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A method for polyaniline coatings on solid polystyrene surfaces and electroless copper deposition

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Abstract

A new efficient method is presented for electroless copper deposition on solid polystyrene surfaces via polyaniline (PANI) coatings. It was demonstrated that, partial polymerization of aniline by catalytic air oxidation in the presence of dissolved polystyrene (PS) (M_n: 87.000 K) gives viscous solution of PANI-PS mixture in aniline. Direct application of the polymerization mixture with copper catalyst onto polystyrene sheets (5 × 15 cm) resulted in extension of the polymerization by air oxygen to give a smooth PANI-PS composite layer on the host surface. Treatment of the surface with a similar PANI solution without PS gave Emeraldine base film with homogenously dispersed copper. Reduction of the surface copper by diluted hydrazine (5%) yielded zero-valent copper serving as seed points for accumulation of more copper from an electroless plating solution in the following process. Experiments showed that, the method presented offers a simple pathway to produce excellent copper deposits on PS substrate. This method is superior to traditional electroless plating process, since tedious surface etching and expensive palladium activation steps are being avoided. The surface characteristics were examined by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), adhesion tests and contact angle measurements. The results showed that, the electroless plating process gives a homogeneous and highly robust copper layer with 34.2 µm of thickness within 48 h. Adhesion of the copper layer to the underlining surface was satisfactory as inferred from pull-off measurements (1.6 N/mm^2).
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Keywords: Surface metallization; Electroless plating; Copper deposition; Polyaniline; Coating

1. Introduction

Electroless metal plating (EMP) is a versatile method for surface metallization of plastics and ceramics [1,2]. Common EMP process involves; i) surface modification ii) surface activation by Pd (II) and $SnCl_2$ solutions and iii) electroless metal deposition steps. The surface modification step is of prime importance to attain good adhesion of the metal layer to the substrate surfaces.

Numerous techniques, such as ion assisted laser treatment [3], plasma modification [4], excimer UV laser [5] and dielectric barrier discharge [6] have been developed for modification of polymer surfaces. Beside those high energy-irradiation methods, wet chemical methods such as nitration and sulfonation have been reported to be efficient in modification of relatively polar polymer surfaces [7].

Moreover, coating of a polymer substrate with a reactive layer has been considered as a more direct way of surface modification [8] for the electroless metal deposition. However the organic solvent involved in the process may cause swelling and distortion of the underlining polymer surfaces [9].

Graft copolymerization of a reactive monomer such as glycidylmethacrylate [10] from the surface has been reported to be a useful method for modification of the surfaces to be metallized.

Dai and Wang [11] described fabrication and selective metallization of high aspect ratio cured SU-8 polymer microstructures on silicon substrate using UV lithography technique and selective electroless copper deposition method, yielding honey cell patterned surfaces. Henry and McCarley [12] reported a general method for amine modification of poly methyl methacrylate sheets and selective metal deposition on the surfaces. Some polymer surfaces are reactive enough to deposit zero-valent metals and do not need additional surface modification. For instance polyaniline

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(PANI) films were demonstrated to be capable of undergoing spontaneous metallization via chemisorption from Pd (II) and $SnCl_2$ solutions [13]. In the following studies, Kang and coworkers [14] reported that, Pd-laden PANI films can be used for electroless plating of copper.

Simplicity of this process has prompted us to obtain PANI coated surfaces for metallization of plastic surfaces. However adhesion of preformed PANI to any surface cannot be achieved by ordinary coating methods.

In a recent work, we have demonstrated that, aniline can be polymerized by air oxygen in presence of Cu (II) as catalyst [15] to give Emeraldine base. In the present work this chemistry was employed for preparing PANI films well adhered to solid polystyrene surfaces. To the best of our knowledge there appear no reports dealing with metallization of plane polystyrene surfaces by wet chemical methods. So this work would be the first report on the subject. In the present work viscous solution of PANI-aniline mixtures were obtained by the catalytic air oxidation and applied onto planar PS surfaces. These robust PANI layers were used to deposit elemental copper from electroless copper solutions. The processing conditions and surface characterizations were investigated using analytical measurements, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) techniques.

