
Plasma-Enhanced Vapor Deposition Process for the Modification of Textile Materials

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Abstract

Nowadays many techniques are used for the surface modification of fabrics and textiles. Two fundamental techniques based on vacuum deposition are known as chemical vapor deposition (CVD) and physical vapor deposition (PVD). In this chapter, the effect of plasma-enhanced physical and chemical vapor deposition on textile surfaces is investigated and explained.

Keywords: Chemical vapor deposition, textile, fabric, modification

1. Introduction

Textile industries have been experiencing fast development with versatile products for a wide spectrum of applications being developed through technological innovations. The surfaces of textiles offer a platform for functional modifications to meet specific requirements for various applications. Surface modification of textiles gives the textile product the desired properties. Many techniques ranging from conventional wet treatments to biological methods are used for the surface modification of textiles.

In recent years, a great attention to the functionalization of textile surfaces has been attracted with the help of new technologies, such as high-energy beam processes, vapor deposition, and nanoparticle coatings.

The coupling of electromagnetic power into a process gas volume generates the plasma medium comprising a dynamic mix of ions, electrons, neutrons, photons, free radicals, metastable excited species, and molecular and polymeric fragments.

Vapor deposition (either physical or chemical) is a coating process, where the coating material is condensed from vapor phase, forming a thin film, or modifies the surface of the substrate

by creating functional groups on the surface. Different types of deposition techniques are used to meet this criterion. Most of these techniques, including vacuum deposition, are used to minimize unwanted reaction with the free space and to shape the film composition easily. Two fundamental techniques based on vacuum deposition are known as chemical vapor deposition (CVD) and physical vapor deposition (PVD).

In the CVD technique, thin film design is achieved by chemical reaction between precursors. The reaction needs hot substrate or high-temperature medium. Due to the need of gas phase for surface coating, the CVD technique is suitable for large and complex-shaped surfaces. Physical processes such as evaporation and sputtering are used in the PVD technique.

By contacting effects of the gases, numerous sputtering methods are used to form plasma. Different surfaces can be coated with deposition flux using PVD methods. To select the deposition method, some parameters are very important, such as thin film material, substrate type, uniformity, and control of the thickness.

Conventional finishing techniques applied to textiles (dyeing, stain repellence, flame retardance, antibacterial treatments, wrinkle recovery improvement, sizing, desizing, washing, and so on), generally wet chemical process, produce a lot of wastewater. Vapor phase treatment is an eco-friendly and dry technology offering an interesting replacement to add new abilities and functionalities. Some abilities such as antibacterial properties, electrical and mechanical properties, hydrophilicity, water repellence, and biocompatibility of textiles and fibers can be modified. On the other hand, bulk properties and touch of the textiles remain unaffected [1].

In this chapter, the effect of both plasma-enhanced physical and chemical vapor deposition processes on textile surfaces is investigated and explained.

2. Vapor deposition

In vapor deposition process, materials in a vapor state are condensed through condensation, chemical reaction, or conversion to form a solid material. These processes are used for coatings to alter the mechanical, electrical, thermal, optical, corrosion resistance, and wear properties of the substrates. Vapor deposition processes usually take place within a vacuum chamber [2].

Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are two categories of vapor deposition processes.

Vapor deposition (either physical or chemical) is a coating process where the coating material is condensed in vacuum at the substrate from vapor phase, forming a thin film ($\leq 10 \mu\text{m}$ in the case of physical deposition and $\leq 1000 \mu\text{m}$ in the case of chemical deposition). Sometimes, the deposited material further reacts with the gaseous substances to form a final compound coating. Generally, metals and nonmetals can be deposited; a certain case depends on the applied method [3].

It is well known that thin film coating can be realized with a thickness of a few nanometers. Different types of deposition techniques are used to meet this criterion. All these techniques,

including vacuum, are used to minimize unwanted reaction with the free space and to shape the film composition easily. Two main techniques based on vacuum deposition are known as CVD and PVD. In the CVD technique, thin film design is realized by chemical reaction between precursors. In the PVD technique, some processes such as sputtering, thermal evaporation, molecular beam epitaxy, and electron beam evaporation are used. In sputtering techniques, by contacting effects of the gases in the background, plasma is formed. PVD techniques are very useful and efficient for surface modifications [4].

2.1. Chemical vapor deposition (CVD)

CVD is a chemical process used to fabricate high-quality and high-performance solid materials. The process has many applications in different industries. In this process, volatile precursors can react or decompose on the substrate surface to create the proper coating. Some by-products that are produced through this process should be removed through the chamber by gas flow technique.

Some microfabrication processes, such as polycrystalline, monocrystalline, epitaxial, and amorphous, are used in CVD techniques to deposit materials in different forms. Silicon compounds, carbon nanofibers, carbon nanotubes, carbon fiber, fluorocarbons, filaments, titanium nitride, and various high-k dielectrics can be modified by this method. CVD is also used to produce synthetic diamonds [5].

CVD is practiced in a variety of formats. These processes generally differ in the means by which chemical reactions are initiated and classified by operating pressure and are listed as below:

1. APCVD (Atmospheric pressure CVD).
2. LPCVD (Low-pressure CVD) – In this method, unwanted gas-phase reactions reduced and film uniformity also improved.
3. UHVCVD (Ultrahigh vacuum CVD) – In this method, pressure is below 10^{-6} Pa ($\sim 10^{-8}$ torr).

Modern CVD is either LPCVD or UHVCVD, which is classified by the physical characteristics of vapor as follows:

- AACVD (Aerosol-assisted CVD) – CVD in which the precursors are transported to the substrate by means of a liquid/gas aerosol.
- DLICVD (Direct liquid injection CVD) – CVD in which the precursors are in liquid form. Liquid solutions are injected in a vaporization chamber toward injectors.
- MPCVD (Microwave plasma-assisted CVD).
- PECVD (Plasma-enhanced CVD) – PECVD technique allows deposition at lower temperatures.
- RPECVD (Remote PECVD) – Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region. Removing the wafer from the plasma region allows processing temperatures down to room temperature.

- ALCVD (Atomic-layer CVD) – Deposits successive layers of different substances to produce layered crystalline films.
- CCVD (Combustion CVD) – Combustion CVD or flame pyrolysis is an open-atmosphere, flame-based technique for depositing high-quality thin films and nanomaterials.
- HFCVD (Hot filament CVD) – This process uses a hot filament to chemically decompose the source gases.
- HPCVD (Hybrid physical–chemical vapor deposition) – This process involves both chemical decomposition of precursor gas and vaporization of a solid source.
- MOCVD (Metal organic CVD) – This CVD process is based on metal organic precursors.
- RTCVD (Rapid thermal CVD) – This CVD process uses heating lamps or other methods to rapidly heat the wafer substrate.
- VPE (Vapor-phase epitaxy).
- PICVD (Photo-initiated CVD) – This process uses UV light to stimulate chemical reactions [6].

2.1.1. CVD uses

CVD is commonly used to deposit conformal films and augment substrate surfaces in ways that more traditional surface modification techniques are not capable of. CVD is useful in the process of atomic layer deposition. A variety of applications for such films exist. Also, polymerization by CVD, perhaps the most versatile of all applications, allows for super-thin coatings that possess some very desirable qualities, such as lubricity, hydrophobicity, and weather resistance, to name a few [6].

For many years, wet chemistry methods have been the main method used for coating the surfaces. Liquid processes have many disadvantages, such as the need to dispose of organic solvents, incomplete wetting of high aspect ratio structures, diffusion-limited transport of reactants, and poor control of reactant supply, compared with gas-phase processes. The CVD method is often called nanoparticle vapor deposition (NVD). In NVD, two binary chemicals are injected simultaneously or when the other chemical is present. Currently, CVD has mostly been applied in coating industries, but the use of CVD in other areas, such as in the production of powders, fibers, monoliths, and composites, is growing rapidly [7–9].

2.1.2. PECVD and its applications

PECVD is a process used to deposit thin films from a gas state (vapor) to a solid state on a substrate. In this process, thin film can be deposited on the substrate at low temperature. Reacting gases created plasma and chemical reactions are also involved. By DC discharge or RF (AC) frequency, plasma is created between two electrodes, and the reacting gases are filled between the electrodes [6].

