coatings

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Review

Sputtering Physical Vapour Deposition (PVD) Coatings: A Critical Review on Process Improvement and Market Trend Demands

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Abstract: Physical vapour deposition (PVD) is a well-known technology that is widely used for the deposition of thin films regarding many demands, namely tribological behaviour improvement, optical enhancement, visual/esthetic upgrading, and many other fields, with a wide range of applications already being perfectly established. Machining tools are, probably, one of the most common applications of this deposition technique, sometimes used together with chemical vapour deposition (CVD) in order to increase their lifespan, decreasing friction, and improving thermal properties. However, the CVD process is carried out at higher temperatures, inducing higher stresses in the coatings and substrate, being used essentially only when the required coating needs to be deposited using this process. In order to improve this technique, several studies have been carried out optimizing the PVD technique by increasing plasma ionization, decreasing dark areas (zones where there is no deposition into the reactor), improving targets use, enhancing atomic bombardment efficiency, or even increasing the deposition rate and optimizing the selection of gases. These studies reveal a huge potential in changing parameters to improve thin film quality, increasing as well the adhesion to the substrate. However, the process of improving energy efficiency regarding the industrial context has not been studied as deeply as required. This study aims to proceed to a review regarding the improvements already studied in order to optimize the sputtering PVD process, trying to relate these improvements with the industrial requirements as a function of product development and market demand.

Keywords: PVD optimization process; PVD technique; sputtering; magnetron sputtering; deposition improvement; reactors

1. Introduction

The physical vapour deposition (PVD) process has been known for over 100 years, and plasma-assisted PVD was patented about 80 years ago [1]. The term "physical vapour deposition" appeared only in the 60s. At that time, the evolution of vacuum coating processes was needed, which was carried out through the development of well-known technologies, such as sputtering, vacuum, plasma technology, magnetic fields, gas chemistry, thermal evaporation, bows, and power sources control, as described in detail in Powell's book [2].

In the last 30 years, plasma assisted PVD (PAPVD) was divided into several different power source technologies such as direct current (DC) diode, triode, radio-frequency (RF), pulsed plasma, ion beam assisted coatings, among others. In the beginning, the process had some difficulties in being understood at a fundamental level and necessary changes were introduced to provide benefits, such as excellent adhesion from the coating to the substrate, structure control, and material deposition at low temperatures [3].

On the other hand, many additional surface treatments have appeared to meet the industrial and commercial needs, developing the performance of a huge number of products. In the last decades, the development of PVD deposition technologies has been focused essentially on the coating of tools, considering the strong evolution of the computer numerical control (CNC) machining processes, since new machining approaches have arisen [4].

PVD technique is a thin film deposition process in which the coating grows on the substrate atom by atom. PVD entails the atomization or vaporization of material from a solid source, usually called target. Thin films usually have layers with thicknesses as thin as some atomic layers to films with several microns. This process causes a change in the properties of the surface and the transition zone between the substrate and the deposited material. On the other hand, the properties of the films can also be affected by the properties of the substrate. The atomic deposition process can be made in a vacuum, gaseous, plasma, or electrolytic environment. Moreover, the vacuum environment in the deposition chamber will reduce the gaseous contamination in the deposition process to a very low level [5].

The last decades showed an evolution of the PVD techniques, aiming to improve coating characteristics and deposition rates without putting aside initial surface cleaning to remove possible contaminations [6,7]. This technique has suffered relevant improvements, mainly in carbides and nanocomposite transition metal nitrides substrates [8–12]. Research has been focused on improving the characteristics of coatings, although the enhancement of the deposition rate effectiveness regarding this process has been the main concern of the industry linked to this kind of techniques [13–15].

The most common surface coating methods in a gaseous state regarding the PVD process are evaporation and sputtering. These techniques allow for particles to be extracted from the target at very low pressure to be conducted and deposited onto the substrate [16].

The reactor that was used in the evaporation process requires high-vacuum pressure values. Generally, these characteristics and parameters have lower atomic energy and less adsorption of gases into the coatings deposition. As a result, a transfer of particles with larger grains leads to a recognized lesser adhesion of the particles to the substrate, compared with the sputtering technique. During deposition, some contaminant particles are released from the melted coating material and moved onto the substrate, thereby reducing the purity of the obtained coatings. Thus, the evaporation process is usually used for thicker films and coatings with lower surface morphological requirements, although this technique presents higher deposition rates when compared with the sputtering process.

Therefore, the sputtering process appears as an alternative for applications that require greater morphological quality of surfaces where roughness, grain size, stoichiometry, and other requirements are more significant than the deposition rate. Due to the stresses generated during the cooling process with the decrease in temperature or the melting temperature of the substrate (polymers), the deposition process presents temperature limitations for certain applications [17–21]. This leads to the Sputtering process becoming more relevant among PVD deposition techniques without forgetting the appearance of new techniques based on the sputtering process to meet the continuous increase in market requirements.

New coating properties, following market and researchers' requirements, have been developed with the emergence of new systems based on conventional processes. Even though the deposition rates that were obtained by the evaporation process are the desired, the truth is that the sputtering deposition techniques made an unquestionable progress in terms of quality and increase in deposition rate, responding to industry and researchers demands interested in this area, even serving as interlayer for further coatings obtained by chemical vapour deposition (CVD) [22].

CVD is another method of deposition under vacuum and is the process of chemically reacting a volatile compound from a material to be deposited with other gases, in order to produce a non-volatile solid that is deposited onto a substrate. This method is sometimes used as pre-coating with the aim of increasing the durability of the substrates, decreasing the friction, and improving the thermal properties—this means that one can combine deposition methods, like layers of PVD and CVD, in the same coating [23–26].

There are also a large number of studies in mathematical modelling and numerical simulation that contribute to the improvement of this process, which may be an advantage over other processes. These studies have a great impact on the improvement of the reactors characteristics that lead in the future to the costs reduction, as well as in the improvement of the mechanical properties of the films [27–32].

This work has as main focus the magnetron sputtering technique since its development will be focused on the improvement of these specific reactors in the future.

2. PVD Coatings

PVD is an excellent vacuum coating process for the improvement of wear and corrosion resistance. It is highly required for functional applications, such as tools, decorative pieces, optical enhancement, moulds, dies, and blades. These are just a few examples of a wide range of already well-established applications [33–35]. The equipment used in this technique requires low maintenance and the process is environmentally friendly. Benefits of PVD coatings are many. PVD can provide real and unique advantages that add durability and value to products. Deposition techniques have an important role in machining processes. Machining tools are probably one of the most exigent applications, which require characteristics, such as hardness at elevated temperatures, high abrasion resistance, chemical stability, toughness, and stiffness [36–45]. In addition, PVD is also able to produce coatings with excellent adhesion, homogeneous layers, designed structures, graduated properties, controlled morphology, high diversity of materials and properties, among others [46–50].

PVD processes allow the deposition in mono-layered, multi-layered and multi-graduated coating systems, as well as special alloy composition and structures. Among other advantages of this process, the variation of coating characteristics continuously throughout the film is undoubtedly one of the most important [32,51,52]. Their flexibility and adaptability to market demands led to the development and the improvement of techniques for the various processes and thus multiple variants have arisen, some of them presented in Figure 1.

