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Surface plasma functionalization of polycarbonate: Application to electroless nickel and copper plating

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Abstract

Electroless metallization of polymers requires different steps including (i) the preconditioning of the surface to render it chemically reactive, (ii) the chemisorption of a catalyst (Pd) to activate the so-modified surface towards subsequent metallization, and (iii) the metallization itself. In the present work, electroless metallization was carried out on poly(carbonate) substrates, and step (i) was performed using plasma treatments in various gaseous atmospheres (NH_3, N_2, O_2). When a sufficiently high surface concentration of nitrogenated groups is grafted it is shown from X-ray photoelectron (XPS) analyses that the so-functionalized surfaces can chemisorb Pd^{2+} ions directly from a simple $PdCl_2$ solution. Thus, step (i) allows simplification of the conventional electroless processes commonly used up to now. Moreover, XPS analyses indicate chemical reduction of Pd^{2+} ions to Pd(0) during the more or less long initiation time before the start of metallization. This reduction is easily performed in nickel plating baths thanks to the hypophosphite reducer. On the other hand, this reduction is possible with formaldehyde, the reducer of copper plating baths, only if Sn^{2+} ions (brought by the conventional processes using $SnCl_2$ and $PdCl_2$ solutions) are present.

1. Introduction

Polymers can be metallized chemically using aqueous solutions. This process is known as electroless or autocatalytic plating and the metal deposition is the result of a redox reaction. This reaction can only take place on contact with a catalyst (Pd in general) whose chemisorption on the polymer surface is the essential step in the process. The conventional method to activate such a surface consists in either a two-step or a one-step process [1–10]. In both cases, the polymer surface is preconditioned using chemical treatment, generally by immersion in a sulfo-chromic bath at 75 °C. In the two-step process the treated substrate is immersed in aqueous, acidic $SnCl_2$ (sensitisation) and $PdCl_2$ (activation) solutions successively [1–9]. In the one-step process this substrate is immersed in a mixed $SnCl_2$–$PdCl_2$ colloidal solution [6, 7, 10]. Because of the easy oxidation of Sn^{2+} ions, these conventional processes require careful monitoring of the solutions.

On the basis of previous work [11–16], it is shown here that, if nitrogenated groups are plasma-grafted on the polymer surfaces, palladium can be easily chemisorbed on the nitrogenated species through mere immersion in a dilute $PdCl_2$ solution. As a consequence, a new, simplified process developed to catalyse polymer surfaces is under investigation. The reaction mechanisms of the palladium chemisorption and redox reaction initiation, leading to Ni or Cu plating, are studied and proposed from X-ray photoelectron spectrometry (XPS) analyses.

2. Experimental details

Plasma treatment of polymer surfaces was performed in a capacitive reactor (RIE 80 model from Plasma Technology) working in the RF mode. The sample to be surface-modified was placed on the powered electrode. The base pressure in the reactor was 1×10^{-3} torr and the different adjustable experimental parameters were the nature of the gas or gas mixture, flow-rate, working pressure, power density and treatment time.

Surface chemical modifications were determined by XPS using a Riber SIA 200 spectrometer equipped with a nonmonochromatic AlK_α excitation source. All spectra were referenced to the C 1s peak (C–C and C–H bonds of the polymer used) whose binding energy was fixed at 285.0 eV.

Electroless metallization was carried out according to the experimental procedure previously described [11, 12].

When the conventional procedure was used to graft the palladium species on the surfaces, only the two-step way was operated in order to control surface modifications after every step of the treatment. For this purpose, the samples were successively immersed for 2 min in the sensitisation solution (0.1 g L^{-1} $SnCl_2$ and 0.1 mL L^{-1} concentrated HCl) then, after rinsing in water, in the activation solution (0.1 g L^{-1} $PdCl_2$ and 0.1 mL L^{-1} concentrated HCl). In the alternative method developed in our laboratory, palladium grafting was performed using only the activation $PdCl_2$ solution (the same as that of the two-step conventional process). The nickel metallization bath (36 g L^{-1} $NiSO_4 \cdot 6\ H_2O$, 10 g L^{-1} $NaH_2PO_2 \cdot H_2O$, 29 mL L^{-1} lactic acid (85%)) was operated at pH 5 and 85 °C. The copper metallization bath [17] which operates in alkaline medium (pH $\sim$ 12) at room temperature was composed of one volume of HCHO (37%) and five volumes of the following solution: $KNaC_4H_4O_6 \cdot 4\ H_2O$ (0.6 M), NaOH (0.14 M), $CuSO_4 \cdot 5\ H_2O$ (0.28 M), EDTA (0.03 M).

