ELSEVIER

Polymer 43 (2002) 4137–4146

polymer

www.elsevier.com/locate/polymer

Electroless plating of copper on polyimide films modified by surface grafting of tertiary and quaternary amines polymers

Z.J. Yu, E.T. Kang*, K.G. Neoh

Department of Chemical Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore, Singapore 119260

Received 4 December 2001; received in revised form 9 April 2002; accepted 15 April 2002

Abstract

Argon plasma-pretreated polyimide (PI, Kapton® HN) films were subjected to UV-induced surface graft copolymerization with *N*,*N*′-(dimethylamino)ethyl methacrylate (DMAEMA) and 2-(trimethylammonium)ethyl methacrylate chloride (TMMAC). The DMAEMA *graft*-copolymerized PI (DMAEMA-*g*-PI) surfaces were also quaternized and amino-functionalized with 3-bromopropylamine hydrobromide (the Q-DMAEMA-*g*-PI surfaces). The surface composition and the degree of quaternization of the *graft*-modified PI films were determined by X-ray photoelectron spectroscopy. The DMAEMA-*g*-PI, Q-DMAEMA-*g*-PI and TMMAC *graft*-copolymerized PI (TMMAC-*g*-PI) surfaces can be activated directly by $PdCl_2$, in the absence of prior sensitization by $SnCl_2$ (the 'Sn-free' activation process), for the subsequent electroless plating of copper. A shorter induction time for the electroless deposition of copper was found for the palladium-activated Q-DMAEMA-*g*-PI and TMMAC-*g*-PI surfaces than for the palladium-activated DMAEMA-*g*-PI surface. The T-peel adhesion strength of the electrolessly deposited copper with the Q-DMAEMA-*g*-PI surface was enhanced to above 6 N/cm, in comparison to only about 4 N/cm for the DMAEMA-*g*-PI surface, about 2.5 N/cm for the TMMAC-*g*-PI surface, or about 0.5 N/cm for the PI surface with argon plasma treatment alone.

Keywords: Polyimides; Graft copolymerization; Electroless plating

1. Introduction

Polyimides (PIs) are widely used as dielectric materials in microelectronics. They have the desirable properties of high-temperature resistance, good mechanical strength, good dimensional stability and low dielectric constants [1,2]. The adhesion of a metal to the PI film is generally poor, unless the PI surface is pretreated prior to metallization. A number of surface modification techniques, such as wet-chemical treatment [3], plasma treatment [4,5], UV excimer irradiation [6], and pulse ion beam irradiation [7], have been applied to PI substrates to enhance their adhesion to metals. Recently, surface modification of PI films by graft polymerization with nitrogen-containing monomers, such as *N*-vinylimidazole, has been carried out to enhance their adhesion with the evaporated copper [8,9]. A great deal of effort has also been devoted to the surface modification and functionalization of PI films for adhesion enhancement with the electrolessly deposited metals [10–15]. More recently, adhesion improvement of PI films with the electrolessly deposited copper was achieved via the UV-induced surface graft copolymerization of PI films with the N-containing monomers [16].

Copper metallization of PIs and fluoropolymers, which have good thermal stability and low dielectric constants, has always been of great interest to the microelectronics industry [17–19]. Arising from its inherent simplicity, the technique of electroless plating of copper has clear advantages over the conventional electroplating process. Historically, two methods, viz. the 'two-step' process [20,21] and the 'one-step' process [22,23], have been used for the surface sensitization and activation of substrates prior to the electroless plating of copper. The one-step process involving a colloidal mixture of $SnCl_2$ and $PdCl_2$ has gained popularity due to its simplicity. In both processes, the substrate surface is sensitized first by $SnCl_2$ to facilitate the chemisorptions of $PdCl_2$. However, from the economic and environmental points of view, the simplicity in process operation, and the fact that $SnCl_2$ is not an active catalyst for the electroless plating process [24], it is of interest to develop a Sn-free, one-step activation process for the electroless plating of copper.

In the present work, surface modification of argon plasma-pretreated PI films via UV-induced graft copolymerization with a tertiary amine monomer, *N*,*N*′-(dimethylamino)ethyl methacrylate (DMAEMA) and a quaternary

* Corresponding author. Tel.: +65-874-2189; fax: +65-779-1936.
E-mail address: cheket@nus.edu.sg (E.T. Kang).

0032-3861/02/$ - see front matter
PII: S0032-3861(02)00263-X

amine monomer, 2-(trimethylammonium)ethyl methacrylate chloride (TMMAC) is carried out. The DMAEMA *graft*-copolymerized PI surface (the DMAEMA-*g*-PI surface) is further quaternized and amino-functionalized with 3-bromopropylamine hydrobromide (3-BPAH). The surface-modified PI films are activated directly by $PdCl_2$, in the absence of prior sensitization by $SnCl_2$ (the Sn-free activation process), for the subsequent electroless plating of copper. The graft concentration, the degree of quaternization (DQ), and the chemical states of the adsorbed palladium species on the surface-modified PI films are investigated by X-ray photoelectron spectroscopy (XPS). The effect of DQ of the DMAEMA-*g*-PI film on the T-peel adhesion strength of the electrolessly deposited copper is also investigated. Although the individual surface modification techniques, viz. (i) surface modification by graft copolymerization, (ii) surface functionalization by quaternization, and (iii) electroless deposition of copper via the Sn-free process, have been reported individually, the combination of the three techniques provides a unique approach to the metallization of the PI surfaces. These combined techniques can be readily extended to the functionalization of other polymer surfaces.

