force is higher for acceleration than for deceleration.

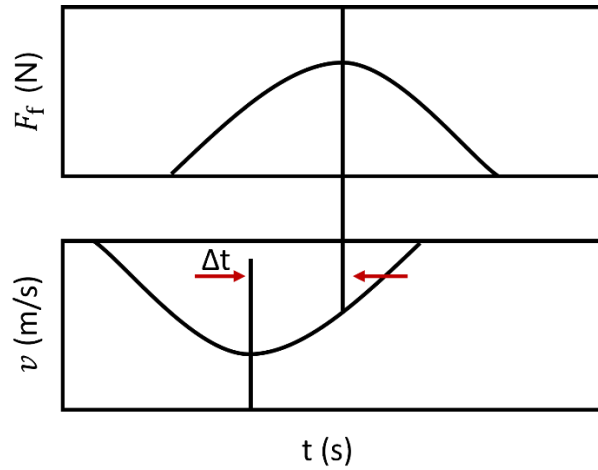


Figure 3.6 - Graphical representation of the frictional lag, showcasing the typical friction-speed shift.

The transition between the pre-sliding and sliding regimes is also an important aspect to consider. By analyzing this passage, it is possible to detect frictional lag. During this transition, the friction force increases until it reaches a maximum value, known as the breakaway force. From this point, the object enters the sliding regime, and the friction force turns into a steady-state curve.

3.4. THEORETICAL FRICTION MODELS

Throughout the years, several friction models have been developed. However, there are many parameters which influence frictional behavior and are difficult to measure, such as the deformation of the surfaces and the accumulation of wear particles. Additionally, the time-varying nature of friction due

to factors such as wear, changing load, or operating temperatures can constraint the applicability of an estimated model. Overall, it is not possible to measure the friction force directly, hence the added difficulty in identifying it in a mechanical system. Nevertheless, some frictional phenomena can be successfully described by friction models [101], allowing the estimation of model parameters which aid the attainment of more quantitatively accurate friction models. There can be two types of friction models, static and dynamic. In short, static friction models describe the dependency of the friction force on the relative sliding velocity, whereas dynamic friction models are characterized for incorporating a spring-like behavior for small forces, that is, no significant displacement is found when the applied force is smaller than the static friction. In general, static friction models possess limitations regarding some frictional characteristics, such as pre-sliding displacement and the frictional lag, hence the development of dynamic friction models. In this section, several dynamic models regarding friction will be briefly discussed, namely the Bristle model [102], LuGre model [103], Leuven model [91] and the generalized Maxwell-slip model [94]. These models were analyzed as they are mostly based on empirical experiences and are the result of adding features to simple models, such as time dependency, thus taking into account more phenomena.

The Bristle model regards the randomness of friction, which derives from the random distribution of asperities on a surface. It assumed that the friction between two contacting surfaces is provoked by many interacting bristles, as illustrated by Figure 3.7. The external forces lead to plastic and elastic deformations of the contacting asperities; thus, the connected bristles can be considered to act as a spring. When the strain of a bristle exceeds a certain level, then the connection breaks, establishing a new one with a random strain.

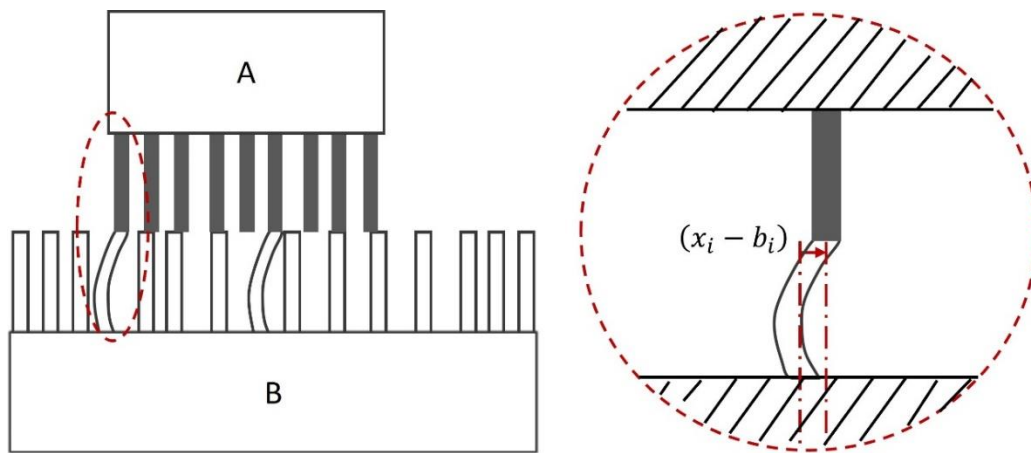


Figure 3.7 - Illustration of the Bristle model

In this model, friction is a function of the velocity, as it is assumed that the number of bristles depends on the relative velocity of the opposing surface. The friction force is given by the total sum of the individual spring forces:

$$F_f = \sum_{i=1}^N \sigma_0 (x_i - b_i) \quad (2)$$

where σ_0 corresponds to the stiffness of the bristles, x_i and b_i represent the relative position of the bristles and the location where a connection takes place, respectively, and N denotes the number of bristles. The LuGre model agrees with the Bristle model, visualizing friction as the force produced by bending bristles with a spring behavior. However, it does not consider a random behavior of friction but is rather based on the average behavior of the bristles. Additionally, this model considers steady-state characteristics, such as the Stribeck effect, by assuming that the average deflection of the bristles at the steady-state motion. Thus, the friction force decreases with increasing velocities. The friction force is given by:

$$F_f = \sigma_0 z + \sigma_1 \dot{z} + f(v) \quad (3)$$

with z corresponding to the average bristle deflection, σ_1 is the micro damping, $f(v)$ represents the viscous friction. In spite of being one of the most utilized models in literature, it still lacks the inclusion of some friction characteristics. Thus, an improvement to this previous model has been developed, known as the Leuven model. This elaborate friction model has the ability to account for several friction characteristics, such as the Stribeck effect, the hysteretic behavior in pre-sliding, the friction lag and the stick-slip phenomenon. After this model, yet another more elaborate friction model was developed, named the Generalized Maxwell Slip model. As represented in Figure 3.8, this model considers a parallel connection of n single massless block-spring models, with all having the same input in terms of displacement or velocity, but with different sets of parameters [104]. The output of this model is the summation of the individual friction forces acting on the blocks. If the elementary model sticks, then the state equation is given by

$$\frac{dF_f}{dt} = k_i v \quad (4)$$

with v and k_i corresponding to the relative tangential velocity and spring stiffness, respectively. If the elementary model slips, the state equation is given by

$$\frac{dF_f}{dt} = \text{sgn}(v) v_i C_a \left(1 - \frac{F_f}{v_i s_i(v)} \right) \quad (5)$$

in which $\text{sgn}(v)$ is the sign function which captures the direction of the velocity, $s_i(v)$ corresponds to

the steady state friction curve and C_a denotes the attraction parameter.

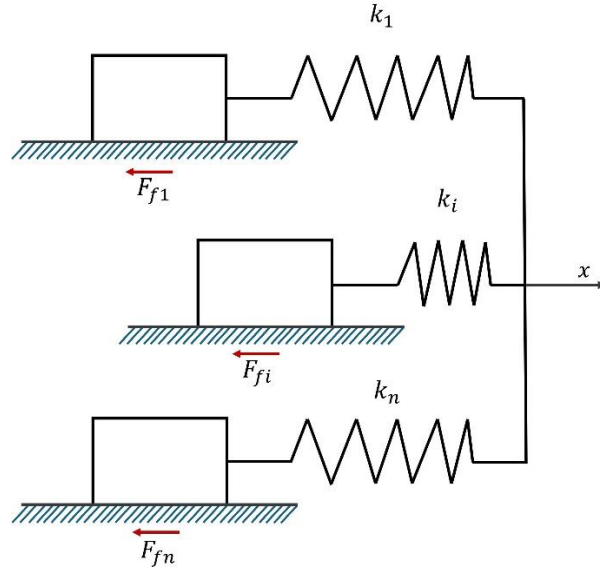


Figure 3.8 - Illustration of the generalized Maxwell-slip model.

This improved model allows not only the proper simulation of the frictional lag behavior and the transition between pre-sliding and sliding behavior, but also the breakaway force and stick-slip behavior.

4. WEAR CHARACTERIZATION

Wear can be defined as the surface damage or removal of material from one or both of the contacting surfaces in a system of relative motion [105-106]. This phenomenon is a function of the tribo-system, which is composed by several elements, such as the body, counterbody, interfacial element and environment [107], as illustrated in Figure 4.1. Thus, a material's susceptibility to wear is dependent on not only its mechanical properties, but also on environmental factors, namely the conditions to which it is exposed.

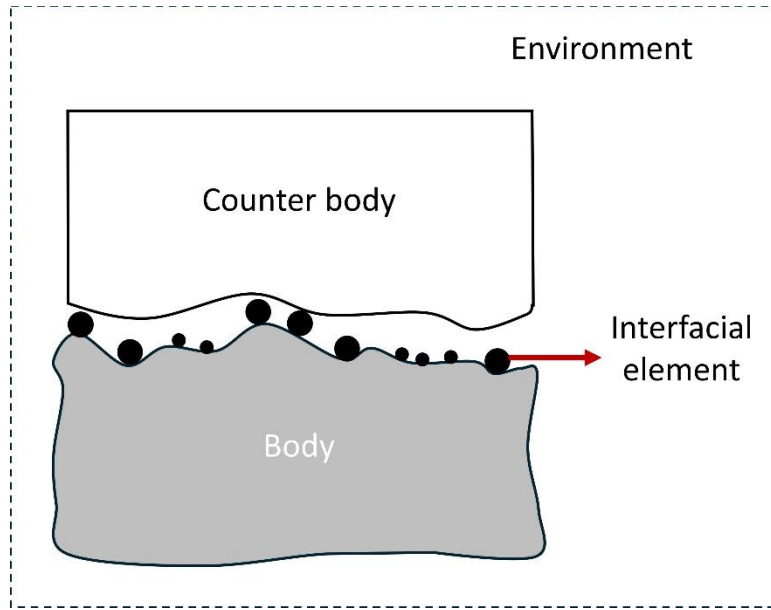


Figure 4.1 - Illustration of the tribo-system.

The main properties which influence wear are the sliding speed, hardness, temperature and the material composition. The applied load can also influence wear, as it leads to the increase of the shear force, as well as the frictional momentum, resulting in the increase of the wear rate [108]. The wear rate can be defined as the amount of material per unit of time.

The worn material resulting from the sliding between two bodies can be quantified through Archard's law [109]. This law states that the volume of worn material (V) is proportional to the normal load and the sliding distance (L), and inversely proportional to the material hardness (H), as shown through the following equation:

$$V = K_w \frac{F_N L}{H} \quad (6)$$

in which K_w denotes a dimensionless constant corresponding to the wear coefficient.

There can be various types of wear mechanisms, such as adhesion, abrasion, tribochemical reaction and surface fatigue [110], as illustrated in Figure 4.2, which will be explained in the following sub-sections.

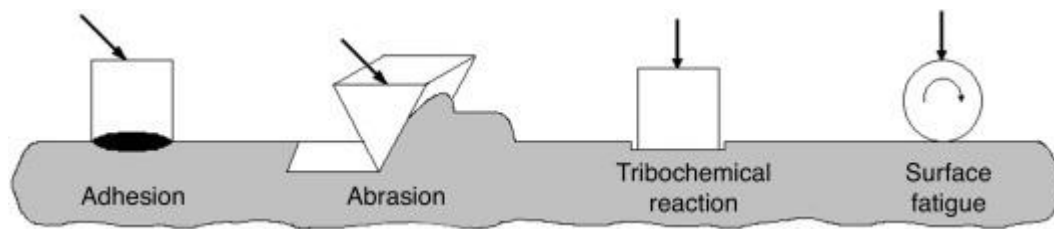


Figure 4.2 – Schematic representation of wear mechanisms [107].

4.1. ADHESIVE WEAR

Adhesive wear occurs when the atomic forces between the materials of contacting surfaces under relative pressure outweigh the inherent material properties of each surface [111-112]. In other words, adhesion occurs at the asperity contacts at the interface, which are sheared by relative motion [113]. This can result in the detachment of a fragment from one surface and attachment to the other. As sliding continues, loose wear particles may form, as illustrated in Figure 4.3.

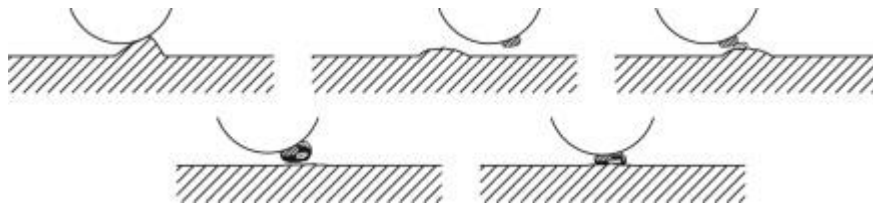


Figure 4.3 - Representation of the adhesive wear mechanism [87]

A detailed list of steps which lead to the formation of adhesive-wear particles is provided below, based on information from [114]:

1. Deformation of the contacting asperities
2. Removal of the surface films
3. Formation of the surface films
4. Failure of the junctions and material transfer
5. Modification of transferred fragments
6. Removal of transferred fragments and creation of loose wear particles

The volume of material removed through adhesive wear can be estimated from Archard's law, Eq. (6).

4.2. ABRASIVE WEAR

Abrasive wear takes place when the asperities of a hard rough surface slide on a softer surface, provoking damage on the interface due to fracture or plastic deformation. The abrasive wear caused by plastic deformation can occur in various deformation modes, which include ploughing, wedge formation and cutting [115].

There can be two types of abrasive wear, according to the type of contact, two-body abrasion and three-body abrasion. The term two-body abrasion is given when the ploughing is caused by an asperity from the harder material, whereas the term three-body abrasion is conferred when the ploughing occurs through the contact with a wear particle which is trapped at the interface of both contacting bodies [107,116], as shown in Figure 4.4.

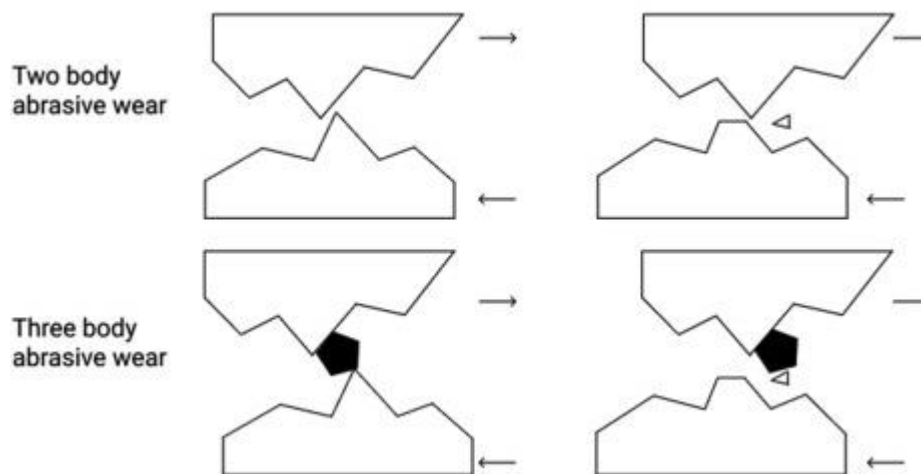


Figure 4.4 - Schematic of the formation of two and three body abrasive wear [117].

Within the category of abrasive wear, there can be three main mechanisms: plowing, cutting and fragmentation [117-118]. Plowing consists of the displacement of material to the sides, resulting in ridges adjacent to grooves, which may be removed by the passage of abrasive particles. This formation of grooves does not involve direct material removal [118]. Cutting can be defined as the removal of material from the surface in the form of microchips, with little or no material being displaced to the sides of the grooves. Lastly, fragmentation is characterized as the separation of material from the surface due to cutting and crack formation, leading to a localized fracture and crack formation around the grooves. This results in an additional material removal by fragmentation, in which the debris are produced in the form of flakes [117].

The volume of material removed during this process (V) can be estimated by considering the diagram from Figure 4.5, in which a hard conical asperity is traversing a softer surface with an angle (θ), under the action of a normal load, leading to the following equation:

$$V = \frac{2 \tan \theta}{\pi} \frac{F_N L}{H} \quad (7)$$

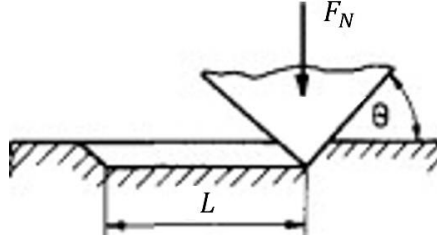


Figure 4.5 - Representation of a conical asperity traversing a softer surface under the action of a normal load [114].

Similarly to Eq. (6), this equation constitutes a simplified model, as it only considers hardness as a material property.

