Review

Recent advances in the plasma-assisted synthesis of silicon-based thin-films and nanostructures

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Abstract: Silicon-based thin-films and nanostructures are of paramount importance in a wide range of applications, including microelectronics, photovoltaics, large area sensors, as well as biomedicine. The wide accessibility of silicon and its relatively low cost have driven a continuous improvement of the technology based on this element. Plasma technology has been widely used for the synthesis of coatings and nanostructures based on silicon. Moreover, it has given a fundamental contribution for continuously improving the control of the physicochemical properties of silicon-based materials, and for allowing the synthesis of nanometric structures with well-defined shape and morphology. In this work, we have reviewed the most interesting developments of plasma-assisted processed for the synthesis of Si-based materials, both inorganic and organic, in the last five years. A special attention has been given to the new techniques, or modifications of already existing ones, that open new possibilities for the synthesis of materials with new properties, as well as nanostructures with novel characteristics.

Keywords: silicon; thin-films; nanostructures; growth; plasma-assisted.

1. Introduction

The development of microelectronics has given a paramount importance to the study of silicon-based semiconductors. In fact, while the early developments of transistor devices were based on germanium, silicon has quickly become the semiconductor of choice for the fabrication of the most diffused electronic devices [1]. Nowadays silicon, in its monocrystalline, polycristalline, and amorphous forms, is also of great importance for the production of low cost photovoltaic cells, which play a primary role in the renewable energy production [2]. Another important application field for this material is biomedicine, thanks to the promising bioactive [3], antibacterial [4] and antiviral [5] properties of silicon and silicon alloys.

A huge amount of research has been devoted, over the years, to the study of the physicochemical properties of silicon and silicon-based materials, such as silicon oxide, silicon nitride and silicon carbide, and the techniques for the processing of these materials, such as etching, thin-film deposition or doping, have been continuously improved [6]. Among the different types of growth and processing techniques, plasma-assisted ones have played a major role, due to their great flexibility and their ability to lower processing temperatures. As an example, *plasma enhanced chemical vapor deposition* (PECVD) has been intensively used for the growth of silicon-based thin-films in microelectronics, photovoltaics, as well as biomedical applications [7, 8]. Moreover, *reactive ion etching* (RIE) has played a paramount role for the realization of complex geometries in silicon-based devices [9]. In fact, plasma assisted techniques are able to activate chemical reactions at low temperatures, enabling the production of ions, atoms and radicals, that can be exploited for the modification of surface morphologies and for the synthesis of thin-films and nanostructures [10].

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In this work, we report the most interesting developments in the field of plasma-assisted techniques for the synthesis of silicon-based thin-films and nanostructures, as well as for the modification of surfaces containing silicon, in the last five years. The research has been carried out using the *Scopus* and *Web of Science* databases, limiting the research to the publication years between 2018 and 2023, although in some cases older sources have been included, if they contained a more detailed explanation of a technique that was briefly described in another paper. A preliminary selection of the papers was carried out by carefully reading the abstracts, than the selected papers were carefully evaluated, especially considering the experimental sections. Only experimental works that involved the synthesis or the surface modification of silicon-based materials by means of plasma-assisted techniques have been included in the review. Researches in which silicon-based materials were used only as substrates for the growth of other materials have not been included, unless they exerted a functional role, such as in the case of adhesion improvement layers. Materials in which silicon was used as a dopant only have been excluded as well. We have divided the discussion in two parts: the first is dedicated to techniques that work at pressure lower than the atmospheric one, thus requiring the use of vacuum technology, while the second deals with techniques that work at atmospheric pressure. We have given a special focus to unusual applications of plasma discharges for the synthesis of silicon-based materials with special properties.

2. Synthesis by means of low pressure discharges

Low-pressure discharges have been used for more than three decades for the synthesis of several types of silicon-based thin-films, especially for applications in the fields of microelectronics, large area electronics, and photovoltaics. *Radio frequency*, *capacitively-coupled plasma enhanced chemical vapor deposition* (RF-PECVD) and *sputtering*, with several variations, have been the most commonly used techniques, due to their high flexibility, but several other types of plasma-assisted techniques have been developed, including the use of *inductively coupled plasmas* (ICP), *hollow cathode/anode plasmas*, *microwave plasmas*, as well as *electron cyclotron resonance* (ECR) discharges. In this section, the most recent developments of low pressure discharges for silicon-based materials are reviewed, dividing them respect to the type of excitation used to produce the plasma discharge: capacitively-coupled direct current (DC) and radio-frequency (RF), inductively-coupled (ICP) or microwave (MW) discharges, while a separated paragraph is dedicated specifically to the synthesis of polymer-like coatings.

2.1. CCP-DC discharges

Low-pressure plasma discharges activated by means of a DC bias are usually less expensive compared to the ones activated by a RF bias, since the latter typically require a more expansive generator, as well as the use of a matching network to prevent or limit the reflected power [10]. However, despite of the lower cost, the use of DC-activated discharges is less common, due to their lower versatility compared to RF ones, and the limitations concerning the use of insulating electrodes, due to the problem of surface charging. Moreover, they typically provide a strong ion bombardment on the substrate and the growing film, which may be detrimental for the film properties in some cases, e.g. by increasing the formation of defects in semiconductor materials.

