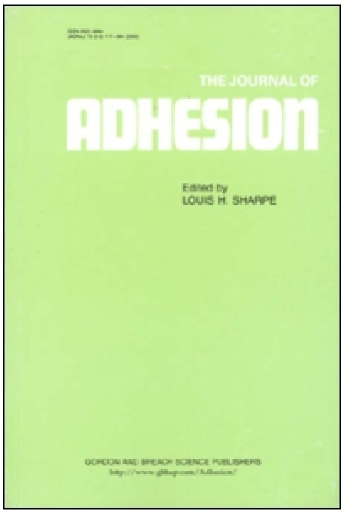

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Charbonnier, Marlene , Romand, Maurice , Esrom, Hilmar and Seeböck, Robert(2001) 'Functionalization of Polymer Surfaces Using Excimer VUV Systems and Silent Discharges. Application to Electroless Metallization', The Journal of Adhesion, 75: 4, 381 — 404

To link to this Article: DOI: 10.1080/00218460108029612

URL: http://dx.doi.org/10.1080/00218460108029612

J. Adhesion, 2001, Vol. 75, pp. 381–404
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Functionalization of Polymer Surfaces Using Excimer VUV Systems and Silent Discharges. Application to Electroless Metallization

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(Received 24 July 2000; In final form 27 October 2000)

New approaches for electroless plating of nonconductive polymers or polymer-based materials are described. In this work, polyimide substrates were surface-functionalized (i) in nitrogenated (ammonia at reduced pressure) and oxygenated (air at atmospheric pressure) atmospheres under assistance of vacuum-ultraviolet (VUV) irradiation (use of a xenon silent discharge excimer source) or (ii) directly in air at atmospheric pressure using a dielectric-barrier discharge (DBD) device. After functionalization, the substrates were "activated" by dipping in a dilute acidic $PdCl_2$ solution or by spin-coating of a thin metal-organic film (from a solution of palladium acetate (PdAc) in chloroform). The catalytic activity of the so-deposited palladium species toward the electroless deposition of nickel was studied before and after a VUV post-irradiation (in air at atmospheric or reduced pressure) with a view to understanding better the role of the reducer (sodium hypophosphite) within the electroless bath.

This work confirms the specific interest of grafting nitrogenated functionalities onto polymer surfaces for attaching covalently the palladium-based catalyst (in particular in the case of the $PdCl_2$ route), forming thus strong Pd—N—C bonds at the metal/polymer interface. This results from the strong chemical affinity of palladium toward nitrogen. On the other hand, when oxygenated functionalities are surface-grafted, the conventional two-step procedure using $SnCl_2$ and $PdCl_2$ solutions can be proposed due to the strong chemical affinity of tin toward oxygen. The Ni deposits obtained under these different conditions pass the standard Scotch®-tape test and, therefore, exhibit a good

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practical adhesion. For this same purpose, it is interesting to note that the DBD treatment operating in air at atmospheric pressure causes an increase of the surface roughness and, therefore, an improvement in adhesion of metallic films when their initiation is catalyzed through the PdAc route. In addition, this work demonstrates that extensive research still has to be performed to understand and improve the Ni/polymer adhesion when the PdAc route associated with a VUV irradiation is considered.

Keywords: Polymers; Surface modification; Surface functionalization; Surface activation; Silent discharges; Incoherent excimer lamps; UV/VUV irradiation; Palladium chemisorption; Electroless metallization; XPS analysis

INTRODUCTION

Electroless plating is one of the most widely used industrial processes for metallizing non-conductors such as polymers and polymer-based materials. For example, metallized plastics produced from such a technology find a lot of applications in appliance, automotive and microelectronics industries [1].

Basically, electroless plating is an autocatalytic process consisting of a redox reaction in aqueous solution between ions of the metal to be deposited (usually nickel or copper) and a strong reducer such as hypophosphite (in case of Ni deposits) or formaldehyde (in case of Cu deposits). The reactions involved are:

$$Ni^{+2} + 2H_2PO_2^- + 2H_2O \rightarrow Ni^0 + 2H_2PO_3^- + H_2 + 2H^+$$

and

$$Cu^{+2} + 2HCHO + 4OH^- \rightarrow Cu^0 + 2HCOO^- + H_2 + 2H_2O,$$

respectively. Let us remind here that, when such reactions are initiated, the metal deposited serves as catalyst, thus ensuring continuous buildup of the metal film (hence the commonly used term "autocatalytic process"). However, in the case of non-conducting substrates, the metallization initiation itself has to be preceded by an activation procedure, the primary purpose of which is to provide catalytic sites on the material surface. The earlier version of activation consists of a two-step process [2–8]. Step 1 involves the substrate treatment in a stannous chloride/hydrochloric acid solution (sensitization step) and leads to the adsorption of stannous ions (Sn^{+2}) onto the surface. After rinsing, step 2 involves the treatment of the sensitized substrate in a palladium chloride/hydrochloric acid solution (actual activation step). This second step is sometimes reported as allowing the deposited Pd^{+2} ions to be reduced to Pd^0 by the Sn^{+2} ions [2]. The so-formed Pd^0 sites then catalyze the initiation of electroless metallization. Further, a second version of activation (also known as the one-step process) was developed and is today in current industrial use [4, 9–14]. This approach involves the substrate treatment in a mixed stannous chloride/palladium chloride/hydrochloric acid solution (colloidal solution) and leads to the formation of colloidal particles consisting of a Sn/Pd alloy core surrounded by a protective layer of stannous hydroxide. This surface excess of stannous ions must be removed with a view to leaving the colloidal particles and, therefore, the palladium sites to act as a catalyst for starting the metal deposition in the electroless bath. This post-activation step (also known as the acceleration step) is accomplished by solubilizing the tin hydroxides of the "activated" surface, for example, in an acidic solution such as a hydrochloric acid solution.