4.3. TRIBOCHEMICAL WEAR

Tribochemical wear occurs when there is a chemical interaction between the mating surfaces. Chemical reactions induced by friction are mainly influenced by the environment and its active interaction with the materials in contact [119]. Typically, the contacting surfaces react with the environment, creating reaction products which are deposited on the surfaces. Then, these reaction products are removed due to crack formation and abrasion, leading once again to the exposure of the surfaces to environmental damage. This process can lead to an increased reactivity due to increased temperature, accelerating the formation of the reaction product. Moreover, it can also lead to an increased brittleness, as a result of the heavy work-hardening [114].

The amount of material loss due to this wear mechanism (V) can be estimated by the following equation, in which it is considered that the surface layers formed by a chemical reaction are removed from the contact zone after a certain critical thickness [113]:

$$V = \frac{k d}{\xi^2 \rho^2} \frac{F_N L}{H} \quad (8)$$

where ξ is the critical thickness of the reaction layer, ρ is the thickness of the reaction layer, k is the velocity factor of oxidation and d is the diameter of asperity contact, as illustrated by Figure 4.6.

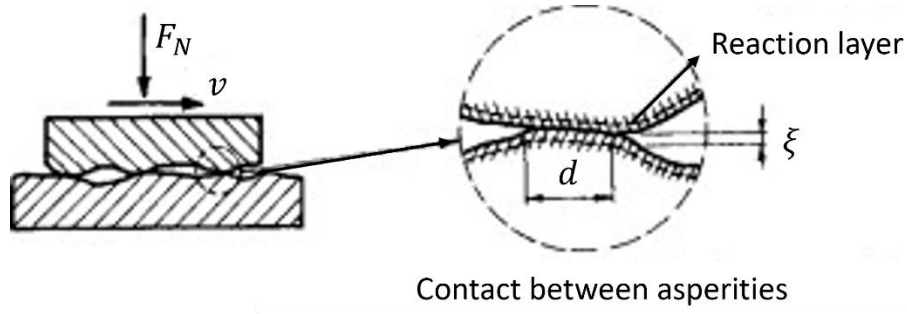


Figure 4.6 - Representation of a conical asperity traversing a softer surface under the action of a normal load [114].

4.4. SURFACE FATIGUE

Surface fatigue wear occurs due to the growth and formation of cracks, being associated with rolling contacts due to the cycling nature of the load [120]. In sliding contacts, the asperities are subject to cycling stress, leading to stress concentration effects, as well as the propagation of cracks. A detailed list of steps which lead to the generation of wear particles is shown below, based on information from [114]:

1. Transmission of stresses at contact points
2. Growth of plastic deformation
3. Crack formation and propagation
4. Creation of wear particles

For sliding contacts, the volume of removed material due to fatigue (V) can be obtained through [114]:

$$V = C\eta\gamma\varepsilon_1^2 \frac{F_N L}{H} \quad (9)$$

where η corresponds to the distribution of asperity heights, γ is a particle size constant, ε_1 is the strain to failure in one loading cycle and C is the fatigue ductility coefficient.

Overall, the analysis of the acting wear mechanisms can provide valuable information for various applications, namely regarding the material selection, the need to improve the design of products and the prediction of failure, aiding the comparison of performance between different materials or designs. For this study, considering the environmental factors involved, one of the key wear mechanisms would be abrasion, as the nanostructured surfaces could be subjected to contacts between particles, such as dust, which can lead to surface degradation, and thus, a possible decrease of their AR properties. In addition, adhesive wear is also a relevant mechanism, as the mechanical stress caused by the interaction between external conditions can lead to an attachment or detachment of material, which could also affect the performance of the nanostructures. Moreover, tribochemical wear could also be an important aspect to

consider, as the nanostructured surfaces could be exposed to elements such as high humidity, as well as to pollutants, leading to chemical degradation. However, in this study, the samples will not be subjected to these types of conditions, hence this wear mechanism will not be considered.

5. EXPERIMENTAL CHARACTERIZATION

The tribological characterization of the moth-eye nanostructures constitutes a valuable approach, as it allows the evaluation of the wear over time, making it possible to verify the existence of significant degradation. The wear of these nanostructures could affect their AR properties, as they depend on the existence of a gradually varying refractive index, provided by the presence of nanostructures, which could be altered by degradation. Moreover, the assessment of the behavior of the structures to wear could provide insights regarding the susceptibility to damage caused by cleaning processes, aiding the selection of appropriate cleaning methods which preserve the surface's integrity. The adhesion properties of the nanostructured surfaces are also relevant to their cleaning, as it can help identify how strongly contaminants such as dust can adhere to the surfaces, and, consequently, the selection of appropriate cleaning agents and techniques. These adhesion properties can be influenced by the roughness of the surfaces, and thus the selection of adequate cleaning protocols. Factors such as the cleaning frequency could also be analyzed through a tribological characterization, and it could also guide the development of novel nanostructured surfaces, based on specific tribological properties.

This chapter presents a detailed description of the testing parameters, namely regarding the utilized equipment, the selected test counterface, the applied loads and the number of cycles. Moreover, the morphological and optical characterization of the nanofabricated samples is showcased, specifically the reflectance spectra of nanostructured surfaces, in comparison with a flat surface, as well as SEM images from the moth-eye structures. In addition, the surface roughness and CA of the nanostructures is characterized. The results of the performed tribological tests are also shown in this chapter, as well as a detailed discussion of the acquired data.

5.1. TEST DESCRIPTION

The assessment of tribological properties of the moth-eye structures was achieved through friction testing, on a tribometer (CETR-UMT2, USA), which is shown in Figure 5.1 (A), utilizing a ball-on-plate test configuration, as presented in Figure 5.1 (B). This equipment performs the acquisition of data every 0.01 s and can detect frictional forces as low as 0.001 N. The selected test counterface consists of a 10 mm diameter bearing steel (AISI 52100) sphere, and the resulting data consists of the variation of the friction coefficient throughout the test length. This test counterface was selected, as this material is well characterized tribologically. Additionally, a spherical surface means that there is only one point in which there is contact with the sample's surface, which facilitates both the characterization and calibration

process. For these tests, two loads were applied, 0.1 N and 0.5 N, having been defined various test cycles: 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 cycles. These test parameters were defined with the purpose of understanding, not only the impact of the applied load, but also the behavior of the structures when exposed to successive cycles. Each test was performed three times, for each load, and cycle has an approximate duration of 17 s and the length of the route performed by the counterface is approximately equal to 15.8 mm.



Figure 5.1 - (A) CETR-UMT2 tribometer utilized for testing and (B) Sample positioned on the tribometer for testing.

To perform the experimental tests, it was necessary to develop a sample support, ensuring an adequate connection to the equipment, as well as a secure positioning of the samples. An image of the sample support printed in polylactic acid (PLA) is shown in Figure 5.2. As seen on the image, the squared central cavity is used to place the sample, containing two additional cavities to accommodate the user's fingers when inserting it. In addition, the support contains four symmetrical mounting holes, which allow the adjustment of the connection to the tribometer through bolts and nuts.



Figure 5.2 – Design of the sample support used in this work, obtained by 3D printing,

5.2. OPTICAL AND MORPHOLOGICAL CHARACTERIZATION

The nanofabrication of the silicon moth-eye structures gave place to samples with an appearance as the one presented in Figure 5.3. The square at the center of the samples corresponds to the area with the nanopattern, obtained through NIL processes, which is approximately equal to 25 x 25 mm. The silicon substrate has an area of 50 x 50 mm.

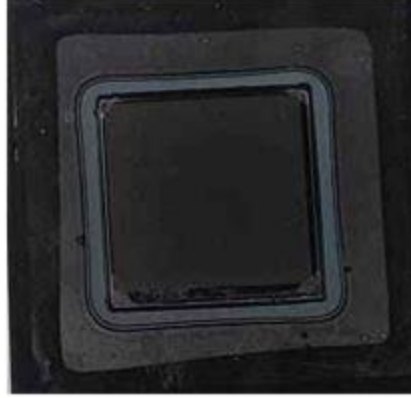


Figure 5.3 - Silicon moth-eye sample obtained through NIL.

These nanostructured surfaces require a morphological characterization, to ensure that the structures are in compliance with the expected results. This characterization was performed through SEM images of the nanostructured surfaces, as shown in Figure 5.4 (A), (B) and (C), from a top view, and Figure 5.4 (D), (E) and (F), with a 30° tilt. According to the images, the structures consist of randomly arranged pillars, with variable diameters, but roughly with uniform height. Further SEM images of the nanostructures can be found in Appendix A: Characterization of the Moth-eye Texturization.

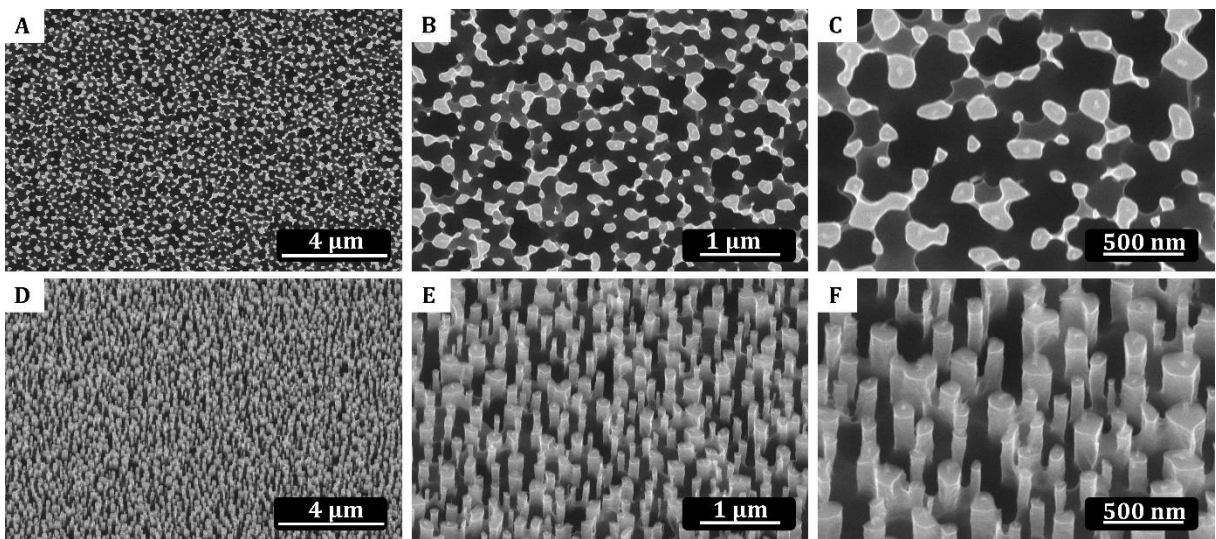


Figure 5.4 - SEM images of Moth-eye structures before tribological testing, (A), (B) and (C) from a top view and (D), (E) and (F) with a 30° tilt.

The mean height of the structures was measured through the image-processing software *Image J*, and five SEM cross-section images, such as the one shown in Figure 5.5, being obtained an average height of 434 ± 32 nm.

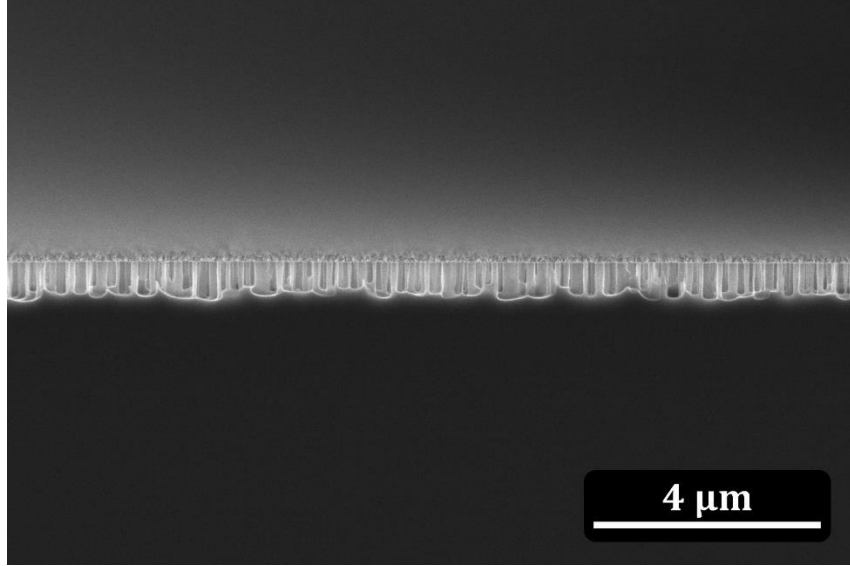


Figure 5.5 - SEM cross-section image of moth-eye sample utilized for measurements.

Subsequent to the nanofabrication of the structures, an optical characterization is required, as the purpose of the implementation of this nanopatterning is the decrease of reflectance. Thus, in order to verify that the optical performance of these architectures is in compliance with the expected results, the total relative reflectance was measured, being presented in Figure 5.6 the results for the total relative reflectance of four samples. The silicon reference refers to a bare silicon sample, without the moth-eye nanostructures.

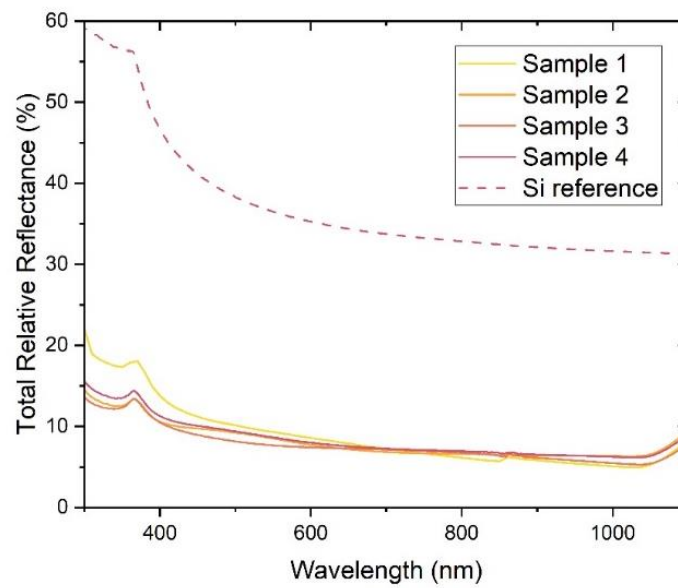


Figure 5.6 - Reflectance spectra of four nanopatterned moth-eye samples and a bare silicon sample.

To further characterize the pillars and to assess their roughness, the AFM technique would be employed, as it is a widely utilized and accurate characterization method for nanostructures [78,123-125]. However, as mentioned in Chapter 2.4, the proximity between the pillars which compose the moth-eye structures prevents the tip of the equipment to accurately register the surface morphology, as shown in Figure 5.7, in which the surface obtained through the AFM technique does not represent the fabricated nanostructures depicted in the SEM images (Figure 5.4).

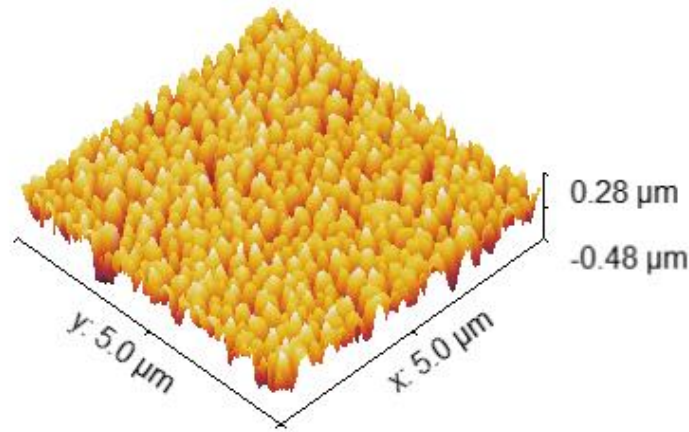


Figure 5.7 - AFM image showcasing an inaccurate profile of the fabricated nanostructures.

As a result, the quantification of the sample's roughness has been performed through an alternative method. In short, the method consists of analyzing the grey scale values of SEM top view images of the moth-eye samples, which constitute the representation of the pillar density in the tested samples. These grey scale values are then correlated to a height scale, given by measurements performed on SEM cross-section images of the pillars through the software *Image J*. Therefore, by combining both data, it is possible to obtain an accurate height profile of the surface, and thus calculate the roughness parameters of the moth-eye samples. To simplify and systematize this process, a *Matlab* code has been developed, being presented in Figures C.1, C.2 and C.3 of Appendix B: Roughness Calculations. In short, this code enables the input of the SEM top view images in the *.tif* format, followed by the selection of the image scale in nm. Then a line needs to be drawn on the image, selecting a row of pillars for the roughness calculations. The developed code generates a graph of the grey scale values as a function of the position along the selected line. In this graph, it is necessary to select different sections, corresponding to the top and bottom of the structures, calculating the respective average minimum and maximum grey scale values. These values will then be related to the previously measured average height scale, obtained through the measurement of SEM cross-section images. By corresponding the maximum and minimum grey scale values to the maximum and minimum height values, respectively, it is possible to obtain an

accurate surface profile and perform the roughness measurements. The average height values were obtained through the measurement of 1400 points, for both the maximum and minimum values of the scale. A step-by-step illustration of the roughness calculation process using this method is also provided in Appendix B: Roughness Calculations.

