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## Sustainability Assessment of Plasma-Assisted Processes for Thin Film Deposition in Space Applications

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### Abstract

In the next years, humankind will return to the Moon. The future of space exploration will allow for the settlement of space bases to study our natural satellite in more detail and prepare for trips to Mars. The coordination of international efforts from different space agencies is required to prepare for this new phase of space exploration. As part of the ESA's (Terra Novae) exploration program and in the context of the ESA's program for exploration, research, and technology (ExPeRT), initiatives named Spaceship have been created in several countries (Germany, England, and France). These innovation environments facilitate the study of new operational concepts and new technologies, with the support of expert engineers, astronauts, and a large-scale network of researchers. As part of this approach, Spaceship FR from the French agency – CNES plays a pivotal role in preparing for the future of space exploration and fostering technologies that can find also many application and inputs on Earth. Within the context of Spaceship FR objectives, this study analyses plasma-assisted technologies for thin film deposition, addressing numerous challenges inherent in lunar exploration and settlement. Emphasizing the efficiency of aerosol-assisted plasmas, particularly in the application of multifunctional coatings, this paper provides a comprehensive review. Special attention is given to the material balance of the global process, emphasizing strategies to optimize sustainability during the deposition phase. Additionally, the economic benefit – cost analysis associated with improved material balance are discussed.

**Keywords:** coatings, thin films, plasma processes, sustainability

### Acronyms/Abbreviations

Atomic Oxygen (AO)  
Centre National d'Études Spatiales (CNES)  
Corporate Social Responsibility (CSR)  
Chemical Vapor Deposition (CVD)  
Diamond-Like Carbon (DLC)  
Direct Liquid Reactor Injector (DLRI)  
European Space Agency (ESA)  
Environmental, Social, and Governance (ESG)  
European Union (EU)  
Hazardous air pollutant (HAP)  
National Aeronautics and Space Administration (NASA)  
Perfluoroalkyl (PFA)  
Plasma-enhanced Chemical Vapor Deposition (PE-CVD)  
Physical Vapor Deposition (PVD)  
Pulsed, Direct Liquid Injection (PDLI)  
Registration, Evaluation, Authorization and Restriction of Chemicals (REACH)  
Scanning Electron Microscope (SEM)  
Sustainable Development Goal (SDG)  
United Nations (UN)

Ultraviolet (UV)  
Volatile Organic Compound (VOC)

### 1. Introduction

In recent years, the space industry has experienced unprecedented growth [1], [2]. This expansion is driven by several factors, including the Artemis program's mission to return to the Moon and the renewed space race involving major players like United States of America, China and Russia [3], [4]. These efforts are pushing for technological innovations that will also support future missions to Mars. Additionally, the private sector's interest is playing a significant role; companies are investing across various domains, fostering the apparition of vibrant ecosystems like the one defined as "New Space" economy [5]. Overall, the global space market is projected to reach \$1.8 trillion by 2035, with an annual growth rate of 9% [1].

As the sector continues to expand, the need for versatile systems that can meet a variety of new innovation policies and their evolving requirements has become essential [6]. To remain competitive in the

current space market and drive disruptive innovation, new technologies enhancing profitability and efficiency become crucial. To understand the significance of these advancements, we must first define what it means to design a system for value in the context of modern space exploration. This approach not only focuses on maximizing the performance and durability of space systems but also ensures their alignment with long-term sustainability goals.

In this review, the concept of designing for value in response to modern space challenges is applied to practical scenarios. Specifically, the objective is to analyse which materials, particularly coatings, can enhance the performance of space systems and support longer, more frequent space missions.

Coatings or, more generally, surface functionalization, aims to bring specific properties to any type of substrate by modifying and/or improving surface performance, or by conferring new functionalities. These methods can be used in many space applications: for the modification or the optimization of the propagation of an electromagnetic field, the adaptation of the thermo-optical properties, the formation of selective optical filters, the development of antistatic and/or charge flow coatings, the electrical bonding on mechanical parts, the improvement of tribological properties (friction, hardening, adhesion) in extreme environments, the development of sensors (pressure, contamination, air and water, etc.), the prevention of the contamination by antibacterial surfaces, the formation of super-hydrophobic and/or oleophobic surfaces to prevent water condensation, icing and/or the lubricant management, the modification of surface reactivity and the formation of barrier layers with a focus on environmental sustainability [7].

This review compares various types of functional coatings and deposition methods, emphasizing their value in addressing the diverse challenges of the space sector, including sustainability. In particular, chemical deposition methods—such as painting, chemical deposition processes, and plasma-assisted techniques—and their resulting deposited coatings, including multi-functional nanocomposite thin films, are examined in greater details. Their main characteristics are explored for their potential use in the space industry as a way to address the sector's multiple demands.