PECVD method is one of the most universal approaches to treat fibers, yarns, and fabrics. Compared to other treatments, such as the traditional chemical methods, plasma treatment is

less material consuming and easier to operate, results in less effluent, and is much more environment friendly. It is also a good way to deposit nonpolymerizable substance at normal conditions on the surface of a substrate. In addition, the PECVD process would only affect a few topmost atomic layers of the substrate surface, ensuring that the bulk of the substrate is not affected, thus allowing a decoupling of the surface properties from the bulk properties of the material and giving the product designer a considerable new degree of freedom. When a chemical is carried into the reactor, it gains energy through inelastic collision with high-energy species especially with the electrons. The bonds of the chemicals are broken up and a new substance would be deposited on the surface of the substrates. The substance and the substrate would be constantly subjected to the plasma until the process is finished. Since high-performance fiber is somewhat inert to normal chemical reactions, the PECVD treatment would be an ideal choice to make chemical or physical changes to these fibers [10].

Low-pressure plasma processes, such as PECVD volatilize organic compounds, and graft functional groups (such as $-NH_2$ and $-OH$) onto hydrophobic polymers. These techniques are used for improving biomedical textiles and materials. Materials and devices' surfaces are functionalized, without any influence on their bulk properties. By plasma deposition treatment, spreading, adhesion, and cells proliferation of biomedical materials' surfaces can be optimized. Density and distribution of the ions and radicals that are produced in the discharge can be tuned by different external plasma parameters such as pressure, power input, gas flow rate, and so on [11].

The lower deposition temperatures are critical in many applications where CVD temperatures could damage the devices being fabricated [12].

Plasma PECVD offers a wide range of cost-effective material processes to manufacturers in the electronic, industrial, and medical sectors.

For separating conductive layers from each other, some dielectrics such as SiN , SiO_2 , SiO , and $SiON$ are used. These dielectrics provide different electrical insulating properties. For military devices, usually diamond-like-carbon (DLC) is used as a capping agent. It has radiation-hardening characteristics. Also A-Si and poly-Si have different conductive properties depending on their doping quantities [13].

The films typically deposited using PECVD are silicon compounds.

Silicon dioxide and silicon nitride are dielectric (insulating) materials commonly used in the fabrication of electronic devices. These films are also used for encapsulation to protect devices from corrosion by atmospheric elements, such as moisture and oxygen [14].

Silicon dioxide can be deposited using a combination of silicon precursor gases, such as dichlorosilane or silane, and oxygen precursors, such as oxygen and nitrous oxide, and has an important influence on infrared and ultraviolet (UV) absorption, stability, mechanical stress, and electrical conductivity.

Silicon dioxide can also be deposited from a tetraethoxysilane (TEOS) silicon precursor in an oxygen or oxygen-argon plasma. High-density plasma deposition of silicon dioxide from

silane and oxygen/argon has been widely used to create a nearly hydrogen-free film with good conformality over complex surfaces [15].

Jin et al. [16] reported the relationship between the PECVD parameters and film properties. The design and synthesis of various functional hybrid film systems for SiO_x film coatings with good mechanical properties at high deposition rates have been reported [16].

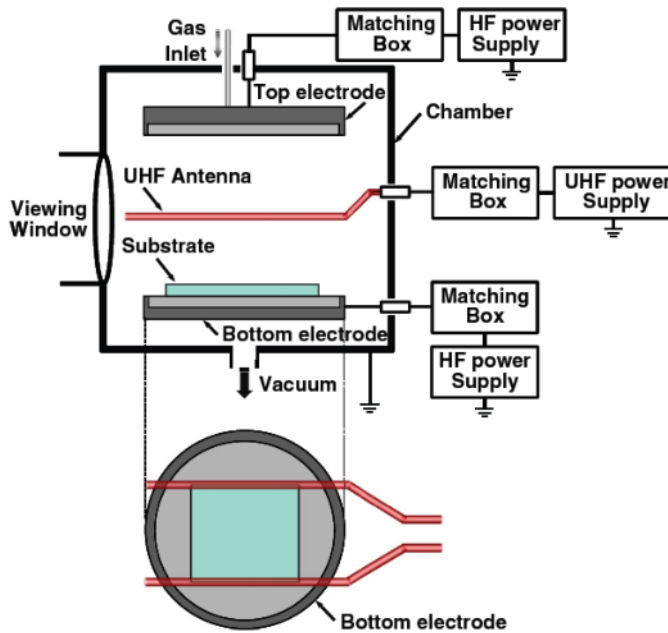


Figure 1. A schematic diagram of the PECVD with the dual frequencies UHF and HF apparatus used to deposit the SiO_x film [16].

Figure 1 shows a schematic diagram of the plasma configuration used for deposition of the SiO_x film. Two circular electrodes covered with a ceramic plate were placed within a cylindrical enclosure containing both electrodes. Two line ultra-high-frequency (UHF) electrodes covered with a ceramic textile tube were placed in the chamber. Table 1 shows the coating parameters.

During the experiment, the base pressure was approximately 3×10^{-2} Pa. A polycarbonate (PC) and Si wafer (100) substrate was placed on the bottom electrode. During the plasma process, a gas composed of octamethylcyclotetrasiloxane (OMCTS) and oxygen gas was allowed to flow to the top electrode. The OMCTS precursor has been used in this study. The SiO_x film thickness was $1 \mu\text{m}$.

SiO_x films were deposited on polycarbonate (PC) substrates at room temperature using a hybrid plasma CVD process. SiO_x films were deposited by applying high-frequency (HF) bias with UHF power.

Parameter	Condition
Base pressure	$<3 \times 10^{-2}$ Pa
Deposition pressure	1.7×10^{-1} Pa– 2.8×10^{-1} Pa
Top electrode (HF, 13.56 MHz)	120 W
UHF power (320 MHz)	0, 80, 150, 220 W
Bottom electrode (HF, 13.56 MHz)	0, 70, 90, 120 W
Film thickness	1 μ m
Temperature	Room temperature
Substrates	PC and Si wafer (100)

Table 1. Deposition parameters [16]

The resulting film showed a Si–O network structure and Si–O–Si intensity [16].

Plasma-enhanced PECVD dielectric films are ubiquitous in the microelectronics industry as well as in other advanced technologies.

Hughey and Cook [17] used silicon nitride for study as a typical PECVD film.

Technologically important materials such as silicon nitride are used as a passivation layer in microelectronic devices, as an etch stop layer in interconnect stacks, and as an active element in optical waveguides. The goals of their study are then to identify specifically the deposition conditions suitable to maintain the mechanical integrity of a silicon nitride film in optical devices.

Results shown in this work provide further evidence for the generality of phenomena observed in different PECVD dielectric materials; primarily, stress increases irreversibly on thermal cycling and is caused by a reduction in the amount of bonded hydrogen [17].

In another point of view, DLC is an amorphous carbon film and has good properties like diamond, such as high electrical resistance, high chemical inertness, high hardness, high wear resistance, and low friction. DLCs are used in biotechnology and material science. DLC thin film deposition techniques and conditions strongly influence DLC quality and its thermal and optical properties as well as the adherence degree to the surfaces and its wear resistance. The properties of α -C:H thin films fabricated by PECVD are sensitive to deposition parameters [18].

Dias et al. [18] described that the photoacoustic spectroscopy and the open photoacoustic cell method are employed in the thermo-optical characterization of hydrogenated amorphous carbon thin films. The samples were fabricated in a modified PECVD system with varying deposition times.

The spectroscopic results showed that the best absorption and smallest transmission around 330–500 nm occurred in samples with 30 s to 10 min of deposition. DLC-coated glass with a 2 min deposition time showed UV transparency. Furthermore, the thermal diffusivity increased with decreasing film thickness.

Therefore, considering the heat dissipation and the absorption intensity, α -C:H-coated glass at 10 min can be suggested for coatings of aerospace carcasses. On the other hand, the α -C:H-coated glass at 2 min could be used as an anti-reflective coating on crystalline silicon solar cells as a device for generating clean energy.

A very important conclusion was that the thickness of the films (deposition time) is a relevant parameter. The changes in deposition time limit the UV transparency and dehydrogenation of thin films [18].