2. Experimental

2.1. Materials

The PI films used in present work were poly[*N*,*N*′-(oxydiphenylene)pyromellitimide]. They were obtained from the Du Pont Chemical Company of Wilmington, DE as Kapton® HN in rolls of 40 mm in width and 75 μm in thickness. The surfaces of the PI films were cleaned with reagent grade acetone in an ultrasonic water bath before use. The monomers, DMAEMA and TMMAC, used for the surface graft copolymerization were supplied by the Aldrich Chemical Company of Milwaukee, WI and Röhm GmbH of Darmstadt, Germany, respectively. The quaternizing agent, 3-BPAH, was also obtained from the Aldrich Chemical Company. The chemical structures of the monomers and the quaternizing agent are shown below:

DMAEMA: $CH_2{=}C(CH_3)CO_2CH_2CH_2N(CH_3)_2$
TMMAC: $CH_2{=}C(CH_3)CO_2CH_2CH_2N^+(CH_3)_3Cl^-$
3-BPAH: $BrCH_2CH_2CH_2NH_3^+Br^-$

2.2. Argon plasma pretreatment and surface graft copolymerization

The PI films were cut into strips of about 20 mm × 40 mm in size. They were pretreated with argon plasma before the UV-induced graft copolymerization. A cylindrical type glow discharge cell, Model SP100, manufactured by Anatech Ltd of Springfield, VA, USA was used for the plasma treatment. The plasma power applied was kept at 32 W at a radio frequency of 40 kHz. The film was placed between the two parallel plate electrodes and subjected to the glow discharge under an argon pressure of about 0.5 Torr. The argon plasma-pretreated polymer films were then exposed to the atmosphere for 10–20 min to facilitate the formation of surface peroxides and hydroperoxides for the subsequent UV-induced graft copolymerization experiments [16].

UV-induced surface graft copolymerization with DMAEMA and TMMAC was carried out according to the procedure reported earlier for other vinyl monomers [25,26]. Each PI film was immersed in 20 ml of the aqueous monomer solution (10 vol%) in a Pyrex® tube. Each reaction mixture was thoroughly degassed and sealed under an argon atmosphere. It was then subjected to UV irradiation from a 1000 W high-pressure mercury lamp for a fixed period of time in a Riko RH400-10W rotary photochemical reactor. The reactor was manufactured by Riko Denki Kogyo of Chiba, Japan. It was also equipped with a constant temperature water bath. The UV graft copolymerization time was varied from 5 to 30 min. All UV-induced graft copolymerization was carried out at about 25 °C. After each grafting experiment, the PI films were removed from the viscous homopolymer solution and washed with a jet of doubly distilled water. It was then immersed in a water bath with continuous stirring for at least 24 h to remove the residual monomer and adsorbed homopolymer. The DMAEMA and TMMAC *graft*-copolymerized PI surfaces are denoted as the DMAEMA-*g*-PI and TMMAC-*g*-PI surfaces, respectively.

2.3. Quaternization of the tertiary amine groups on the DMAEMA-g-PI surface: the Q-DMAEMA-g-PI surface

The DMAEMA-*g*-PI films were immersed in an excess volume of a freshly prepared 3-BPAH aqueous solution. The 3-BPAH concentration was kept constant at 1 M. The mixture was kept in a constant temperature water bath under stirring for a predetermined period of time. The films were then transferred into the 3 M NaOH solution to neutralize the acidity introduced by the 3-BPAH, followed by rinse with a 90:10 (v/v) acetone/water mixture to remove the unreacted 3-BPAH. The films were finally washed with acetone before being dried under reduced pressure.

2.4. Electroless deposition of copper on surface-modified PI films

The DMAEMA-*g*-PI, the TMMAC-*g*-PI and the Q-DMAEMA-PI films were activated via the immobilization of the palladium catalyst, in the absence of prior sensitization by $SnCl_2$, for the subsequent electroless plating of copper. In this Sn-free activation process, the surface-modified PI film was immersed directly in an aqueous solution containing 0.1 mg/ml $PdCl_2$ and 10 mg/ml HCl (37 wt%) for a predetermined period of time and then rinsed twice with the doubly distilled water. The surface-activated

PI film was then immersed in the electroless copper-plating bath for 5–20 min to allow the deposition of a copper layer of about 200 nm in thickness. The thickness of the deposited metal was determined gravimetrically. The solution of the copper plating bath was prepared afresh and the composition of the copper plating bath was as following: 0.7 wt% $CuSO_4 \cdot 5H_2O$, 2.5 wt% potassium sodium tartrate, 0.4 wt% sodium hydroxide and 0.4 wt% formaldehyde. The Cu-plated PI films were then rinsed thoroughly with copious amounts of doubly distilled water, before being dried by pumping under reduced pressure.

