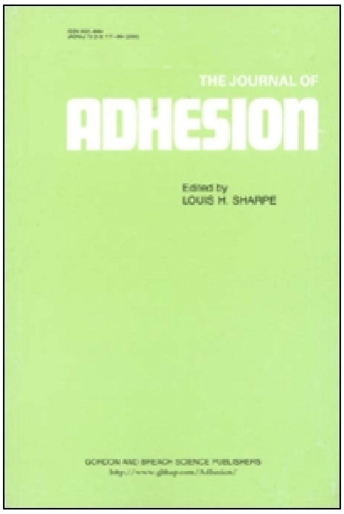


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

ELECTROLESS PLATING OF GLASS AND SILICON SUBSTRATES THROUGH SURFACE PRETREATMENTS INVOLVING PLASMA-POLYMERIZATION AND GRAFTING PROCESSES

Marlene Charbonnier[a]; Yves Goepfert[a]; Maurice Romand[a]; Didier Leonard[b]
[a] Laboratoire de Sciences et Ingénierie des Surfaces, Villeurbanne cedex, France [b] UMR des Sciences Analytiques, Villeurbanne cedex, France

To cite this Article Charbonnier, Marlene , Goepfert, Yves , Romand, Maurice and Leonard, Didier(2004) 'ELECTROLESS PLATING OF GLASS AND SILICON SUBSTRATES THROUGH SURFACE PRETREATMENTS INVOLVING PLASMA-POLYMERIZATION AND GRAFTING PROCESSES', The Journal of Adhesion, 80: 12, 1103 — 1130

To link to this Article: DOI: 10.1080/00218460490884132
URL: http://dx.doi.org/10.1080/00218460490884132

The Journal of Adhesion, 80: 1103–1130, 2004
Copyright © Taylor & Francis Inc.
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460490884132

ELECTROLESS PLATING OF GLASS AND SILICON SUBSTRATES THROUGH SURFACE PRETREATMENTS INVOLVING PLASMA-POLYMERIZATION AND GRAFTING PROCESSES

Marlene Charbonnier
Yves Goepfert
Maurice Romand
Laboratoire de Sciences et Ingénierie des Surfaces, Université Claude Bernard—LYON 1, Villeurbanne cedex, France

Didier Leonard
UMR des Sciences Analytiques, Université Claude Bernard—LYON 1, Villeurbanne cedex, France

Electroless plating of nickel (or copper) was carried out on glass (or silicon) substrates that were previously surface modified by using plasma-polymerization and grafting processes, and then activated by immersion in a simple acidic $PdCl_2$ *solution. Three pretreatments based on the deposition of plasma-polymerized thin films (PACVD process) on* O_2 *plasma-cleaned substrates were investigated. They include film deposition of (1) amorphous hydrogenated carbon (a-C:H) grown from* CH_4*, whose surface is subsequently plasma-functionalized in* NH_3 *or* N_2*; (2) amorphous hydrogenated carbon nitride (a-*CN_x*:H) grown from* CH_4/NH_3 *or* CH_4/N_2 *mixtures; and (3) amorphous hydrogenated carbon nitride grown from volatile organic precursors (allylamine, acetonitrile).*

In the three cases, X-ray photoelectron spectroscopy (XPS) results show that chemisorption of the catalyst occurs on the nitrogen-containing functionalities created by plasma polymerization and grafting and thus that the electroless deposition is possible. Differences were observed depending on the nature and thickness of the plasma-polymerized thin films, as well as on the nature and concentration of the nitrogen-containing functionalities present or grafted at the surface. Practical adhesion of Ni films was investigated using a Scotch® tape test. Ni films up to 3 or

Received 20 October 2003; in final form 29 March 2004.

Presented in part at the 26th Annual Meeting of The Adhesion Society, Inc., Myrtle Beach, South Carolina, USA, 23–26 February 2003.

Address correspondence to Maurice Romand, Laboratoire de Sciences et Ingénierie des Surfaces (LSIS), Université Claude Bernard–LYON 1, Bât. J. Raulin, 43 Boulevard du 11 Nov. 1918, F-69622 Villeurbanne cedex, France. E-mail: Maurice.Romand@univ-lyon1.fr

4 μm in thickness were shown to pass this test successfully, i.e., without causing any metal detachment.

Keywords: Glass; Silicon; Ceramics; Substrate pretreatment; Plasma polymerization; PACVD process; Plasma grafting; Palladium chemisorption; Electroless plating; Peel test; Adhesion; XPS analysis

INTRODUCTION

Electroless plating [1–3] is a chemical process widely used in the automotive, aerospace, packaging, appliance, optics, and microelectronics industries to metallize (generally using Ni or Cu) a variety of insulating materials including glasses, ceramics, and engineering plastics or composites. Numerous applications involving, for example, capacitors, sensors, activators, solar cells, ohmic contacts, chip level interconnections and printed circuit boards, magnetic disks, plastic enclosures for electronic devices (EMI/RFI shielding), masks for photolithography ... are reported [1, 4−15]. However, the electroless plating of nonconducting substrates requires the use of complicated, time-consuming and often environmentally unfriendly procedures [16, 17]. Consequently, it is highly desirable to develop new, more economically and ecologically attractive routes prior to the final metallization step. More precisely, in comparison with the conventional methods in common industrial use (see next section), the prerequisites are that the new approaches should be applicable to various substrates, reduce the use of hazardous chemicals as well as the number of processing steps, minimize the material surface roughening and finally provide a strong chemical adhesion at the "metal/substrate" interface through a strong attachment of the catalytic species (generally, the Pd-based catalysts needed to initiate the metal deposit) to the substrate surface [18].

The main purpose of the present work is to show how an electroless plating process, previously developed by some of the authors of this article for metallizing polymer surfaces, can be extended to the case of glasses, silicon, and ceramics substrates. First, the process is described in the case of polymer substrates.

ELECTROLESS PLATING OF POLYMER SUBSTRATES

Electroless plating is basically a process that operates in an aqueous solution containing the ions of the metal to be deposited (generally nickel or copper ions) and a reducing agent such as sodium hypophosphite or formaldehyde (case of Ni or Cu deposit, respectively). The process is considered as "electroless" because the electrons required for the reduction of the metallic cations (Ni^{+2} or Cu^{+2}) are supplied by the reducing agent and not by an external electrical source. The overall equation for the deposition of nickel or copper by their respective reducing agents can be written as follows:

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

and

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

Note that Ni^{+2} or Cu^{+2} reduction only takes place on specific catalytic surfaces constituted by Ni or Cu themselves in the metallic state, which makes the reduction process autocatalytic and ensures the continuous building up of the metal film. It is also worthwhile to point out that the reducing agents provide the electrons for the aforementioned reactions, and furthermore they are responsible for the incorporation of additional elements into the metal coatings. For example, when sodium hypophosphite is used in an electroless Ni bath, the resulting deposit is, in fact, a nickel–phosphorus (Ni–P) alloy. In addition, the commercial electroless baths contain various additives, including complexing agents that control the amount of free metal ions as well as buffering and wetting agents, step-coverage and ductility promoters, and stabilizers/inhibitors that prevent the spontaneous decomposition of the plating baths.

In the case of nonconducting substrates, the initiation of metallization is conventionally preceded by an activation procedure to provide catalytic sites at the material surface. The first developed process [19–25] consisted of two steps (Figure 1, route on the left). After solvent cleaning, chemical etching (generally in chromic acid/sulfuric acid solutions), and rinsing, step 1 involves the substrate treatment in a stannous chloride/hydrochloric acid solution (sensitization step), which leads to the surface adsorption of stannous species (Sn^{+2}). After rinsing, step 2 requires 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+} species to be chemically reduced to the Pd^0 state by the Sn^{2+} species, according to the redox reaction [17]

$$Pd^{2+} + Sn^{2+} \rightarrow Pd^0 + Sn^{4+}.$$

The so-formed Pd^0 sites are then capable of initiating the electroless metallization. Another process of activation (also known as the *one-step process*) was later introduced and is commonly used in industry today [21, 26–30]. This procedure (Figure 1, route on the right) involves the

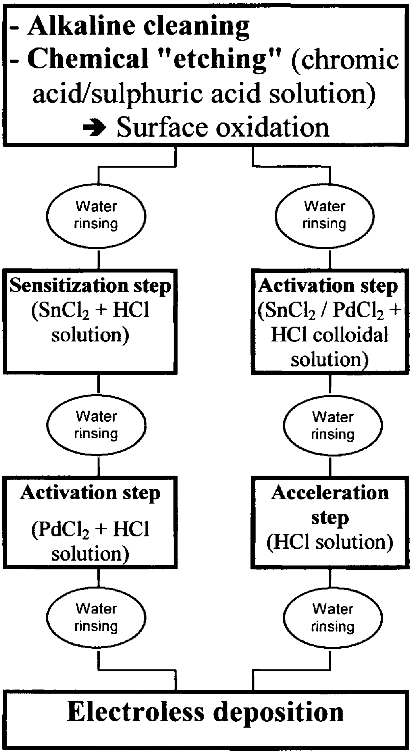


FIGURE 1 Schematic diagram of the conventional electroless plating processes using chemical pretreatments and the two-step (on the left) or one-step (on the right) route, leading to the surface activation of insulating substrates—in particular, of polymer substrates.

