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Review article

APPLICATION OF PECVD IN THE CONSERVATION OF METALLIC CULTURAL HERITAGE: A REVIEW

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***Abstract**:*
Plasma technology is a modern, non-conventional technique with a wide range of applications in various fields. Plasma-based material processing technology aims to modify the chemical and physical properties of metallic, polymer, textile, and dielectric surfaces. Plasma processing techniques include plasma etching, cleaning, plasma surface activation and functionalization, and plasma deposition. Plasma processing has attracted the attention of cultural heritage restoration due to its low temperature, selectivity, durability, and effectiveness. The goal of this work is to introduce readers to previous studies on the different uses of plasma-based technology in the conservation and restoration of metallic cultural and historical artifacts. It focuses on the role of the different plasma-based coating techniques especially plasma enhanced chemical vapor deposition (PECVD) for archaeological and artistic metallic artifacts that need reversible coatings with a pleasing aesthetic appearance and a good barrier effect against atmospheric pollution at low temperatures.

1. Introduction

Plasma is a fully or partially ionized gas in which the free electric charges, electrons, and ions make plasma electrically conductive, internally interactive, and strongly responsive to electromagnetic fields [1-3]. The constituents of plasma are free-charged particles, such as electrons, positive and negative ions, free radicals including reactive oxygen species (ROS) and reactive nitrogen species (RNS), neutral gas atoms, ground or excited molecules, and electromagnetic radiation (including ultraviolet and VUV radiation) [1,4], fig. (1). Plasmas provide opportunities for numerous applications in material processing such as etching deposition, nanoparticle synthesis, surface treatment, lasers etc.,. Plasma status can be achieved by applying energy in various forms, including thermal, electrical, and electromagnetic energy. Applying electric fields (DC, pulsed, audio, and RF) to a gas is the most common method for plasma generation in laboratories (gas discharge), which increases the kinetic energy of background electrons, leading to increased collisions of the free electrons, resulting in excitation and ionization of the working gas [5]. Several specific gases can be used, either inert or reactive, such as helium, argon (Ar), heliox (a combination of helium and oxygen), air to create plasma [6], as well as NH_3, CO_2, H_2 and nitrogen Unlike oxygen, plasma is able to oxidize organic materials at room temperature, into carbon monoxide and water. Hydrogen plasma is able to reduce certain corrosion products back to metal [7].

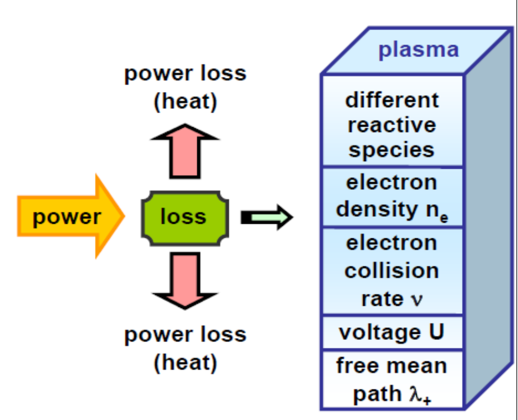

Figure (1) Shows schematic of plasma generation (*After, Krčma, et al., 2014*) [8]

