Chapter

Plasma Based Approaches to Achieve Self-Cleaning Surfaces

Deepanjana Adak and Raghunath Bhattacharyya

Abstract

The role of gaseous plasma has proven to be very beneficial in creating self-cleaning of various surfaces. Few references are there, in the published literature, on plasma enhanced hydrophilicity/hydrophobicity behavior of surfaces. A range of atmospheric pressure plasma spray systems are gaining popularity for creating self-cleaning surfaces, with some unique features, as also to fabricate new types of self-cleaning materials. In this chapter a brief introduction to essentials of plasma processing will be first presented, followed by examples of plasma assisted surface modification. This will include plasma cleaning, plasma etching, plasma polymerization/deposition, etc. Subsequently, various plasma assisted techniques to achieve a variety of self-cleaning surfaces will be highlighted. A unique combination of plasma-based approaches and sol–gel derived coating will also be discussed.

Keywords: self-cleaning, atmospheric-plasma, cold-plasma, superhydrophilic, superhydrophobic

1. Introduction

1.1 What is plasma?

> *The term has been first used to describe ionized gas by Irving Langmuir in the year 1929. Plasma can be defined as a quasi-neutral gas of charged and neutral particles characterized by collective behavior.*

Depending on the energy of particle constituting matter, the matter can be broadly divided into 3 states – solid, liquid, and gases. However there exist energetically fourth state of matter apart from these three states, known as, *Plasma*. Generally, the transformation from one state to another is achieved in the presence of energy sufficient enough to overcome intermolecular forces. Likewise the transformation to fourth state of matter, plasma state, from gaseous state takes place when the gas molecules are heated to extremely high temperature or subject to high energy radiation [1]. The most common examples of species that exist in plasma state are interstellar matter such as sun and other stars. The primary benefit of plasma-assisted solid processing arises from the ability to conduct chemical reactions at substrate temperatures significantly lower than those achievable through standard reactions occurring at thermal equilibrium [2].

Plasma, with its fascinating characteristics, arises from the electromagnetic interactions among charged particles. It comprises electrons, ions, neutrals, electromagnetic radiation (photons), and electromagnetic fields, all contributing to its unique properties [3–9]. One notable attribute of plasma is its striking quasi-neutrality, where the positive and negative charges are intricately balanced, leading to an overall state of electrical neutrality [10].

Plasma can be broadly classified into two groups based on temperature and equilibrium conditions. The first group is thermal or equilibrium plasma, characterized by high ionization and thermal equilibrium among charged particles at temperatures around 10^4 K. The second group is non-thermal or non-equilibrium plasma, commonly known as cold plasma. In cold plasma, ionization is milder, and electrons do not reach thermal equilibrium with heavier particles. As a result, the gas temperature remains close to room temperature or slightly elevated, typically ranging from 40 to 150°C. Additionally, the electron density in cold plasma is typically below 1000 m^{-3} [11]. Non-thermal or cold plasmas can be generated under both low-pressure and atmospheric-pressure conditions. Generally, the temperature of each species within the plasma is determined by the average kinetic energy of the individual particles.

The fundamentals of cold, low-pressure plasmas has been discussed in an extensive detail in the book "*Cold Plasma in materials fabrication*" *by Alfred Grill, IBM Research Division, T.J Watson Research Center, New York* [10]. The behavior of plasma closely resembles the behavior of neutral gas, and it is possible to somewhat explain its property as described by *Kinetic Theory of Gases.* In contrast to neutral gas molecules, the movement of particles composing plasma results in localized concentrations of positive and negative charges. These concentrations of charge give rise to long-range coulombic fields that influence the trajectories of charged particles. Consequently, a charged particle in plasma tends to follow a path that, on average, aligns with the electric field present.

Plasma is broadly characterized by the following basic parameters,

- The densities of electrons & ions: $n_e = n_i =$ which represents the plasma density.

- The density of neutral particles (n_n)

- The energy distributions of neutrals, f_n (w), ions, f_i (w) and electrons f_e (w)

- Electron Energy (T_e)

- Debye length λ_D which serves as a characteristic dimension indicating regions where the breakdown of neutrality can occur.

$$T_e = 1\,\mathrm{eV}, n_e = 1010\,\mathrm{cm}^{-3}, \lambda_D = \sqrt{\frac{\varepsilon_o k T_e}{n_e e^2}} = 74\,\mu\mathrm{m} \quad (1)$$

- The presence of a plasma sheath near a surface is a result of electrons moving at significantly greater speeds than ions, causing them to depart from the plasma and create a positive charge in the surrounding area of the surface.

Near the surface, an electric field emerges that hinders the motion of electrons and accelerates ions. As a result, the surface acquires a negative potential, referred to as a negative self-bias, relative to plasma. In contrast, the plasma itself maintains a positive potential. The localized concentration of charged particles is confined within a volume equivalent to the Debye length (λ_D). It is important to highlight that beyond this volume, the charge density of ions matches the charge density of electrons, leading to the plasma's overall electrical neutrality. This property is the key reason why plasma is commonly regarded as a quasi-neutral gas.

1.2 Cold-plasma generation

To create and maintain cold plasma, gaseous molecules are typically exposed to direct current (DC), radio frequency (RF), or microwave (MW) power. In 1923, Irving Langmuir discovered the distinctive characteristics of DC glow discharge in a discharge tube and coined the term "plasma." It was observed that when voltage is applied to the gas in the discharge tube, the number of free electrons gradually increases and accelerates in response to the applied electric field, leading to a steady rise in the current (I). Once the applied voltage reaches a certain threshold value, known as the breakdown potential (V_b), an avalanche process occurs due to the interplay of three simultaneous processes:

- Accelerated ions collide with the cathode, resulting in the emission of secondary electrons.
- The newly generated ions, in turn, produce additional electrons through collisions as they accelerate toward the cathode, leading to the creation of more ions.
- The electrons produced in this manner are either removed from the plasma through recombination with oppositely charged ions or diffuse/drift toward the walls of the tube.

When equilibrium is reached between rate of formation and recombination of electrons, the discharge becomes self-sustaining. This leads to a significant breakdown in the gas, causing it to emit a glowing effect. Consequently, there is an abrupt rise in current accompanied by a voltage drop. The following schematics (**Figure 1**) summarize what prevails in plasma reactors commonly used in most laboratories.

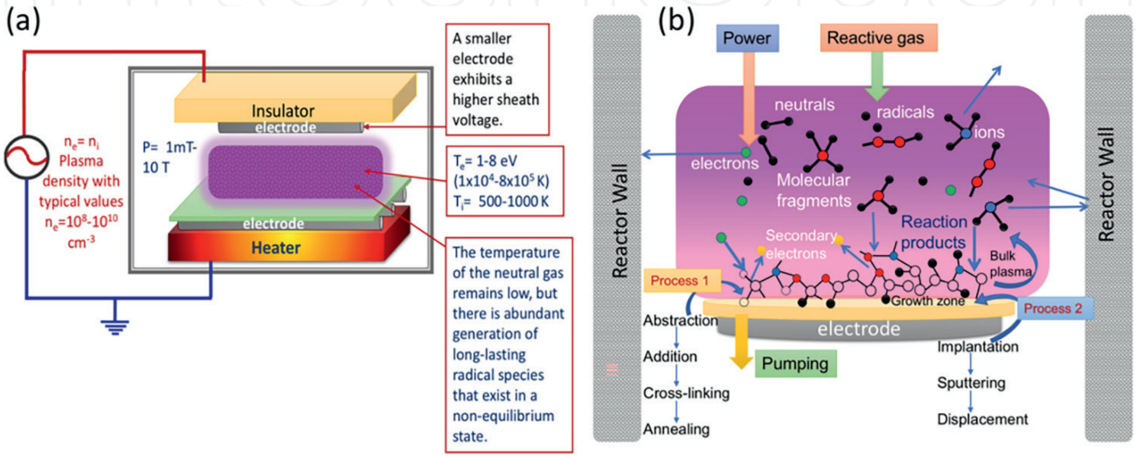

Figure 1.
Schematic depicting typical processes inside the plasma reactor.