The selected roughness parameters were the arithmetical mean deviation (R_a), root mean square roughness (R_q), the maximum peak-to-peak-valley height (R_t), lowest valley height (R_v) and the highest peak height (R_p). The average values of these parameters and the respective standard deviations (SD) were calculated, being displayed in Table 5.1.

Table 5.1 - Average values of the respective roughness parameters and SD.

Parameter	Mean value (nm) $\pm$ SD
R_a	195 $\pm$ 9
R_q	219 $\pm$ 10
R_t	797 $\pm$ 75
R_v	282 $\pm$ 35
R_p	515 $\pm$ 52

The surface roughness is an important aspect to consider when performing a tribological characterization, as it has been shown that the roughness, particularly the amplitude parameters, can influence the wear and frictional behavior of surfaces [127]. For example, the surface height influences friction, especially in a lubricated regime, in which a smoother surface hinders liquid retention, whereas a rougher surface promotes it, assisting the decrease of friction. Moreover, the lack of roughness can also lead to an extreme form of adhesive wear [128], known as seizure, which can provoke the welding of material to the adjacent surface [129]. Under dry friction, which is the case of this study, the impact of the roughness depends on the type of contact, having been reported that at the initial point contact between surfaces, the wear of the surfaces can be higher for a smaller roughness height [127]. This is possibly due to the fact that the maximum pressure for smoother surfaces at the initial contact point is higher for smoother surfaces, than for a rougher surface [130]. However, it has been shown that higher surface roughness corresponds to a higher tendency for fatigue [131-133], and that a decrease in roughness height can lead to a higher corrosion resistance [133]. Therefore, it could be inferred that structures which confer a lower roughness to the surface would provide better tribological properties, namely a better wear resistance. In addition to the roughness, the water CA of the nanostructured surfaces

has also been measured, as shown in Figure 5.8, obtaining an average of $97.7^\circ \pm 5.5$, achieved through 10 measurements. As this value is between 90° and 180° , the surface is considered hydrophobic. As a reference, a bare silicon sample, without the moth-eye pattern, has also been measured, obtaining a CA of $28.4^\circ \pm 1.6$.

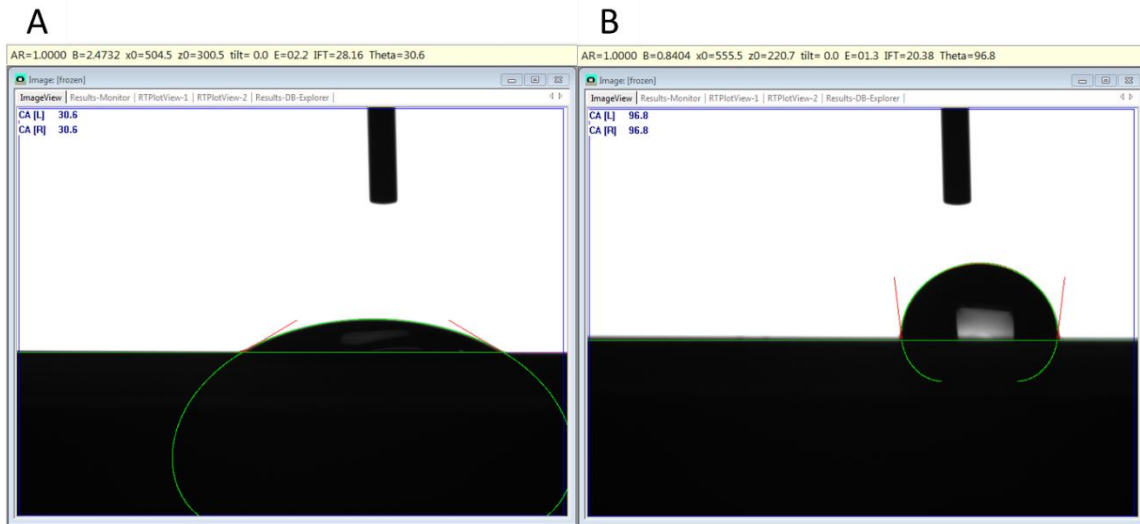


Figure 5.8 – Drop Shape Analysis software during water CA measurements of a (A) bare silicon sample and a (B) moth-eye nanostructured surface.

Given the intention of these nanostructures to be positioned on the upper surface of solar modules, where they could be exposed to environmental elements such as rain, their hydrophobic properties can be considered advantageous. This surface hydrophobicity enables efficient water drainage from the surface, which could enhance the durability and performance of the devices by minimizing accumulation and potential contamination.

5.3. TRIBOLOGICAL CHARACTERIZATION

The optical and morphological characterization of the moth-eye samples is followed by the tribological characterization of the surfaces. After the employment of the testing parameters described in Chapter 5.1, the nanostructured surfaces underwent an extensive analysis of both wear and frictional properties, being also submitted to morphological investigations. Upon a first visual inspection, the tested surfaces revealed a well-defined test track, corresponding to the places where the tests occurred, as shown in Figure 5.9. In this figure, the sample's surface presents some flaws on the top and bottom right side of the patterned area, which are not related to the tribological testing, but are a result of defects during the nanofabrication processes. Hence, these faulty areas were not utilized for testing.

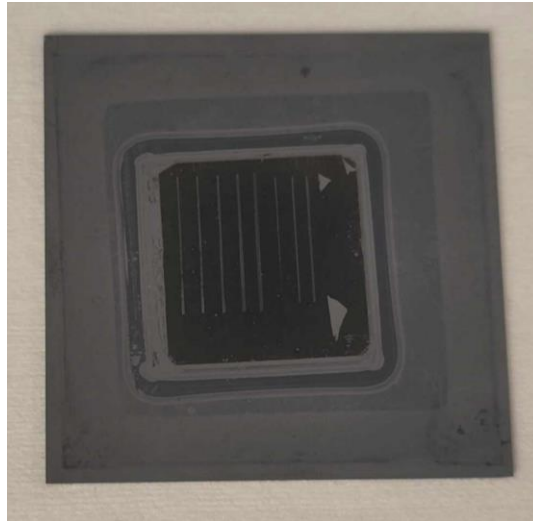


Figure 5.9 - Moth-eye sample after tribological testing.

Further investigation of the tracks revealed a correlation between the width of the tracks, the number of cycles and the applied load. Through OM, the respective measurements were performed, being presented in Table 5.2 an average of 10 measurements and the respective standard deviations, whose values are presented in Table C.1 and Table C.2 of Appendix C: Optical Microscopy Measurements. From these results, it is possible to conclude that the increase of test cycles, for the same load, leads to a larger width of the track. A higher load also gives place to a greater track width. Figure 5.10 (A), (B) and (C) contains images of the test track measurements for 0.1 N and Figure 5.10 (D), (E) and (F) for 0.5 N tests, where the boundary between the test track and the rest of the sample is evident. It must be noted that the values displayed in Figure 5.10 only represent one of the ten measurements, therefore, they do not exactly match the results of Table 5.2.

Table 5.2 - Mean test path width and SD for tests performed with 0.1 N and 0.5 N.

Number of cycles	Mean width of tested track (μm) $\pm$ SD	
	0.1 N	0.5 N
1	113 $\pm$ 6	160 $\pm$ 7
2	140 $\pm$ 7	229 $\pm$ 37
3	155 $\pm$ 20	270 $\pm$ 27
15	206 $\pm$ 20	344 $\pm$ 34
50	252 $\pm$ 11	388 $\pm$ 23

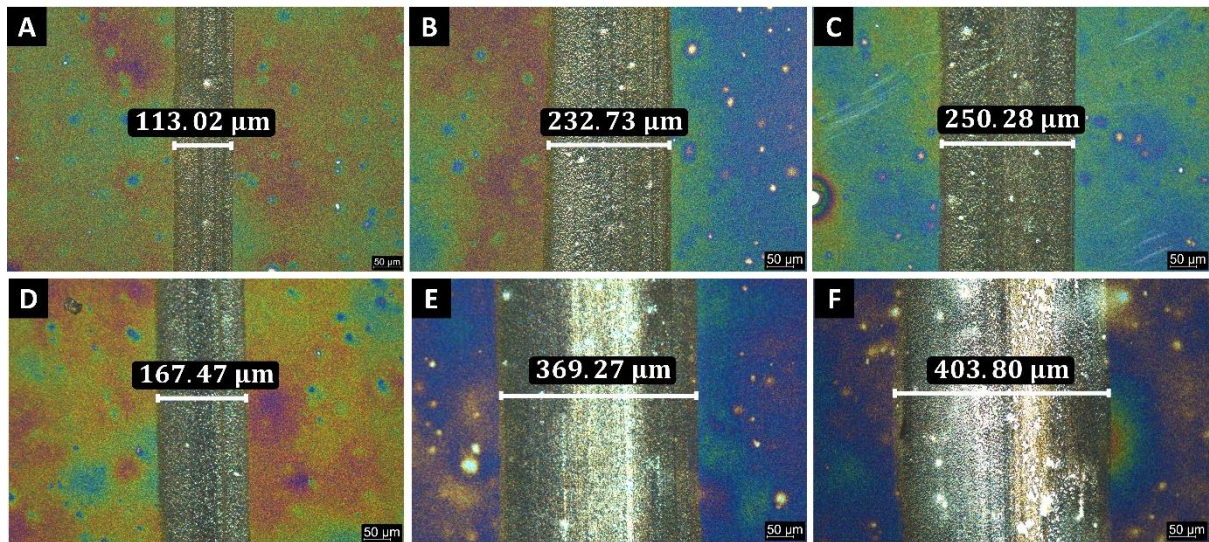


Figure 5.10 – Images obtained by OM for (A) 0.1 N test and 1 cycle, (B) 0.1 N test and 15 cycles, (C) 0.1 N test and 50 cycles, (D) 0.5 N test and 1 cycle, (E) 0.5 N test and 15 cycles, (F) 0.5 N test and 50 cycles.

The increase of the track width between both loads was approximately equal to 1.4 times for 1 cycle, increasing to approximately 1.7 for 3 cycles. This difference gradually decreases to 1.5 times for 50 cycles. The difference of track width between both loads was an expected phenomenon, as there is a higher sinking of the test counterface on the surface. However, the significant increase in width with the number of cycles was an unexpected finding. From the graphical input of these results, it is possible to detect a tendency to stabilize the track's width for both applied loads, as shown in Figure 5.11.

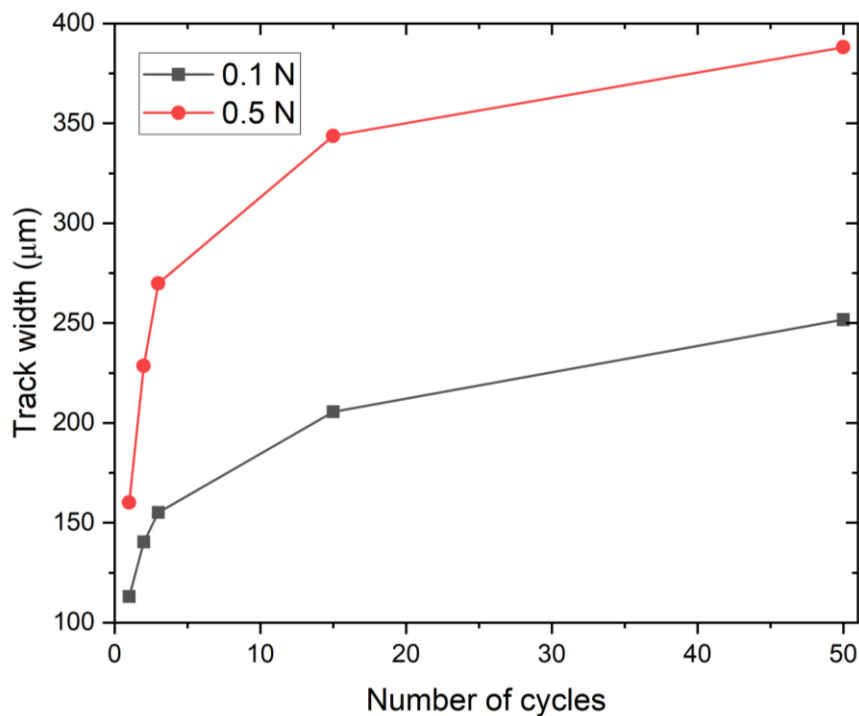


Figure 5.11 – Track width of the tested moth-eye samples with 0.1 N and 0.5 N, as a function of the number of cycles.

This verified track width's saturation means that from a certain number of cycles, the track maintains the same width. The increase of width could have been caused by the test configuration, as there is a possibility of the counterface not following the exact same track when passing back and forth, hence leading to an increase of its width with the number of cycles. Additionally, this could also be due to material accumulation, as the fractured pillars at the boundary could affect the untested area. The increase of cycles would translate into a larger material accumulation, and thus a wider test track.

Subsequent to OM, further investigation of the surface was performed, namely to the worn nanostructures. Firstly, low magnification SEM images were taken for both tested loads, as presented in Figure 5.12. Here, it is possible to verify the presence of abrasive wear, manifested through the appearance of nitid shear bands, which correspond to the previously inspected tracks.

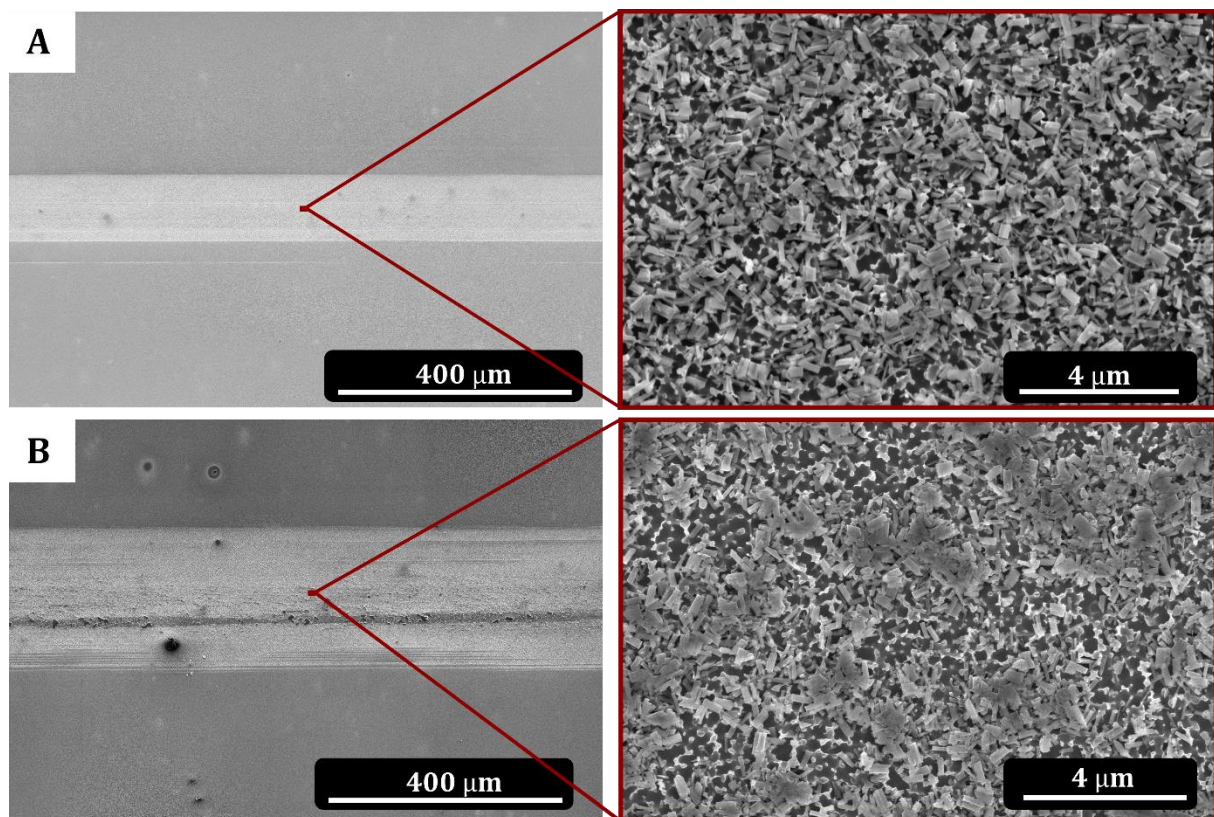


Figure 5.12 - SEM top view images of moth-eye samples tested for 1 cycle with (A) 0.1 N and (B) 0.5 N.