Despite of their intrinsic limitations, DC discharges are quite often used for the deposition of carbon-based materials, such as diamond-like carbon (DLC) or carbon nanotubes (CNT). In fact, they can provide a high electron energy, which is necessary for the dissociation of gases such as CH_4, with strong molecular bonds, that are often used for the synthesis of these materials. In this context, an interesting study was carried out by Delfani et al. [11] to investigate the effectiveness of silicon-based thin films such as a-Si:H, a-SiC:H and a-SiN:H, deposited by means of pulsed DC-PECVD, to enhance the adhesion of DLC thin films on steel substrates. The Si-based layers and the DLC coatings were

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grown in succession in the same deposition chamber by means of a pulsed DC discharge, analyzing especially the effect of substrate temperature on the adhesion strength of the DLC films. The authors found that a-SiN:H films grown a temperatures higher than 150 °C provided the best results in terms of adhesion of the DLC films.

Silicon-based interlayers for carbon based materials were also studied by Lakhonchai and coworkers [12], who investigated the corrosion resistance of hydrogenated amorphous carbon (a-C:H) thin films grown on chromium-plated substrates, which were coated with a-Si, a-Si:N, a-Si:H and a-Si_XC_Y:H layers. In this case the silicon-based layers, as well as the a-C:H films, were grown by means of an hybrid PECVD/DC-*sputtering* deposition system, in which Ar, H_2 and C_2H_2 were introduced in different amounts, depending on the material to be grown. In this study, the authors found a better effectiveness of a-Si:H interlayers for improving the adhesion of the carbon-based films, compared to the other silicon-based materials investigated, while the worst behavior was observed for the a-Si_XC_Y:H material.

Silicon-carbon hybrid materials show interesting properties for the production of anodes for lithium-ion batteries with enhanced stability, as was recently investigated by Sun and coworkers [13]. In their study, an *active screen plasm*a was used for the deposition of SiO_x/C nanostructured materials by dispersing ordered mesoporous carbon (CMK3) on a silicon substrate and then activating a discharge at low pressure in a H_2 atmosphere. According to the active screen process, the DC bias was applied between the chamber walls and an *active screen mesh* (ASM), composed by a metal grid that surrounded the substrate. The plasma discharge produced radicals that were able to reach the substrate by diffusing through the ASM, while the ion bombardment impinged on the mesh, that protected the substrate from it. Such a configuration allows to use a DC discharge, while strongly reducing substrate and film damage by the ion bombardment. The process resulted in the formation of nanostructures of different shapes, composed by a mixture of SiO_x and amorphous carbon, that revealed interesting properties for the production of battery anodes.

Silicon-carbon based materials are also suitable for biomedical application, as in the case of the recent studies of Grenadyorov and coworkers [14, 15], who investigated the use of a pulsed DC-PECVD discharge for the synthesis of hybrid a-C:H:SiO_x materials onto Ti–6Al–4V alloy substrates. The hybrid deposition system exploited both a pulsed DC generator and a hot filament to achieve the dissociation of the *polyphenylmethylsiloxane* (PPMS) vapor used as precursor. The grown a-C:H:SiO_x layers showed good biocompatibility and adhesion, as well as high wear resistance, making them good candidates for application to biomedical devices.

Plasma spray is a kind of *physical vapor deposition* (PVD) technique, often used in applications where thick and porous coatings are required such as in thermal insulation and some kind of biomedical surfaces. In this process, a powder precursor is injected in a flow of plasma, being melted or evaporated and then transported to the substrate, where it typically adhere in the form of *microlamellae*. The technique can be carried out at atmospheric or reduced pressure, depending on the application, and the flow of plasma can be excited by a DC or a RF bias. An original type of hybrid DC/RF plasma spray at low pressure was used by Ohta and koworkers [16] for the production of *silicon nanoparticles* (Si NP) intended for use in the fabrication of cathodes for lithium-ion batteries. A considerable production rate of 17 g min^{-1} was obtained with optimized conditions, with an average nanoparticle diameter of 50 nm. Plasma spray was also used by Harder [17] for depositing Si-HfO_2 coatings onto SiC substrates, with the aim to obtain a protection of this materials against oxidation in a steam environment, although the author found that the coatings effectiveness resulted limited.

2.2. CCP-RF discharges

Low-pressure, *capacitively-coupled radiofrequency* (CCP-RF) *discharges* are the most common type of applications of cold plasmas, and their use is widespread, due to their

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versatility. More specifically, the use of RF-PECVD and RF *magnetron sputtering* [10] is very common thanks to the ability of these techniques to grow a large number of materials, including silicon-based ones, on substrates of different types, including plastic materials, and to achieve a good control of the material stoichiometry during the synthesis of alloys. These techniques require the use of RF generators, which are often more expensive than DC ones, and matching networks, which are used to tune the impedance of the load coupled with the generator, in order to minimize the amount of power reflected to it. The use of an RF bias provides a greater versatility, allowing for the deposition on insulating substrates and reducing the amount of ion bombardment on the surface of the substrate and the growing film, which is detrimental in some applications.

