Critical review

Plasma diagnostics for the low-pressure plasma polymerization process: A critical review

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ABSTRACT

Since the 1980s, functionalized plasma polymer films have attracted a considerable attention owing to their promising utilization in a wide range of modern applications. For such materials, controlling the chemistry of the coatings by a clever choice of the process parameters represents the main challenge. And yet, it became quickly obvious that in view of the complexity of the growth mechanism, fine control of the layers properties can only be reached by understanding at a fundamental level the mechanistic formation of the layers. In this context, a detailed comprehensive study of plasma chemistry is therefore of crucial importance as the numerous interlinked chemical reactions occurring in the discharge govern the film properties. In this paper, the most common plasma diagnostics methods employed in the context of plasma polymerization process, namely Mass Spectrometry, in-situ Fourier Transform Infrared Spectroscopy, Optical Emission Spectroscopy, Langmuir and Ionic probes are reviewed. After a light description of each technique, the main achievements for improving the mechanistic understanding of the layer formation are exposed. Moreover, the use of theoretical calculations based on Density Functional Theory (DFT) to support the understanding of the acquired data is highlighted. In view of the better control of the process allowed by the plasma phase investigation, some general conclusions and perspectives describing future developments in the field of plasma polymerization are finally discussed.

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1. Introduction

The interactions of a solid with its surrounding are mainly defined by the physico-chemical properties of its surface. It is therefore not surprising that since many decades, continuous research and developments in materials science have contributed to the rapid growth of surface and coating technologies which nowadays still increasingly attract considerable attention. Surface technologies refer to the modification of the surface (e.g., chemical functionalization, etching, coating,…) of a material without changing its bulk properties. For instance, tailor-made coatings allow adjusting mechanical (wear, friction), chemical (corrosion, permeation, temperature insulation, biocompatibility, wettability), electrical (conductivity), and optical (transmission, reflection, absorption, color) properties of materials [1].

Through the years, numerous processes have been developed for the modification of surfaces via the synthesis of thin films. A non-exhaustive list includes chemical vapor deposition, pulsed laser deposition, spin coating, sol gel, spin casting, thermal evaporation and plasma-based technologies [1–4]. Among them, the plasma-based processes are of particular interest by combining significant advantages such as their low process temperature, enabling the treatment of a wide range of materials including polymers, and the absence of solvents making these techniques compatible with the modern quest for environmentally friendly technology. Another key advantage of these processes is their versatility enabling one to modulate the properties of a given surface over a wide range (e.g., crystallinity, morphology, chemical composition of the deposited material) by adjusting the synthesis conditions [5–9]. All these attractive properties justify the popularity gained by plasma technologies and their important development in numerous industrial fields such as automotive, aeronautics and microelectronics [1,10,11].

If in the past, research and applications have often focused on the development of inorganic thin films, the design of organic surfaces is nowadays more and more important with applications in the fabrication of antibacterial surfaces [12], protein biochips [13,14] or platforms for biomolecules immobilization [15,16]. These surfaces can also be synthesized using plasma-based technology, more specifically by means of the plasma polymerization method, allowing the formation of solid organic thin films referred to as plasma polymer films (PPF). Despite the use of the word "polymer", PPF present little resemblance to the conventional polymers except for their organic nature [17]. Indeed, PPF are not characterized by the assembling of a repeating unit, but by a random network presenting a cross-linking density significantly higher than conventional polymers (see Fig. 1). In order to avoid confusion between plasma and conventional polymers, the term "precursor" is sometimes preferred instead of monomer to name the molecule from which the material is built. Nevertheless, both terms are accepted and currently employed in the plasma polymerization community.

