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Comparison between single monomer versus gas mixture for the deposition of primary amine-rich plasma polymers

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ABSTRACT

Primary amine-based plasma polymer films (NH_2-PPFs) attract great attention due to their potential for various biomedical applications. In this context, in order to better understand the growth mechanism of such coatings, we investigate the impact of the precursor mixture on plasma chemistry and ultimately, on PPFs properties. PPFs are synthesized from both cyclopropylamine (CPA) and ammonia/ethylene (AmEt) mixture in low pressure (2.7 Pa) inductively-coupled plasma discharges, keeping the N/C ratio constant in the precursor flow rate. Optical emission spectroscopy (OES) is performed to study the plasma phase while PPFs chemistry is investigated by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy (combined with chemical derivatization). The results show that, for similar energetic conditions, the use of CPA allows a better nitrogen incorporation in the film compared with the use of the AmEt mixture. This is attributed to the initial presence of C—N bonds in the CPA molecule. In addition, it is shown that primary amine retention decreases when the power increases due to a strong dehydrogenation of the monomers that promotes the formation of multiple and conjugated CN bonds. Using OES, etching reactions of the growing PPFs surfaces are highlighted and are shown to strongly influence the plasma chemistry.

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1. Introduction

The synthesis of primary amine-rich surfaces has attracted great attention due to its potential for various applications in biotechnology, such as cell colonization [1], microfiltration membranes [2] or biosensor development [3–5]. These surfaces are well-known reactive platforms for the covalent immobilization of biomolecules [6]. Indeed, primary amine groups, being positively charged in aqueous environments at physiological pH values, are supposed to attract the negatively-charged molecules (e.g., fibronectin or vitronectin), as well as RGD peptides, which are important for cell adhesion and growth [7].

Different plasma processes have been reported to allow obtaining primary amine-rich surfaces. The simplest technique consists of grafting NH_2 groups by exposing the surface, for example, to an ammonia (NH_3) or a nitrogen/hydrogen (N_2/H_2) discharge [8]. However, this technique suffers from unstable functionalization due to reptation phenomena [6]. On the contrary, plasma polymerization is known to enhance the stability and reduce the ageing effect encountered in the grafting approach [9]. Different kinds of precursor have been used to synthesize the plasma polymer films (PPFs). Both single monomers (allylamine (AA) [10–12], diaminocyclohexane (DACH) [12–14], ethylenediamine (EDA) [12,15], heptylamine (HA) [12,16], cyclopropylamine (CPA) [9, 17], …) and gas mixtures (N_2/ethylene (C_2H_4), NH_3/C_2H_4 [7,18], NH_3/acetylene (C_2H_2) [19], NH_3/butadiene (C_4H_6) [18], …) have been employed.

Based on this important set of data, it is preferable for some researchers to work with a single monomer that already contains the chemical group of interest to promote a better incorporation of this group in the deposited layer [7]. Nevertheless, for other groups, the use of a gas mixture allows a more flexible surface chemistry by tuning the monomer gas flow ratio [18]. It is well known that the chemical structure of the precursors has a direct impact on the physicochemical characteristics of the resulting PPF in "mild" plasma conditions of low or pulsed power [20,21]. However, the initial precursor structure is no more conserved when extensive molecular fragmentation occurs in the discharge (high power conditions), and one could think in this case that the nitrogen to carbon ratio in the precursor would prevail on the precursor structure.

Denis et al. [17] show for example that the retention of primary amine groups in PPFs deposited from two different isomeric precursors, namely AA vs CPA, only differs in low power conditions for which the monomer fragmentation leads to species of different nature. However, Ryssy et al. [12] show more recently, by studying both plasma and

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thin film chemistries for four precursors having more different structure with well-distinct nitrogen to carbon ratios (AA, EDA, DACH and HA), that the choice of the precursor strongly influences the primary amine content and PPF stability whatever the energetic conditions, even if they conclude that the nitrogen to carbon ratio is not a good predictor of surface functionality. They correlate the primary amine retention to the binding energies implied in the different molecules and to the stability of the resultant precursor ions and other ionic oligomeric species in the discharge, which can, depending on their energies and masses, either take part to thin film growth or be responsible for ablation and densification of the already deposited material. Similarly, Buddhadasa and Girard-Lauriault [18] conclude on the importance of the hydrocarbon molecule structure in NH_3/C_xH_y mixtures on the resultant polymer cross-link density and thus on the stability of the plasma layer.

In this context, we aim, in this work, to compare the use of a single monomer (cyclopropylamine) with the use of a gas mixture (ammonia/ethylene) in order to better understand how the precursor mixture influences the PPFs chemistry and to conclude on the best choice for obtaining NH_2-rich PPFs. To be consistent, we choose to keep the same nitrogen to carbon ratio in the precursor flow rate. In addition to thin film synthesis and characterization, optical emission spectroscopy and mass spectrometry are employed to support our description of the PPF growth mechanism.

2. Experimental

The plasma polymer films (PPFs) are deposited on intrinsic, two faces polished silicon wafers ((100) orientation, thickness 500–550 μm) from Siltronix, which are infrared-transparent in the 1500–4000 cm^{-1} region. Prior to deposition, substrates are cleaned with methanol and dried with nitrogen. PPFs are synthesized from cyclopropylamine (Alfa Aesar, purity 98%) and ammonia/ethylene (Air Liquide, purity >99.9%) mixture.