The RF-PECVD technique is also called *plasma assisted chemical vapor deposition* (PACVD) and usually, if not specified otherwise, involves the use of a capacitively-coupled plasma (CCP) generated by the application of a radiofrequency bias between two planar electrodes. Nonplanar configurations and inductive coupling are also possible, but less common. The most common choice for the excitation frequency is 13.56 MHz, since it is an industrial standard for RF generators and lies between typical electron and ion plasma frequencies, allowing a separation between their behavior [10]. However, higher frequencies, such as 40 MHz of 75 MHz are also used in order to achieve specific material properties, and in this case the technique is often called *very high frequency PECVD* (VHF-PECVD).

One of the most typical applications of RF-PECVD is the growth of amorphous silicon-based materials [18], such as a-Si, a-SiO_x, a-SiN_x, a-SiC_x, a-SiO_xC_y, a-SiO_xN_y, and even a-$SiC_xO_yN_z$ [19], the composition of which can be tuned efficiently by the control of precursor gases concentrations. In recent years, a great interest was dedicated to the application of PECVD techniques for depositing silicon-based amorphous thin films for the passivation of heterojunction photovoltaic cells, which are considered very promising for improving the efficiency of solar energy production devices [20-27]. Hydrogenated amorphous silicon (a-Si:H) is the material which was more intensively studied for this application [20-25], but doped amorphous silicon oxide (a-SiO_x) was also considered [26, 27]. Wang and coworkers [23] compared the effectiveness of a-Si:H passivating layers grown by PECVD using RF (13.56 MHz) and VHF (40 MHz) plasma excitation frequencies, founding a better performance of the former compared to the latter. VHF excitation (40.68 MHz) was also used by Ruan and coworkers [20], but in their work it was applied for growing the doped layers of the cell, while the intrinsic a-Si:H passivating layer was grow using standard 13.56 MHz excitation frequency. The groups of Chen and Truong [26, 27] used an hybrid dual-mode PECVD for the deposition of a-SiO_x passivating layers, exploiting the synergistic action of microwaves (2.46 GHz) and radiofrequency (13.56 MHz) excitation in the plasma discharge. Of particular interest is the study of Ouaras and coworkers [25], who developed a novel type of PECVD reactor with interdigitated electrodes, by which they were able to perform a patterned deposition of a-Si:H on a solar cell of area 156 mm x 156 mm, without the need of a lithographic step.

Silicon-based nanoparticles, as well as nanocrystalline materials, in which nanocrystals are usually embedded in an amorphous matrix, are interesting for several applications, including solar energy production, and PECVD is a very common way to synthesize them. In fact, in recent years, several research groups carried out research studies on the use of RF-PECVD techniques for the synthesis of nanocrystalline silicon-based materials [28-30] and nanoparticle-based materials [31-33]. In most cases, a standard RF-PECVD system with parallel-plates electrodes was used to synthesize the material, but a careful study on the process parameters, especially precursors dilution and power density, was usually required to achieve a good control on the material properties. In the work of Ghosh and coworkers [31], an a-SiN layer was grown on the rear of PV devices, and SiN nanoparticles were subsequently produced by an hydrogen plasma etching, after which an a-Si:H layer was deposited to embed the SiN nanoparticles.

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Microcrystalline and polycrystalline silicon layers were grown by PECVD. Li and coworkers [34] used a VHF (75 MHz) excitation frequency PECVD system for growing intrinsic mc-Si layers on glass substrates, investigating the effect of deposition rate on the film microstructure. Liu and coworkers [35] achieved the synthesis of polycristalline silicon thin films on polymeric substrates at a temperature of 100 °C by means of a RF-PECVD system. In order to promote film crystallization, they exploited a variable DC negative bias on the substrate to achieve a tunable ion bombardment. They found that a transition between amorphous and polycrystalline structure was obtained for biases higher than 50 V, and the optimal bias value was obtained at 100 V, over which a degradation of the film structure was observed.

The synthesis of silicon-based ternary compounds is another interesting application of RF-PECVD techniques, which allow for a fine-tuning or the elements incorporation in the material, thanks to the possibility of tuning the amount of precursors radicals in the plasma discharge, by regulating the gas flow rates and the RF power [18]. Song and coworkers [36] investigated the growth of silicon-carbon-oxygen amorphous ternary alloys (a-SiC_xO_y), doped with nitrogen, by means of VHF-PECVD, with a specific focus on their photoluminescence properties. Hang and coworkers [37] studied the growth of silicon-nitrogen-oxygen amorphous ternary alloys by means of standard RF-PECVD, while Ke and coworkers [38] investigated the deposition of silicon-boron-nitrogen amorphous alloys (a-SiB_zN_y) on steel.

Silicon-based nanowires (NWs) are another material which was effectively grown by means of PECVD techniques. Recently, silica and silicon NWs were grown by Wang and coworkers [39] using a standard RF-PECVD reactor, after having prepared the substrate with mixed catalyst of Sn and Cu. Silicon-tin NWs were also grown by Azrak and coworkers [40] using a procedure which included the formation of a silane plasma by means of a RF-PECVD reactor.