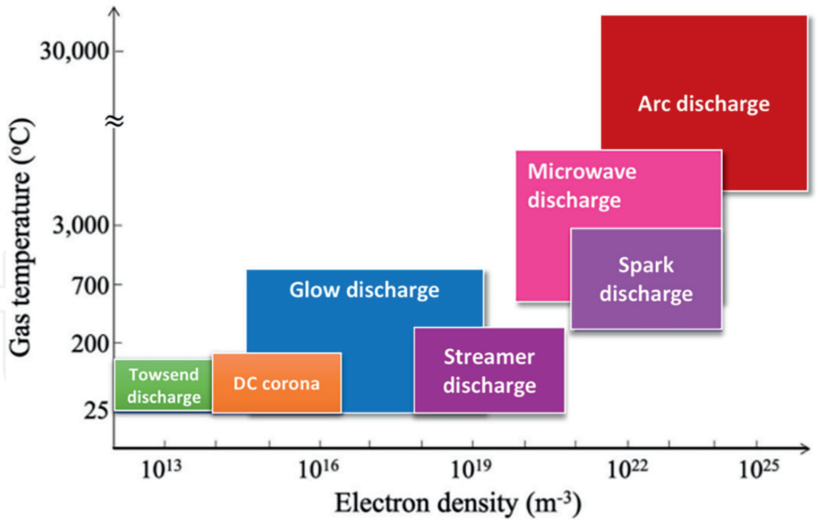

Figure 2.
Variation of electron density with gas temperature for gas discharges of the typical atmospheric cold plasma. (Adapted from ref. [5].)

In recent studies, cold plasmas have gained significant attention and are generated using methods such as corona discharges, dielectric barrier discharges, and plasma jets. These plasmas are created at atmospheric pressure by employing pulses with durations ranging from 10^{-6} to 10^{-9} seconds. In this type of plasma, known as 'Cold Atmospheric Plasma' (CAP), electrons with high energy levels are generated. CAP has shown great potential for a wide range of surface engineering application [12] (**Figure 2**).

2. Plasma assisted surface modification

The plasma-based surface modification majorly involves: *Plasma treatment*, *plasma etching*, and *plasma polymerization*. In case of plasma treatment of materials as well as plasma polymerization on a substrate, the plasma can be majorly divided into following three categories [13]:

- Chemically non-reactive plasma i.e. plasma generated by ionizing inert gas such as Ar, He, etc.
- Chemically reactive plasma i.e. plasma generated through inorganic and organic molecular gases such as O_2, N_2, CF_4, etc.
- Polymer forming plasma i.e. plasma resulting from organic or inorganic vapor.

Every year the substantial increase in the number of research papers and patents on the use of plasma technology for producing a variety of new materials and functional coatings is indicating the myriad of opportunities created by plasma technology [14]. Plasma-based methods are highly prevalent in surface treatment technologies and find extensive application in areas such as cleaning, surface activation, enhancing adhesion, corrosion resistance, biomedical applications, and the development of self-cleaning coatings [14–20].

Plasma techniques are employed in various processes related to substrate treatment, including cleaning the substrate using gaseous plasma prior to coating, as well as modifying the surface after applying the desired coating material [21, 22]. Plasma etching also known as dry etching, has emerged as a crucial technique in microfabrication processes for microelectronic devices, aligning with advancements in the field of microelectronics [10]. However, so far plasma-based approaches were not extensively used to develop self-cleaning surfaces in commercial scale. Vacuum based plasma techniques impose major challenges with respect to cost-effective large area deposition in ambient conditions. Though, one can find in several published literatures the use of plasma deposition techniques for developing functional self-cleaning coatings.

2.1 Plasma cleaning

Plasma treatment is a highly effective method for preparing materials for subsequent processing, as it enhances their surface energy and removes contaminants introduced during the production process. This treatment significantly improves the quality, durability, and adhesive properties of coatings or printing applied to the surface. By subjecting materials to plasma treatment, their surface is modified in a way that optimizes their compatibility with secondary manufacturing applications [23]. The process involves a reactive treatment wherein positive and negative ions, electrons, and radicals interact and collide in the presence of an electric potential difference. Through this energetic interaction, plasma treatment primes the surface, creating an environment that enhances the acceptance and bonding of subsequent manufacturing processes. By increasing the surface energy and eliminating contaminants, plasma treatment ensures that adhere more effectively, resulting in superior quality and longer lifespan of the applied materials. *Roger L. Shannon* and *Roger B. Gillette* together filed a patent that claims a plasma cleaning device for cleaning contaminated surfaces present in a high vacuum [24]. Basic steps involved in plasma cleaning of a substrate have been presented in **Figure 3**.

2.2 Plasma etching

Extensive research has been conducted on plasma-assisted surface modification techniques, aimed at customizing various surface properties through the treatment of target substrates with gaseous plasma. The etching process facilitated by chemically reactive plasma involves a combination of physical and chemical mechanisms, which depend on the stability and volatility of the products formed through the interaction between the etching gas and the material [13]. Etching by chemically non-reactive plasma occurs by a physical deposition process such as magnetron sputtering [25, 26].

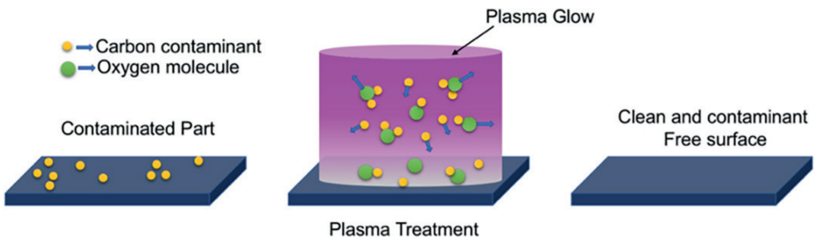

Figure 3.
Steps involved in typical plasma cleaning process.

The plasma etching is carried using a gaseous discharge containing reactive species such as atoms and radicals that react with the surface to form volatile compounds that evaporate from the surface under proper reaction condition leaving an etched target substrate. It is also possible to create desired nanostructure on the substrate by varying the process parameters and underlying plasma chemistry of the reactive etchant gas [27, 28].

The reactive ion etching (RIE) is one of the most widely used dry etching techniques. The etching in this system is achieved by suitable combination of chemical reactivity of plasma species and the physical effects caused by ion bombardment [29]. A schematic depiction of a typical RIE system is given **Figure 4**.

It should be noted that in RIE systems both the chemical reaction on the surface of target substrate and the removal of the volatile products so formed on the etched surface are enhanced by ion bombardment of gaseous plasma. Basic steps involved in plasma cleaning of a substrate have been presented in **Figure 5**.

