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Copper patterned polystyrene panels by reducing of surface bound Cu (II)-sulfonyl hydrazide complex

Niyazi Bicak *, Bunyamin Karagoz

Istanbul Technical University, Dept. of Chemistry, Maslak 34469 Istanbul, Turkey

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Abstract

A modified electroless metal deposition method has been developed for copper plating of polystyrene (PS) surfaces. The modified procedure avoids the plasma conditioning and surface activation steps in the classical electroless metal plating process.

First step of the present procedure is chlorosulfonation of PS surface by soaking into chlorosulfonic acid, yielding chlorosulfonated surface with density of 0.046–0.110 mmolcm^{-2} depending on contact time (10–60 min).

In the second step chlorosulfone groups on the surface are converted to sulfonyl hydrazides almost quantitatively by reaction with hydrazine solution (80%). Green Cu (II)-sulfonylhydrazide complex is formed at the surface, in the third step, by interaction with ammoniacle Cu (II) solution at room temperature. The copper in the complex is reduced rapidly in the fourth step, by immersing the specimen into 5% of hydrazine solution. The elemental copper deposited onto the surface serves activating sites to accumulate more (5–7 mg per cm^2) elemental copper from electroless copper solutions in the final step. The present method avoids the surface activation with palladium and allows preparing copper patterns with reasonably high pull-off strengths (3.77 Nmm^{-2}) on PS panels.

In the study the copper deposition has been investigated using standard analytical procedures, X-ray photoelectron spectrometry (XPS) and Scanning Electron Microscopy.
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Keywords: Electroless copper plating; Chlorosulfonation; Polystyrene, Sulfonylhydrazide; Copper deposition

1. Introduction

Zerovalent metal deposits on polymer surfaces have found potential applications in various fields such as electronics and optical devices.

Alternative methods, high vacuum deposition [1], sputtering of metal powder dispersions [2] and electroless plating [3] have been used to obtain metal coated particles and two-dimensional metal layers. The electroless plating is of special interest due to simplicity of its processing [4].

Using this method it is also possible to obtain patterned polymer surfaces in which metal deposits are created only on confined arrays and islands. This method involves three steps; i) pretreatment of the surface with X-ray, plasma or chemical oxidants, ii) activation (sensitizing) with Pd $(OOCCH_3)_2$ and $SnCl_2$, iii) electroless metal plating.

Last two steps of this approach proceed without difficulty. But the first step is crucial for successful metal plating. The X-ray exposure and plasma treatment with noble gases, in this step, provide surface wettability to adhere to the metal layer deposited in the following steps. Any failure of this step results in peeling of metal layers. Plasma induced hydrophylicity increases physical sorption ability of the surface. Ion-assisted plasma process using N_2 and O_2 has proven to be much more efficient [5,6]. However in those procedures adhesion limitation is the main problem.

It has been evidenced that, high peel strengths can be achieved by covalently attached ligating functions on the substrate surface. But covalent attachment depends strictly on chemical structure of the surface and the reagent employed. Plasma enhanced-surface modification [7], excimer laser irradiation for C–Cl bond scission of PVC and following amination [8] are some examples of surface functionalization with low-molecular weight metal chelating compounds. Most common approach in this method is graft copolymerization of some functional monomers such as 4-vinyl pyridine, 1-vinyl

* Corresponding author.
E-mail address: bicak@itu.edu.tr (N. Bicak).

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imidazole [9], glycidyl methacrylate [10] and aniline [11] from polymer surfaces and subsequent metal deposition from electroless metal solutions. High peel strengths, as high as 21 have been attained by this method.

In another metallization approach, silver salt of polyamic acid is heated to give polyimides with extremely reflective silver mirror on the surface [12]. However, this method needs high temperatures i.e. 400 °C and seems to be confined to silvering of polyimides.

In our previous paper we have described a new method in which metal deposition from ammoniacle Ni (II), Cu (II) and Ag (I) solutions has been achieved by polymer bound hydrazine as reducing agent [13]. Advantage of polymer bound reducing agent is formation of metal plates only on the polymer surface, but not in the solution. This method is very successful in preparing spherical bead polymers with the metal contents up to 23% by weight and avoids the surface sensitizing employed in typical electroless plating processes.