The increase of magnification revealed the existence of fractured pillars for both loads, as shown in Figure 5.12 (A) and (B). In the low magnification image of Figure 5.12 (B), it is possible to detect a darker nitid line near the center of the track. This highlighted track could have been provoked due to the existence of dirt particles on the surface of the counterface or of the sample, which would have led to a three-body abrasion phenomenon and aggravated the wear of the area in which it contacted the surface. Another possible explanation would be that the highlighted track is formed from an asperity of the test

counterface. However, this could not be proved due to the complexity of the roughness calculation of the spherical counterface, as it would have to be performed based on SEM imaging, in which it is difficult to focus on a round surface's asperities.

The friction evolution curves as a function of the test time are presented in Figure 5.13 (A). These curves correspond to the average of three tests performed for one cycle and are representative of the frictional behavior of the moth-eye nanostructured surfaces, as this curve morphology repeats throughout the various test cycles. As can be seen in Figure 5.13 (B), each friction coefficient curve is characterized by two distinct phases: (I) a pre-sliding phase, and (II) sliding phase. The pre-sliding phase is characterized by an initial rapid increase in friction, in which mechanical interlocking of the asperities occurs, giving place to a strong abrasive interaction, due to the relative motion of the contacting surfaces. The curve relative to this phase showcases a relation between its duration and the applied load, having been detected that for a higher load (0.5 N), phase I lasts longer (average of 2.09 s) than for the lower applied load (0.1 N), which lasts for approximately an average of 1.79 s. This is due to a more mechanically aggressive truncating of the asperities' extremities provoked by a higher load, which delays the beginning of the polishing effect gradually verified on the increasingly longer tests. As the tests continue, the friction coefficient values tend to stabilize, although some small oscillations are verified, possibly due to the random distribution of differently shaped pillars, as seen in the previous section. The pre-sliding phase duration measurements can be seen in Appendix D: Pre-sliding Measurements.

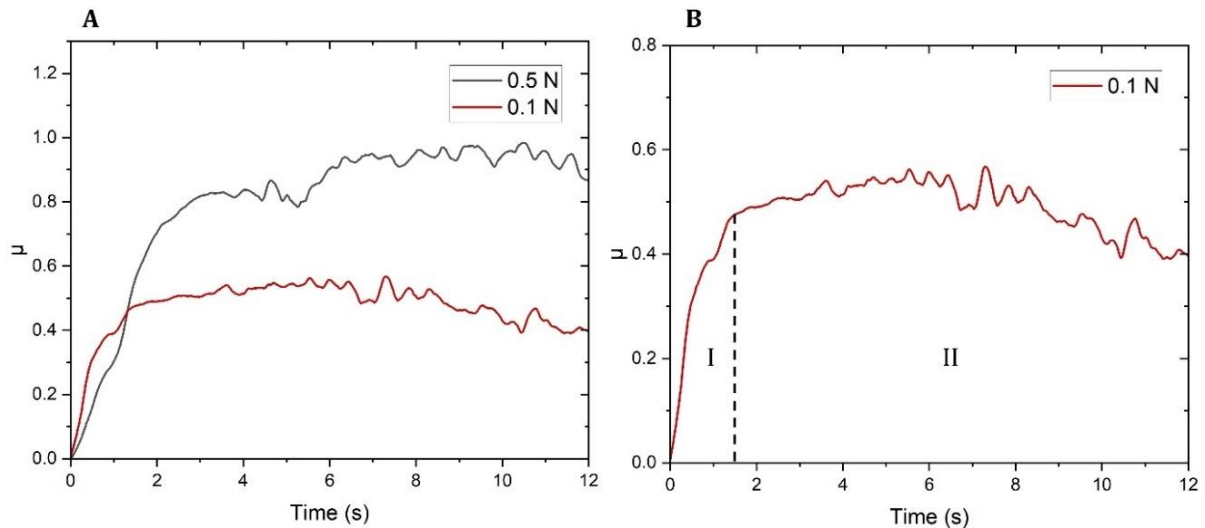


Figure 5.13 - Friction coefficient curves, as a function of the test time, (A) for 0.1 N and 0.5 N, (B) illustrating pre-sliding (I) and sliding (II) phases.

The sliding phase of the friction coefficient has also been analyzed, through the average friction values of the three tests, with the resulting data being presented in Table 5.3. For this study, it would also be interesting to analyze frictional mechanisms such as the stick-slip phenomenon. This analysis can be

performed if the system would have to be flexible enough to enable a change in the velocity of the sliding body, which is the case of this study. However, this evaluation could not be accomplished, as the utilized tribometer does not allow the measurement of the counterface's velocity during testing, preventing a correlation between the friction coefficient variation and the velocity profile. In addition, it would also be of relevance to analyze further acting mechanisms, such as the Stribeck effect, which manifests as a nonlinear dependence of friction force on the sliding speed, and the frictional lag, which is characterized by a lag in the friction force relative to the sliding velocity. Seen as in the sliding phase the friction force becomes predominantly a function of the velocity, it was also not possible to perform this analysis. Hence, the analysis of the frictional behavior during phase II of the tests was performed through the data presented in Table 5.3.

Table 5.3 - Mean friction coefficient values relative to the sliding phase of the tribological tests, for both tested loads (0.1 N and 0.5 N).

Cycle number	0.1 N	0.5 N
1	0.42 ± 0.06	0.85 ± 0.22
2	0.48 ± 0.10	0.70 ± 0.09
3	0.47 ± 0.08	0.74 ± 0.09
4	0.40 ± 0.07	0.71 ± 0.08
5	0.41 ± 0.01	0.77 ± 0.09
10	0.44 ± 0.08	0.76 ± 0.07
15	0.56 ± 0.06	0.87 ± 0.13
20	0.48 ± 0.07	0.82 ± 0.08
25	0.52 ± 0.08	0.93 ± 0.12
30	0.48 ± 0.07	0.88 ± 0.08
35	0.52 ± 0.06	0.97 ± 0.06
40	0.48 ± 0.08	0.87 ± 0.06
45	0.51 ± 0.07	0.97 ± 0.05
50	0.50 ± 0.06	1.01 ± 0.04

The friction data resulting from the tests performed with the lower load (0.1 N) reveal that the backward stroke (2 cycles) showcased higher friction values, in comparison with the forward slide (1 cycle). These differences between the forward and backward friction are common observations at the micro and nanoscale [126], and have been reported previously [31]. This phenomenon occurs due to the

fracture and deformation of the structures during the first slide, which results in an increased true area of contact during the backward stroke. This is shown in Figure 5.14 (B), in which horizontally stacked fractured pillars can be observed, contrary to Figure 5.14 (A), which mainly shows vertically stacked fractured pillars.

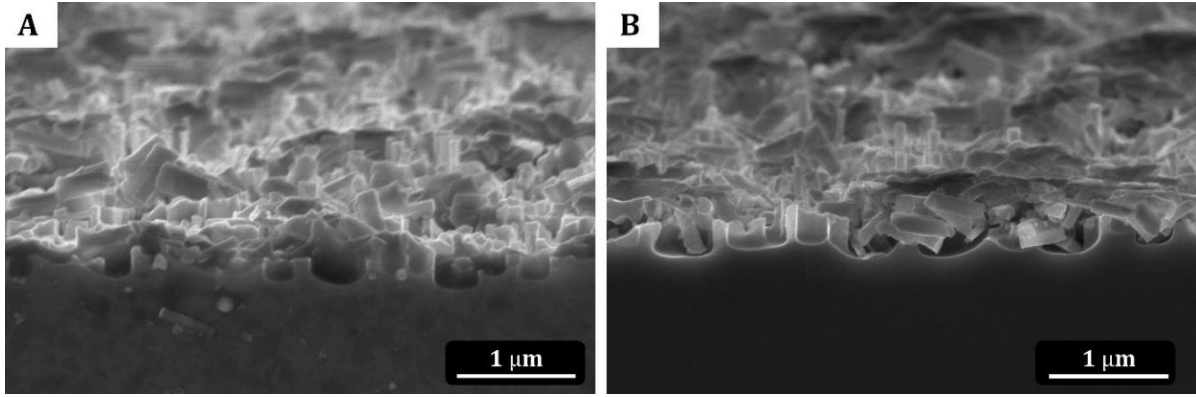


Figure 5.14 - SEM cross-section images of samples tested for 0.1 N and (A) 1 cycle and (B) 50 Cycles.

When analyzing the following frictional behavior, it was verified a significant increase of the friction coefficient at 15 cycles, approximately equal to 1.3 in comparison with the 10-cycles tests, corresponding to the highest detected friction of the lower load tests. This can be justified by the chemical composition of the sample's tested area. Through EDS (Figure 5.15 (C) and (D)), it was found that at 15 cycles, the tested surface revealed the presence of oxygen and iron, which arose from the test counterface, in addition to silicon from the substrate. When analyzing the surfaces tested for less than 15 cycles, it was only verified the existence of silicon (Figure 5.15 (A) and (B)). Therefore, it seems that the adhesion mechanism between both sliding surfaces is the main cause for the increase of friction for the lower load tests. It is important to note that EDS is a qualitative method, which depends greatly on the selected point of the sample. Thus, the objective with the employment of this technique in this study was to get an idea of the sample's composition and not to perform a quantitative study regarding the atomic composition of the samples.

The chemical composition of the tests that are longer than 15 cycles also revealed an increase of the adhesion with the number of cycles, as shown in the SEM images contained in Figure 5.15. For these tests, the overall friction coefficient values were higher than the ones obtained previously, presenting average values within the range of 0.50 ± 2 .

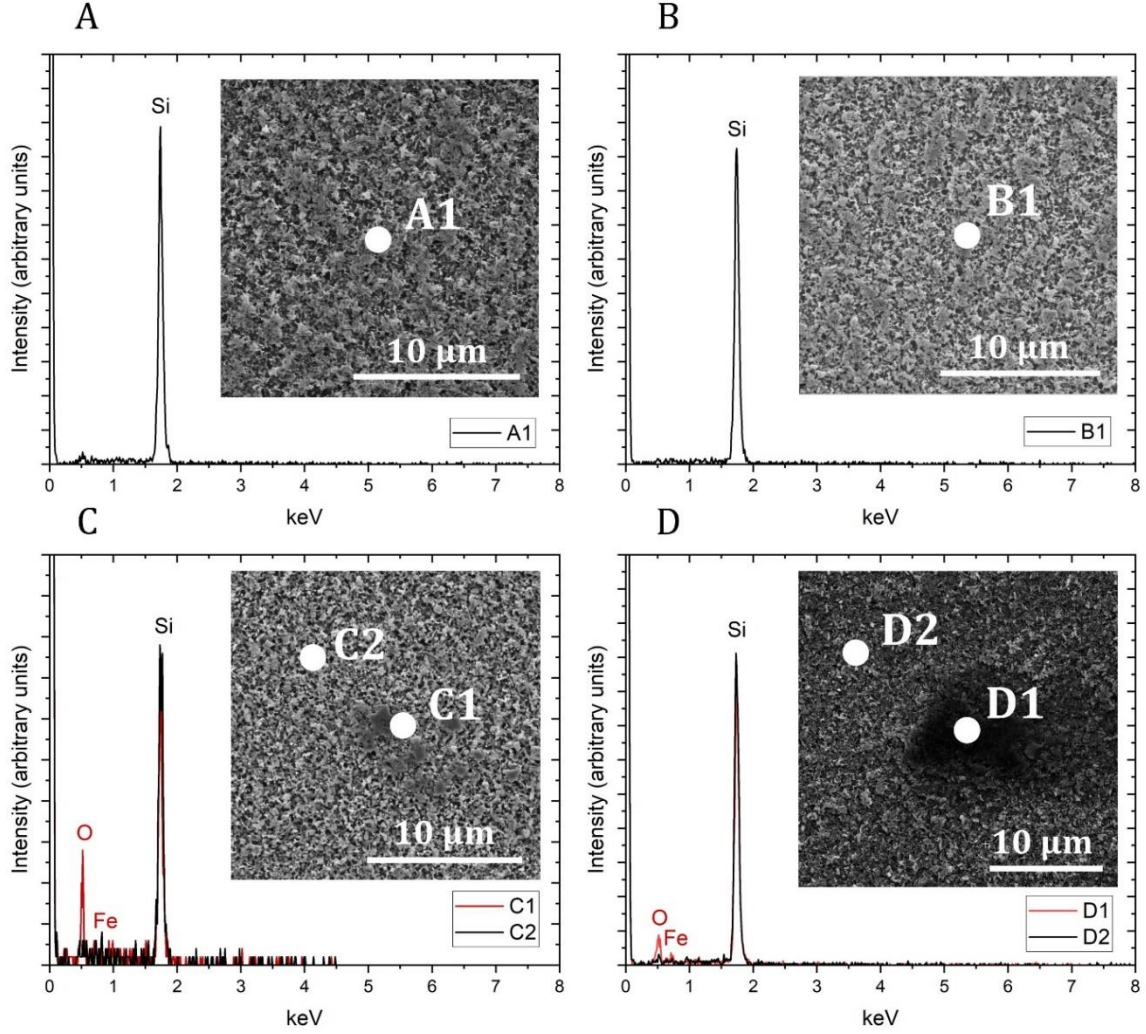


Figure 5.15 - EDS spectrum of moth-eye samples tested with 0.1 N for (A) 1 cycle, (B) 3 cycles, (C) 15 cycles and (D) 50 cycles.

A trend in the frictional behavior has been detected throughout the test cycles. As seen in Figure 5.16, it is observed that the friction coefficient increases for the odd cycle numbers and decreases for even cycle numbers. This occurs for both applied loads, except for the 50 cycle tests performed with 0.5 N. The observed phenomenon could be justified by the type of test setup, as a slight tilt of the samples, provoked by an uneven sample support, could have been the cause for the decrease in friction in a certain direction, as there is less contact with the sample. Another possible justification could be due to the fracture of the pillars to same side as the movement is performed on the first passage. As the counterface performs the returning movement, it will have to overcome more resistance from the structures, due to its tilt to the opposite side, hence the repetitive increase and decrease in friction coefficient.

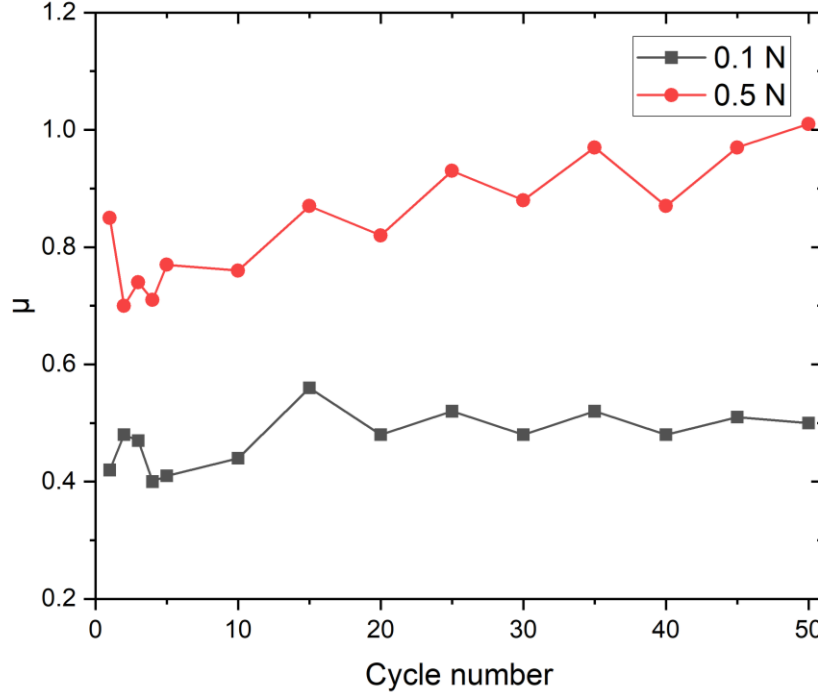


Figure 5.16 - Average friction coefficient values for the various test cycles, for a load of 0.1 N and 0.5 N.

The higher load tests (0.5 N) reveal a significant increase of the friction coefficient. Contrary to the lower load tests, the 2-cycle tests showcased lower friction than the first stroke (1 cycle). This phenomenon can be justified by the stronger abrasive interaction between the asperities during the 1-cycle test, which led to the fracture and severe deformation of the nanostructures, as shown in Figure 5.17 (A). This event lead to the delay of the polishing effect, as the worn structures now form an intermediate rough surface. With the increase of the test cycles, a polishing phenomenon becomes progressively prominent, as seen in Figure 5.17 (B), leading to gradually higher friction values, as the real contact area increases with each pass of the sphere.