The formation of solid deposits from organic compounds using glow discharges is not new. It was indeed first reported by Dutch researchers in 1796 [18]. These materials adhered tightly to the walls of the glass-made reactors and were observed to be insoluble in most solvents.
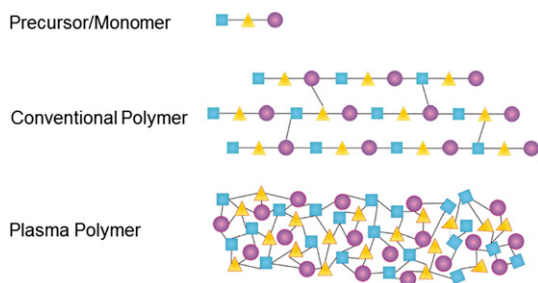
Nevertheless, they were considered as a nuisance until the work of Goodman who demonstrated that a 1 μm thick plasma-polymerized styrene film deposited on a titanium foil made a satisfactory dielectric for a nuclear battery [19]. Since that time, the potential of these organic coatings has been revealed and a systematic investigation of the plasma polymerization process has been carried out. More information about the history of the plasma polymer science can be found in Refs. [20–22].

It is now demonstrated and accepted that PPF exhibit interesting physico-chemical properties for organic materials such as high thermal, mechanical and chemical stabilities [4]. Moreover, due to their intrinsically good adhesion properties, numerous materials (e.g., glass, polymers, metals), even with complex geometry (e.g., carbon nanotubes [23–26], micro/nanoparticles [27–31]), can be homogeneously covered [4]. All these features justify their use in a wide range of applications. Historically, they were first developed in the search of physical barriers with applications in the field of corrosion protection [32,33] and food packaging [34,35]. In this context, highly cross-linked PPF were needed. Such PPF are obtained when a high level of precursor fragmentation occurs in the plasma. Thus, highly energetic conditions have usually been employed due to the precursor fragmentation dependence on the energy dissipated in the system [21]. As a result of these extensive fragmentation reactions, poor control of the PPF chemistry was achieved.

Since the 1980s, with the rise of micro- and nano-technologies, plasma polymerization has been further developed in the search for PPF with controlled and tailored chemistry while keeping their other inherent properties. In this context, functionalized PPF containing/supporting —COOH [36–41], —OH [42,43], —NH$_2$ [44–51], —COOR [52–56], —COR [57–59], —CF$_x$ [60–62], —Br [20,63], —SH [27,64–68], thiophene-based units [69,70] have been developed. The interest in this class of materials arises from their potential use in modern fields of applications including the development of supports for biomolecules immobilization [71–77] or cell growth [78–80], interlayers for promoting adhesion of metal coatings [81], biocompatible [82] or antibacterial coatings [12,83], controlled drug release coatings [84–87], super-hydrophobic surface [62], conductive layers [70],etc.

For these applications, the chemical composition of the coatings is one of the most important criteria defining its performances. Therefore, scientists have focused their efforts toward fine control of the plasma polymer chemistry. It quickly appeared that this control can be obtained through the understanding of the PPF growth mechanism and more specifically of the phenomena taking place at the plasma–substrate interface. Accordingly, investigating the plasma chemistry rapidly turned out to be a necessity. Numerous works have therefore been focused on the investigation of the plasma phase during the PPF growth. Surprisingly, while other aspects of the field have been reviewed such as the growth mechanism of the layers [8,21], their behavior in liquid medium [82], their use for biological applications [72], their nanostructure [88] and their surface analysis [89,90], there are no documents summarizing the efforts made for a precise evaluation of the plasma phase. Therefore, the present paper aims at reviewing the principal works developed to evaluate the plasma chemistry during the low-pressure plasma polymerization process. Particularly, we pay special attention to describe how these works have contributed to enlarging the knowledge of plasma polymer growth at a molecular level.

This review is organized as follows. In the first part, the plasma polymerization mechanism is described. Then, an overview of the main achievements obtained by several research groups in the field of plasma diagnostics related to the plasma polymerization process is presented. The most popular diagnostics methods employed for probing the species constituting the plasma are described, namely, mass spectrometry, gas phase Fourier transform infrared spectroscopy and optical emission spectroscopy. The main results obtained by Langmuir and ionic probes to determine the plasma parameters and ion flux, respectively, are also discussed. In addition, throughout the paper, it is shown how theoretical calculations based upon the density functional theory method have proven to be a powerful tool for assisting in the interpretation of

Fig. 1. Schematic comparison of a plasma polymer film and a conventional polymer material obtained from the same precursor/monomer.