These techniques are constantly evolving and continue to be inspiration sources for many studies. Many books and articles spread out the information on these variants, making it difficult to quantify all existing techniques. Sputtering (or cathodic spraying) and Evaporation are the most commonly used PVD methods for thin film deposition.

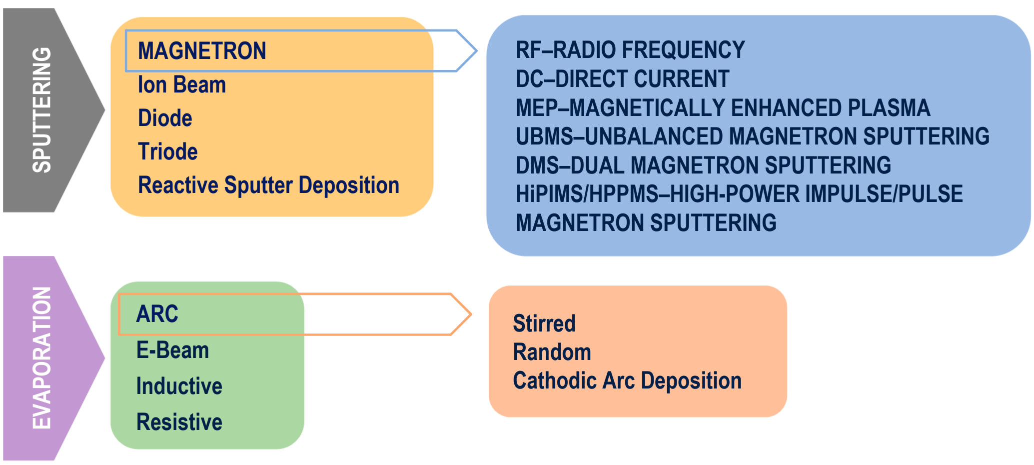

Figure 1. Segmentation of the current physical vapour deposition (PVD) techniques for advanced coatings.

2.1. Evaporation and Sputtering Principles

In PVD techniques, a thermal physical process of releasing or collision transforms the material to be deposited—the target—into atomic particles, which are directed to the substrates in conditions of gaseous plasma in a vacuum environment, generating a physical coating by condensation or the accumulation of projected atoms. A higher flexibility in the types of materials to be deposited and a better composition control of the deposited films are the results of this technique [21,53,54]. Two electrodes connected to a high voltage power supply and a vacuum chamber constitute the PVD reactors, as seen in Figure 2 [21,53,55].

Regarding the sputtering process, fine layers of several materials are applied while using the magnetron sputtering process. The raw material for this vacuum coating process takes the form of a target. A magnetron is placed near the target in sputtering processes. Then, in the vacuum chamber, an inert gas is introduced, which is accelerated by a high voltage being applied between the target and the substrate in the direction of the magnetron, producing the release of atomic size particles from the target. These particles are projected as a result of the kinetic energy transmitted by gas ions whose have reached the target going to the substrate and creating a solid thin film. The technology allows for previous contaminations located on the substrate to be cleaned from the surface—this is by reversing the voltage polarity between the substrate and the target, usually called cathodic cleaning [21].

When considering the technique of e-beam evaporation, this method involves purely physical processes, where the target acts as an evaporation source containing the material to be deposited, which works as a cathode. Note that the system evaporates any material as a function of the e-beam power. The material is heated at high vapour pressure by bombarding electrons in high vacuum, and the particles released. Then, a clashing occurs between the atomic size released particles and gas molecules—inserted into the reactor, with the aim of accelerating the particles, by creating a plasma. This plasma proceeds through the deposition chamber, being stronger in the middle position of the reactor. Successively compressed layers are deposited, increasing the adhesion of the deposited film to the substrate [17–21].

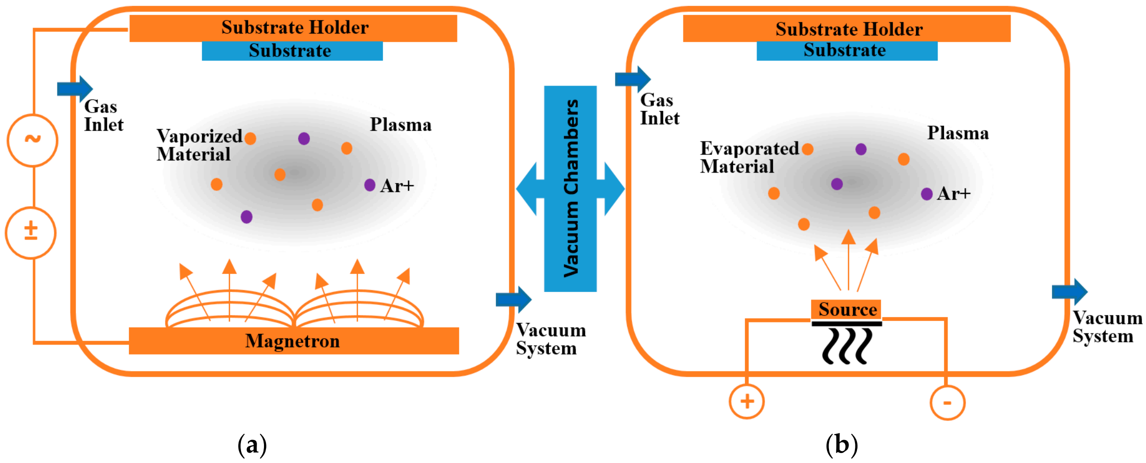

Figure 2. Schematic drawing of two conventional PVD processes: (**a**) sputtering and (**b**) evaporating using ionized Argon (Ar+) gas.

Being a cleaner deposition process, sputtering permits a better film densification, and reduces residual stresses on the substrate as deposition occurs at low or medium temperature [56–58]. Stress and deposition rate are also controlled by power and pressure. The use of targets with larger area facilitates a good uniformity, allowing the control of the thickness by an easy adjustment of the process parameters and deposition time. However, the process may cause some film contamination by the diffusion of evaporated impurities from the source, thus, there are still some limitations in the selection of the materials that were used for the coatings due to their melting temperature.

Furthermore, this process does not allow an accurate control of film thickness. However, it allows for high deposition rates without limit of thickness [59]. For better understanding, a comparison between evaporation and sputtering techniques is summarized in Table 1.

Table 1. Typical features of the PVD [17–21].

Parameters	Sputtering	Evaporation
Vacuum	Low	High
Deposition rate	Low (except for pure metals and dual magnetron)	High (up to 750,000 A min^{-1})
Adhesion	High	Low
Absorption	High	Less absorbed gas into the film
Deposited species energy	High (1–100 eV)	Low (∼0.1–0.5 eV)
Homogeneous film	More	Less
Grain size	Smaller	Bigger
Atomized particles	More Dispersed	Highly directional

2.2. Sputtering Process Steps

To obtain better thin film deposition, it is important to know all process steps regarding the equipment related to the reactor, keeping in attention what takes place in the chamber during the deposition cycle. A preparation process before deposition is necessary, namely cleaning the substrate to achieve a better film adhesion between the coating and substrate. Nonetheless, cleaning the substrates in an ultrasonic bath, outside the vacuum chamber, is also suggested before the substrates are placed on the satellites [60]. An advantage of a vacuum sputtering chamber is the fact that it can be used both for cleaning the substrates, and afterwards, a coating deposition [21,54]. On the other hand, the duration of the cleaning process is considerable, being a disadvantage in terms of industry competition, as it raises final product costs. In order to control the costs, a management of the machine's breakdown times and setups is necessary. As this fact is a drawback to the industry, an optimization of the process' parameters is required to reduce production times. An important parameter to be optimized is the deposition rate, regarding an improvement in the plasma density and energy available in the process. Thus, it is necessary to take into account all of the steps of the process and parameters studied, in order to comply with industry demands [61]. Contamination of the films can be avoided with correct substrate handling and efficient maintenance of the whole vacuum system, as the contamination sources come from bad surface conditions or system related sources. The process cycle time depends mainly on the vacuum chamber size and its pumping system [17].