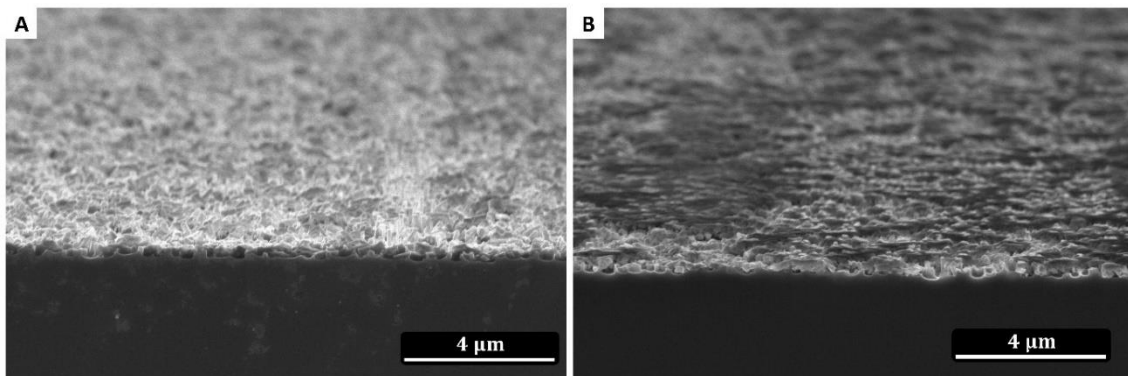


Figure 5.17 - SEM cross-section images with a 10° tilt of samples tested for 0.5 N and (A) 1 cycle and (B) 50 Cycles.

When analyzing the chemical composition of the samples, the presence of iron and oxygen was detected for all tested cycles, as shown in Figure 5.18. This further justifies the significant increase in friction, in comparison with the lower load tests.

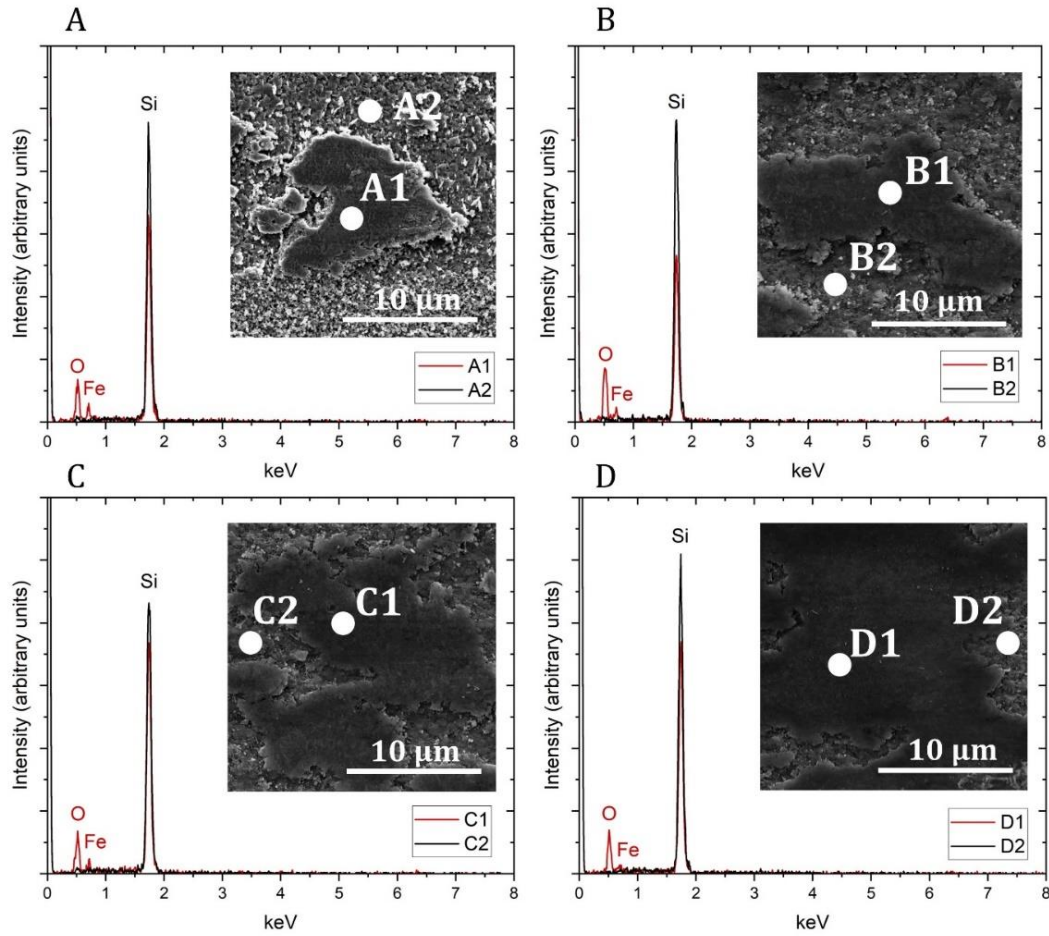


Figure 5.18 - EDS spectrum of moth-eye samples tested with 0.5 N for (A) 1 cycle, (B) 3 cycles, (C) 15 cycles and (D) 50 cycles.

A morphological analysis of the tested surfaces revealed that as the number of cycles increases, the adhesion of counterface material became more prominent, as shown in Figure 5.19. It is possible to determine a relation between the number of cycles and the compression of the structures. Through the Figure 5.19 (A), it is possible to observe that the adhesion is mainly located towards the center of the track, with this area presenting a higher visible compression of the structures, manifested through the appearance of plateaus. These plateaus are a result of a self-polishing mechanism, that is, the fractured remains of the structures became trapped in the interstices between the structures. This phenomenon is better illustrated in Figure 5.20 through high magnification images of the structures after (A) 3 cycles and (B) 15 cycles.

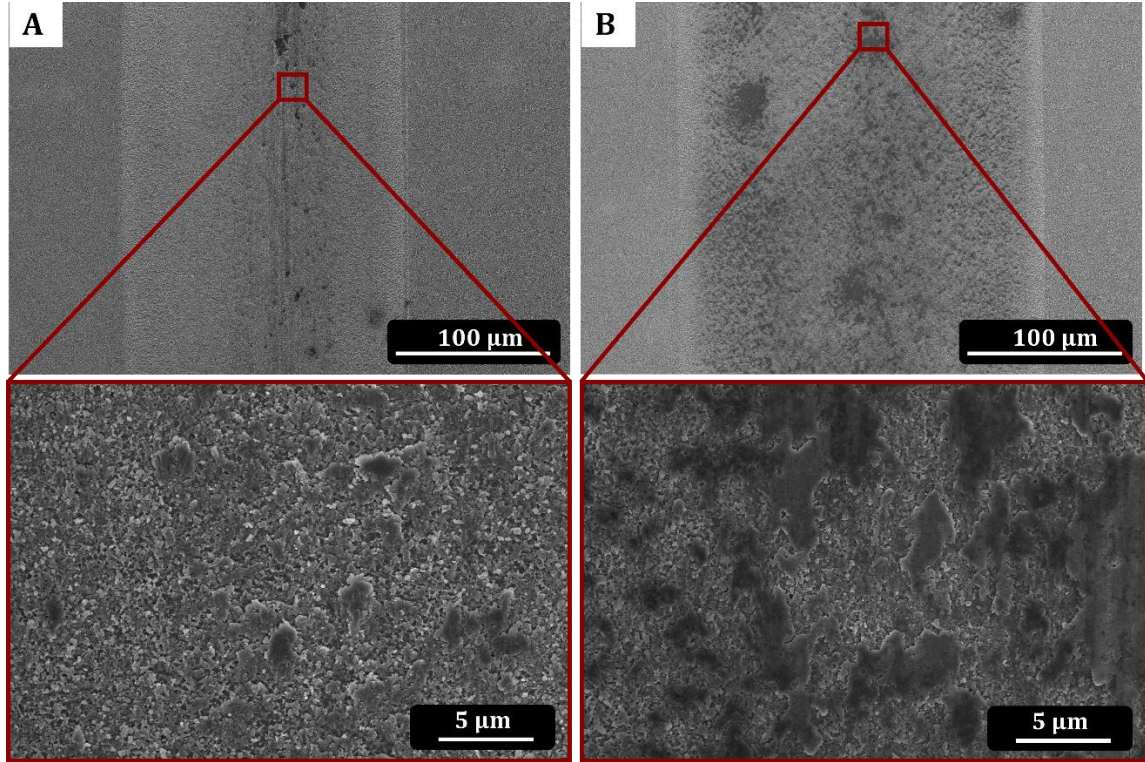


Figure 5.19 - SEM top view images of moth-eye samples tested with 0.5 N for (A) 3 cycles and (B) 15 cycles.

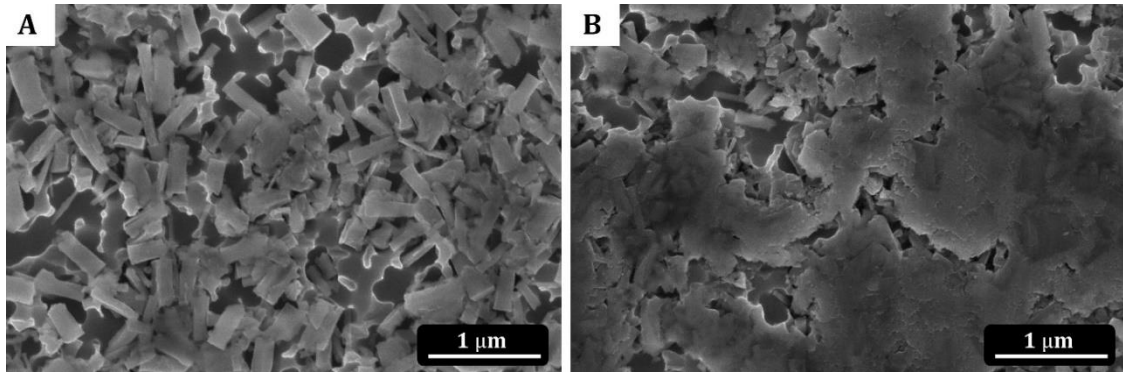


Figure 5.20 - SEM top view images of moth-eye samples tested with 0.5 N for (A) 3 cycles and (B) 15 cycles.

As contact and sliding between the structures continued, the surface eventually became smoother, as a result of the compression and subsequent flattening of the pillars, as seen in Figure 5.19 (B) and Figure 5.20 (B). However, with the increase of cycles it was observed that both adhesion and the compression of the structures became more prominent on the sides of the track (Figure 5.19 (B)).

Regarding the optical performance after tribological testing, it was not possible to assess the influence of the wear caused by the applied loads and number of cycles on the AR properties of the nanostructured surfaces. This can be due to the fact that the wear track resulting from the tests does not possess a large enough area to perform the optical measurements on the UV-vis equipment.

5.4. STRUCTURAL-TRIBOLOGICAL CORRELATION

An additional investigation has been conducted into different types of moth-eye structures. During the nanofabrication phase of this project, a calibration of the etching equipment was necessary, which also required a recalibration of the moth-eye pattern nanofabrication. During this process, two new types of structures were obtained, with one consisting of agglomerated pillars, as shown in Figure 5.21, which appear to be shorter than the previously obtained structures, as shown in Figure 5.22. The other obtained structures are morphologically similar to those structures characterized in Chapter 5.2, except for the height, as they appear to be taller than the previous structures.

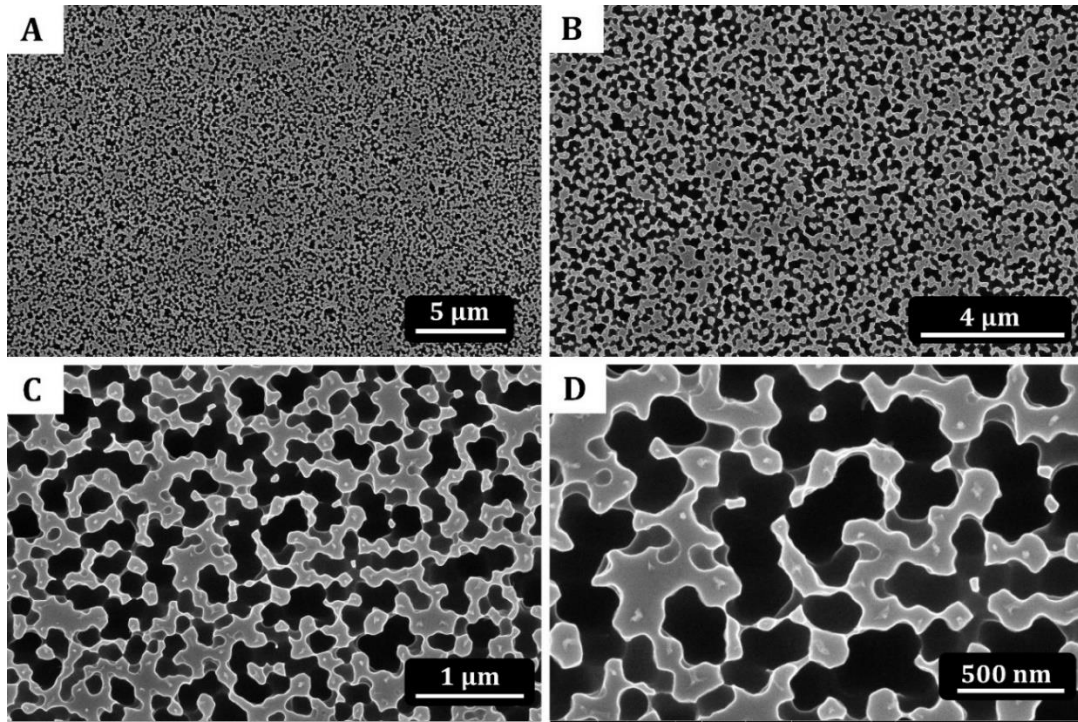


Figure 5.21 - SEM top view images of moth-eye sample (Structure B) for different horizontal field widths (HFW): (A) 30 μm HFW; (B) 15 μm HFW, (C) 5 μm HFW and (D) 2.5 μm HFW.

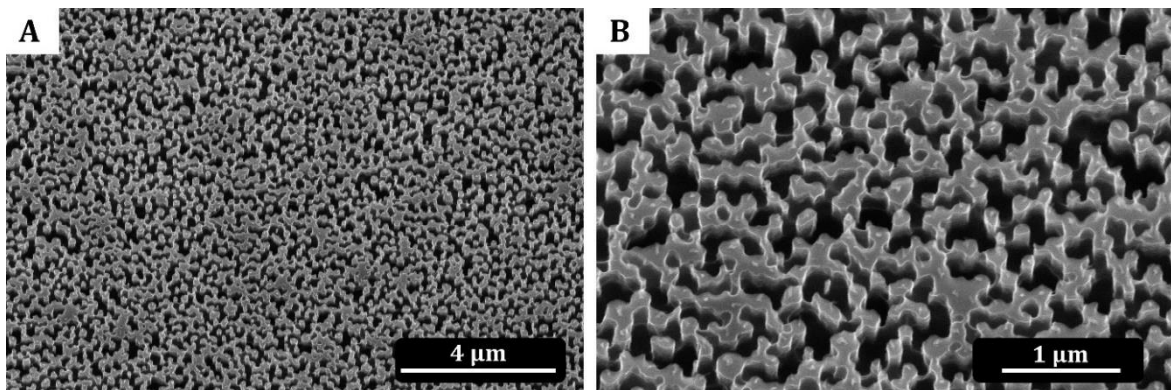


Figure 5.22 - SEM images of a moth-eye sample (Structure B) with a 30° tilt, for (A) a HFW of 15 μm and (B) a HFW of 5 μm.

Through SEM cross-section images (Figure 5.23), the heights of the individual (Structure A) and of the agglomerated (Structure B) pillars were measured, obtaining average values of 578 ± 58 nm and 290 ± 34 nm, respectively. These measurements were performed on the image-processing software *ImageJ* and were the result of 1400 measurements.

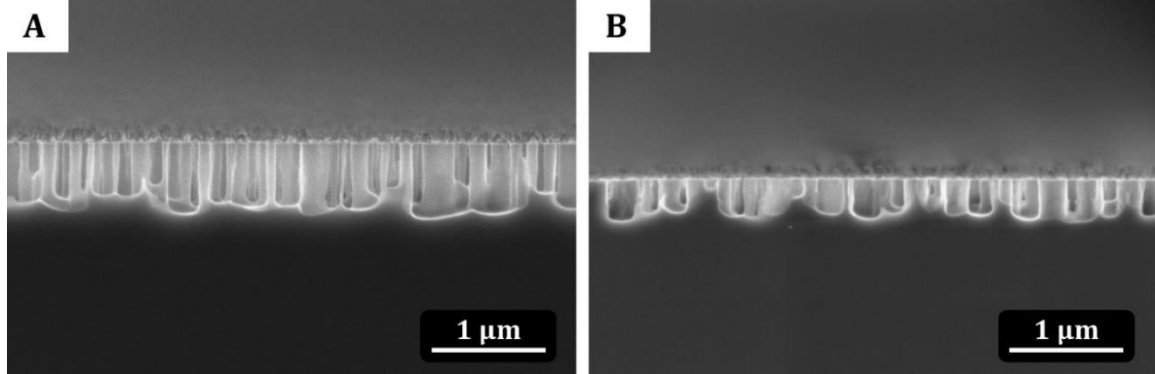


Figure 5.23 - SEM cross-section images for a HFW of 5 μm of (A) Structure A and (B) Structure B.