The deposition chamber used in this study is a cylindrical stainless steel vacuum chamber, which is described and sketched in references [22–24]. The chamber is pumped to a residual pressure of 8×10^{-4} Pa before to introduce the precursors. CPA is progressively heated from 318 K (container) to 328 K (manifold) until 333 K (line) before to be introduced as a vapor in the deposition chamber, thanks to a Minisource injection system from Omicron. Gas flow rate are fixed at 20 sccm (standard cubic centimeters per minute) for CPA and 20 sccm/30 sccm for the NH_3/C_2H_4 mixture, in order to have the same N/C = 1/3 ratio. The working pressure is regulated at 2.66 Pa. The substrates are located at 10 cm from the copper coil connected to the RF power supply (13.56 MHz) and kept at the floating potential during the depositions. All thin films are synthesized in continuous wave mode.

Deposition rates are measured with a Dektak150 mechanical profilometer from Veeco, using a diamond tip with a 2.5 μm curvature radius and an applied force of 0.1 mN.

Fourier transform infrared spectroscopy (FTIR) analyses are performed in transmission mode with a FTIR Bruker IFS 66 V/S spectrometer. Spectra are only measured in the 1500–4000 cm^{-1} region to avoid perturbations by the strong absorption peaks coming from the Si wafer below 1500 cm^{-1}, which could lead to wrong interpretations. Spectra are acquired using OPUS software with a 4 cm^{-1} resolution and averaged over 32 scans. The spectra are then baseline corrected using a concave rubberband correction with 6 iterations and finally normalized in the 2800–3100 cm^{-1} to more easily compare the relative intensities of the different peaks.

X-ray photoelectron spectroscopy (XPS) analyses are performed using a PHI 5000 VersaProbe (ULVAC-PHI) hemispherical analyzer from Physical Electronics, with a highly focused (beam size 200 μm) monochromatic Al Kα radiation (1486.6 eV, 15 kV, 50 W), at a pressure $< 3 \times 10^{-7}$ Pa. X-ray photoelectron spectra are collected at the takeoff angle of 45° with respect to the electron energy analyzer. Surface charging is compensated by a built-in electron gun (2 eV, 20 μA) and an argon ion neutralizer (10 V). The pass energy is 117.4 eV for survey spectra and 23.5 eV for high resolution spectra. For elemental quantification, each point has been reproduced twice, with <2 at.% deviation between the measured values.

The surface concentration of primary amine groups is determined using the chemical derivatization method with 4-trifluoromethyl benzaldehyde (TFBA, purity 98%, Sigma Aldrich) [17,18,25]. The reaction is carried out in a 2.4 L glass desiccator wherein ~0.5 mL of TFBA are dripped onto a ~1 cm thick layer of glass beads, placed at the bottom of the desiccator. 24 h after deposition, the samples are placed on the porcelain disk of the desiccator. The desiccator is then flushed with an argon flow during 10 min, to remove the air inside, and placed in an oven at 45 °C for 3 h. The primary amine selectivity is calculated using the following equation:

$$\frac{[NH_2]_u}{[N]_u} = \frac{[F]_d}{3 \times [N]_d} \quad (1)$$

where [N] and [F] are the relative concentration of nitrogen and fluorine, respectively, determined by XPS, and the u and d subscripts correspond to “underivatized” and “derivatized” samples, respectively.

Mass spectrometry measurements of the gas phase are performed in residual gas analysis mode (RGA) using a quadrupole HAL EQP 1000 mass spectrometer supplied by Hiden Analytical, and connected to the deposition chamber by a 100 μm extraction orifice located at about 50 cm from the coil. Neutral species entering the mass spectrometer are ionized by electron ionization to allow their detection. The electron energy is fixed at 20 eV in the ionization source of the spectrometer in order to avoid excessive fragmentation of the precursors in the ionization chamber.

Optical emission spectroscopy (OES) measurements are performed using a portable multichannel spectrometer AVS-MC2000–5 from Avantes. 5 different entrance slits allow to study the light from the plasma over 5 different wavelength ranges (200–350 nm, 330–465 nm, 440–610 nm, 590–735 nm and 720–970 nm). Light is collected through an optical fiber located at 10 cm from the coil and connected to the desired slit of the spectrometer depending on the studied wavelength range. Spectra are acquired with an integration time of 300 ms and averaged over 3 measurements.

3. Results and discussion

First, the deposition rates of plasma polymer films (PPFs) synthesized from both cyclopropylamine (CPA) and ammonia/ethylene (AmEt) mixture have been measured as a function of the power injected in the discharge in the range 30–100 W. The measurements are presented in Fig. 1. To compare more easily these data with those found in the literature, the Yasuda parameter W/F [20], corresponding to the energy applied per injected monomer molecule, has been calculated for each condition according to the following equation:

$$\frac{W}{F}(eV) = \frac{W}{\frac{F}{V_m}} \times \frac{1}{N_A} \times \frac{1}{|e|} \quad (2)$$

where W is the power injected in the discharge in W or J s^{-1}, F is the monomer flow rate in L s^{-1}, V_m is the molar volume of the gas (24 L mol^{-1}), N_A is the Avogadro constant (6.02×10^{23} mol^{-1}) and $|e|$ is the modulus of the elementary charge (1.602×10^{-19}), used as a conversion factor between J and eV (Table 1).

For both kinds of precursor, the deposition rates increase with the power in the studied range. This is consistent with a higher energy transfer from the power supply to the species present in the deposition chamber, leading to a stronger fragmentation of the monomers and to a greater number of active radicals and other energetic species that can take part to thin film growth. The fact that the deposition rates

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