## 2. Aerospace system structures and aging

### 2.1 Materials in system design

Before discussing coating materials, it is important to first examine the materials commonly used in space systems structures to better understand the need for functionalization.

To appreciate how structural materials can be chosen and combined in a system, it is helpful to trace the

evolution of materials used in aeronautics, which laid the groundwork for those employed in modern spacecraft. In less than a century, airplanes evolved from being constructed with wood, wire, and fabrics to becoming high-tech machines built from advanced materials. Recognizing aviation's potential to revolutionize commercial transport, the industry embarked on a path of material evolution as early as the beginning of the 20th century. Starting with Hugo Junkers' J 1 prototype of the first full metal aircraft, this progress focused on making aircraft stronger, lighter, faster, and more efficient. In time, steel alloys were progressively flanked by aluminium alloys and then titanium. The advantages and disadvantages of these materials can be summarized as follows [8]:

- Aluminium Alloys: low cost, easily malleable and machinable, but weakens under stress and warps at high temperatures;
- Steel Alloys: Stronger and stiffer, but heavier and less resistant to corrosion;
- Titanium Alloys: high heat resistance, lightweight, more corrosion-resistant, tough, and easily malleable and machinable, but very expensive.

Starting from the 1970's, composite materials began to be incorporated in aircraft manufacturing, with the goal of reducing the weight of the airplanes while still improving performance. These materials consist of a matrix reinforced with fibres, often of carbon or glass. The advantages and disadvantages of composite materials are [8]:

- Composite materials: lightweight, good fatigue resistance, corrosion-resistant, and easily malleable but sensitive to impacts and perforations, prone to aging in humid conditions, poor lightning resistance, and costly.

For their characteristics, all of these components are and need to be used in today's commercial airplanes, to compromise between important requirements like weight, reliability, durability and prize of access and procurement ease. A trade-off in the distribution of these materials is part of the design choices that needs to be accomplished when building an airplane. An example of how this is done in commercial airplanes is shown in Fig. 1, which illustrates the material distribution in a Dreamliner. This diagram points out design decisions such as limiting the use of steel, a material that, while highly durable, is heavy and has a temperature-dependent expansion coefficient. A quantitative summary of what material compose a few examples of commercial airplanes can be found in Tab. 1, highlighting the families of materials that are often used in aeronautics.

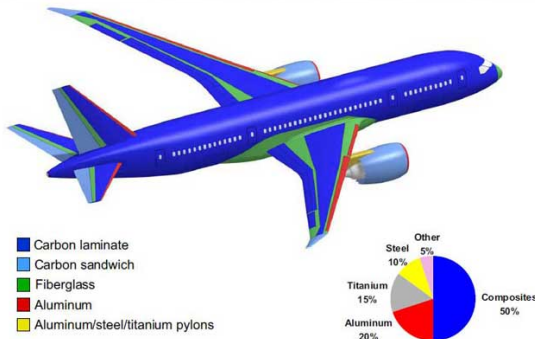


Fig. 1. Distribution of materials on the Boeing 787 Dreamliner [9].

Con-structor	Model	Al	Ti	Steel	Compo-sites	Others
Boeing	767	81%	14%	2%	3%	<1%
Airbus	A320	72%	6%	9%	10%	3%
Airbus	A350	19%	14%	6%	54%	7%
Boeing	Dreamliner	20%	15%	10%	50%	5%

Table 1. Examples of new materials use in commercial airplanes [9], [10], [11], [12].

With respect to airplanes, spacecraft systems need, most of the time, to resist even harsher conditions. It is no wonder that depending on the type of mission, a more complex combination of elements is needed. Although, some of the most common structure elements are shared with aeronautics [13]. In a spacecraft system, one can expect to find [14], [15]:

- Aluminium Alloys (e.g., 2024, 6061, 7075): as for aviation, common for structural components, good strength, low weight, and ease of manufacturing;
- Heat-resistant Alloys (e.g., Inconel 718, A-286): excellent tensile strength and heat resistance.
- Ferrous alloys: (e. g. stainless steel): ferromagnetic, higher thermal resistance, high strength and toughness.
- Magnesium: low density and good vibration damping, though prone to corrosion.
- Titanium (e.g. Ti-6Al-4V): as for aviation, appreciated for its high strength, lightweight, and corrosion resistance.
- Beryllium: very high specific rigidity but is restricted due to toxicity;
- Composite materials (e. g. Graphite/Epoxy, Aramid/Epoxy or Glass/Epoxy): offer customizability in strength, rigidity, and thermal expansion, and are versatile and widely used in spacecraft for their tailored mechanical properties.
- Other advanced materials like super alloys, metallic alloys composites, intermetallic

materials, ceramic matrix, glass and glass-ceramic matrices offer advantages for some specific requirements.