All experiments were carried out on polycarbonate (PC) substrates previously cleaned in an ethanol ultrasonic bath. The substrates were 1 mm thick sheets (Goodfellow).

3. Results

3.1. *Palladium chemisorption mechanisms*

Before chemisorption of palladium on PC substrates, the surface of the latter was either oxidized by chemical treatment in a sulfochromic bath (78.7 g L^{-1} $K_2Cr_2O_7$, 868 cm^3 L^{-1} concentrated H_2SO_4) operating at 75 °C for 1 min, or plasma-treated using various gases (O_2, NH_3, N_2) in the following conditions: flow rate 100 sccm, working pressure 100 mtorr, power density 0.5 W cm^{-2} and time treatment 1 min. Surface modifications due to these treatments were investigated by XPS. The corresponding spectra (Figure 1) show a strong oxygen uptake after the surface treatments by the chemical and O_2 plasma routes (spectra (b) and (c), respectively) and both an oxygen and nitrogen uptake after those carried out by N_2 and NH_3 plasmas (spectra (d) and (e), respectively). When nitrogenated plasmas are used, the grafted oxygenated groups are due, on the one hand, to competitive reactions on the solid surface between the nitrogenated species created in the gas used and the oxygenated species due to residual O_2 and H_2O vapour still present in the reactor atmosphere, on the other hand to the natural oxidation taking place after the plasma treatment itself when the samples are returned to atmospheric pressure.

Different treatments were then performed to graft palladium species on the modified surfaces. These included immersion of the sample in (i) a $SnCl_2$ solution for 2 min, (ii) a $SnCl_2$ solution, and then a $PdCl_2$ solution, both for 2 min, and (iii) a $PdCl_2$ solution for 2 min. For example, Figures 2 and 3 show the result of these treatments performed on an oxygen-rich surface (O_2 plasma-treated PC) (Figure 2) and on a surface grafted with both nitrogenated and oxygenated groups (NH_3 plasma-treated PC) (Figure 3). As shown in Figure 2, an oxygen-rich surface (spectrum (a)) easily chemisorbs tin species (spectrum (b)), and then palladium species (spectrum (c)) after the complete two-step conventional procedure, but cannot chemisorb palladium directly (spectrum (d)) through the use of the simple $PdCl_2$ solution. On the other hand, a surface on which both oxygenated and nitrogenated species were grafted (Figure 3, spectrum (a)) does not chemisorb any tin species (spectrum (b)), while the complete two-step conventional procedure (spectrum (c)), as well as the $PdCl_2$ treatment alone (spectrum (d)) graft palladium species directly onto the polymer surface.

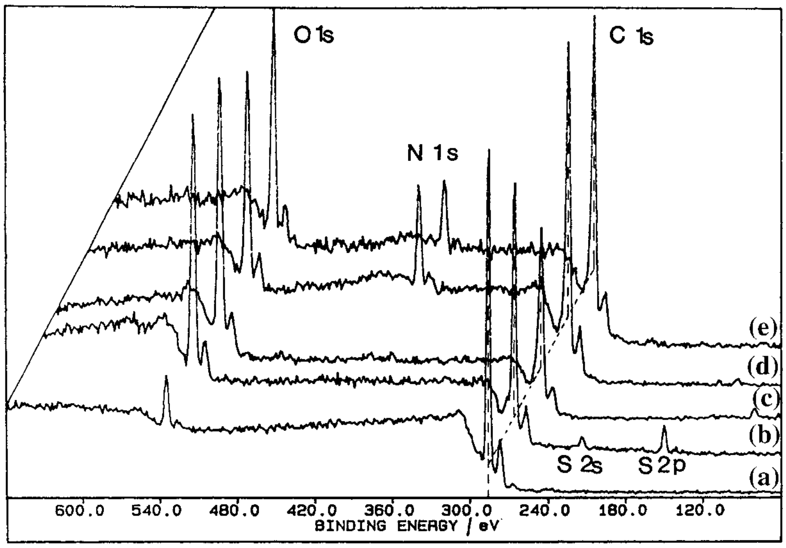

Fig. 1. Survey XPS spectra of virgin polycarbonate (a), the same after sulfochromic chemical treatment (b), O_2 (c), NH_3 (d) and N_2 (e) plasma treatments.