An optical characterization was performed to analyze the influence of both types of structures on the total relative reflectance, as shown in Figure 5.24. The structures present very similar optical performances, with Structure B showcasing a slightly better performance, equivalent to 1 PP, in comparison with Structure A. This was a positive finding, as it is predicted that both structures will present very different tribological behaviors, due to their significant morphological differences. Therefore, an ideal structure can be selected, solely based on their tribological performances.

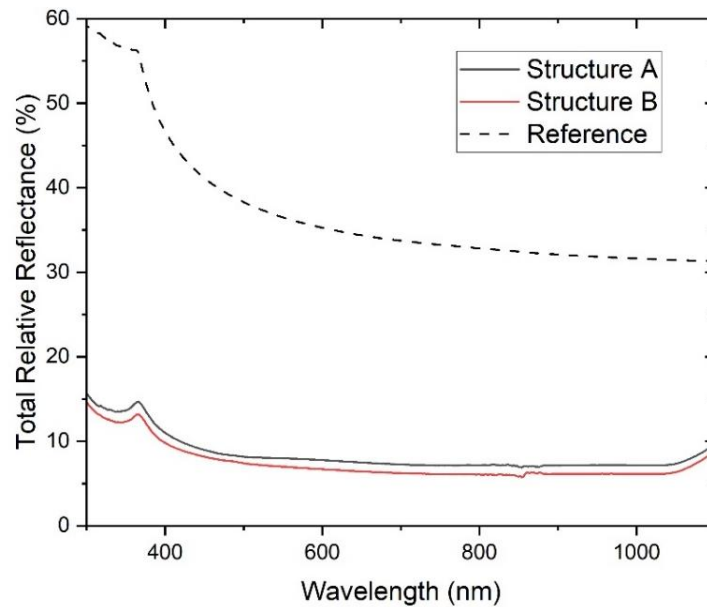


Figure 5.24 - Reflectance spectra of moth-eye samples with Structure A and B, in comparison with a bare silicon sample.

Regarding the morphological characterization, the average pillar diameter for both structures was analyzed through the software *ImageJ* and SEM top view images. This analysis was performed through an average of 30 measurements, which are presented in Appendix A: Characterization of the Moth-eye Texturization, and concluded that the average diameter of structures A and B was equal to 163 ± 65 nm and 509 ± 218 nm, respectively.

The roughness of both structures was also analyzed through the method described previously in Chapter 5.2. The average values of the roughness parameters are presented in Table 5.4 and represent an average of 30 measurements, which are shown in Table B.1 and Table B.2 of Appendix B: Roughness Calculations. From these results, it is possible to conclude that structure A possesses a larger roughness, in comparison with the other type of structures. The conclusions drawn in Chapter 5.2 regarding the surface roughness have stipulated that a lower roughness could indicate a better wear resistance, in comparison with rougher surfaces. Hence, it could be predictable that structure B will confer better tribological properties to the surface.

Table 5.4 - Mean roughness parameters and the respective SD for Structure A and B.

Parameter	Mean value (nm) $\pm$ SD	
	Structure A	Structure B
R_a	250 ± 15	138 ± 8
R_q	278 ± 17	160 ± 11
R_t	979 ± 112	614 ± 89
R_v	337 ± 60	226 ± 44
R_p	641 ± 75	388 ± 59

Regarding the tribological testing, two samples of each type of structure were tested, with a load of 0.1 N, being performed from 1 to 50 cycles, as in the previous tests. The ball-on-plate test configuration was also employed, utilizing a spherical bearing steel (AISI 52100) counterface. The results of these tests are presented in Table 5.5 and show that the friction coefficient is overall lower for structure B than for structure A, signifying that these structures are ideal if lower conditions are desired. These results are in agreement with experiments performed by Afshar-Mohajer et al [31], which have been mentioned in Chapter 1.1. Similarly to the conclusions drawn in this study, the shorter pillar-like structures showcased the lower friction values, in comparison with the taller structures.

Table 5.5 – Mean friction coefficient variation for a 0.1 N load, as a function of the cycle number for Structure A and B, with the respective SD.

Cycle number	Structure A	Structure B
1	0.48 ± 0.26	0.36 ± 0.10
2	0.50 ± 0.28	0.38 ± 0.09
3	0.49 ± 0.22	0.38 ± 0.06
4	0.41 ± 0.16	0.36 ± 0.06
5	0.51 ± 0.21	0.42 ± 0.06
10	0.48 ± 0.15	0.40 ± 0.06
15	0.54 ± 0.16	0.41 ± 0.05
20	0.48 ± 0.14	0.46 ± 0.08
25	0.60 ± 0.22	0.40 ± 0.06
30	0.48 ± 0.14	0.46 ± 0.09
35	0.49 ± 0.13	0.39 ± 0.06
40	0.47 ± 0.13	0.46 ± 0.08
45	0.59 ± 0.23	0.38 ± 0.07
50	0.49 ± 0.13	0.47 ± 0.05

On a structural level, the results presented in Table 5.5 were expected. Considering that the pillared-like moth-eye structures can be regarded as equivalent to beams with a fixed end and free at the tip, with a load being applied perpendicularly to the structure as illustrated by Figure 5.25. In this case, it is evident that the stress concentrates at the bottom of the structures, as highlighted in Figure 5.25, and increases with the height of the beam [134].

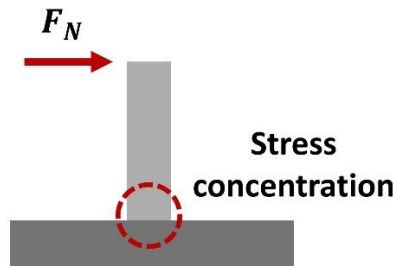


Figure 5.25 - Illustration of stress concentration on a pillar-shaped structure.

Further analysis shows that for structure A, the highest average friction coefficient value was equal to 0.60, at 25 cycles, whereas for structure B it was 0.47, at 50 cycles. This indicates that a significant decrease in friction can be obtained with the implementation of structure B. Additionally, through the analysis of Figure 5.26, it is evident that the average values vary less than the results from structures A,

which show a sudden increase in friction at 45 cycles (1.25 times), presenting an average friction coefficient close to the maximum value ($\mu = 0.59$).

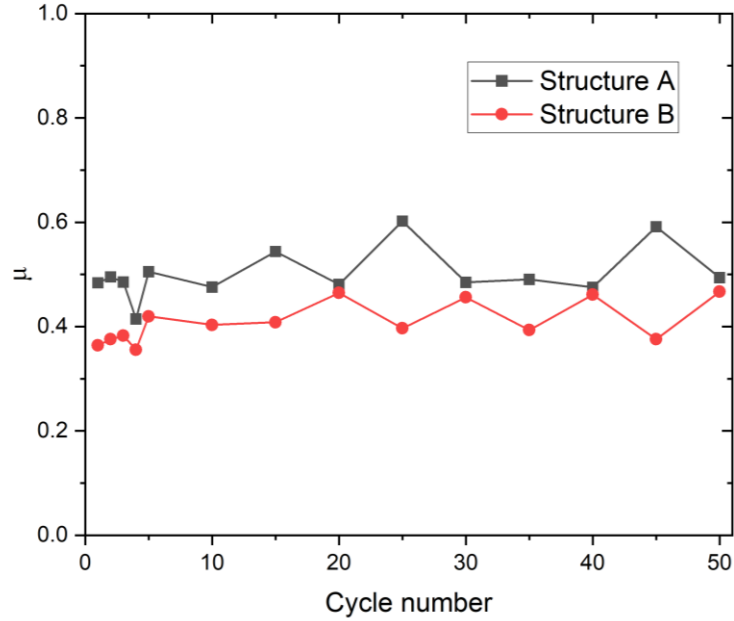


Figure 5.26 - Average friction coefficient of tested moth-eye samples for Structure A and B.

As shown in Figure 5.26, the same trend in the frictional behavior was also detected for both tested structures, as the friction coefficient increases and decreases successively. This occurrence can be justified by the same reasons as in the previous tests, which correspond to the test setup and the initial fracture direction of the structures. The wear resistance of both types of structures has also been investigated. A visual inspection of the samples which contain structures B revealed the lack of a visual test track, contrary to the samples with structures A, which presented wear tracks similar to the ones showed in Figure 5.9. The SEM analysis of samples with structures B also revealed the absence of wear on the sample's surface for all test cycles, whereas for structures A the wear was similar to the structures presented in Chapter 5.3, as shown in Figure 5.27.

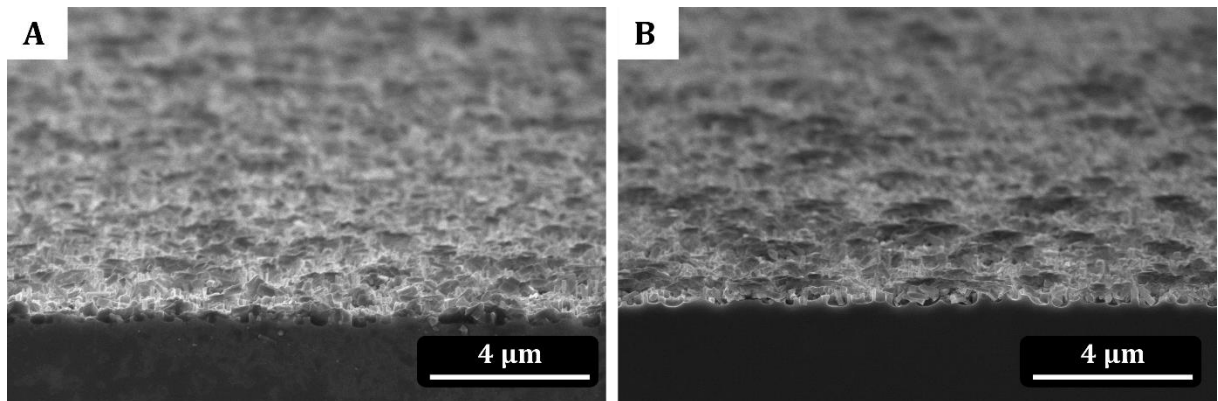


Figure 5.27 - SEM cross-section image of sample with structure A tested for 0.1 N and (A) 1 cycle and (B) 50 cycles.

6. CONCLUDING REMARKS

6.1. SUMMARY AND CONCLUSIONS

The presented work aims to provide a thorough tribological analysis of the frictional behavior of nanostructured surfaces with AR properties, which are intended to be placed on the top surface of solar modules. In addition, a brief review of AR strategies for solar cells was performed, particularly regarding the addition of nanostructures to the top surface, with emphasis on the moth-eye pattern. These bio-inspired nanostructures enable a broadband, omnidirectional and angle-independent AR, which results from a gradually changing refractive index, as light travels from air to the bottom of the structures. For this study, the moth-eye nanostructures were obtained through nanoimprint lithography, in a cleanroom environment, being fabricated in silicon substrates. As these structures work best when placed on the outside of a solar panel, it is worth characterizing their behavior in terms of weariness.

It was proposed to perform a tribological characterization of the moth-eye texturization, by conducting friction tests for different loads, as well as for various test cycles. Prior to these tests, it is necessary to perform an optical characterization, through a UV-vis spectrophotometer, ensuring they possess the desired AR properties. Additionally, a morphological characterization is required to compare the structures before and after tribological testing. This was achieved through techniques such as SEM and SEM-EDS, as well as through optical microscopy. Further morphological characterization was performed, through the calculation of several surface roughness parameters (R_a , R_q , R_t , R_v , R_p), which can greatly influence the frictional behavior of a surface, as well as contact angle measurements, which revealed that these structures can be regarded as hydrophobic.

Regarding the tribological characterization, the samples were submitted to two loads, 0.1 N and 0.5 N, applied through a spherical 5 mm radius counterface. For both loads, various test cycles were defined, being performed for 1 to 50 cycles. These parameters were established with the purpose of analyzing the behavior of the structures when exposed to successive degradation, as well as to study the effect of the applied load. The friction data resulting from these tests consists of the variation of the friction coefficient with the test time. The results from these tests revealed that the friction coefficient variation curves possess a repetitive morphology, being characterized by two phases, an initial pre-sliding phase and a posterior sliding phase, in which the movement has effectively begun, and the friction coefficient has stabilized. For the lower load (0.1 N), the pre-sliding phase has revealed to be shorter than for the higher load (0.5 N). This longer pre-sliding phase derives from a more mechanically aggressive interaction

between the counterface's surface and the sample's asperities, which correspond to the moth-eye nanostructures. This leads to the formation of an intermediate rough surface, which translates into a delay of the polishing mechanism, which is verified for the successive test cycles.

The lower load tests have shown that for 2 cycles, the friction coefficient increases, a phenomenon which is common at the nanoscale and can be justified by the increased true area of contact, a result of the fracture and deformation of the structures during the first cycle. When analyzing the friction coefficient values, it is possible to detect an increase of the friction coefficient for 15 cycles, a point from which the friction coefficient values maintained within the 0.50 ± 2 range. This increase is justified by the predominance of an adhesion mechanism, as iron from the counterface was detected on the sample's surface through SEM-EDS.

The higher load tests revealed that contrary to the lower load, the 2-cycle tests revealed a decrease in friction, due to the previously explained phenomenon, regarding the formation of an intermediate rough surface, as the more mechanically aggressive interaction led to a decrease of the true area of contact. For these tests, an adhesion mechanism predominates in all test cycles, as the presence of iron from the counterface has been detected for all test cycles, explaining the higher friction coefficient values, in comparison with the lower load tests. For lower test cycles, it was detected that the adhesion and compression of the structures was mainly located at the center of the test track, manifested by the presence of plateaus on the surface. These plateaus were the result of a polishing mechanism, provoked by the trapping of fractures structures in the interstices between pillars. Through the analysis of SEM images throughout the test cycles, it was verified that both features appeared to also be more prominent on the sides of the tracks with the increase of the number of cycles. Furthermore, a broad inspection of the friction coefficient variation revealed a trend in its behavior, showing an increase for odd cycle numbers and a decrease for even cycle number. This could be justified by the type of test setup, namely due to a tilt of the sample, or could also be due to the initial fracture direction of the structures, which implies a larger resistance of the structures when performing the returning movements.

Through optical microscopy, a correlation between the number of cycles, the width of the test track and the applied load has been verified. Thus, it was possible to conclude that the test track width gradually increased with the number of cycles for both applied loads, presenting smaller widths for the lower load tests, in comparison to the higher load tests. This increase of width between both loads was expected, as there is a higher sinking of the test counterface when a higher load is applied. The increase of width with the number for cycles could have been caused by the counterface, which could be performing slightly different paths when passing back and forth, leading to the increase of width as the number of cycles

increases. Moreover, it could have also been caused by accumulation of worn material from the nanostructures, leading to increasingly wider test tracks as the number of cycles increases.

Moreover, through a recalibration of the nanofabrication procedure, different moth-eye structures were obtained, consisting of (A) individual and (B) agglomerated pillars, with average heights of 578 ± 58 nm and 290 ± 34 nm, respectively, and average pillar diameters of 163 ± 65 nm and 509 ± 218 nm, respectively. These structures present identical optical performances, as the difference between each reflectance spectra is approximately equal to 1 PP. This means that an ideal structure can be selected based solely on their tribological behaviors, which will differ due to their very different morphologies. As a part of the morphological characterization, the roughness parameters were calculated for both structures, being concluded that structures B confer a lower roughness to the surface, presenting an average R_a of 138 nm, whereas structures A confer an average R_a of 250 nm. Based on this analysis, it was predicted that structures B would confer better tribological properties to the surface, due to their lower roughness, namely a lower tendency for fatigue and higher corrosion resistance.

Regarding the tribological testing of both structures, a load of 0.1 N was applied for 1 to 50 cycles. Similarly to the previous tests, the employed equipment was a tribometer and a spherical 5 mm radius counterface was utilized. The results of these experiments revealed that structures B showcased lower friction coefficient values, with the maximum friction values being obtained for 50 cycles. Structures A presented the highest friction values during the 25-cycles tests. Similarly to the previous tests, a trend in the frictional behavior of both structures was also detected, which can be justified by the same reasons, namely the type of test setup and the initial fracture direction of the structures.

Lastly, it was concluded that besides providing lower friction, structure B also possesses a higher wear resistance, as no visible wear was detected on the sample's surface. Contrary to these structures, surfaces with structures A showcased nitid wear tracks, similar to the presented results in the initial study performed for similar structures.