However extension of this method to flat surfaces is challenging, not only because of the difficulty in preparing soluble polymers having reducing groups but also for their compatibility with the substrate material.

In the present work we report a relatively simple procedure for preparing copper patterned polystyrene sheets by using polymer bound sulfonyl hyrazide groups. Chlorosulfonation of PS by direct immersion in chlorosulfonic acid and following interaction with hydrazine yields sulfonyl hydrazide functions on the surface. The resulting surface is suitable for complexation with Cu (II) solutions. The copper complex on the surface is reduced by dilute hydrazine solution. Minute amounts of zero-valent copper formed serves as activating sites to accumulate copper from electroless plating solutions. In the study effects of process conditions have been investigated and morphology of the metallized surfaces has been studied by conventional chemical methods, XPS and SEM techniques.

2. Experimental

2.1. Materials

All the chemicals used were analytical grade commercial products; chlorosulfonic acid (Aldrich), hydrazinium hydroxide (85%) (J. T. Bakers), $CuCl_2.2H_2O$ (E. Merck), they were used as supplied.

2.2. Chlorosulfonation of PS panels

Commercial PS panel (3 mm thickness) was cut into small pieces (5 × 15 cm) and immersed in chlorosulfonic acid for predetermined time intervals (20–150 min) at room temperature. The samples were taken out and soaked into ice-water. After washing with cold water the samples were dried by air flow. The samples were stored in desiccators.

2.3. Determination of the chlorosulfone density

The edges of the chlorosulfonated sample were removed by cutting (4 × 4 cm) with a blade and boiled in 40 mL of 2 M NaOH solution for 30 min. The aqueous solution was decanted and transferred into a beaker. The sample was washed with water. The mother liquor and washings were combined in a volumetric flask. Then 5.6 mL of 65% HNO_3 was added to the flask and the solution was diluted to 100 mL. It was filtered and 10 ml of the filtrate was used for chloride analyses. The chloride concentration was determined by colorimetric method using mercuric sulfocyanide [14]. Thus, 4.42×10^{-4} M chloride concentration of the solution (for 20 min of the chlorosulfonation time), corresponds to;

$$4.42 \times 10^{-4}\left(\mathrm{molL}^{-1}\right) \times 0.1\mathrm{L}/32\mathrm{cm}^2 \\ = 1.38 \times 10^{-6}\mathrm{mol\ per\ cm}^2\mathrm{of\ the\ surface\ area}$$

2.4. Reaction with hydrazinium hydroxide

The chlorosulfonated samples (4.5 × 10 cm) were soaked into hydrazinium hydroxide and the reaction contents were shaken for 15 min at room temperature. The samples were taken out, washed with 0.1 M NaOH solution (20 mL), rinsed with water and dried by means of a soft paper. They were stored in tightly closed vessels to avoid oxidation by air oxygen.

2.5. Determination of the Sulfonyl hydrazide Content

The sulfonyl hydrazide content was assayed by iodometric method as follows; a half gram of iodine was dissolved in 25 mL methanol and the PS sample (4 × 4 cm) was placed in this solution. The bottle was closed and shaken for 30 min. Ten mL of the methanol solution was pipetted and titrated with standard $Na_2S_2O_3$ solution. Thus, 1.0 mL of the titer consumption corresponds to 1.32×10^{-6} mol sulfonyl hydrazide per cm^2.

2.6. Preparation of copper patterned PS panels

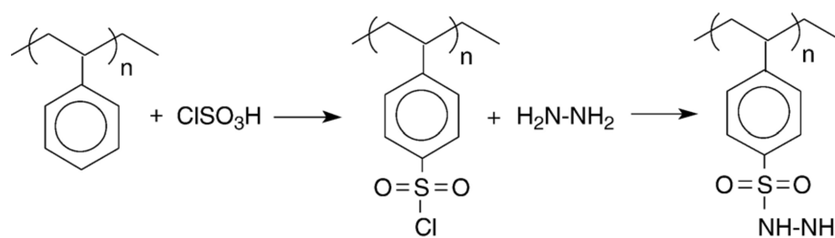
Both surfaces of a polished PS sample (5 × 10 cm) was masked by using self-adhesive polyethylene ribbon with 3 mm of wide. The distance between the parallel tapes was adjusted to be 5 mm, with the helps of a cylindrical guide. Non-masked areas of the slides were subjected to chlorosulfonation and following reaction with hydrazine as described above.

