



Chemical reactivity of plasma polymerized allylamine (PPAA) thin films on Au and Si: Study of the thickness influence and aging of the films

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ABSTRACT

In this work, we investigate the surface reactivity of substrates coated with thin layers (estimated thickness ≤ 30 nm) of plasma polymerized allylamine films (PPAA), an amine-functionalized polymer deposited by plasma-enhanced chemical vapor deposition (PECVD) with radiofrequency (RF) discharges. Our results show that very thin layers, or islands, can retain on their surface molecules that are able to react through their NH_2 functions. We have tested and assessed by X-Ray Electron Spectroscopy (XPS) and Quartz Crystal Microbalance (QCM) the surface density of chemical functions vs. layer thicknesses by using chemical derivatization with two types of agents: imine formation by a reaction of primary amine from the coating with aldehyde (Pentafluorobenzaldehyde, PFBA) and amide-bond formation by reaction with an activated carboxylic group (Succinimidyl Succinate Terminated Polyethylene glycol, EGSS). Results show that the PPAA coatings—even for very thin layers of a few nanometers—promote the chemisorption of the tagging molecules. The aging under air and evolution of reactive amine surface concentration with time under air are also presented.

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1. Introduction

Surface modification of materials by cold plasma techniques is a hot topic in applied research as well as in industry. Among the numerous plasma-based techniques able to etch [1,2], modify [3,4] or coat a wide range of materials, plasma polymerization of monomers stands out for its ability to produce thin polymeric films with good adhesion to their substrates [5]. Depending on the experiment, the resulting polymer presents on its extreme surface various chemical functions, such as nitrile, carboxy [6,7] or amino groups [8]. The presence of such functions decreases the hydrophobicity [8], increases the biocompatibility [9,10] and makes possible the covalent binding of biomolecules [11]. Amine functions on solids (e.g. nanoparticles) can also aid their dispersion in solution [12] by electrostatic charge repulsion, because they become positively charged in an acidic pH

[13]. Most of the time, these benefits are obtained thanks to the deposition of a polymeric layer of several tenths of a nanometer onto the substrate [14]. In this work, we investigate the surface reactivity towards aldehydes and activated carboxylic acids of substrates coated with thin layers (estimated thicknesses ≤ 30 nm) of PPAA, an amine-functionalized polymer deposited by PECVD in RF discharges. There are several advantages to produce very thin films as opposed to thicker ones, if one can do so without degrading the properties of the films: it saves process time, it reduces waste, and it spares the monomer. In industrial processes, these points easily lead to substantial economic and ecological benefits. In this work, we tried to determine the minimum deposition time needed to guarantee a sufficient number of amine functions at the modified surface. To assess this, we used two different techniques devoted to extreme surface characterization: the first is the spectroscopy of photoelectrons induced by X-Rays (XPS) after the derivatization of amine functions, and the second is the use of Quartz Crystal Microbalance (QCM) under liquid, to probe in real time the covalent adsorption of a “tagging polymer” on the layer. We have also evaluated the aging of such polymeric thin films, in terms of their loss of reactive amine functions, when exposed to ambient atmosphere.