2.3 Plasma polymerization

Plasma polymerization is a process that involves the deposition of an organic polymer through plasma-enhanced chemical vapor deposition (PECVD). This process entails the decomposition of an organic monomer gas, followed by the deposition and polymerization of the excited species onto the substrate's surface. Films deposited through plasma polymerization can have thicknesses ranging from several

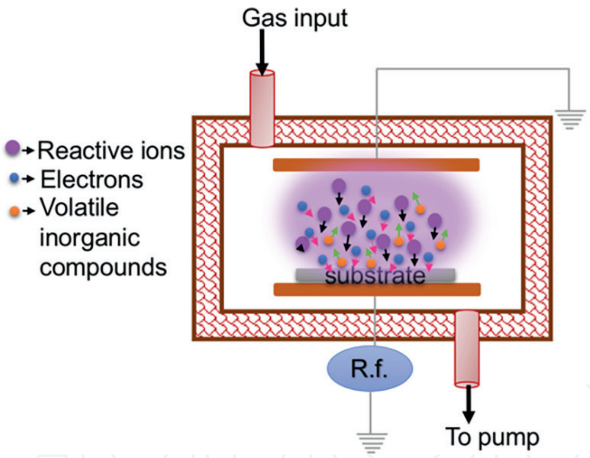

Figure 4.
Schematic depicting dry etching in a reactive ion etching system.

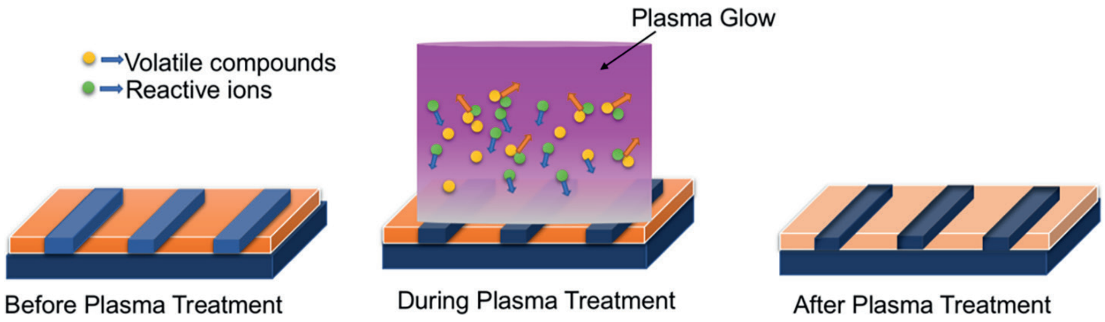

Figure 5.
Steps involved in a typical plasma assisted etching.

tens to several thousands of angstroms. These deposited films, known as plasma polymers, exhibit chemical and physical properties that differ from conventional polymers. Starting materials for plasma polymerization can include hydrocarbons, fluorocarbons, and organic compounds containing nitrogen, oxygen, or silicon. Plasma polymers do not possess distinct repeating units like conventional polymers. Instead, their properties are primarily determined by the plasma parameters used during the deposition process. For example, it is not possible to identify a specific product as a plasma polymer of ethylene, as various products can be obtained from an ethylene plasma. Therefore, plasma polymers derived from ethylene are not equivalent to polyethylene. It's worth noting that the presence of functional groups, such as double bonds, is not a prerequisite for the monomer used in plasma polymerization. The process can occur even without such functional groups. Furthermore, the process of plasma polymerization yields a polymer coating through a rapid step growth reaction mechanism [13]. Plasma polymerization does not rely on a single species for its occurrence; instead, a diverse range of active species generated during the process actively participate in the polymerization reaction. The specific type and quantity of these activated species are contingent upon the reaction conditions employed during plasma polymerization [30]. Since both the kind of reactive species (monoradical and diradicals) are formed simultaneously, reaction between them is also very much likely to occur by cross cycle reactions, depending on the concentration of both the species.

Important factors that determines the deposition of films by plasma polymerization processes are type of monomer, carrier/reactive gas and it mass flow, pressure, temperature, input power, and reactor type [31]. Another important factor that ascertains the several important surface properties of plasma assisted modification is the frequency source used to generate plasma.

Srivatsa et al. developed a custom plasma polymerization deposition system (**Figure 6**) to enhance both surface wettability and hardness [24]. Subsequently, a four-layer antireflective coating (ARC) is applied in the same chamber on a polycarbonate (PC) substrate, consisting of alternating thin films of titanium dioxide and

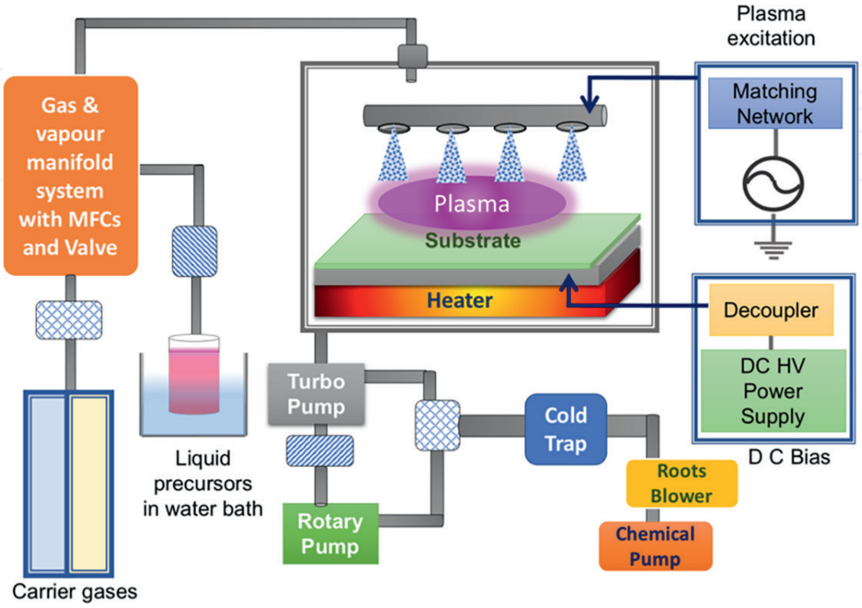

Figure 6.
Typical plasma polymerization deposition system set up. (Reproduced from ref. [24].)

silicon dioxide with varying thicknesses. This results in the creation of a robust and durable ARC on the PC substrate.

Jung *et al.* demonstrated effect of microwave and rf plasma on the photocatalytic properties and wetting behavior of TiO_2 thin films deposited on glass substrate using dip-coating techniques [32]. Han *et al.* adopted the plasma polymerization processing method for obtaining a broadband transparent, superhydrophobic surfaces usingCH_4, C_4F_8, and He gas mixture in an Rf plasma reactor at atmospheric pressure [33]. Ji et al. conducted a study where they presented the production of a superhydrophobic coating using a combination of atmospheric pressure middle frequency (Mf) and radio frequency (Rf) plasmas in an in-line process [34]. The coating was created by utilizing a mixture of Ar gas and HMDSO solution.

Barankin et al. developed a novel low-temperature atmospheric pressure plasma technique for polymerizing liquid fluoroalkylsilane (FAS) precursors, providing an effective method for producing hydrophobic coatings on glass and acrylic surfaces [35]. This innovative approach involves the atmospheric plasma curing of liquid FAS precursors, resulting in films with exceptional properties. The coatings exhibited a total surface energy of 11 dynes/cm, characterized by 10% polarity and average water contact angles ranging from 106° to 110°. To enhance adhesion between the FAS molecules and the surfaces, oxygen plasma activation was utilized, proving crucial in achieving strong bonding. The hydrophobic coatings generated through this method exhibit excellent transparency, stability, and long-lasting performance for over a year. This durability is attributed to the robust bonding between the fluoroalkyl ligands and the surfaces, preventing degradation and ensuring sustained hydrophobic characteristics.

2.4 Atmospheric pressure plasma

Various plasma sources (ion sources) which worked under vacuum conditions have long been used to tailor material properties [36]. In a major development in recent years their counter parts for processing under atmospheric conditions have started becoming available.