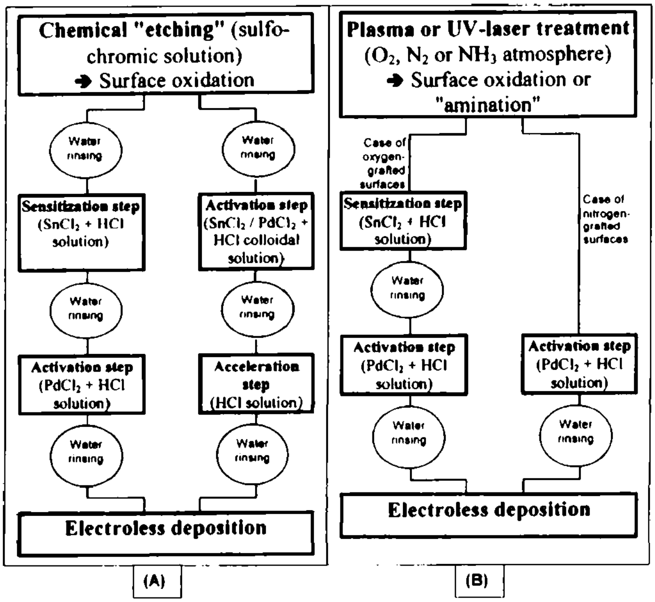
It must be mentioned at this point that, irrespective of the activation procedure considered here (two-step or one-step process), the reducing agent (hypophosphite, formaldehyde ...) present in the electroless bath is able to bring the palladium species into a reduced form which makes the substrate surface to be plated catalytically active. This explains why a more or less long incubation time often takes place before starting the deposition reaction.

Obviously, the afore-mentioned tin-palladium processes, as well as other activation methods proposed as alternative approaches [14], and conditioning chemical methods for cleaning, etching and oxidizing the "virgin" polymer surfaces, encounter various drawbacks. Indeed, they need the use of hazardous chemicals (for example, sulfochromic mixtures used as etchants, sodium bisutfite solutions or any of the proprietary products designed to neutralize the excess of etchants, hydrochloric acid used in sensitization/activation baths ...) and, therefore, are responsible for serious environmental problems. In addition, it is proved that the management of the activating solutions is often difficult. For example, the maintenance of the colloidal tin-palladium solution requires a continuous monitoring of the stannous tin content to prevent the bath from becoming useless. Even when the bath is not being used, stannous species oxidize to the stannic state (Sn^{+4}) and the bath no longer can work correctly.

For various reasons including those cited above, there exists a continually growing demand for developing new and efficient processes which allow the reduction of the number of wet chemical surface conditioning steps as well as the minimization or even avoidance of environmental problems. For example, there has been proposed a simplified method which involves, at first, the surface conditioning of polymer substrates through plasma treatments in oxygenated and nitrogenated (O_2, N_2 and NH_3) atmospheres [13–20]. Under these conditions, the polymer surfaces are functionalized with oxygenated or nitrogenated species, respectively. In the case of oxygen-grafted surfaces, the sensitization/activation baths (two-step or one-step operation) must be used to graft palladium species. This fact results from the strong chemical affinity of tin species and the non-affinity of palladium ones toward oxygenated species. On the other hand, in the case of nitrogen-grafted surfaces, only a dilute palladium chloride/hydrochloric acid solution (simplified one-step operation) allows one to produce the surface "activation". This results from the strong chemical affinity of palladium species toward nitrogenated species. This new alternative does not require baths containing tin chloride. By taking into consideration such a chemical affinity, it was further shown that the simplified surface activation could be accomplished through ultraviolet (UV) laser pretreatments in an ammonia environment [21, 22]. For the same purpose, aiming at simplifying the surface conditioning before the electroless deposition, it has been demonstrated in the past few years that the Pd nucleation of non-catalytic surfaces could also be produced by decomposition of thin, solid metal-organic films through the use of UV or VUV (vacuum-ultraviolet) sources emitting high photon fluxes [23–38]. Especially, thin palladium acetate ($Pd(OCOCH_3)_2$, PdAc in abbreviated form) films deposited by spin-on, spraying or dip-coating methods directly on polymer surfaces (*i.e.*, without any pretreatment susceptible of improving wettability) from a suitable solution (*e.g.*, in chloroform) have been irradiated, for example at the wavelengths $\lambda = 193$ and 248 nm using ArF* and KrF* excimer lasers, as well as at $\lambda = 172$ and 222 nm using Xe_2^* and KrCl* incoherent excimer lamps [23–38]. In these different works, the PdAc films have been reported to be thermally and/or photolytically decomposed. The so-formed thin "palladium" films are then able to act as catalysts for a subsequent electroless metal deposition.

Figure 1 represents schematic diagrams of the different preparation processes: (A) conventionally used and (B) newly developed and/or already proposed to activate catalytically the surface of polymer or polymer-based materials.

In the present paper, special attention is focused on the surface processing of polymer substrates through the use either of a dielectric barrier discharge (DBD) device operating in air at atmospheric pressure or of a DBD-driven excimer source (Xe_2^* lamp emitting VUV radiation at 172 nm) which allows one, for example, to treat sample surfaces in air at atmospheric pressure or in ammonia at reduced pressure. It is easy to imagine that approaches involving surface treatments at atmospheric pressure can offer various advantages, especially in industrial applications. In a first series of experiments, the



Xe_2^* lamp has been used to study the influence of some experimental parameters on the surface composition of polycarbonate (PC) substrates. In a second series of experiments, the incoherent excimer source and the DBD device have been used to compare the surface modifications generated on polyimide (PI) substrates. The potential of these treatment methods is discussed in terms of surface activation (chemisorption of palladium species) and initiation of the electroless metal deposition. After each surface pretreatment step, surface analysis is mainly carried out by X-ray photoelectron spectroscopy (XPS) with a view to understand and quantify the influence of the experimental parameters on the surface atomic concentration of the elements of interest (C, O, N, Sn, Pd ...).

EXPERIMENTAL

In this work, surface treatments were carried out on polycarbonate (PC) and polyimide (Kapton® 500 HN) foils obtained from Goodfellow (UK) and Dupont (USA), respectively. PC substrates were used to study the surface modifications as a function of the experimental conditions, while Kapton® substrates were considered with a view to investigate the subsequent electroless metallization. In all cases, the sample surface was first degreased with ethanol in an ultrasonic bath.