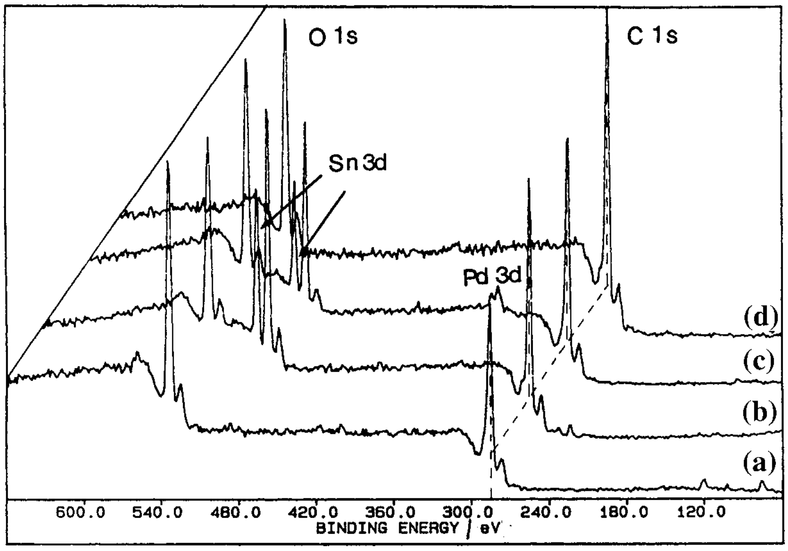

Fig. 2. Survey XPS spectra of O_2 plasma-treated polycarbonate (a), the same after sensitization by $SnCl_2$ (b), sensitization by $SnCl_2$, then activation by $PdCl_2$ (c) and activation only by $PdCl_2$ (d).

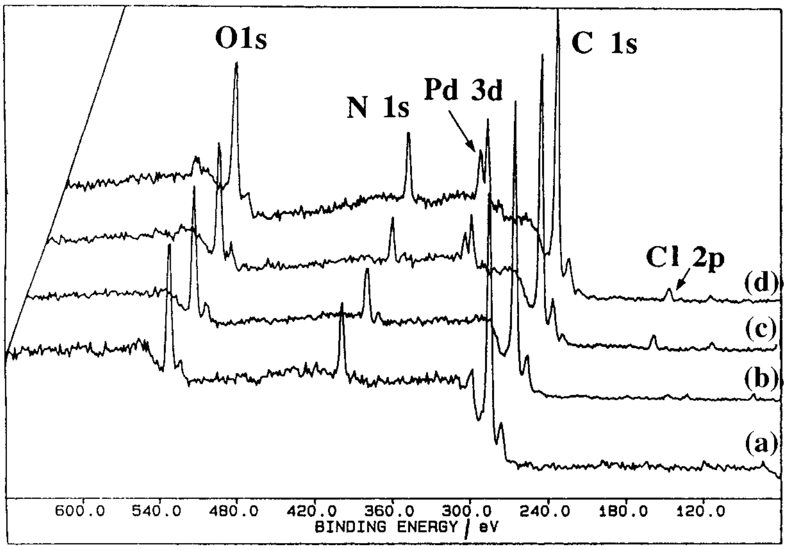

Fig. 3. Survey XPS spectra of NH_3 plasma-treated polycarbonate (a), the same after sensitization by $SnCl_2$ (b), sensitization by $SnCl_2$, then activation by $PdCl_2$ (c) and activation only by $PdCl_2$ (d).