2. The Significance of Plasma Treatment in cultural heritage materials

Plasma processing is not a single but a "field of opportunities" [4], as it is considered a modern non-conventional technique [5] and has had a wide range of applications in various fields since the 80$_{s}$. It attracted the attention of cultural heritage restoration mainly because of its low temperature [9,10]. Plasma technology can also be used to develop thin protective layers [11]. In the last twenty years, scientists from various fields have turned their attention to the application of unconventional cleaning methods to metal artifacts. The so-called cold high frequency plasma has come to be considered as a viable, non-destructive, and ecological method [12]. The principal applications of plasma treat-ments concern the processes that lead to a selected, limited transformation of the outer surface layer (nanometric scale) [11]. Since 1979, cold plasma has been investigated in the field of conservation and restoration as a method to clean and disinfect cultural and historical objects without making them more fragile. It is due to characteristics such as low temperature and high energy, as well as a large array of industrial uses. Since plasma treatments are non-destructive and conducted under low pressure and atmospheric conditions, they are recommended in the field of cultural heritage protection for cleaning and preserving many types of artifacts, from paper to metallic art works. Several studies show how plasma-based technologies can be used to help preserve both inorganic and organic cultural heritage materials. Vaprek et al. [13] reported that the plasma treatment method developed at their institute to be relatively quick, effectively in treatment of corroded iron artifacts. In particular, De Graaf [14] highlighted that the preservation of shipwreck artifacts using plasma, followed by post-treatment and chlorine removal, has been proved successful in experiments. As long as the diffusion length of active particles is not too short in low-pressure hydrogen-based plasmas, active particles can infiltrate the pores or holes in the surface, enabling the treatment of virtually the whole surface. Favre-Quattropani [15] demonstrated that argon-hydrogen mixtures can be utilized to restore corroded metallic artefacts to their original condition and coating silver substrates. The effects of the plasma pencil in a liquid environment on corroded bronze objects and archaeological glasses were explored by Janca et al. [16] also the HF plasma pencil (13.56 MHz) has been used to reduce cor-rosion on historical objects since it is simple to use and manage. The HF plasma pencil destroyed the corroded layer of bronze artifacts efficiently. During the treatment of archaeological glasses, layers of soil solution precipitates were peeled off, but the most important layer of gelous glass that was breaking down was only treated moderately. According to Kern and Schuegraf [17] plasma deposition can provide very thin coatings with a customizable structure that have a minimum effect on the surface's look and provide good corrosion protection. Francassie, et al. [18] indicated that plasma enhanced chemical vapor deposition (PECVD) with organosilicon precursors appear to be a promising technique for enhancing the corrosion resistance of metallic materials. Schmidt-Otta [19] demonstrated that, for conservation purposes, low ionization plasma composed of ions, electrons, and neutral gas is utilized to clean and conserve iron artifacts and this plasma could achieve a number of benefits. Argyropoulos, et al. [20] demonstrated that plasma enhanced chemical vapour deposition (PECVD) barrier films are approved for usage on intentionally and naturally aged metal reference alloys, since PECVD coatings on bronze and silver-based alloys [19]. Moreover, D'Agostino, et al [21]. stated that PECVD coatings permit the protection of metallic and artistic artefacts that require reversible coatings with an acceptable aesthetic appearance. Furthermore, Grassini, et al. [22] explained that low pressure plasmas-the so-called cold plasmas-exhibit some advantages which suit their applications in the field of metal conservation, such as dry processes easily performed at room temperature to preserve the metallurgical characteristics and applications that can be made directly on the exterior or the interior of complex shaped objects. Grassini, et al. [23] demonstrated that PECVD coatings deposited under optimum circumstances protect silver artifacts from environmentally harsh chemicals. Angelini and Grassini [7] explained that this technology is becoming increasingly significant because it is extremely versatile, environmentally friendly, and permits the deposition of thin films (100-10,000) as polymers and silica-like coatings with good barrier properties for metallic artefacts against aggressive agents and vapors. Faraldi, et al. [24] reported that plasma-enhanced chemical vapor deposition (PECVD) is an environmentally friendly process used to deposit a variety of nano-structured coatings for the protection or surface modification of metallic artifacts, such as the SiO_2-like films that have been successfully tested on ancient silver, bronze, and iron artefacts as barriers against aggressive agents. Water-based dispersions attach to hydrophobic surfaces treated with plasma; according to Pflugfelder [25] this method is highly effective for revitalizing lime plaster facades. It's possible that plasma-blasters could be used to remove graffiti. Nettesheim [26] explained that employing a plasma jet helped to remove varnish coats thicker than 1 mm when peeling paint and cleaning surfaces with atmospheric plasma. There was relatively minimal combustion, thermal stress, and mechanical damage. As a result, a smooth surface with a fine sanding has been generated, which has been optimized for later processing. Concerning the cleaning of historical textiles with metal threads, the plasma beam's surface activation, which does not cause chemical harm to silk or copper, may be useful in removing corrosion products and surface organic filth [27]. El-Gohary and Metawa [28] studied the role of the radio frequency (RF) hydrogen plasma (H_2), which proved that it was able to remove some metallic stains (iron and copper) from the historic brick surfaces of Prince Yousef Kamal's location. With respect to organic objects, Daniels, et al. [29] clarified the role of low-pressure hydrogen plasma in the restoration of daguerreotypes. Abd Jelil [30] illustrated some of the promising outcomes for textile treatment as plasma treatments allow for the creation of traditional textile finishes without affecting critical textile qualities. Pflugfelder [25] mentioned that for temperature-sensitive materials, the DBD-jet is preferable, such as cleaning ancient documents and books, as their preservation presents a challenge. Ioanid, et al. [31] demonstrated that to make the heritage photographs look better, a cleaning process that involved either physical or chemical etching was used. This did not cause any major physical or chemical changes on the surface that had been treated with plasma. Alatter, et al, [32] demonstrated that DBD Ar. plasma, a non-contact approach, when mixed with the aqueous extract, cleaned the surface of historical images without leaving stains or causing damage. Abdel-Maksouda, et al. [33] described the role of plasma cleaning in removing iron stains from archaeological bone artefacts and demonstrated that plasma-based technology is one of the most promising techniques for the preservation of cultural heritage. Abdel-Maksoud, et al. [34] explained that the pulsed coaxial plasma pistol is an excellent and quick technique to remove invisible oil coatings, dust deposits, corrosion products, and other contaminants from bone. The best way to clean iron stains depends on the type and size of the bone piece, as well as the thickness and type of the iron stains.

3. Plasma Classification

There are two primary types of plasma: thermal plasma and non-thermal plasma:

3.1. *Thermal plasma (fully ionized gas)*

It is a fully ionized gas (high temperature plasma). It is also called thermal equilibrium plasma since all plasma species have the same temperature (Te = Ti = Tn = 10^4 k where T_e is the electron temperature, Ti ion temperature, and Tn neutral gas temperature). Note that the term "temperature" for plasma constituents means kinetic energy. Plasmas like these can be made with a plasma torch, an arc, or a microwave and high gas temperatures (10,000 k) [6].