2.5. Surface characterization

The surface composition of the samples was determined by XPS. XPS measurements were carried out on a Kratos Analytical AXIS HSi spectrometer using a monochromatized Al Kα X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The X-ray source was run at a reduced power of 150 W (15 kV and 10 mA). The anode voltage was set at 15 kV, while the anode current was set at 15 mA. The pressure in the analysis chamber was maintained at 5.0×10^{-8} Torr or lower during each measurement. The PI films were mounted on the standard sample stubs by means of the double-sided adhesive tapes. The core-level signals were obtained at a photoelectron take-off angle of 90° (with respect to the sample surface). All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. In peak synthesis, the linewidth (full width at half maximum or FWHM) of the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to ±10%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

The surface morphology of the PI films was investigated using a Nanoscope IIIa atomic force microscope (AFM). All images were collected in air using a tapping mode under a constant force (scan size: 10 μm, set point: 3.34 μV, scan rate: 1 Hz).

2.6. Adhesion strength measurement

The metallized PI film was thermally cured in a vacuum oven at 120 °C for 2 h and then adhered to a copper sheet backing (0.1 mm in thickness), using a commercial epoxy adhesive (Araldite Stand® from Ciba-Geigy Chemical Co. of Toms River, NJ, USA), for the subsequent T-peel adhesion strength measurement. The assembly was thermally treated in a vacuum oven at 120 °C for 2 h prior to the adhesion strength measurement. The adhesion strength of the electrolessly deposited copper on the *graft*-modified PI films was determined by measuring the T-peel adhesion strengths on an Instron tensile tester (Model 5544) from the Instron Corp. of Canton, MA, USA. All measurements were carried out at a cross-head speed of 10 mm/min. Each adhesion strength value reported was the average of at least five sample measurements, which usually did not vary by more than ±0.5 N/cm.

3. Results and discussion

Surface modification of PI film via argon plasma pretreatment, followed by UV-induced graft copolymerization with DMAEMA or TMMAC, is shown schematically in Step 1 of Fig. 1. The process of quaternization with 3-BPAH to introduce the quaternary and primary amine groups on the DMAEMA-*g*-PI surface is illustrated in Step 2 of Fig. 1. The processes of Sn-free surface activation by $PdCl_2$ and the subsequent electroless plating of copper on the surface-modified PI film are illustrated schematically in Step 3 of Fig. 1. Details of the surface modification and electroless deposition processes are described later.

3.1. Surface modification of PI films by graft copolymerization

Fig. 2 shows the C 1s and N 1s core-level spectra of the pristine (part (a)) and the 60 s argon plasma-treated (part (b)) PI films. The C 1s core-level spectra of the pristine PI film can be curve-fitted with five peak components with BEs at about 284.6, 285.6, 286.4, 288.6 and 291.1 eV, attributed to the *C*H species, the *C*H–N and *C*H–C(O) species, the *C*–O species, the N–*C*=O species and the $\pi-\pi^*$ shake-up satellite, respectively [26,27]. Surface modification of PI film by argon plasma treatment, followed by air exposure, results in the formation of two additional carbon species at BEs of about 287.4 and 289.3 eV (Fig. 2(b)). These two peak components are attributable, respectively, to the carbonyl species, which differs from the carbonyl species of the imide group in the pyromellitic dianhydride chain, and to the carboxyl species [28]. The [O]/[C] ratio of the pristine PI film is about 0.21. The ratio increases to about 0.30 after 60 s of argon plasma treatment, followed by air exposure, in agreement with the results generally reported in the literature [29]. It has also been suggested that argon plasma treatment of the PI film can result in the cleavage of imide linkages and give rise to the formation of carboxyl and secondary amine groups [4]. The formation of the secondary amine species is discernible in the N 1s core-level spectra as a new lower BE component at about 399.7 eV. On the other hand, the N 1s core-level spectrum of the pristine PI surface consists of a single peak component at the BE of 400.6 eV, attributable to the imide species ($-N-(C=O)_2$) [26,30].