These analyses show unambiguously that a surface on which only active oxygenated functional groups are present requires tin species to chemisorb palladium. Under these conditions, tin grafts onto the oxygen atoms as shown by the O 1s spectra (not presented here). Indeed, the O 1s spectrum of the tin-grafted sample, compared to that of the oxygen-plasma treated sample, presents only a slight broadening towards the low binding energy side which is characteristic of Sn–O bonds. This small chemical effect is due to the fact that (i) the electronegativity of tin (1.8) is not very different from that of carbon (2.5), and (ii) the surface density of C–O bonds is much higher than that of Sn–O bonds. As a result, the small binding energy shift due to Sn–O bonds and the low intensity of the corresponding component do not lead to a noticeable shift of the O 1s peak, but only to its broadening. The tin species so-grafted on oxygen atoms create bridges between the oxygenated surface and palladium. This behaviour results from the strong mutual chemical affinity between Sn and O and from the non-affinity between Pd and O. As a consequence, tin is grafted as Sn^{2+} onto oxygen atoms as shown in Figure 4. The latter compares reference Sn $3d_{3/2,5/2}$ XPS spectra of Sn(0), Sn^{2+} and Sn^{4+} species (spectra (a), (b) and (c) recorded, respectively, from Sn metal and from solid $SnCl_2$ and $SnCl_4$) with those of PC surfaces which were activated by O_2 plasma, then treated either by the $SnCl_2$ solution (spectrum (d)) or successively by the $SnCl_2$ and $PdCl_2$ solutions (spectrum (e)). Clearly, the chemical shift of the 3d spin doublet for the (d) and (e)-treated samples is characteristic of a +2 state.

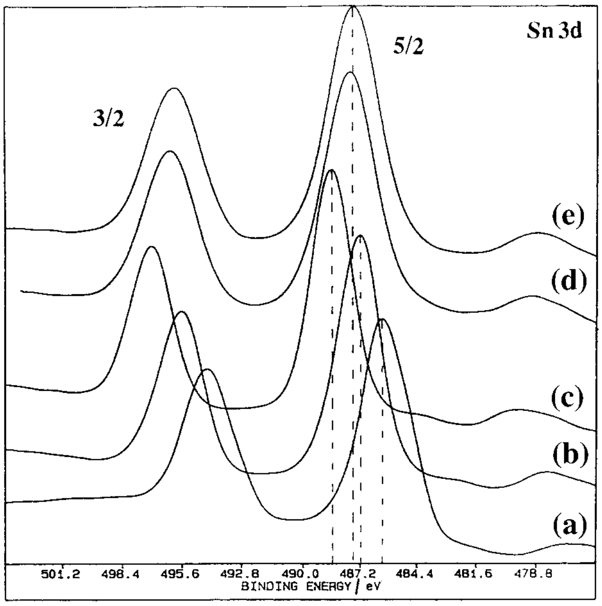

Fig. 4. Sn $3d_{3/2,5/2}$ spectra of metallic Sn (a), $SnCl_2$ (b), $SnCl_4$ (c), O_2 plasma-treated polycarbonate after sensitization by $SnCl_2$ (d) and the same after sensitization by $SnCl_2$, then activation by $PdCl_2$ (e).

When a surface possesses oxygenated and nitrogenated functionalities both uptaken on carbon atoms, everything happens as if the oxygenated groups do not exist since no Sn^{2+} ions are grafted through the mere $SnCl_2$ treatment (Figure 3 (b)). The presence of only nitrogen at the surface of the polymer inhibits the reaction of Sn^{2+} ions from the solution with the oxygen atoms and favours the direct chemisorption of palladium onto the nitrogen atoms. This results from the strong mutual chemical affinity between these species. However, the formation of Pd–N bonds cannot be directly demonstrated from the N 1s spectra. Indeed, the N 1s peak cannot show an energy shift after Pd grafting because (i) the Pd surface concentration is very low (~1 at %), and (ii) the electronegativity of palladium (2.2) is very close to that of carbon (2.5) so that C–N and Pd–N bonds have similar polarities. Figure 5 compares reference Pd $3d_{3/2,5/2}$ XPS spectra of Pd(0) and Pd^{2+} species (spectra (a) and (b) recorded respectively from Pd metal and solid $PdCl_2$) with those of PC surfaces which were treated by NH_3 plasma, then either in a $PdCl_2$ solution (spectrum (d)) or successively in $SnCl_2$ and $PdCl_2$ solutions (spectrum (c)). Clearly, palladium is surface-grafted as Pd^{2+} in the first case, and both as Pd^{2+} and Pd(0) in the second case, even though the Pd^{2+} species are largely predominant. Indeed, when palladium is uptaken on tin, the 3/2 and 5/2 peaks (spectrum (c)) are slightly shifted (−0.8 eV) in comparison with those of the Pd^{2+} species alone and are broadened toward the low binding energy side, which indicates the presence of some metallic palladium sites on the treated surface.

In conclusion, surfaces carrying oxygenated functionalities chemisorb Pd^{2+} ions only through Sn^{2+} ions which are themselves chemisorbed onto oxygen atoms. Surfaces carrying both oxygenated and nitrogenated functionalities chemisorb Pd^{2+} ions directly onto nitrogen atoms and hinder Sn^{2+} ion grafting.