From the wide list of materials proposed above, it is clear that selecting materials for space structure design involves navigating a complex array of factors. This complexity is increased by the variety of space systems, making it difficult to even classify all of the materials existent and their combination into one framework. Despite these challenges, many families of materials, such as composites and metals, frequently recur both in aeronautic and space systems because they effectively address a wide range of requirements. These materials are chosen for their specific properties, including strength, rigidity, ductility, fracture toughness, thermal conductivity, thermal expansion, corrosion resistance, volatility, fabrication ease, and procurement ease.

Even with careful selection and distribution of materials, no single material can meet all structural requirements, particularly those impacting performance throughout its lifecycle. A key example is aging, a process that inevitably affect structures whether during storage or operation, as a result of various environmental factors. This challenge has been identified in the roadmap of the World Competitiveness Cluster Aerospace Valley as a critical bottleneck in the Aerostructure, Materials, and Processes sector [16].

Ageing is typically driven by a combination of environmental factors such as weathering, temperature fluctuations, and mechanical stress. One effective way to mitigate this is through the use of specialized coatings. Protective and (multi-)functional coatings with the appropriate physical and mechanical properties play a vital role in shielding materials from environmental stress and significantly slowing down the ageing process.

## 2.2 Ageing and protective layer

As previously mentioned, one key aspect to determine a design choice in space systems is the possibility to prevent the system from structural ageing. This factor is intrinsically related to operations and maintenance costs, including materials and repairs, all while affecting the system’s lifespan and performances [17]. In some cases, like for reusable space systems, aging of materials can constitute a major concern from an economic standpoint, while for longer mission durations, resisting aging can become a necessity for mission success.

In general, the aging of materials is due to physical, mechanical, chemical or even biological causes. In space, some of the factors that cause the most concern with respect to the aging of materials are [18]:

- Temperature: thermal cycling due to extreme temperature jumps can cause mechanical stress and cracking;

- Radiations (Ultraviolet (UV) and charged particles): damage the structures on a molecular level changing their chemical and physical properties;
- Atomic Oxygen (AO): affects prevalently (but not only) metals leading to oxidation reactions and consequent erosion of surface materials;
- Debris and Micrometeoroids: impact from these objects can cause physical damage to the surface and structure;
- Microbial Growth: biological factors like microbial growth can occur on surfaces, particularly in habitats or environments with water, leading to different levels of degradation.

To prevent from aging, solutions have often been found in coatings.

One of the most used coating to prevent the aging of materials is paint. Various type of paints can serve different purposes: white or black, high temperature resistant and other type of paints as for example metallic paints or ceramics, are commonly used for thermal regulation of external and internal spacecraft structures, protection from stray light, radiations, UV and AO [18]. For this reason, paints are used for both short- and long-term missions, depending on the specific requirements. For example, ceramic white paint can be preferred for long-term missions, such as the BepiColombo mission to Mercury, due to its lower degradation rate. In contrast, polyurethane based paints can be chosen for shorter missions because of their high reflectivity and lower outgassing rate [19].

Overall, paints are relatively easy to apply and have a long history of use, with established standards for space missions. They can also be composite materials, such as metallic paints that contain metal flakes or particles to enhance protection against light and UV radiation. Additionally, paints can be used as finishing topcoats to add colour depth to a structure. However, paints face challenges such as adhesion (often requiring a primer and/or a surface pre-treatment), degradation and wear (often requiring additional topcoats) and they must be applied at the right thickness to optimize performance and durability [20]. To address these issues, multi-layer painting techniques are commonly employed to ensure effective protection. Although, this multi-process increases the coating thickness, contributing to an augmentation in volume and mass of the spacecraft structure and can affect the coating lifetime.

Reducing the mass of spacecraft systems can significantly lower launch, maintenance and operational costs, thus decreasing the overall mission expenses. To address the challenge of coating thickness, alternative coatings than painting may be considered. Evaluating these alternatives in terms of mass and performance is crucial, as estimated mass serves as a key parameter in mission design [21], [22], [23].

To answer the need for mass-optimization, a solution can be found in thin films. Among coatings, thin films are defined as materials in the thickness range of a few nano- to about micrometres [24]. Such as other type of coatings, these films are deposited on a substrate to modify its surface properties. Thin films have a broad impact on the characteristics of materials, including their optical, electrical, and mechanical properties, such as resistance to wear, fatigue, and corrosion [25]. Their applications in aeronautics is already established and is of growing interest due to their wide range of use. For example, they were used in the past as part of thermal regulation and optical systems [26], [27], power production and storage systems [28], [29].