In a first series of experiments, the surface modification of the polymer foils was performed in air at atmospheric pressure or in ammonia (NH_3) at reduced pressure using a Xe_2^* incoherent excimer source (Excivac Laboratory System, Heraeus Noblelight, Germany) and the experimental setup described in Figure 2(A). The latter consists of two contiguous chambers which can be, if necessary, evacuated individually (primary vacuum). The upper chamber which contains the excimer lamp is separated from the reactor by a 5 mm thick calcium fluoride (CaF_2) window. The discharge in the lamp is operated at a frequency of about 275 kHz and at a voltage amplitude of 4 kV. The incoherent radiation emitted by this device peaks at a wavelength of 172 nm with a full-width-at-half-maximum (FWHW) of about 15 nm. The upper chamber is evacuated ($p = 10^{-2}$ mbar) so that the sample surface is irradiated with a maximal flux estimated at

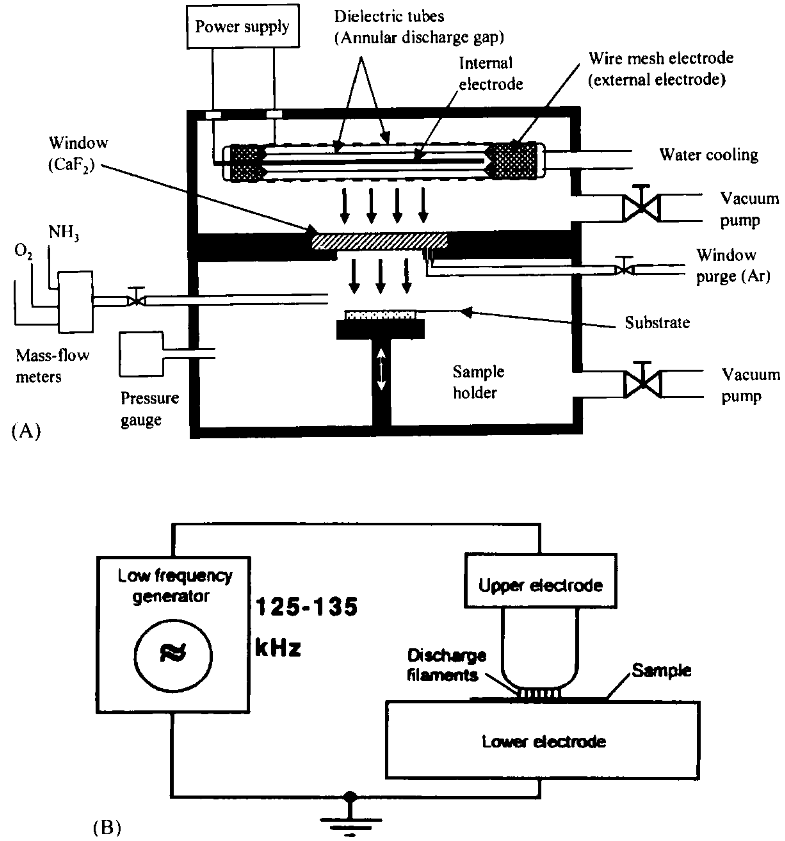


FIGURE 2 Schematic diagrams of: (A) the VUV treatment chamber using an incoherent excimer lamp, and (B) the dielectric barrier discharge (DBD) device operating directly in air at atmospheric pressure.

between 2.5 and 3.3 × 10^{16} photons $cm^{-2}\,s^{-1}$ (*i.e.*, with a flux between 30 and 40 mW cm^{-2}) [39].

In a second series of experiments, the surface modification of the polymer foils was performed in air at atmospheric pressure using a DBD discharge and the electrode arrangement shown in Figure 2(B). In this arrangement [40, 41], the samples are placed on the lower grounded electrode and act as the dielectric barrier. The lower electrode is a circular copper disk (25 mm in diameter) while the upper electrode is a rod (up to 20 mm in diameter). The position of the lower electrode can be varied with a view to changing the distance between electrodes. Only a very limited range of discharge gap lengths (0.1 to 0.5 mm) is accessible for discharge ignition to take place with the power (typically between zero and 80 W) and frequencies (125 – 135 kHz) available from the generator used (ENI HRG-2 model operating without matching network).

The two-step operation leading to surface activation was carried out using, successively, the sensitization solution containing $0.1\,\mathrm{g\,l^{-1}}$ $SnCl_2$ and $0.1\,\mathrm{cm^3\,l^{-1}}$ concentrated HCl, and the activation solution containing $0.1\,\mathrm{g\,l^{-1}}$ $PdCl_2$ and $0.1\,\mathrm{cm^3\,l^{-1}}$ concentrated HCl. After each treatment, the samples were rinsed in distilled water for 1 min. When using the simple activation process, a solution containing $0.1\,\mathrm{g\,l^{-1}}$ $PdCl_2$ and $0.1\,\mathrm{cm^3\,l^{-1}}$ concentrated HCl was employed.

In the experiments using the photo-decomposition of metal-organic precursors, the palladium acetate (PdAc) films were deposited by spin-coating from a PdAc solution in chloroform ($CHCl_3$). During the spin-on process, the chloroform evaporates immediately and homogeneous ultra-thin solid films are obtained. Depending on the spin-speed, PdAc concentration of the solution and number of drops deposited, different film thicknesses can be produced. Subsequently to their photo-chemical reduction (by VUV irradiation or DBD treatment in air) the non-decomposed part of the films was removed by rinsing in a ultrasonic bath of chloroform for 1 min. In the present work, the cleaned substrates were spin-coated at 10^3 rpm with a PdAc solution (0.015 M).

The metallization bath leading to Ni deposition (in fact Ni-P deposition) consists in an aqueous solution containing $36\,\mathrm{g\,l^{-1}}$ $NiSO_4 \cdot 6H_2O$, $10\,\mathrm{g\,l^{-1}}$ $NaH_2PO_2 \cdot H_2O$ and $29\,\mathrm{g\,l^{-1}}$ lactic acid. This solution (pH 5) operates at the temperature of 85°C. The metallization duration was fixed for all specimens at 2 minutes, which generates films of about 0.5 μm in thickness.

In this work, surface analysis was carried out by XPS using a RIBER SIA 200 spectrometer equipped with a non-monochromatic AlK_α excitation source and a MAC 2 analyzer. Spectra were recorded at a take-off angle of 65° with respect to the sample surface. Survey scans were recorded at overall resolution of 2.3 eV and core level spectra at 0.9 eV. All XPS peaks were referenced to the C 1s signal, at a binding energy of 285 eV characteristic of C—C and C—H bonds.