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 hydroxides. This surface excess of stannous ions must be removed from the colloidal particles to allow the palladium sites to act as a catalyst for initiating the metal deposition in the electroless bath. This postactivation step (also known as the acceleration step) is accomplished by dissolving the stannous hydroxides, for example, in a hydrochloric acid solution.

As seen above, the wet chemical processes employed to prepare the polymer surfaces before metallization use environmentally unfriendly and often hazardous chemicals. That means that manufacturers must deal with the production of by-products, and therefore with waste treatments and recyclability operations. Specific problems are also encountered with the use of the one-step process because the colloidal solutions exhibit activity and stability strongly dependent on the chloride and stannous ion concentrations. It is why a continual maintenance of the activating solutions is required through chemical analysis [16]. In addition, the postactivation (acceleration step) is far from being a simple operation [16, 17]. As highlighted by Brandow *et al.* [30], an incomplete removal of the outer Sn^{+2} shell leaves dormant catalytic sites, which inhibit the action of the electroless bath. In contrast, an excessive removal of the stannous shell leads to the detachment of many activating species adsorbed at the polymer surfaces, which makes the plating initiation in the electroless bath difficult. For all these reasons as well as others [16, 17] not described here, there exists a growing demand for new processes that lead to an efficient electroless metallization through a reduced number of surface-conditioning steps that avoid any use of environmentally harmful chemicals, and are tin free.

An approach was developed in our laboratory [31–41] on the basis of the specific chemical affinity of palladium towards nitrogen-containing groups. This process uses a simple acidic $PdCl_2$ solution for Pd^{2+} seeding of polymer surfaces which were previously functionalized using N_2 and/or NH_3 plasma or vacuum ultra violet (VUV) irradiation treatments (Figure 2, route on the right). It was also shown that O_2–plasma-treated polymer surfaces do not graft palladium directly and require the use of the conventional route (*i.e.*, that of acidic $SnCl_2$ and $PdCl_2$ solutions) to obtain the palladium seeding through the chemisorption of tin species (Figure 2, route on the left). This is explained by the specific chemical affinity of tin towards oxygenated groups and the lack of the palladium affinity towards these same groups. These results dealing with the adsorption of palladium species (in fact, Pd^{2+} species as shown by XPS) show the selectivity of the chemisorption phenomenon and prove that Pd^{2+} species are not simply physisorbed on the surface-modified polymers [42].

The routes described in Figure 2, and particularly those using plasma or VUV treatments in a nitrogenated atmosphere, were shown to operate quite well when electroless Ni plating is carried out in laboratory-made baths. It was not so easy (long initiation times resulting in low deposition rates and poor covering deposits) when electroless Cu plating was performed using laboratory-made baths or when Ni or Cu metallizations were undertaken using proprietary electroless formulations. Formaldehyde, the reducing agent present in the Cu plating baths, was shown to be not strong enough to reduce the surface-grafted Pd^{2+} species to the Pd^0 state [41]. Consequently, it was necessary to perform Pd^{2+}

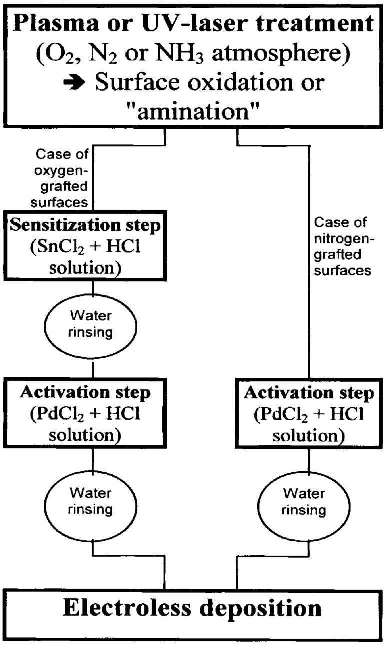


FIGURE 2 Schematic diagram of the electroless plating processes using plasma or VUV pretreatments of polymer surfaces in oxygenated (route on the left) or nitrogenated (route on the right) atmospheres.

reduction prior to dipping the activated substrates in the electroless Cu solution. Furthermore, it was emphasized that stabilizers present in the proprietary Ni baths prevent the Pd^{2+} to Pd^0 reduction, probably because of adsorption of these stabilizers on the Pd^{2+} catalytic sites. All of these problems were overcome by treating the Pd^{2+}-grafted surfaces in a hypophosphite ($H_2PO_2^-$) solution prior to their immersion in the Ni or Cu plating baths (Figure 3). It was demonstrated that (1) Pd^0 is the real catalyst initiating the electroless redox reaction at the polymer surface, and (2) it is possible to develop an industrial process allowing the electroless Ni or Cu metallization *via* the chemisorption of nitrogen-containing groups [41].

In all the experiments carried out recently using this new process and commercial electroless baths, the use of a Scotch® tape peel test (cross-hatched peel test) has shown that a good practical adhesion of some micrometer-thick Ni or Cu coatings to polyimide substrates is obtained because no metal part is stripped off by the tape [42]. Identically, substrates such as poly(butylene terephthalate) (PBT) or poly (phenylene sulfide) (PPS), which are known as very resistant to metal

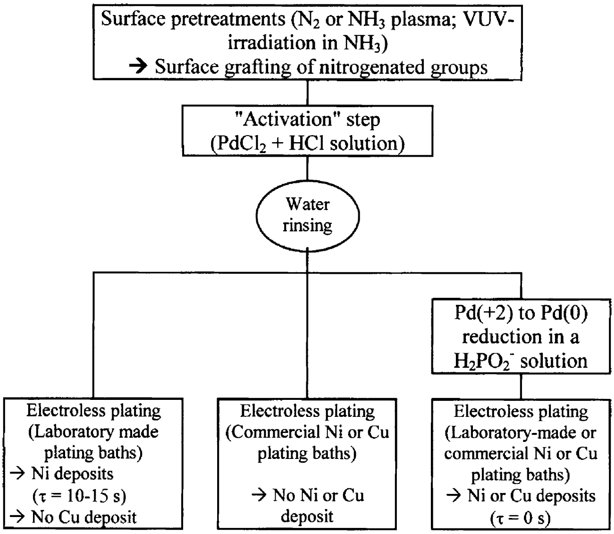


FIGURE 3 Schematic diagram of the routes that were investigated in order to establish an industrial, viable electroless plating process, through to the grafting of nitrogenated functionalities on polymer surfaces (plasma or VUV-assisted treatments) and the subsequent activation of the functionalized surfaces (immersion in an acidic $PdCl_2$ solution). The initiation time τ (in seconds) is the time required to observe the starting of the metal deposition when the pretreated substrates are immersed in the electroless plating solution.

deposition when standard electroless processes are implemented, pass the Scotch® tape test when they are coated with some micrometer-thick Ni or Cu films, or even when the latter are overplated with a Cu film by electroplating [43]. In addition, thin electroless Ni films (less than 1 μm thick) were shown to be very adherent to poly(carbonate) or poly(imide) substrates when coated specimens are subjected to a fragmentation test in conjunction with an original approach. The latter consists of recording the changes in the relative electrical resistance of the metal coatings when the coated specimens are strained under uniaxial tension [42, 44–46].

OTHER TIN-FREE PROCESSES USED TO PRODUCE ELECTROLESS METALLIZATION OF POLYMER AND CERAMIC SUBSTRATES

Vargo *et al.* [47] first described a process to deposit blanket or patterned metal films through a tin-free way on fluoropolymer substrates.

This process involves hydroxylation of the substrate surface by plasma treatment in a H_2–H_2O or H_2–CH_3OH flowing vapor mixture, covalent attachment of an organosilane (solution of N-(2-aminoethyl)-3 aminopropyltrimethoxysilane (EDA)) to the hydroxylated surfaces, coordinative bonding of Pd^{2+} species (from tin-free aqueous catalyst solutions) to the silanized surface, and metallization by immersion in a Ni electroless plating bath. Calvert and coworkers also plated a variety of nonconducting substrates such as polyimide, silicon, or silica [18, 30, 48–50]. These authors produced ligand-bearing surfaces by self-assembly of appropriate aminosilanes such as N-2-(trimethoxysilyl) ethyl-2-pyridineor(aminoethylaminomethyl)phenethyltrimethoxysilane, and they carried out the catalysis of the chemisorbed ligand-bearing organosilanes by immersion in an acidic $PdCl_2$ solution. These approaches lead to a selective attachment of the Pd^{2+} species on the amine groups. On the other hand, no catalyst adsorption occurs when the deposited organosilanes are not bearing nitrogen functionalities. Films produced by self-assembly yield a covalently bonded organic film approximately one monolayer thick (0.5–2.5 nm), and the process can be used to fabricate high-resolution metal patterns through microlithographic technologies (film exposure to masked UV/VUV radiations from excimer lasers or lamps). In addition, the method described by Hidber *et al.* [51] for forming micrometer- and submicrometer-scale patterns of copper on glass, (SiO_2/Si), and polymers must be reported. This method uses a patterned elastomeric stamp (poly(dimethylsiloxane)-based fabrication) to deliver the catalyst (palladium colloids stabilized with tetraalkylammonium bromides) to the substrate surfaces that were previously submitted to silanization (substrate immersion in a solution of an organosilane in ethanol or heptane). Under these conditions, the contact between the stamp and the substrate allows the transfer of the colloid, the subsequent electroless metallization, and the formation of structures with micrometer-scale features. Various organosilanes with different terminal groups were used. The use of a Scotch® tape test shows that silanization with organosilanes carrying nitrogen-containing terminal functionalities (amino groups) provides a "complete adhesion" of the metal film to the surface.