The formation of nanocomposite of metal oxide/carbon nanotubes has been extensively studied because of their potential industrial applications in optics, catalysis, microelectronics, and many other areas. A corona discharge enhanced CVD method has been shown to synthesize NiO-loaded carbon nanotubes (CNTs) by Yu et al. [19]. In a synchronous system, formation of CNTs and embedment with NiO nanoparticles are carried out. Preparation time is reduced significantly and the reaction temperature is much lower compared with previous methods. The diameter of these NiO nanoparticles is about 5 nm, which is characterized by TEM. Surface of NiO nanoparticles is reduced into metallic Ni and they are all encapsulated into the CNTs walls [19].

2.1.3. Application of PECVD in the textile industry

In view of the wide employment of PECVD in the surface functionalization of various materials, researchers studied different methods [20, 21].

Here are further descriptions of some of these examples.

According to Mossotti et al. [22], hexamethyldisiloxane (HMDSO) plasma polymerization of thin films using low-pressure plasma equipment was successfully developed for several applications on different substrates.

A Si:Ox:Cy:Hz film was deposited on scoured knitted wool fabrics by PECVD at different applied powers. HMDSO was used as the monomer, and argon and oxygen was used as feed gases. The polymerization was preceded by a stage of activation of substrates to make the wool fabrics more reactive to the deposition [22].

The polymerization was performed in a mixture of gases at constant flow rate: argon (20 sccm), oxygen (20 sccm), and HMDSO (3 sccm) for 8 min at a constant pressure of 2×10^{-2} mbar. Applied power varied from 30 to 50 W.

The experimental arrangement used for the plasma process was the lab-scale low-pressure equipment. A schematic diagram of experimental setup is shown in Figure 2. Two capacitively coupled cylindrical electrodes are used in the reaction chamber. Sample was placed on a roller below the electrodes. At different speeds, this roller could rotate; 4 rpm was chosen for working speed. Because of homogeneous deposition on different substrate surfaces, this configuration was excellent for plasma polymerization.

The reactor was made of steel. The power electrode was connected to an RF (13.56 MHz) generator tuned with the plasma system by an impedance matching network.

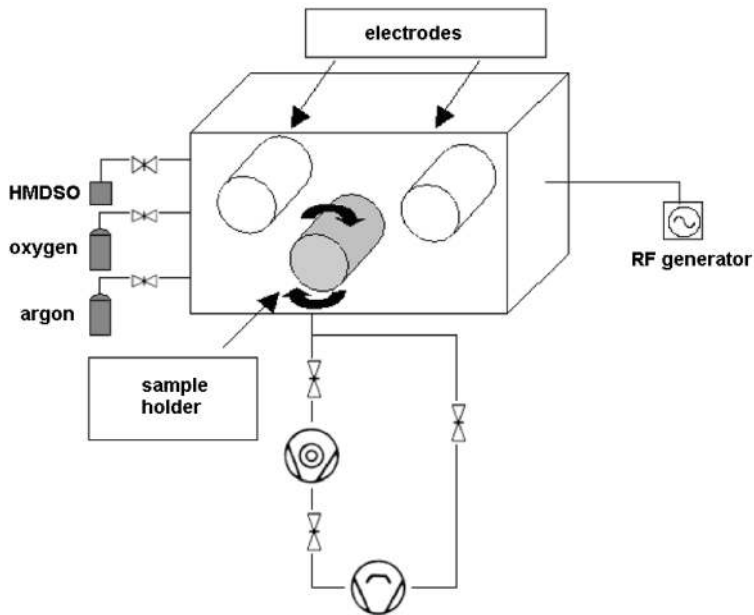


Figure 2. A schematic diagram of experimental setup [22].

Thin films (Si:Ox:Cy:H_z) were deposited on knitted wool fabrics. The achieved results of their research revealed the formation of films with a prevalent inorganic character. The results showed that this kind of treatment could represent an efficient technique to reduce pill formation on knitted wool fabrics. This plasma treatment did not affect the whiteness index of the fabric, while an increase in bursting resistance was pointed out.

Aramid fibers are one of the most popular choices for making soft body armor because of its high modulus and high strength as well as its good flexibility. Generally speaking, the ballistic performance of soft body armor is affected by parameters from two aspects, that is, the parameters associated with the projectile, including the mass, the geometry, the velocity, and the material, and those with the ballistic panel, including the fiber property, the inter-yarn friction, and the structural characteristics of the ballistic panel. To date, friction between yarns has been found to be one of the important parameters in the soft body armor design. The research of Chu et al. [10] focused on coating the aramid yarns with the PCVD technology at the atmospheric pressure (APPCVD); the schematic of the setup is shown in Figure 3. An organosilicon compound (CH₃)₂Cl₂Si was selected as the precursor substance to be deposited on the surfaces of yarns [10].

The APPCVD treatment included two steps: (i) the surface activation of the Twaron yarns by nitrogen gas plasma and (ii) precursor disassociation and deposition on the activated Twaron yarns using chemical (CH₃)₂Cl₂Si. The chamber in the APPCVD reactor was designed to be rectangular with a size of 10 cm × 5 cm. The Twaron yarns to be processed were positioned in

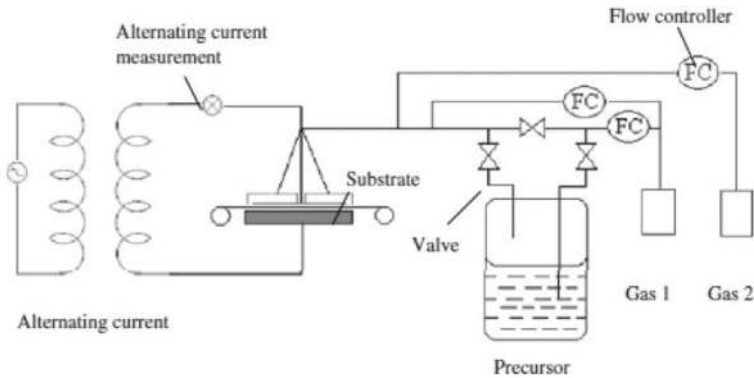


Figure 3. Schematic diagram for the setup of atmospheric pressure plasma-enhanced vapor deposition used [10].

the sample holder statically after being wrapped on a thin and smooth paper tape. The precursor chemical $(\text{CH}_3)_2\text{Cl}_2\text{Si}$ was thermostabilized outside the APPCVD reactor and was then carried into the reactor by the carrier gas, which was nitrogen. Figures 3 and 4 depict the APPCVD reactor used in the experiment for the production of plasma, which was established in Salford University. The plasma source is alternate current (AC) with the specified input voltage of 21.9 V and the frequency of 3.25 kHz. The flow rate of nitrogen gas was set to be 5 L/min and the chemical flow rate was set to be 0.2 L/min. The gap between two electrodes was set to be 3 mm in the APPCVD reactor.

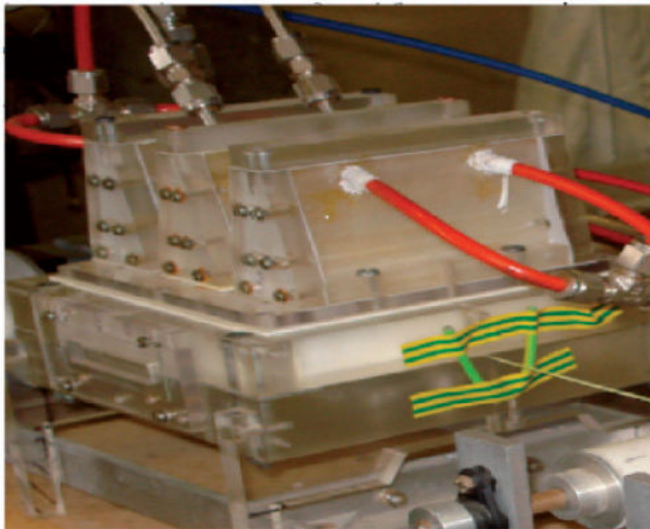


Figure 4. Photograph of the atmospheric pressure plasma-enhanced vapor deposition reactor [10].