Contact angle measurements were performed within less than one minute after the surface treatment using the sessile drop method with an automatic apparatus (Digidrop model from GBX Scientific Instruments, France). The water drop was 5 µl in volume. Every contact angle value obtained with a precision of about ± 1° results from ten successive measurements carried out within a few seconds.

The surface morphology of some polyimide samples was also studied by atomic force microscopy using an AFM Nanoscope® III apparatus (Digital Instruments, USA). Images were obtained in air in the tapping mode using a standard silicon nitride tip oscillating at a resonant frequency of 270 kHz.

RESULTS AND DISCUSSION

Excimer Lamp Experiments: Effects of Experimental Parameters

The use of the Xe_2^* excimer lamp setup shown schematically in Figure 2(A) requires, at first, a study of the influence of the experimental parameters (distance between the CaF_2 window and the sample, working pressure in the reactor, treatment time, power delivered by the generator to the lamp) on the chemical characteristics of the polymer surface subjected to the VUV irradiation. This study was carried out using polycarbonate (PC) substrates. The results show that:

(i) When the treatments are performed in air at atmospheric pressure, grafting of oxygenated functionalities and improving of the substrate wettability are observed. However, these characteristics decrease drastically when the CaF_2 window-sample distance increases because of the absorption of the VUV radiation by O_2 molecules of air. Therefore, surface treatments in air at atmospheric pressure must be carried out with the sample located as closely as possible to the CaF_2 window. In the experimental setup shown in Figure 2(A), the CaF_2 window-sample distance commonly used is 1 cm.

(ii) When the treatments are performed in air at reduced pressure (1 mbar), the residual oxygen content is sufficient to allow a significant grafting of oxygenated functionalities. In addition, it is interesting to note that the CaF_2 window-sample distance plays a less critical role than in the case of experiments performed at atmospheric pressure, given that a higher photon flux reaches the sample surface. However, as there is no particular interest in working in air at reduced pressure, the easier way for attaching oxygenated functionalities on the polymer surfaces consists in operating at atmospheric pressure with a short CaF_2 window-sample distance (1 cm).

(iii) When the treatment time in air at atmospheric pressure increases, grafting of oxygenated functionalities increases while water contact angles decrease. These characteristics tend to a limit beyond a treatment time of about 2 min (Fig. 3).

(iv) When the power delivered by the generator increases, the efficiency of the surface treatment improves, which possibly allows one to decrease the treatment time.

In summary, the Xe_2^* excimer lamp is, therefore, used in the following conditions: generator power: 80%; treatment time: 1 min; CaF_2 window-sample distance: 1 cm.

VUV Treatments of Polyimide Substrates

Results presented in this section are related to polyimide substrates (Kapton® 500 HN samples), *i.e.*, to polymer materials which, unlike

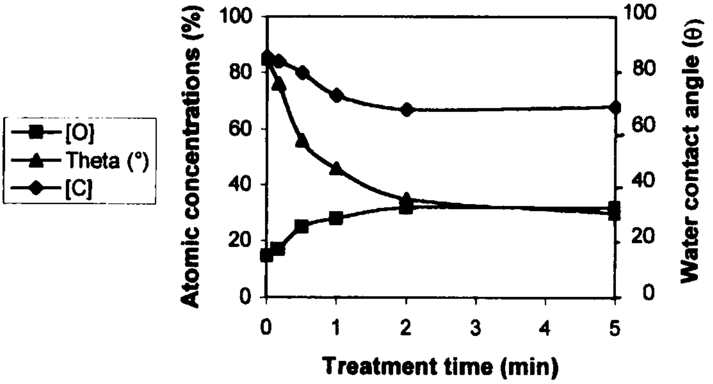


FIGURE 3 VUV treatment of polycarbonate substrates in air at atmospheric pressure. Influence of the treatment time on oxygen and carbon surface concentrations (at. %) and on water contact angle (θ in degrees). Experiments carried out at a CaF_2 window-sample distance of 1 cm and a power of 80%.

PC samples, naturally contain nitrogen atoms in their chemical formula. Figure 4 shows XPS survey spectra of such substrates (a) after degreasing, (b) and (c) after VUV irradiation for 1 min in air at atmospheric pressure and in NH_3 at reduced pressure (5 mbar), respectively, at constant Xe_2^* lamp power ($W = 80\%$). For such experimental conditions, XPS analyses show that VUV irradiation in air causes a noticeable increase of the oxygen surface concentration (from 17.4 to 27.8 at. %) while the nitrogen surface concentration does not change significantly (from 6.4 to 6.6 at. %). On the other hand, the VUV irradiation in NH_3 for 1 min leads, in particular, to a strong increase of the nitrogen surface concentration (from 6.4 to 17.6 at. %) while the oxygen surface concentration is observed to decrease slightly from 17.4 to 16.2 at. %. It should be noted here that the nitrogen surface concentration reaches 23.5% when the polyimide substrate is VUV-treated for 3 min, which is of prime interest for the objective of this work. It should also be mentioned that, as far as photon energy is concerned, the radiation at 172 nm emitted by the

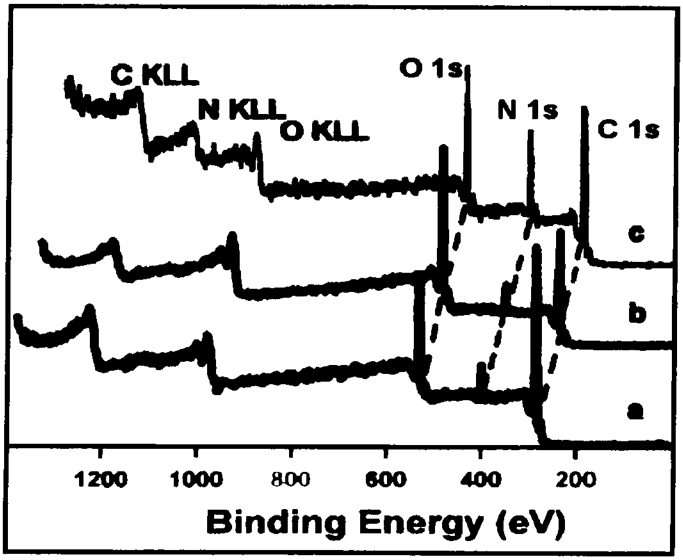


FIGURE 4 XPS survey spectra of a Kapton® 500 HN sample (a) ethanol-degreased, (b) and (c) the same as (a) after a VUV treatment in air at atmospheric pressure for 1 min and in NH_3 at 5 mbar, respectively. In both cases, the CaF_2 window-sample distance was 1 cm and the power 80%.