Following the placement of the substrates on the holders' vacuum chamber, the deposition process takes place regarding the following four important steps, featured in Figure 3:

- The first step—Ramp up—involves the preparation of the vacuum chamber, which consists in a gradual increase of the temperature, induced by a tubular heating and a modular control system; at the same time, the vacuum pumps are activated in order to decrease the pressure inside the chamber. In this type of sputtering reactors, two pumps are used, the first one (primary vacuum) produces a pressure up to 10^{-5} bar, the second one (high vacuum) reaches 10^{-7} bar pressure.
- The second step—Etching—is characterized by cathodic cleaning. The substrate is bombarded by ions from plasma etching to clean contaminations located on the substrate surface. This is an important preparation step for a deposition because it helps to increase adhesion. Indeed, the substrate properties have a direct influence on adhesion, such as substrate material, hardness and surface quality [62,63].
- In the third step—Coating—takes place. The material to be deposited is projected to the substrate surface. Several materials can be used; among these are titanium, zirconium, and chromium nitrides or oxides, among others.
- The last step—Ramp downstage—corresponds to the vacuum chamber returning to room temperature and ambient pressure. In order to achieve this, a specific cooling system is

used—chiller—with two sets of water knockout drums: one is used for the vacuum pumps and the other for cooling targets. Equipment unloading and cooling should not damage coatings' properties. The need for a cooling system is a drawback because it decreases production rate and rises energetic costs.

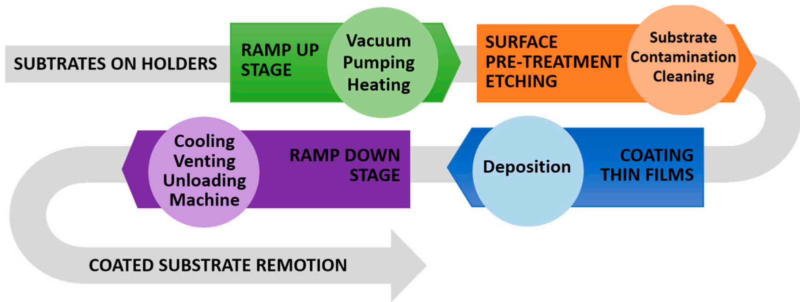

Figure 3. The processing flow for a classic PVD sputtering process.

A global industrial concern is energy consumption to help reduce costs [64]. New policies are expected to drive more innovation, encourage better industry performance, and lead to more energy savings.

The CVD process reveals a higher consumption compared to the PVD when considering all of the process steps. This has been demonstrated by several studies, such as sustainability assessments regarding manufacturing processes, energy consumption, and material flows in hard coating processes [65,66].

A comparative study issued by Gassner et al. [65], revealed a consumption of 112 kWh (process cycle time $\approx$ 5 h; coating thickness $\leq$ 6 µm) regarding the TiN deposition, using Magnetron Sputtering (MS) technique, which can be compared with the 974 kWh consumed in the $TiCN/Al_2O_3$ deposition using CVD technique, (process cycle time: 18 h 30 min; coating thickness $\leq$ 30 µm). PVD process, particularly the sputtering process, does not require very high temperatures, such as the high-temperature that was usually developed in the CVD process. Thus, in the CVD technique, the highest energy consumption is centred in the heating step, which is justified since the temperature parameters range between 750–1150 °C in the CVD case, and in the MS deposition, are usually done at lower temperatures, in the range of 350–600 °C. A possible way of reducing energy consumption costs is recovering the residual heat through heating exchange modules. Furthermore, in MS deposition processes, three-quarters of the total energy is usually consumed in the coating step. In order to increase energy coating efficiency, recycling target materials must be considered. Thus, it is possible to conclude that heating, etching, and refrigeration have a much lower contribution to energy consumption. Figure 4 compares the energy consumption for the PVD (using MS) and CVD during the deposition steps [65].

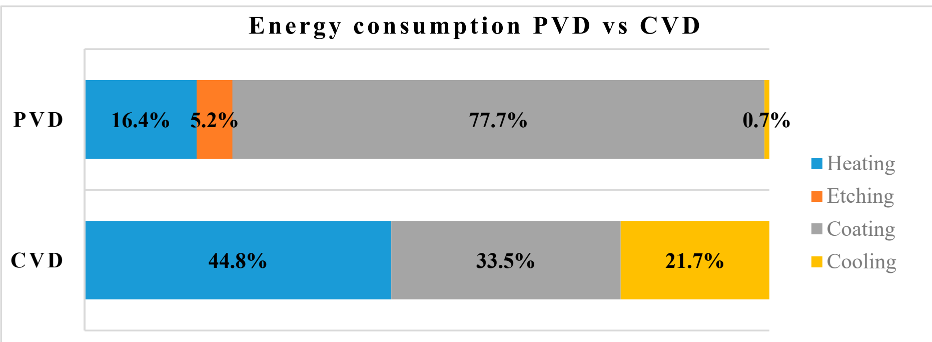

Figure 4. Energy consumption in the different steps of the PVD process: Heating, Etching, Coating, and Cooling. Energy consumption in the steps of the CVD process: Heating, Coating, and Cooling.

The way to sustainability and energy efficiency needs to be thought as an opportunity in reducing costs. The investment in terms of quality improvement of the coatings includes an increasing in adhesion between those and the corresponding substrates, extending their lifespan. This means that the reactor must be deeply studied in terms of parameters and external devices used to improve the deposition process. Beyond the solutions above referred, other possible solutions can be based on the improvement of the cleaning step within the reactor, minimizing the reactor occupation and saving costs in terms of energy and assistant gases. The reduction of dark areas into the reactor through the modelling of the plasma region would increase the useful volume of the chamber, contributing to a more homogeneous thickness of the coating in a large number of coated parts regarding each batch. Moreover, if the quality of the coatings is improved regarding its function, the lifespan of the coating will be enlarged, contributing by this way to energy savings, thus increasing its sustainability.

2.3. Deposition Process Influence Coatings Properties

In the last decades, one has observed an evolution in the approach of researchers regarding the impact of the deposition processes on coating properties.

The quality and variety of thin films has been a focus over the years and has progressed ever since. Currently, due to efficiency and optimization reasons of the industrial processes, new techniques and reactors have emerged with various combinations and possible derivations. However, these new techniques have a great impact on the influence of coating properties. The appearance and evolution of new simulations software also contribute positively to the continuous improvement need.

Having a focus on process improvement, it is important to know the parameters that can be adjusted during coating deposition and substrate cleaning. Some of these parameters can be the number of pumps, the number of targets, type of targets, substrate geometry, reactor occupancy rate, pressure, gas type, gas flow, temperature, current density, bias, among others.