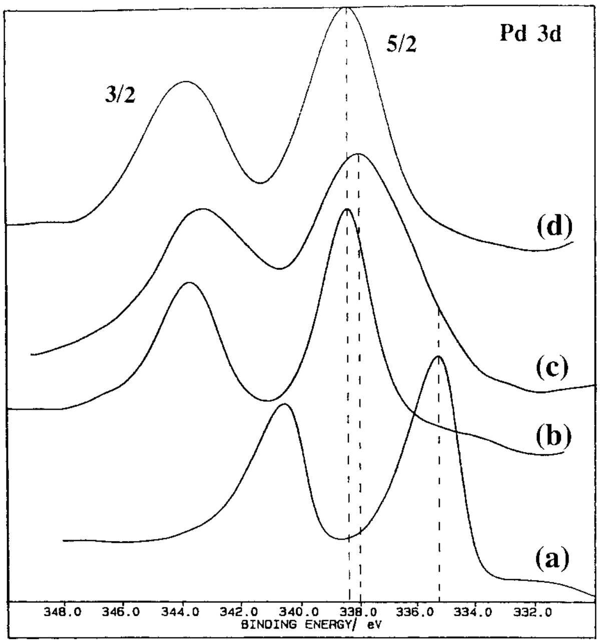

Fig. 5. Pd $3d_{3/2,5/2}$ spectra of metallic Pd (a), $PdCl_2$ (b), O_2 plasma-treated polycarbonate after sensitization by $SnCl_2$, then activation by $PdCl_2$ (c), NH_3 plasma-treated polycarbonate after activation only by $PdCl_2$ (d).

As shown in previous work [11–16] nickel metallization of a polymer can be obtained using the simplified process we have developed. XPS analyses have pointed out the efficiency of NH_3 or N_2 plasma treatments for the surface-grafting of nitrogenated species and, above all, the efficiency of palladium chemisorption onto such grafted functionalities. On all the studied substrates (PC, PS, PTFE, PA, PEI ...) we have found a higher palladium surface concentration (1.5 to 1.8 at %) with our simplified process than with the one- or two-step conventional process (0.8 to 1.0 at %). As palladium is grafted on the top surface of the polymer, it is evident that the more Pd^{2+} ions are chemisorbed, the stronger is the adhesion of the electrolessly deposited metallic film.

3.2. *Metallization initiation mechanisms*

3.2.1. *Nickel metallization of PC*

When a PC sample, first exposed to an oxygen plasma treatment and then to the two-step conventional process (use of $SnCl_2$, then $PdCl_2$ solutions), is immersed in a nickel plating bath, metallization starts after a very short initiation time (2 s). During this period of time, Pd^{2+} ions are partly reduced to atomic palladium by the $H_2PO_2^-$ ions of the plating bath [14]. To understand what happens during the initiation time, Pd 3d XPS spectra were recorded after the initiation step (Figure 6). To avoid the masking of XPS information concerning the initiation step by the nickel deposition, the analyses were carried out on a sample subjected to the initiation

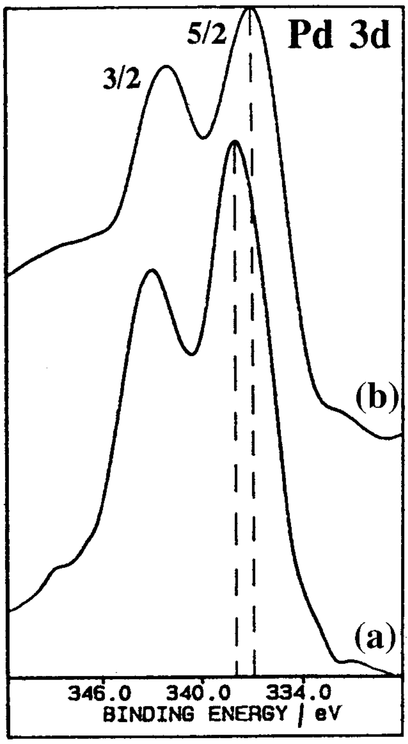

Fig. 6. Pd $3d_{3/2,5/2}$ spectra of O_2 plasma-treated polycarbonate after sensitization by $SnCl_2$, then activation by $PdCl_2$ (a), the same after treatment for 2 s in a 0.1 M NaH_2PO_2 solution (85 °C, pH 5) (b).