Overall, the objectives of this study were accomplished, as a tribological characterization of the moth-eye structures was performed. The results from this study are in accordance with previous experiments found in literature, for similar structures, and are in agreement with theoretical concepts. In spite of the fact that the outcomes from this study constitute preliminary results, they allow the understanding of the tribological behavior of the nanostructures when contacting with another surface. In summary, it could be concluded that the height and roughness of the nanostructures plays an important role regarding the wear, as it was found that the initial contact against a counterbody leads to fracture, which marks the presence of degradation mechanisms. This indicates that a longer lifetime of the

structures can be achieved with the increase of the fracture resistance, which is possible with the employment of shorter structures. This statement is supported by the experiments performed in this work, as the shorter structures showcased the absence of degradation, even after 50 cycles of repetitive relative sliding with a steel counterface, and still confer the desired anti-reflection properties. Therefore, this study comprises results which are beneficial for the prediction of the wear of these structures and enable structural optimizations. Moreover, the results drawn from this study could provide valuable insights into the cleaning processes of the nanostructured surfaces, namely regarding their susceptibility to damage, which could be assessed through the analysis of the adhesive properties of the structures. This study demonstrated that the moth-eye structures could allow the presence of adhesion, as it was found that iron from the test counterface was detected on tested surfaces. Hence, further testing would be required to better assess the ideal approach to the cleaning of these surfaces. Additional conclusions could also be drawn from this study, such as that the degradation caused to these nanostructures influences the nearby areas, as the contact time increases, proving that their wear is not a localized phenomenon. The increase of the applied load appeared to aggravate this phenomenon, leading to a larger affected area of the nearby nanostructures. This could indicate that when the nanostructures are applied on solar modules, the successive wear caused during their operational period could majorly affect the performance of this technology, even if the wear is applied on only the same point. It is important to remark that this study is still in its early stages, and that further research regarding the tribological behavior of nanostructured surfaces could still be performed.

6.2. CONTRIBUTIONS

This study provided a general overview of the benefits of nanostructured surfaces, namely regarding the anti-reflection properties which are conferred by its implementation. Additionally, a review of wear and friction-enhancing strategies which involve the addition of nanostructures is provided, highlighting the low friction and wear properties, in comparison with smooth surfaces.

An industry-friendly fabrication process for the development of nanostructured surfaces was described, being also presented an overview of advanced characterization techniques adequate for such nanoscale architectures.

A brief review of relevant friction models was conducted, highlighting the continuous improvement of the models over the years, as well as of several wear mechanisms, which greatly influence the lifetime of nanostructured surfaces.

Lastly, a comprehensive tribological characterization of bio-inspired anti-reflective nanostructured surfaces was performed. For this, a sample holder was developed, as well as a systematic testing procedure, which establishes comparison parameters and enables the analysis of wear and frictional behavior.

6.3. FUTURE WORK

The tribological characterization of nanostructured surfaces is an area which holds significant promise, as advancements in nanotechnology are continuously made. Understanding friction and wear can be crucial to enhance the performance and lifespan of nanostructured materials. Hence, it would be valuable to continue the investigations carried out in this study, through the utilization of test counterfaces with different geometries, materials, sliding velocities and applied loads. Further characterization of the moth-eye nanostructures could also be performed, namely regarding their mechanical properties. This could be achieved by the employment of other types of tests, such as fatigue testing, as well as compressive and impact tests, aiming to evaluate the resilience of the nanostructures under loading conditions. For these tests, it would be of relevance to employ loads which are similar to those to which the nanostructures could be exposed when implemented on the top surface of the solar modules.

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APPENDICES

APPENDIX A: CHARACTERIZATION OF THE MOTH-EYE TEXTURIZATION

Additional SEM images of the moth-eye texturization are showcased in Figure A.1, Figure A.2, Figure A.3 and Figure A.4.

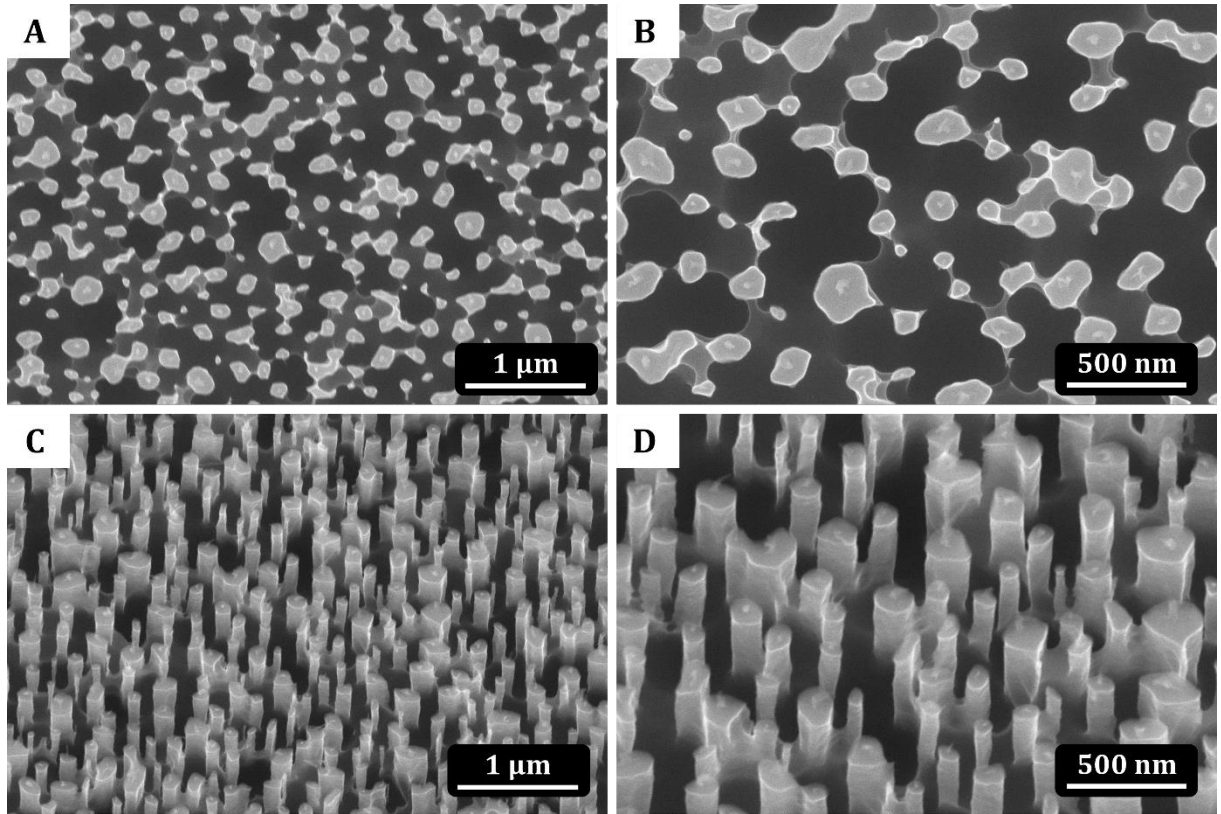


Figure A.1 - SEM images of moth eye nanostructures from a (A) top view and a HFW of 5 μm, (B) top view and a HFW of 2.5 μm, (C) 30° tilt and a HFW of 5 μm and (D) 30° tilt and a HFW of 2.5 μm.

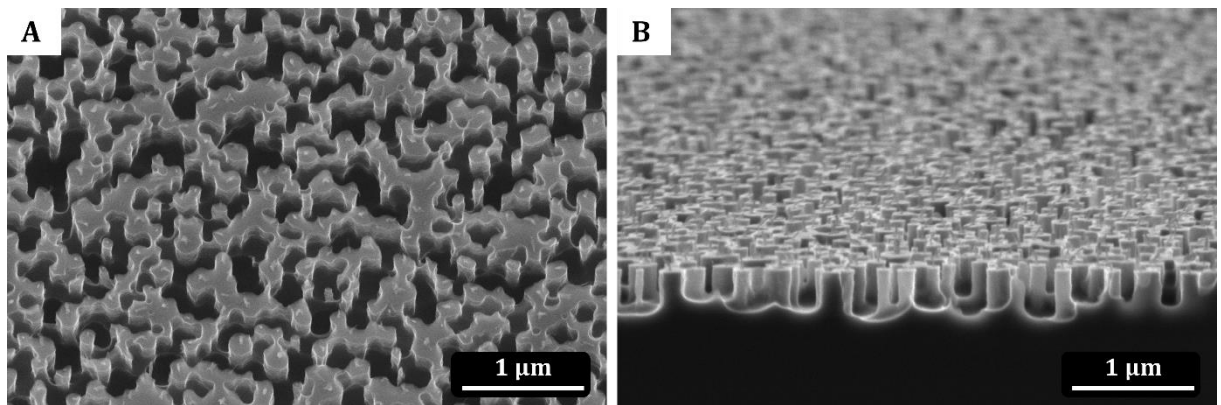


Figure A.2 - SEM images of moth-eye nanostructured surfaces with structure B with a (A) 30° tilt and (B) from a cross-section view and a -10° tilt.

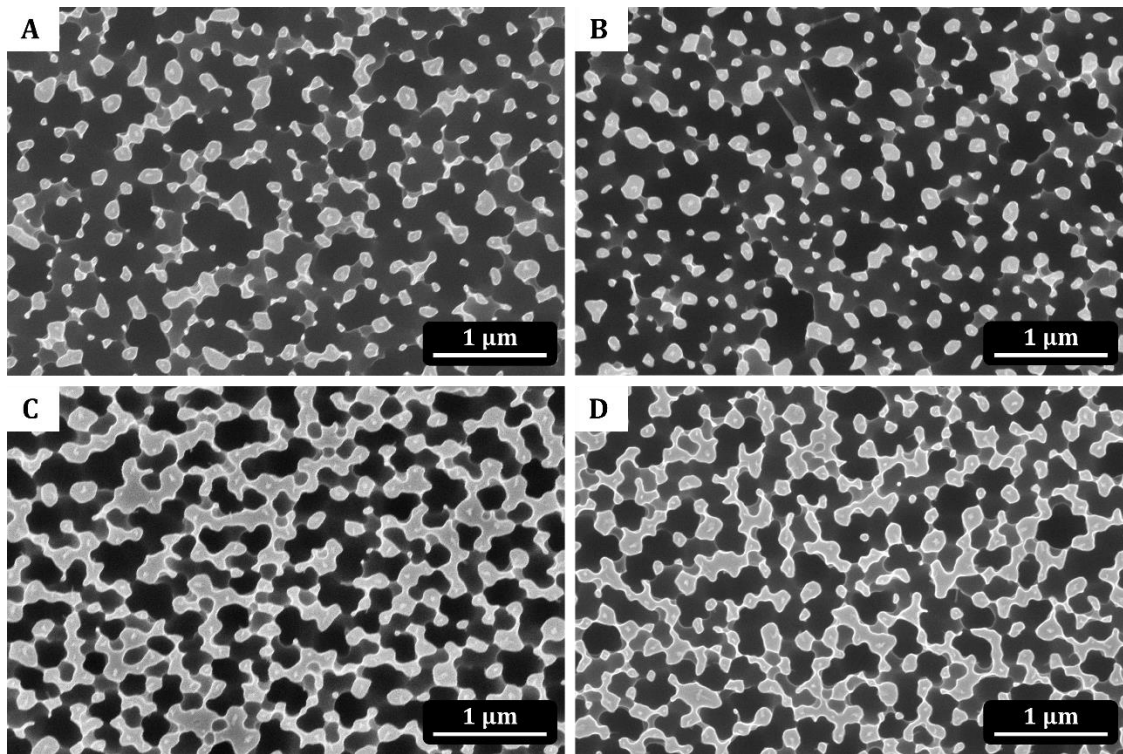


Figure A.3 - SEM top view images of moth-eye nanostructured samples with (A) and (B) structure A and (C) and (D) structure B.

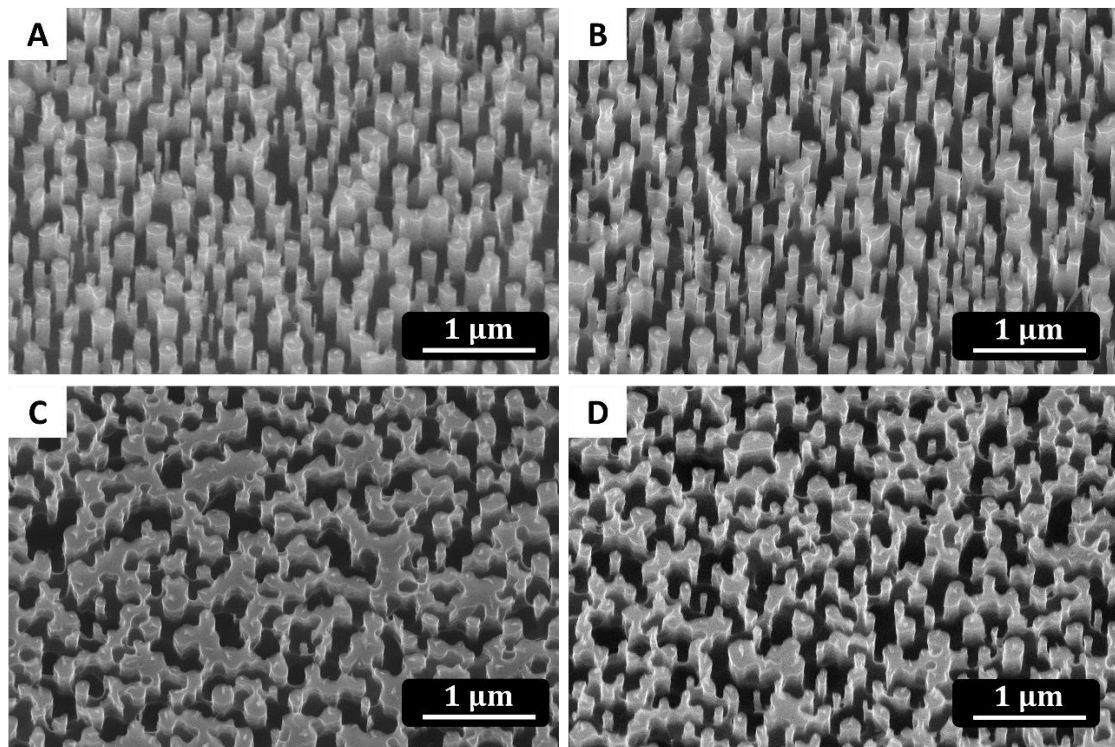


Figure A.4 - SEM images with a 30° tilt of moth-eye nanostructured samples with (A) and (B) structure A and (C) and (D) structure B.

The average diameters of the nanofabricated moth-eye structures A and B were obtained through 30 measurements, which are presented in Table A.1.

Table A.1 - Measurements of the diameter of pillars from structure A and B.

Diameter of the pillars (nm)		
	Structure A	Structure B
1	225	487
2	243	208
3	204	654
4	220	227
5	208	681
6	191	207
7	257	265
8	148	498
9	145	778
10	118	383
11	192	621
12	147	654
13	164	532
14	129	1038
15	135	163
16	68	520
17	152	782
18	229	443
19	100	487
20	78	664
21	121	522
22	393	660
23	116	399
24	158	207
25	121	140
26	143	525
27	152	391
28	106	573
29	111	716
30	107	836

APPENDIX B: ROUGHNESS CALCULATIONS

As previously mentioned, the roughness calculations were performed with the aid of a *Matlab* code, which is presented below, in Figure B.1, Figure B.2 and Figure B.3.

```
clear all
close all
clc

% Ask the user to select an image in the .tif format
[filename, pathname] = uigetfile('*.tif', 'Select the .tif image');
filepath = fullfile(pathname, filename);

% Verify if the user selected an archive
if filename == 0
    error('No selected image.');
```

end

```
% Read the image
img = imread(filepath);

% Convert the grey scale if the image is colored
if size(img, 3) == 3
    img = rgb2gray(img);
end

% Show the image
figure;
imshow(img);
title('Draw a line on the image scale');
```

```
% Allow the user to draw a line on the image scale
hScale = images.roi.Line;
positionScale = wait(hScale); % Wait until the user finishes the scale line

% Ask the user the real length of the drawn line
prompt = {'Type the real length of the drawn line (nm):'};
dlgtitle = 'Define the real length';
dims = [1 35];
definput = {'100'}; % Standard value
answer = inputdlg(prompt, dlgtitle, dims, definput);

% Convert the user input to a number
realLength = str2double(answer{1});

% Calculate the scale in the x axis
%numPointsScale = size(get(hScale, 'Position'), 1);
scaleLength = sqrt((positionScale(2,1) - positionScale(1,1))^2 +
    (positionScale(2,2) - positionScale(1,2))^2);
xScaleFactor = realLength / scaleLength;

% Show the image again
figure;
```