Fig. 3(a) and (b) shows the respective N 1s core-level spectra for the 60 s argon plasma-pretreated PI films after having been subjected to 15 and 30 min of UV-induced graft copolymerization in 10 vol% DMAEMA. Fig. 3(c), on the other hand, shows the N 1s spectrum of the 60 s argon plasma-pretreated PI film after having been subjected to 15 min of UV-induced graft copolymerization in 10 vol%

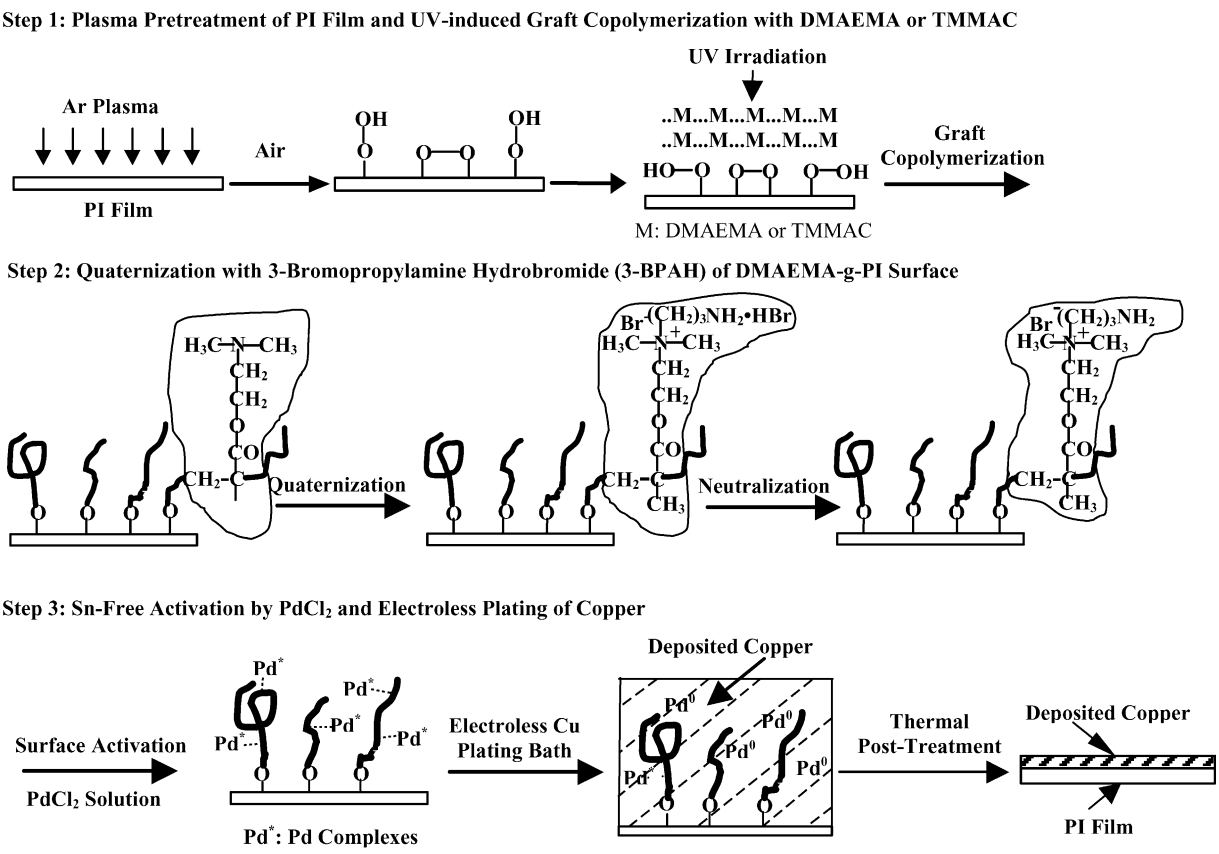

Fig. 1. Schematic diagram illustrating the processes of (Step 1) argon plasma pretreatment of PI film, UV-induced graft copolymerization, (Step 2) quaternization with 3-BPAH, and (Step 3) the Sn-free activation by $PdCl_2$, and electroless deposition of copper on the surface-modified DMAEMA-*g*-PI film.

TMMAC solution. The respective PI surfaces after modification by graft copolymerization are referred to as the DMAEMA-*g*-PI and TMMAC-*g*-PI surfaces. The presence of surface grafted DMAEMA polymers can be deduced from the appearance of the N 1s core-level signal at about 399.1 eV, attributable to the tertiary amine ($-N(CH_3)_2$) species [31]. The presence of surface grafted TMMAC polymers, on the other hand, is suggested by the appearance of the N 1s peak component at about 402.3 eV for the quaternary amine ($-N^+(CH_3)_3$) species [31]. The persistence of the imide peak component ($-N-(C{=}O)_2$) of a fairly strong intensity at about 401.6 eV in the N 1s core-level spectra of Fig. 3(a) and (c) suggests that the thickness of the grafted DMAEMA or TMMAC polymer layer for these two samples is less than the probing depth of the XPS technique (about 7.5 nm in an organic matrix [32]). On the other hand, the barely discernible N 1s peak component at the BE of 400.6 eV, as shown in Fig. 3(b), indicates that the PI surface is almost fully covered by the grafted DMAEMA polymer to a thickness comparable to the probing depth of the XPS technique.