However, parameters changes will have an impact on the film deposition rate and its adhesion. Consequently, one can have changes in the grain size and film thickness that will determine the coating characteristics, namely its hardness, Young's modulus, morphology, microstructure, and chemical composition [67].

The preparation of vacuum chambers for deposition is very important. The presence of oxygen in the vacuum chamber must be removed in order to ensure further vacuum and cleanliness conditions. Reactor cleanliness is also an important factor to keep the coatings free of impurities resulting from other previous materials used in the reactor. It is advised that the pressure must be maintained in the range of 101 and 104 Pa, being the last one the base pressure. Setup conditions will contribute to the creation of homogeneous plasma and an efficient cathodic cleaning. Etching process makes it easier to remove oxides and other contaminants from the substrate surface. The duration of the etching and bias sub-processes is also very relevant. A good plasma etching and excellent substrate surface cleanliness surely provide good adhesion [63]. In addition to adhesion, microstructural and mechanical properties, as well as corrosion properties of thin films have been studied. Gas flow and type are responsible for changes in the microstructural and mechanical properties. To improve the corrosion properties of materials, they have been developed new PVD coating techniques with magnesium alloys [34].

Effect of nitrogen-argon flow ratio on the microstructural and mechanical properties of AlSiN and AlCrSiN coatings that were prepared by high power impulse magnetron sputtering has been studied [68,69]. For AlSiN coatings, the N_2/Ar flow ratios from 5% to 50% had a strong impact on the results obtained. As a result, the hardness of the AlSiN coating increased with increasing nitrogen-argon flow ratio and reached a maximum value of 20.6 GPa [68]. In AlSiN coatings with an increase of N_2/Ar flow ratio, with nitrogen content in the range from 28.2% to 56.3%, prepared by varying the flow ratio from 1/4 to 1/1, resulted in higher hardness and better tribological behaviour with the contribution of the increasing crystallinity [69].

In recent years, in the high-power impulse magnetron sputtering (HiPIMS) process, reactive gases, such as oxygen or nitrogen, have been used. This technique is being applied to improve and adapt the properties of the growing films by their high fraction of ionized sputtered material during the process [70].

Regarding corrosion properties, studies show that this characteristic is tightly influenced by the deposition conditions and coating microstructure. However, it has less influence on the density of the defects [34]. The operating conditions have an effect on the homogeneity of the coating. Since these conditions interfere with the properties of the films, it is important to optimize the substrate and holders' rotation, the number of satellite holders, different initial positions of the substrate face, and take advantage of the chamber area and satellites occupancy space [60,71].

To conclude, the properties of the films are directly related to the deposition process. For this reason, it is unquestionable that progress continues to focus on solving problems that the industry is looking for, with a focus on improving reactors in terms of performance and film properties.

3. Sputtering Depositions Improvements

Process optimization and PVD technique improvements have been the focus of many studies, thus contributing to its success. Recently, the increase in plasma ionization has been the main goal of improvement, increasing the deposition rate. Other attentions are paid to decrease dark areas in the deposition chamber, recycle or improve targets, select gases, and increase atomic bombardment efficiency. The use of responsible energy practices has sensitized users of this technique, even though it is still an area to improve. Enlightening the energy efficiency of the whole process has an impact on costs, but also on the environment [68,72,73].

3.1. Reactors' Parameters and Characteristics

In general, the vacuum chambers that are applied to the coating of tools and components are constantly evolving. However, the industry already presents a wide range of solutions in this field [32,38,39]. The emergence and development of dedicated software that is easy and quick to use through remote control, have contributed to the technological evolution of PVD reactors [74–77]. Manual labour has been replaced by technology because the main purpose is to make the equipment more autonomous and automatic. This will reduce maintenance and management costs, and, on the other hand, increase production by making the investment more profitable.

One of the great advantages of this type of reactors and technology is its ability to deposit a wide range of films into parts with complex geometries of different materials, making the process quite flexible. Loading and unloading workpieces is a simple task since access to the coating areas is extremely easy. Currently, the characteristics of the reactors contribute to its handling. In summary, the main characteristics and parameters of the reactors can be seen in Figure 5.

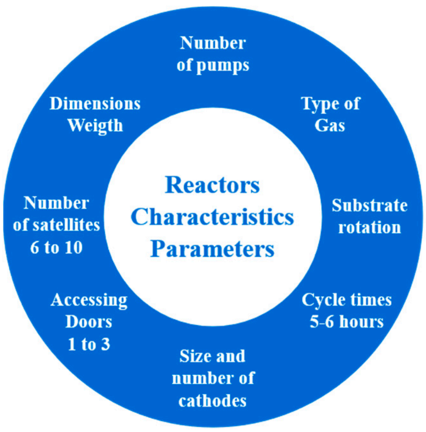

Figure 5. Characteristics and parameters chambers.

It is essential to highlight the importance of the useful diameter of the vacuum chambers, because this parameter will limit the working pressures, and, consequently, the substrates size. The chamber diameter can vary between 400 and 850 mm [74–77] but it can reach up to 2500 mm under customer request [74]. Cycle time is relatively fast, for example for a deposition of 3 μm, usually, takes between 5–6 h. Regarding the number of satellites, this can reach twenty, being more common the use of six or ten satellites.

The rotation systems of the substrates are very important in an industrial context. Its efficiency can reduce costs and improve film properties, with the rotation speed being determinant in the deposition sequence of the layer. Studies have shown that this effect is reflected in the morphologic properties of the coated substrates [60,71,78].

As described in Section 1, in the last years, new pulsed techniques with many potentialities have emerged. The technique with the greatest impact on its development, taking into account all sputtering techniques, is undoubtedly the one using Magnetron. However, it can also be used Diode, Triode, Ion Beam, and Reactive Sputtering systems. The studies on the evolution of the sputtering magnetron technique in DC and RF contribute to the emergence of techniques, such as dual magnetron sputtering (DMS), reactive bipolar pulsed dual magnetron sputtering (BPDMS), modulated pulsed power magnetron sputtering (MPPMS), HiPIMS, dual anode sputtering (DAS), among others.

One of the cheaper power supplies with easy process control is the DC power supply and hence is the most used although the sputter yield is generally much lower [79]. This makes the DC power source the most used in magnetron or pulsed systems. Its major disadvantage is the low rate of ionization. Studies show that only about a fraction of 1% of the target species is sprayed ionized [17]. The DC source only applies when the targets are made of conductive materials. On the other hand, the RF source is only applicable to the use of non-conductive or low conductivity targets. An alternative to using DC and RF sources is the Mid Frequency source (MF). To maintain the plasma in the sputtering process, an alternating high-frequency signal is applied, which allows the current to pass through the target, thus avoiding the accumulation of charges.

The dual magnetron sputtering (DMS) process uses MF power supply and it has been widely used for reactive deposition. It has become increasingly sophisticated, being usually used in systems for industrial applications using magnetron rotation [80,81]. In particular, this method is characterized by a different composition of the targets and way as the film grows. Surface oxidation is one of the sensitive aspects of this technique. To counter oxidation, it is necessary to take into account parameters, such as reactive gas partial pressure, voltage, and sputter rate [80]. Furthermore, in order to receive DC power and apply pulsed-DC power sources in the magnetrons, components need to be configured to switch power. This is possible while using a pulsed power supply [80].