To enable affordable access to plasma techniques, researchers are now extensively exploring atmospheric pressure-based methods. There is a wide variety of atmospheric-pressure plasmas used in the processing of materials. Traditional sources of plasma, such as transferred arcs, plasma torches, corona discharges, and dielectric barrier discharges, are being employed. These sources generate plasmas with electron and neutral temperatures exceeding 5000°C, and the density of charged particles generally ranges from 1016 to 1019 cm^{-3} [37, 38]. They are primarily used in metallurgy applications due to their high-temperature nature. On the other hand, non-equilibrium plasmas created by corona discharges and dielectric barrier discharges have gas temperatures ranging from 50 to 400°C, and the density of charged particles falls within the range of 1010 to 1015 cm^{-3} [39, 40]. In order to create a dielectric barrier discharge (DBD) plasma, a high-frequency voltage is applied to a ceramic material, which leads to the generation of plasma within the ceramic's holes. Consequently, objects like an endless fabric tape can be passed over the ceramic, allowing for a significant surface area to be activated in a short amount of time. It is important to note that DBD plasma production results in the generation of ozone (O_3) [41]. Therefore, it is crucial to utilize an extraction system when operating DBD for extended periods in enclosed spaces. Popular atmospheric plasma deposition has been presented in **Figure 7**.

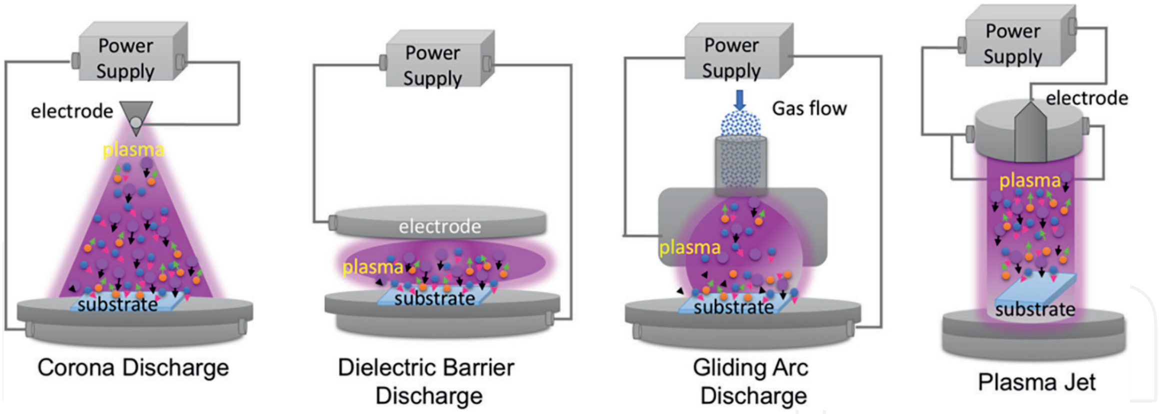

Figure 7.
Various atmospheric plasma deposition processes.

Among various atmospheric plasma processes, DBD plasma technique is highly advantageous due to its ability to generate high-energy electrons and facilitate rapid reactions. Moreover, it can be employed with various gases without causing electrode corrosion. As a result, this technique has found wide applications in diverse fields, including sterilization, material surface cleaning, semiconductor manufacturing, and surface treatment. Owing to its versatility and effectiveness, further research can explore its potential for optimizing deposition parameters and investigating the long-term stability and durability of plasma-treated surfaces in different environmental conditions. However, their non-uniform nature limits their use in materials processing.

In contrast, the atmospheric-pressure plasma jet shares similarities with a conventional low-pressure glow discharge [40, 42–44]. The plasma jet typically maintains a gas temperature between 25 and 200°C, with charged-particle densities at approximately 1011 cm^{-3}. Additionally, there are high concentrations of reactive species, ranging from 10 to 100 ppm. An important advantage of this plasma source is that it can operate without requiring a vacuum chamber, which significantly broadens its range of potential applications. In summary, atmospheric-pressure plasma jets present a promising solution for a wide range of materials processing applications. They offer moderate gas temperatures, relatively high particle densities, and a rich presence of reactive species. The absence of a vacuum requirement enhances their versatility, allowing them to be effectively utilized in various material processing scenarios. Moreover, to address the constraint imposed by the reactor size, which limits the use of moderate-sized substrates for functionalization or modification, a recent technology called air plasma spray has emerged. This technology aims to enhance the adhesion, uniformity, mechanical hardness, and other surface properties of the target substrate.

In a recent study by Marchand et al., they showcased the preparation of long-lasting superhydrophobic films on various substrates under ambient conditions, eliminating the need for a vacuum chamber. They achieved this by utilizing a tetramethylsilane (TMS) precursor [45]. A superhydrophobic coating was successfully demonstrated by Jin et al. using an in-line process that incorporated atmospheric pressure middle frequency (Mf) and radio frequency (Rf) plasmas [34]. The process involved the utilization of a mixture of Ar gas and HMDSO solution. Han et al. introduced a single-step processing technique for achieving broadband transparency (covering wavelengths from visible to near-infrared range) and super-hydrophobicity on surfaces. This was accomplished using a mixture of helium (He), methane (CH_4), and octafluorocyclobutane (C_4F_8), gases in a radio frequency (RF) plasma reactor operating at atmospheric pressure [33]. By employing atmospheric pressure, He/CH_4 plasma, it is possible to achieve a chemically dominant hydrophobicity without the need for etching agents. The effects of plasma treatment on hydrophobicity and transparency were investigated and a large contact angle ~165° and low hysteresis of 4.9° was obtained.

Hossain et al. investigated tetramethylsilane (TMS) and 3-aminopropyl methyl silane (APDMES) as precursors to apply superhydrophobic coatings onto glass substrates. The deposition process involved a plasma jet that relied on dielectric barrier discharge [46]. The resulting films demonstrated exceptional water repellency properties, with a water contact angle of 163° and a sliding angle of only 5°. Additionally, the films exhibited a surface roughness of 50 nm, which further enhanced their superhydrophobic characteristics and self-cleaning abilities. The deposition process utilizing the dielectric barrier discharge plasma jet proved to be a straightforward and efficient technique for creating superhydrophobic coatings on various substrates.

In a separate study, Lin et al. utilized a CO/N_2 DBD plasma along with acrylic acid as a precursor to alter the surface of a PTFE film [47]. This process led to creation of hydrophilic functional groups such as –COOH, C–O, C–C, and others on the PTFE surface. Through two reaction treatments, the water contact angle decreased to 140°, and after twenty reactions, it reached less than 5°, indicating a significant improvement in surface wettability.

Fakhouri et al. introduces a novel approach for depositing TiO_2 coatings using atmospheric pressure plasma jet (APPJ) coupled with a liquid precursor spray (droplet size~100 μm) [48]. The developed technique enables high deposition rates, and the resulting coatings exhibit a highly porous structure with pore sizes ranging from 100 to 1000 nm, leading to a large specific surface area. The coatings deposited by APPJ demonstrate several notable advantages over the RF-sputtered coatings. Firstly, they exhibit a significantly higher specific surface area, which is beneficial for enhanced photocatalytic activity. The increased surface area provides more active sites for reactions, leading to improved catalytic performance. Moreover, the porous nature of the APPJ coatings further contributes to their enhanced specific surface area and catalytic activity. In comparison to RF sputtering, the APPJ technique offers superior deposition properties, including higher deposition rates and improved coating characteristics. These findings highlight the effectiveness of the APPJ technique in depositing TiO_2 coatings with high specific surface areas and improved photocatalytic activity compared to RF-sputtered coatings.

3. Plasma assisted self-cleaning surface

Plasma coatings represent an exciting field within plasma technology, with significant potential for enhancing the functionality and value of materials across a wide range of applications. These coatings provide two primary surface properties: complete repellency to liquids (such as water and oil) or complete wetting ability. The process involves the formation of a nanoscale polymer layer across the entire surface of an object when it is exposed to plasma. This coating process is rapid, typically taking only a few minutes to complete. It is a very thin (few nanometers to microns) permanent coating, firmly bound to the material surface on an atomic scale.