Xe_2^* excimer lamp is energetic enough (7.20 eV) to break the N—H bonds (4.03 eV) of NH_3 molecules, but not to break the $N\equiv N$ bonds (9.76 eV) of N_2 molecules. This is the reason why NH_3 is used as the nitrogenated gas phase and why N_2 cannot be employed in such experiments, although it is commonly used for plasma treatments. On the basis of previous results [13–20], the samples irradiated in air were subjected to the conventional sensitization-activation process (immersion successively in acidic $SnCl_2$ and $PdCl_2$ solutions) while those irradiated in NH_3 were treated in the simple acidic $PdCl_2$ solution. Figure 5 represents XPS survey spectra of these samples after water rinsing. In the first case, Sn and Pd species are grafted at a surface concentration of 4.4 and 1.1 at. %, respectively, and in the second case, Pd species are at 1.2 at. %. On the other hand, when a sample VUV-irradiated in air is only immersed in the acidic $PdCl_2$ solution, Pd is also grafted but at a low surface concentration (0.3 at. %). Such a result, never observed for PC samples treated in the same way, is due here to the chemisorption of palladium species on the nitrogen atoms

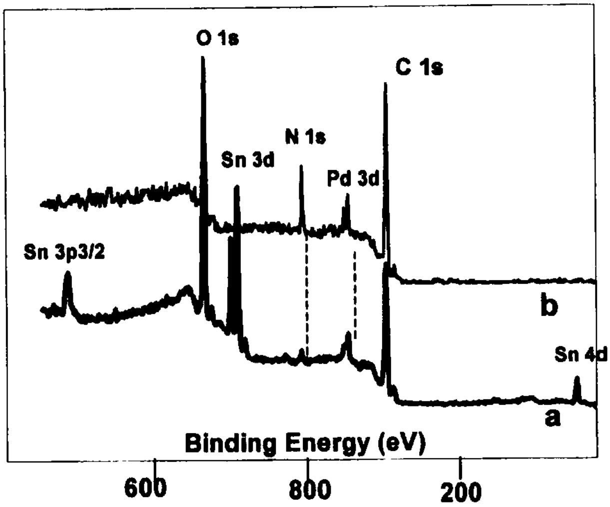


FIGURE 5 XPS survey spectra of a Kapton® 500 HN sample (a) VUV-treated in air at atmospheric pressure (treatment time: 1 min, power: 80%), then immersed successively in acidic $SnCl_2$ and $PdCl_2$ solutions and water rinsed, (b) VUV-treated in NH_3 at 5 mbar (treatment time: 1 min, power: 80%), then immersed in an acidic $PdCl_2$ solution and water rinsed.

which are naturally present at the surface of the polyimide. These results confirm that the use of the conventional sensitization-activation procedure requires the prerequisite grafting of oxygenated functionalities on the polymer surface, while the simplified activation procedure (sample immersion in a $PdCl_2$ acidic solution) requires the grafting of nitrogenated functionalities.

Consider now the route involving the deposition of palladium acetate (PdAc) films (Fig. 6(A)). As already pointed out in the "Introduction" section of this paper, the UV/VUV-induced decomposition of spin-coated PdAc films, *via* excimer lamps or lasers, has been extensively investigated by different authors [23–38] with a view to produce palladium-activated layers for a subsequent metal deposition in electroless plating baths. Given the specific behavior, previously emphasized in this work, of palladium species toward oxygen or nitrogen-grafted polymer surfaces, it was of considerable interest to study, at first, the chemical interactions capable of occurring between PdAc and such modified surfaces. XPS analysis

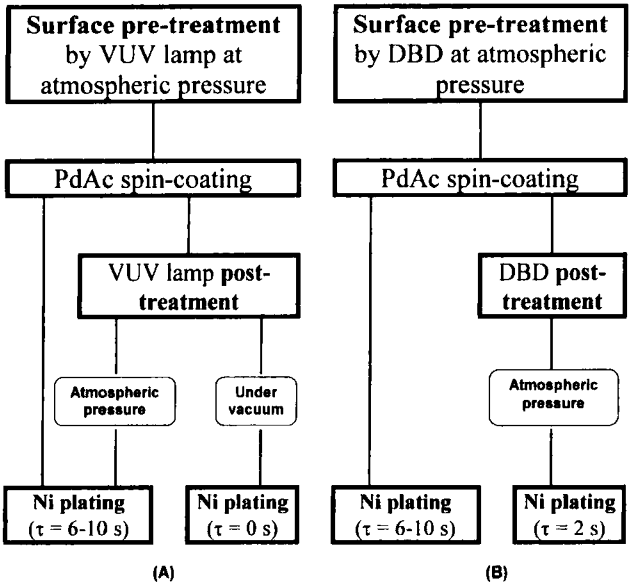


FIGURE 6 Schematic diagrams of the electroless plating processes involving the PdAc routes and using: (A) the VUV excimer lamp, (B) the DBD device.

shows that, after a VUV treatment in air for 1 min, the Pd surface concentration is about 7.3 at. %, while after the CH_3Cl rinsing this concentration decreases down to 0.2 at. %. Clearly, the PdAc molecules are weakly bonded to the oxygen-grafted surfaces since the solvent rinsing removes the major part of them. On the other hand, after a VUV treatment in NH_3 for 1 min, the Pd surface concentration is quite similar to that determined after the VUV treatment in air, but after rinsing this concentration remains noticeable (in the range 2–3 at. %). This means that some of the nitrogenated species grafted onto the polymer surface form strong "N—Pd" bonds.