Atomic layer deposition (ALD) is a technique which relies on the alternate injection of different precursors in the reaction chamber, exploiting specific and highly selective chemical reactions to form extremely conformal alloy coatings with thickness control at the atomic level. Its variant called *plasma enhanced ALD* (PEALD) exploits the use of a plasma discharge to produce radicals that are then injected in the reaction chamber to be used in the chemical reactions, increasing the technique versatility. This technique has risen in importance with the continuous increase of complexity of nanodevices, the fabrication of which often requires to cover conformally surfaces with very small features such as pores or spikes, and the deposition of layers with nanometric thickness. Recently, Baranov and coworkers [41, 42] studied the growth of GaP/Si superlattices for photovoltaic applications, using a hybrid deposition process that exploited both standard RF-PECVD and PEALD, in which the plasma was obtained by a radiofrequency, capacitively-coupled discharge. The obtained superlattices resulted of purely crystal structure, without an amorphous phase.

Radio-frequency activated sputtering was used for the deposition of silicon-based materials in recent years. As an example, an interesting study of Zhang and coworkers [43] studied the incorporation of deuterium in silicon carbide thin films grown by means of a conventional RF sputtering system using an atmosphere of deuterium gas.

A simple O_2 RF plasma activation of 1.4404 stainless steel parts, industry relevant as components of microreactors for the production of PVP in aqueous solution, through a radical polymerization of N-vinylpyrrolidone, was applied [44] for the deposition of an ultra-thin 1H, 1H, 2H, 2H perfluorooctyltriethoxysilane (FOTS) antifouling coating. If compared to the standard sol-gel method (precursors: FOTS and Zirconium(IV)-acetylacetonate ($Zr(acac)_4$), the plasma assisted process showed outstanding anti-adhesive properties with almost no PVP-deposit formation on the steel components, though their surface roughness remains higher.

Another comparative study involved (3-aminopropyl)trimethoxysilane (APTMS) [45] as grafting molecule for a type of cross-linked polyethylene which is produced

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through the silane method, generally known as organosilane-grafted moisture-crosslinked polyethylene or silane-crosslinked polyethylene (Si-XLPE), compounds that are widely used in the electrical and biomaterials industry and can take advantage from the integration of trifunctional organosilanes, such as APTMS. Indeed, this molecule is capable of polymerizing in the presence of water, which gives rise to a different possible configuration structure based on 2-dimensional and 3-dimensional surface-induced polycondensation, through covalent attachment.

Chemical vapor deposition (CVD) and plasma-facilitated *in situ* grafting methods (*grafting-from* and *grafting onto*) were employed to immobilize APTMS. The reactor for the plasma-assisted processes was a low-pressure plasma system operating at a maximum power of 100W and low frequencies (40-100 kHz). The characteristics of obtained samples with the same main preparation principles were compared with each other, in terms of surface chemistry (XPS, EDX, and ATR-FTIR), morphology (by AFM and FESEM), and wettability (by contact angle measurement), thus showing that plasma *grafting-from* deposition method favoured the highest attachment of APTMS to the surface, by forming multilayer structures instead of monolayers and leading to the creation of hydrophobic surfaces.

2.3. ICP-RF discharges

Inductively coupled plasma (ICP) discharges exploit the generation of a time-varying magnetic field, by means of an alternating current flowing in one or more coils, which in turns provides the generation of a variable electric field, able to accelerate electrons and ions to generate a plasma discharge [10]. Compared to CCP discharges, ICP ones typically provide a higher plasma density and have the advantage to avoid the ion bombardment, due to the absence of sheaths. However, when an ion bombardment is required to achieve specific effects during the process, it can be obtained by adding a DC or RF bias to the sample surface, the intensity of which can be tuned as required. ICP discharges were used in recent years to perform the growth of silicon-based materials by means of PECVD [46, 47], PEALD [48, 49], as well as *sputtering* [50] processes. Rumyantsev et al. [46] exploited an ICP-PECVD reactor to achieve the synthesis of amorphous hydrogenanated silicon-carbon (a-SiC_x:H) and silicon-carbon-nitrogen (a-SiC_xN_y:H) alloys from examethyldisilazane (and nitrogen for N containing films). Also Yang and coworkers [47] investigated the use of an ICP-PECVD technique for the synthesis at very low temperature (20 °C) of silicon dioxide and silicon thin-films, using silane (SiH_4) and oxygen as precursor gases, for the fabrication of metal-oxide-semiconductor (MOS) and thin-film-transistor (TFT) devices.

A variant of the PEALD techniques involves the use of ICP for the formation of the required radicals and was recently exploited for the synthesis of silicon nitride and oxinitride as well as silicon dioxide. In fact, Song and coworkes [48] used a multi-ICP system with seven coils connected in parallel to generate N radicals to be incorporated in SiN and SiCN alloys, while Jung and coworkers [49] exploited a remote ICP plasma for the growth of SiO_2 layers from bis(tertiary-butylamino) silane (BTBAS) and oxygen.

Takenaka and coworkers [50] exploited an ICP sputtering system, in which low-inductance antenna (LIA) modules were arranged near rectangular silicon sputtering targets, to produce an intense and homogeneous ion bombardment on them, resulting in the deposition of Si thin films with crystallinity in range 73-78% without intentional substrate heating.