3.2. *Non thermal plasma (partially ionized gas)*

Non-equilibrium plasma "non-thermal" (NTP), also called "cold plasma" or "near ambient temperature plasma" in which electron temperature is much greater than ion or neutral gas temperature (Te >> Ti = Tn) [35] This kind of plasma includes direct current (DC) plasma, [capacitive coupled radio frequency plasma (CCP-RF),pulsed plasma, and audio frequency plasmas [11].

4. Reactions Involved in the Plasma

The main types of reactions occurring in volume plasma are divided into two basic categories: homogenous and heterogeneous reactions [5].

4.1. *Homogeneous gas phase reactions*

Homogenous inter-species interactions occur in the gaseous phase as a result of inelastic collisions between electrons and heavy species or collisions between heavy species [12, 36] for example, the synthesis of ozone from oxygen[5, 9].

4.2. *The heterogeneous reaction*

Heterogeneous reactions occur involving the interaction between the plasma species and the solid surface immersed or in contact with the plasma [37] (or sometimes liquid) surface [9], as schematically shown in fig. (2-a). Cold plasma can cause several effects on substrates depending on the plasma mode and the process gases used [4], the choice of the precursors and the discharge conditions [38,39]. There are several mechanisms that can be used [4], such as: fine cleaning, grafting (surface activation or functionalization), (utilizable ablation) etching, coating deposition and cross-linking, and sterilization [13, 40], fig. (2-b).

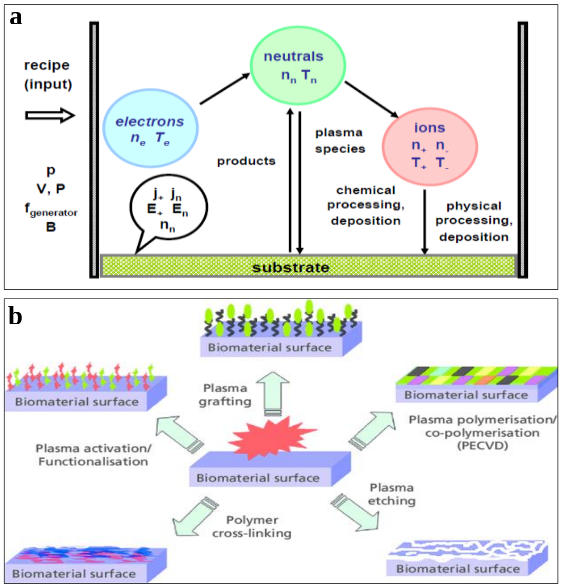

Figure (2) Shows **a.** schematic of plasma processing (*After, Krčma, et al., 2014*) [8], **b.** schematicof different processes involved in plasma processing (*After, Angelini, et al., 2007*) [41]

4.2.1. Plasma etching (PE) or (utilizable ablation)

Plasma etching or sputtering [42] or ablation, namely one in which material is removed from the solid surface by etching induced by the plasma [36]. It allows the ablation of the surfaces by the reaction with active species generated in a plasma discharge to form volatile products [7], also increasing the wettability and adhesion properties of subsequent finishing treatments. A direct plasma is normally needed in order to carry out an effective etching process. So ablation affects only the contaminant layers and the outermost molecular layers of the substrate material, leading to a controlled nano-or micro-roughness, increasing diffuse reflectance and minimizing the specular component, so etching requires the removal of several hundred nanometres and etching processes are therefore slow[40].

4.2.2. Grafting (modification)

This method is also referred to as "plasma activation," "plasma alteration," and "plasma therapies" [42]. In this process, neither material is added to nor withdrawn from the solid in meaningful amounts, but the surface is chemically and/or physically transformed during exposure to plasma particles and radiation [4,9]. By plasma treatment, it is possible to graft species that allow for the development of a wide range of properties and functionalities of the chemical composition of the treated surfaces and, consequently, of their chemical and physical properties (*wettability, changing from hydrophilic to hydrophobic and vice versa, adhesivity, dyebility, refractive index, printability, or oleophobicity*, etc.) [4]. This process never occurs on its own but always precedes or follows plasma cleansing. Plasma grafting and cross-linking of chemical functionalities in inert or reactive gases, such as Ar, H_2, CO_2, NH_3, etc., affect the hydrophilic or hydrophobic nature of a surface, as well as its acidic or basic behavior [7].

4.2.3. Sterilization

Plasma sterilization operates differently due to its special active agents, UV photons and radicals (atoms or atomic assemblies with unpaired electrons, hence chemically reactive, such as O and OH, respectively) [4].