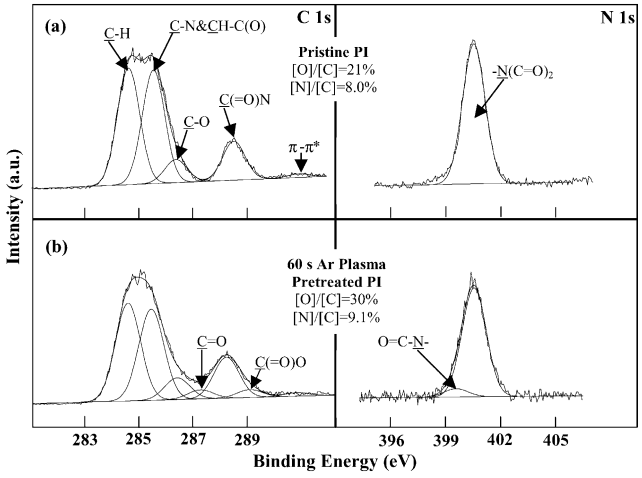

Fig. 2. C 1s and N 1s core-level spectra of (a) the pristine PI film and (b) the 60 s argon plasma-treated PI film.

The graft concentration of the DMAEMA or TMMAC polymer on the PI surface is defined as the number of repeat units of the graft chain per repeat unit of the substrate chain. The surface graft concentration is determined from the peak area ratio of the tertiary ($-N(CH_3)_2$) or quaternary ($-N^+(CH_3)_3$) amine peak component to the corresponding imide ($-N-(C{=}O)_2$) peak component in the curve-fitted N 1s spectrum. These components are associated, respectively, with the DMAEMA graft chains, the TMMAC graft chains, and the substrate PI polymer. The concentration of the surface grafted DMAEMA or TMMAC polymer is, thus, expressed as the $2[-N(CH_3)_2]/[-N-(C{=}O)_2]$ or the $2[-N^+(CH_3)_3]/[-N-(C{=}O)_2]$ molar ratio, respectively. The

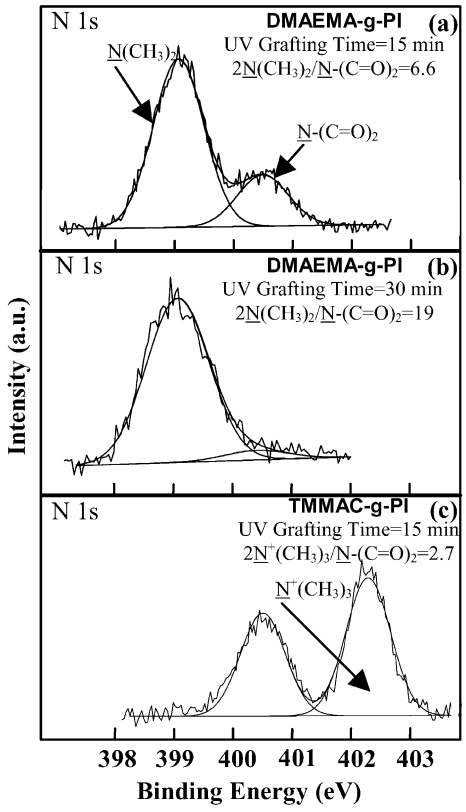

Fig. 3. N 1s core-level respective spectra of the surface-modified PI films from UV-induced graft copolymerization in the 10 vol% DMAEMA monomer solution (a) for 15 min and (b) for 30 min or in the 10 vol% TMMAC monomer solution (c) for 15 min.

factor 2 in the numerator is introduced to account for the fact that there are two functional $-N-(C{=}O)_2$ groups in every repeat unit of the PI molecule.

One of the key factors that affect the graft concentration of DMAEMA or TMMAC polymer on the PI surface during the UV-induced graft copolymerization is the UV graft copolymerization time. In this work, the variation in graft concentration of the DMAEMA polymer on the PI surface was studied by varying the UV irradiation time from 5 to 25 min, while keeping the plasma pretreatment time of the PI films at 60 s and the DMAEMA or TMMAC monomer concentration in the graft copolymerization medium at 10 vol%. Earlier studies [16,33] have shown that 60–80 s of argon plasma pretreatment of the PI film under similar glow discharge conditions is optimum or close to optimum for the surface peroxides formation. It is observed in Fig. 4 that the graft concentration increases sharply with the UV graft copolymerization time. It is also found that when the UV graft copolymerization time is above 30 min, the N 1s peak component signal at 400.6 eV for the PI substrate is no longer discernible. Thus, the graft concentration, based on the present definition and XPS-derived surface composition, becomes 'infinity' for these two monomers.

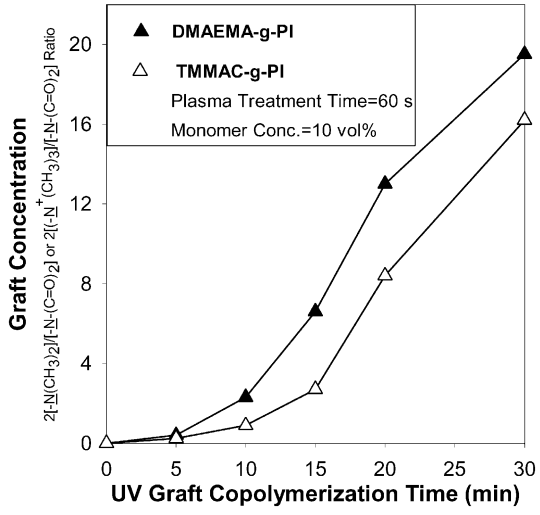

Fig. 4. Dependence of the graft concentration of the DMAEMA and TMMAC polymer on UV grafting copolymerization time (plasma pretreatment time = 60 s and monomer concentration = 10 vol%).