DAS is a technology that allows switching from the commonly used alternating current—mid frequency (AC-MF) mode to a DC power process to reduce the heat load on the substrate.

The BPDMS technique is followed by the DMS technique. The interesting fact about this technique is that it also uses an MF source like DAS. Rizzo et al. [82] used in their study an MF band of 80–350 kHz. Using this technique, it was possible to prevent arc formation and its results showed a high deposition rate of around 0.044 μm min^{-1} using ZrN coating.

The deposition rate is always the focus of improvement when one thinks to upgrade a reactor for industrial purposes. The need of the industry thus obliges it, and, in that sense, in the last years, studies have been conducted also following industrial needs. Some recent investigations have been focused on the increase of spray ionization, on process stability, on new segmented targets, on gas flow optimization of different gases, on the bias influence, on obtaining better absorbers, among others. However, in order to obtain low-cost absorbers as compared to industrial techniques, a laboratory-tested sputtering unit was tested and the results pointed out that the deposition rates were low [83]. On the other hand, in studies regarding the gas flow in sprayed zirconia coatings on flat substrates, the deposition rate results reached 20 μm h^{-1}, which represents a good deposition rate. Other studies regarding the influence of bias voltage and gas flow showed that the temperature increase in the substrate and the application of a bias voltage resulted in a decreased deposition rate. For example, having a substrate temperature of 650 °C and applying a bias voltage at −10 V, it is possible to obtain a deposition rate of 20 μm h^{-1}. However, the deposition rate is reduced to 5 μm h^{-1} if −20 V bias voltage is applied [84,85].

Another approach in an industrial context using the reactor CemeCon® CC800/9 is the study of Weirather et al. [86]. They used the Reactive Pulsed DC magnetron sputtering technique with triangle-like segmented targets. That work contributed to show the potential of this technique in an industrial context, reducing the costs in thin film deposition. $Cr_{1-x}Al_xN$ ($0.21 \leq x \leq 0.74$) was used as a coating material, having obtained low friction values of 0.4 and wear coefficients up to 1.8×10^{-16} m^3 N m^{-1}, in order to obtain good results regarding the tribological properties. The maximum hardness obtained was 25.2 GPa, which proved to be a good result.

A study carried out regarding the plastics industry compared conventional DC, MF pulsed and HiPIMS techniques considering the deposition rate and coating's hardness. It is noteworthy that the complex geometry of the injection moulding tools was an additional challenge in this study, taking into account the three technologies that were used. For the three different technologies, five different targets configurations were used, varying the chemical composition of the $(Cr_{1-x}Al_x)N$ coatings. The HiPIMS technique provided the best results for aluminium deposition rate, which was reflected in an increase from 1.32 to 1.67 μm h^{-1}. In this case, the deposition rates of DC and MF coatings decrease from about 2.45 to 1.30 μm h^{-1}. On the other hand, chromium deposition rate presented the worst results for the HiPIMS technique as compared to DC and MF ones. The morphology, surface, and roughness that were obtained by the HiPIMS technique showed almost constant coatings behaviour [87].

HiPIMS technology allows for combining technologies, such as cathodic arc plasma deposition and ion plating, with this being its greatest advantage [88]. Although this type of reactor appeared in the 1990s, with the evolution of sputtering magnetron technology, just in recent years it has known more interest in its improvement and in exploring its potentialities. Since then, it has been used in the improvement of the spray ionization through the pulsed power that influences the plasma conditions and the coating's properties. When compared to conventional magnetron sputtering, the studies about this technique have shown significant improvements in coating structure, properties, and adhesion [89,90]. On the other hand, the combination of HiPIMS and DC-Pulsed also shows evidence in improving adhesion and morphology while using TiSiN coating [91]. Although versatile, it is necessary to have some care in the process and in the evaluation of results, given the difficulty in obtaining consistent and repeatable results [92].

One variation of the HiPIMS is the power pulses method MPPMS. This technique uses a pulsed high peak target power density for a short period of time and creates high-density plasma with an elevated degree of ionization of the sputtered species [93].

Deep oscillation magnetron sputtering (DOMS) is another variant of HiPIMS. A study that was carried out using this system led to seeking a relation between the ionization of the sputtered species and thin film properties [94]. This investigation had the purpose of identifying the mechanisms which influence the shadowing effect in this technique. To effectively reduce the atomic shadows, it was necessary to accelerate the chromium ions in the substrate sheath in the DOMS, which reduces significantly the high angle component of its collision. A high degree of ionization allows the deposition of dense and compact films without the need for the bombardment of high-energy particles during the coating growing process.

Plasma enhanced magnetron sputtering (PEMS) is an advanced version of conventional DC magnetron sputtering (DCMS). In conventional MS, the discharge plasma is generated in front of the magnetrons, as can be seen in Figure 6a. On the other hand, PEMS assisted deposition has the advantage of generating an independent plasma through impact ionization by accelerating electrons that are emitted from hot filaments in the chamber, which expands through the entire vacuum chamber, as shown in the illustration of Figure 6b. Lin et al. [95] carried out a comparative study between the techniques DCMS and HiPIMS with and without PEMS assistance regarding the deposition of

TiSiCN nanocomposite coatings, concluding that PEMS assistance improves the microstructure and mechanical properties of coatings that are produced by DOMS or DCMS, as well as the reduction of residual stress.

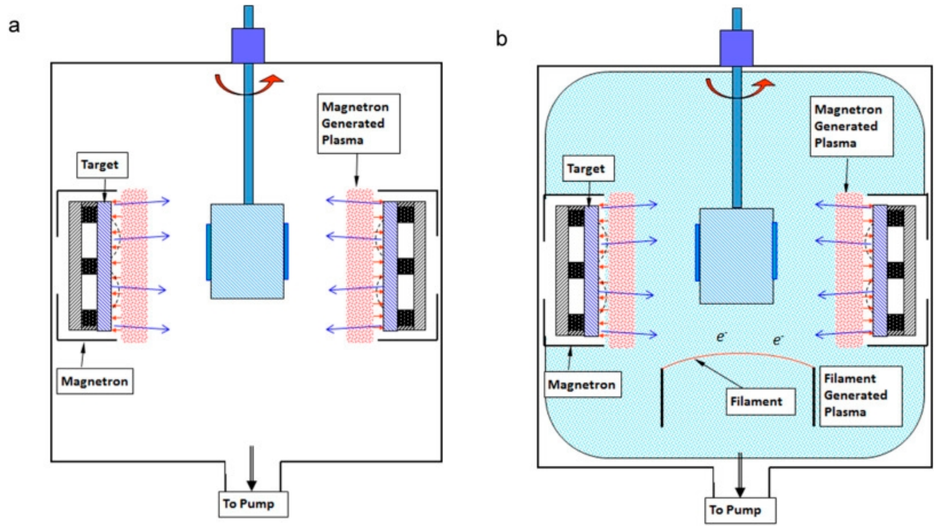

Figure 6. Schematic comparison between (**a**) conventional magnetron sputtering (MS), and the (**b**) plasma enhanced magnetron sputtering (PEMS) assisted process. Reproduced from [95] with permission. Copyright 2018 Elsevier.