Meanwhile an ammoniacle cupric sulfate solution was prepared by mixing 30 mL of 1 M $CuSO_4$ solution with 20 ml of NH_3 solution (25%). The chlorosulfonated PS sheet was dipped into this solution while shaking occasionally. A blue-green copper-sulfonyl hydrazide complex formed on the surface.

After 10 min, the sample was taken out, washed with distilled water and immersed in hydrazine solution (5%) at room temperature for another 10 min. Residual Cu (I) or Cu (II) contaminants are reduced in this process. This process can be termed as “developing step”. Since the copper layer formed is very sensitive to air oxidation, the resulting samples must be stored in tightly closed vessels.

2.7. Determination of copper content of the panel

The trace copper deposited on PS panel in developing stage was determined by stripping the zerovalent copper with HNO_3



Scheme 1. Chlorosulfonation of PS.

solution. This was carried out as follows: In an efficient fume cupboard, the PS sample (5×5 cm) having copper deposit was dipped into 50 mL of 10% HNO_3 solution. The solution was stirred with a magnetic bar until all the copper stains on the slide disappear (approximately 45 min). 10 mL of this solution was transferred into a volumetric flask, neutralized by NaOH solution and diluted to 100 mL. The cupric ion concentration of the solution was assayed colorimetrically by using diethanolamine-CS_2 as color reagent according to the procedure described in the literature [15]. Surface density of the copper after the developing stage was found 6.4×10^{-7} $mmolcm^{-2}$.

2.8. Electroless plating with copper

The copper plating was performed by using typical electroless solution as suggested in the literature [16]. The composition of the plating solution was as follows: 0.7 wt.% $CuSO_4.5H_2O$, 2.5 wt.% sodium potassium tartarate, 0.4 wt.% NaOH and 0.4 wt.% formaldehyde. The specimen containing trace amount of elemental copper on the surface was immersed into this solution for 3 h. Progress of the copper deposition was followed visually by increasing thickness of the surface. Average values of the copper contents of the specimens were found to be $(9.6\pm0.2)\times10^{-5}$ $molcm^{-2}$ by the diethanolamine-CS_2 method. The total mass increases of those specimens were found to be 0.161 ± 0.005 g.

2.9. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) pictures were taken with a Jeol 1540 instrument at 10 kV, using gold coated samples.

2.10. X-ray Photoelectron Spectrometer (XPS)

The XPS measurements of copper plated samples (1×2 cm^2) were carried out by SPECS PHOIBOS-150 Electron Analyser equipped with a SPECS XR-50 X-ray source. Monochromatized Al Kα radiation(1486.6 eV) was used for the excitation. Survey spectra were acquired from 0 to 1200 eV with a pass energy of 80 eV. All the peaks were referenced to a C1s signal at 285 eV, representing C–C bonds of PS substrate. The pressure of the analyser chamber was 10^{-8} to 10^{-9} Torr.

2.11. Adhesion tests

Adhesion tests were performed by Adhesion-master 525 MC pull-off apparatus equipped with a cylinder (20 mm of diameter) acting 10 kN maximum force and a control unit. The specimens were placed at the bottom of the cylinder and attached by means of commercial two-component epoxy adhesive. After drying at room temperature for 24 h, the specimens were subjected to linearly increased pull forces until the rupture from the surface. The pull-off forces were measured as Nmm^{-2}.

2.12. Contact angle measurements

The contact angles were measured according to the sessile drop technique by Goniometer (KSV Instruments Model CAM 101). A drop of distilled water with a tight syringe was placed on the surface. Advancing contact angles associated with the hydrophobic character and receding contact angles indicating hydrophilic character of the surface were measured at both left and right sides of the drop. The contact angles of surfaces were calculated from the average of the measured values.

3. Results and discussion

Chlorosulfonation of commercial PS sheets (with 3 mm of thickness) with chlorosulfonic acid and subsequent treatment with hydrazinium hydroxide yield sulfonylhydrazide functions on the surface (Scheme 1).