2.4. MW discharges

The use of microwaves (MW) for the excitation of plasma discharges is usually exploited to achieve a more intense plasma and more energetic electrons, but microwave-assisted techniques are usually more expensive, compared to RF-activated ones. Kim and coworkers [51] studied the growth of low-resistivity polycrystalline silicon thin-films by

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means of a PECVD technique activated by MW at 2.45 GHz at a pressure of about 67 Pa in a showerhead reactor, with two different gas injection points: one before the showerehead, where a mixture of Ar and H_2 was injected, and second one downstream of the showerhead, where SiH_4 and PH_3 where inserted near the substrate. A remote-plasma reactor activated by microwaves (2.45 GHz) was used by Wrobek and coworkers [52] to achieve the deposition of hard a-SiCN coatings at a pressure of 75 Pa using a mixture of aminosilane and silazane precursors. Microwave discharges were also investigated for the synthesis of nanostructures: Wollny and coworkes [53] exploited a microwave-assisted PECVD reactor for the growth of silicon nanoparticles using a mixture of Ar, H_2 and SiH_4 at a reduced pressure of abut 10 kPa. They also developed a theoretical model to explain the synthesis process. A microwave-assisted technique was also used by Daoudi and coworkers [54, 55] for the deposition from silane of silicon nanoparticles with diameter in range 7-37 nm, which were then decorated by silver nanoprisms.

A particular type of microwave-assisted plasma discharge is the *electron cyclotron resonance* (ECR), in which the synergist action of microwaves and a static magnetic field is used to achieve high electron energies. In this kind of discharge, the magnetic field intensity is tuned in such a way that the electron cyclotron frequency equals the microwave frequency, thus allowing resonant absorption of the microwave energy by the plasma electrons [56] (pp. 492–512.). In recent years, Miller and coworkers [57] reported an interesting study, regarding the synthesis of terbium-doped silicon oxide (a-SiO_x:Tb) by means of a novel hybrid deposition system, in which the silicon oxide was grown exploiting an ECR plasma of silane and oxygen, while Tb atoms were generated by a magnetron sputtering source located in the same vacuum chamber.

2.5 Other discharges

Apart from DC, RF and MW activated discharges, other types of discharges were also successfully used for the deposition of silicon based materials, including gas-jet and, hollow electrode ones. The *gas jet electron beam chemical vapor deposition* (GJEB-CVD) technique [58, 59] exploits the formation of a supersonic jet of gas, which is then dissociated by a beam of high energy electrons that cross the gas flow, producing a flow of radicals that impinge directly on the substrate surface. Zamchiy and coworkers [58] exploited this technique to achieve the synthesis of silicon oxide nanowires using a tin film as catalyst.

The *hollow electrode* (anode or cathode) discharge exploits the generation of a CCP discharge between two electrodes, one of which has at least a portion of it shaped in the form a cylinder, inside which the gas flows. The particular electrode shape allows the formation of a more intense plasma, compared to a conventional parallel-plates CCP discharge, with a higher electron density. Tabuchi and coworkers [60] investigated the use of a hollow-anode PECVD reactor, activated with a VHF-RF frequency of 105 MHz in an atmosphere of silane and hydrogen, to achieve the deposition of microcrystalline silicon at 300 °C.

2.5 Plasma polymerization

Since many decades, the plasma polymerized organic thin films are of great interest and, in particular, the thin organosilicon films can be produced from different precursors/methodologies and aimed to a wide range of applications as multifunctional materials. Low pressure plasma processes based on hexamethyldisiloxane (HDMSO) as a precursor were intensively studied and reviewed few years ago only [61], thus hereinafter the most recent and peculiar advances will be reported. Kleines and coauthors obtained by MW (2.45 GHz) excitation in a PECVD reactor plasma polymerized ultra-smooth SiOCH coatings deposited on polydimethylsiloxane (PDMS) substrates in order to get membranes [62] for the control of gas separation. According to process parameters (oxygen carrier to HDMSO monomer ratios and of microwave power input), weaker

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cross-linking of the siloxane bonds as well as a more organic structure with an increased proportion of bound methyl groups was found advantageous for a high permeability and separation performance of the coatings. Especially for the separation of He and N_2, but also partly for other gas pairings (He/CO_2 and CO_2/N_2), the selectivity for all test points decreased with increasing oxygen content in the process gas. Furtherly, the same authors explored the effect of energy density [63] on the coated membrane permeation properties by varying over the MW power level as well as the MW pulse duration. They found out the highest permeation and separation performance of the produced layers for the low energy density range of the process, as the low power prevented strong fragmentation of the monomer, which resulted in less dense and cross-linked growth of the layers. Due to the low pulse durations, rearranging processes were suppressed and the layer structure did not become denser due to further energy input. The conclusions were proven through several characterizations: ellipsometry, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) Fourier Transform InfraRed spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM).