3.2. Surface morphology of the graft-copolymerized PI films

The changes in surface morphology of the PI films after modification by graft copolymerization with the respective DMAEMA and TMMAC monomer are studied by AFM. The respective AFM images of the pristine PI film surface and the DMAEMA-*g*-PI (graft concentration = 6.6) surface and the TMMAC-*g*-PI (graft concentration = 2.7) surface are shown in Fig. 5. The root mean square surface roughness (R_a) of the pristine PI film is about 0.75 nm. The R_a values for the DMAEMA-*g*-PI and TMMAC-*g*-PI surfaces increase to about 2.6 and 1.6 nm, respectively. The graft polymer exists as a distinctive overlayer on the PI surface, while the surface of the pristine PI film is comparatively flat. The more rugged surface morphology of the *graft*-copolymerized films will facilitate, to some extent, the spatial interactions of the graft layer with the incoming metal atom or ions in the subsequent Sn-free activation and electroless copper plating processes.

3.3. Quaternization of the DMAEMA-g-PI surface: the Q-DMAEMA-g-PI surface

The tertiary amine species on the DMAEMA-*g*-PI surface were quaternized by the alkyl halide, 3-BPAH, in Menschutkin reaction [34] and subsequently neutralized in a base (NaOH) solution to produce the primary amine and the quaternary ammonium species. Fig. 6(a) shows the Br 3d and N 1s core-level spectra of the quaternizing agent, 3-BPAH. The Br 3d core-level spectrum of 3-BPAH consists of two spin–orbit split doublets of about equal sizes/areas, with the Br $3d_{5/2}$ components lying at about 68.8 and 71.1 eV and attributable to the ionic (Br^-) and covalent (–Br) bromine species [32], respectively. The N 1s core-level spectrum with the BE at 401.1 eV is attributable to the NH_2 species in the form of the protonated amine salt ($-NH_2{\cdot}HBr$) [32]. The N 1s and Br 3d core-level spectra of

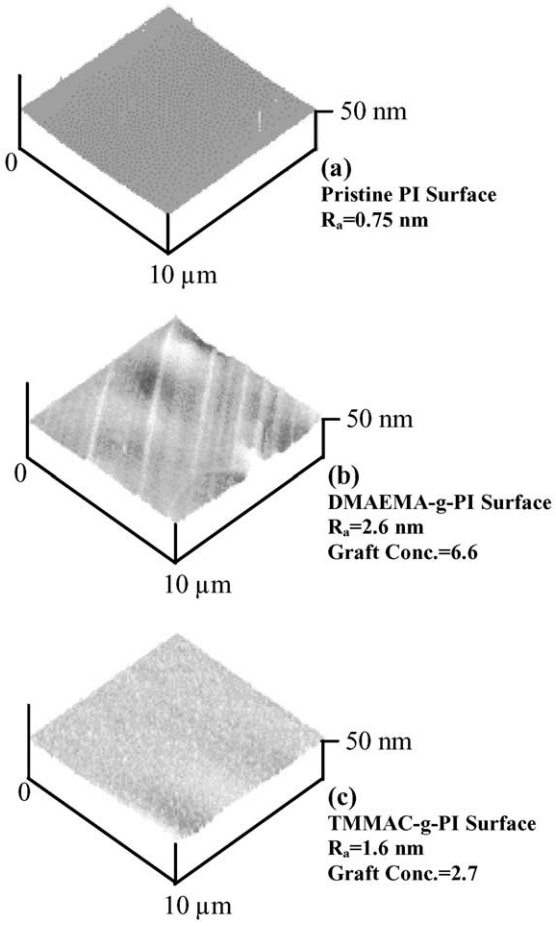

Fig. 5. AFM images of (a) the pristine PI surface, (b) the DMAEMA-*g*-PI surface, and (c) the TMMAC-*g*-PI surface.

two DMAEMA-*g*-PI films (UV graft copolymerization = 30 min, graft coverage comparable to the probing depth of the XPS technique) quaternized in 1 M 3-BPAH at 50 °C for 1 and 8 h, respectively, followed by neutralization in NaOH solution, are shown in Fig. 6(b) and (c). The appearance of a new peak component in the N 1s core-level spectrum of the DMAEMA-*g*-PI surface at 402.3 eV, which can be assigned to the nitrogen of the quaternary amine [32], suggests that some of the tertiary amine species of the DMAEMA-*g*-PI surface have been converted into the quaternary amine species ($-N^+(CH_3)_2R(Br^-)$). The quaternization by 3-BPAH is also confirmed by the presence of only the ionic doublet in the Br 3d core-level spectrum of the quaternized DMAEMA-*g*-PI surfaces. Furthermore, no imide ($-N-(C{=}O)_2$) peak component signal at the BE of 400.6 eV for the PI substrate is discernible on the quaternized surfaces.