The research of Chu et al. was concerned with the surface modification of Twaron yarns to increase the inter-yarn friction for the efficient improvement of ballistic fabrics.

The chemical particles were deposited onto the surface of fibers with treatment time being 21 s, 2 min, and 4 min, and SEM photography provided evidence for the surface modification. FTIR spectra supported the existence of Si–O–Si vibration, which can be attributed to the chemical deposition. EDX analysis confirmed the deposition of the chemical through the obvious increase of Si element on the surface of the fiber. The surface modification has led to obvious increase in both the frictional coefficients (static and kinetic) and frictional force between the yarns. The yarn–yarn static frictional coefficient showed an increase from 0.1617 to 0.2969 and the kinetic frictional coefficient showed an increase from 0.1554 to 0.2436. It was also found that the tensile strength, Young's modulus, and breaking strain of the Twaron yarns are not negatively affected by the APPCVD treatment but show a slight increase.

Their research has led to the establishment of a feasible and valid method to increase the inter-yarn friction within ballistic fabrics to achieve enhanced ballistic energy absorption and to provide better protection against high-velocity projectile impact [10].

Surface modification (physical or chemical treatments) can be used for creating fire-retardant properties onto the polymer surface (where the flammability occurs) and would thus allow preserving the bulk properties of the material. In the work of Jimenez et al. [23], a new route to improve the fire-retardant properties of a polymer by depositing a thin film on its surface using plasma-assisted polymerization technique has been investigated. The plasma-assisted polymerization of organosilicon compounds is an interesting technique to create thin polysiloxane-based films on the surface of various substrates. Polysiloxane-based films are known to show good thermal stability, interesting flame properties, and an interesting hydrophobicity.

The experimental setup used to make the polysiloxane-based deposit is shown in Figure 5.

The monomer (TMDSO), premixed with oxygen, is injected into the cold remote nitrogen plasma through a coaxial injector. First, the samples were treated by the cold remote nitrogen plasma to increase the adhesion quality of the organosilicon film on the polymer. Then, the deposition step is performed without air re-exposure. Moreover, they reported that this solution gives even better performances in terms of Limited Oxygen Index (LOI) values, rate of heat release (RHR), and ignition time (IT) [23].

In the other research work, to improve textile fabric abrasion resistance, a $\text{SiO}_x\text{C}_y\text{H}_z$ thin film was realized by low-pressure plasma CVD (PCVD) at room temperature using HMDSO as the precursor compound. Organosilicon compound hexamethyldisiloxane (HMDSO) as a best reagent precursor was chosen because of its availability, liquid state, volatility at room temperature, low flammability, low toxicity, and low cost. HMDSO plasma can produce coatings with different surface properties (e.g., hydrophobic or hydrophilic behavior, friction-reducing or wear-resistant coatings, and barrier coatings); it also shows good adherence to substrates and high transparency to visible radiation. To study the film properties, different plasma exposure times on several fabrics were investigated in the range of 4–12 min by Rosace et al. [24].

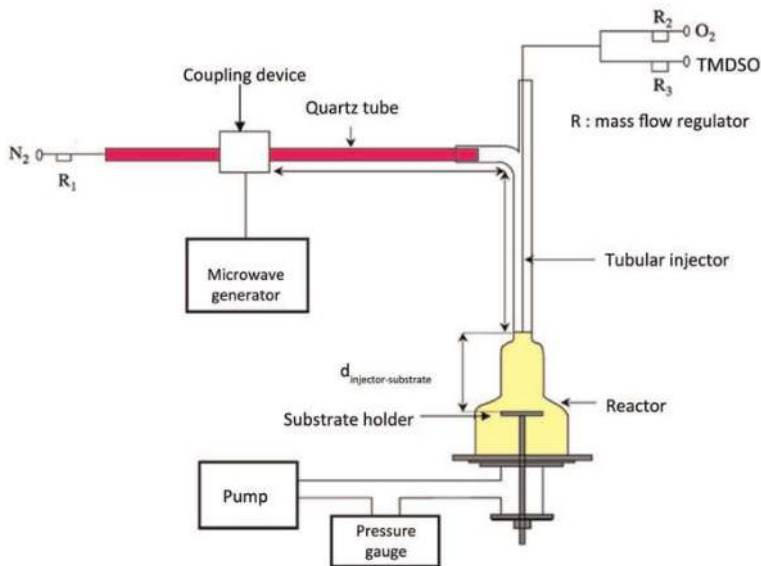


Figure 5. Experimental setup of PECVD. TMDSO: 1,1,3,3-tetramethyldisiloxane [23].

Four different textile fabrics have been used in their study to investigate the effect of HMDSO plasma deposition on different morphological kinds of fabric. The process consists of a first stage of activation of the textile fiber surface using O_2 plasma followed by a second stage based on the deposition of thin films onto previously activated textile fiber surfaces.

From the results obtained by FTIR-ATR, SEM, and EDX elemental analysis measurements, Rosace et al. concluded that organosilicon thin film on the textile fabric surface was successfully performed. Organosilicon film is an anti-wear coating against the abrasion of textile fabrics. In fact, after the application of thin layer, all tested textile fabrics showed a remarkable improvement of abrasion resistance, a lower weight loss, and a higher endpoint of Martindale test than untreated samples. But the adhesion of the coating to the substrate is not optimal. In fact, after five washing cycles, the deposited film seems to be removed from the treated fabrics. Poor washing fastness is in the relevance to the fabric's end use. Functional coatings do not involve any of the solvents and do not require high temperatures. They also have high long term and wash stability. This environment-friendly finishing can replace some wet chemical with no emissions of volatile organic compounds (VOCs) in a closed vacuum system [24].

In the other research work, plasma surface activation was made on the Polyethylene terephthalate (PET) nonwoven in a Europlasma CD 400M/PC laboratory system, as illustrated in Figure 6, by Wei et al. [25]. The material was subjected to oxygen plasma treatment at 100 W power with a gas flow rate of $1.67 \text{ cm}^3/\text{s}$ for 60 s. Plasma-induced polymerization was performed on the same PET needle-punched nonwoven material using grafting chemical (acrylic acid). First, polyester nonwoven sample was treated for 60 s and a power of 200 W with argon plasma. Then, to facilitate polymer grafting and formation of peroxides on the fiber surface,

sample was exposed to atmospheric air for 15 min. Thereafter, sample was treated with 20% (w/v) aqueous acrylic acid at 50°C for 5 h. After the grafting reaction, the material was rinsed in boiling deionized water to remove any acrylic acid homopolymer and monomer and then was dried at 40°C for 24 h [25].

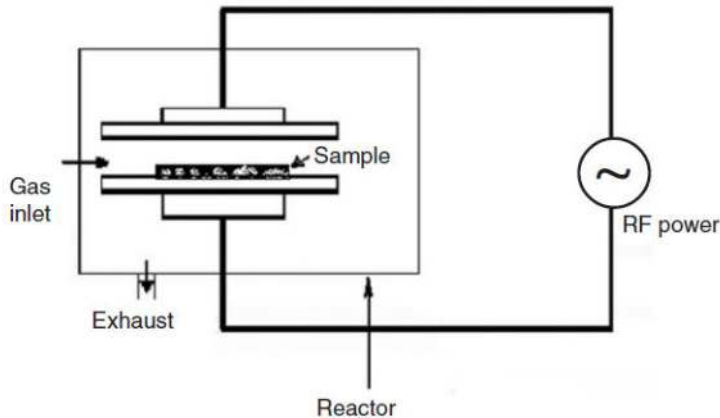


Figure 6. Plasma treatment system [25].

The PCVD deposition was performed on the PET nonwoven material using tetraethoxysilane (TEOS) and oxygen as the precursors. The RF source used was 13.56 MHz. The deposition of SiO₂ was made at the pressure of 150 Pa with a power of 100 W. The deposition lasted for 5 min.

They concluded that textile materials can greatly be modified by plasma treatments. Different effects on the textile surfaces can observe with different gas plasma treatments. Plasma-based modifications have many advantages. Plasma treatment is applicable in various forms on different substrates and materials. Biological, optical, electrical, and chemical properties and also morphology of the treated samples can be modified. It is environment-friendly and a green technique. Therefore, the great potential for significant improvements in the properties of textiles by plasma-enhanced modification is highly promising [25].