Due to their potential, thin films continue to be studied through various deposition methods, aiming to achieve performance levels comparable to chemical treatments and paint adhesion. However, the wide range of deposition techniques available makes it challenging to establish a comprehensive classification system for them [24].

An often used approach is to divide techniques by the method used for their deposition (physical or chemical processes), and by the phase of the precursor used to deposit the coating (liquid or dry processes). While, for example, spraying is considered a liquid chemical process, widely used methods for deposition like Chemical Vapor Deposition (CVD) are considered dry chemical processes, as they involve the use of a precursor in a gaseous phase. In particular, CVD has been used and studied for application in the past to produce coatings for different type of systems and components, as for example to create ultra-lightweight thin films solar arrays for space [30], [31], [32].

The principle of CVD involves the flow of one or more gaseous precursors into a chamber containing heated substrates. The precursors are decomposed into radical species through increased collisions between high-temperature species. These radical species can then diffuse to the substrate where the deposition of the thin film occurs.

In general, films deposited by CVD are known for their homogeneity, as the thickness of the sidewalls is comparable to that of the surface. This feature is advantageous for the fabrication of complex components. Additionally, a wide range of high-purity materials is available for deposition. Nevertheless, CVD films are typically produced at very high temperatures (400 to even 2000°C), which limits the choice of substrate types [33]. A solution to overcome this limitation can be found in plasma processing [34].

### 2.3 Plasma processes for thin film deposition

Plasmas are electrically conducting gas formed of electrons, ions, photons, excited species, radicals and

molecular fragments with neutrals. Non-equilibrium plasmas, where electrons and ions do not reach thermal equilibrium, are particularly valuable for industrial applications due to their ability to create a highly reactive environment at near-ambient temperatures. In non-equilibrium, low-temperature plasmas, electron-neutral collisions predominate, enhancing the interaction of plasma species with precursors of the matrix that will compose the desired film. Fig. 2 provides an explanation of how a typical plasma process works, illustrating the mechanisms generally involved in deposition when a precursor is injected in the system.

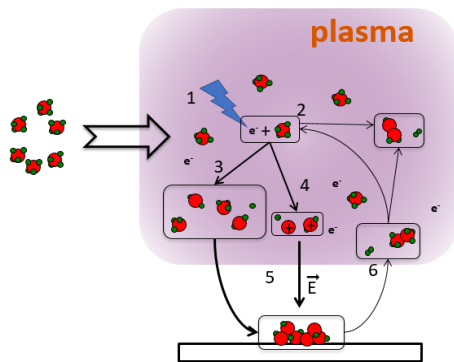


Fig. 2. Typical steps of plasma-based deposition process. In the order, the process involves: (1) electron heating, (2) electron-neutral collisions inducing (3) molecular dissociation and (4) ionization. The (5) transport reactive species at the surface, together with the presence of radicals, lead to the formation a thin film, through mechanisms of recombination, adsorption and (6) desorption [35].

In particular, the mechanisms depicted in Fig. 2 are commonly associated with the Plasma Enhanced Chemical Vapor Deposition (PE-CVD), where the plasma facilitates the typical chemical vapor deposition reactions, often from a gaseous precursor. In this type of reactors, the plasma is often confined between two electrodes powered by a high-frequency generator. This setup allows for the confinement of charged plasma species and provides them with energy. The energy of the electrons is lost through collisions with the neutral precursor species, causing molecular dissociation and leading to excitation, ionization, or the creation of radicals. The ions are transported by the electric field towards the surface, where the radicals can also diffuse. Upon reaching the substrate, mechanisms at the surface such as recombination, adsorption, and desorption of species due to the energy of the transported species contribute to the growth of the thin film.

In PE-CVD and plasma processes, higher densities of reactive species can be achieved compared to conventional CVD processes at similar temperatures, thanks to the unique properties of the plasma. Moreover,

the ability to work, at atmospheric temperatures, enables deposition on temperature-sensitive substrates and can potentially reduce manufacturing energy costs with respect to CVD. Other plasma processes used for coating manufacturing involve for example Physical Vapor Deposition (PVD), where the plasma is used to physically vaporize a solid or liquid precursor and then condensed onto a substrate, with no involvement of any chemical process.

Overall, plasma processes, and particularly PE-CVD, offer the flexibility to use a wide range of precursors and deposition conditions, making them a valuable tool for the development of innovative thin films [36], [37], [38].

#### 2.4 Examples

Although the industrial transfer of methods such as CVD and plasma processes like PVD and PE-CVD for thin film deposition is still under development, some examples of their application in industry can be found.