The specific reactivity of palladium species towards nitrogen-containing functionalities was also used to metallize (electroless Ni coatings) carbon [52, 53] and glass [54–56] substrates through processing involving deposition of thin films by plasma techniques. In the former case (carbon substrate), hydrogenated carbon nitride (a-CN_x:H) films were produced by magnetron sputtering of a graphite target using various Ar/N_2 sputtering gas combinations. In the latter case, the a-CN_x:H films were also produced by plasma polymerization (PACVD process) of CH_4/N_2 or CH_4/NH_3 mixtures. Wang *et al.* [57] have recently carried out electroless plating of copper on polyimide substrates pretreated by Ar plasma, then coated by plasma-graft copolymerization of 4-vinylpyridine. Subsequently, these films were activated directly in an acidic $PdCl_2$ solution (*i.e.*, through a tin-free process) and then metallized by deposition of copper in a laboratory-made electroless bath.

Another strategy consists in performing the UV/VUV photodecomposition of suitable organometallic compounds such as palladium acetate (PdAc) deposited on polymer surfaces from chloroform solution [31, 32, 58–73]. The so-formed Pd films acts as a catalyst for a subsequent metal deposition.

EXPERIMENTAL

All surface treatments and subsequent electroless metallizations were carried out on glass slides provided by Labonord, France and on silicon wafers covered with a native oxide (SiO_2) layer. Before use the substrates were ultrasonically cleaned in ethanol.

Plasma processing was performed in a parallel plate radio-frequency (RF) reactor operating in the Reactive Ion Etching mode (RIE 80 reactor from Plasma Technology, Bristol, England). The base pressure was 10^{-3} Torr. Plasma cleaning was done using O_2 under the following experimental conditions: working pressure = 100 mTorr, flow rate = 100 sccm, power density = $0.5\,W\,cm^{-2}$, treatment time = 2 min. Amorphous hydrogenated carbon (a-C:H) films were deposited by a PACVD process from a CH_4 gas phase (working pressure = 100 mTorr, flow rate = 50 sccm, power density = $0.5\,W\,cm^{-2}$) and subsequently functionalized using NH_3 or N_2 (100 mTorr, 100 sccm, $0.5\,W\,cm^{-2}$). Similarly, amorphous hydrogenated carbon nitride (a-CN_x:H) films were deposited from various CH_4/NH_3 or CH_4/N_2 gas mixtures (100 mTorr, 100 sccm, $0.5\,W\,cm^{-2}$). Post-functionalization of these films was carried out using NH_3 or N_2 plasma treatment. In addition, a-CN_x:H films were deposited by plasma-graft polymerization using allylamine ($H_2C{=}CH_2{-}CH_2{-}NH_2$) (AA) and acetonitrile ($CH_3{-}C{\equiv}N$) (AN) as precursor monomers. In these experiments, the monomer molecules were allowed to flow freely into the plasma reactor from the saturated vapor at room temperature (boiling point = 58°C for AA and 84.6°C for AN).

The glass substrates were seeded with Pd^{2+} species from a solution containing 0.1 g/l $PdCl_2$, and 0.1 ml/l concentrated HCl was used to perform the activation process. Prior to metallization, the activated surfaces were dipped in a hypophosphite ($H_2PO_2^-$) solution (10 g/l, 85°C, 3 min) in order to reduce the surface-grafted Pd^{2+} species to Pd^0.

Metallization was carried out in a commercial electroless nickel plating bath (Enplate® Ni 426) supplied by Enthone-OMI, Marne la vallée, France.

XPS (X-ray photoelectron spectroscopy) analyses were performed using a Riber SIA 200 spectrometer (Riber, Rueil Malmaison, France) using a nonmonochromatized Al K_α X-ray source and a take-off angle of 65° with respect to the specimen surface. All spectra were referenced to the C 1s peak at a binding energy of 285.0 eV characteristic of C–C and C–H bonds. The standard deviation of binding energy measurements was determined to be ±0.15 eV. Low-energy electron-induced X-ray spectrometry (LEEIXS) analyses were conducted with a wavelength-dispersive X-ray spectrometer (WDS) in which the excitation source is an electronically stabilized gas discharge tube (cold cathode tube) [74–77]. This source is used to generate a nonfocused electron beam under the primary vacuum of the X-ray spectrometer. In the present experiments, a 3 keV electron beam (current density $= 0.1\,\mathrm{mA\,cm^{-2}}$) was used to bombard the sample surface. Characteristic X-rays (C K_α radiations in this study) were dispersed using an octadecyl hydrogen maleate crystal (interspacing distance $2d = 6.35$ nm) and detected with a ($Ar + 10\%\ CH_4$) flow-proportional counter necessary to perform WDS in the soft and ultrasoft X-ray range.

Water contact angles were measured with an automated sessile drop apparatus (Digidrop model from GBX Scientific Instruments, Romans/Isère, France). Metal-to-glass adhesion was evaluated using a standard Scotch® tape test (ASTM D 3359–97). If no metal squares are removed by the Scotch® tape, test value (TV) is equal to 5. If metal squares are removed, the adhesion is then qualified by smaller TV values (4 to 0).

ELECTROLESS PLATING OF GLASSES: RESULTS AND DISCUSSION

The results obtained are quite similar for glasses and silicon wafers with native oxide layer. Therefore, only glass substrates will be discussed in this report.

The solvent cleaning in ethanol was not efficient enough to remove the hydrocarbon contamination (20 at. % C are still detected after this step by XPS analysis). On the other hand, O_2 plasma treatments led to a strong decrease in this contamination (9 at. % C) to a complete disappearance of sodium and magnesium from the outermost surface layers of glass and, consequently, to a strong increase of the surface energy (water contact angle <2°). Under these conditions, subsequent experiments were all performed on such O_2 plasma-treated samples.

Since previously obtained results on the chemical reactivity of palladium-based catalysts on N-functionalized polymer surfaces, an attempt was made to attach nitrogen-containing groups directly on glass substrates from NH_3 or N_2 plasmas. These experiments were unsuccessful in terms of metallization. This can be explained by the difficulty in binding electronegative nitrogen species to oxygen-rich surfaces; also, when some of these species are present they are dragged into the acidic $PdCl_2$ solution. To overcome these problems, other alternatives were considered. They are described in Figure 4.

The first approach (Figure 4a) consists of PACVD deposition of thin films of amorphous hydrogenated carbon (a-C:H) using CH_4. The surface of such films is then functionalized using NH_3 or N_2 plasma treatment in the same reactor, *i.e.*, without any vacuum break. The second approach (Figure 4b) aims at bringing together the two previous steps in one unique process. A PACVD process is

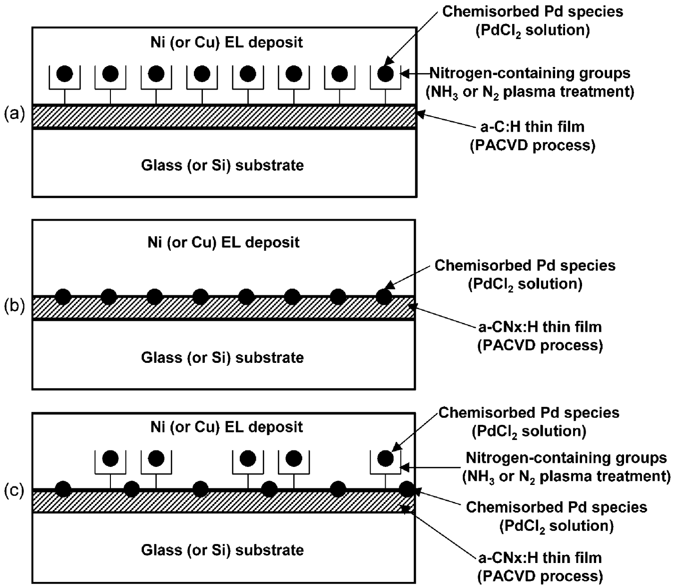


FIGURE 4 Methods used in the present work to metallize glass (or silicon) substrates *via* electroless plating (Ni or Cu deposition). Routes (a) to (c) require substrate pretreatments (PACVD and surface-grafting processes), leading to the chemisorption of nitrogenated functionalities at the surface.

used to deposit thin films of amorphous hydrogenated carbon nitride (a-CN$_x$:H) from CH_4/NH_3 or CH_4/N_2 mixtures. Some plasma post-treatments in NH_3 or N_2 were also carried out (Figure 4c) in order to increase the surface density of nitrogen-containing functionalities of the (a-CN$_x$:H) films. These three processes are based on approaches used in previous works. The route (a) described in Figure 4 and involving the deposition by plasma of a-C:H films and their subsequent functionalization by NH_3 plasma was investigated in order to promote bonding of such films (deposited on stainless steels) with epoxy resins [78]. As already mentioned, the routes (b) and (c) also described in Figure 4 and involved the deposition of a-CN$_x$:H films and their possible postfunctionalization by NH_3 or N_2 plasma were reported in order to metallize carbon [52, 53] and glass [54–56] substrates using electroless Ni.