2. Experimental

2.1. Materials

Aniline (E.Merck) was redistilled before use. Polystyrene (PS) (M_v: 87.000 K) was obtained by suspension polymerization of styrene monomer using azo-bis(isobutyronitrile) as radical initiator according to the procedure given in the literature [16]. Cu $(NO_3)_2 \cdot 2H_2O$ (E.Merck), $CuCl_2 \cdot 2H_2O$ (E.Merck) and all the other chemicals were analytical grade commercial products. They were used as purchased.

2.2. Preparation of PANI-PS solution by partial polymerization of aniline (Solution-1)

Ten milliliter (1.1 mol) of redistilled aniline and 1 g of PS were added to a 100 mL volume of two necked flask equipped with an air inlet. The mixture was stirred until complete dissolving of the polymer. Then 0.223 g (1 mmol) Cu $(NO_3)_2 \cdot 2H_2O$ was dissolved in the mixture by vigorous stirring (ca. 1 h). The air delivery tube was dipped into the flask cautiously and an air stream was passed through the solution by means of an air pump (approx. 10 mL/min) under continuous stirring. This process resulted in the darkening of the mixture immediately. The viscosity gradually increased (400–460 cP) and after 1 h the air flow was closed. The resulting pitch dark solution was stored in a closed vessel at room temperature.

2.3. Preparation of copper-rich PANI solution (Solution-2)

The above procedure was performed without PS, except 0.762 g (4 mmol) $CuCl_2 \cdot 2H_2O$ was used as polymerization catalyst for preparation of this solution. Viscosity of the solution was around 380 cP after 1 h of air bubbling.

2.4. Copper plating

2.4.1. Coating of PS surface with PANI-PS film (step-1)

The specimens were obtained by cutting (5 × 15 cm) commercial PS panels (with 3 mm of thickness) and cleaned by sonication in ethanol for 30 min. The above viscous solution of PANI-PS (Solution-1) was diluted with 3 mL acetone and applied onto plane surface of the PS support by means of an applicator with 60 μm of aperture. The sample was left to stand open to air exposure for extension of the polymerization (24 h). This procedure gave dry and homogenous PANI-PS composite layer as primer coating on the substrate.

To obtain patterned surfaces Solution-1 was employed on the pre-patterned specimens obtained by masking simply with commercial self adhesive tapes mounted on a roller, side by side (with 2 mm space of each). Application of Solution-1 onto non-protected areas of the surface by means of pipette and wiping excess of the polymer with a doctor blade and following air exposure resulted in PANI-PS patterned surfaces.

2.4.2. Top coating with PANI (step-2)

Solution-2 was slightly diluted with acetone (3 mL) and applied onto primer coating layer by using the same procedure. Continued polymerization of the residual aniline by air exposure for 24 h yielded a smooth copper-rich PANI layer.

2.4.3. Reduction of the surface copper with hydrazinium hydroxide (step-3)

The PANI coated specimens were soaked into aqueous solution with 5% (wt) hydrazinium hydroxide and 5% (wt) ammonia to reduce surface copper. The copper reduction was visually followed by simultaneous evolution nitrogen from the coated surface. Five minutes of contact with the solution at room temperature was found to be enough to produce zero-valent copper seeds for the activation of the surface. The samples were taken out, rinsed with water and dried by means of a soft paper. They were stored in tightly closed vessels to avoid re-oxidation of the copper by air oxygen.