In this sense, the industrial group Oerlikon-Balzers is an emblematic example. The Swiss company offers a great variety of coatings deposited through plasma-assisted process for the aerospace industry [39]. In aviation, for example, Diamond-like Carbon (DLC) coatings can protect the actuation system from extreme friction, wear and contact with other parts. In extreme environments, the high hardness of a DLC coating – along with a corresponding low coefficient of friction – can prevent parts from pitting, galling, seizing and ultimately failing in the field [40]. DLC coatings are deposited mainly through PE-CVD and PVD plasma processes [41]. Depending on the specifics of the coating material, these thin films can show also good corrosion resistance and reduction of sticking. DLC films can also reduce wear and erosion in turbines, making them more resistant to repeated cycles even under high thermal conditions [42]. In all, the Oerlikon-Balzers group highlights how PE-CVD and PVD coatings are especially suitable for precision components due to the coating uniformity, repeatability and no need for post-finishing.

Another example is the IHI Ionbond, a part of the Japanese business unit IHI Group. IHI Ionbond uses CVD, PVD, and PE-CVD processes to produce coatings for the aerospace industry. These coatings have numerous applications, including in satellites and launch vehicles. For space systems, Ionbond DLC coatings, deposited via PVD or PE-CVD processes, are used in cryogenic fuel systems to prevent galling and improve functionality, while their CVD coatings support plasma thrusters in space probes and satellites. Additionally, Ionbond's film coatings are applied to structural components of airplanes and spacecraft to protect against wear, friction, galling, and mechanical damage, as well as in turbo-reactors to ensure reliability under extreme

conditions, such as high temperatures, abrasion, hot corrosion, oxidation, and wear [43].

While research continues to advance the industrial transfer of thin film deposition methods, companies like OC Oerlikon and IHI Ionbond illustrate the increasing interest and potential of thin film coatings for various industrial applications.

### 3. From functional to multifunctional coatings

#### 3.1 Probability of success

In the precedent section, thin films were proposed as coating solutions for different applications. In fact, thin films have the potential to reduce costs by minimizing mass, all while granting performance competitiveness with respect to well-established methods like painting.

In this section, additional factors that significantly influence decision-making when selecting a specific system design are considered, particularly when designing for value. As highlighted in a National Aeronautics and Space Administration (NASA) technical paper on life support technology selection by H. Jones, the system's mass-cost index need to be leveraged with the probability of success of a certain design choice [21]. This means that the coating material selection must be carefully balanced against the probability of success in meeting the mission objectives that the design is intended to achieve.

Consider spacecraft designed for interplanetary travel, potentially with astronaut crews on-board. These spacecraft must withstand harsh environments for extended durations of time without opportunities for maintenance or repair. As materials age, their performance becomes critical to mission success. Addressing multiple challenges—such as radiation, thermal cycling, corrosion, microbial growth, and micrometeoroid impacts—with a single coating is exceptionally demanding. In such scenarios, minimizing mass is crucial, making it even more challenging to develop a single thin coating that can effectively combat all these aging factors.

To address this issue, nanocomposite coatings, such as thin films with embedded nanoparticles, are emerging as new protective materials [44]. These coatings can combine multiple physical and chemical properties, such as anti-scratch, anti-corrosion, anti-fouling, self-healing, anti-UV, or super-hydrophobic characteristics, among others [35].

Of course, the advantages of nanocomposite thin films go beyond their asset to become a key technology to assure the success of interplanetary travels. Their ability to fulfil multiple requirements without the need for multi-layers' coatings, the optimization of their mass due to their thinness, often combined with ameliorated coatings' performances, make them an attractive product

for a variety of space systems in the market [35], [45], [46].

#### 3.2 Nanomaterials and nanocomposites

To better understand nanocomposites, it's helpful to first define a broader category: nanostructured materials. These are materials where at least one dimension falls within the nanoscale range (1-100 nanometres). The nanoscale dimension can be found either inside the material or on its surface, and this added dimension can induce changes in the properties of a material.

A notable example of nanostructured coatings are the ones exhibiting what is known as the "lotus effect." These coatings are bio-inspired as they tend to reproduce the super-hydrophobic and self-cleaning characteristics of lotus flowers. Such bio-inspired coatings have attracted considerable attention across various domains, including their potential use in aerospace applications, where keeping surfaces clean is essential for optimal performance and efficiency in harsh environments [47]. The unique design of these nano-coatings involves a double structure. Microscale bump-like formations, combined with micro- and nanoscale branch-like structures, work together to reduce the surface contact of water droplets. By minimizing adhesion forces, the material becomes both repellent and super-hydrophobic (Fig. 3) [48]. However, despite their promising features, the lotus inspired nanostructures are prone to scratches, which limits their long-term viability, particularly for space travel or reusable systems. While anti-scratch coatings exist, a more advanced approach might involve combining these technologies by dispersing nanoparticles into a thin film matrix to create a multifunctional thin film.