Figure 5 displays XPS wide-scan spectra of PACVD films deposited from CH_4 in 2 min (a), then plasma treated for 10 s in NH_3 (b) or N_2 (c), and finally immersed in an acidic $PdCl_2$ solution ((d) and (e), respectively). Figures 6 and 7 show those of PACVD films deposited from CH_4/NH_3 and CH_4/N_2 mixtures, respectively (treatment time: 2 min), either after their subsequent immersion in an acidic $PdCl_2$ solution

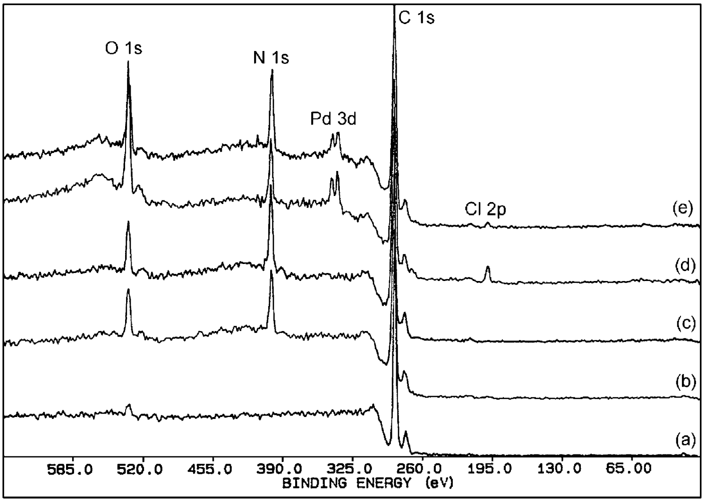


FIGURE 5 XPS wide-scan spectra of a glass substrate (a) covered with a thin amorphous hydrogenated carbon film, (b) and (c) being similar to (a) after a plasma treatment in NH_3 and N_2, respectively, and (d) and (e) similar to (b) and (c), respectively, after the activation by immersion in an acidic $PdCl_2$ solution.

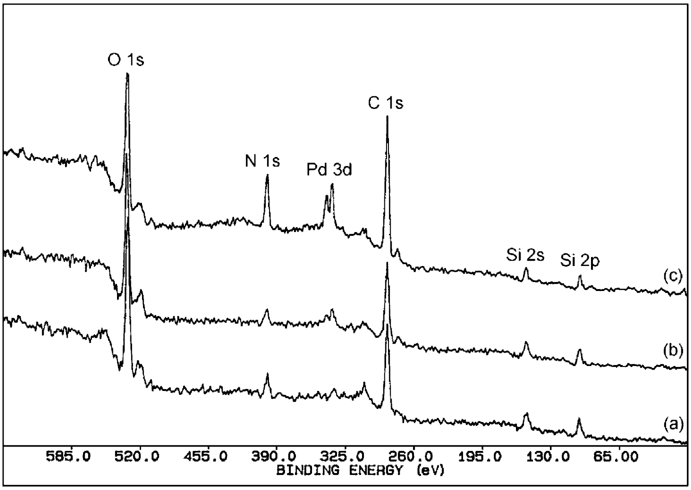


FIGURE 6 XPS wide-scan spectra of a glass substrate (a) covered with a thin amorphous hydrogenated carbon nitride film produced by PACVD from a CH_4/NH_3 mixture (flow rate ratio = 50/10); (b) is similar to (a) after an activation by the immersion in an acidic $PdCl_2$ solution, and (c) is similar to (a) after successively a plasma treatment in NH_3 and an activation by immersion in an acidic $PdCl_2$ solution.

(case (b)) or after their plasma treatment for 5 s in NH_3 or N_2 and their immersion in an acidic $PdCl_2$ solution (case (c)). Figure 5 shows that the plasma post treatment is required to graft nitrogen functionalities on a-C:H films and to further attach palladium to the so-functionalized surfaces. As previously mentioned, the palladium species are attached as Pd^{2+} [42]. Nitrogen groups are naturally present at the surface of a-CN_x:H films. The purpose of the post treatment in NH_3 or N_2 plasma is to add new nitrogen functionalities to enhance the attachment of palladium species after immersion in an acidic $PdCl_2$ solution. Table 1 reports the surface-preparation processes of the glass substrates, the quantitative XPS data (C, O, N, Pd, Si, and Cl atomic concentrations), as well as results inferred from the Scotch® tape test, namely the maximal electroless Ni film thickness for which no metal squares are removed by the Scotch® tape (TV = 5).

From the data displayed in Table 1, it is clear that the experimental conditions used to deposit the PACVD films result in thicker a-C:H coatings than a-CN_x:H coatings, given that the Si 2p signal coming from the glass substrates is practically not observed in the former case, while it is in the latter case. The presence of the Si 2p peaks

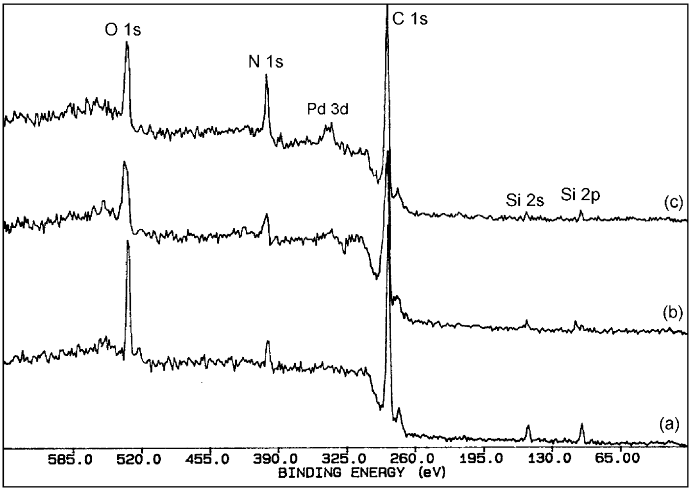


FIGURE 7 XPS wide-scan spectra of a glass substrate (a) covered with a thin amorphous hydrogenated carbon nitride film produced by PACVD from a CH_4/N_2 mixture (flow rate ratio = 30/30); (b) is similar to (a) after an activation by the immersion in an acidic $PdCl_2$ solution, and (c) is similar to (a) after successively a plasma treatment in N_2 and an activation by immersion in an acidic $PdCl_2$ solution.

suggest that the thickness of the a-CN_x:H films is less than the sampling depth of the XPS technique (*i.e.*, less than about 5–10 nm for organic compounds). The N_2-plasma treatment of PACVD films leads to higher nitrogen surface concentration than is obtained using NH_3-plasma. However, the concentration of chemisorbed Pd is higher on the NH_3 plasma-treated surfaces than on the N_2 plasma-treated surfaces. Note that a sufficient adhesion of plated metal is usually obtained when the surface concentration in Pd as measured by XPS is higher than about 1 at. % [41–43]. The lower performances in adhesion for specimens plasma treated in N_2 in comparison with those plasma treated in NH_3 result from the difference in the chemical nature of the grafted nitrogen-containing species. Once again, this confirms that the nitrogen functionalities grafted from the N_2 and NH_3 plasmas are not identical [41–43]. These results are in full agreement with previous observations by other authors. For example, it was found for a variety of polymers (XPS analysis) that the use of NH_3 instead of N_2 leads systematically to a reduced uptake of nitrogen [79–82]. In addition, it was shown that the surface chemistry of the treated polymers is also different insofar as NH_3 plasma treatments

TABLE 1 Surface Atomic Concentration (at. %) (XPS Analysis) of a-C:H and a-CN_x:H Thin Films that were Deposited on Glass Substrates (PACVD Process), Subsequently Plasma Functionalized in N_2 or NH_3, and Activated by Immersion in an Acidic $PdCl_2$ Solution

	Surface concentration (at. %)						Ni film thickness (μm) (TV = 5)
Surface conditioning	C	O	N	Pd	Si	Cl	
PACVD (CH_4, 2 min) + NH_3 pl. (10 s)	80	7	13				
PACVD (CH_4, 2 min) + NH_3 pl. (10 s) + $PdCl_2$ (Route (a))	73	12	12	1	<1	1	2.6
PACVD (CH_4, 2 min) + N_2 pl. (10 s)	77	7	16				
PACVD (CH_4, 2 min) + N_2 pl. (10 s) + $PdCl_2$ (Route (a))	74	11	14	1	<1	1	1.7
PACVD (CH_4/NH_3 = 50/10, 2 min)	66	15	9		10		
PACVD (CH_4/NH_3 = 50/10, 2 min) + $PdCl_2$ (Route (b))	63	17	8	1	10	1	2.3
PACVD (CH_4/NH_3 = 50/10, 2 min) + NH_3 pl. (5 s)	51	24	12		13		
PACVD (CH_4/NH_3 = 50/10, 2 min) + NH_3 pl. (5 s) + $PdCl_2$ (Route (c))	53	22	11	2	13	1	2.8
PACVD (CH_4/N_2 = 30/30, 2 min)	76	12	8		4		
PACVD (CH_4/N_2 = 30/30, 2 min) + $PdCl_2$	74	14	8	1	4	1	0.6
PACVD (CH_4/N_2 = 30/30, 2 min) + N_2 pl. (5 s) (Route (b))	73	9	15		3		
PACVD (CH_4/N_2 = 30/30, 2 min) + N_2 (5 s) + $PdCl_2$ (Route (c))	69	12	14	1	3	1	1

The adhesion data are relative to the Ni film maximum thickness, which is obtained without any metal squares removed (cross-hatched tape test: Test Value (TV) = 5). Routes (a), (b), and (c) are relative to schemes given in Figure 4.

almost exclusively introduce amine functionalities, whereas N_2 plasma treatments introduce both amine and imine functionalities [79–82].