step for 2 s in a solution containing only the reducer (NaH_2PO_2) at the same concentration (0.1 M), pH (5) and temperature (85 °C) as in the Ni plating bath. As the Pd 3d spectra present similar modifications for both the 3/2 and 5/2 peaks, we only consider, here, the most intense $3d_{5/2}$ peak. Figure 6 shows that after the initiation period, this peak shifts from 338.0 to 337.0 eV. Even though the peak does not appear at the energy position of the metallic palladium (335.2 eV as shown in Figure 5), its shift indicates the presence of some reduced Pd(0) species which initiate the metallization when a sufficient surface density of these species is obtained [14].

PC samples grafted with nitrogenated functionalities and exposed to the simplified treatment by immersion in a $PdCl_2$ solution have different behaviour when immersed in the nickel plating bath. The initiation time (12 s) before the metallization starting, is longer than in the previous case. It is used here, too, to reduce the Pd^{2+} ions grafted on the PC surface as shown in Figure 7. Spectrum (a) concerns a sample after immersion in the $PdCl_2$ solution, while spectrum (b) is characteristic of this same sample after treatment at 85 °C for 12 s in the 0.1 M NaH_2PO_2 solution. The latter shows a broadening of the Pd $3d_{5/2}$ peak toward the low binding energy side which indicates the presence of metallic palladium. This presence, even at a low level, makes catalysis of the Ni deposition possible. Spectra (c) to (f) will be discussed later in this paper.

In the case of the conventional processes, the presence of Sn^{2+} ions capable of being oxidised to Sn^{4+} ions provides a redox couple that favours the rapid reduction of Pd^{2+} ions. Such a reduction was proposed by different authors [2, 3, 5, 10] who considered that the Pd^{2+} reduction occurred during the treatment using $SnCl_2$ then $PdCl_2$ solutions, that is to say before immersing the sample in the plating bath. In the case of the non-conventional process, the Pd^{2+} ions are only reduced by the $H_2PO_2^-$ ions present in the metallization bath which explains the extra delay to the metallization initiation compared to that of the conventional process.

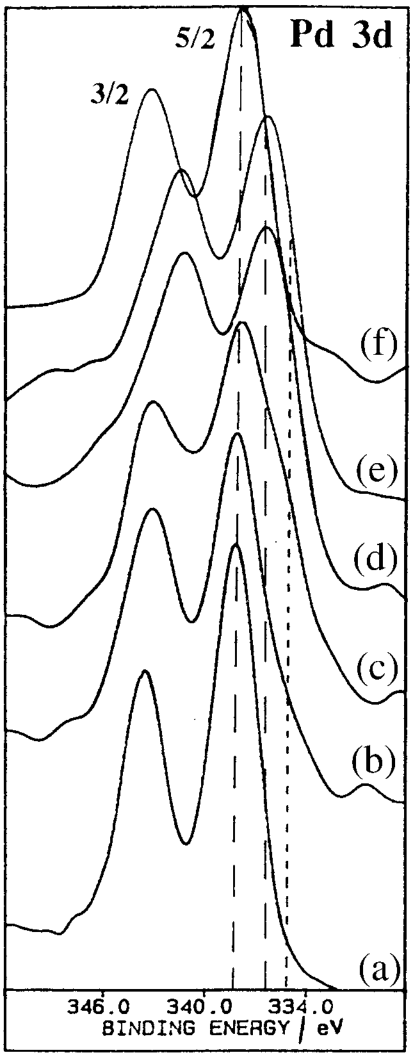

Fig. 7. Pd $3d_{3/2,5/2}$ spectra of N_2 plasma-treated polycarbonate after activation by $PdCl_2$ (a), the same after 12 s (b), 1 (c), 5 (d) and 10 min (e) in a 0.1 M NaH_2PO_2 solution (85 °C, pH 5), the same after photon irradiation for 3 min using an incoherent excimer lamp (λ = 172 nm) (f). Small dashed line corresponds to binding energy for the Pd(0) state.