Nanoparticles are defined as particles where at least one dimension is smaller than 1 micrometre. When incorporated into materials, they create a special category of nanomaterials known as nanocomposites. Due to the high surface-to-volume ratio, nanoparticles surface effects—such as chemical reactions or bonding—become much more crucial than in bulk materials. Moreover, the interaction between the nanoparticles and the surrounding matrix also significantly impacts the material's overall properties, including strength, conductivity, and flexibility [49]. Therefore, the size, shape, distribution, concentration and nature of the nanoparticles in the matrix induces novel chemical and physical properties in the material.

Going back to our example, it has been shown in a study conducted by G. Carnide, R. Clergereaux and M. L. Kahn that a thin film composed of a DLC matrix with embedded Zinc Oxide nanoparticles can exhibit hydrophobic and water-repellent properties as well as high mechanical resistance without the need for micro-texturation [45].



As the potential of nanocomposite thin films for commercial use becomes clear, the challenge on the deposition methods to assure the insertion of the nanoparticles in the thin films needs to be explored, in particular for the plasma-assisted processes.

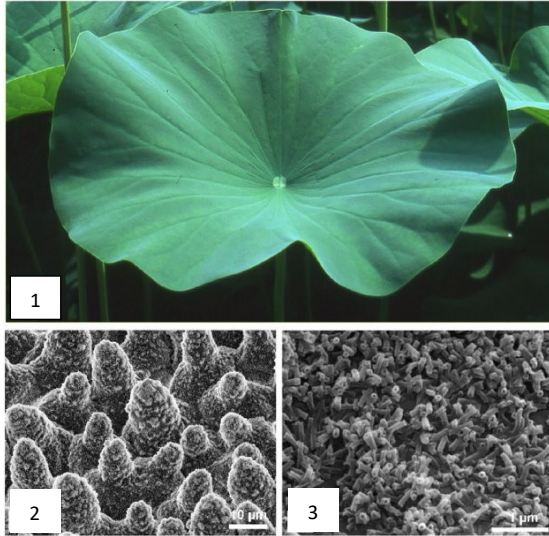


Fig. 3. (1) Typical lotus leaf, with Scanning Electron Microscope (SEM) images highlighting for different magnifications the (2) bump-like microstructures recovered in (3) branch-like nanostructure [50].

### 3.3 Nanocomposite thin film deposition

Numerous plasma-assisted deposition techniques were implemented to introduce nanoparticles into thin films, including PE-CVD processes. When injecting a matrix's precursor in a PE-CVD process, for example, clusters of reactive species and radicals can aggregate to form nanoparticles directly in the plasma volume, or *in-situ*. Thanks to the forces in action in the system, the nanoparticles can be transported to the growing site and contribute to the thin film formation (see Fig. 4).

Therefore, PE-CVD can lead to the formation of nanoparticles using a mixture of precursors. Other methods include combinations of techniques such as using PE-CVD for matrix deposition and sputtering for nanoparticle deposition, or integrating multiple methods like PVD and PE-CVD. Additionally, many other non-PE-CVD techniques like the direct injection of solid nanoparticles into plasma deposition systems via gas aggregation sources have been explored [49], [51]. Overall, the precursor materials for these processes can be introduced either as a vapor from a solution or through solid delivery systems. Via this gaseous and dry methods, though, nanoparticles are always created *in-situ*, limiting the control over important parameters like their size, shape, concentration, etc.

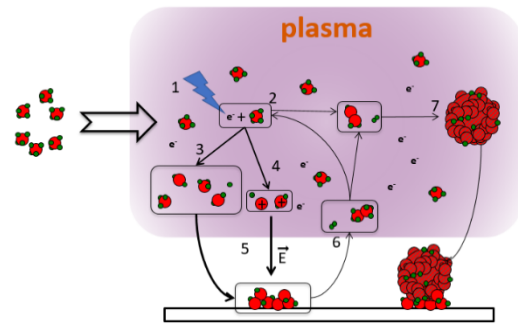


Fig. 4. Aggregation (7) of reactive species and radicals in the plasma volume can lead to the formation of nanoparticles. These participate in the formation of nanocomposite thin films [35].

### 3.4 Aerosol-assisted plasmas

Recently, an increasing trend has appeared in the scientific community, seeing the production of nanomaterials or nanocomposite thin films by combination of liquid- and gas-phase processes [52]. This is achieved by creating an aerosol—a suspension of micrometric liquid droplets in a gaseous medium—from a nanoparticle colloidal solution and directly injecting this colloidal solution into a plasma. The nanoparticles are dispersed in the liquid matrix precursor as a colloidal solution and are injected into the plasma phase using a spraying mechanism to atomize the liquid and produce the aerosol. The flexibility offered by aerosol-assisted deposition processes is notable compared to those where nanoparticles are generated *in-situ*. The colloidal solutions can be prepared *ex-situ*, allowing for the combination of nanoparticles with any compatible conventional precursor.