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2. Experimental

The layers were synthesized using a PVD-PECVD facility manufactured by AJA Systems Inc. The chamber is equipped with a turbomolecular pump that produces a base vacuum better than 3.10^{-4} Pa prior all experiments. The sample holder (stainless steel) is electrically connected to an RF generator (13.6 MHz). A glass vacuum flask is filled with the monomer (allylamine 98%, purchased at Sigma-Aldrich) and connected to the chamber. All depositions of allylamine were made under a 100% allylamine atmosphere, with a flow of 80 sscm (mass-flow regulated feeding) of monomer, leading to a pressure of 8 Pa. For PPAA deposition, the RF power supply was fixed at 6 W (power regulated), which is the lowest power that produced a stable plasma in our equipment. By working at low power, we expect to get the highest concentration of amines [15,16] in the resulting material. To determine the deposition rate, a thick layer (about 100 nm) was deposited onto a clean floated glass substrate. Then, its thickness was precisely measured by stylus profilometry (Veeco Dektak). The ratio between the thickness and the deposition time gives the equivalent deposition rate. This ratio was determined at 0.070 ± 0.008 nm s $^{-1}$. The different films with decreasing thicknesses were obtained by shortening the deposition time. Supposing a linear increase in the thickness of the PPAA film with the deposition time, the corresponding equivalent thicknesses were 30, 15, 7.5, 3.75, and 1.9 nm for the samples deposited during 430, 214, 107, 53, and 26 s, respectively. Prior to the plasma deposition, the samples (ca. 1 cm 2 of commercial silicon wafers) were thoroughly cleaned in pure ethanol under ultrasonication for 20 min, and then dried with N $_2$. The samples called “silicon substrate” were used immediately after this cleaning. The “gold” wafers were actually silicon substrates, covered by (i) 5 nm chromium, followed by (ii) 50 nm thick layer of gold (classical metal thin films deposition by magnetron sputtering, without breaking the vacuum). The role of chromium is just to create an interlayer that promotes adhesion between the gold film and the silicon substrate [17]. The elemental composition of the PECVD deposited layers was determined by XPS (Surface Science Instruments SSX-100, excitation source was a monochromatized Al K α (1486.6 eV) radiation). The reactivity of the samples was characterized with XPS and QCM. XPS spectra were recorded after a derivatization with PFBA (in excess, 15 h, 50 °C in pure ethanol), according to the procedure described in Choukourou et al. [18]. The Scofield factor was 1.00 for C $_{1s}$, 1.68 for N $_{1s}$ and 3.33 for F $_{1s}$ peaks, and the compositions were determined by measuring the peak areas. The PFBA that did not bind to the layer was removed by several rinsing steps in various solvents (ethanol, dichloromethane, acetone and hexane) assisted by ultrasonication. The QCM experiments were carried out with the Q-Sense E4 device, equipped with QSX 301 crystal coated with 100 nm of gold (used as received). After the rinsing and stabilization steps, the EGSS (Succinyl

midyl Succinate Terminated Polyethylene glycol, purchased at Sigma-Aldrich) solubilized in bi-distilled water (200 μ g/ml) was introduced in the cell. The resonance frequency of the third and fifth harmonic was recorded over the time. All QCM experiments were carried out at a stabilized temperature of 25 °C, and the water flow was regulated at 50 μ l/min.

3. Results and discussion

3.1. XPS results

XPS spectra of the films reveal the presence of carbon, nitrogen and oxygen and, depending on the substrate and the deposition time of the film, the characteristic peaks of Si or Au. Fig. 1 shows the relative atomic concentration of the films. All PPAA layers deposited on gold exhibit an oxygen content of about 15 at.% coming from both oxygen contained in molecules adsorbed on the vacuum chamber and then released during the plasma process, as well as from the post-deposition reactions with atmospheric contaminants [19]. The oxygen proportion is higher for the PPAA films deposited on Si, mainly due to the presence of oxygen coming from the underlying layer of Si, which is naturally oxidized. For deposition times beyond 100 s, it is clear that the layers did not change a lot in terms of the composition (quality) of the deposits. The dramatic change in carbon content only occurs for the first sample (26 s of deposition time). As an indicator of the reactive proportion vs. the “total” nitrogen content (in depth measurement), we have calculated the following ratio, based on XPS measurements: $\frac{NH_2}{N_{total}} = \frac{[F]_{at.\%}/5}{[N]_{at.\%}} \times 100$. This formula takes into account the fact that each imine bond corresponds to an immobilization of five new fluorine atoms at the surface. The higher the ratio (amino selectivity), the lower the proportion of nitrogen implied in other C and N chemical combinations (nitrile groups, etc.) and those coming from oxidized amine forms (such as nitro and amides groups). This ratio is also lowered if the nitrogen-based functions are “slightly” buried: in this case, they are not accessible for surface chemistry but can still be probed by XPS. The results are plotted in Fig. 2. The amino selectivity is around 5%, lower than what it is expected for allylamine films deposited by plasma techniques (around 10%, see [20,21]). This is probably due to the type of reaction used for the derivatization step (liquid phase in this work, instead of gas-phase in the previous cited references). One can see that the amino selectivity is higher for the PPAA deposited on gold, compared to the PPAA lying on bare silicon. The fact that this difference is higher for the thinnest layers could suggest that the oxygen present at the surface of the substrate (Au or Si) can diffuse and therefore would be able to react with the nitrogen atoms present in the deposited layer. It would oxidise the primary