The HDMSO precursor was studied also for an opposite scope [64], *i.e.* to produce a SiO_x based barrier coating to atomic oxygen (AO) erosion when deposited on Kapton® (polyimide) by means of a RF activated plasma discharge by varying the ratio of O_2/Ar in the reactor atmosphere, ranging from a 50 to 1000 W power. Kapton® is employed in the thermal blankets covering the external surface of spacecraft due to its and thermo-optical properties and durability in harsh environments. By testing it in a coaxial ground-based AO simulation facility, it was found that for an AO fluence up to 1.09×10^{22} atoms/cm^2, the uncoated sample was eroded and completely broken. On the contrary, when the coated polyimide film was under AO attack, the HDMSO belonging methyl group were decomposed into volatile products (such as CO_2, CO, H_2O), and the silicon formed a dense glassy SiO_x layer resistant to further AO erosion.

HDMSO and hexamethyldisilazane (HDMSN) [65], were compared as precursors for SiO_x based O_2 permeation barrier coatings and/or interlayers deposited on polyethylene terephthalate (PET) an polypropylene (PP) substrates by MW (2.45 GHz) activated low pressure plasma polymerization. By means of mass spectrometry, the probability for dissociation of HMDSN at a given energy of incident electrons was higher than for HMDSO. Due to the higher number of smaller fragments, HDMSN coatings showed lower oxygen transmission rates (OTRs) for thicknesses larger than 2.5 nm (measured by ellipsometry), compared to HDMSO coatings. By increasing the content of oxygen in the process mixture, HDMSN seemed to produce highly cross-linked SiO_x barrier coating directly well adhering on PP without the presence of a nanometric organic interlayer, instead needed for PET.

The mechanism of organosilicon based thin-film deposition is still under investigation. Typically, the chemical interpretation considers mainly the recombination of free radicals, which is dominated by neutral radicals over ionic radicals. Thus, free radicals formed by the dissociation of precursor molecules diffuse to the surface of the film, where they are first physisorbed and migrate along the surface until they are desorbed or chemisorbed at a binding site on the film surface.

Recently, an interesting study of these fundamentals [66] was published, focused on tetravinylsilane (TVS) and its plasma polymerization in a low pressure PE-CVD reactor with the capacitively coupled discharge operated at 13.56 MHz in pulsed mode. The power dependence of the plasma species was studied by mass spectrometry. Moreover, it was found that the deposition rate correlates with the flux of these species chemisorbed on the film surface, if distinct sticking coefficients are taken into account. Then, the carbon to silicon ratio in the deposited film strongly correlates with the C/Si flux ratio for the various power-controlled plasmas.

Considering other kinds of organosilicon precursors, tetraethoxysilane (TEOS) [67] was found to be a good candidate to obtain by low pressure RF plasma polymerization an efficient thin film for the increase of biocompatibility of metal implants. The coating was

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deposited on sanded and nanotextured Ti6Al4V alloys, and surface, electrochemical properties and biological behaviour was evaluated through the use of mesenchymal stem cells. This well-known precursor for the SiO_2 production by a sol-gel method can be exploited with higher versatility of resulting thin film properties by plasma polymerization techniques, starting from the possibility of getting nanometric thicknesses. In particular, the samples sanded and polymerized by plasma showed a number of viable stem cells higher than the nanotextured and polymerized surface by plasma.

For specific chemical functionalities, plasma polymerization, for instance, was applied to get nanometric organosilicon based NH_2-terminated films on silicon and aluminium samples by using (3-Aminopropyl)triethoxysilane (APTES) [68]. A pulsed and remote plasma (pulsed RP-PACVD) was used in order to produce a very soft plasma polymerization process and thus promoting the growth of organic, highly ordered coatings. The plasma was ignited in the discharge tube and the generated reactive species flowed out into a second reaction tube where the substrate holder was located and the influence of the frequency, the duty cycle, t_{on} and t_{off} was investigated thoroughly. In addition to weight and spectroscopical characterizations, the Atmospheric pressure Matrix Assisted Light Desorption Ionisation (MALDI) Mass spectrometry was applied: oligomers containing up to eight APTES derived monomers ($C_3H_9NO_2Si$) and eight primary amine groups were undoubtedly detected and a density increases along with the duration of the t_{off} was observed. Among them, silsesquioxanes (cages) which are uncommon as species obtainable by plasma processes and cyclosiloxanes (rings) were clearly identified.

Fluorine containing organosilicon monomers were widely used to tune the surface water adsorption/spreading/wetting for applications such as aerospace industry, self-cleaning, heat exchangers, power generation, low-friction coatings, anti-fogging properties or oil spill clean-up processes.

Aside from the above reported example concerning the O_2 RF plasma activated functionalization by FOTS to get antifouling surfaces, Giner et al. focused on the effects of FOTS grafted, by means of a two-stepped chemical vapor deposition process (CVD) (the organosilane cross-linking, forming Si-O-Si surface bonds, was thermally promoted), on a substrate coated by HDMSO plasma polymerized films [69], that is, composed by flat SiO_x. Actually, there is still the need to improve the analytical understanding of different states of adsorbed ultra-thin and extended water layers on nanorough substrates both for macroscopically hydrophilic and hydrophobic surfaces. Thus, this kind of surface was compared to the one consisting of SiO_x microparticles deposited from a water suspension and successively FOTS functionalized, in order to explore the combined effect of chemistry and roughness on water adhesion behaviour. The FOTS layer on the particles is more defect-rich than the one on the smooth PECVD SiO_x-film and capillary bridges are formed at the contact points between the particles: an increased water adsorption is so observed notwithstanding the presence of the water repulsive FOTS functionalization.