The DQ is the most important characteristic of the Q-DMAEMA-*g*-PI surfaces. However, the DQ value obtained is somewhat dependent on the analytical method used, such as ^{1}H NMR and gel-permeation chromatography [35,36]. In the present work, XPS is employed to measure the surface composition of the graft layer in the first few

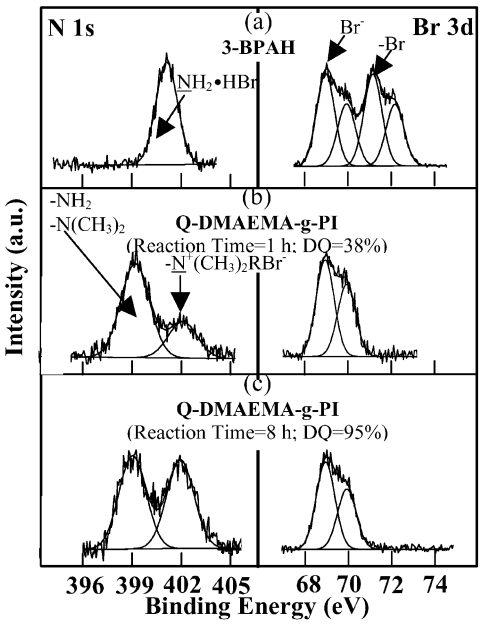

Fig. 6. N 1s and Br 3d core-level spectra of (a) 3-BPAH, and the DMAEMA-*g*-PI surfaces quaternized in 1 M solution of 3-BPAH at 50 °C for (b) 1, and (c) 8 h.

nanometers before and after quaternization. The DQ value is then deduced from the surface composition. The N 1s peak component at about 399.1 eV for the Q-DMAEMA-*g*-PI surface actually originates from two photoelectron signal sources, one from the nitrogen of the unquaternized tertiary amine species ($-N(CH_3)_2$) of the grafted DMAEMA polymer and the other from the NH_2 species of the coupled 3-BPAH. Therefore, the DQ of the graft layer is derived from the following equation:

DQ = (Area of N 1s component at 402.1 eV)

/(Area of N 1s component at 399.1 eV)

as the conversion of each tertiary amine nitrogen of the grafted DMAEMA unit into the quaternized nitrogen by 3-BPAH is also accompanied by the introduction of a NH_2 species at the BE of 399.1 eV. Furthermore, when the thickness of the quaternized graft layer exceeds the probing depth of XPS, there is no N 1s component signal at 401.6 eV from the PI substrate. Thus, according to the above definition, the DQs for the quaternized DMAEMA-*g*-PI surfaces at the quaternization time of 1 and 8 h are about 38 and 95%, respectively. Thus, for all quaternization experiments, only DMAEMA-*g*-PI films with a graft copolymerization time of 30 min, and with a surface coverage (by the grafted DMAEMA polymer) comparable to the probing depth of the XPS technique, are used.

Two identical DMAEMA-*g*-PI films were quaternized at 30 and 50 °C, respectively, in a 1 M aqueous solution of 3-BPAH for 1–24 h. As shown in Fig. 7, the DQ value increases with the reaction time at both temperatures over the entire reaction period of 24 h. For quaternization carried

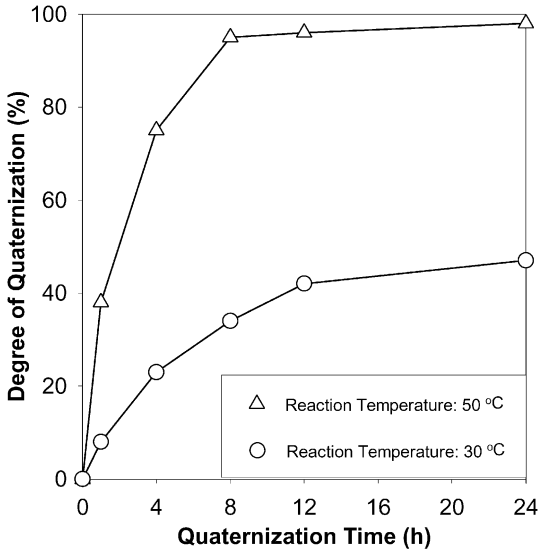

Fig. 7. The dependence of DQ of the DMAEMA-*g*-PI surface on the quaternization time in the 1 M solution of 3-BPAH at 30 and 50 °C.

out at 30 °C, the DQ is only about 41% after 12 h and increases slowly thereafter. At the higher temperature of 50 °C, the DQ has already reached 95% after 8 h in the 1 M 3-BPAH solution.

