Production and preliminary characterization of DC plasma polymerized allylamine film (PPAA) by NRA, ERD and XPS

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Abstract

Due to its surface properties, especially the presence of amine groups, plasma polymerized allylamine (PPAA) is involved in a large range of applications. Most of them are related to biology and biochemistry. In this work, we demonstrate a quick and simple way to produce PPAA thin films by conventional DC magnetron sputtering. To the best of our knowledge, this is the first method not involving radiofrequency (RF) or microwave discharges. In this paper, we show preliminary characterizations on the produced films (bulk analysis) carried out by ion beam techniques. The Hydrogen content in the whole layers was measured by ERD. The surface composition was probed by XPS on pentafluorobenzaldehyde (PFBA) derivatized films: the maximum concentration of amine groups is 1.6%.
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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. Cold plasma treatments of materials can graft in a short time and with high yield a wide range of chemical functions at their surface, providing a strong modification of their reactivity. Depending on the experimental conditions, a plasma treatment can etch the substrate (cleaning of surfaces [1]), modify the surface by its functionalization [2], generate thin layers with fine tuning of thickness and composition (plasma deposition techniques [3]) or produce a macromolecular network (plasma polymerisation of monomers [4]). This paper deals with this last application. Surface treatment by plasma can modify the biocompatibility of materials [5], but can also be the starting point for more complex surface biochemistry. It can provide immobilization of antibodies [6] and enzymes immobilization [7]. PPAA films were widely studied among the literature, mainly for their involving in biological applications: the presence of amine groups can promote a wide range of chemical reactions with biomolecules [8]. To the best of our knowledge, all papers imply RF or microwave discharges in order to generate the plasma and not DC

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magnetron sputtering. The purpose of this work was to demonstrate a quick and simple way to produce PPAA by conventional DC magnetron sputtering. The produced PPAA films were characterized by nuclear reaction analysis (NRA) and elastic recoil detection (ERD), whereas surface chemistry was probed by X-ray photoemission spectroscopy (XPS) on samples derivatized with pentafluorobenzaldehyde (PFBA). The preliminary results of our experiments gave evidence of $-NH_2$ reactive sites on the surface of the PPAA layers. In a plasma discharge, it is well established that the power has a great influence on the composition of the deposited layer. Therefore, among a lot of experimental parameters, we have chosen to study how the power influences the composition of the layer, while all the other parameters were kept constant.

2. Experimental

PPAA films were deposited in a vacuum chamber equipped with a 2″ balanced DC magnetron sputtering system. A carbon target was mounted on the cathode. This chamber was pumped down with a turbomolecular pump, allowing a base pressure of 10^{-3} Pa. The monomer (allylamine 98%, purchased from Sigma-Aldrich) was introduced in a glass vacuum flask and connected to the vacuum chamber. In order to maintain a constant pressure during all experiments, a flow control valve was placed between the flask and the chamber. All experiments were carried out at a stabilized pressure (probed near the cathode by a Baratron gauge) of 2.5 (±0.1) Pa in pure allylamine atmosphere. In this work, two sets of substrates were used, depending on the analysis. For NRA and XPS of as-deposited layers, the substrate was polycrystalline copper, mechanically polished in order to obtain a smooth (mirror like) surface. For deposition rate measurements and chemical derivatization of $-NH_2$ groups, Si wafers (without any pre-treatment) were used. In all cases, the substrates were electrically grounded during deposition and the distance between the cathode and the sample holder was 80 mm. The DC power supply connected to the cathode was regulated in power. Typical voltages were comprised between 326 V (3 W) and 510 V (100 W) at the beginning of the deposition.