The receptivity of the industry to the HiPIMS technique has been very positive bearing in mind the range of reactor power supply. Emerging technologies allow gains around the 30% in the ionization rate and higher charge states of the target ions. This high degree of ionization results in increased advantages of some coating properties, such as improved adhesion and the possibility of consistently covering surfaces with complex geometry [79,96]. Thus, the scientific community has focused on the development of high power magnetic pulsed technologies, since these results are very interesting concerning the industrial context.

3.2. Improvements and Applications of External Devices

Studies show a great interest in using the HiPIMS technique due to its versatility in the production of the PVD coating. This technique has as a disadvantage the deposition rate, which is lower when compared with the conventional sputtering DC. This factor needs to be improved. Some studies have been developed around this concern, trying to overcome the above-mentioned problems by the use of external devices, such as magnetic fields, although the improvements have not been significant yet.

In order to increase the deposition rate of thin films and improve the performance of HiPIMS, Li et al. [97] tested two different vacuum chamber approaches, using five different substrates positions: 0°, 45°, 90°, 135°, and 180°, based in the magnetron cathode in both studies. The first study was focused on the application of an external unbalanced magnetic field. This method indicates that, in the 0° angle substrate position, a substantially higher ion current in the substrate was reported. An increase in plasma density in the substrate region has occurred, showing that this method achieved the expected results. Following the first goal to increase the deposition rate, the second work focuses on more simplified and efficient ion discharge using external electric and magnetic fields with the auxiliary anode. To optimize the magnetic field distribution, the authors used a coaxial electromagnetic coil. This method allowed for a better distribution of the electric field and electric potential in the reactor, increased discharging, plasma intensification, and uni-directionality. The amplitude of the plasma density was five times greater in all positions when compared to the discharging without outer-field HiPIMS [98]. Figure 7 shows the vacuum system during HiPIMS discharge, measuring the ionic current of the substrate in different positions regarding both studies.

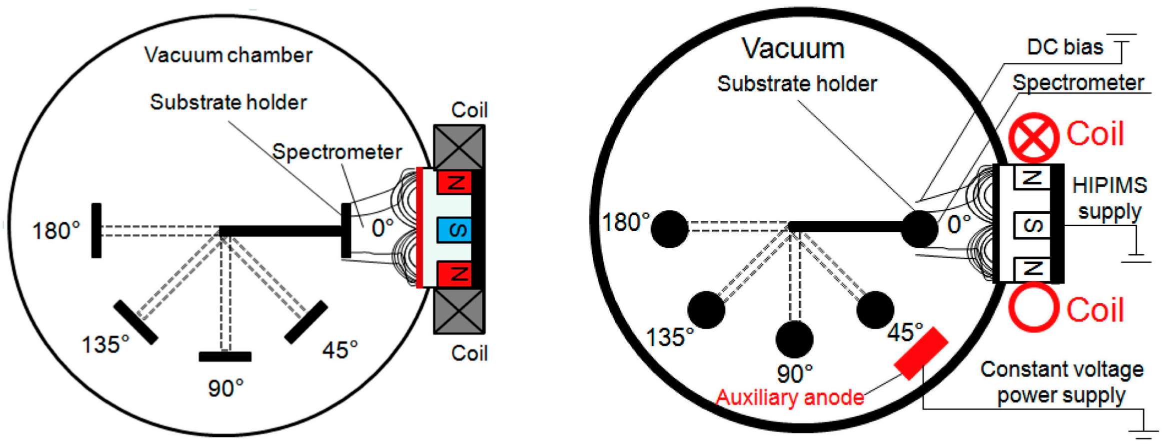

Figure 7. Vacuum system setup using (**a**) external unbalanced magnetic field, (**b**) external electric and magnetic fields, with the auxiliary anode. (**a**) Reproduced from [97] with permission. Copyright 2016 Elsevier. (**b**) Reproduced from [98] with permission. Copyright 2017 Elsevier.

Other examples using an auxiliary magnetic field as external device showed more ambitious results, presenting increased deposition rates between 40% and 140% when considering the inclusion of an external device with different types of targets that were chosen due to their relevance in technological applications. The results were compared with the HiPIMS process without the external device under similar experimental conditions (working gas pressure, average power). Figure 8 shows the configuration of the setup used. However, it is possible to improve the system, as described by the researchers that are involved in that work. It was shown a great potential for deposition improvement in HiPIMS through the control of the magnetic field and pulse configuration [99].

Using magnetic fields, Ganesan et al. [100] showed that it is possible to increase the deposition rate, guiding the ion flux in the direction of the substrate with the application of an external magnetic field using a solenoidal coil, excited with a DC current pulse. This is the scheme that is used in this study, as depicted in Figure 9; it is possible to see in the centre of the chamber the additional solenoidal coil that provides an external magnetic field.

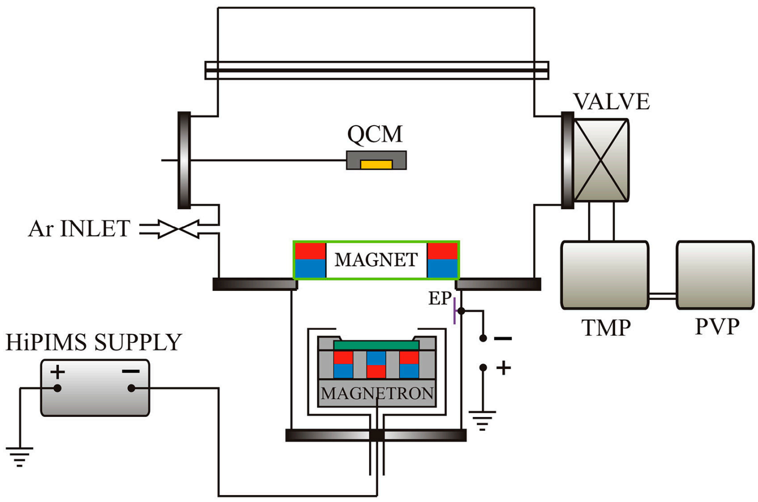

Figure 8. Schematic drawing of the experimental setup used in the work. Reproduced from [99] with permission. Copyright 2018 Elsevier.

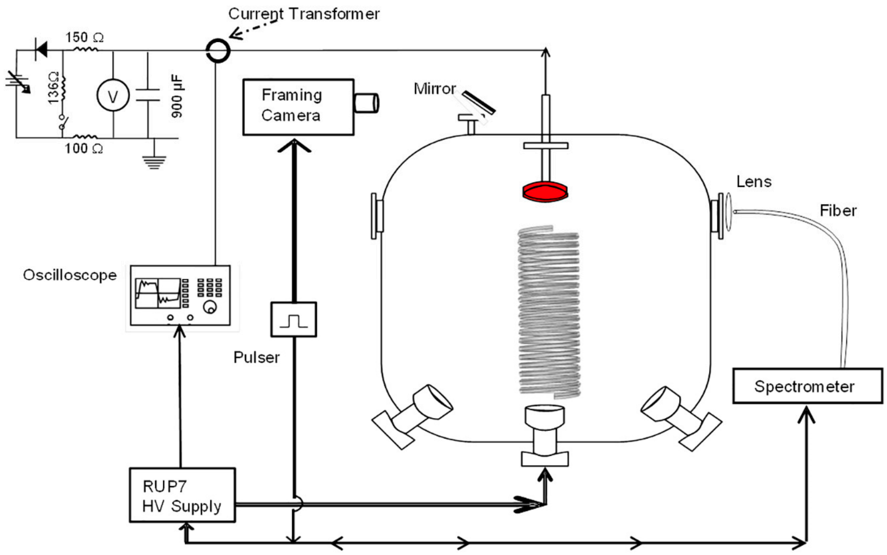

Figure 9. Experimental unit high power impulse magnetron sputtering (HiPIMS) deposition system showing the additional solenoidal coil. Reproduced from [100] with permission. Copyright 2019 Elsevier.