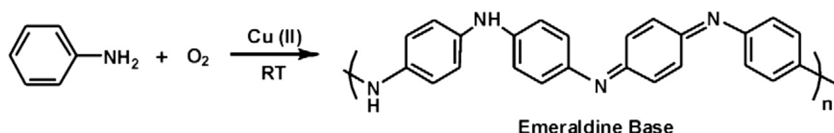
2.4.4. Electroless plating with copper (step-4)

The electroless copper plating solution constituting with 0.7 wt.% $CuSO_4 \cdot 5H_2O$, 2.5 wt.% sodium potassium tartarate, 0.4 wt.% NaOH and 0.4 wt.% formaldehyde was prepared as suggested in the literature [17]. The specimens having trace amount of elemental copper on the surface were soaked into this solution for 16 h. Progress of the copper deposition was followed by increasing thickness of the surface. Copper content of the specimen was found to be 9.6×10^{-5} mol/cm^2 by the diethanolamine-CS_2 method.

2.5. Surface characterization

2.5.1. FT-IR spectra

FT-IR spectra were taken by a Mattson 1000 FT-IR Spectrometer.



Scheme 1. Polymerization of aniline by catalytic air oxidation.

2.5.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) pictures were taken with a Jeol 5410 instrument at 10 kV. Samples were gold coated in order to achieve a good conductance.

2.5.3. X-ray photoelectron spectra (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.

2.5.4. Adhesion tests

Adhesion tests were performed by Adhesion-master 525 MC pull-off apparatus equipped with a control unit and a cylinder (20 mm of diameter) acting 10 kN maximum force. 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 N/mm^2.

3. Results and discussion

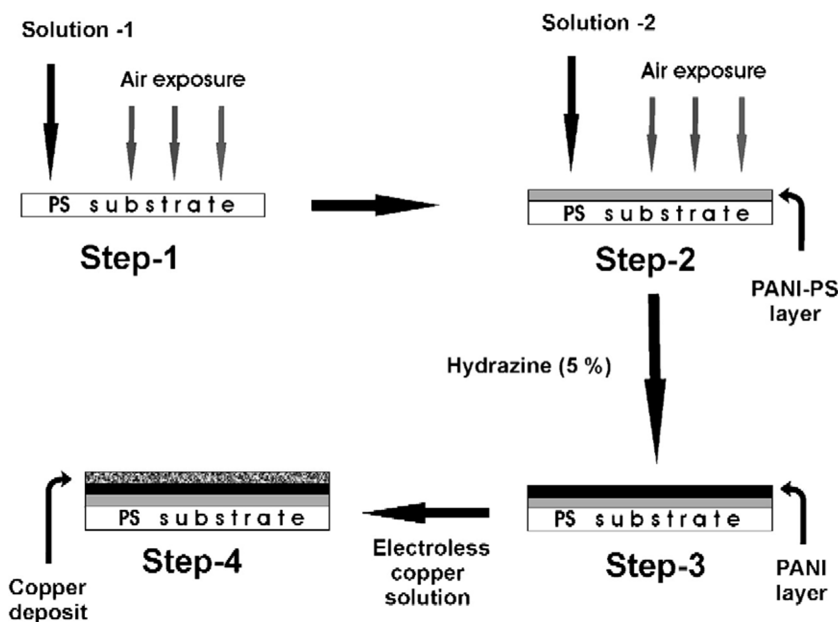
Copper (II) catalyzed air oxidation of aniline yields organo-soluble polyaniline in Emeraldine base form as described in our previous paper (Scheme 1) [15]. Herein we describe extension of this chemistry to PANI coatings on flat PS surfaces for electroless copper deposition. The polymerization is believed to occur by oxidation of aniline with Cu (II) yielding Cu (I). Re-oxidation of the later by air oxygen allows regeneration and recycling of Cu (II).

In this work, first, two PANI solutions, Solution-1 and Solution-2 were prepared by copper catalyzed air oxidation of aniline. Air oxidation of aniline solution containing 10% (w/w) polystyrene gave a viscous solution of PANI-PS mixture (Solution-1) due to partial polymerization of aniline. Viscosities of the dark polymer solutions so obtained were 400–460 cP at 30±0.2 °C. In this process aniline was exploited as a kind of reactive diluent which acts as polymerizing monomer and solvent. The polymerizations for longer than 2 h, however, gave the solutions with higher viscosities containing solid particles in some cases. Due to this reason Solution-1 was stored in tightly closed bottles to avoid further polymerization upon standing.