4.2.4. Cleaning

Cold plasma has been tested in disinfection and cleaning operations as a non-toxic and non-invasive alternative in the field of cultural heritage [43] by removing substances previously deposited on the substrate [44]. For instance, the application of low-pressure hydrogen plasma has been developed for cleaning iron artifacts [45]. Plasma and laser therapies represent promising alternatives to the aforementioned methods [46]. Because organic contamination in many cases consists of weakly bound hydrocarbons, oxygen plasma cleaning will cause both H and C to react with oxygen and leave the substrate surface as volatile H_2O and CO_2 [4].

4.2.5. (Coating deposition) ion implantation polymerization)

This process refers to the precipitation of chemicals (plasma polymerization) to impart some desired properties to the substrate [40]. Whereby material is added to the surface in the form of an increased thin film deposition during plasma polymerization [36] a process known under the collective name of "plasma-enhanced chemical vapor deposition," or PECVD [9]. Thin films can be obtained by three general deposition methods: mechanical, physical, and chemical deposition, fig. (3). Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are two types of deposition methods that can be used to make thin films. These techniques were developed in the semiconductor industry [47]. As is the case with conventional coatings, the technique should be applied under optimized conditions in order to achieve the best surface coverage of the nano coating in terms of uniformity, smoothness, adhesion, crack-free surfaces, etc. [38].

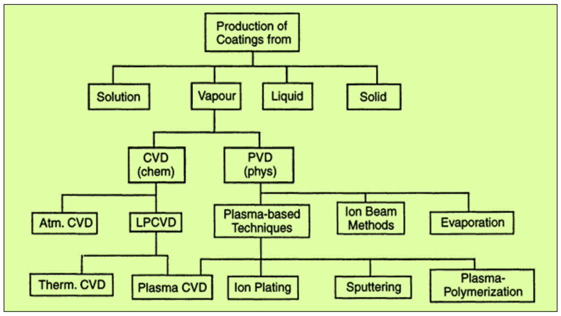

Figure (3) Shows systematic of deposition techniques (*After, Droes, et al., 1997*) [48]

5. Classification of thin film deposition processes

5.1. *Physical vapor deposition (PVD) processes*

In classic PVD processes, there are no chemical reactions. Instead, a sample ingot of the desired composition is evaporated (either by e-beam, thermal evaporation, or some other method), moved, and deposited on a suitable substrate [49]. CVD techniques are different from PVD techniques because they involve chemical reactions that change the composition of the final film from what it was before [50]. Plasma is used to generate and direct ions toward the substrate. This is referred to as physical vapor deposition. The technique is divided into two primary methods: reactive sputtering and activated reactive sputtering. However, the coatings are carried out at low pressure, so there is a high cost to implement the process and a subsequent one to keep it working [39]. Figure (4) shows a schematic diagram of the sputtering process.

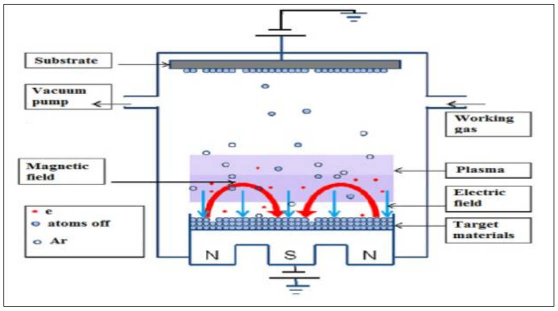

Figure (4) Shows schematic diagram of sputtering process (*After, Boscom, et al., 2012*) [51]

5.2. *Chemical vapor deposition (CVD)*

As shown in figure (5), CVD is a simple homogeneous deposition technique that produces films with good step coverage, even on complex shapes. Chemical vapor deposition (CVD) is the process of chemically reacting volatile compound with other gases to produce a nonvolatile solid that deposits on a suitable cleaned substrate. Chemical vapor deposition is a method of creating solid films from chemically reactive gas mixtures [10]. Various types of CVD methods and reactors are used depending on the reactants, reaction conditions, and the forms of energy used to activate the reactions on the surface of the substrate, as follows: **1)** When using a previous organometallic compound, the process is called metal-organic CVD (MOCVD), as CVD processes are based on metal-organic precursors [52]. **2)** When using plasma to enhance the precursor reaction rates of the precursors, the process is known as plasma enhanced CVD (PECVD) or electrical discharge (plasma enhanced or activated CVD) [53]. Radio frequency PECVD (RF-PECVD), electron cyclotron resonance PECVD (ECR-PECVD), and inductively coupled PECVD (IC-PECVD) are all variations of PECVD [54,55]. **3)** There are modified CVD processes such as low-pressure CVD (LPCVD), low-pressure CVD (LPCVD)-CVD processes at sub-atmospheric pressures, laser enhanced CVD, and aerosol-assisted CVD (AACVD). **4)** Atmosphere-pressure CVD (APCVD): It is a CVD process at atmospheric pressure and the choice of activation method depends on the substrate material used [50].