The reaction with chlorosulfonic acid proceeds at room temperature [17] and gives chlorosulfonated PS as in the case for benzene derivatives. The substitution takes place mostly at *para*-position of the phenyl ring. The reaction provides a means of easy functionalisation of PS. Solution of linear PS in CH_2Cl_2, however,

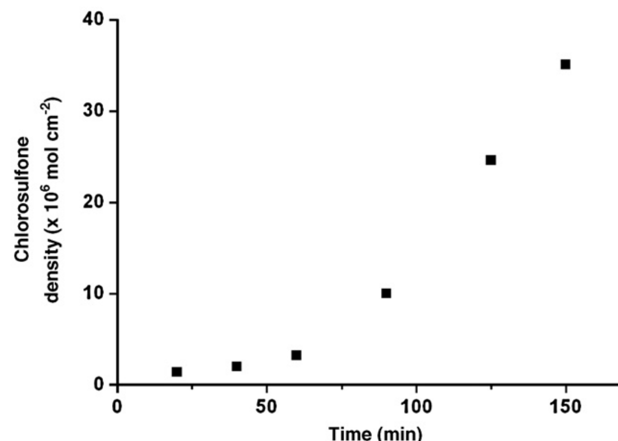
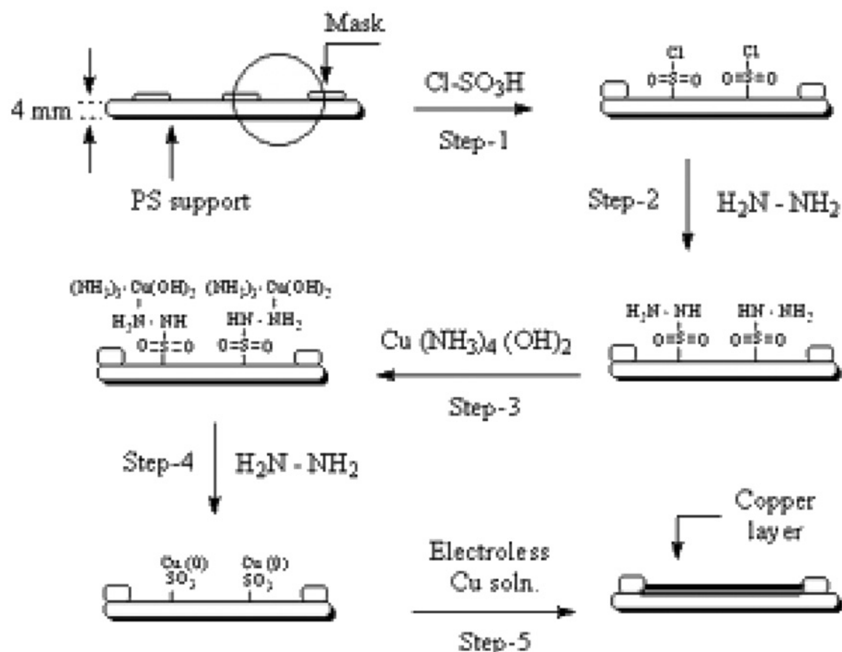


Fig. 1. Chlorosulfone density (mol per cm^2) versus time plots of PS sheets. (The data produced are average of two independent chlorine analyses with 4% of maximum deviation).



Scheme 2. Schematic layout of the copper patterning of PS surface.

undergoes rapid crosslinking upon addition of chlorosulfonic acid due to bridging sulfone formation between phenyl rings as side reaction. Nevertheless this crosslinking is beneficial to create robust chlorosulfonated layers on flat PS surface.

Chlorosulfonation of PS surface can be achieved simply, by immersing PS plaque samples ($5 \times 15 \times 0.3$ cm) into chlorosulfonic acid in a suitable glass container equipped with a $CaCl_2$ guard tube. Time-dependent chlorosulfone density of the surface is shown in Fig. 1. The figure shows a sharp increase of the chlorosulfonation around 1 h, due to increasing hydrophylicity of the surface.

As the reaction proceeds the samples become opaque. Loss of the transparency indicates formation of a surface layer with different refractive index. It was shown that 20 min of the contact with chlorosulfonic acid is enough to attain visually followed surface roughness and yields a chlorosulfone density of 1.38×10^{-6} mol per cm^2, which is satisfactory for the further surface modifications. This step is completed after rinsing with cold water and subsequent drying with air-blow.