Plasma coating technology generates surfaces with exceptional hydrophobic properties, exhibiting a “lotus effect” where water is repelled. These surfaces also possess dirt-repellent characteristics, enabling self-cleaning without the need for manual cleaning methods. Promising applications for plasma coatings include the coating of automotive components like aluminum wheel rims, as well as window frontages and glass panes [49].

Song *et al.* reported a one-step nanostructure fabrication process using plasma-assisted reactive ion etching (RIE) processing [50]. Mazumder *et al.* reported a similar hierarchical nanostructured transparent antireflection glass material with superomniphobic properties. The two-tier roughness was found to consist of primary nanopillars (~100–200 nm) superimposed with nanoparticles (~10–30 nm). The nanopillars were fabricated by metal dewetting followed by RIE and the nanoparticles are deposited using combustion chemical vapor deposition (CCVD). They have been able to achieve contact angles ~170° and 160° for water and oil, respectively and an average transmission of 93.8% in the wavelength range 400 to 700 nm using CF_4 and O_2 gas mixture, exhibits very high optical transmission and antifogging effects [51].

3.1 Versatility of low temperature plasma

In recent times, the advancement of low temperature plasma technology has emerged as a flexible and efficient approach for manipulating the surface structure of materials [52]. One specific technique, known as low temperature plasma-enhanced chemical vapor deposition (PECVD), offers several notable advantages. These include direct surface pretreatment, modification at low temperatures, low organic content, and the absence of post-processing requirements [53, 54]. PECVD utilizes the energy and reactivity of electrons, ions, free atoms, and free radicals present in the plasma to induce physical and chemical transformations on the material surface. Consequently, this process enables the formation of new functional groups with desirable properties or the creation of film layers with unique structures, making it a crucial method in the treatment of superwetting surfaces.

The significance of plasma-based process to achieve surface superwettability is evident from the surge in research publications. In the year 2000, the number of papers published on this topic was less than 3500. However, by 2010, this number had increased to nearly 9000, highlighting the expanding interest in the field. As of the current year, approximately 20,000 papers have been published in the area of plasma control of surface superwettability, demonstrating its continued relevance and widespread research focus [55].

Two widely used approaches for surface modification are atmospheric pressure plasma treatment and low-pressure plasma treatment [56, 57]. Atmospheric pressure plasma treatment includes techniques like dielectric barrier discharge plasma and atmospheric pressure plasma jet treatment. On the other hand, low-pressure plasma treatment involves methods such as radiofrequency (Rf) discharge plasma treatment and glow discharge plasma treatment. These methods enable the application of plasma to the surface, leading to the creation of nano-scale roughness [58]. Alternatively, by introducing precursors that are chemically linked to diverse functional groups, the desired surface wettability can be achieved [59].

Zhang et al. explored the potential of an atmospheric pressure air plasma jet, generated using a dielectric barrier structure with hollow electrodes (HEDBS), as a means to spray TiO_2 films inside tubular substrates [60]. The results obtained from the self-cleaning test indicate that the proposed HEDBS approach, utilizing air as the working gas, offers a practical and efficient method for synthesizing thin TiO_2 nanofilms, while simultaneously reducing costs and saving time. This approach holds significant promise for various applications, particularly for coating tubular substrates with TiO_2 films.

Chemin et al. presented innovative method for synthesizing anatase TiO_2/SiO_2 nanocomposite coatings at atmospheric pressure, offering transparent anti-fogging and self-cleaning properties on polymer substrates [61]. The concomitant injection of titania and silica precursors in a blown-arc discharge allows for the efficient production of durable coatings with excellent performance characteristics. The findings of this study pave the way for the development of advanced coatings applicable in various industries where transparency, anti-fogging, and self-cleaning properties are highly desirable. The use of anatase TiO_2 nanoparticles in conjunction with SiO_2 in the nanocomposite coatings contributes to their enhanced durability and desirable properties. The combination of these materials not only imparts super-hydrophilicity, which facilitates water spreading and evaporation, but also harnesses the photocatalytic nature of TiO_2, enabling the degradation of organic pollutants and further promoting self-cleaning functionality.

This plasma-based surface pre-treatment using air plasma gun results in clean and highly activated surfaces that can be easily wetted by water, eliminating the need for volatile organic compounds (VOCs) and the associated processes of drying and wastewater disposal. This technology finds application in various areas such as enhancing structural adhesive bonds in the automotive industry, creating seals for electronics applications, or achieving quick and bubble-free wet labelling with strong initial adhesion in the packaging industry. Moreover, the use of plasma gun has been reported for depositing thin film coatings like organosilicate and ceria nanocomposites, which provide improved hardness, adhesion, and UV-absorbing properties [62, 63].

Deicing and self-cleaning processes have gained significant global attention due to their crucial importance in various industries. One major challenge faced by these industries is the formation of atmospheric ice caused by super-cooled dewdrops in icy rain. This phenomenon poses a significant threat to aircraft, wind turbines, electric and telecommunication wires, highways, bridges, and other outdoor equipment and systems. Plasma-treated superhydrophobic (SH) coatings have emerged as a highly relevant solution for both deicing and self-cleaning applications in aircraft and other systems. Subeshan et al. the use of plasma-treated superhydrophobic coatings provides an effective solution for both deicing and self-cleaning requirements in aviation industries [64]. This study contributes valuable insights into the characteristics and performance of plasma-treated SH coatings on the AA 2024-T3 alloy, showcasing their ability to repel water, prevent ice formation, and maintain a clean surface under diverse atmospheric conditions.

The utilization of an air plasma gun for plasma-based surface pre-treatment leads to the formation of clean and highly activated surfaces that readily wet with water. This eliminates the need for volatile organic compounds (VOCs), as well as the associated processes of drying and wastewater disposal. The technology has diverse applications, including enhancing adhesive bonds in the automotive industry, creating seals for electronics, and achieving efficient and bubble-free wet labelling with strong initial adhesion in the packaging industry. Additionally, the plasma gun has been proven effective for depositing thin film coatings like organosilicate and ceria nanocomposites, which exhibit improved hardness, adhesion, and UV-absorbing properties [54, 55]. Hovish et al. presented a technique for growing a superhydrophilic organotitanate thin film with excellent thermomechanical properties using atmospheric plasma deposition. This thin film demonstrated an effective antifogging property, with a contact angle (θ) less than 5° [65]. Asadollahi et al. described the development of an anti-icing coating on Al-6061 sheets. This involved pre-treating the surface and depositing organo-silane (HMDSO) using an atmospheric pressure plasma jet (APPJ) [66].

Additionally, Plasma jet printing (PJP) is a highly versatile and scalable printing method that utilizes plasma to interact with aerosolized inks, offering precise control over material characteristics. PJP represents an innovative approach for high-quality material printing, as it is environmentally friendly and can utilize lower quality inks. The process involves transforming the material into aerosol form, introducing it into the print head, and generating plasma through an electromagnetic field. The reactive species within the plasma interact with the ink, allowing for dynamic in situ tailoring of electronic properties. PJP's gas-phase operation eliminates liquid waste and toxic by-products, while enabling the use of unprocessed, low-grade inks to produce high-quality prints [51].