Irrespective of the means chosen to functionalize the PI surfaces (VUV irradiation in air or in NH_3) and to attach the palladium species ($SnCl_2/PdCl_2$, $PdCl_2$ or PdAc routes) the problem is now to render these species catalytically active for the subsequent electroless metallization and, obviously, to create the desired adhesion between the electrolessly-deposited metal films and the palladium-activated substrates. For such a purpose, it is at first useful but not necessary to convert a sufficient surface density of the uptaken palladium species into Pd(0) nuclei. Although there is still considerable controversy on the question of whether palladium acts as a catalyst in the Pd(+2) or Pd(0) form, we have shown in different studies dealing more particularly with Ni deposition [18] that the chemical reduction takes place in the electroless bath thanks to the action of the reducing agent (sodium hypophosphite in the present case). It is interesting to note that the rate at which such reduction phenomena occur in the electroless solution would explain the more or less long initiation time from which the metallization itself starts. As UV/VUV irradiation has been shown to be able to initiate the photo-reduction of some metal-organic compounds such as PdAc, the possibilities offered by the Xe_2^* excimer lamp have also been investigated in this work with a view to reducing palladium species such as are attached onto the polymer surface ($PdCl_2$ or PdAc routes), *i.e.*, before the dipping of the substrate in the electroless bath. Such a reduction, when it takes place, can be shown by XPS from the binding energy of the Pd 3d5/2 peak. In the Pd(+2) form, this energy is located at about 338.0 eV and in the reduced Pd(0) form at 335.3–335.5 eV. Table I brings together some analytical results. They show that VUV post-treatments in air of samples Pd-grafted by the $PdCl_2$ and PdAc routes never cause the

TABLE I Surface atomic concentrations (at. %) and Pd $3d_{5/2}$ binding energy (eV) of Kapton® HN substrates which were surface functionalized in air (atmospheric pressure, 1 min) or NH_3 (5 mbar, 1 min), and then subjected to "activation" processes ($PdCl_2$ and PdAc routes)

Surface	*Subsequent surface treatments*	*Surface composition (at. %)*						E_b *(eV)*	*Comments*
functionalization	*before metallization*	*C*	*O*	*N*	*Cl*	*Sn*	*Pd*	*Pd* $3d_{5/2}$	*(Ni metallization)*
VUV/air (Atmospheric pressure, 1 min)	$SnCl_2 + PdCl_2$ + WR*	62.3	28.8	3.3	–	4.4	1.1	338.0	Bright and adherent Ni deposits ($\tau = 2$ s)
	$PdCl_2$ + WR*	70.8	22.7	6.1	–	–	0.3	338.1	No deposit
	$PdCl_2$ + WR* + VUV/AIR, 3 min	71.7	21.3	6.8	–	–	0.2	338.0	No deposit
	$PdCl_2$ + VUV/air, 3 min + WR*	73.0	19.9	7.1	–	–	0.0	–	No deposit
	PdAc	54.7	29.4	8.6	–	–	7.3	338.0	Poor adhesion of Ni deposits ($6 < \tau < 10$ s)
	PdAc + CR**	67.6	26.2	6.1	–	–	0.2	338.1	Poor adhesion of Ni deposits ($6 < \tau < 10$ s)
	PdAc + CR** + VUV/AIR, 3 min	64.3	27.2	8.3	–	–	0.2	338.0	Poor adhesion of Ni deposits ($6 < \tau < 10$ s)
	PdAc + VUV/air, 3 min + CR**	54.8	28.0	8.0	1.6	–	7.6	338.0	Poor adhesion of Ni deposits ($6 < \tau < 10$ s)
	PdAc + VUV/1 mbar, 3 min + CR**	62.0	16.3	5.5	1.8	–	14.4	**335.3**	Poor adhesion of Ni deposits ($\tau = 0$ s)
VUV/NH_3						–			
(5 mbar, 1 min)	$PdCl_2$ + WR*	65.5	23.3	10.1	–	–	1.2	338.1	Bright and adherent Ni deposits ($\tau = \sim 10$ s)
	$PdCl_2$ + WR* + VUV/AIR, 3 min	59.8	28.8	10.3	–	–	1.1	338.2	Bright and adherent Ni deposits ($\tau = \sim 10$ s)
	$PdCl_2$ + VUV/air, 3 min + WR*	62.1	26.6	10.8	–	–	0.5	338.2	Bright and adherent Ni deposits ($\tau = \sim 10$ s)
	$PdCl_2$ + VUV/1 mbar, 3 min + WR*	69.7	20.3	9.4	–	–	0.6	338.1	Bright and adherent Ni deposits ($\tau = \sim 10$ s)
	PdAc	54.8	26.1	11.2	–	–	7.9	338.1	–
	PdAc + CR**	58.0	22.9	16.8	–	–	2.3	337.9	Poor adhesion of Ni deposits (blisters)
	PdAc + CR** + VUV/AIR, 3 min	56.2	26.9	13.4	2.0	–	1.5	337.9	Bright and adherent Ni deposits ($6 < \tau = 10$ s)
	PdAc + VUV/air, 3 min + CR**	48.2	26.0	15.4	1.9	–	8.5	338.1	Bright and adherent Ni deposits ($6 < \tau = 10$ s)
	PdAc + VUV/1 mbar, 3 min + CR**	47.1	21.9	11.9	3.4	–	15.7	**337.5/ 335.6**	Bright and adherent Ni deposits ($\tau = 0$ s)
	PdAc + VUV/1 mbar, 5 min + CR**	52.9	19.4	8.7	2.2	–	16.7	**335.5**	Bright Ni deposits ($\tau = 0$ s) but poor adhesion (blisters)

* WR: water rinsing.
** CR: chloroform rinsing.

formation of metallic Pd. On the other hand, when the same samples are VUV post-treated in vacuum ($p = 1$ mbar) for 1 to 5 min, a chemical reduction takes place for the Pd species grafted from the PdAc route while it does not for the Pd species grafted from the $PdCl_2$ route. It can be concluded that VUV photons do not act in the same manner on the Pd(+2) species chemisorbed from $PdCl_2$ solutions as on the molecular PdAc species attached from PdAc solutions. The chemical reduction of the PdAc species is evidenced: (i) by the progressive shift, when the VUV treatment time increases, of the binding energy of the Pd 3d5/2 peak from about 338.0 eV (energy characteristic of Pd(+2) species) to about 335.5 eV (energy characteristic of metallic palladium), (ii) by the increase of the palladium surface concentration during the VUV/vacuum irradiation. This fact confirms (mass spectrometry results) that gaseous products such as H_2O^+, CO_2^+, CH_3C^+, CH_3CO^+ and CH_3^+ are produced during VUV exposure [28, 34]. Obviously, the results presented in Table I are only characteristic of the material thickness analyzed by XPS (*i.e.*, a few nm). Nevertheless, they confirm previous studies [23–29, 35] carried out by UV transmission spectroscopy on thicker PdAc films which were spin-coated on quartz substrates and irradiated with UV/VUV photons emitted by different incoherent excimer lamps or special silent discharge devices of various configurations.