First characterization of the layers was performed with $^3He^+$ ion beam produced by ALTAÏS,[1] the linear accelerator installed at the LARN Lab. This ion allowed us to be sensitive to each element present in the analysed sample that was tilted at 25° (see Fig. 1). Indeed, the 2.385 MeV $^3He^+$ produces forward recoils of hydrogen that were detected by the ERD detector placed at 30°. The incident ions also make some usable nuclear reactions on carbon ($^{12}C(^3He,p_i)^{14}N$ with $i = 0–4$), nitrogen ($^{14}N(^3He,p_i)$ ^{16}O with $i = 0–7$ and $^{14}N(^3He,\alpha_0)$ ^{13}N) and eventually on oxygen ($^{16}O(^3He,p_i)$ ^{18}F with $i = 0–2$ and $^{16}O(^3He,\alpha_0)$ ^{15}O). The pro-

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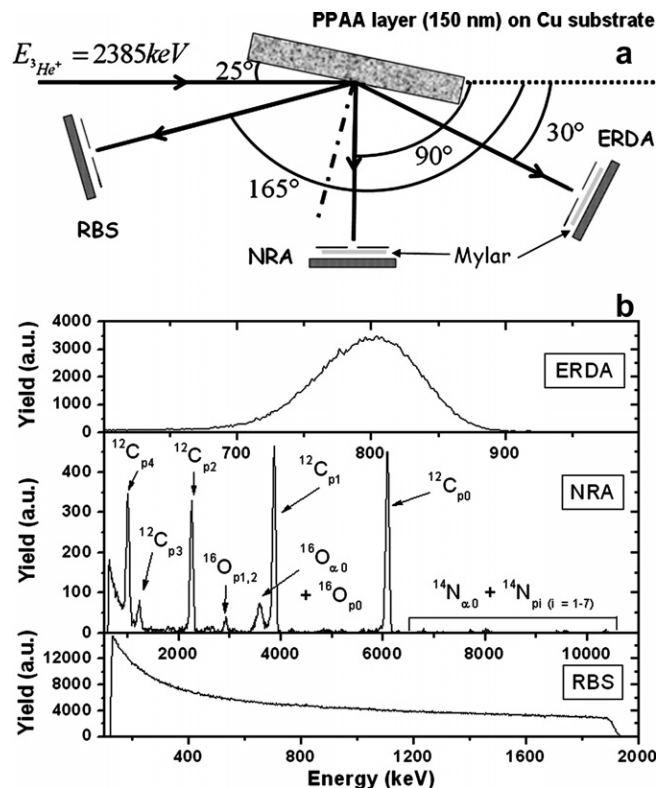

Fig. 1. (a) Experimental set-up for NRA and ERD measurements; (b) ^3He induced spectra for PPAA (20 W) 150 nm-thick layer PPAA deposited on polished Cu substrate.

tons and alpha particles were detected by the NRA detector placed at 90°. A 15.2 μm Mylar foil is placed in front of the ERD and NRA detectors to stop the scattered primary $^3He^+$. A RBS detector, placed at 165°, was used to monitor the number of incident particles. The simultaneously obtained spectra (see Fig. 1b) were treated with the software SIMNRA [9] to provide the concentration of the elements in layers analysed. The procedure has been checked against a well known standard: to achieve this, polyimide film (Kapton) was used. In Fig. 1b, one can see the presence of hydrogen, carbon, nitrogen and oxygen. Their concentrations versus the power applied during the deposition are presented in the result paragraph. XPS measurements were performed with SSX-100 spectrometer (Surface Science Instruments), with incident X-Ray beam of 1486.6 eV (Al K_α). Scofield factors used are given by the spectrometer manufacturer: 1.00 for C_{1s} and 3.33 for F_{1s}.

Surface amine groups were derivatized into imine with pentafluorobenzaldehyde (PFBA), according to an experimental protocol adapted from Park et al. [10]. Substrates were placed overnight at 50 °C in anhydrous ethanol (10 mL) under nitrogen atmosphere with ca. 100 mg of PFBA. After that, the samples are thoroughly cleaned ultrasonically 3 × 3 min in ethanol, dichloromethane, acetone and hexane in order to release PFBA molecules non covalent-bound to the substrate. The thickness of the deposited film was measured by a stylus profiler (Veeco Dektak). For the five different powers, the deposition rates

were determined by measuring the film thickness and the deposition time.