The challenge with aerosol-injection systems is primarily related to their interaction with the plasma phase. Injecting a liquid-phase precursor into a plasma chamber can modify the characteristics of the plasma. This is why methods to restore an equilibrium state between aerosol injectors have been studied. One alternative for continuous aerosol injection into the plasma is Pulsed Direct Liquid Injection (PDLI), a method that delivers the precursor (colloidal) solution in the form of pulsed injections [53]. It has been shown that, with respect to continuous injection, this kind of pulsed system optimizes the ionization rate and overall deposition process [54].

## 4. Impacts of plasma processes

### 4.1 Sustainability

When making design decisions, it is crucial to consider the associated benefits of a system. In the process of comparing different designs that meet requirements and ensure mission success, the benefits of



a particular choice—when weighed alongside costs and the probability of success—become decisive in selecting the final architecture. However, estimating these benefits is challenging, especially when comparing them to competitors in the market. As the space market evolves, value and benefit creation depend on various factors, including customer needs, both visible and latent stakeholder values, and the economic advantage of developing a specific system or service.

Recently, sustainability has emerged as a key factor in calculating the benefits of a design choice. This is evidenced by the growing inclusion of sustainability in the trade-off matrices used in space systems design and the increasing number of global initiatives focused on this issue [55]. Sustainability is intrinsically linked to concepts like Environmental, Social, and Governance (ESG) criteria, which affect a company's economic performance, and Corporate Social Responsibility (CSR), which reflects a company's core values. Ultimately, sustainability is increasingly tied to the overall benefits of a system and has become a relevant factor to consider when designing large-scale space missions [56].

Sustainability, however, is a broad term encompassing multiple pillars: economic, environmental, and social. The pursuit of a sustainable system is often referred to as sustainable development. To understand what sustainable development entails today, it is useful to look at the 2030 Agenda. This is a program of actions for Sustainable Development, adopted by all United Nations (UN) member states in 2015, which includes 17 Sustainable Development Goals (SDGs) aimed at ending poverty, protecting the planet, and ensuring prosperity for all by 2030 [57]. In Fig. 5, the SDGs are reported as presented on the official government websites of the UN member states.



Fig. 5. The table of the 17 SDGs as defined by the UN in the Agenda 2030 [58].

By examining the UN's criteria for sustainable development and applying them to the manufacturing of industrial products, several challenges emerge. Key aspects include promoting industrial innovation alongside responsible consumption and production, which means for example balancing material and

energetic inputs and outputs, making responsible choices in raw material use, reducing waste, and increasing recycling opportunities. Environmental concerns are intrinsically linked to industrial production, from the manufacturing process to the impact of effluents resulting from product degradation on the ecosystems. Additionally, promoting a sustainable process also means incorporating measures for health and well-being of users and operators all along the material's life cycle.

For the variety and the complexity of the challenges related to sustainable development, it is difficult to outline a comprehensive way to determine the best design choice comprising every aspect of the coating life-cycle. However, certain parameters can help outlining challenges, problematics and advantages of coating solutions with respect to the above-mentioned concerns. Some of these criteria, like durability and deposition rate of a thin film, together with the material balance and energy assessment of the process, are discussed for the coatings and deposition methods presented in this review.

For instance, paint coatings have a fast deposition rate, and the overall energy consumption required for the deposition process can be relatively low if compared to CVD or plasma-assisted technologies [59]. Although, producing a sufficient thickness of paint requires large volumes of material, and much of the manufacturing by-products—such as hazardous air pollutants (HAPs) solvents and volatile organic compounds (VOCs)—are toxic and hazardous to both the environment and humans. As a consequence, these effluents need to be recirculated through expensive machines [60]. Moreover, as paint is prone to degradation, the HAPs and VOCs toxic components can be released in the atmosphere during the coating life-cycle, contributing to air pollution. Depending on the type of paint, other harmful and persistent effluents, such as perfluoroalkyl substances (PFAs), may also be emitted [61]. Overall, even with this well-established deposition method, the toxicity of painting by-products and the effluents released during the coating's life cycle, along with the large volume of material required for deposition, can raise sustainability concerns.