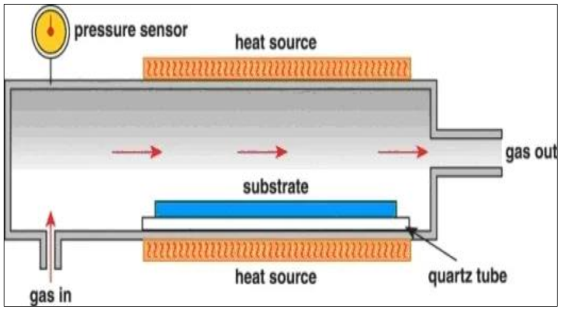

Figure (5) Shows schematic diagram of sputtering process (*After, Popoola, et al., 2016*) [51]

6. Types of Plasma Enhanced Chemical Vapor Deposition

6.1. *Atmospheric pressure PECVD*

Atmospheric pressure plasma chemical vapor deposition (APECVD) shows a high potential for the field of cultural heritage as an alternative conservation method to current, non-sustainable methodologies [56]. **Atmospheric pressure sources**: at atmospheric pressure, plasma can be generated by a variety of electrical discharges, including micro hollow cathode discharges [37], gliding arc discharges and flame discharges, and dielectric plasma needle barrier discharge (DBD) [1,37]. DBDs exist at both low and atmospheric pressures [5]. In recent years, however, impressive developments in atmospheric pressure plasma technologies, so-called dielectric barrier atmospheric pressure glow discharges (DBD or APGD for short), and atmospheric pressure plasma jets (APPJ) have occurred, and these technologies will increasingly compete with low-pressure deposition, treatment, and etching processes, primarily for economic reasons [57]. As illustrated in fig. (6), atmospheric pressure plasma chemical vapor deposition (APECVD) has great potential in the realm of cultural heritage conservation as an alternative to current and non-sustainable methods.

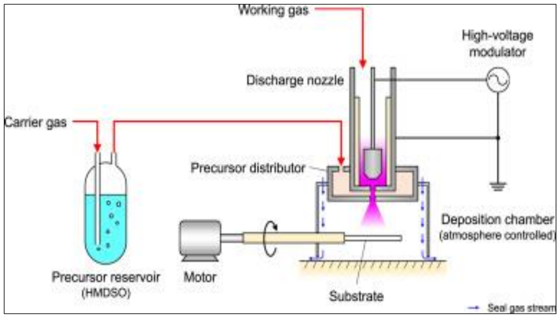

Figure (6) Shows schematic diagram of sputtering process (*After, Gosar, et al., 2019*) [58]

6.2. *PECVD generated under vacuum*

Low-pressure PECVD technology is also referred to as vacuum plasma technology [10,53] or vacuum plasma spray [37]. The pressure which operates at vacuum pressure (10 mTorr or 1 Pa) and moderate pressure (= 1 Torr or 100 Pa), so plasma can be formed and sustained even at room temperature. Low pressure PECVD can be generated at lower air gas pressure by some sources such as microwave, radio frequency (RF), DC, pulsed DC, and audio frequency plasmas:

6.2.1. Microwave PECVD

Microwave plasma-assisted CVD (MPCVD): The CVD process uses a microwave energy source to analyze the precursor to conserve plasma. It is a kind of high frequency electromagnetic radiation in the GHz range (MW, mainly 2.45 GHz) [36].

6.2.2. Radio frequency PECVD (RF-PECVD)

The radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) technique has the additional benefits of low deposition temperature [36], high purity, and straightforward control of reaction parameters [7,11].

6.2.3. Pulsed direct current. PECVD

Direct current plasma (dc) PECVD excited by d.c. power supplies has a region in which electrons are accelerated to energies sufficient to ionize gas molecules, and the positive ions so formed gain enough energy to eject electrons from the cathode [35].

7. Deposition Mechanism of PECVD

The PECVD technique is a complex method due to the complex gas phase chemistry [52]. In PECVD reactors, the plasma is in close proximity to the substrate and is typically at very low discharge power levels such that gas-phase reactions do not occur [57]. In a more detailed description, the process can be defined as ionization proceeds via interactions between energetic electrons and gas molecules. Electrons, ions, radicals, precursor fragments, neutral atoms, molecules, and other highly excited species are all found in plasma [40]. The interaction of all of these species with the substrate results in either surface etching or low-temperature film deposition [5]. So, to summarize the deposition process, the reactant gases or vapors are decomposed primarily at surfaces (substrate, electrodes, walls) by the glow discharge, leaving the desired reaction product as a thin solid film [17], as only in 1995 did vacuum plasma technology become widely used [59]. Despite the fact that there are many different experimental setups for PECVD, there are three main parts in every PECVD process: *the gas feeding system*, *the vacuum chamber*, and *the plasma generator*, fig. (7). The type of interaction between the plasma and the sample surface and the rate at which species are created can be controlled by adjusting the bulk plasma parameters [6], such as: The type of working gas (es), the pressure and flow rate of the gas (es), the intensity and frequency of the power supply used to excite the plasma, the treatment time, the surface material of the sample, the shape of the reactor and the frequency of the plasma, and the distance between the device and the sample [60].