3. Results and discussion

The deposition rate as a function of the power is shown in Fig. 2. These experimental points can be fitted by an exponential growth. We have to emphasize that the deposition rate determination is correct under the assumption that it is constant over the time.

Polymeric materials are known to be sensitive to the ion beams used in nuclear analysis. The size of the 15 nA ^{3}He beam is determined by a 1 mm circular collimator. During irradiation, the temperature rises of ca. 30 °C. Because the desorption rate is not the same for every element in the layer, its composition is changing during the analysis. For all samples, the charge-normalized signal of C, N, O do not change with irradiation time, whereas ERD signal (H concentration) was affected by irradiation, indicating a hydrogen desorption in the layer during the analysis. Bulk composition of the coatings, determined by treatment of spectra by SIMNRA, is given in Fig. 3 for the five different samples. The curves of nitrogen and oxygen concentration have the same profile, showing a minimum between 6 and 10 W. The hydrogen concentration curve displays the same shape, whereas on the C curve one can guess a maximum located at 10 W. However, when considering experimental errors (shown on the Fig. 3), these minima/maxima are not really convincing. Consequently, these slight differences in atomic compositions have to be confirmed by performing more experiments (plasma deposits and ion beam measurements). Monomer (allylamine) has a theoretical atomic composition of 27% of C, 64% of H and 9% of N. By analysing the Fig. 3, we can observe that the layer composition is rather different than the one of the monomer. In particular, PPAA is much less hydrogenated
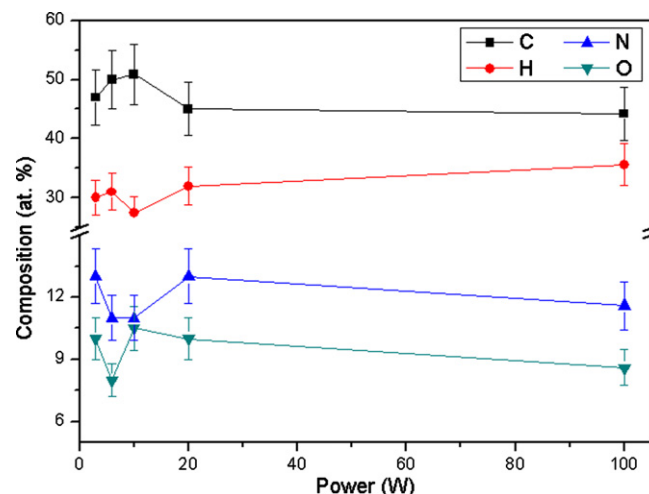

Fig. 3. Bulk composition of PPAA layers probed by NRA and ERD measurements.

than the monomer. This was already observed by Krishnamurthy et al. [11].