The data in Table 1 also show that the thickness of the PACVD films obtained from CH_4/NH_3 or CH_4/N_2 mixtures is largely dependent on the flow rate ratios of the two gases. Indeed, in these gas mixtures, NH_3 and N_2 are nonpolymerizable by themselves, but when they are associated with a polymerizable gas (CH_4 in the present case) they are involved in both etching and copolymerization processes. As a consequence, the relative flow rate of the nitrogen-containing gas must be chosen in order to avoid that the etching level outweighs the copolymerization process. In the experiments reported in Table 1, the flow rate ratios for the CH_4/NH_3 and CH_4/N_2 mixtures were 50/10 and 30/30 (sccm/sccm), respectively. The low flow rate for NH_3 (10 sccm) in comparison with that for N_2 (30 sccm) can be justified since NH_3 etches these PACVD coatings faster than N_2 does [78]. This is supported by Figure 8, which shows how the thickness of the a-CN_x:H films varies as a function of the deposition time for different flow rate ratios of CH_4/NH_3 and CH_4/N_2 gas mixtures. The corresponding data were obtained by LEEIXS through intensity measurement of the C K_α radiation. It must be noted that, for very thin a-CN_x:H films (as well as for very thin a-C:H films), the C K_α intensity

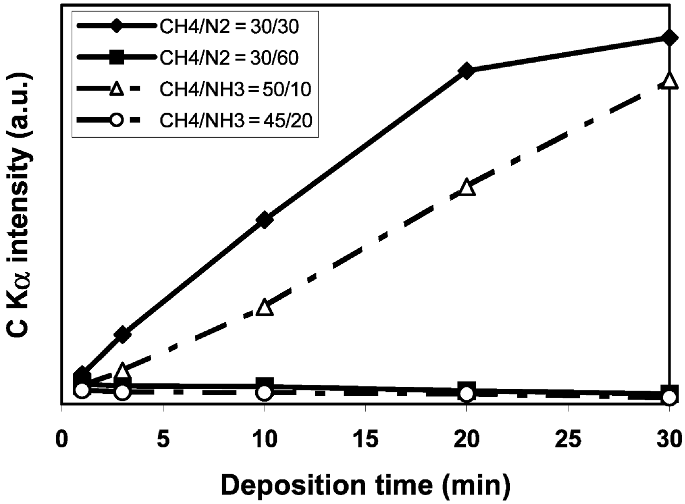


FIGURE 8 Intensity changes (LEEIXS analysis) of the C K_α radiation emitted from a-CN_x:H thin films deposited for different times on glass substrates: influence of the CH_4/NH_3 or CH_4/N_2 flow rate ratios.

is directly proportional to the film thickness insofar as the latter does not exceed a few tens of nanometers. This proportionality extent depends on the energy of the incident electron beam (here 3 keV) and on the chemical nature of the film [83]. Figure 8 indicates that the chosen CH_4/NH_3 and CH_4/N_2 flow rate ratios (50/10 and 30/30, respectively) lead to the formation of films whose thickness linearly increases with deposition time. On the other hand, the flow rate ratios of 45/20 (for the CH_4/NH_3 mixture) and 30/60 (for the CH_4/N_2 mixture) lead to the formation of very thin a-CN_x:H films, which are presumably deposited as islands. Indeed (see Table 1), Si from the substrate is always detected by XPS analysis. This is due to the high etch rate of the a-CN_x:H film during formation when NH_3 or N_2 concentration is high. The flow rate ratio control is then a critical parameter. The etching characteristics of the NH_3 or N_2 plasmas also explain why plasma treatments of a-CN_x:H films in these gaseous atmospheres were operated for very short times (5 or 10 s). Again, lower performances in adhesion for samples plasma treated in N_2 are observed in comparison with those plasma treated in NH_3 (cases of CH_4/N_2 and CH_4/NH_3 flow rate ratios reported in Table 1).

Note that the purpose of the PACVD deposition carried out in this work is not to obtain thick films but very adhering thin films capable of playing the role of a bridge between the metal coating and substrate. It is worth pointing out that Ni-P films thicker than those reported in Table 1 fail the Scotch® tape test, with the locus of failure always occurring at the "metal/plasma polymer" interface. Figure 9 shows XPS spectra obtained from the metal side and the thin a-CN_x:H side after the Scotch® tape test in the case of a 5 μm thick Ni-P film. The failure mode is adhesive in nature at the interface since nitrogen is observed only on the a-CN_x:H film side and not at all on the Ni-P film side.

a-CN_x:H films can also be deposited directly from volatile organic liquids containing nitrogen atoms. Two polymerizable monomers, namely allylamine (AA) and acetonitrile (AN), were used in the second part of the present study. In these experiments, the whole process leading to electroless plating can also be described by the scheme (b) in Figure 4, the a-CN_x:H films being produced by plasma polymerization of the AA and AN monomers. Figure 10 displays XPS wide-scan spectra of the PACVD films deposited on glass substrates (deposition time: 2 min). The spectra (a) and (b) are characteristic of the films obtained from AA and AN, respectively, while the spectra (c) and (d) are recorded after activation of the AA and AN substrates by immersion in an acidic $PdCl_2$ solution. Although the starting monomers do not contain oxygen, XPS analyses show a relatively high concentration

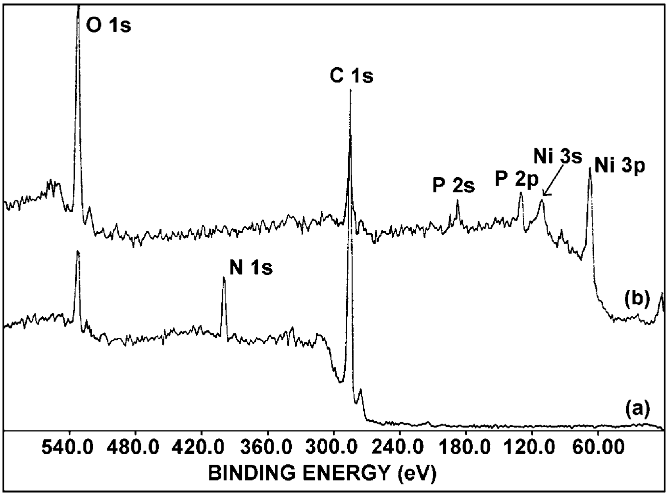


FIGURE 9 XPS wide-scan spectra of (a) the a-CN_x:H surface and (b) the Ni-P surface after delamination (Scotch® tape test) of a "Ni-P/ a-CN_x:H/ glass" system (thickness of the electroless Ni-P film = 5 µm).

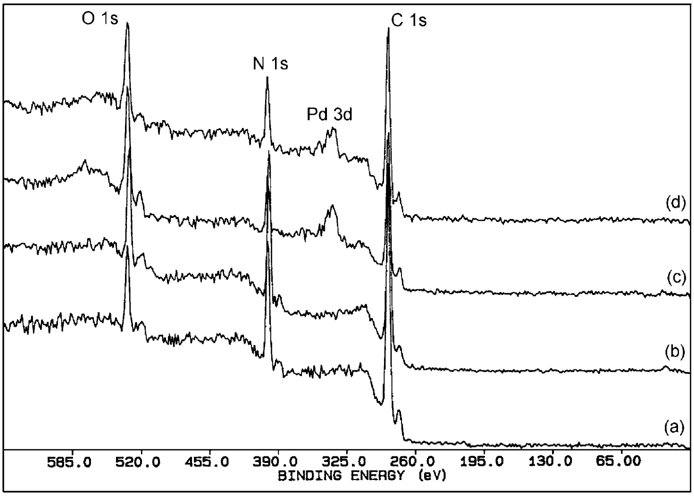


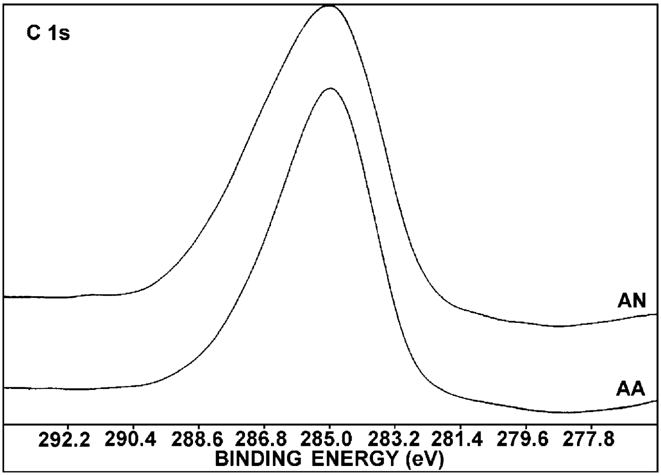
FIGURE 10 XPS wide-scan spectra of a glass substrate covered with a thin amorphous hydrogenated carbon nitride film obtained by plasma polymerization of (a) allylamine and (b) acetonitrile; (c) and (d) are similar to (a) and (b), respectively, after the activation by immersion in an acidic $PdCl_2$ solution.