In addition, data in Table I show that adhesion of Ni films (as determined using the standardized Scotch® tape test) is strongly influenced by the chemical groups formed on the polymer surface. The best electroless deposition results (formation of bright and well-adherent Ni deposits) are obtained when the substrate is first VUV-treated in NH_3, *i.e.*, when nitrogenated groups are grafted on the polymer surface. In all cases, the "activation" process using the $PdCl_2$ route has to be recommended as quite reproducible and as achieving continuous metallized films. On the other hand, extremely different results are observed when the PdAc route is followed, the adhesion level of the Ni films being very dependent on the pre-deposition conditions (irradiation atmosphere, irradiation time, ...). Nevertheless, some of these conditions also allow the deposition of electroless Ni layers which cannot be removed with the adhesive tape, therefore, which adhere well to the polymer surface. It can also be seen from data in Table I that the "activated" surface becomes catalytically active only after a certain period of time ($\tau = 6-10\,s$) in the electroless bath, when the VUV treatments in air or in vacuum do not lead to the chemical reduction of the palladium species such as deposited (in case of both $PdCl_2$ and PdAc routes). Under these conditions, the reducer (hypophosphite) of the electroless bath is responsible for the chemical reduction, hence, for the starting of the metallization itself. On the other hand, when the VUV post-treatments in vacuum cause the chemical reduction of the palladium species (in case of the PdAc layers), metallization starts as soon as the samples are dipped in the plating bath, *i.e.*, without any initiation time ($\tau = 0$). Clearly, these results support, once again, the key role that metallic palladium plays in the catalysis of the electroless plating. Lastly, it should be noted that too-high surface amounts of metallic palladium have sometimes been observed to lead to a decomposition of the electroless bath (home-made solution used in a small volume in the present work). It should be borne in mind that industrial baths contain ions of the metal to be plated, reducer, buffers and chelating agents, as well as stabilizers which are required to inhibit a rapid decomposition. Furthermore, all the experimental investigations carried out in this section clearly demonstrate the difficulty of obtaining reproducible results concerning the surface composition of samples treated through the PdAc route, in comparison with those obtained for samples which are surface-modified through the $PdCl_2$ route.

DBD Treatments in Air at Atmospheric Pressure

This series of experiments is also related to Kapton® 500 HN samples. The DBD surface treatments were carried out in air at atmospheric pressure by using the device shown in Figure 2(B). As found in our AFM investigations, such treatments are responsible for a noticeable etching of the material surface. For example, the average roughness (R_a) as determined over a $1\,\mu m^2$ area for a sample DBD-treated for 1 min, increases from 1.3 ± 0.5 to 10.6 ± 7.8 nm. For example, Figure 7 represents optical micrographs of a Kapton® HN surface before and after a DBD treatment in air for 1 min (power = 35 W), as well as the corresponding AFM images of a $1\,\mu m^2$ area scanned zone. In both cases, the surface roughness can be clearly seen. In comparison, it should be mentioned that no change in R_a is observed for the same

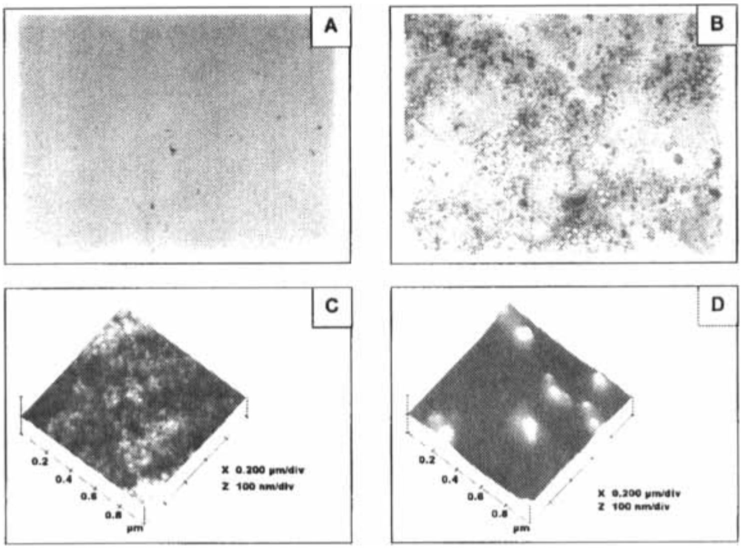


FIGURE 7 Optical micrographs (magnification × 300) and AFM images (scanned zone = 1 × 1 µm) of the surface of a Kapton® 500 HN sample (A) and (C) before, and (B) and (D) after a DBD treatment in air for 1 min.

substrate after an excimer VUV irradiation in air for 1 min using the setup shown in Figure 2(A). On the other hand, a polyimide sample containing alumina particles as inorganic fillers (Kapton® MT samples) has its R_a strongly enhanced from 9.6 ± 5.6 to 85.0 ± 19.9 nm after a DBD treatment in air for 1 min [39]. This results from the selective etching of the organic part of this sample, which lays the fillers bare.

Moreover, the DBD treatment of the Kapton® HN substrate leads to surface oxidation. For a 1 min treatment time, the oxygen surface concentration increases from 15.0 to 18.4 at. % while that of carbon decreases from 78.6 to 70.0 at. % and that of nitrogen increases from 6.4 to 11.7 at. % (XPS results). Indeed, after the DBD treatment, the O 1s peak is somewhat broadened toward the low-binding-energy side, suggesting the presence of oxygen atoms bonded to other electronegative atoms. This surface oxidation is confirmed by the intensity decrease of the $\pi \rightarrow \pi^*$ shake-up satellite envelope on the high-energy side of the O 1s peak. In other words, this decrease results from a partial opening of the aromatic rings, which makes nitrogen and carbon atoms available for oxidation. In addition, this surface

TABLE II Surface atomic concentrations (at. %) and Pd $3d_{5/2}$ binding energy (eV) of Kapton® HN substrates which were DBD surface treated in air (atmospheric pressure, 1 min) and then subjected to "activation" processes ($PdCl_2$ and PdAc routes)