3.2.2. *Copper metallization of PC*

After the conventional procedure (use of $SnCl_2$, then $PdCl_2$ solutions), the metallization starts after a period of about 15–30 s in the copper bath used in this work. Since the $CuSO_4$ bath is dark blue the determination of the onset of the reddish copper deposit appearance on transparent PC substrates is rendered difficult. The longer initiation time observed for copper (15 to 30 s) than for nickel (2 s) deposition indicates that the reducer of the copper bath (HCHO in alkaline solution) is less active toward the Pd^{2+} reduction than that (NaH_2PO_2 in acidic solution) of the nickel bath. This is confirmed by the absence of a copper deposit after an ammonia or nitrogen plasma treatment followed by either the conventional or the new simplified ($PdCl_2$) procedure. In both cases, only Pd^{2+} ions are grafted on the PC surface and the copper metallization bath is unable to reduce the Pd^{2+} ions to Pd atoms as revealed by XPS spectra of palladium (not shown here). Indeed, a simulation of what may happen during the initiation time in the copper plating bath was done on a PC sample previously treated by NH_3 plasma and $PdCl_2$, then immersed for 5 min at room temperature in a HCHO 37% aqueous solution (1:5 vol.) whose pH was adjusted to 12 by NaOH addition. Only a slight shift from 338.5 to 338.0 eV of the maximum of the Pd $3d_{5/2}$ peak was observed. This suggests that the reduction of Pd^{2+} species to Pd(0) ones is quantitatively too low. Under these conditions, copper metallization initiation cannot proceed.

Comparatively, similar XPS analyses were performed, on the one hand on a PC sample treated by oxygen plasma, then by the two-step conventional process (Figure 8(a)), on the other hand on the same sample after immersion for 5 min in the HCHO solution as in the previous case (Figure 8(b)). The presence of Sn^{2+} ions appears to play a significant role since the maximum of the Pd $3d_{5/2}$ peak before the HCHO treatment, located at 338.1 eV (i.e., at a lower value than in the case of the NH_3 plasma treatment), shifts to 337.7 eV after the treatment. In this case, the Sn^{2+} ions are probably involved in the Pd^{2+} reduction and the surface density of palladium atoms seems sufficient to catalyse the Cu^{2+} reduction and allow the PC plating.

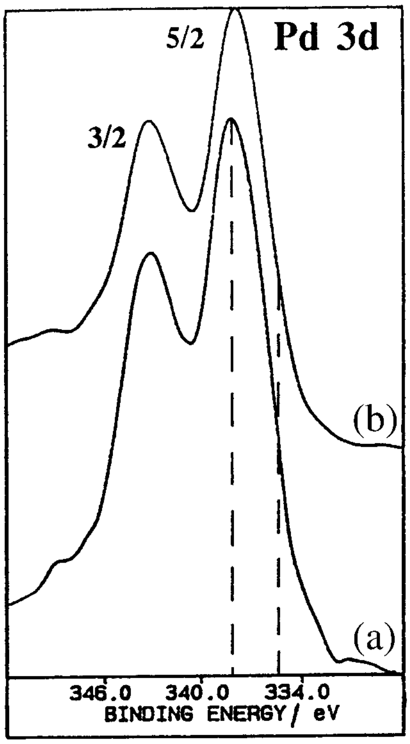

Fig. 8. Pd $3d_{3/2,5/2}$ spectra of O_2 plasma-treated polycarbonate after sensitization by $SnCl_2$, then activation by $PdCl_2$ (a), the same after immersion in an aqueous solution (1:5 vol) of HCHO 37% at pH 12 for 5 min (b). Dashed line at right hand side corresponds to binding energy for the Pd(0) state.