in oxygen is incorporated in these plasma polymers, which is often seen in plasma polymerization of organic compounds [84–86]. In the present examples, the oxygen surface concentrations (9 and 12 at. %, respectively) are about half of those in nitrogen (17 and 24 at. %, respectively). Table 2 displays the surface elemental concentrations of the AA and AN coatings prior to and after the activation step, as well as the maximum thickness of the electroless Ni films with optimal adhesion performances (TV = 5). Palladium is chemisorbed after immersion of the AA- and AN-coated specimens in the acidic $PdCl_2$ solution at relatively high surface concentrations (2 and 1.5 at. %, respectively), *i.e.*, at values that usually allow an easy electroless metallization. In addition, it can be noted that the surface concentration in Pd for the activated AA-coated specimen (2 at. %) is slightly larger than that (1.5 at. %) for the activated AN-coated specimen in spite of the fact that the nitrogen surface concentration at the AA polymer surface is less (17 at. %) than that at the AN polymer surface (24 at. %). Most probably, this trend results from the fact that nitrogen groups present in AA and AN plasma polymers are not in the same chemical environment. In particular, one can expect the formation, among others, of amine species in (and therefore, at the surface of) the AA plasma polymer, while this is not the case in (and therefore at the surface of) the AN plasma polymer. Under these conditions, the high Pd concentration at the surface of the AA plasma polymer is only due to the significant reactivity of the Pd species towards the amine groups [41, 42]. On the other hand, the AN plasma polymers probably contain a relatively high surface concentration in functional groups, which should be much less favorable to the chemisorption of Pd^{2+} species. Figure 11 displays the C 1s and N 1s XPS spectra of AA and AN plasma polymers when introduced into the spectrometer within 2 min after their deposition on a glass substrate. The N 1s spectra do not exhibit noticeable differences (full width at half maximum = 3.0 and 3.2 eV for AA and AN plasma polymers, respectively). On the other hand, the C 1s spectra give evidence that a distinction could be made about the surface content of both materials. Although both C 1s peaks show an asymmetry on the high-binding energy side, the one related to the AN plasma polymer is substantially broadened (full width at half maximum = 3.3 and 4.2 eV for AA and AN plasma polymers, respectively). As seen in Table 2, the surface content in oxygen is similar (~10 at. %) for both materials. That could mean that during plasma polymerization of AN many nitrile (cyano) groups are converted in species (*e.g.*, imines) whose C 1s component occurs at a higher binding energy (+0.7 eV for imines) in comparison with the amine groups resulting from the plasma polymerization of

TABLE 2 Surface Atomic Concentrations (at. %) (XPS Analysis) of a-CN_x:H Thin Films that Were Deposited on Glass Substrates (PACVD Process) Using Allylamine (AA) or Acetonitrile (AN) Monomers and Subsequently Activated by Immersion in an Acidic $PdCl_2$ Solution

	Surface concentrations (at. %)						
Surface conditioning	C	O	N	Pd	Si	Cl	Ni film thickness (μm) (TV = 5)
PACVD (AA, 2 min)	74	9	17				
PACVD (AA, 2 min) + $PdCl_2$	68	14	14	2		2	3.9
PACVD (AN, 2 min)	64	12	24				
PACVD (AN, 2 min) + $PdCl_2$	69.5	14	14	1.5		1	0.6

The adhesion data are relative to the Ni film maximum thickness, which is obtained without any metal squares removed (cross-hatched tape test: Test Value (TV) = 5).



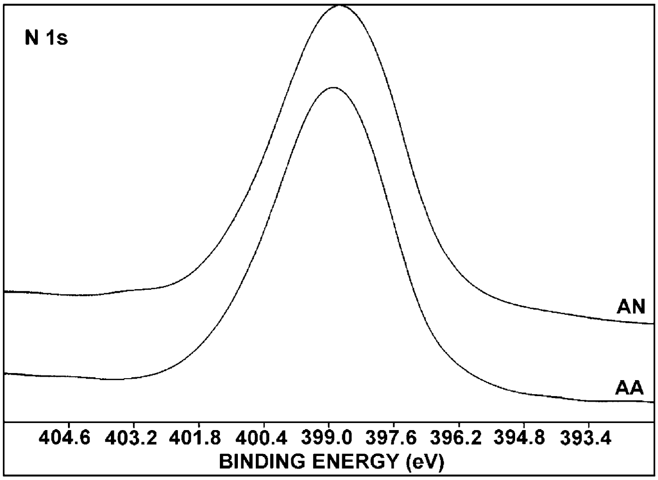


FIGURE 11 C 1s and N 1s XPS spectra of freshly deposited AA and AN plasma polymers deposited on a glass substrate.

AA. This hypothesis is consistent with the conclusion of work carried out by Inagaki *et al.* [83, 84] that deals with the plasma polymerization of acrylonitrile. From XPS and Fourier transform infrared (FTIR) investigations, these authors established that most of the cyano groups of this monomer precursor are converted into imine, ketene-imide (-C=C=N-) and amide groups, although some of the cyano groups still remain in the deposited material. As the C 1s and N 1s spectra provided in Figure 11 were obtained with a nonmonochromatic X-ray source, they cannot be unambiguously curve-fitted, and further information about the fine structure of such spectra presently would be highly speculative. Complementary experiments are in progress to give more insight into the difference observed between AA and AN plasma polymers.

In addition, some experiments were made using a tin-free process similar to that developed by Calvert and coworkers. [18, 30, 48–50]. This process consists of chemisorbing on glass substrates a γ-aminopropyltriethoxysilane (γ-APS) from a 1 wt% APS solution in a 95/4 wt% methanol/water mixture. After drying, attachment of Pd^{2+} species on the nitrogen-containing functionalities is accomplished by immersion in an acidic $PdCl_2$ solution. Adhesion of the corresponding "Ni-coating/glass substrate" systems are similar [54] to those obtained using the PACVD processes (see Tables 1 and 2). Comparison of these different routes leading to electroless metallization can obviously be a subject of debate. However, it clearly appears that the silanization process requires rigorous control of the chemisorption step and undoubtedly is more time-consuming for this application than those required to implement the PACVD process [54]. On the other hand, it is also evident that a plasma reactor requires a significant investment.

Finally, it is important to shed light on the changes with time (aging) of the AA and AN plasma-polymerized thin films, as well as prior to and after its postfunctionalization in a N_2 or NH_3 atmosphere. These aging effects govern the quality of the subsequent operations and consequently that of the "coating/substrate" interface. Gengenbach and coworkers [89–93] studied the aging in air of plasma polymers obtained from polymerizable nitrogen-based organic monomers (n-heptylamine, 1,3-diaminopropane, N,N-dimethylformamide, ethylenediamine, n-butylamine, N,N-dimethylacetamide...), as well as that of N_2 or NH_3 plasma-treated polyolefins (polyethylene (PE), polypropylene (PP)) and perfluorinated polymers polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)). XPS and contact-angle measurements showed that freshly treated or deposited materials consist of a random hydrocarbon network with a considerable amount of unsaturation and a high concentration of such nitrogen-containing functional groups as primary/secondary amines and imines (N 1s binding energy at ~399.1 eV). On the other hand, storage in air (aging) predominantly causes oxidation of the carbon atoms that have amine groups attached to them, which mainly leads to amide groups. This is inferred from the progressive shift of the N 1s peak up to a binding energy of ~399.8 eV, a value characteristic of amides. In addition, these authors showed that plasma polymers must be deposited under relatively "mild" conditions (*e.g.*, at low powers) in order to retain the highest possible percentage of the precursor functionality without compromising the physical integrity of the deposit. In the framework of the work described in the present article, the results of Gegenbach and coworkers strongly suggest that the activation process (immersion of the substrates modified with surface nitrogenated functionalities in a $PdCl_2$ solution) must be performed within a few hours after the plasma treatment.

CONCLUSIONS

The work presented in this article shows that different strategies can be used to simplify the processing leading to the electroless deposition of nickel (or copper) on dielectric substrates such as glasses (or silicon wafers covered with a thin film of silica). Based on an approach previously developed for the metallization of polymer or composite substrates, these processes use plasma-assisted deposition (PACVD or plasma-polymerization process) of thin films containing (or grafted with) nitrogen functionalities. They are used as sites to chemisorb the palladium-based catalyst required to initiate the electroless metal deposition. This essential step is performed by immersing the nitrogen groups carrying substrates in a simple acidic $PdCl_2$ solution. This method differs from the conventional processes since the sensitization step (adsorption of tin species) that usually takes place prior to the activation step (adsorption of palladium species) is left out. In this step, palladium is covalently attached to the PACVD thin films as Pd^{2+}. However, it is shown that the chemical reduction of these species to Pd^0 must be carried out first (immersion in a hypophosphite solution). This means that palladium at the zero oxidation step acts as the true catalyst of the electroless reaction initiation. Particularly, it must be noted that this extra step is required when commercial electroless plating baths are used. Indeed, some additives (stabilizers) present in such baths are shown to poison the catalytic sites when they are formed through the activation step in the acidic $PdCl_2$ solution.