Finally, a double step process composed by a hexamethyldisilazane (HMDSZ) plasma polymerization (PP) step and an Acrylic Acid (AA) grafting polymerization (GP) for materials used in dental implants, titanium (Ti) [70] and its alloys and zirconia (ZrO_2) ceramics [71] was reported. In the former case, at first, a Micro-arc oxidation (MAO) process, also called plasma electrolytic oxidation (PEO), was applied to Ti specimens in an electrolyte containing sodium silicate pentahydrate, potassium hydroxide, and ethylenediaminetetraacetic acid) in distilled water, then a RF (13.56 MHz) LP plasma discharge in presence of HDMSZ vapours was activated to get a PP-SiO_x coating and, lastly, a O_2 plasma pre-treatment was carried out to form peroxide groups on the surface and thus facilitate the UV light-induced AA GP by liquid immersion in the precursor of the pre-treated specimens. In the latter case, the zirconia ceramic surface was coated through RF-LP plasma discharge with the PP-SiO_x which was subsequently plasma activate to promote the AA surface grafting. In both cases, the carboxylic terminations

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were used to immobilize biopolymers (chitosan, chitosan/poly-g-glutamic acid, and gelatin) that enhance the materials biocompatibility and cell viability assays.

3. Synthesis by means of atmospheric pressure discharges

Atmospheric pressure plasma (APP) discharges allow the synthesis of materials, or their surface modification, while working at atmospheric pressure, thus avoiding the use of vacuum technology [72]. The interest in this kind of techniques has risen considerably in recent years, especially due to their lower cost and better applicability to in-line industrial processes. While the first applications of APP techniques were mostly dedicated to the surface modification of textiles and polymeric materials [73, 74], their use for the synthesis of materials and nanostructures, including silicon-based ones, has increased considerably [75]. In the following, the most recent applications of APP techniques for the synthesis of silicon-based materials are reviewed, dividing them depending on the technique used for generating the atmospheric plasma. The last section has been dedicated specifically to the APP synthesis of Si-based polymeric materials.

3.1 Plasma spray

Atmospheric plasma spray (APP) is a technique in which precursor powders are injected in a flow of plasma at atmospheric pressure, generated by means of a DC or RF discharge, and then transported to the substrate, where they adhere to form a coating material. A similar technique was used by Wan and coworkers [76] to achieve the deposition of silicon nanospheres and nanosheets, by injecting raw silicon powders in a flow of Ar plasma, generated by a DC discharge at atmospheric pressure. More recently, Yang and coworkers [77] exploited the injection of self-produced SiO_x nanopowders with high silicon content in a flow of Ar plasma, generated at atmospheric pressure using a RF-ICP excitation. The process resulted in the deposition of SiO_x nanowires with high silicon content, to be used in the production of high-performance lithium-ion battery anodes.

Zheng and coworkers [78] exploited an APP technique to achieve the deposition of nanostructured and conventional Yb_2SiO_5 coatings on SiC substrates, for application as environmental barrier coatings, to prevent the oxidation of SiC-based turbines in aeromotive engines. The different film morphologies were achieved using different kinds od precursor powders to be injected in the plasma flow. An APP technique was also used by Ma and coworkers [79] to achieve the formation of an Al-Si graded layer on the internal surface of cylindrical mechanical parts, such as pipes sections, made of aluminum. The composition of the graded layer was changed during the deposition, starting from a pure SiAl layer and adding Cu and Fe in increasing quantity as the growth proceeded, with the aim to improve the layer adhesion on the Al surface.

3.2 Plasma jet

Plasma jet is a type of plasma technique, usually working at atmospheric pressure, in which a plasma discharge is activated in a reaction chamber, and a flow of plasma is then extracted from it and sent to a substrate, where it exert its action of material growth or surface modification. Differently from the case of *plasma spray* techniques, the precursors for the material growth are usually in the form of gases that are ionized and dissociated directly in the plasma stream. Wang and coworkers [80, 81, 82] used an array of six plasma jet sources to achieve the deposition of SiO_x on a cylindrical aluminum surface. The plasma jet source was activated by an high-voltage AC power supply, using tetraethylorthosilicate (TEOS) as precursor and Ar as carrier gas. A plasma jet surface treatment was also used by Xiong and coworkers [83] for the synthesis of nanocomposite coatings containing aluminum nitride (AlN) and methyltrimethoxysilane (MTMS). An Ar plasma jet, generated using a high voltage power source working at 10 kHz, was sent to the polyimide substrate, on which a mixture of AlN powders and MTMS had been previously deposited, transforming the two separated AlN and MTMS phases in the nanostructured material formed by AlN nanoparticles embedded in a polymer matrix. A

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specific type of plasma jet technique, called HelixJet, was recently exploited by Dworschak and coworkers [84] for the synthesis of silicon nanocrystals (Si NC). The HelixJet plasma source exploits an original electrode configuration, in which two metal electrodes are wired around a quartz tube, forming two spiral paths. One of the electrodes is grounded, while the other one is biased with a RF (13.56 MHz) bias, giving rise to a synergistic action between the spiral-arranged electric field and the plasma filaments. The system allowed the synthesis of SiO_X particles of amorphous and crystalline structure, as well as Si nanocrystals embedded in SiO_X.