Thin film coatings, produced via plasma processes, tend to offer more sustainable alternatives in terms of material usage. The inputs for thin films are generally low compared to paint, due also to the thinness of the coatings, with minimal waste, as most of the material is effectively utilized in the coating. This is especially true for PE-CVD processes, while lower material utilization efficiency is attained for other PVD or plasma-assisted processes like sputtering [62]. Moreover, the thin films produced through plasma-assisted processes are thinner than paint, making them less prone to delaminating and degrading, thus reducing the risk of harmful emissions over time. They also tend to have good adhesion and only sometimes nanometric under layers are needed to

enhance attachment to the substrate. Plasma processes, however, require highly complex machines and are energy-intensive, with significant electrical consumption needed to sustain operations over extended periods due also to their lower deposition rate compared for example to painting processes [62], [63]. Processes like PE-CVD, can create some undesired by-products, though these are often managed through exhaust systems, vacuum pumps, and chamber cleaning.

Similarly, CVD coatings share the benefits of thin films in terms of lower material inputs and durability. However, CVD has significant energy demands due to the need for high temperatures over long periods, making it less sustainable in terms of energy efficiency. The use of such energy-intensive processes can counterbalance some of the environmental benefits derived from lower material waste. Just as PE-CVD, CVD also carries the risk of creating by-products for some kind of deposition processes. Due to the high temperatures of the processes, the CVD by-products can be an even more concerning source of hazard and needs to be handled more carefully [62].

With respect to nanocomposite thin films, more sustainability concerns are raised by the presence of nanoparticles. In fact, it remains significant uncertainty about the health and environmental risks associated with these components [64]. Research has shown that nanoparticles can cause serious health issues, including cancers, organ damage, protein denaturation, and asthma attacks. As a result, regulatory bodies are currently implementing laws to regulate nanoparticle usage, like the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) law imposed by the European Union (EU).

In response to these concerns, green synthesis methods have been developed to minimize health and environmental risks. One example is the Direct Liquid Reactor Injector (DLRI), a system patented by the research group led by R. Clergereaux and M. L. Khan [65]. This system allows for the production of nanoparticles directly in the injector system, creating the desired colloidal solutions without the need for operators to treat the nanoparticles *ex-situ*. This reduces the risks related to operators' health as well as reducing contact of both people and the environment with contaminated wastes.

Although their industrial transfer is under development, technologies like the DLRI highlight the dual necessity of advancing nanotechnologies while also assessing their potential dangers. In this sense, adopting "safe-by-design" solutions is essential for fostering innovations that support sustainable development, while also delivering value to companies committed to meeting sustainability standards.

## 5. Conclusions

In this review, functional thin films were compared to more traditional coating methods, namely painting, to guide design choices for modern space systems. The advantages and disadvantages of some relevant coating and deposition methods were analysed, focusing on the recent history and market needs of the space sector, which now involves a diverse range of missions with longer and more frequent journeys to space. Sustainability, driven by economic and political factors, has emerged as a new value source and was also considered as a key element for the comparisons.

A comprehensive summary comparing the main design-relevant characteristics of paints and thin films deposited by CVD, plasma processes, and more specifically PE-CVD can be found in Table 2.

Additionally, a specific focus was placed on nanocomposites due to their potential application in future space missions. Composite materials can, in fact, meet multiple requirements with minimal increases in mass and volume. Although these materials are still under development and raise concerns related to the use of nanoparticles, "safe-by-design" solutions like DLRI show promising advancements that could facilitate the industrialization of nanocomposite materials.

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Coating deposition processes	Painting	CVD	Plasmas	PECVD
Composites	Yes	No	Under development	Under development
Finishing	Depends on the requirements	Thermal constraints	Yes	Yes
Substrate types	All	Only low temperature substrate	All	All
Adhesion	Low, necessitate surface treatment	Good, can necessitate under layer	Good, can necessitate under layer	Good, can necessitate under layer
Durability and in-use sustainability	Long term desorption	Good	Good	Good
Inputs	High volume >>	Low volume <<	Dependent on the specific process	Low volume <<
Effluents and by-products	High volume >> and potentially hazardous	Low volume << but potentially hazardous	Low volume << and controlled	Low volume << and controlled
Thickness - masse	>> 100 µm + multilayers + homogeneous composition	> 10 nm	> 10 nm	> 10 nm
Deposition rate	>> µm/s or mm/s	10-1000 nm/min	10-1000 nm/min	10-1000 nm/min
Energy assessment	Low	High due to high T°	Dependent on the specific process	Dependent on the specific process
Industrial transfer	Established	Under development	Under development	Under development
Savoir-faire	Ordinary process	Under development	Under development	Under development
Formation	Low	Specialized operators	Specialized operators	Specialized operators
Recycling	Key challenge	Key challenge	Key challenge	Key challenge

Table 2. Summary of some characteristics of different coating technologies for design choices in space systems.

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