This is the most crucial stage of the whole process. Experiments showed that prolonged contacts with chlorosulfonic acid, longer than 1 h result in brittle materials and yield some pinholes on the surface owing to further diffusion of the acid through the samples.

Patterned surfaces can be obtained by prior masking of the surfaces with self-adhesive polyethylene sheet having any desired shape and frame of the board.

The first step of the process involves the chlorosulfonation step discussed above.

Overall process of the copper patterning is depicted in Scheme 2. The hydrazide formation in the second step is performed by

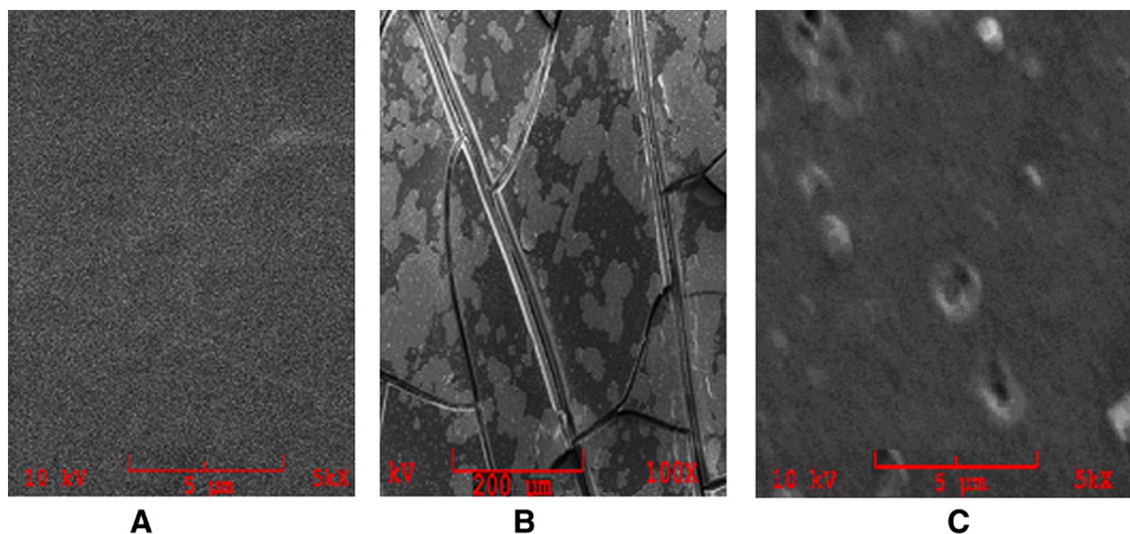


Fig. 2. SEM picture of PS surface with copper seeds (A) and the electroless copper plated surface (B) and its magnified view (C).

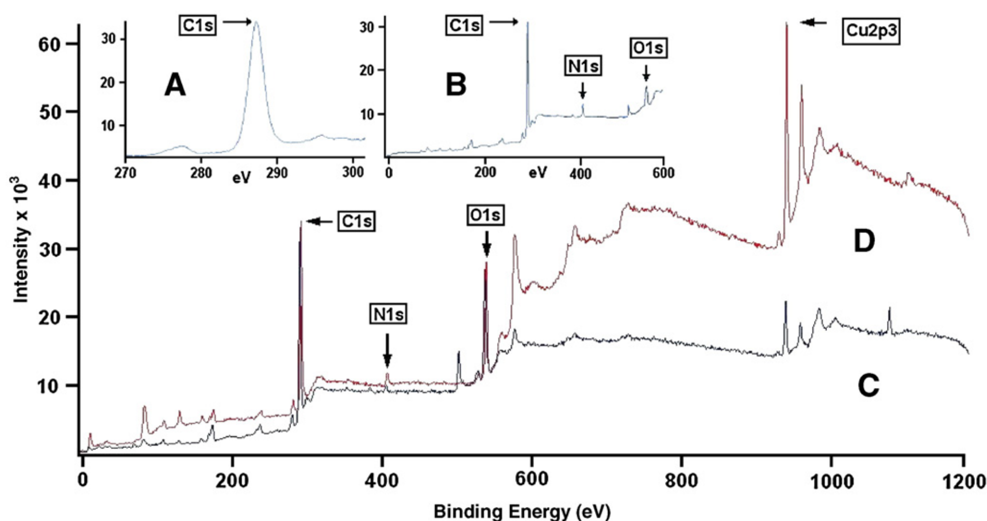


Fig. 3. Wide scan XPS of naked PS surface (A), sulfonylhydrazide functional surface (B), surface with copper seeds (C) and electroless copper plated surface (D).