3.3 Other APP techniques

Apart from plasma spray and plasma jet, several other techniques can be used that work at atmospheric pressure, such as *corona discharges* and *dielectric barrier discharge* (DBD), both of which are characterized by the formation of filamentary discharges, produced by the accumulation of *streamers* [85]. Among the most interesting ones that were used recently for the growth of silicon-based materials, there is the technique used by Post and coworkers [86] for the synthesis of core-shell nanoparticles, exploiting a vapor-phase process at atmospheric pressure, in which the plasma generated in Air by a DBD reactor was used to generate radicals, that were then injected in a thermal reactor, together with a previously generated nanoparticles areosol and a *tetraethyl orthosilicate* (TEOS) or *hexamethyldisiloxane* (HMDSO) vapor flow.

Silicon-based materials were also synthesized exploiting APP-PECVD discharges, in which a uniform plasma, in contrast to filamentary discharges such as corona or DBD, is obtained at atmospheric pressure. Of particular interest are the results obtained by Kakiuchi and coworkers [87, 88], who achieved the deposition of a-Si thin films at low temperature and atmospheric pressure, exploiting a parallel plate reactor with a VHF excitation at 150 MHz (with an without pulsing) and a distance between the electrodes of 500 µm using a mixture of He, H_2 and SiH_4 precursor gases.

3.4 Plasma polymerization

Plasma polymerization processes at atmospheric pressure (APP) are of large domain in the industrial applications. Nowadays, HDMSO is still the most used monomer to produce a plethora of modifications of the materials surface properties such as the reduction of the flammability of fir-wood as well as the control of its wettability [89], the superhydrophobicity to glass substrates [90] and the corrosion resistance [91] of steel specimens. The final thin film is, in the three cases, a SiO_x coating with different chemical characteristics according to the desired function to be imparted and the type of atmospheric pressure plasma reactor and process conditions. A dielectric barrier discharge (DBD) apparatus, conceived for cotton textile processing, was applied to fir-wood [89] thanks to the ease of formation and production of a large-scale stable discharge, by using a carrier gas of pure argon containing the monomer vapor flowing between the two electrodes. The cross-linked nature of the macromolecular structures based on Si-C and Si-O-Si bonds, PDMS-like, clearly explains the water-repellent and fire-retardant nature of plasma-modified wood substrates, after extensive characterization by means of FESEM, AFM, XPS, FTIR, EDX, and DTA-TG.

Interestingly, for the glass substrates coatings, an argon plasma jet at a relatively low power frequency (11.5 kHz) was applied [90] with or without the use of several shielding gases. The XPS characterization proved the different effects on chemical composition: N_2 shield preserved a high carbon content (in CH_3 groups) from the precursor, while minimizing the incorporation of oxygen into the coating surface. Also, it was found that O (from O and OH radicals) replaced C to form silica-like coating in the case where shielding gas was not present or with Ar and He shields. The plasma jet system used to treat the SAE 1020 steel surface [91] comprised a commercial AC power supply operated

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at 19.0 kHz to excite the discharge in Ar/HDMSO atmosphere. Among the tested deposition modes (continuous or alternated), deposition time, and number of deposition steps, the most stable coatings, aiming to the formation of inorganic quartz-like material, were obtained with a three-step deposition and in both continuous and alternated modes.

A peculiar and very interesting organosilicon precursor, 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS), was, instead, chosen by Profili et al. [92] for the morphological and chemical modification of bleached, unrefined Kraft paper, that is, one of the by-products derived from woody biomass. TMCTS precursor was selected for its ability to produce organosilicon coatings with relatively high deposition rates with respect to more conventional HDMSO. Plane-to-plane dielectric barrier discharges at atmospheric pressure were activated in the presence of the precursor. It is worth noting that, during plasma processing of Kraft paper substrates, the amplitude of the applied voltage and its frequency were constantly adjusted to keep a homogeneous discharge regime. At such conditions, the neutral gas temperature did not exceed 50 °C.

Finally, it was observed a low plasma-assisted fragmentation of the TMCTS precursor and a partial oxidation of the TMCTS precursor fragments during the plasma deposition process to form a Si-O-Si network, thus resulting in a high hydrophobicity imparted to the coating and so improving the chemical and mechanical stability of cellulosic fabric subjected to humid environments.

4. Conclusions

In this work, we have reviewed the most important improvements in the synthesis of silicon-based materials by means of plasma-assisted techniques, that were published in recent years. A wide range of techniques have been included, ranging from classical RF-PECVD and *sputtering* to more innovative and exotic techniques, and several types of silicon-based thin-films, both inorganic and organic, as well as nanostructures of different types and shapes have been described. The results confirm that plasma-assisted techniques constitute a very versatile and powerful collection of methods for the synthesis of silicon-based materials, and new and innovative techniques were developed in the recent years, that promise important developments in the silicon-based technology.

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