3.2 Integration of sol–gel and gaseous plasma-based approaches

The combination of sol–gel and plasma-based techniques has led to the development of coatings with unique optical and surface properties. Jung et al. conducted a study that specifically explored surface modification using plasma treatment on a sol–gel derived TiO2 film, which served as a photocatalyst [32]. The study investigated the effect of gaseous plasma treatment (Ar/O_2) on the enhancement of wetting behavior, specifically the attainment of a superhydrophilic property. In one of our own research work, we investigated sol–gel derived V-TiO_2:SiO_2 coatings and applied subsequent O_2 plasma treatment [59]. Different weight percentages of V-doped TiO_2 in the SiO_2 sol were tested to achieve the best combination of optical transparency and self-cleaning properties. The resulting coatings demonstrated antireflective properties, superhydrophilicity, and visible photo-catalytic activity. O_2 plasma treatment significantly reduced the contact angle of all V-TiO_2:SiO_2 formulations, reaching 0°. In another study, we combined sol–gel self-assembly with a plasma-based approach to create highly transparent, self-ordered, superhydrophilic, and photoactive TiO_2 thin film coatings [60]. The TiO_2 sol contained a block copolymer that facilitated the formation of regular pores in the film, resulting in reduced refractive index values (~1.31) and improved transparency (4% antireflection gain). The mesoporous TiO_2 coatings exhibited excellent photocatalytic activity for VOCs. Nitrogen plasma treatment enhanced mechanical stability and hydrophilicity without affecting optical transmission. Under optimized conditions, the coatings achieved superhydrophilicity with a water contact angle of less than 5°. Optimal conditions were determined by varying the Rf self-bias potential and duration of plasma treatment.

Noppakun Sampo conducted research on the utilization of sol–gel methods in the development of a multifunctional magnetic iron-based solution for thermal spray techniques [61]. The study focuses on preparing liquid feedstocks for the solution precursor plasma spray (SPPS) process. By exploring sol–gel methods in thermal spray applications, valuable insights were gained into the development and characterization of the magnetic iron-based solution. The research specifically investigates the effects of organic chelating agents on the topography, physical properties, and phase composition of cobalt ferrite splats. These findings contribute to a deeper understanding of the mechanisms involved and have significant potential for practical applications in various fields. Similarly by employing the SPPS technique, Cai et al. successfully developed ceramic superhydrophobic coatings with desirable properties [67]. The deposition process has been shown in **Figure 8**. The chosen rare earth oxide as the

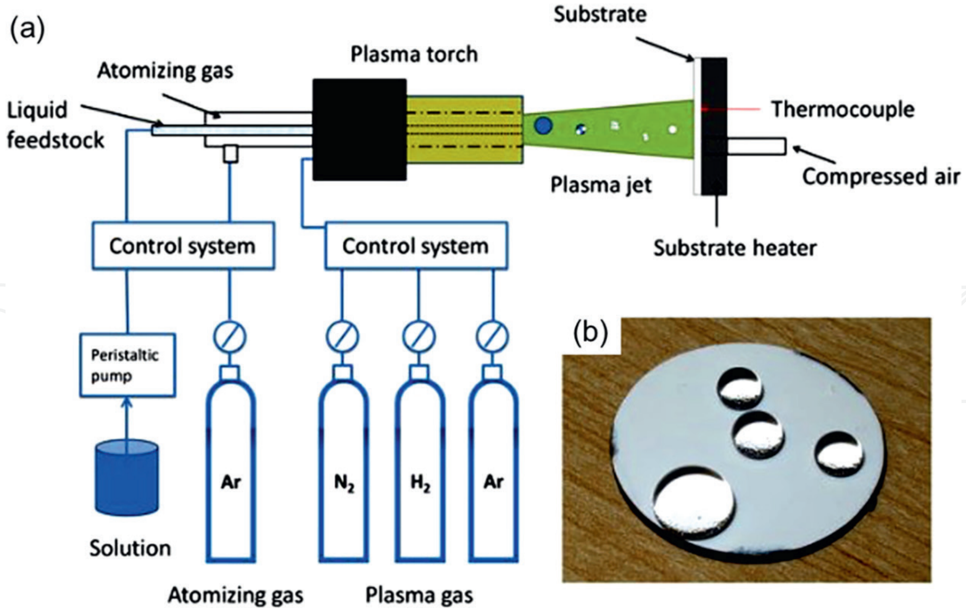

Figure 8.
(a) Schematic of the SPPS deposition system. (b) Water droplets of varying sizes on the coated surface (with permission, Copyright © 2016 Yuxuan Cai et al.).

coating material, along with the optimized spraying conditions, resulted in coatings with excellent hydrophobicity, mimicking the natural superhydrophobic surfaces. The outcomes of this study have significant implications for various applications where enhanced water repellency and self-cleaning properties are desirable, such as anti-icing coatings, corrosion protection, and efficient fluid flow management.

The sol–gel process is a commonly used method for synthesizing powders, coatings, and bulk materials. However, as a wet chemical technique, it has certain limitations, especially when applied as a coating method using aqueous colloidal solutions. The commonly utilized techniques such as dip and spin coating face challenges when applied to complex substrates. To overcome these limitations, the aerosol gel deposition method provides a promising solution. Pietrzyk et al. reported a novel technique to deposit Al_2O_3 coating by plasma enhanced aerosol-gel method [68]. By combining the aerosol-gel deposition of thin films with low-temperature plasma treatment, an innovative approach is established, introducing a novel method known as plasma-enhanced aerosol-gel for coatings production. This combined approach brings forth numerous advantages. Firstly, it enables the application of coatings on more complex substrates, which are difficult to coat using traditional techniques. Secondly, the aerosol-gel deposition method provides a homogeneous and controlled deposition of thin films. Lastly, the subsequent low-temperature plasma treatment enhances the properties of the deposited coatings, such as adhesion, durability, and functionality. This integration of aerosol-gel deposition and low-temperature plasma treatment represents a significant advancement in the field of coatings production, providing a versatile and efficient approach for the synthesis of high-quality coatings with improved properties.

4. Conclusion

Gaseous plasma, also known as cold plasma, exhibits an ion/electron density of around 1000 cm^{-3} and an electron temperature of 1 eV. Different types of plasma reactors, such as DC, Rf, VHf, and MW, with varying excitation frequencies, play a crucial role in film processing. Pulsing the discharge subtly affects the film's characteristics.

Cold plasma finds applications in surface cleaning, etching, deposition, and grafting during film growth. Plasma polymerization overcomes limitations imposed by plasma chemistry, as plasma polymers' properties depend on plasma parameters rather than the monomer used. Surface superwettability control using gaseous plasma treatment (e.g., Ar/O_2) has been extensively explored, resulting in improved superhydrophilic properties.

Recent advancements allow the generation of cold plasma at atmospheric pressure using techniques like Corona, DBD, Gliding Arc discharge, and Plasma jet, overcoming the need for vacuum-based reactors. The atmospheric pressure plasma jet (APPJ) technique proves effective in depositing TiO_2 coatings with high specific surface areas and improved photocatalytic activity compared to vacuum-based plasma reactors. These approaches enable surface bombardment with plasma, creating nano-scale roughness. By introducing functionalized precursors, desired surface wettability can be achieved. Open-air plasma deposition is used for various thin film coatings, offering enhanced hardness, adhesion, and UV-absorbing properties. Plasma-treated superhydrophobic (SH) coatings are highly relevant for de-icing and self-cleaning applications in aircraft and other systems. An innovative method demonstrates the synthesis of anatase TiO_2/SiO_2 nanocomposite coatings at atmospheric pressure, providing transparent anti-fogging and self-cleaning properties on polymer substrates. Additionally, an atmospheric pressure air plasma jet generated using a dielectric barrier structure with hollow electrodes (HEDBS) shows promise for spraying TiO_2 films inside tubular substrates.