	Surface composition (at. %)					E_b *(eV)*	*Comments*
Treatments	*C*	*O*	*N*	*Pd*	*Sn*	*Pd* $3d_{5/2}$	*(Ni metallization)*
(a) DBD/air,1 min	70.0	18.4	11.6	–	–	–	–
(b) the same as (a) + $PdCl_2$ + WR*	74.2	18.5	6.6	0.7	–	338.1	Bright and adherent Ni deposits ($\tau = 20$ s)
(c) the same as (a) + PdAc	65.3	27.5	9.0	3.2	–	338.0	Bright/dull Ni deposits – Poor adhesion (blisters) – Immediate bath decomposition
(d) the same as (a) + PdAc + CR**	72.3	20.1	7.0	0.6	–	338.0	
(e) the same as (c) + DBD/air, 1 min + CR**	71.8	19.7	7.3	1.2	–	338.1	Dull and well-adherent Ni deposits (bath decomposition after 16 s)
(f) the same as (a) + $SnCl_2$ + $PdCl_2$ + WR*	65.4	25.4	5.2	1.2	3.1	338.0	Bright and adherent Ni deposits ($\tau = 2$ s)

•WR: water rinsing.

**CR: chloroform rinsing.

oxidation is also clearly observed from the appearance of a new component at about 407.4 eV in the N 1s spectrum. This component, located at about +6.2 eV in comparison with the binding energy of nitrogen atoms from the imide rings (401.2 eV), is due to the formation of NO_2/NO_3-type groups [41] which can be explained by the strong oxidizing power of ozone molecules (O_3) and atomic oxygen (O) produced by the silent discharge operating in air. This result is interesting to note since no similar effect has ever been observed under oxygen plasma or VUV irradiation in air by using the Xe_2^* incoherent excimer lamp. On the other hand, the formation of NO_2 groups has already been reported by Foerch and co-workers [42]. These authors have subjected polyethylene and polystyrene substrates to a two-step process consisting in a nitrogen-plasma treatment followed by a corona-discharge treatment in air. Under these conditions, nitrogen atoms from the nitrogenated species grafted during the plasma treatment are oxidized during the corona discharge.

In addition, Table II brings together some data concerning the surface atomic concentrations of samples DBD-treated then activated using the $PdCl_2$ and PdAc routes, respectively. Several comments can be made from the analysis of these data:

- The DBD-treated surface contains both enough oxygenated and nitrogenated groups to allow the deposition of bright and adherent Ni deposits after the "activation" sequence using either the simplified $PdCl_2$ route (sample (b)) or the conventional $SnCl_2/PdCl_2$ two-step procedure (sample (f)). In the first case, it can be assumed that the Pd surface concentration (0.7 at. %) is due to the chemisorption of the Pd(+2) species on the nitrogenated functionalities (nitrogen surface concentration ~6.6 at. %). However, it is also possible that the surface roughness created by the DBD treatment which increases the surface area and lays more nitrogenated groups bare, favors the palladium grafting. In the second case, the relatively high Pd surface concentration (1.2 at. %) is associated with the significant tin surface concentration (3.1 at. %), the Sn(+2) species being chemisorbed onto the oxygenated functionalities.
- When the PdAc route is considered after the DBD pre-treatment (Fig. 6(B)), bright/dull Ni deposits with poor adhesion (appearance

of blisters) are achieved (samples (c) and (d)). On the other hand, an additional DBD post-treatment in air allows one to obtain dull and well-adherent Ni deposits (sample (e)). When the DBD post-treatment is used, it causes a decrease of the Pd surface concentration (etching action of the DBD treatment on the PdAc layer) which avoids rapid bath decomposition. It should also be noted that dull deposits result probably from the increase of the surface roughness while deposits obtained after VUV irradiation (see previous section) are always bright.

As was shown after a surface pre-treatment by VUV, a surface pre-treatment by DBD followed by an activation procedure through the $PdCl_2$ route provides much more reproducible results in terms of surface composition than those obtained using the PdAc route. In other respects, it should be emphasized that more homogeneous Ni deposits are formed through the $PdCl_2$ (or the $SnCl_2/PdCl_2$) route than through the PdAc one.

CONCLUSIONS

The results described in this paper demonstrate:

1. The specific interest of grafting nitrogenated functionalities (through the use of the Xe_2^* excimer lamp as the VUV source and ammonia as the working atmosphere) for promoting the subsequent attachment of the palladium-based catalyst on the polymer surface. The relevant chemisorption is rendered possible thanks to the strong chemical affinity of palladium toward nitrogen. Palladium can be grafted either as Pd(+2) from a $PdCl_2$ solution or in the molecular form from a PdAc solution in chloroform. In both cases, the chemical reduction to the Pd(0) state can be performed in the plating bath, thanks to the presence of a strong reducer (hypophosphite). However, when the PdAc route is used, it is possible to reduce the PdAc molecules *via* a VUV post-treatment in primary vacuum which allows an immediate plating. In all cases, bright and well-adherent Ni deposits are obtained.
2. The potential of the conditioning treatments carried out in air at atmospheric pressure either by DBD or by excimer lamp. These

treatments graft oxygenated functionalities and increase wettability. Furthermore, the DBD treatment causes a surface roughness. In both cases, the conventional process ($SnCl_2/PdCl_2$ route) used to render the surface catalytic leads to the deposition of well-adherent nickel films. In both cases too, PdAc can be attached in a molecular form on the surface oxygenated functionalities but without a true chemisorption since the solvent rinsing eliminates the major part of the PdAc layer. However, Ni deposits can be obtained just after the PdAc spin-coating (*i.e.*, without the rinsing step) but they are little-adherent. On the other hand, a VUV treatment in air of the PdAc film allows the anchoring of the PdAc molecules while a VUV treatment in primary vacuum leads to their decomposition and to the formation of Pd(0) nuclei. In the latter case, metallization starts immediately and leads to bright but little-adherent Ni films (blisters). Finally, even though a DBD treatment in air of the PdAc films does not reduce the PdAc molecules, it allows the formation of well-adherent Ni films thanks to the surface roughness that it creates.

Lastly, it should be pointed out that extensive researches have still to be carried out to get a better adhesion of Ni deposits when the surface "activation" is performed through the PdAc route. Indeed, the question of how the PdAc layer (before and after its chemical reduction *via* a VUV irradiation or a DBD treatment) "adheres" to the surface of the polymeric substrate remains largely unanswered.

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