In the other example, the influence of flow rate and proportion of reactive gas and pressure in the reactive chamber on the growth of diamond films fabricated by PECVD has been studied by Deng and Zhu [26]. The samples were fabricated by PECVD. n-Si(100) wafers were used as substrates with a resistance of 90 Ω. The wafers were cleaned by standard method. The power of RF source was 500 W, and the frequency was 13.56 MHz. The temperature of substrates during the deposition process was 950°C. Before the reactive gases were introduced, the n-Si substrate was pretreated in H plasma under 200°C for 20 min. They found that these parameters (flow rate and proportion of reactive gas and pressure in the reactive chamber) influence the growth process as a whole rather than individually. It can be deduced that diamond films

with different ratios of SP2 bonds will be fabricated by controlling GH_2 in the range of 16–40 ms to meet different applications [27]. The low-temperature synthesis of carbon nanofibers by microwave PECVD using a $\text{CO}/\text{Ar}/\text{O}_2$ system and their characterizations were performed by Mori and Suzuki [27].

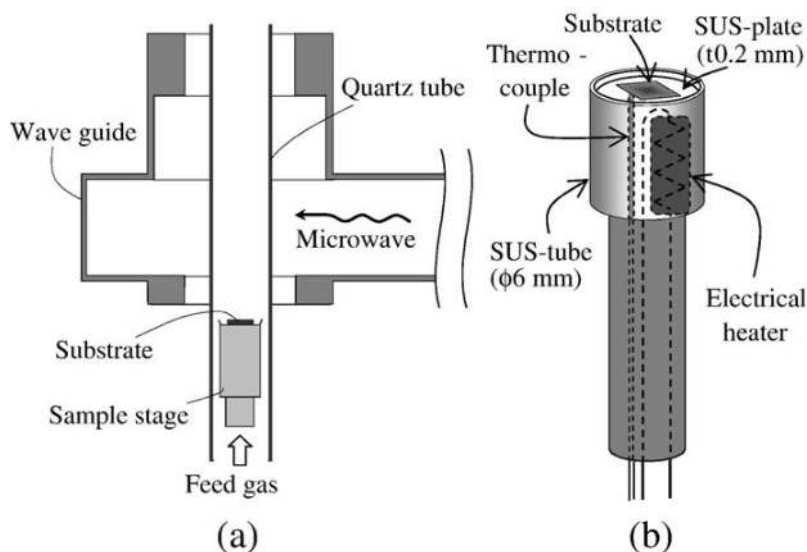


Figure 7. A schematic diagram of experimental apparatus: (a) plasma reactor and (b) sample stage [27].

Figure 6 shows a schematic diagram of the microwave plasma CVD system of Mori and Suzuki [27].

Borosilicate glass and CaF_2 plates with a thin Fe catalyst layer were used as substrates. For the CNF deposition, $\text{CO}/\text{Ar}/\text{O}_2$ microwave discharge plasma was used. In this process, CO flow rate was 10 sccm, Ar flow rate was 30 sccm, O_2 flow rate was 0–1.0 sccm, total pressure was 400 Pa, microwave power was 80 W, and deposition time was 10 min.

The diameter of bulk CNFs was about 50–100 nm and the surface of CNFs was covered by branching fibers and their nuclei with a diameter of about 5–20 nm. The growth rate of CNFs is about 4–6 nm/s [27].

A method most often used to synthesize titanium dioxide thin films for photocatalytic applications is a sol-gel technique. Other ways to deposit these films comprise reactive magnetron sputtering, ion beam sputtering, spray pyrolysis, hydrothermal technique, CVD, and metal organic CVD method. Thin TiO_2 films, deposited using the above-listed techniques, exhibit both photocatalytic properties and receptiveness to the modification of their hydrophilicity under the effect of UV light. A synthesis method that is useful for the deposition of titanium oxide films is PECVD technique.

Many researches and studies have been done about low-temperature plasma and enhancement of chemical reactions in recent years. To deposit semiconducting, insulating, and conducting thin films, RF glow discharges have used. It is also used for electrical and optical devices like optical filter systems. With PECVD technique, titanium dioxide films were stimulated and used as optical filter application.

Szymanowski et al. [28] reported an application of the RF PECVD method to the deposition of titanium oxide films, exhibiting such photo-induced properties as change of water contact angle under illumination with UV light and photocatalytic activity with respect to chemical and biological contamination of water. They have achieved good results for the RF PECVD-treated material [28].

A low-temperature process, PECVD, has been used for the synthesis of TiO_2 for optical applications. By RF PECVD technique, thin films of titanium oxide were deposited and designed for photocatalytic applications. Homogeneous films were obtained and optical properties like stoichiometric TiO_2 method were obtained. Their bactericidal activity in a combination with n UV irradiation was tested.

From the result, it can be concluded that PECVD produced titanium oxide coatings with a large degree, photocatalytic properties, and good antibactericidal activity. By increasing refractive index, bactericidal inhibition of the coated samples increases. Films whose optical parameters approach those of stoichiometric TiO_2 were obtained best results. The results showed a substantial enhancement of the bactericidal activity of UV irradiation for the surfaces modified with the presented process [29].

The aim of the work of Sobczyk-Guzenda et al. [30] was to use the RF PECVD method to place a photocleaning titanium dioxide coating onto the surface of a cotton woven fabric.

The power of RF discharge was varied from 100 to 300 W. The optimum value found to be 200 W. The coating uniformly covers each fiber with no signs of splintering and stability of the coating remains unchanged after washing the fabric in a detergent solution even after 18 months of storage. By increasing the power, single cracks appear in the coatings and their number substantially increases after washing. A very thin film with low strength was deposited on the surface of cotton in lower used power (100 W).

It was concluded that deposition of TiO_2 coatings significantly enhanced the photocleaning properties of cotton under UV light as compared with untreated cotton. In addition, change of the surface character from hydrophobic to strongly hydrophilic under UV illumination is observed in TiO_2 -coated fabric under optimum conditions. Both the above effects of photocleaning and photowetting were introduced to the cotton fabric by means of its modification with the RF PECVD-deposited TiO_2 coating [30].

In the work of Potocký et al. [31], polyvinyl alcohol (PVA) fibers were used as a polymer matrix containing ultradispersed diamond (UDD) nanoparticles. The growth of diamond fiber-like structures and films by microwave PECVD was studied as a function of UDD concentration in the PVA matrix. The composite PVA polymer nanofiber with UDD powder is a suitable pretreatment layer for diamond growth by the microwave PECVD method.

By careful and mechanical separation of polypropylene (PP) cloth from the PVA nanofiber textile, the composite PVA and UDD nanofiber textile was transferred from PP cloth to Si substrates. From the PP cloth pattern, the fingerprint was maintained and then the PVA composite was transferred to the Si substrate by tweezers. In a CVD chamber (cavity resonator reactor), these substrates were loaded.

The composite PVA polymer nanofibers with UDD nanoparticles is a quick, easy, and economical method for the pretreatment of different substrate materials with three-dimensional geometry in large scale [31].

Struszczyk et al. [32] described the studies on the surface modification of so-called ballistic materials (materials commonly used to protect the human body against firearms; i.e., fragments or bullets). Two materials, an ultrahigh molecular weight polyethylene (UHMWPE) composite and aramid fabric, were investigated. The surfaces of these fibrous materials were modified using plasma-assisted CVD (PACVD) to examine the effects of the modification on the material properties, which are important for designing ballistic protections.

The aim of their study was to investigate the effects of low-temperature plasma treatment in the presence of two low molecular mass organic derivatives containing fluorine or silicon on the most critical properties of two types of ballistic raw materials, a p-aramid woven fabric and UHMWPE fiber composite [32].

They investigated the influence of the surface modification of two different materials by PACVD based on their properties (especially those critical for ballistic applications). Specifically, the materials studied were Kevlar and the Dyneema SB51 composite (ultrahigh molecular weight polyethylene); both materials are usually used to design soft ballistic inserts for bullet- and fragment-proof vests.