Various plasma-assisted deposits were compared. In a first investigation, amorphous hydrogenated carbon (a-C:H) thin films were produced from a CH_4 gas phase. These films were subsequently plasma functionalized in NH_3 or N_2. As a variant, amorphous hydrogenated carbon nitride (a-CN_x:H) thin films were obtained from a CH_4/NH_3 or CH_4/N_2 gas phase. These films can also be plasma functionalized in NH_3 or N_2 to increase their surface density of nitrogen-containing species. In a second investigation, carbon nitride (a-CN_x:H) thin films were grown from two volatile organic monomers (allylamine and acetonitrile). All of these processes were shown to lead to the formation of electroless Ni (or Cu) films that are well adherent to their substrates when PACVD thin films are produced with a sufficient thickness and surface density of nitrogen-containing species. In a sense, such PACVD films are used as adhesion promotion layers for the electroless Ni (or Cu) deposition.

In these experiments, the practical adhesion of the Ni films to their substrates was characterized using a cross-hatched peel test and, when successful results were achieved, about 3 µm thick Ni films pass this test without any delamination. In addition, XPS results confirm—as was already shown in previous works dealing with plasma functionalization of polymers—that palladium chemisorption on nitrogen-containing functionalities is largely dependent on the chemical nature of latter. Most probably, the amino groups such as those introduced by NH_3 plasma functionalization or plasma polymerization of allylamine favorably influence the chemisorption of the Pd^{2+} species.

Finally, the present work shows that the best way to electroless metallization of glass or ceramic substrates should consist in carrying out plasma polymerization of methane (or another hydrocarbon) and surface functionalization of the so-obtained plasma polymer through a NH_3 plasma treatment. Indeed, this simple way of operating in the gas phase allows easy control of all experimental parameters. On the other hand, the process using nitrogen-containing organic monomers presents two major drawbacks, namely the toxicity of the precursors and the difficulty of controlling their flow rate to avoid any significant etching effect on the catalytic sites by the gas.

REFERENCES

[1] Mallory, G. O. and Hajdu, J. B., Eds., *Electroless Plating: Fundamentals and Applications* (American Electroplaters and Surface Finishers Society, Orlando, FL, 1990).

[2] Paunovic, M. and Schlesinger, M., *Fundamentals of Electrochemical Deposition* (John Wiley, New York, 1998).

[3] Lowenheim, F. A., *Electroplating* (McGraw-Hill Book Co., New York, 1978).

[4] Ohno, I., *Mat. Sci. Eng. Soc.* **A 146**, 33–35 (1991).

[5] Stone, F. E., In: *Electroless Plating: Fundamentals and Applications*, G. O. Mallory and J. B. Hajdu, Eds. (American Electroplaters and Surface Finishers Society, Orlando, FL, 1990), pp. 331–375.

[6] Ebneth, H., In: *Metallizing of Plastics, Handbook of Theory and Practice*, R. Suchentrunk, Ed. (ASM International, Materials Park, OH, 1993), 89–111.

[7] J. Hajdu, *Plat. Surf. Finish.* **83**, 29–33 (1996).

[8] Yoshiki, H., Hashimoto, K., and Fujishima, A., *Metal Finish.* **94**, 28–29 (1996).

[9] Baumgartner, C. E. and Scott, L. R., *J. Adhesion Sci. Technol.* **9**(7), 789–799 (1995).

[10] Karas, B. R., Foust, D. F., and Dumas, W. V., *J. Adhesion Sci. Technol*. **6**(11), 1205–1219 (1992).

[11] Lee, K.-W. and Viehbeck, A., *IBM J. Res. Develop*. **38**(4), 457–474 (1994).

[12] Shacham-Diamand, Y., Dubin, V., and Angyal, M., *Thin Solid Films* **262**, 93–103 (1995).

[13] Rye, R. R., Howard, A. J., and Ricco, A. J., *Thin Solid Films* **262**, 73–83 (1995).

[14] Dressick, W. J., Dulcey, C. S., Georger, J. H., and Calvert, J. M., *Chem. Mater*. **5**, 148–150 (1993).

[15] Dressick, W. J. and Calvert, J. M., *Jpn. J. Appl. Phys*. **32**, 5829–5839 (1993).

[16] Stone, F. E., In: *Electroless Plating: Fundamentals and Applications*, G. O. Mallory and J. B. Hajdu, Eds. (American Electroplaters and Surface Finishers Society, Orlando, FL, 1990), Chap. 13, pp. 331–375.

[17] Kuzmik, J. J., In: *Electroless Plating: Fundamentals and Applications*, G. O. Mallory and J. B. Hajdu, Eds. (American Electroplaters and Surface Finishers Society, Orlando, FL, 1990), Chap. 13, pp. 377–399.

[18] Dressick, W. J., Dulcey, C. S., Georger, J. H., Calabrese, G. S., and Calvert, J. M., *J. Electrochem. Soc*. **141**, 210–220 (1994).

[19] Cohen, R. L., D'Amico, J. F., and West, K. W., *J. Electrochem. Soc*. **118**, 2042–2046 (1971).

[20] De Minjer, C. H. and Boom, P. F. J. V. D., *J. Electrochem. Soc*. **120**, 1644–1650 (1973).

[21] Meek, R. L., *J. Electrochem. Soc*. **122**, 1478–1481 (1975).

[22] Sard, R., *J. Electrochem. Soc*. **117**, 864–870 (1970).

[23] D'Amico, J. F., de Angelo, M. A., Henrickson, J. F., Kenney, J. T., and Sharp, D. J., *J. Electrochem. Soc*. **118**, 1695–1699 (1971).

[24] Feldstein, N. and Weiner, J. A., *J. Electrochem. Soc*. **120**, 475–479 (1973).

[25] Tsukahara, M., *J. Metal Finishing Soc. Japan* **23**, 83–89 (1972).

[26] Cohen, R. L. and West, K. W., *J. Electrochem. Soc*. **120**, 502–508 (1973).

[27] Feldstein, N., Schlesinger, M., Hedgecock, N. E., and Chow, S. L., *J. Electrochem. Soc*. **121**, 738–744 (1974).

[28] Horkans, J., Kim, J., Mc Grath, C., and Romankiw, L. T., *J. Electrochem. Soc*. **134**, 300–304 (1987).

[29] Burrell, M. C., Karas, B. R., Foust, D. F., Dumas, W. V., Lamby, E. J., Grubb, W. T., and Chera, J. J., In: *Metallized Plastics 1: Fundamental and Applied Aspects*, K. L. Mittal, Ed. (Plenum Press, New York, 1989), pp. 223–233.

[30] Brandow, S. L., Dressick, W. J., Marrian, C. R. K., Chow, G.-M., and Calvert, J. M., *J. Electrochem. Soc*. **142**, 2233–2243 (1995).

[31] Charbonnier, M., Romand, M., Kogelschatz, U., Esrom, H., and Seeböck, R., In: *Metallized Plastics 7: Fundamental and Applied Aspects*, K. L. Mittal, Ed. (VSP, Utrecht, The Netherlands, 2001), pp. 3–26.

[32] Charbonnier, M., Romand, M., Esrom, H., and Seeböck, R., *J. Adhesion* **75**, 381–404 (2001).

[33] Charbonnier, M., Alami, M., and Romand, M., *J. Electrochem. Soc*. **143**(2), 472–480 (1996).

[34] Alami, M., Charbonnier, M., and Romand, M., *Plasmas Polym*. **1**(2), 113–126 (1996).

[35] Alami, M., Charbonnier, M., and Romand, M., *J. Adhesion* **57**, 77–90 (1996).

[36] Charbonnier, M., Alami, M., and Romand, M., *J. Appl. Electrochem*. **28**, 449–453 (1998).

[37] Charbonnier, M., Romand, M., Alami, M., and Duc T. M., In: *Polymer Surface Modification: Relevance to Adhesion*, K. L. Mittal, Ed. (VSP, Utrecht, The Netherlands, 2000), pp. 3–27.

[38] Charbonnier, M., Romand, M., and Alami, M., In: *Polymer Surface Modification: Relevance to Adhesion*, K. L. Mittal, Ed. (VSP, Utrecht, The Netherlands, 2000), pp. 29–43.

[39] Charbonnier, M., Romand, M., Stremsdoerfer, G., and Fares-Karam, A., *Recent Res. Devel. Macromol. Res.* **4**, 27–43 (1999).

[40] Romand, M., Charbonnier, M., Alami, M., and Baborowski, J., In: *Metallized Plastics 5 & 6: Fundamental and Applied Aspects*, K. L. Mittal, Ed. (VSP, Utrecht, The Netherlands, 1998), pp. 3–23.

[41] Charbonnier, M., Goepfert, Y., and Romand, M., In: *Polyimides and Other High Temperature Polymers*, K. L. Mittal, Ed. (VSP, Utrecht, The Netherlands, 2003), Vol. 2, pp. 289–314.

[42] Charbonnier, M. and Romand, M., *Int. J. Adhes. Adhes.* **23**, 277–285 (2003).

[43] Charbonnier, M., Goepfert, Y., Romand, M., and Fares-Karam, A., In: *Proc. 16th International Symposium on Plasma Chemistry*, Taormina, Italy, 22–27 June 2003, d'Agostino, R., Favia, P., Fracassi, F. and Palumbo, F., Eds., Abstract Po6.24 p. 348, Full Papers CD, (IMP/CNR, Bari, www.ispc16.org).