To overcome challenges with complex substrates, traditional techniques like dip and spin coating are supplemented by the aerosol gel deposition method. This approach integrates aerosol-gel deposition with low-temperature plasma treatment, enabling the novel plasma-enhanced aerosol-gel method for coatings production. Moreover, plasma jet printing offers a versatile and scalable printing method that leverages plasma's interaction with aerosolized inks, allowing precise control and customization of material characteristics.

These advancements in plasma technology offer exciting possibilities for self-cleaning applications. Plasma treatments can modify surface properties to achieve superhydrophilic or superhydrophobic behavior. The integration of plasma techniques with innovative deposition methods paves the way for improved coating performance and functionality on various substrates.

Author details

Deepanjana Adak[1]* and Raghunath Bhattacharyya[2]

1 Surface Engineering Division, CSIR-National Aerospace Laboratories, Bangalore, India

2 School of Advanced Materials, Green Energy and Sensor Systems, Indian Institute of Engineering Science and Technology, Shibpur, India

*Address all correspondence to: deepanjana.adak@gmail.com

References

[1] John PI. Plasma Sciences and the Creation of Wealth. Tata McGraw-Hill Publishing Company; 2005. ISBN: 9780070585577

[2] Lee DH, Song Y-H, Kim K-T, Jo S, Kang H. Current state and perspectives of plasma applications for catalyst regeneration. Catalysis Today. 2019;**337**:15-27

[3] Pham VP, Jo YW, Oh JS, Kim SM, Park JW, Kim SH, et al. Effect of plasma–nitric acid treatment on the electrical conductivity of flexible transparent conductive films. Japanese Journal of Applied Physics. 2013;**52**(7R):075102

[4] Pham VP, Kim KH, Jeon MH, Lee SH, Kim KN, Yeom GY. Low damage pre-doping on CVD graphene/Cu using a chlorine inductively coupled plasma. Carbon. 2015;**95**:664-671

[5] Kim KN, Pham VP, Yeom GY. Chlorine radical doping of a few layer graphene with low damage. ECS Journal of Solid State Science and Technology. 2015;**4**(6):N5095

[6] Pham VP, Kim DS, Kim KS, Park JW, Yang KC, Lee SH, et al. Low energy BCl3 plasma doping of few-layer graphene. Science of Advanced Materials. 2016;**8**(4):884-890

[7] Pham VP, Kim KN, Jeon MH, Kim KS, Yeom GY. Cyclic chlorine trap-doping for transparent, conductive, thermally stable and damage-free graphene. Nanoscale. 2014;**6**(24):15301-15308

[8] Pham PV. A library of doped-graphene images via transmission electron microscopy. C. 2018;**4**(2):34

[9] Pham P et al., editors. 21st Century Surface Science: A Handbook. IntechOpen; 2020. DOI: 10.5772/intechopen.87891

[10] Grill A. Cold Plasma in Materials Fabrication. New York: IEEE Press; 1994. p. 272

[11] Tendero C, Tixier C, Tristant P, Desmaison J, Leprince P. Atmospheric pressure plasmas: A review. Spectrochimica Acta Part B: Atomic Spectroscopy. 2006;**61**(1):2-30

[12] Bruggeman PJ, Iza F, Brandenburg R. Foundations of atmospheric pressure non-equilibrium plasmas. Plasma Sources Science and Technology. 2017;**26**(12):123002

[13] Yasuda H. Plasma Polymerization. Elsevier Science; 1985. ISBN: 9780127687605

[14] Jafari R, Asadollahi S, Farzaneh M. Applications of plasma technology in development of superhydrophobic surfaces. Plasma Chemistry and Plasma Processing. 2013;**33**(1):177-200

[15] Isabell TC, Fischione PE, O'Keefe C, Guruz MU, Dravid VP. Plasma cleaning and its applications for electron microscopy. Microscopy and Microanalysis. 1999;**5**(2):126-135

[16] Carosio F, Alongi J, Frache A. Influence of surface activation by plasma and nanoparticle adsorption on the morphology, thermal stability and combustion behavior of PET fabrics. European Polymer Journal. 2011;**47**(5):893-902

[17] Liston EM. Plasma treatment for improved bonding: A review. The Journal of Adhesion. 1989;**30**(1-4):199-218

[18] Friedrich JF, Mix R, Kühn G. Adhesion of metals to plasma-induced functional groups at polymer surfaces. Surface and Coatings Technology. 2005;**200**(1):565-568

[19] Singh H, Sidhu BS, Puri D, Prakash S. Use of plasma spray technology for deposition of high temperature oxidation/corrosion resistant coatings: A review. Materials and Corrosion. 2007;**58**(2):92-102

[20] Chu PK, Chen JY, Wang LP, Huang N. Plasma-surface modification of biomaterials. Materials Science and Engineering: R: Reports. 2002;**36**(5):143-206

[21] d'Agostino R, Favia P, Kawai Y, Ikegami H, Sato N, Arefi-Khonsari F, editors. Advanced Plasma Technology. John Wiley & Sons; 2007. DOI: 10.1002/9783527622184

[22] Adak D, Bhattacharyya R, Barshilia HC. A state-of-the-art review on the multifunctional self-cleaning nanostructured coatings for PV panels, CSP mirrors and related solar devices. Renewable and Sustainable Energy Reviews. 2022;**159**:112145

[23] Pham PV. Cleaning of graphene surfaces by low-pressure air plasma. Royal Society Open Science. 2018;**5**(5):172395

[24] Shannon RL, Gillette RB, inventors; US Patent assignee. Plasma cleaning device. 1978

[25] Hossain MM. Plasma Technology for Deposition and Surface Modification. Logos Verlag Berlin GmbH; 2009. ISBN: 978-3-8325-2074-8

[26] Pham PV. The new etching technologies of graphene surfaces. In: 21st Century Surface Science: A Handbook. London, UK: IntechOpen; 2020. DOI: 10.5772/intechopen.92627

[27] Xu S, Levchenko I, Huang SY, Ostrikov K. Self-organized vertically aligned single-crystal silicon nanostructures with controlled shape and aspect ratio by reactive plasma etching. Applied Physics Letters. 2009;**95**(11):111505

[28] He B, Yang Y, Yuen MF, Chen XF, Lee CS, Zhang WJ. Vertical nanostructure arrays by plasma etching for applications in biology, energy, and electronics. Nano Today. 2013;**8**(3):265-289

[29] Bondur JA. Dry process technology (reactive ion etching). Journal of Vacuum Science and Technology. 1976;**13**(5):1023-1029

[30] Yasuda HK. Some important aspects of plasma polymerization. Plasma Processes and Polymers. 2005;**2**(4):293-304

[31] Hegemann D, Hossain MM, Körner E, Balazs DJ. Macroscopic description of plasma polymerization. Plasma Processes and Polymers. 2007;**4**(3):229-238

[32] Jung C-K, Bae IS, Song YH, Boo JH. Plasma surface modification of TiO_2 photocatalysts for improvement of catalytic efficiency. Surface and Coatings Technology. 2005;**200**(5):1320-1324

[33] Han D, Moon SY. Rapid formation of transparent Superhydrophobic film on glasses by $He/CH_4/C_4F_8$ plasma deposition at atmospheric pressure. Plasma Processes and Polymers. 2015;**12**(2):172-179

[34] Ji Y-Y, Hong Y-C, Lee S-H, Kim S-D, Kim S-S. Formation of super-hydrophobic and water-repellency surface with hexamethyldisiloxane (HMDSO) coating on polyethyleneteraphtalate

fiber by atmosperic pressure plasma polymerization. Surface and Coatings Technology. 2008;**202**(22):5663-5667

[35] Barankin MD, Gonzalez E, Habib SB, Gao L, Guschl PC, Hicks RF. Hydrophobic films by atmospheric plasma curing of spun-on liquid precursors. Langmuir. 2009;**25**(4):2495-2500