Solution-2 was obtained by the same procedure using four-fold excess of the copper catalyst in the absence of PS. The solution constituting with aniline solution of PANI needs similar precautions for long term storage.

3.1. The copper plating

The electroless copper plating was carried out in four steps, namely i) primer coating with Solution-1, ii) coating with Solution-2, iii) surface activation with hydrazine iv) electroless copper deposition as outlined in Scheme 2.



Scheme 2. Schematic illustration of the electroless copper plating process.

In step-1 Solution-1 was diluted with acetone (2–3 mL per ten mL) to adjust viscosity of the solution. Since acetone is solvent both for PS and PANI, application of the resulting solution onto flat PS specimens (5 × 15 cm) gave a homogenous coating layer (i.e. 60 μm). The specimens coated were left to stand under open air for 24 h at room temperature.

This process resulted in the formation of dry and smooth PANI coatings on the surface (the primer) due to continued polymerization of the unreacted aniline by the catalytic action of copper salt remaining in the polymer matrix. The presence of typical broad bands of PANI in 1500–1600 cm^{-1} range in the FT-IR spectra of the surface revealed its formation [15].

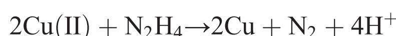
It is important to note that dilution with acetone is essential for homogeneity of the primer. Indeed application of Solution-1 without acetone diluents gave extensive pinholes on the surface due to the water formed in the polymerization. Attempts to remove water by treatment with anhydrous $MgSO_4$ or Na_2SO_4 were found to be impractical and useless. Acetone was chosen due to its volatility and miscibility with water as well.

The PS component in Solution-1 was employed to provide good adhesion and compatibility of outer PANI layer with the PS support. Direct coating without dissolved PS gave imperfect surfaces with poor adhesion.

In the second step aniline solution of PANI (Solution-2) was diluted with acetone as described above and applied onto primer to form a copper-rich PANI layer on the surface. This process resulted in homogenous PANI layers well adhered to the PS surfaces by similar extension of the polymerization of aniline in the mixture.

3.2. The electroless copper plating

The specimens were then, soaked in an aqueous mixed solution of hydrazine with ammonia (5% of each) (step-3).The copper remaining in the PANI layer (40 mmol per mole of aniline repeating units) is reduced to elemental copper in this step. The reaction is believed to occur according to the following reaction [15].



$$2Cu(II) + N_2H_4 \rightarrow 2Cu + N_2 + 4H^+$$

The elemental copper so obtained serves as catalytic sites for further copper deposition from the electroless plating solution. In other words in the present process surface sensitizing is affected by the trace copper instead of $PdCl_2/SnCl_2$ in traditional electroless copper plating process. Obviously the copper only on the outer surface is expected to act as catalyst. The copper embedded within the hydrophobic polymer matrix cannot be reduced by aqueous hydrazine solution and does not induce any catalytic effect. Five minutes of contact with the hydrazine solution was found to be enough to produce active copper seeds. It is important to note that, the use of more concentrated hydrazine solutions is not advisable in this step. Indeed serious peeling of PANI layer was observed when the samples were left to contact with 80% hydrazine solution for longer than 24 h.

Moreover ammonia was determined to be essential for rapid action of hydrazine at room temperature. In the presence of ammonia the nitrogen bubbles evolving from the surface was followed visually, indicating occurrence of the above reaction. The role of ammonia is to retain the intermediate Cu (I) in soluble form by forming tetramine-cuprous complex, rather than adjusting pH of the reaction medium. This assumption was further confirmed by a separate experiment in which CuCl precipitated instead of Cu (0), in aqueous mixture of $CuCl_2$ with hydrazine. In the presence of ammonia, however, an instantaneous zero-valent copper precipitation was observed. This result revealed that the copper on the PANI surface is first reduced to Cu (I) and it forms water soluble cuprous-complex tetramine complex. The complex is then rapidly reduced to Cu (0) as soon as it forms.