XPS measurements were done for chemically derivatized layers, by tagging amine groups with pentafluorobenzaldehyde. This experiment gives evidences of –NH$_2$ reactive sites at the surface of PPAA layers. The major interest of PPAA films seems linked to the presence of amine functional groups. To be able to quantify the potentially reactive amine functions at the surface of the PPAA layer, we have performed chemical derivatization of amino groups with the PFBA tagging group. Because PFBA only reacts with amine groups, this technique enables us to demonstrate that the surface is decorated with NH$_2$ functional groups. Adapted from Choukourov et al. [12], the following formula was used to determine the –NH$_2$ amount relative to carbon by measuring by XPS the Fluorine concentration [F] linked to the tagging group (PFBA) and taking into account the C introduced by the PFBA molecule: $[NH_2] = \frac{[F]/5}{[C]-7[F]/5} \times 100$. The results are plotted
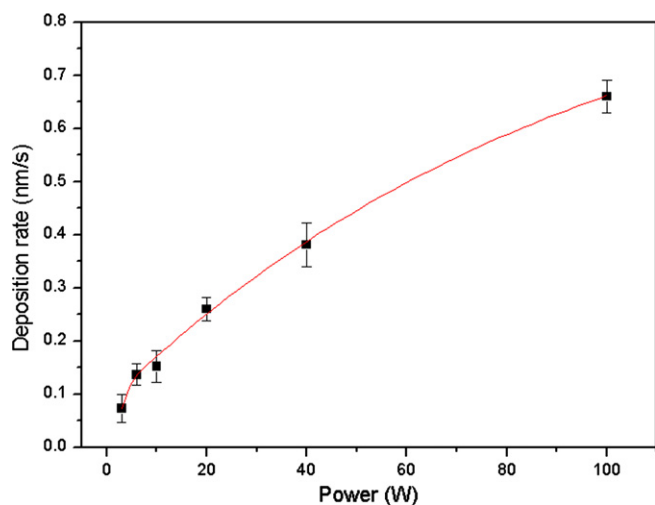

Fig. 2. Deposition rate of PPAA as a function of applied power. Errors bars are related to the standard deviation obtained by two or more experiments.
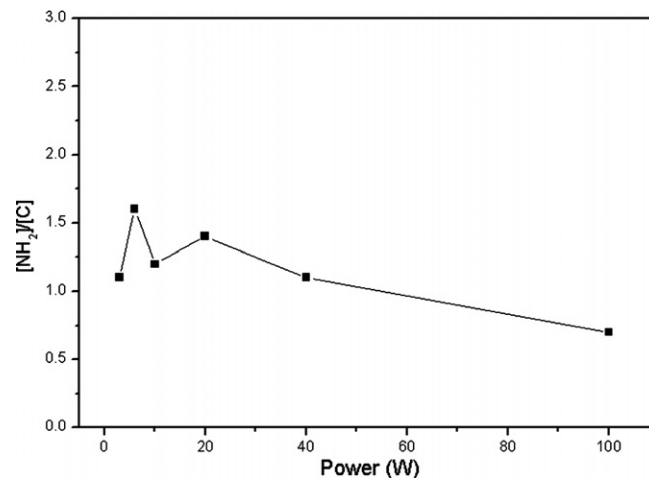

Fig. 4. NH$_2$ concentration as a function of power probed by XPS on derivatized samples.

in Fig. 4. By reproducing the whole experiment (plasma deposition, chemical derivatization and XPS on derivatized samples) and taking into account the standard deviation of the amine concentration value, we have estimated the relative error on these amine concentrations at maximum 12%. The maximum of amine density is obtained for the 6 W sample, but the amine concentration remains quite constant when varying the power. From NRA and ERD measurements, the 6 W sample shows a high concentration of carbon and the lowest concentration of oxygen. Fig. 4 shows that increasing power decreases the amount of amine functions because high power increases the energy input per unit mass of the monomer [4], leading to a more extensive fragmentation of the starting monomer. Therefore, more rearrangements and cross-reactions between these highly reactive species occur, leading to a polymerized compound very different than the monomer.

4. Conclusions

We have demonstrated that the PPAA synthesis is feasible in a simple DC-magnetron sputtering system. The influence of the power on the deposited layer was probed by NRA and ERD (for the composition) and XPS technique. Considering the potential applications of as-synthesized PPAA layers, the best power seems to be located at 6 W. This power gives a rather high amount of amine functions (up to 1.6%) on the surface of the layer. We have shown by organic chemistry that these amine groups are reactive. Furthermore, the results of derivatization experiment give insights about the resistance of the PPAA layer against organic solvents, potentially important for "real life" applications. When deposited onto Si wafer, PPAA layers are well resistant to ethanol, dichloromethane, acetone and hexane. Since most of the results reported in this paper were obtained with a reduced number of experiments, these conclusions require confirmation by performing more experiments.

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