[44] Romand, M., Charbonnier, M., and Goepfert, Y., In: *Metallization of Polymers 2*, E. Sacher, Ed. (Kluwer Academic/Plenum Publishers, New York, 2002), pp. 191–205.

[45] Goepfert, Y., Charbonnier, M., and Romand, M., In: *Proc. 25th Annual Meeting of the Adhesion Society*, A. V. Pocius, and J. C. Dillard, Eds. (The Adhesion Society, Blacksburg, VA, 2002), Poster Vol., pp. 51–53.

[46] Goepfert, Y., Charbonnier, M., and Romand, M., In: *Proc. 26th Annual Meeting of the Adhesion Society*, G. L. Anderson, Ed. (The Adhesion Society, Blacksburg, VA, 2003), pp. 231–233.

[47] Vargo, T. G., Gardella, J. A., Calvert, J. M., and Chen, M.-S., *Science* **262**, 1711–1712 (1993).

[48] Calvert, J. M., Dressick, W. J., Dulcey, C. S., Chen, M. S., Georger, J. H., Stenger, D. A., Koloski, T. S., and Calabrese, G. S., In: *Polymers for Microelectronics. Resists and Dielectrics*, L. F. Thomson, C. G. Wilson, and S. Tagawa, Eds., ACS Symposium Series 537 (ACS, Washington, DC, 1994), Chap. 14, pp. 210–219.

[49] Brandon, S. L., Chen, M.-S., Wang, T., Dulcey, C. S., Calvert, J. M., Bohland, J. F., Calabrese, G. S., and Dressick, W. J., *J. Electrochem. Soc.* **144**(10), 3425–3434 (1997).

[50] Chen, M.-S., Brandow, S. L., Dulcey, C. S., Dressick, W. J., Taylor, G. N., Bohland, J. F., Georger, J. H., Pavelchek, E. K., and Calvert, J. M., *J. Electrochem. Soc.* **146**(4), 1421–1430 (1999).

[51] Hidber, P. C., Helbig, W., Kim, E., and Whitesides, G. M., *Langmuir* **12**, 1375–1380 (1996).

[52] Touchais-Papet, E., Charbonnier, M., and Romand, M., *Appl. Surf. Sci.*, **138–139**, 557–562 (1999).

[53] Touchais-Papet, E., Alami, M., Charbonnier, M., Romand, M., and Mikou, A., In: *Proc. 22nd Annual Meeting of the Adhesion Society*, D. R. Speth, Ed. (The Adhesion Society, Blacksburg, VA, 1999), pp 48–51.

[54] Charbonnier, M. and Romand, M., *Surf. Coat. Technol.* **162**, 19–30 (2003).

[55] Charbonnier, M., Goepfert, Y., and Romand, M., In: *Proc. 26th Annual Meeting of the Adhesion Society*, G. L. Anderson, Ed. (The Adhesion Society, Blacksburg, VA, 2003), pp. 124–126.

[56] Charbonnier, M., Goepfert, Y., and Romand, M., In: *Proc. 16th International Symposium on Plasma Chemistry*, Taormina, Italy, 22–27 June 2003, CD, R. d'Agostino, P. Favia, F. Fracassi, and F. Palumbo, Eds. Abstract Po7.2 p. 364, Full-Papers (IMP/CNR, Bari, www.ispc16.org).

[57] Wang, W. C., Kang, E. T., and Neoh, K. G., *Appl. Surf. Sci.* **199**, 52–66 (2002).

[58] Esrom, H., Demny, J., and Kogelschatz, U., *Chemtronics*. **4**, 202–208 (1989).

[59] Esrom, H. and Wahl, G., *Chemtronics* **4**, 216–221 (1989).

[60] Esrom, H. and Kogelschatz, U., *Appl. Surf. Sci.* **46**, 158–162 (1990).

[61] Kogelschatz, U., *Appl. Surf. Sci.* **54**, 410–423 (1992).

[62] Esrom, H. and Kogelschatz, U., *Thin Solid Films* **218**, 231–246 (1992).

[63] Zhang, J.-Y., Esrom, H., and Boyd, I. W., *Appl. Surf. Sci.* **96**–**98**, 399–404 (1996).

[64] Zhang, J.-Y., Boyd, I. W., and Esrom, H., *Appl. Surf. Sci.* **109**–**110**, 253–258 (1997).

[65] Esrom, H., Zhang, J.-Y., Kogelschatz, U., and Pedraza, A.J., *Appl. Surf. Sci.* **86**, 202–207 (1995).

[66] Zhang, J.-Y., King, S. L., Boyd, I. W., and Fang, Q., *Appl. Surf. Sci.* **110**, 487–492 (1997).

[67] Zhang, J.-Y., and Boyd, I. W., *Thin Solid Films* **318**, 234–238 (1998).

[68] Zhang, J.-Y., Boyd, I. W., and Esrom, H., *J. Mater. Sci.* **17**, 2037–2040 (1998).

[69] Geretovszky, Z. and Boyd, I. W., *Appl. Surf. Sci.* **138**–**139**, 401–407 (1999).

[70] Macauley, D. J., Kelly, P. V., Mongey, K. F., and Crean, G. M., *Appl. Surf. Sci.* **138**–**139**, 62–67 (1999).

[71] Macauley, D. J., Kelly, P. V., Mongey, K. F., and Crean, G. M., *Appl. Surf. Sci.* **138**–**139**, 622–626 (1999).

[72] Zhang, J.-Y., Boyd, I. W., and Draper, S., *Surf. Coat. Technol.* **100**–**101**, 469–473 (1998).

[73] Horn, H., Beil, S., Wesner, D. A., Weichenhain, R., and Kreutz, E. V., *Nucl. Instrum. Meth. Phys. Res. B* **151**, 279–284 (1999).

[74] Romand, M., Bador, R., Charbonnier, M., and Gaillard, F., *X-ray Spectrom.* **16**, 7–16 (1987).

[75] Gaillard, F. and Romand, M., *Surface Interface Anal.* **16**, 429–434 (1990).

[76] Romand, M., Gaillard, F., and Charbonnier, M., *Adv. X-ray Anal.* **35B**, 767–781 (1992).

[77] Romand, M. and Charbonnier, M., *J. Adhesion Sci. Technol.* **15**(8), 945–965 (2001).

[78] Deshayes, L., Charbonnier, M., Prakash, N. S., and Romand, M., *J. Adhesion*. **43**, 209–221 (1993).

[79] Lub, J., van Vroonhover, F. C. B. M., Bruninx, E., and Benninghoven, A., *Polymer*, **30**, 40–44 (1989).

[80] Klemberg-Sapieha, J. E., Küttel, O. M., Martinu, L., and Wertheimer, M. R., *J. Vac. Sci. Technol.* **A9**(6), 2975–2981 (1991).

[81] Klemberg-Sapieha, J. E., Martinu, L., Sapieha, S., and Wertheimer, M. R., In: *The Interfacial Interaction in Polymeric Composites*, G. Akovali, Ed. (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993), pp. 201–222.

[82] Gerenser, L. J., In: *Handbook of Thin Films Process Technology*, D. A. Glocker and S. I. Shah, Eds. (IOP Publishing Ltd, Bristol, 1995), pp. E3.1:1–E3.1:21.

[83] Inagaki, N., Takada, S., and Yamada, Y., *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 2003–2010 (1992).

[84] Inagaki, N., Takada, S., Ohmori, H., and Mibu, S., *J. Adhesion Sci. Technol.*, **10**(3), 241–256 (1996).

[85] Romand, M., Charbonnier, M., and Baborowski, J., In: *Adv. X-ray Anal.* **40**, J. V. Giltrich, T. C. Huang, C. R. Hubbard, I. C. Noyan, P. K. Predecki, D. K. Smith

and R. L. Snyder, Eds. (International Centre for Diffraction Data, CD-Rom Publication, Newton Square, PA, 1997).

[86] Yasuda, H., *Plasma Polymerization* (Academic Press Inc., London, 1965).

[87] Inagaki, R., *Plasma Surface Modification and Plasma Polymerization* (Technomic Publishing Company Inc., Basel, 1996).

[88] D'Agostino, R., *Plasma Deposition, Treatment and Etching of Polymers* (Academic Press Inc., San Diego, CA, 1990).

[89] Gengenbach, T. R. and Griesser, H. J., *J. Polym.Sci.: Part A: Polym. Chem.*, **37**, 2191–2206 (1999).

[90] Gengenbach, T. R., Vasic, Z. R., Li, S., Chatelier, R. C., and Griesser, H. J., *Plasmas and Polymers*, **2**, 91–114 (1997).

[91] Gengenbach, T. R., Chatelier, R. C., and Griesser, H. J., *Plasmas and Polymers*, **4**, 283–307 (1999).

[92] Gengenbach, T. R., Chatelier, R. C., and Griesser, H. J., *Surf. Interface Anal.*, **34**, 611–619 (1996).

[93] Griesser, H. J., Gengenbach, T. R., Dai, L., Li, S., and Chatelier, R. C., In: *Mittal Festchrift*, W. J. Van Ooij and H. R. Anderson, Eds. (VSP, Utrecht, 1998), pp. 307–328.