The surfaces of these materials were modified using a low temperature RF (13.56 MHz) plasma generator. The PACVD system (CD 400 PLC R/R model; Europlasma, Belgium) consisted of two parallel rectangular aluminum electrodes. The right one was connected to an alternative voltage (RF 13.56 MHz), whereas the left one was grounded. The surface to be modified was placed between the electrodes, facing the right one. During the process, the material to be deposited was injected (in the gas phase) into the chamber simultaneously with the gas used for the plasma initiation.

The surface modification of both Kevlar and Dyneema was performed in five stages: (a) proper evacuation of the chamber, (b) surface cleaning, (c) surface activation, (d) deposition of the material on the surface, and (e) conditioning of the deposited layer.

The results indicate that the use of PACVD to deposit a polymer layer on the fiber (Kevlar) and UHMWPE composite (Dyneema) surfaces might significantly improve the water resistance of the p-aramid fibers, and consequently, the ballistic protections can be used for a longer period of time without a significant loss of product performance and safety. The surface properties of both studied ballistic materials can be changed in a controlled way, which is helpful, for example, for the fabrication of a hybrid composite consisting of more than one type of ballistic or nonballistic material. The combination of materials with different performances

might significantly improve the main functionality of the fabricated composites and provide them with new functionalities.

They concluded that PACVD is promising for ergonomics studies and the transformation of textiles, such as Kevlar and Dyneema, into materials used for protection against firearms [32].

2.2. Physical vapor deposition (PVD)

To deposit nanometer to thick layers of organic, inorganic, or metallic material at fiber surface, plasma is used. Several methods of plasma-assisted deposition such as sputtering, thermal evaporation, or anodic arc evaporation at low pressure to vaporize metals and polymers and to condense the gasified material onto a substrate (PVD) on textiles have been proposed. [33]. Vaporization and subsequent condensation of a coating species on a surface involves PVD, which is an atomistic deposition process. With the random (heterogeneous) nucleation of crystallites, growth and coating deposition begin. Growth and nucleation process will depend on different parameters, such as nucleation sites availability, energy of the substrate surface, atomic structure of the coating as a bulk material, and mobility of the deposited species.

Microcrystallites have a random variety of orientations possibly which influenced by epitaxy with the substrate crystal lattice, during the initial stages of growth. These regions of condensation will act as preferential nucleation sites from which will grow columns of textured material as the film grows [34].

Physical vapor deposition PVD coating is a product that is currently being used to enhance a number of products, including automotive parts such as wheels and pistons, surgical tools, drill bits, and guns [35, 36].

The PVD technique is based on the formation of vapor of the material to be deposited as a thin film. The material in solid form is either heated until evaporation (thermal evaporation) or sputtered by ions (sputtering) [37].

2.2.1. Different types of PVD

Cathodic arc deposition: In cathodic arc deposition process, a high-power electric arc discharged at the target or source material blasts away some into highly ionized vapor to be deposited on the sample or workpiece.

Electron beam PVD: In electron beam PVD, by electron bombardment in high vacuum, material to be deposited is heated to a high vapor pressure and is transported by diffusion to be deposited by condensation on the cooler workpiece.

Evaporative deposition: In evaporative deposition, by electrically resistive heating in “low” vacuum, the material to be deposited is heated to a high vapor pressure.

Pulsed laser deposition: In pulsed laser deposition, a high-power laser ablates material from the target into a vapor.

Sputter deposition: In sputter deposition process, glow plasma discharge, which is usually localized around the target by a magnet, bombards the material sputtering some away as a vapor for subsequent deposition [38, 39].

2.2.2. Application of PVD in different branches of industry

PVD technology is very versatile, enabling one to deposit virtually every type of inorganic materials, such as metals, alloys, compounds, and mixture, as well as some organic materials. Wear resistance, hardness, and oxidation resistance can be improved by PVD coatings. These coatings are used in surgical/medical, automotive, aerospace, dies and moulds for all manners of material processing, cutting tools, optic, watches, thin films, window tint, food packaging, firearms, and textile industry. This chapter is a review of the science and technology related to plasma-enhanced PVD (PEPVD) use in the textile industry.

Cathodic arc plasma deposition is one of the oldest and most modern emerging technologies. Cathodic arc plasma deposition is a coating technology with great potential, because cathodic arc plasmas are fully ionized with very energetic ions, promoting the adhesion and formation of dense films.

According to Hsu et al. [40], undoped ZnO films were successfully deposited on the glass substrate at a low temperature ($<70^{\circ}\text{C}$) using cathodic arc plasma deposition. ZnO films were deposited onto the glass substrate in a cathodic arc plasma deposition (CAPD) system. As a cathode target, 100-mm diameter metallic Zn 99.99% purity in an alumina ceramic tube was held, and as the reactant gas, 99.99% purity O_2 gas was used. Glass substrates were washed by alcohol before deposition and then ultrasonically cleaned in alcohol for 10 min. In the depositions of ZnO films, the base pressure was kept at 3×10^{-4} torr. Substrate rotation of 2 rpm and substrate-anode electrode distance of approximately 21 cm remained constant during the deposition work. Without extra heating, the depositions of ZnO films were performed at room temperature. The result of the confirmed experiment showed that the transmittance increases and the resistivity decreases, indicating that the result of the final confirmed experiments could be certainly improved [40].

However, sputter deposition is a PEPVD method, in which a glow plasma discharge (usually localized around the “target” by a magnet) bombards the material sputtering some away as a vapor for subsequent deposition. Now, the sputter deposition is able to deposit most materials.

DC (diode) sputtering, RF (radiofrequency) sputtering, magnetron sputtering, and reactive sputtering are the basic techniques in sputter deposition. DC sputtering is the simplest sputtering technology. In DC sputtering, the sputter voltage is typically -2 to -5 kV; also, the substrate is being bombarded by electrons and ions from target and plasma. Sputtering film has neutral atoms deposit independently and put negative bias on the substrate to control this; also, it can significantly change film properties during deposition.

RF sputtering works well with insulating targets. Plasma can operate at lower Ar pressures (1–15 mtorr). In RF sputtering, for frequencies less than 50 kHz, electrons and ions in plasma are mobile, and it follows the switching of the anode and cathode.

For frequencies above 50 kHz, ions (heavy) can no longer follow the switching and there are enough electrons to ionize gases (5–30 MHz). Typically, 13.56 MHz is used.

To confine the glow discharge plasma to the region closest to the target plate, magnetron sputtering technique uses powerful magnets; ions with higher density can make the electron or gas molecule collision process much more efficient and improve the deposition rate [41].

Sputter deposition is a widely used technique for depositing thin metal layers on semiconductor wafers. The range of applications of sputtering and the variations of the basic process are extremely wide.

In another point of view, PVD, especially sputtering technology, has been regarded as an environment-friendly technique for the functionalization of textile materials. By sputter coatings of polymers, metals, and metal oxides, different functions can be achieved. By using co-sputtering methods, composite coatings can also be achieved. The functional textiles obtained include magnetic, optical, conductive, and biocompatible materials and can be used in different applications and industries [42].

Antimicrobial properties, electrical conductivity, or a shiny metallic appearance for decorative purposes by textile metallization show a growing interest for textile applications. Ag-coated yarns using electroless Ag plating technique are produced increasingly. Only on nylon fibers, good adhesion of the Ag layers could be achieved and washing fastness is an important technological challenge.

Hegemann et al. [43] described an alternative technique to deposit Ag on textiles, namely, plasma sputtering, which allows cleaning and deposition in a one-step process. They obtained excellent adhesion on polyester fibers with smooth coatings. Also, electrical conductivity was obtained with low amounts of deposited Ag maintaining their textile properties while showing metallic appearance and antimicrobial activity [43].

Fungal and bacterial infestation can cause material damage to fabrics, where damage becomes visible through discoloration and stains. Some fungi and bacteria are pathogenic. Antimicrobial active coatings might be a possible protection against an infestation of the fabrics. Fabrics consisting of SiO₂ fibers were coated with precious metal PVD layers using the magnetron sputtering technique by Scholz et al. [44]. Layers of silver, copper, platinum, platinum/rhodium, and gold were characterized according to their bonding strength and antimicrobial effectiveness. They found that copper was most effective against fungi and bacteria. But silver is effectiveness against fungi but it is effective against bacteria. The other tested metals did not have antibacterial properties. Due to a plasma treatment, the bonding strength between the coatings and the substrates was sufficient [44, 45].