Figure B.1 – *Matlab* code developed to calculate the roughness of the moth-eye texturization

```

imshow(img);
title('Draw a line on the image for analysis');

% Allow the user to draw line on the image for analysis
hTrace = imline;
positionTrace = wait(hTrace); % Wait until the user finishes the scale line

% Obtain the coordinates of the points along the drawn line
xTrace = positionTrace(:,1);
yTrace = positionTrace(:,2);

% Obtain the grey scale values along the drawn line
numPoints = 3000; % Number of points along the drawn line
xi = linspace(xTrace(1), xTrace(2), numPoints);
yi = linspace(yTrace(1), yTrace(2), numPoints);
TraceLength = sqrt((xTrace(2) - xTrace(1))^2 + (yTrace(2) - yTrace(1))^2);

% Interpolate the grey scale values along the drawn line
grayValues = improfile(img, xi, yi);

% Calculate the x position along the drawn line using the scale factor
x_positions = linspace(0, TraceLength, numPoints) * xScaleFactor;

% Show the grey scale values along the drawn line
figure;
plot(x_positions, grayValues, '-');
xlabel('Position along the line (nm)');
ylabel('Grey scale value');
title('Grey scale value along the line');
hold on;

% Allow the user to select rectangular sections
disp('Select areas long the line to calculate the average grey scale values
(first the minimum values and then the maximums).');
disp('Press Enter when the selection is finished.');
```

```

regionMeans = [];
while true
    h = imrect;
    position = wait(h);

    if isempty(position)
        break;
    end

    % Determine the index from the points within the selected regions
    x1 = position(1);
    width = position(3);

    % Convert the position in the x scale
    [~, startIndex] = min(abs(x_positions - x1));
    [~, endIndex] = min(abs(x_positions - (x1 + width)));

    % Calculate the average grey scale values of the region

```

Figure B.2 - *Matlab* code developed to calculate the roughness of the moth-eye texturization (continuation).

```

regionMean = mean(grayValues(startIndex:endIndex));
regionMeans = [regionMeans; regionMean];

% Plot the average of the region on a graph
plot(x_positions(startIndex:endIndex), repmat(regionMean, 1, endIndex-
startIndex+1), 'r', 'LineWidth', 2);

%     keypressed = getkey;
%     if keypressed == 13; break; end

end

hold off;

% Show the average of the regions
disp('Average grey scale values on the selected regions:');
disp(regionMeans);

Mean_lim = input('How many minimum regions have been selected? ');

Mean_min = mean(regionMeans(1:Mean_lim));
Mean_max = mean(regionMeans(Mean_lim+1:end));

Min_roughness = 0; % nm
Max_roughness = 578.1643; % nm

HeightValues = (grayValues - Mean_min + Min_roughness) * (Max_roughness-
Min_roughness)/(Mean_max-Mean_min);

figure;
plot(x_positions, HeightValues, '-');
xlabel('Position along the line (nm)');
ylabel('Height (nm)');
title('Height (Cross section)');
hold on;

zj = HeightValues;
z_mean = mean(zj);
rj = zj - z_mean;

Ra = (1 / numPoints) * sum(abs(rj)); % Arithmetical mean deviation. The
average deviation of all points roughness profile from a mean line over the
evaluation length
disp('Roughness parameters:');
fprintf('Ra = %g\n', Ra)

Rq = sqrt((1 / numPoints) * sum(rj.^2)); % The average of the measured height
deviations taken within the evaluation length and measured from the mean line
fprintf('Rq = %g\n', Rq)

Rt = abs(min(rj)) + abs(max(rj)); % Maximum peak-to-peak-valley height. The
absolute value between the highest and lowest peaks
fprintf('Rt = %g\n', Rt)

Rv = abs(min(rj)); % Lowest valley. This is the depth of the deepest valley
in the roughness profile over the evaluation length
fprintf('Rv = %g\n', Rv)

Rp = abs(max(rj)); % Highest peak. This is the height of the highest peak in
the roughness profile over the evaluation length
fprintf('Rp = %g\n', Rp)

```

Figure B.3 - *Matlab* code developed to calculate the roughness of the moth-eye texturization (continuation).

A step-by-step illustration of the roughness calculation is provided by Figure B.4 and Figure B.5.

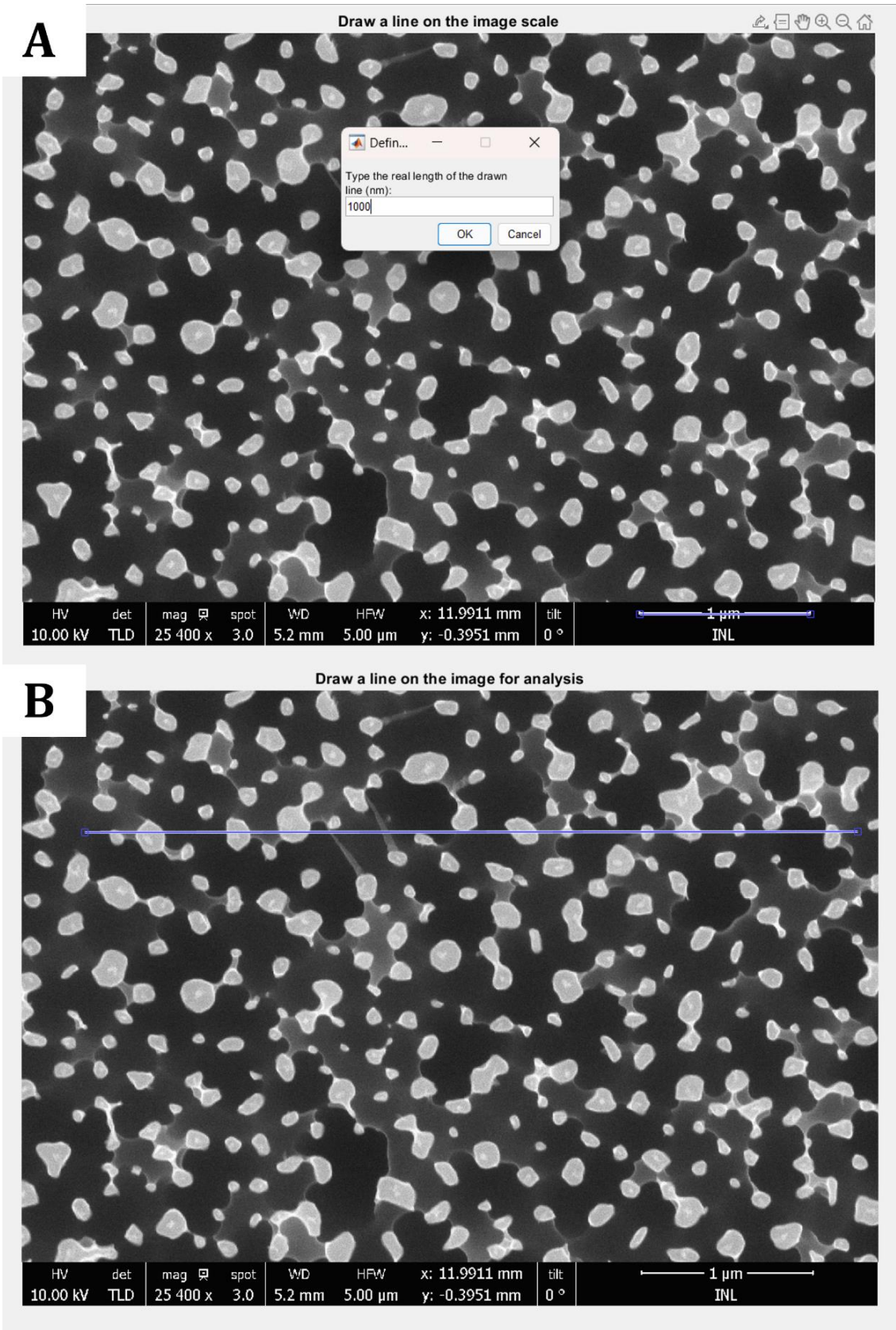


Figure B.4 - Execution of the *matlab* generated code. (A) showcases the input of the image and the selection of the scale. (B) illustrates the row of pillars which will be analyzed.

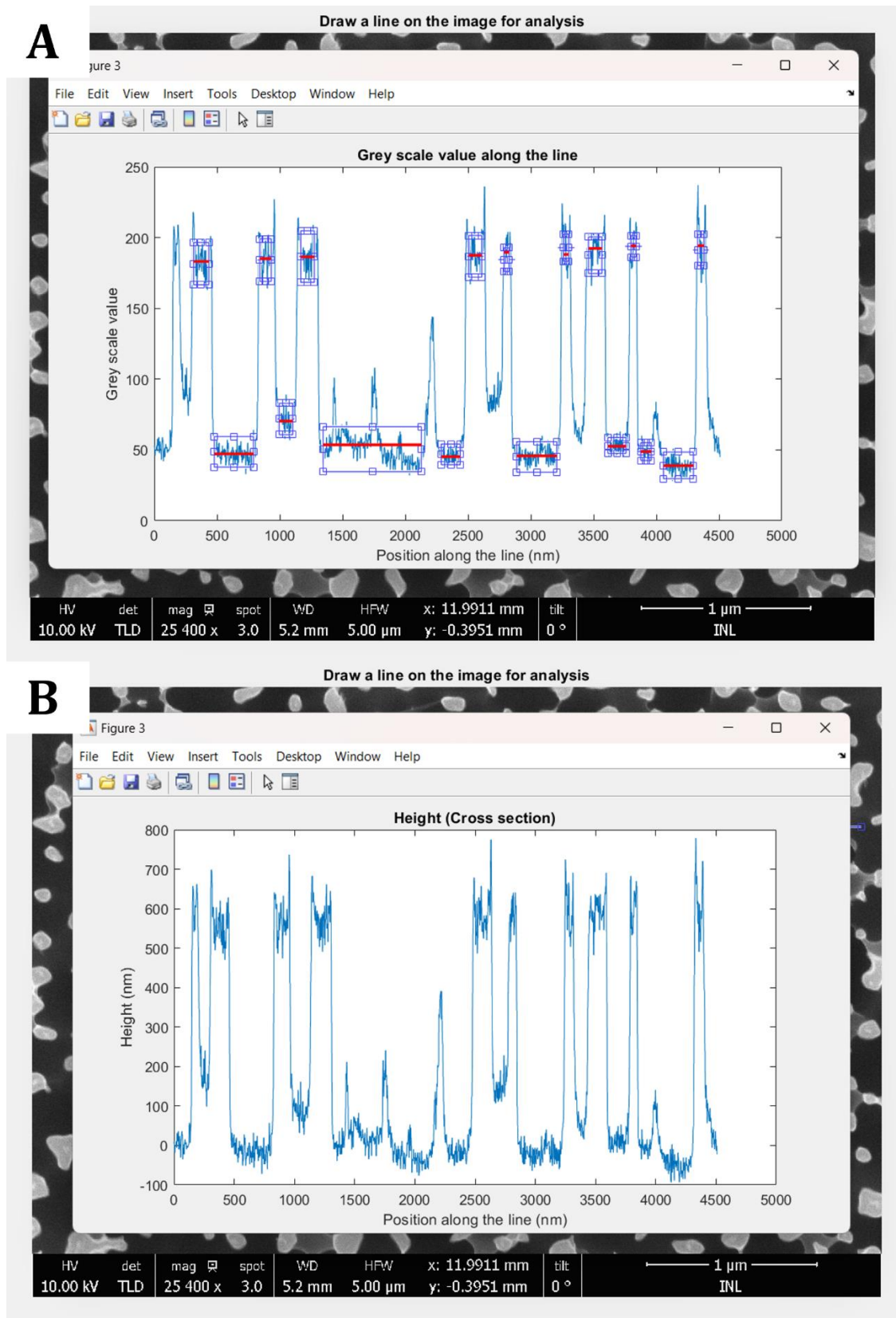


Figure B.5 - Execution of the *matlab* generated code. (A) showcases the selection of minimum and maximum values, which will be correlated with the actual height values. (B) presents the corrected surface profile, which will be utilized to calculate the roughness parameters.

The results of the 30 performed measurements for Structure A and B are included in Table B.1 and Table B.2, respectively.

Table B.1 - Results of the performed roughness measurements for Structure A.

	R_a	R_q	R_t	R_v	R_p
1	276.606	294.171	926.495	341.814	584.682
2	253.837	271.316	858.590	297.037	561.553
3	246.196	272.067	946.240	287.498	658.741
4	231.872	256.622	854.546	287.941	566.605
5	249.449	270.379	846.262	320.074	526.188
6	222.738	254.719	880.215	269.934	610.281
7	221.157	245.407	890.643	259.285	631.358
8	268.270	283.702	915.680	334.190	581.490
9	254.330	274.703	906.716	317.735	588.981
10	248.106	271.895	952.466	316.326	636.141
11	241.231	274.900	911.824	319.734	592.090
12	237.879	269.295	944.922	292.266	652.656
13	230.452	260.153	1004.620	292.261	712.363
14	266.933	292.796	1030.700	394.080	636.621
15	246.973	270.688	1092.870	311.400	781.474
16	245.962	271.510	930.628	290.016	640.612
17	225.702	256.718	874.095	279.155	594.940
18	252.843	276.139	974.417	388.963	585.454
19	241.234	270.113	989.763	278.981	710.781
20	279.610	298.663	1044.120	392.337	651.779
21	240.795	274.292	978.458	313.671	664.787
22	258.766	322.586	1301.740	539.201	762.538
23	240.222	261.069	843.922	308.980	534.942
24	275.286	290.370	935.068	377.477	557.591
25	242.266	277.746	1019.720	379.250	640.472
26	256.935	307.728	1303.000	455.575	847.423
27	271.398	296.690	1117.250	350.638	766.616
28	265.982	295.317	1046.430	324.190	722.242
29	263.009	291.264	1031.540	417.203	614.335
30	261.751	294.126	1019.340	376.579	642.757

Table B.2 - Results of the performed roughness measurements for Structure B.

	R_a	R_q	R_t	R_v	R_p
1	134.355	149.337	554.087	194.920	359.168
2	138.871	154.586	540.043	202.194	337.849
3	143.121	158.784	558.202	183.761	374.441
4	132.030	155.277	604.352	249.712	354.640
5	149.805	174.663	687.071	254.618	432.453
6	134.553	157.402	653.858	207.544	446.314
7	137.527	156.072	524.616	216.960	307.656
8	129.150	143.226	498.837	180.770	318.067
9	133.392	161.327	663.546	274.325	389.221
10	162.642	190.293	724.231	264.031	460.199
11	133.583	158.516	613.838	259.673	354.165
12	132.179	148.917	532.554	170.217	362.337
13	138.223	157.281	608.385	204.301	404.084
14	148.403	168.857	635.848	207.118	428.730
15	143.678	175.507	714.203	285.152	429.051
16	134.969	149.388	497.000	196.144	300.856
17	135.566	161.595	689.221	235.327	453.894
18	138.173	157.017	620.821	183.844	436.977
19	123.834	154.051	673.523	299.524	373.999
20	130.523	148.593	558.991	212.993	345.998
21	147.032	166.570	618.986	192.430	426.557
22	141.895	169.688	672.797	212.815	459.981
23	148.319	168.109	597.295	243.817	353.478
24	127.213	145.104	571.724	171.605	400.119
25	146.467	163.422	547.545	223.493	324.052
26	136.040	151.979	544.918	189.567	355.351
27	135.388	153.246	552.331	199.298	353.033
28	150.083	191.002	957.352	369.719	587.633
29	121.552	157.587	657.150	286.425	370.726
30	144.302	160.764	562.887	219.417	343.470

APPENDIX C: OPTICAL MICROSCOPY MEASUREMENTS

Table C.1 and Table C.2 contain the measurements of the test track width for tests performed with 0.1 N and 0.5 N, respectively.

Table C.1 - Test track width measurements of tests performed with 0.1 N.

	Number of cycles				
	1	2	3	15	50
1	113.02	132.20	179.94	232.73	250.28
2	118.05	141.08	178.07	213.29	257.20
3	124.29	150.22	140.86	200.58	252.41
4	124.32	132.92	174.68	218.57	229.17
5	104.37	140.35	159.79	171.56	260.35
6	105.09	140.13	156.44	207.05	253.13
7	107.49	132.45	137.91	208.03	232.74
8	109.41	133.40	110.90	236.81	264.39
9	110.37	152.35	157.64	189.54	257.94
10	114.47	148.51	155.78	178.27	259.12

Table C.2 - Test path width measurements of tests performed with 0.5 N.

	Number of cycles				
	1	2	3	15	50
1	167.47	210.18	235.61	363.04	333.02
2	161.27	232.52	238.01	366.22	368.76
3	153.07	214.97	276.47	377.88	379.81
4	157.88	293.19	258.64	369.27	398.28
5	159.55	299.03	231.10	376.95	400.02
6	161.72	199.40	272.58	369.59	410.29
7	162.43	186.45	284.81	317.69	404.75
8	175.88	232.51	293.91	314.81	403.80
9	148.53	223.13	308.82	297.81	405.71
10	154.34	194.36	299.00	284.08	376.20

APPENDIX D: PRE-SLIDING MEASUREMENTS

The values resulting from the measurements of the pre-sliding phase length of the friction coefficient variation for both tested loads (0.1 N and 0.5 N) are contained in Table D.1.

Table D.1 - Measurements of the pre-sliding phase durations for 0.1 N and 0.5 N.

	Time (seconds)	
	0.1 N	0.5 N
1	1.048	1.533
2	1.371	2.258
3	1.442	2.631
4	1.572	2.731
5	2.025	2.803
6	0.232	2.309
7	2.580	2.609
8	2.591	2.451
9	2.520	3.054
10	2.510	1.018
11	2.561	2.147
12	1.240	0.645
13	1.209	1.301
14	1.744	1.311
15	2.220	2.614