Higher ammonia concentrations were also studied. Those experiments showed that the solutions with 20% ammonia results in formation of copper powders in the solution too. This might be ascribed to quick extraction of the copper as tetramine

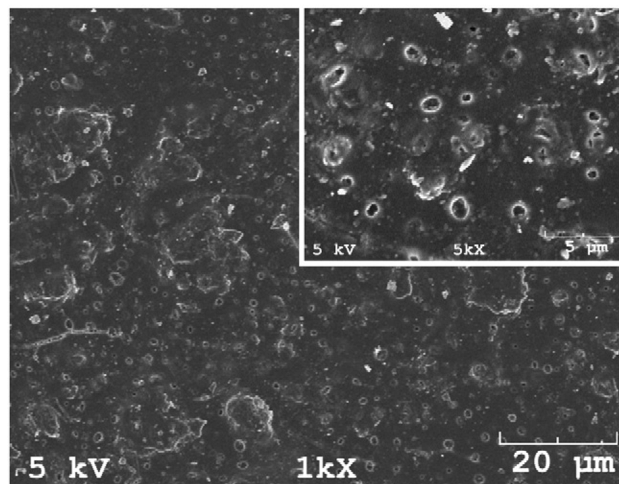


Fig. 2. SEM images of the PANI layer formed on PS after second step of the coating process, Magnification: 1000×, magnification: 5000× (in window).

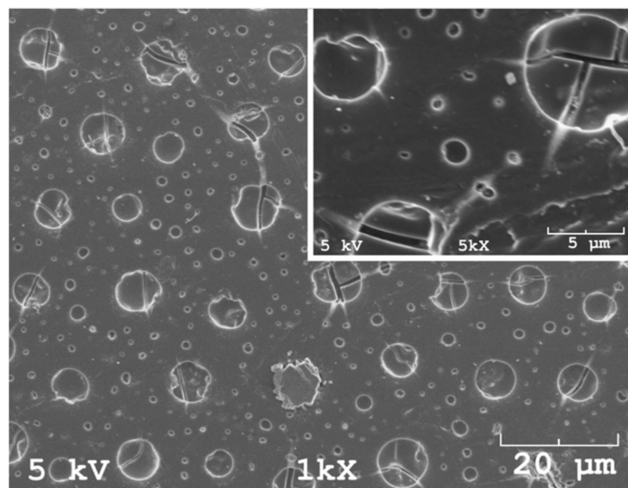


Fig. 1. SEM image of the PANI layer formed on PS after first step of the coating process, Magnification: 1000×, magnification: 5000× (in window).

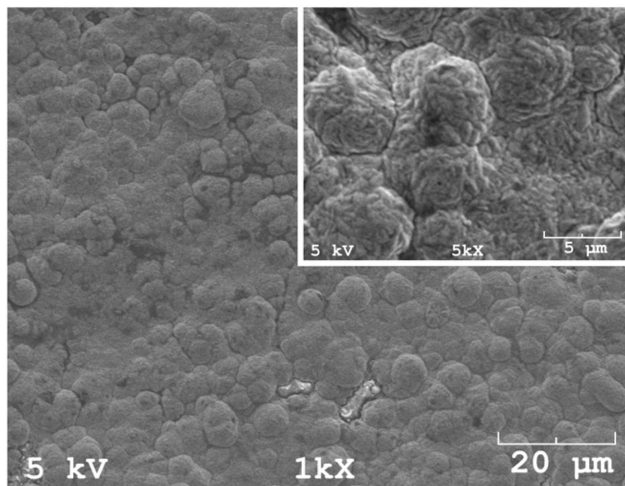


Fig. 3. Surface morphology of the electroless copper deposits formed on the PANI coated surfaces (step-4), Magnification: 1000×, magnification: 5000× (in window).

complex from PANI layer and its reduction in solution. It was found that 5% of hydrazine is suitable for the reduction to avoid copper leakage from the surface.