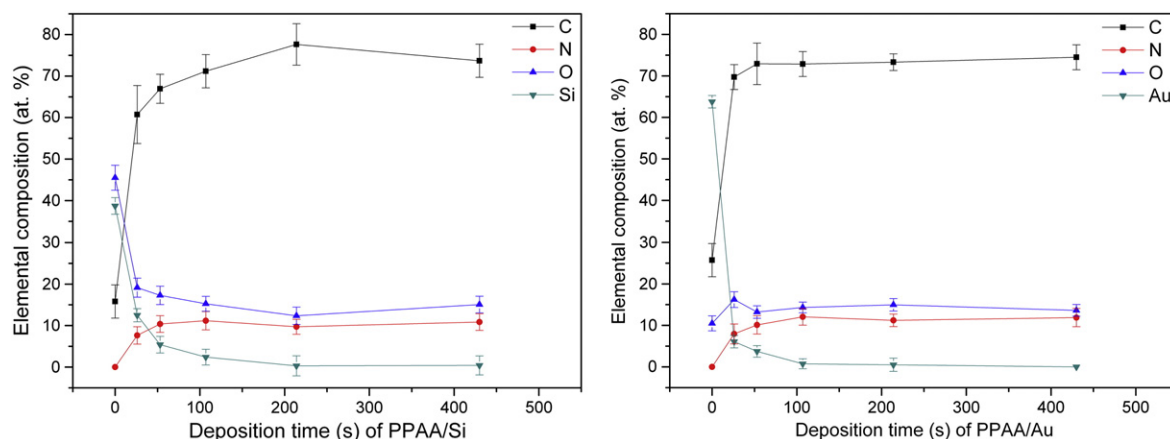


Fig. 1. Evolution of elemental composition (at.%) probed by XPS signals over the deposition time.

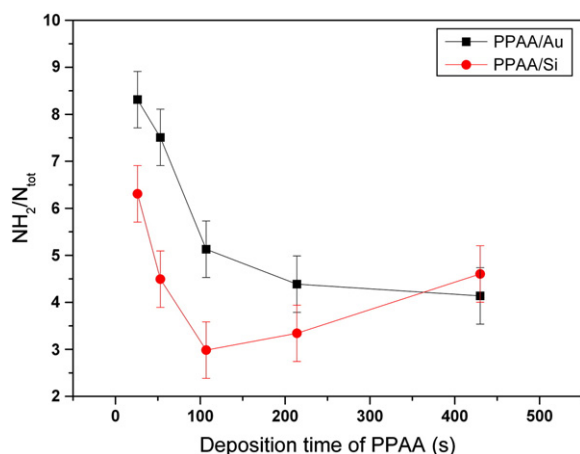


Fig. 2. NH₂/N_{tot} ratio vs. deposition time of PPAA film, after derivatization.

amine functions and make them non-reactive. As a noble metal, gold does not react with oxygen, whereas bare silicon wafers are oxidized on their surface (natural oxide layer), making them a possible source of oxidizing agent. In the case of very thin layers, the substrate type seems to have importance, with a loss of amine functionalities. This hypothesis is corroborated by considering Fig. 3, which shows high resolution spectra of the C_{1s} core level recorded for the thinnest samples (26 s of deposition on both Au and Si). These spectra suggest a higher proportion of oxidized carbon for the PPAA film deposited on Si substrate (the decomposition of the C_{1s} peaks was made according to Ref. [22]). A very important piece of data for biotechnological applications is the “total” density of reactive amino groups on the surface. To determine this, we have divided by five the concentration of fluorine expressed in atomic % (over all other elements probed by the technique). This ratio slightly increases from 0.48 to 0.64, for the Au substrate, whereas this ratio only ranges from 0.32 to 0.48 in the case of Si substrate.

3.2. QCM results

Five samples were prepared by plasma deposition onto Q-Sense gold-coated quartz, tested in a typical QCM experiment. The deposition time was varied from 0 to 430 s. During the stabilization step, the raw results (not shown) indicate that the polymeric layers were all stable under flowing water, whatever their deposition time (drift of less than 2 Hz during 1 h). As expected, the mass of the layer

increases just after EGSS injection. After the rinsing step, the frequency signal remained quite stable, at a lower frequency than before the EGSS injection. This latter point is the proof that the polymer is strongly attached to the layer.