To achieve copper metallization after NH_3 or N_2 plasma treatment and Pd^{2+} grafting, it is necessary to reduce the Pd^{2+} ions to palladium atoms before immersing the sample into the copper plating bath. For this, two methods were investigated. The first consisted in immersing the Pd^{2+} grafted samples in 0.1 M NaH_2PO_2 at 85 °C for different times, in rinsing them in water for 1 min, before dipping in the copper metallization bath. XPS results for the Pd 3d peaks are gathered in Figure 7. The latter shows the reference spectrum before the NaH_2PO_2 treatment (a) and spectra obtained after 12 s (b), 1 (c), 5 (d) and 10 (e) min. After 12 s or 1 min, the Pd $3d_{5/2}$ peak broadens toward the low binding energy side suggesting the presence of metallic palladium. After 5 or 10 min, the 5/2 peak is shifted to 336.3 eV. This peak includes a significant component located at about 335.2 eV due to metallic palladium and another one located at 338.9 eV corresponding to the non-reduced Pd^{2+} species. Account being taken of this experimental observation, the PC samples were immersed in the hypophosphite solution for various times, and then immersed in the copper bath. Under these conditions, the Cu metallization proceeded after an initiation time that was all the shorter as the previous treatment duration in the hypophosphite solution was long. Indeed, after 5 to 10 min of treatment in the hypophosphite solution, the Pd(0) surface density is sufficient to allow the start of metallization. The second attempt to reduce the Pd^{2+} ions before copper plating consisted in subjecting the sample to a VUV irradiation ($\lambda = 172$ nm), through the use of an incoherent excimer lamp [18]. PC samples previously treated by N_2 or NH_3 plasma then by $PdCl_2$ were located 1 cm away from a CaF_2 window separating the VUV source and the reactor. Specimens were irradiated for 3 min under a residual air pressure of 1 mbar. As shown by spectrum (f) in Figure 7, the Pd^{2+} ions are partly reduced to Pd(0) since the Pd $3d_{5/2}$ peak is located at 337.5 eV. However this energy position close to that of Pd^{2+} shows the necessity of using a longer treatment time or a higher lamp intensity to obtain a more complete reduction. For a sample irradiated for 3 min, copper metallization needs an initiation time of about 10 s.

4. Discussion

Our previous work [14] has shown that electroless reactions require, on the surface to be coated, the presence of palladium metal for metallization initiation to occur. The present results show that a very strong reducer such as NaH_2PO_2 can reduce Pd^{2+} ions in all cases, that is to say when they are chemisorbed onto tin ions or onto nitrogenated species. Indeed, the potential of the $H_2PO_3^-/H_2PO_2^-$ redox couple at pH 5 under the operative conditions of the electroless reaction is $E_0 = -0.804$ V. On the other hand, although formaldehyde is a strong reducer in alkaline medium (E_0 ($HCOO^-/HCHO$) $= -0.913$ V at pH 12), it does not reduce the Pd^{2+} ions when the latter are chemisorbed onto the grafted nitrogenated species. It is clear, in this case, that the kinetics of the Pd^{2+} reduction are infinitely slow. However, when Sn^{2+} ions are grafted onto the PC surface just before the Pd^{2+} ions, according to the two-step conventional process, the formaldehyde partly reduces the Pd^{2+} ions as shown in Figure 8. It is very likely that the Sn^{2+} ions either participate directly in the Pd^{2+} reduction or catalyse the Pd^{2+} ions reduction by HCHO, by lowering the activation energy. This hypothesis is supported by work of Ohno et al. [19] concerning the catalytic activity of different metals for oxidation of various reducers. These authors have shown that, among the autocatalytic metals, Cu is the most catalytically active and Pd the least, for oxidation of a solution containing a mixture of formaldehyde and EDTA of pH 12. In the same work, these authors have also studied the oxidation by different metals of a NaH_2PO_2/Na-citrate solution (pH 9) and found a significant catalytic activity for palladium. This agrees with our XPS analyses (Figure 7) which point out the effective reduction of the Pd^{2+} ions grafted onto a solid surface when the latter is immersed in a NaH_2PO_2 solution whose characteristics (concentration, pH, temperature) are identical to those of the Ni plating baths.

5. Conclusion

This work used XPS to study the reactions proceeding during the preparation of surfaces for electroless metallization as well as those leading to the catalyst chemisorption and metallization initiation. The potential of NH_3 or N_2 plasma treatments of polymer surfaces to graft nitrogenated functionalities that can directly chemisorb palladium ions through immersion in a dilute $PdCl_2$ solution was shown. As a result, a new simplified process was developed to make a polymer surface catalytic toward a subsequent nickel electroless metallization. The examination of palladium XPS spectra has shown that, during the initiation time (i.e., before the start of metal deposition) the Pd^{2+} ions grafted onto the surface during the catalyst chemisorption step were partly reduced to Pd(0), and that this reduction was necessary for achieving metal deposition. This reduction is efficiently performed by the reducer ($H_2PO_2^-$ ions) of nickel plating baths. On the other hand, the reduction is only possible with the reducer (HCHO in alkaline medium) of copper plating baths if Sn^{2+} ions are jointly present with Pd^{2+} ions on the surface to be plated. Account being taken of the redox potentials of the different couples involved, there is no thermodynamical hindering of the corresponding reduction reaction and we may consider that the Sn^{2+} ions play the role of catalyst in the reduction of Pd^{2+} ions by formaldehyde.

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