The study shows evidence of intensification in the ionization zone that increases the plasma extension and density, leading to an increase in the deposition rate through the combination of magnetic and reactor magnetron fields. This evidence can be interpreted in Figure 10, where (a) represents a conventional situation of deposition by the generation of transporting ions in neutral (N) and ionized fluxes (I) plasmas, those are deposited on the substrate. The same happens on (b), although applying the magnetic field. The ionization zone will be extended, activating additional ions that will be directed to the substrate, increasing the deposition rate. The results show that an increased maximum peak current and/or in the power density corresponds to a significant improvement in the pulverized ions flow. It has further been found that an increase of about 25% in peak current is seen when a 150 A magnetic field at the start of the HiPIMS pulse is used, inducing a 25% increase in the rate of the target ion emission as compared to the case where no external magnetic field is applied [100].

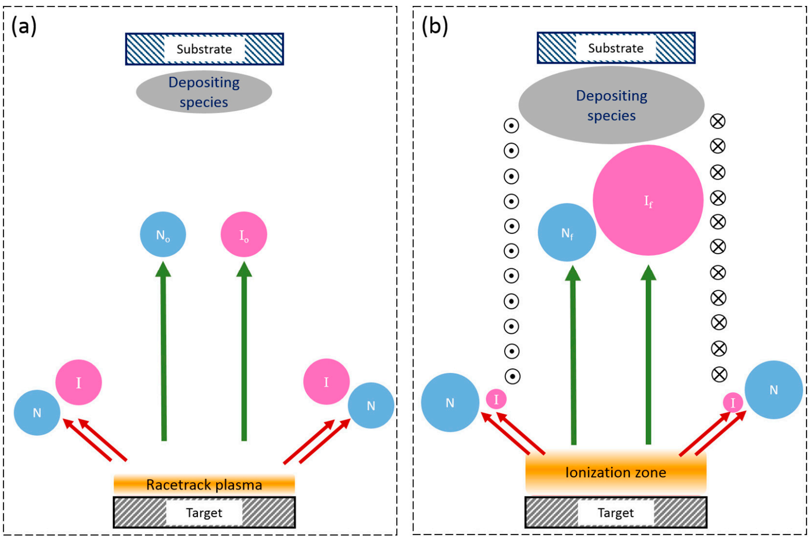

Figure 10. Schematic illustration of a film deposition, (**a**) without the external device and (**b**) with the application of an external magnetic field. Reproduced from [100] with permission. Copyright 2019 Elsevier.

In order to improve Cu films, Wu et al. [101] studied the utilization of a modified HiPIMS system using a positive kick voltage after an initial negative pulse, being possible to control the magnitude and the pulse width of the reverse pulse. This result is interpreted by a bipolar pulsed effect that was studied in detail in this type of deposition. Figure 11 shows the results that were obtained in the deposition of Cu films using three different kick pulses, comparing three different systems: DC magnetron sputtering (DCMS), conventional HiPIMS, and Bipolar Pulsed. It was found that the increase in the voltage amplitude and pulse width of the kick pulse can promote an increase of the deposition rate relatively to the conventional HiPIMS, but even so, the deposition rate that was achieved by the DCMS process showed to be higher. To conclude, the HiPIMS bipolar pulse shows great potential and this new approach can improve Cu film properties such as electronic conductivity and adhesion. However, in order to achieve deposition rates higher than DCMS, the substrates positioning needs to be planned in the centre of the reactor, where the deposition rate is more effective.

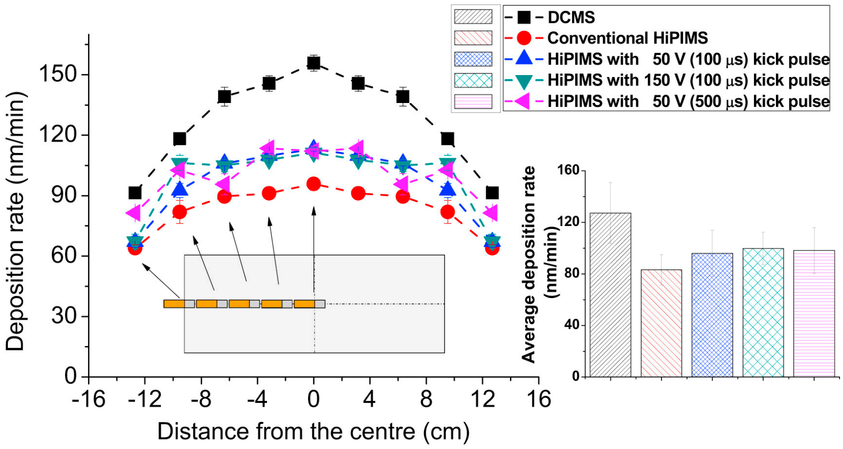

Figure 11. Results relatively to Cu films deposition rate. Average deposition rates for all the samples at different positions in the reactor. Reproduced from [101] with permission. Copyright 2018 Elsevier.

The combination of two or more vacuum chambers in improving the process and its efficiency should be considered. This approach can be seen in the recent work of Bras et al. [102], which simulates an industrial in-line vacuum production of solar cells using as a deposit compound the copper indium gallium selenide (CIGS). The use of the sputtering technique in the industrial context applied in the production of solar cells was demonstrated. In this study, automated arms were used to load and unload the cells. The system presents a process sequence using two vacuum chambers and 25 cathodic spray stations, which has its own heating and helium cooling arrangement. Following the simplified process in Figure 12, it can be seen: (a) in chamber A sputtering stations 1 to 5, where the substrate cleaning and absorber metal layers are carried out; (b) in the transition chamber A to B, the heating station increases the substrate temperature to improve deposition; (c) in chamber B, sputtering stations 6–18 promote the deposition of CIGS layers and the substrate is then rapidly cooled down in the intermediate chamber, and, finally, back to the chamber A; and, (d) sputtering stations 19–25 are producing the buffer layer in an oxygen-containing atmosphere. To finalize the cells, the addition of resistive transparent conductive oxide (TCP) bilayers is needed. The efficiency was demonstrated for cells with a total area of 1 cm^2 and 225 cm^2 with values of 15.1% and 13.2%, respectively.