soaking the chlorosulfonated sample into concentrated hydrazinium hydroxide solution (80%) at 0 °C for 5 min. Density of sulfonyl hydrazide function was determined by H_2O_2 method and found to be 1.32×10^{-6} mol per cm^2.This value indicates a 95.6% of transformation yield of chlorosulfone groups on the surface. After rinsing with demineralized water (2×50 mL) the sample is dipped into ammoniacle Cu (II) solution (step 3) at room temperature for 5 min. An immediate green copper complex forms on the exposed areas of the plaque. Considering with complex forming ability of the sulfonyl hydrazide function with transition metal ions [18], greenish color of the surface can be ascribed to copper (II)-sulfonyl hydrazide complex via electron donating NH_2 group of the later.

The copper in the complex undergoes complete reduction with hydrazine hydrate solution (80%) in step 4. This step can be termed as "developing stage" and gives a typical bright color of the elemental copper. This is an alternative approach to typical "surface activation" by Pd (II)-$SnCl_2$ solution in the classical electroless plating process. The zero-valent copper deposit on the surface serves seeding points to accumulate more copper in the next step. However, the fresh copper layer is very sensitive to air oxidation. For this reason the washed surfaces were dried with nitrogen flow.

At the beginning we attempted to reduce copper directly by the surface bound sulfonyl hydrazide groups. Because sulfonyl hyrazides are known as reducing agents for Ni (II), Cu (II) and Ag (I) ions. Indeed we have obtained surface copper by soaking specimens into Cu (II) solution above 80 °C. Similar results were obtained by heating of the samples in an oven at this temperature. However, surface and shape deformations were observed of the PS supports.

So the hydrazine reduction at room temperature was taken into consideration to avoid the deformation. Needless to say, this approach can be employed for the case of heat resistant supports.

In the final step the sample was subjected to electroless copper plating. Analysis of the surface layer (by diethanolamine-CS_2 method) obtained in this step indicated an average copper density of $(9.6\pm0.2)\times10^{-5}$ molcm^{-2} (for the exposure time of 3 h) which is good agreement with the mass increase, 6.1±0.3 mg per square centimeter.

SEM pictures of the surface with hydrazine-reduced copper (Fig. 2A) represents a very homogenous surface. The electroless

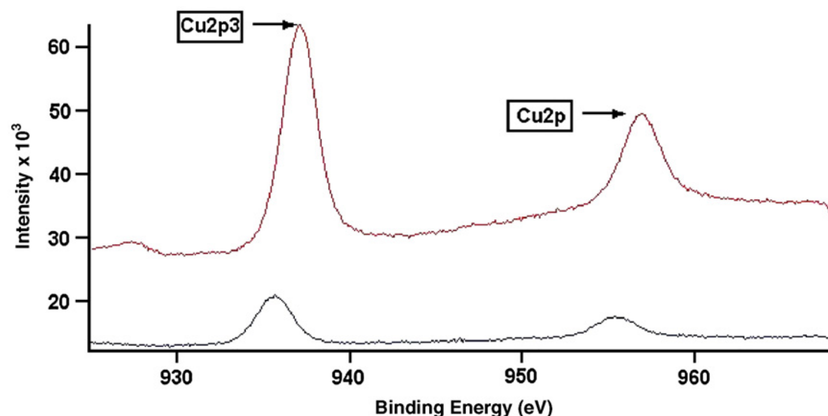


Fig. 4. Cu2p$_{3/2}$ and Cu2p core level XPS of the PS surface with copper seeds (a) and electroless copper plated surface (b).