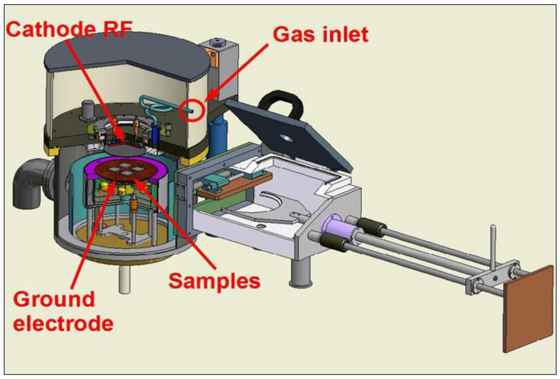

Figure (7) Shows Set-up of vacuum chamber for collection of optical emission data (*After, Li, et al., 2016*) [60]

PECVD is a method for making thin films of metals and semiconductors. The process incorporates the following four fundamental steps: ***)** Plasma formation resulted in the formation of active gas types. ***)** Active species are transported to the target substrate surface. ***)** The reaction on the target substrate's surface. ***)** Reaction by-products are pumped down.

8. Precursors Used for anticorrosive Deposition on Metallic Surfaces

As a matter of fact, one of the major concerns of conservators is the preservation of artifacts from the excavation sites [62]. For centuries, organic coatings, paints and varnishes have been used, providing permanent or temporary protection to various metals against severe or corrosive environments [11,50]. Another well investigated solution to produce functional layers without affecting the environment concerns deposition [11]. There is a pattern of the various properties required for protection against corrosion which is particular to the application, good coating standards should include the following requirements: **a)** as a matter of fact, the ethics of restoration and conservators require the maintenance of the aesthetic appearance and the integrity of the object without removing or modifying parts of it. **b)** good strength, adhesion and hardness of such films are highly significant and the possibility of depositing the coating at relatively low temperatures, **c)** protective coatings should provide a continuous barrier against aggressive agents, so any defect can become a focal point when a localized corrosion attack can start [61]. **d)** high temperature resistant, high thermal fatigue, chemically inert, low coefficient of friction and low cost, **e)** to satisfy curator requirements, protective coatings should include light transparency, with high chemical stability, oxygen and water low permeability and reversible in order to allow the recovery of the initial state of the object [29,63]. PECVD can extend the applicability of the vapor deposition process to various precursors, including reactive organic (silicone-PEO, Teflon-like, etc.), inorganic (SiO_x, diamond, etc.), and inert materials [42]. A suitable CVD precursor would have the following characteristics: volatile and stable during transport to the CVD reactor; easily decomposes under reaction conditions to form the desired coating; low toxicity; cost-effective; not damaging to deposition apparatus. Table (1) shows the different precursors used in PECVD.

Table (1) shows the different precursors used in PECVD [64]

Material	**Precursors**	**Remark**
SiO_2:H	Silane /oxygen or nitrous oxide: SiH_4/O_2or N_2O	Gas (hazardous, flammable)
SiO_2:H:C	Tetraethoxysilane (TEOS):$Si(OC_2H_5)_4$	Liquid
	Hexamethyldisiloxane (HMDSO)	Liquid
	Tetramethyldisiloxane(TMDSO)	Liquid
SiO_2:F	SiH4/O_2/CF_4	Gas
SiO_2:F:C	TEOS /C_2F_6	Liquid/gas
	TEOS /O2/CF	Liquid/gas
	Fluorotriethoxsilane(FTES):$(C_2H_5O)_3SiF$	Liquid
PPFC	C_2F_4,C_4F_8, etc	Gas
	Hexafluoropropylene(HEPO)	Liquid
	Fluoro-alky silanes(FASs)	Liquid
	Perfluoro-1, 3-dimethylcyclohexene (PFDCH)	Liquid
Al_2O_3:C:H	Trimethyl-aluminum(TMA):($(CH_3)_3Al/O_2$ or N_2O	Liquid
	Trimethl-amine alane(TMAA):$(CH_3)_3NAIH_3/O_2$ OR N_2O	liquid
$SiN_{1.3}$:H	SiH_4/N_2 (or NH_3)	Gas
$SiN_{1.3}$:H:C	Hexamethyldisilazane(HMDSN)	Liquid
	Hexamethylcyclotrisilazane(HMCTSZN):$[SiN_{1.3}H(CH_3)_2]_3$	Liquid
SiO_XN_Y:H	$SiH_4/O_2/N_2$ or $SiH_4/N_2O/NH_3$	gas
AlO_XN_Y	$AlBr_3/H_2/N_2O$	gas
$TiO_{2:}$ C:H	Tertraisopropyltitanate (TIPT): $Ti(OC_3H_7)_4/O_2$	Liquid
	Tetraethoxytitante(TEOT): $Ti(C_2H_5)_4/O_2$	Liquid
Ta_2O_5	TaF_5/O_2	solid
Ta_2O_5:H:C	Tantalum pentaethoxide: $Ta(OC_2H_5)_5/O_2$ & $Ta(OCH_3)_5/O_2$	
a-C:H	Methane CH_4 , C_nH_{2n+2}, CnH_{2n}, etc	Gas, liquid
GeO2:H:C	Tetramethyelgermanium(TMGEe):$Ge(CH_3)_4/O_2$	Liquid
Y_2O_3-ZrO_2	Acetylacetonatozirconium $Zr(acac)_4$:$(C_5H_7O_2)_4Zr$	Solid
(YSZ)	Dipivaloymethanato yttrium $Y(dpm)_3$:$(C_{11}H_{19}O_2)Y$	Solid
$BaTiO_3$	Dipivaloymethane barium $Ba(dpm)_2$: $(C_{11}H_{19}O_2)_3Y/TIPT/O_2$	solid
$SrTiO_3$	Dipivaloymethane strontium $Sr(dpm)_2$: $(C_{11}H_{15}O_2)_3Y/TIPT/O_2$	solid