[36] Bhattacharyya R. Indigenous ion sources for material processing. Defence Science Journal. 2009;**59**(4)

[37] Kruger CH, Owano TG, Laux CO. Experimental investigation of atmospheric pressure nonequilibrium plasma chemistry. IEEE Transactions on Plasma Science. 1997;**25**(5):1042-1051

[38] Schutze A, Jeong JY, Babayan SE, Park J, Selwyn GS, Hicks RF. The atmospheric-pressure plasma jet: A review and comparison to other plasma sources. IEEE Transactions on Plasma Science. 1998;**26**(6):1685-1694

[39] Goldman M, Sigmond RS. Corona and insulation. IEEE Transactions on Electrical Insulation. 1982;**17**(2):90-105

[40] Eliasson B, Kogelschatz U. Nonequilibrium volume plasma chemical processing. IEEE Transactions on Plasma Science. 1991;**19**(6):1063-1077

[41] Dielectric Barrier Discharge. Available from: https://www.plasma.com/en/dielectric-barrier-discharge/diener

[42] Jeong JY, Babayan SE, Tu VJ, Park J, Henins I, Hicks RF, et al. Etching materials with an atmospheric-pressure plasma jet. Plasma Sources Science and Technology. 1998;**7**(3):282

[43] Herrmann HW, Henins I, Park J, Selwyn GS. Decontamination of chemical and biological warfare (CBW) agents using an atmospheric pressure plasma jet (APPJ). Physics of Plasmas. 1999;**6**(5):2284-2289

[44] Jeong JY, Park J, Henins I, Babayan SE, Tu VJ, Selwyn GS, et al. Reaction chemistry in the afterglow of an oxygen−helium, atmospheric-pressure plasma. The Journal of Physical Chemistry A. 2000;**104**(34):8027-8032

[45] Marchand DJ, Dilworth ZR, Stauffer RJ, Hsiao E, Kim J-H, Kang J-G, et al. Atmospheric rf plasma deposition of superhydrophobic coatings using tetramethylsilane precursor. Surface and Coatings Technology. 2013;**234**:14-20

[46] Hossain MM, Trinh QH, Nguyen DB, Sudhakaran MSP, Mok YS. Formation of plasma-polymerized superhydrophobic coating using an atmospheric-pressure plasma jet. Thin Solid Films. 2019;**675**:34-42

[47] Lin L, Rui L, Li C, Liu Q, Li S, Xia Y, et al. Study on CO_2-based plasmas for surface modification of polytetrafluoroethylene and the wettability effects. Journal of CO_2 Utilization. 2021;**53**:101752

[48] Fakhouri H, Salem DB, Carton O, Pulpytel J, Arefi-Khonsari F. Highly efficient photocatalytic TiO_2 coatings deposited by open air atmospheric pressure plasma jet with aerosolized TTIP precursor. Journal of Physics D: Applied Physics. 2014;**47**(26):265301

[49] Surface modification using PlasmaPlus® nanocoating. Available from: https://www.plasmatreat.com/en/what-is-plasma/plasma-surface-treatment/plasma-coating/functional-coating/plasmatreat

[50] Mazumder P, Jiang Y, Baker D, Carrilero A, Tulli D, Infante D, et al.

Superomniphobic, transparent, and antireflection surfaces based on hierarchical nanostructures. Nano Letters. 2014;**14**(8):4677-4681

[51] Song YM, Park GC, Kang EK, Yeo CI, Lee YT. Antireflective grassy surface on glass substrates with self-masked dry etching. Nanoscale Research Letters. 2013;**8**(1):505

[52] Lei Z, Xin C, Yang J, Zhang L, Hao S, Min L, et al. The denitration mechanism of fly ash catalysts prepared by low-temperature plasma technology. Vacuum. 2020;**181**:109695

[53] Kim J, Hwang JH, Kwon YW, Bae HW, An M, Lee W, et al. Hydrogen-assisted low-temperature plasma-enhanced chemical vapor deposition of thin film encapsulation layers for top-emission organic light-emitting diodes. Organic Electronics. 2021;**97**:106261

[54] Leszczynski S, Strobel C, Leszczynska B, Waurenschk S, Röhlecke S, Stahr F, et al. Dynamic deposition system for fabrication of amorphous/crystalline silicon heterojunction solar cells combining linear hot-wire and plasma enhanced chemical vapor deposition methods. Thin Solid Films. 2022;**754**:139296

[55] Li D, Xu K, Zhang Y. A review on research Progress in plasma-controlled superwetting surface structure and properties. Polymers. 2022;**14**(18):3759

[56] Haye E, Job N, Wang Y, Penninckx S, Stergiopoulos V, Tumanov N, et al. ZnO/carbon xerogel photocatalysts by low-pressure plasma treatment, the role of the carbon substrate and its plasma functionalization. Journal of Colloid and Interface Science. 2020;**570**:312-321

[57] Takenaka K, Machida R, Bono T, Jinda A, Toko S, Uchida G, et al. Development of a non-thermal atmospheric pressure plasma-assisted technology for the direct joining of metals with dissimilar materials. Journal of Manufacturing Processes. 2022;**75**:664-669

[58] Chang FJ, Nishijima D, Tynan GR. Rough-surface effect on sputtering of Cr bombarded by low-energy He plasma. Nuclear Materials and Energy. 2021;**29**:101077

[59] Ma X, Mao Z, Xu D, Ding Y, Xu C. High-rate synthesis of SiCN films using single-source silicon precursor with high-density helicon plasma. Vacuum. 2020;**177**:109397

[60] Zhang L, Yu S, Wang K, Zhang J, Fang J. A cost- and time-saving strategy of spraying TiO_2 self-cleaning coatings in tubular substrates by air cold plasma. Chemical Physics Letters. 2017;**687**:205-208

[61] Chemin J-B, Bulou S, Baba K, Fontaine C, Sindzingre T, Boscher ND, et al. Transparent anti-fogging and self-cleaning TiO_2/SiO_2 thin films on polymer substrates using atmospheric plasma. Scientific Reports. 2018;**8**(1):9603

[62] Cui L, Ranade AN, Matos MA, Pingree LS, Frot TJ, Dubois G, et al. Atmospheric plasma deposited dense silica coatings on plastics. ACS Applied Materials & Interfaces. 2012;**4**(12):6587-6598

[63] Ding Y, Dong S, Hilt F, Dauskardt RH. Open-air spray plasma deposited UV-absorbing nanocomposite coatings. Nanoscale. 2018;**10**(30):14525-14533

[64] Subeshan B, Usta A, Asmatulu R. Deicing and self-cleaning of plasma-treated superhydrophobic coatings on the surface of aluminum alloy sheets. Surfaces and Interfaces. 2020;**18**:100429

[65] Hovish MQ, Hilt F, Rolston N, Xiao Q, Dauskardt RH. Open air plasma deposition of Superhydrophilic Titania coatings. Advanced Functional Materials. 2019;**29**(19):1806421

[66] Asadollahi S, Farzaneh M, Stafford L. On the Icephobic behavior of organosilicon-based surface structures developed through atmospheric pressure plasma deposition in nitrogen plasma. Coatings. 2019;**2019**:9

[67] Cai Y, Coyle TW, Azimi G, Mostaghimi J. Superhydrophobic ceramic coatings by solution precursor plasma spray. Scientific Reports. 2016;**6**(1):24670

[68] Pietrzyk B, Miszczak S, Szymanowski H, Kucharski D. Plasma enhanced aerosol–gel deposition of Al_2O_3 coatings. Journal of the European Ceramic Society. 2013;**33**(12):2341-2346