The Sauerbrey equation gives the correspondence between the frequency shift (df) and the mass changes (dm): $df = -\frac{n}{c} \frac{dm}{c}$ where c is $17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ and n the considered overtone. We have applied it for the third and fifth overtone frequency shift data between the stabilization with pure water (actually 0 Hz) and the stabilized mass during the washing step. The results in terms of retained mass are presented in Fig. 4. As previously seen with the XPS results, a few nanometers of PPAA deposited on the substrate dramatically changes its properties in terms of chemical reactivity. Beyond a deposition time of 107 s of PPAA, there is no substantial evolution in the retaining ability of the substrate. Furthermore, the best efficiency seems to be obtained for the very thin layers (26 s of deposition time). Fig. 4 also shows on the same plot the results of the concentration of reactive amine functions probed by both XPS and QCM techniques, as a function of the deposition time. We have chosen the fluorine peak area in XPS (F_{1s}) as the most relevant indicator of quantity of amine functions at the surface, whereas in QCM, the total adsorbed mass of the tagging polymer (EGSS) after rinsing was selected. In QCM experiments, EGSS is linked to the substrate through an amide bond (vs. imine bond in XPS results). Therefore, this technique is less specific than the method used in derivatization with PFBA, because this latter reagent is specific to primary amines functions. Notwithstanding this fact, the behavior of the substrate functionality over the deposition time is similar in both techniques. The PPAA deposition always promotes the covalent bonding of molecules that have a strong affinity for amine functions. It indicates that the surface reactivity is strongly enhanced by a short deposition time, producing a very thin layer of allylamine.

3.4. Film aging

Because the simultaneous action of oxidative agents present in the air and in UV light, it is well known that polymeric thin films are unstable [10,23]. This is a major drawback for the use of PPAA films in “real life” applications. We have evaluated here the stability of the polymer deposited on Si substrate, in terms of the loss of reactive amine functions, under exposure to an uncontrolled atmosphere. To quantify how long these nitrogen-based functions are still under primary amine form and able to react with PFBA, we have carried out the very same experiment of derivatization just after the synthesis ($t=0$), 3 days, 7 days, 15 days and 30 days after the deposition. All samples were deposited at the same time in the PECVD reactor,

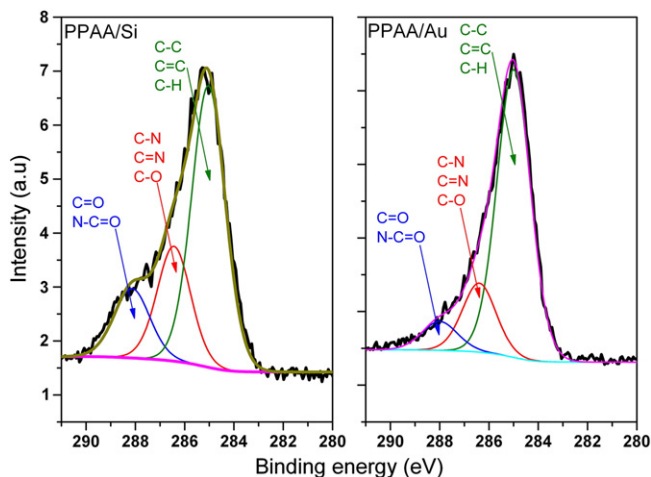


Fig. 3. High resolution XPS spectra (C_{1s} core level) of PPAA very thin films (deposition time: 26 s) deposited on Au and Si.

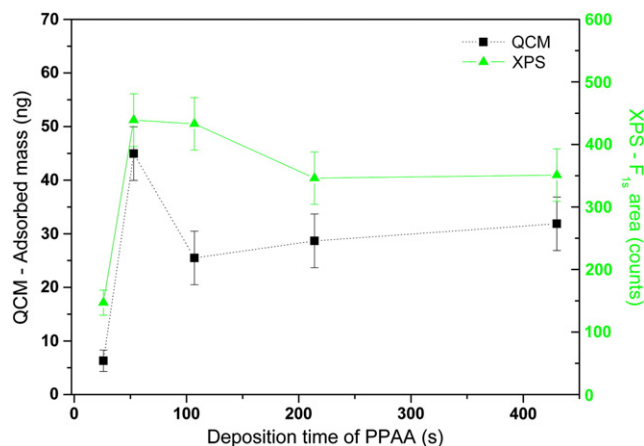


Fig. 4. QCM experiment results, for surface reaction of EGSS (50 µl/min, water, 25 °C) compared to XPS results, as a function of deposition time of PPAA.