In the last step the PANI coatings with few percent of zero-valent copper (i.e. 2.4%) seeds were subjected to electroless copper plating. This was achieved by immersion of the specimens into the electroless solution for 2 to 24 h. Bright and homogenous copper layers were obtained by this process.

3.3. The surface characteristics

SEM picture of the primer (Fig. 1) exhibits homogenously distributed pores with sizes varying from 1–10 µm on the surface. Within the large pores small cracks were also formed. The presence of the pores implies micro phase separation due to the water eliminated in the course of the polymerization by air oxygen. Application of the primer without acetone gave visible islands indicating macro phase separation.

Apparently such phase separation produces non-covered regions on the substrate surface. Addition of acetone to the primer coating formulation provides mixing of water with aniline solution of PANI-PS and fine distribution of Solution-l open regions as tiny dots (0. 3 µm) and small pores with average diameter of 7 µm. Drying of Solution-1 with Na_2SO_4 prior to application was not helpful to avoid formation of the pores, as described above. This is due to formation of additional water by continued polymerization of aniline after application of the solution onto the surface.

SEM picture of the copper-rich PANI layer (Fig. 2) shows a less porous surface. Only micron and sub micron sized pores are observable on the surface. This phenomenon implies that open circles are being filled by Solution-2 in the second step. Homogenously distributed grey points represent copper salt remaining on the surface.

SEM photograph of the sample obtained in the third step exhibited similar appearance with Fig. 2. Such a similarity reveals that reduction with hydrazine, in the third step occurs without changing initial positions of the copper salt.

Visual appearance of copper plated surface is smooth and homogenous. SEM image of the copper deposits (Fig. 3) exhibited a nodular growth on the surfaces. This might be due to rapid formation of the amorphous copper seeds in the hydrazine reduction step.

Increasing thickness of the copper layer by time-length of the electroless plating is clearly seen in Fig. 4. Cross-sectional view of the specimen plated for 24 h indicated a copper thickness of 14.8 µm, with a marked damage of the section (Fig. 4 left). The copper thickness rises up to 32.4 µm for 48 h of electroless plating time (Fig. 4 right). Unfortunately, we were not able to take similar pictures of the other specimens for the plating times shorter than 24 h. It was observed that the cross sections of those samples had burned up during electron bombardments. This might be due to fact that long scan times are essential to attain better contrasts. However organically rich cross sections readily undergo destruction by the electron bombardment.

XPS of the specimens showed similar patterns with typical peaks of carbon, nitrogen, oxygen and copper elements, as expected. Fig. 5 is given as representative example. The figure shows XPS of the copper plated sample given. In each spectrum the reference carbon peak (C1s core) appears at 285 eV. This peak originates mainly from the PS support and PANI layer.

Intensity of this peak is almost the same with those observed in XPS of the other samples. The peak around 75 eV must be due to Cu3p3 core level. This peak is not observed clearly in the spectra of the other samples obtained in the previous steps. Also Cu 3s core level peak around 120 eV is invisible. N1s core level

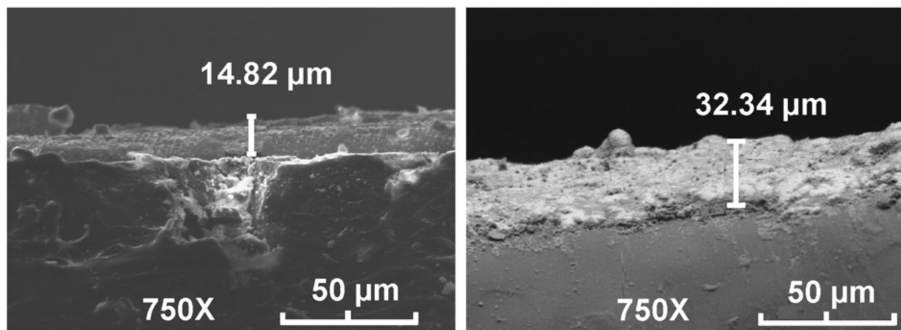


Fig. 4. SEM photos of cross sections of the electroless copper deposited specimens.