8.1. *Inorganic coatings*

PECVD of inorganic thin films are oxides, nitrides and carbides of metals or semiconductors. PECVD from silicon containing organic compounds (i.e. organo-silicons precursors) appears particularly promising for employment in the field of corrosion protection of metallic materials, also of artistic and historic interest, as a matter of facts being PECVD a highly versatile technique the production of a variety of coatings with a wide range of properties simply by means of a proper selection of the experimental conditions is easily achieved: the SiO_2-like coatings are characterized by high chemical and thermal stability, good dielectric properties, low gas permeability, etc [29,53,63]. It allows the deposition of thin films (100-10,000 Å) as polymers [43]. The polymerization of monomer molecules – like hexamethyldisiloxane (HMDSO) [5, 11] which yields glassy, ultrafine layers – can be effectively by plasma-assisted chemical vapor deposition techniques (RF-assisted plasma activation) [11].

8.2. *Organic coatings*

Organic thin films are soft materials or "plasma polymers," hard carbon films, and crystalline diamond. Polymer products will stratify onto the substrate surface if an organic precursor containing structures capable of forming a polymer is introduced into the plasma (under suitable energy conditions). Precursor activation occurs when precursors collide with high-energy free electrons in the plasma, resulting in precursor fragmentation and the formation of highly reactive radical and ionic species [64].

9. Advantage and Disadvantage of PECVD in the Cultural Heritage Field

9.1. *Advantages*

Plasma is a technique of appealing a thin film to particles because; it can be applied in a cold state (at room T) or in (300 ° C) [47,57]. This technique allowing restorers to work with temperature-sensitive materials while not deteriorating the substrate and thus preserving its features [64]. Due to the significantly higher pressures as compared to PVD and lower deposition temperatures as compared to thermal CVD, this technique allows the convenient coating of complex shaped three dimensional objects at temperatures below the annealing temperature of a lot of alloys [47]. Films in a thickness range of 10 nm to 5 µm with customized properties can be deposited quickly and cost-efficiently by PECVD coating. A wide variety of void-free, well-adherent thin films (100-10.000 angstrom) [7]. The thin films deposited also have low mechanical stress. This can prevent the films from being deformed and becoming non-uniform because of the uneven mechanical stress on the films. Good conformal step coverage and excellent uniformity are also provided by the PECVD process [64]. PECVD coatings are ideal candidates for archaeological and artistic artifacts that need reversible coatings with a satisfactory esthetic appearance and a good barrier effect against atmospheric pollution. So it does not change bulk material properties and does not lose material (preserve the authenticity). The reaction is limited to the surface (a selective) so that the process can be timed to stop when the original surface of the object is reached in order to avoid damage [65]. Moreover, it allows the design of new devices with unique surface properties and suitable for all sizes of objects (large and small-sizes) through the control of the device dimensions [47]. PECVD has high deposition rates compared to reactive sputtering and a lower cost of materials. Conventional PECVD technologies have fallen short of this promise due to electrode coating, poor uniformity, and powder formation. General Plasma, Inc. (GPI) has developed a new linear plasma source technology that addresses these problems and enables PECVD on large area substrates [66]. Plasma treatments are by definition dry processing methods at room temperature in order to preserve the metallurgical feature, thus avoiding the use of water and solvents, minimizing emissions and the overall environmental burden [67]. This also prevents further corrosion, which may be caused by the presence of an aqueous environment. Also, there is no dissolution of the metal itself [68]. Even though inorganic materials (stones, minerals, glass, ceramics, and metals) are temperature stable, temperature plays a significant role in surface treatment. When surface-treating organic materials such as paper, leather, wood, and so on, protection against high temperatures is extremely crucial. In addition, several ancient artefacts, such as polychromatic paints on wooden statues and brocade textiles, demonstrate the mixture of inorganic and organic substances. Because of these facts, any plasma application on cultural heritage items must be confirmed and any potential hazards addressed before use. In many applications, a low substrate temperature is necessary, as is the capacity to generate unique materials. Plasma processing happens at temperatures close to ambient, which helps prevent heat-related process yield loss [69]. Thermal stress and degradation in polymer devices are minimized by the room-temperature plasma process [70]. Furthermore, direct application to the exterior or inside of complex-shaped items is possible [67]. Depending on the type and size of the device, this can be applied to multiple items at once [69,70]. So that varied substrate shapes, such as flat, hemispherical, cylindrical, inside tubes, etc., can be consistently coated [64]. At the nano-scale, plasma etching may be controlled and selective, and surface ion bombardment can be precisely regulated to prevent damage. Plasma deposition can make very thin coatings with different structures that don't change the look of the surface and protect it well from corrosion. Plasma enhanced chemical vapor deposition (PECVD) processes offer a wide range of configurations (gas mixture ratio, ion energy, continuous or pulsed plasma) to precisely control the growing film characteristics (refractive index, extinction coefficient, thickness, stress) and enable the development of integrated photonic devices on a variety of substrates [63]. Utilizing various plasma processes, metallic nanoparticles can be applied. They are plasma polymerization of organometallics, chemical vapor deposition, and plasma sputtering, a low-pressure method that enables direct application of metallic nanoparticle coatings [71]. In order to optimize the coating substrate performance, it is essential to note the potential of performing preliminary substrate pre-treatments prior to the deposition process in the same reactor [72]. Thin films' great chemical stability, low gas and vapor permeability, and optical clarity distinguish them from other materials [73]. Besides, its high versatility, it allows for the production of high-purity, high-performance conformal coatings in the form of thin nano-structured [37]. Large-area uniformity [7] and precise control over the composition of alloy films [37,74]. Film properties can be altered simply by adjusting a few deposition parameters [40]. Additionally, the processes are easily controllable through RF, DC, or microwave power, time, gas, pressure, and type [56].