Improving the fastness properties and antibacterial activity of dyed cotton samples was the main goal of Shahidi's research work. Cotton fabrics were dyed with various types of dyestuffs and then dyed samples were sputtered using plasma sputtering system for 15 s by silver and copper. A DC magnetron sputtering system for the deposition of metal nanolayer on the surface of samples has been used.

Silver or copper particles were deposited on the surface of cotton samples, and the antibacterial has been developed through the incorporation of metal nanoparticles onto fabric surfaces. It was concluded that the change in properties induced by sputtering can cause an improvement in certain textile products. Also, the results show that the sputtering technique can be a novel method for improving the fastness properties of dyed cotton samples with different classes of dyestuffs [46].

Also, the antibacterial activities of cellulose fabrics were easily achieved with a DC magnetron sputtering device, by coating copper on the surface of a fabric, without any chemical or wet process. The antibacterial activity of the fabrics remained even after laundering for at least 30 cycles [47].

Textiles were treated for the food industry with an original deposition technique based on a combination of plasma-enhanced chemical and physical vapor deposition to obtain nanometer-sized silver clusters incorporated into a SiOCH matrix by Brunon et al. [48]. The plasma tool used in this study was an industrial equipment with a chamber volume of 350 L for transparent and antimicrobial coating (Figure 7).

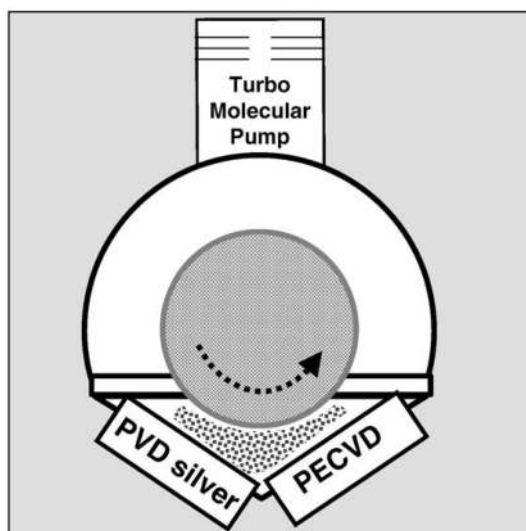


Figure 8. Thin film deposition equipment configuration [48].

The PECVD electrode and the sputtering cathode were installed next to each other to get a material made from both sources. The plasma was a mixed contribution of PECVD source and PVD sourced that are close enough together at an intermediate location. These sources were mounted with a relative angle of 130° and were not in the same plane (Figure 7).

Because of separate generators, both plasma discharges can be run alternately or simultaneously. Because of being uniformly coated, different gasses were mixed in a common pipe and

injected through holes made in a vertical manifold installed next to the plasma sources in the chamber. With a digital liquid mass flow meter, HMDSO injection in the vacuum chamber before being vaporized was controlled.

To quantify the presence at the top surface and inside of the coating of the antimicrobial agent (Ag) as ~10 nm size particles and composition of antimicrobial coatings with acceptable transparency properties, the combination of spectroscopic and microscopic surface analysis was used. Microbiological characterization indicated that the level of antimicrobial activity directly influenced by the variable silver content on the surface [48].

3. Conclusion

This chapter is a study on the plasma-enhanced chemical and physical vapor deposition in textile industry. PECVD is also known as glow discharge CVD. It uses electron energy (plasma) as the activation method to enable deposition to occur at a low temperature and at a reasonable rate. PECVD is widely used in the textile industry. PVD techniques based on sputtering and cathodic arc methods, which are PEPVD, are widely used to deposit coating for various substrates and textiles. The overview concludes with a compilation of typical applications and textile materials.

PECVD has difficulty in depositing high-purity films. This is mostly due to the incomplete desorption of by-products and unreacted precursor at low temperatures, especially hydrogen that remains incorporated into the films. Such impurities, in some cases, are beneficial. PECVD at low frequencies is also prone to induce undesirable compressive stresses in the films. This is especially damaging in thick film for tribological applications, which could lead to cracking or spalling of the films. Toxic by-products and high cost of equipment are the top disadvantages of using PECVD. PECVD methods have some advantages in comparison with CVD methods. They are as follows:

- Flexibility for the microstructure of the deposition and film can be controlled separately
- Deposition can occur at relatively low temperatures on large areas
- To obtain the required film density, the ion bombardment can be substituted for deposition temperature. For temperature sensitive substrates, such low-temperature deposition is important [49].

High vapor pressure metalorganic precursors are available at reasonable prices and the commercial applications of metalorganic-assisted PECVD have been extended from metallic films, dielectric, and semiconductors to new applications, such as powder coating, biomaterials, diamond deposition diffusion barriers, abrasion-resistant coatings on polymer, optical filters, and fiber coatings [50].

In general, the advantages of using plasma-enhanced vapor deposition are low operation temperature, lower chances of cracking deposited layer, good dielectric properties of deposited

layer, good step coverage, less temperature-dependent disadvantages of using PECVD, toxic by-products, and high cost of equipment.

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References

- [1] D. Hegemann, M.M. Hossain, and D.J. Balazs. Nanostructured plasma coatings to obtain multifunctional textile surfaces. *Progress in Organic Coatings* 2007; 58: 237–240.
- [2] www.corrosion-doctors.org.
- [3] A. Surženkov. Aurustussadestatud pinded/Vapour Deposited Coatings/Loengukonspekt, Tallinn University of Technology, ppt.
- [4] M. Esen, I. Ilhan, M. Karaaslan, E. Unal, F. Dincer, and C. Sabah. Electromagnetic absorbance properties of a textile material coated using filtered arc-physical vapor deposition method. *Journal of Industrial Textiles*, published online 12 May 2014. DOI: 10.1177/1528083714534710.
- [5] www.reference.com.
- [6] https://en.wikipedia.org/wiki/Chemical_vapor_deposition.
- [7] P. Aminayi and N. Abidi. Imparting super hydro/oleophobic properties to cotton fabric by means of molecular and nanoparticles vapor deposition methods. *Applied Surface Science* 2013; 287: 223–231.
- [8] M. Gorjanc, V. Bukosek, M. Gorenssek, and A. Vesel. The influence of water vapor plasma treatment on specific properties of bleached and mercerized cotton fabric. *Textile Research Journal* 2010; 80(6): 557–567. DOI: 10.1177/0040517509348330.

- [9] S. Vihodceva and S. Kukle. Low-pressure air plasma influence on cotton textile surface morphology and evaporated copper coating adhesion. *American Journal of Materials Science and Technology* 2013; 2: 1–9. DOI: 10.7726/jac.2013.1001.
- [10] Y. Chu, X. Chen, D.W. Sheel, and J.L. Hodgkinson. Surface modification of aramid fibers by atmospheric pressure plasma-enhanced vapor deposition. *Textile Research Journal* 2014; 84(12): 1288–1297.
- [11] M. Mattioli-Belmonte, G. Lucarini, L. Virgili, G. iagini, L. Detomaso, P. Favia, R. D'Agostino, R. Gristina, A. Gigante, and C. Bevilacqua. Mesenchymal stem cells on plasma-deposited acrylic acid coatings: an in vitro investigation to improve biomaterial performance in bone reconstruction. *Journal of Bioactive and Compatible Polymers* 2005; 20: 343–360.
- [12] www.plasmatherm.com/pecvd.html. Received on 2 August 2015.
- [13] www.plasmaequip.com
- [14] www.plasmatherm.com/pecvd.html. Received 2 August 2015.
- [15] https://en.wikipedia.org/wiki/Plasma-enhanced_chemical_vapor_deposition.
- [16] S.B. Jin, J.S. Lee, Y.S. Choi, I.S. Choi, and J.G. Han. High-rate deposition and mechanical properties of SiO_x film at low temperature by plasma enhanced chemical vapor deposition with the dual frequencies ultra high frequency and high frequency. *Thin Solid Films* 2011; 519: 6334–6338.
- [17] M.P. Hughey and R.F. Cook. Massive stress changes in plasma-enhanced chemical vapor deposited silicon nitride films on thermal cycling. *Thin Solid Films* 2004; 460: 7–16.
- [18] D.T. Dias, V.C. Bedeschi, A. Ferreira da Silva, O. Nakamura, M.V. CastroMeira, and V.J. Trava-Airoldi. Photoacoustic spectroscopy and thermal diffusivity measurement on hydrogenated amorphous carbon thin films deposited by plasma-enhanced chemical vapor deposition, *Diamond & Related Materials* 2014; 48: 1–5.
- [19] K. Yu, J. Zou, Y. Ben, Y. Zhang, and C. Liu. Synthesis of NiO-embedded carbon nanotubes using corona discharge enhanced chemical vapor deposition. *Diamond & Related Materials* 2006; 15: 1217–1222.
- [20] N. De Vietro, C. Annese, L. D'Accolti, F. Fanelli, C. Fusco, and F. Fracassi. A new synthetic approach to oxidation organocatalysts supported on Merrifield resin using plasma-enhanced chemical vapor deposition. *Applied Catalysis A: General* 2014; 470: 132–139.
- [21] J. Musschoot, J. Dendooven, D. Deduytsche, J. Haemers, G. Buyle, and C. Detavernier. Conformality of thermal and plasma enhanced atomic layer deposition on a non-woven fibrous substrate. *Surface and Coatings Technology* 2012; 206: 4511–4517.