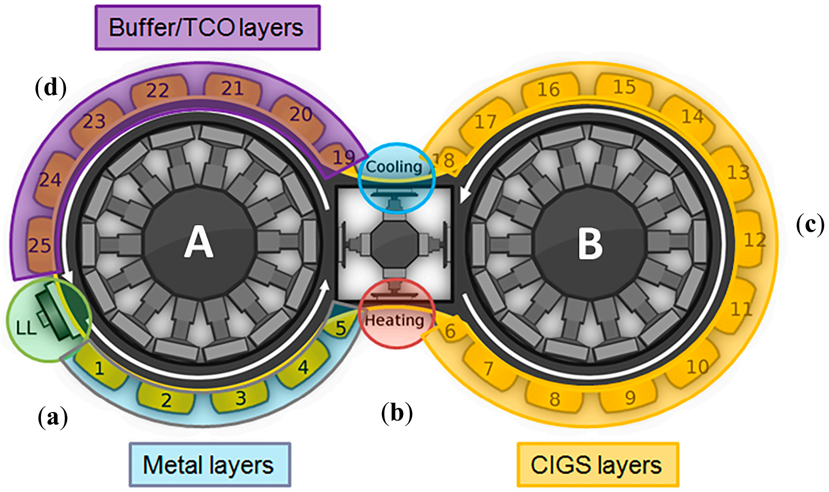

Figure 12. The schematic process sequence of the load-lock DUO solar cell manufacturing system of Midsummer®, (**a**) stations 1 to 5, (**b**) heating station, (**c**) stations 6 to 18 and (**d**) stations 19 to 25. Reproduced from [102] with permission. Copyright 2017 Elsevier.

3.3. Considerations Using CFD Simulation

To study the phenomena that occur in the PVD method, numerical simulation models are usually used. These simulation methods help to solve complex engineering problems in scientific and/or industrial contexts. The most common numerical approaches are finite elements methods (FEM) and computational fluid dynamics (CFD). FEM studies are commonly centred on mechanical properties and CFD is usually focused on process concerns. Initially, studies have been focused mainly on material properties but now the trend is to study the PVD reactor in an industrial context using the simulation, avoiding the cost of stopping the equipment [103,104]. However, the use of numerical methods allows obtaining only an approximate but not exact solution. It is also necessary to have a critical analysis of the results that were obtained through the models because their approximation can introduce errors. Comparing the results that were obtained by the models with experimental results is desirable [105]. FEM helps in studying the phenomenon related to the substrate and coating on their mechanical properties, such as strength, brittleness, adhesion, and performance, among others [31,32,106–108]. CFD is typically focused on the study of fluid flow dynamics, anodic chamber performance prediction, thermal evaluation in a reactor's design, input temperature, the velocity of distribution of the species into the reactor, pressure, and others [109–113]. The quality of the coatings that were obtained in commercial PVD processes is of great importance and therefore its optimization. Thus, it is necessary to take into account the discharge characteristics to know the motion of the neutral gas flow inside the reactor chamber.

Monte Carlo method (DSMC) models are a class of computational algorithms that provide approximate solutions and are widely used in research of thin films [105,114].

Bobzin et al. [28], used direct simulation Monte Carlo method (DSMC) models in CFD analysis to characterized and it assess gas behaviour in the PVD coating process using the Knudsen number (Kn) by means of different approaches: for $Kn \leq 0.1$ the gas flow is described by the Navier–Stokes equations and for $Kn > 0.1$ a kinetic approach was used by the Boltzmann equation. In order to validate the model, they used an argon neutral gas flow and molecular nitrogen gas in an industrial scale reactor CemeCon 800/9® typically used for DC-MS and HiPIMS processes. Considering the developed CFD model, they conclude that it presents limitations in the transition flow regime. To accurately predict flow characteristics, only the kinetic model should be considered. The benefits of each model and the comparison between them were studied and showed that the advances in simulation lead to a detailed analysis on the PVD processes of the formation of coatings that are capable of complying with industrial requirements.

Kapopara et al. [29,30], predicted the gases concentration and distribution (argon and nitrogen), density profiles, velocity profiles, and pressure profiles across the sputtering chamber. They conclude that the locations of both gas inlet port and substrate have a crucial influence on the gas distribution inside the chamber. With this study, it was possible to propose a modification of the reactor geometry for a better gas flow over the substrate. This research showed that the CFD simulation has a great potential and its influence is growing over the time on the PVD reactors studies. After the modulation phase, it allows varying parameters, being a strong advantage in an industrial context due to the capacity of predicting the final results regarding the different phenomena that occur in the reactor during the deposition process. The main goal is a reduction in the production time, with a consequent reduction in costs, maintaining the quality standards.

Trieschmann [115] also used the DSMC to study neutral gas simulation on the influence of rotating spokes on gas rarefaction in HiPIMS. This different approach helps to understand the gas dynamics in the harsh discharge condition. It was concluded that the influence of a rotating plasma ionization zone is limited by a segmented time-modulated sputtering inlet distribution [115].

To conclude, the CFD modelling has been carried out to analyze gas flow and its mixing behaviour within the chamber reactor. However, for a better approximation of a real situation, it is important to use different models and compare them. The models defined and studied are important on the advance of geometry and parameters changes in the reactors that can be simulated, also taking into account external devices, in order to improve the process.

4. Concluding Remarks

PVD techniques are in constant evolution, accompanying the appearance of new technologies that are being adapted to the processes. They also meet the increasing demands of the industry. Furthermore, the focus of researchers in the last years has been on improving reactors and the application of external devices to the detriment of improving the properties of films, which has passed to the background, following the needs of industry.

Optimizing energy consumption of PVD processes is an opportunity for improvement. It is in the deposition step that this improvement can be reflected, since it is in this step of the process that PVD shows greater consumption. In the CVD process, it represents 33.5%, whereas in the PVD process, it represents 77.7% of consumption.

New opportunities in the development of techniques have contributed to the appearance of the MF power source that allowed the combination of DC and RF sources. The DC sources remain the most used type while the RF source is the least used. However, the combination of the sources in the DAS technique allowed for reducing the heat load on the substrate, thus improving the film properties, giving to this technique a huge yield for improvement.

External devices have emerged as a result of the PVD techniques enhancement. The HiPIMS method shows evidence of this application and improvement for high-performance thin films. This technology has had a good acceptance by the industry, which contributed to accelerating the researcher's interest. In addition, the good results obtained with the application of external devices has shown an increase in deposition rates due to plasma intensification. The coatings industry has evolved to the HiPIMS reactors due to the facts above-mentioned, and it is believable that this trend remains in the same way in the near future.

With technology evolution, simulations are currently a reality. Softwares, such as FEM and CFD, support this evolution in reducing production costs and adapting external devices. In addition, they respond to solve complex engineering problems in an industrial context. However, the use of CFD in solving coating problems can still grow in the light of its potential. New developments are expected as technology and software advances in deposition systems.

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Nomenclature

AC-MF	Alternating Current—Mid Frequency
BPDMS	Reactive Bipolar Pulsed Dual MS
CFD	Computational Fluid Dynamics
CIGS	Copper Indium Gallium Selenide
CNC	Computer numerical control
CVD	Chemical Vapour Deposition
DAS	Dual Anode Sputtering
DC	Direct Current
DCMS	Direct Current Magnetron Sputtering
DMS	Dual Magnetron Sputtering
DSMC	Direct Simulation Monte Carlo
E-Beam	Electron Beam Gun
FEM	Finite Elements Methods
HiPIMS	High Power Impulse Magnetron Sputtering
HPPMS	High-Power Pulsed Magnetron Sputtering
MEP	Magnetically Enhanced Plasma
MF	Mid Frequency
MPPMS	Modulated Pulsed Power MS
MS	Magnetron Sputtering
PAPVD	PVD Plasma Assisted
PEMS	Plasma enhanced magnetron sputtering
PVD	Physical Vapour Deposition
RF	Radio Frequency
TCP	Transparent Conductive Oxide
UBMS	Unbalanced Magnetron Sputtering

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