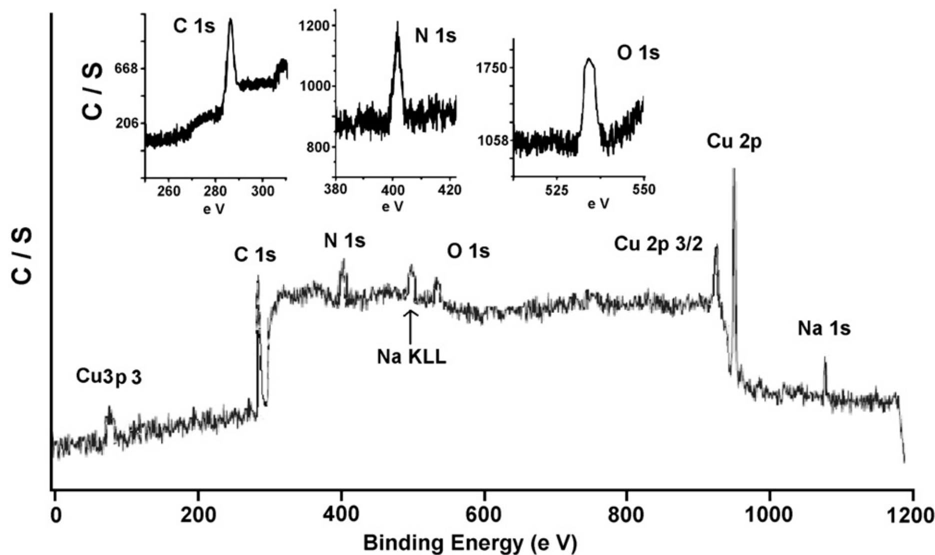


Fig. 5. Wide scan XPS of the electroless copper plated sample (bottom) and typical peaks associated with C1s, N1s and O1s core levels (upper).

of the nitrogen atom of the PANI component yields a peak at 402 eV. O1s core level yielding a weak peak at 535 eV might be due to re-oxidation of the fresh copper on the surface. The small peak at 500 eV must be due to Na-KLL Auger electrons [18]. Another peak of sodium associated with Na 1s core level appears at 1079 eV. The sodium peaks must be due to NaOH component of the electroless copper solution. These two peaks are not observed in the spectra of the other samples, as expected.

Significant difference in XPS of the copper plated sample (Fig. 6) is more intense peaks at 935 eV and 954 eV (indicating Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core levels respectively). The later is major peak in Fig. 5. These two peaks are rather weak in the spectra of the second and third step samples. In the spectrum of the first-step sample only the second peak at 954 eV is visible.

It is fact that these peaks appear at slightly higher energies comparing with those in original core level spectra of zero-valent copper. This is due to rapid oxidation of fresh copper surfaces by air oxygen. The broad peaks in this figure should be ascribed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core levels originating from Cu (0) and Cu (II). These results can be considered as evidence for the copper deposition in the electroless plating process.