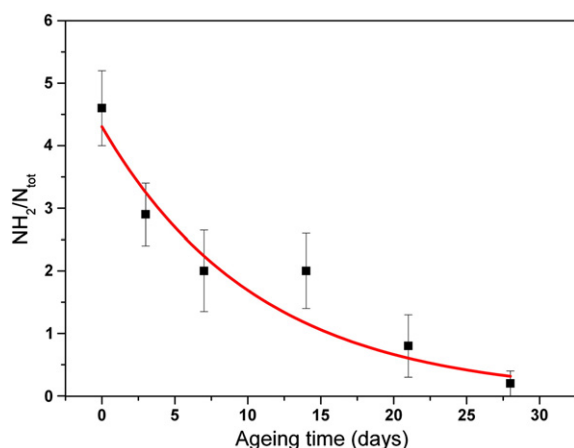


Fig. 5. Chemical reactivity of PPAA thin films on Si towards PFBA (PPAA deposition time: 430 s) over the aging time, probed by XPS.

avoiding possible variability of plasma conditions and their possible impact on layer properties. This aging was carried out for samples deposited during 430 s, 214 s and 26 s on Si substrates. The results are presented in Fig. 5. One can see that the proportion of amine functions (amino selectivity, see Section 3.1) is lowered if the derivatization is carried out a long time after the synthesis, despite the fact that the surface amount of nitrogen remains almost stable. The elemental compositions of the aged films are given in the Table 1. The curve can be adequately fitted with an exponential decay (typical of a first order chemical kinetic) function. This behavior has already been observed by Truica et al. [13]. For the three tested samples (430 s, 214 s and 26 s of deposition time), the half-life time deduced from the fitted exponential curves are 7.6 ± 1.8 days, 10.1 ± 4.8 days, and 7.9 ± 2 days, respectively. Considering the elemental composition given in Table 1, one can see that, for the same layer, the carbon and the fluorine atomic concentrations slightly decrease with the aging time, whereas the oxygen content increases and the nitrogen concentration remains almost constant. Elemental compositions over the aging time, and similar half-life times for the different deposition times, seem to indicate that the aging of the PPAA films does not depend on the layer thickness. This hypothesis is consistent with the model described in Ref. [23] because the aging oxidation process of the amine functions takes place at the extreme surface of the layer and the reactive amine sites probed by derivatization are located in the same place.

4. Conclusions

In this work, we showed that very thin layers of PPAA layers synthesized using an RF discharge are able to greatly increase the chemical reactivity. Our results have shown that this increase rapidly plateaus in terms of the quantity of free amines groups that are able to react with specific taggers. In order to investigate the growth mechanism of the very thin layers of PPAA, more sophisticated approaches (QUASES-Tougaard software package [24]) and other characterizations such as chemical force microscopy will be carried out. The aging of the PPAA films exposed to ambient air was also investigated. The results suggest that the loss of reactivity does not depend on the deposition time (as related to the film thickness). The kinetic half-life time was evaluated at 8.5 days, meaning that after this period, the reactivity of the deposited layers in terms of primary amines is lowered by a factor of two.

Table 1

Elemental composition (at.%) of aged films determined by XPS spectroscopy.

	Deposition time (s)	Aging time 0 days	Aging time 3 days	Aging time 7 days	Aging time 15 days	Aging time 30 days
C (at. %)	430	72	72	70	71	70
	214	77	71	72	72	71
	26	59	60	57	58	60
N (at. %)	430	10	11	11	11	10
	214	9.5	11	12	11	9.8
	26	7.4	6.6	7.9	7.5	7.1
O (at. %)	430	15	15	17	17	19
	214	12	16	15	16	18
	26	19	21	21	23	23
F (at. %)	430	2.4	1.6	1.1	1.2	0.6
	214	1.5	2.4	1.5	1.3	0.2
	26	2.3	2.3	1.3	–	–
Si (at. %)	430	0.4	–	1.4	–	0.6
	214	0.3	–	–	–	0.6
	26	12	10	13	12	9.5

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