Table 1
Functional group densities, adhesion strengths and contact angles in each step of the copper patterning

Steps	Process	Surface function	Functional density ($mol cm^{-2}$)	Adhesion($N mm^{-2}$)	Contact angle[b]
1	Chlorosulfonation	$–SO_2–Cl$	1.38×10^{-6}	ND[a]	ND
2	Hydrazide formation	$–SO_2–NH–NH_2$	1.32×10^{-6}	8.42	68.6 ± 1°
3	Complexation with Cu (II)	$–SO_2–NH–NH_2\ (NH_3)_3\ Cu(OH)_2$	ND	7.31	67.1 ± 0.3°
4	Reduction with hydrazine	$–SO_3^-Cu$ (0)	6.4×10^{-10}	>3.22	72.2<±0.2°
5	Electroless plating	More copper on the surface	9.6×10^{-5}	3.7`7	74.7 ± 0.4°

[a]Not determined, [b]contact angle of the naked PS surface 55.7 ± 0.5°.

process yields surfaces consisting of interconnected copper islands (Fig. 2B). The micro fractures, however, do not result in interruption for the conductivity. In magnified view of this picture (Fig. 2C) some stains are observed. Nevertheless these stains are covered by the elemental copper.

Peel strength test of these samples show reasonably high adhesiveness (3.77 $N mm^{-2}$) of the copper layer.

XPS of fresh PS surface gives only the reference carbon peak (C1s core) at 285 eV (Fig. 3 A). Sulfonyl hydrazide functional surface (step-2) represents nitrogen, N1s core level and oxygen, core level, at 405 and around 534 eV respectively (Fig. 3 B). New peaks arisen at 932.8 and 954 eV in Fig. 3C and D are evidence for accumulation of copper in the last two steps. In Fig. 3C, the peak at 500 eV must be due to Na-KLL Auger electrons [19]. Another peak at 1072 eV represents Na (1 s) which is arisen from adsorbed sodium ions while washing the sulfonyl hydrazide sample with NaOH. These two peaks are almost invisible in the spectrum of the copper plated sample in Fig. 3D. This reveals migration of adsorbed sodium ions in the electroless deposition step. In Fig. 3D the peaks at 75 eV and at 122.5 eV can be ascribed to Cu ($3p_3$) and Cu (3 s) levels respectively. Weakness of those peaks in Fig. 3C (for the case of low copper content) confirms this assumption.

XPS of the electroless copper plated surface (Fig. 4) represents one major peak at 932.8 eV which can be attributed to Cu $2p_{3/2}$ core-level of Cu (0). Another peak observed around 954 eV indicates Cu 2p core level. Average width of this peak is 2.4 eV which is greater than that of the typical value (1.4 eV) observed in XPS spectra of pure elemental copper.

This can be attributed to partial oxidation of the fresh copper surface of the specimen. Interestingly, N1s core level of the nitrogen atom yields a very weak peak around 400 eV. This implies decomposition of the sulfonyl hydrazide groups while reacting of the surface with the electroless solution. Whereas, in the case for core-level spectrum of primary copper layer obtained by hydrazine reduction shows a relatively broad peak around 936 eV. This peak can be assigned to Cu $2p_{3/2}$ of Cu (II) in complex form. This might be due to re-oxidation of the seed copper on the fresh surface with air oxygen.

Adhesion tests revealed that, pull off strength of the primary copper layer (obtained by hydrazine reduction) is above 3.20 $N mm^{-2}$ (Table 1). Electroless deposited copper layer gave a pull-off strength of 3.77 $N mm^{-2}$, which is satisfactory for application of the method for large scale surface treatments.

The contact angle measurements showed that, naked surface of the commercial PS has a contact angle of 55.7 ± 0.5° in the advancing mode. Incorporation of sulfonyl hydrazide function to the surface results in significant rise in the contact angle (to 68.6 ± 1°) in accordance with higher hydrophobicity of this group (Table 1). Slight reduction of the contact angle to 67.1 ± 0.3° (for the case of step-3) might be attributed to hydrophilicity of small amounts of cationic copper complex formed on the surface. Hydrazine reduction (step-4) and following electroless copper deposition increases the contact angles to 72.2 and 74.7° respectively. Such an increment might be due to homogeneity and defect-free nature of the copper layers.

4. Conclusion

In conclusion, the method presented offers preparing robust copper plating with reasonable adhesion on PS sheets. The method omits tedious plasma modification processes and avoids the palladium activations in the typical electroless processes. The copper surface obtained by this method shows reasonably high contact angle (74.7 ± 0.4°) indicating smoothness of the surface. The surface activation by copper itself and homogeneity of the plated surfaces are additional advantages of the present method in preparation of copper patterned surfaces.

Acknowledgement

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