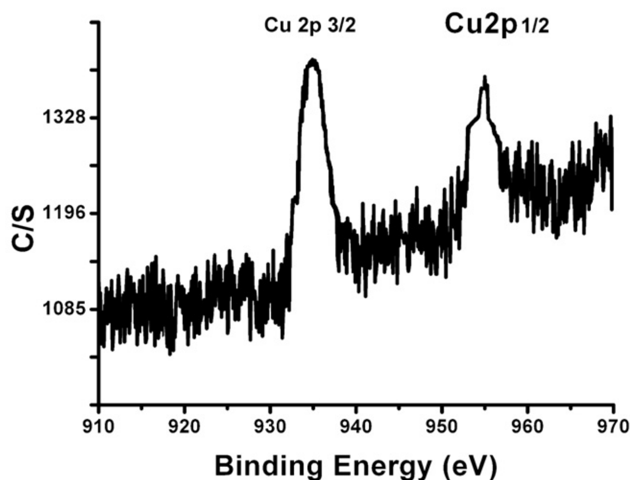


Fig. 6. Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core level XPS of the electroless copper plated surface.

3.4. Contact angles of the surfaces

Contact angle of the primer surface (68.4°) was found to be lower than that of the commercial polystyrene support (75.2°). This implies increasing hydrophilicity of the surface by coating with PAN-PS solution (Table 1).

The surface coated with PANI in the second step indicated even lower contact angle (55.1°) due to much higher hydrophilicity of the PANI-copper mixture on the surface. “Since water is being eliminated in the course of polymerization of aniline, some water might be retained by Cu (II) which is more hygroscopic than Cu (I). Moreover absence of PS is another factor for the hydrophobicity loss in the second layer. All of these factors might be responsible for the low contact angle in the second step.”

We were not able to measure contact angles of the samples obtained in the third step owing to the rapid oxidation of zero-valent copper formed on the surface.

Interestingly reasonable contact angle increment was observed after the electroless copper deposition of the surface. High contact angle of the sample (94.6°) implies reasonable

Table 1
Some physical characteristics of the surfaces in each step

Step	Process	Surface structure	Adhesion strength (N/mm^2)	Copper thickness (μm)	Contact angle [b]
1	Primer coating	PANI-PS	>2.1	–	68.4°
2	Coating with PANI	PANI	>2.1	–	55.1°
3	Surface activation	PANI-Cu(0)	>2.0	nd	nd
4	Electroless plating	Cu (0)	>1.6	32.4 [a]	94.6°

[a] Estimated by SEM.
[b] Contact angle of naked PS substrate was found 75.2°.

increment of the surface hydrohobicity in the final step. This can be ascribed to deposition of the copper as tiny grains in the electroless plating process, as observed in its SEM picture in Fig. 3.

3.5. Surface adhesions

Adhesion is crucial in electroless metal plating process. Adhesion of the coating in each step were estimated by pull-off tests in which maximum pull forces to take apart of the layers are measured. The specimens with primer and with PANI coatings showed pull-off strengths greater than 2.1 N/mm^2 (Table 1). Good adhesion of the PANI layer must be due to the PS component in the primer. Direct application of PANI solution onto specimen without primer gave a PANI layer with poor adhesion. This implies that the adhesion between PS support and upper PANI layer is being enhanced by PS in the primer.

Almost the same adhesion behavior was observed (>2 N/mm^2) for the surface with activated copper obtained in step-3. The copper plated surface attained in the last step showed an average pull off greater than 1.6 N/mm^2.

Overall results of the pull-off experiments can be considered as satisfactory for application view point.

4. Conclusion

PANI-PS solution prepared by partial polymerization of aniline in presence of poly (styrene) yields well-adhered primer on flat PS surfaces open to air atmosphere. Excess of aniline serves as solvent in application to the surface. The wet primer so obtained dries spontaneously due to polymerization of the excess aniline by continued air oxidation. This primer provides good compatibility with the upper copper-rich PANI layer obtained by similar air oxidation.

Reducing of the surface copper with diluted hydrazine solution (5%), in the third step, creates active copper seeds for the deposition of large amounts of copper in the electroless copper plating process.

In other words classical surface activation with Pd (II)-$SnCl_2$ can be avoided by prior reduction of the surface copper.

In conclusion the four-step wet chemistry presented provides smooth copper plated surfaces well adhered to PS support and offers an alternative pathway to large scale applications.

Acknowledgement

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