9.2. *Disadvantage*

There are restrictions on the usage of (LP PECVD) such as the selection of acceptable monomers or a suitable inlet device [66]. Expensive film with a high hydrogen content [75]. Despite the intriguing results obtained by vacuum plasmas, their application is limited due to inherent technological characteristics: the size of the treated artifacts is limited to the vacuum chamber, the entire surface must be treated, and it is expensive, but the most significant limitation is that it cannot be continuously controlled by the restorers in-situ [42]. Non-thermal reactive plasma at low pressure necessitates the use of massive metal vacuum chambers and complicated vacuum equipment (such as vacuum pumps, gas flow controllers, pressure gauges, and gaskets).Moreover, if the treatment is administered at a high capacity and in a continuous mode, the body may be damaged directly or indirectly by overheating or irregular heat stress. Therefore, certain historical information can be disregarded, as well as the significance of the applied force in connection to the object's maximum temperature [38]. In certain instances, in addition to global surface treatment, local treatment may be useful. The primary application of local treatment is for large objects that cannot be treated with low-pressure devices (e.g., objects larger than one meter) or for large installations in ambient air. Although PACVD, a predecessor of organosilicon, appears especially promising for use in the field of corrosion protection of metallic materials, there is little research on this topic in the scientific literature. The most common precursor is hexmethyldisiloxane (HMDSO), and the high corrosion resistance is connected mostly with the film's density and inorganic/ polymeric nature [23]. The application of infrared thermometers is quite restricted due to the fact that the measured object is surrounded by both the plasma reactor wall and the radiating plasma, whose neutral gas temperature is typically between 500 and 1000 K (i.e., much higher than the object temperature). Moreover, object surface properties, such as infrared emissivity, are altered during the process. Lastly, because each object has its own surface qualities, it is impossible to detect the surface temperature online using a simple method. Also, due to object damage, it is impossible to insert a thermometer (such as a thermocouple probe) into the body of the object. There are two techniques to estimate the temperature of an object: **a)** attaching a special thermocouple probe with optical data transfer to the object's surface, **b)** inserting the same probe into an auxiliary new object made of the same material and of similar shape and size, because an object's temperature is affected by its material, thermal capacitance, and shape. Because corrosion product layers, especially those with incrustation, are less thermally conductive than bulk metal, we can infer that the recorded temperature of the object is accurate. Throughout the treatment, the maximum temperature of the object should be maintained at around 100K below the lowest melting point of any metal in the alloy. A similar restriction should also be applied to metallic phases [76].

10. Conclusion

Due of plasma's properties, it is suitable for a variety of applications. Plasma technology is a novel approach to change the surface of materials in a way that doesn't affect the environment. Although there are several advantages and disadvantages of plasma based technology, however, this technology has grabbed the interest of researchers because of its extraordinary features and wide range of prospective applications, and it bears the promise of several future developments. Plasma is widely used in practice, particularly for surface treatment, and NTPs offer some appealing features for cultural heritage restoration because, in the generation of cold plasma, the majority of the electrical energy is directed to an electronic component rather than heating the entire gas stream, allowing the temperature of heavy particles to remain close to room temperature, making it suitable for use in processes where high temperatures are undesirable. It is recommended in the field of cultural heritage protection for cleaning and preserving many types of artifacts, from paper to metallic works of art. Especially plasma enhanced chemical vapour deposition can make very thin coatings with different structures that don't change the look of the metallic artifacts and protect it well from corrosion.

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