- [22] R. Mossotti, G. Lopardo, R. Innocenti, G. Mazzuchetti, F. Rombaldoni, A. Montarso, and E. Vassallo. Characterization of plasma-coated wool fabrics. *Textile Research Journal* 2009; 79(9): 853–861.
- [23] M. Jimenez, H. Gallou, S. Duquesne, C. Jama, S. Bourbigot, X. Couillens, and F. Peroni. New routes to flame retard polyamide 6,6 for electrical applications. *Journal of Fire Sciences* 2012; 30(6): 535–551.
- [24] G. Rosace, R. Canton, and C. Colleoni. Plasma enhanced CVD of $\text{SiO}_x\text{C}_y\text{H}_z$ thin film on different textile fabrics: Influence of exposure time on the abrasion resistance and mechanical properties. *Applied Surface Science* 2010; 256: 2509–2516.
- [25] Q. Wei, Y. Wang, Q. Yang, and L. Yu. Functionalization of textile materials by plasma enhanced modification. *Journal of Industrial Textiles* 2007; 36(4): 301–309.
- [26] N. Deng and C. Zhu. Influence of resident time and proportion of reactive gas on the growth of diamond films. *Journal of Wide Bandgap Materials* 2002; 10(1): 71–75.
- [27] S. Mori and M. Suzuki. Characterization of carbon nanofibers synthesized by microwave plasma-enhanced CVD at low-temperature in a CO/Ar/O₂ system. *Diamond & Related Materials* 2009; 18: 678–681.
- [28] H. Szymanowski, A. Sobczyk-Guzenda, A. Rylski, W. Jakubowski, M. Gazicki-Lipman, U. Herberth, and F. Olcaytug. Photo-induced properties of thin TiO₂ films deposited using the radio frequency plasma enhanced chemical vapor deposition method. *Thin Solid Films* 2007; 515: 5275–5281.
- [29] H. Szymanowski, A. Sobczyk, M. Gazicki-Lipman, W. Jakubowski, and L. Klimek. Plasma enhanced CVD deposition of titanium oxide for biomedical applications. *Surface and Coatings Technology* 2005; 200: 1036–1040.
- [30] A. Sobczyk-Guzenda, H. Szymanowski, W. Jakubowski, A. Błańska, J. Kowalski, and M. Gazicki-Lipman. Morphology, photocleaning and water wetting properties of cotton fabrics, modified with titanium dioxide coatings synthesized with plasma enhanced chemical vapor deposition technique. *Surface and Coatings Technology* 2013; 217: 51–57.
- [31] S. Potocký, T. Ľzák, B. Rezek, P. Tesárek, and A. Kromka. Transformation of polymer composite nanofibers to diamond fibers and films by microwave plasma-enhanced CVD process. *Applied Surface Science* 2014; 312: 188–191.
- [32] M.H. Struszczyk, A.K. Puszczarz, B. Wilbik-Hałgas, M. Cichecka, P. Litwa, W. Urbania-Domagala, and I. Krucinska. The surface modification of ballistic textiles using plasma-assisted chemical vapor deposition (PACVD). *Textile Research Journal* 2014; 84(19): 2085–2093.
- [33] R. Morent, N. De Geyter, J. Verschuren, K. De Clerck, P. Kiekens, and C. Leys. Non-thermal plasma treatment of textiles. *Surface and Coatings Technology* 2008; 202: 3427–3449.

- [34] J.P. Feist, A.L. Heyes, and J.R. Nicholls. Phosphor thermometry in an electron beam physical vapour deposition produced thermal barrier coating doped with dysprosium. *Proceedings of the Institution of Mechanical Engineers, Part G: Journal of Aerospace Engineering* 2001; 215: 333–341.
- [35] <http://en.wikipedia.org/w/index.php?oldid=619209469>.
- [36] M. Aliofkhaezrai and N. Ali. PVD technology in fabrication of micro- and nanostructured coatings. *Comprehensive Materials Processing* 2014; 7: 49–84.
- [37] P. Lu and B. Ding. Nano-modification of textile surfaces using layer-by-layer deposition methods. *Surface Modification of Textiles* 2009: 214–237.
- [38] M. Polok-Rubiniec, K. Lukaszewicz, and L.A. Dobrzański. Comparison of nanostructure and duplex PVD coatings deposited onto hot work tool steel substrate. *Journal of Achievements in Materials and Manufacturing Engineering* 2009; 37(2): 125–192.
- [39] <http://en.wikipedia.org>.
- [40] S.-F. Hsu, J.-H. Chou, C.-H. Fang, and M.-H. Weng. Optimization of the cathode arc plasma deposition processing parameters of ZnO film using the grey-relational Taguchi method, Hindawi Publishing Corporation. *Advances in Materials Science and Engineering* 2014. Article ID 187416, 6 pp. DOI: <http://dx.doi.org/10.1155/2014/187416>.
- [41] www.angstromsciences.com.
- [42] Q. Wei. Textile surface functionalization by physical vapor deposition (PVD). *Surface Modification of Textiles* 2009; woodhead publishing ISBN: 9781845694197
- [43] D. Hegemann, M. Amberg, A. Ritter, and M. Heuberger. Recent developments in Ag metallised textiles using plasma sputtering. *Materials Technology* 2009; 24(1): 41–45.
- [44] J. Scholz, G. Nocke, F. Hollstein, and A. Weissbach. Investigations on fabrics coated with precious metals using the magnetron sputter technique with regard to their anti-microbial properties. *Surface and Coatings Technology* 2005; 192(2–3): 252–256.
- [45] www.chemweb.com.
- [46] S. Shahidi. Plasma sputtering as a novel method for improving fastness and antibacterial properties of dyed cotton fabrics. *The Journal of the Textile Institute* 2015; 106(2): 162-172
- [47] S. Shahidi, M. Ghoranneviss, B. Moazzenchi, A. Rashidi, and M. Mirjalili. Investigation of antibacterial activity on cotton fabrics with cold plasma in the presence of a magnetic field. *Plasma Processes and Polymers* 2007; 4: S1098–S1103.
- [48] C. Brunon, E. Chadeau, N. Oulahal, C. Grossiord, L. Dubost, F. Bessueille, F. Simon, P. Degraeve, and D. Leonard. Characterization of plasma enhanced chemical vapor deposition-physical vapor deposition transparent deposits on textiles to trigger vari-

ous antimicrobial properties to food industry textiles. *Thin Solid Films* 2011; 519: 5838–5845.

- [49] J. Pan. Chemical vapor deposition of one dimensional tin oxide nanostructures: structural studies. *Surface Modifications and Device Applications* 2011.
- [50] K.L. Choy. Chemical vapour deposition of coatings. *Progress in Materials Science* 2003; 48: 57–170.