3.4. Characteristic of the surface-modified PI films and their relevance to electroless plating of copper

3.4.1. Activation of the surface-modified PI films by the Sn-free process

In the present work, the surface-modified PI films are activated directly by immersion in the $PdCl_2$ solution, in the absence of prior surface sensitization by $SnCl_2$, for the subsequent electroless plating of copper. Fig. 8 shows the Pd 3d and N 1s core-level spectra of the corresponding DMAEMA-*g*-PI film (UV graft copolymerization time = 30 min, part (a)), its quaternized counterpart (the Q-DMAEMA-*g*-PI Film, DQ ≈ 91%, part (b)), and the TMMAC-*g*-PI film (UV graft copolymerization time = 30 min, part (c)), after activation in $PdCl_2$ solution for 5, 2 and 2 min, respectively. The presence of surface adsorbed Pd species is revealed by the appearance of the Pd 3d core-level signal on all three activated PI surfaces. The Pd 3d core-level spectrum of each surface consists of three spin–orbit split doublets. The lowest BE doublet with the BEs for the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peak components lying at about 335 and 340 eV, respectively, are assigned to the Pd^0 species. The Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peak components with BEs at about 338 and 343 eV, respectively, are assigned to the Pd^{2+} ions. The major doublet having the intermediate BEs for the respective $3d_{5/2}$ and $3d_{3/2}$ components at about 336.5 and 341.5 eV, respectively, are assigned to the Pd complex (Pd^*) [37]. For the three samples, the area of the Pd^* peak components comprises about 85–95% of the total Pd 3d spectral area. The area of the peak components for the

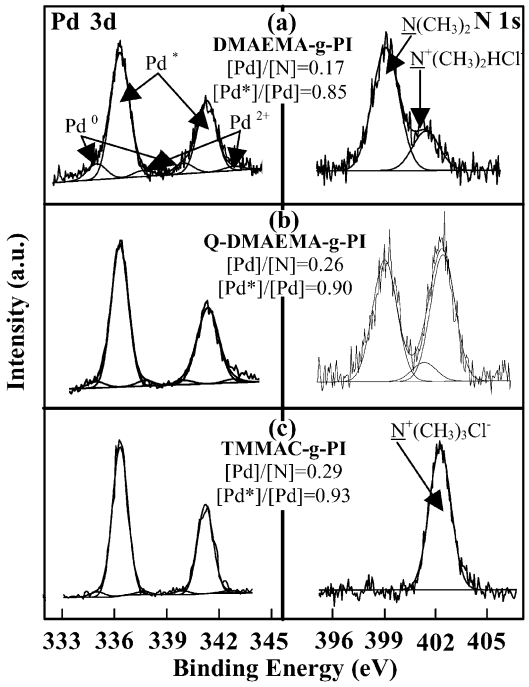

Fig. 8. Pd 3d and N 1s core-level spectra of (a) the DMAEMA-*g*-PI surface, (b) the Q-DMAEMA-*g*-PI (DQ ≈ 91%) surface, and (c) the TMMAC-*g*-PI (UV graft copolymerization time = 30 min) surface activated in the $PdCl_2$ solution by the Sn-free process for 5, 2 and 2 min, respectively.

Pd^{2+} species, on the other hand, contributes less than 5% of the total Pd 3d area. These results indicate that palladium is mainly complexed on the three *graft*-modified PI surfaces. The palladium uptakes, as indicted by the [Pd]/[N] ratios and deduced from the Pd 3d and N 1s core-level spectral area ratios, are 0.17, 0.26 and 0.29, respectively, for the DMAEMA-*g*-PI, the Q-DMAEMA-*g*-PI and the TMMAC-*g*-PI surfaces.

Immersion of the DMAEMA-*g*-PI and Q-DMAEMA-*g*-PI films containing tertiary amine groups on their surfaces into the acidic $PdCl_2$ solution in the Sn-free activation process results in the appearance of a new N 1s peak component at 401.2 eV. The XPS results suggest that in the HCl solution of $PdCl_2$, some of the tertiary amine groups ($-N(CH_3)_2$) on the DMAEMA-*g*-PI surface, as well as some of the primary amine and the tertiary amine group on the Q-DMAEMA-*g*-PI surface, have been partially protonated to give rise to such structures as $-N^+H(CH_3)_2Cl^-$ and $-NH_3^+Cl^-$. The N 1s core-level lineshape of the $PdCl_2$-activated TMMAC-*g*-PI surface, on the other hand, remains practically unchanged after activation in the $PdCl_2$ solution.

3.4.2. Effect of surface functionalization on the induction period for the electroless plating of copper

Palladium exists mainly in the complexed form on the three types of the *graft*-modified PI surfaces. The subsequent redox plating reaction of copper occurs on the

palladium-activated PI surfaces [38]:

$$HCHO + 3OH^- \leftrightarrow HCOO^- + 2H_2 + 2e^- \text{ (pH 14, } E^0 = 1.070 \text{ V)}$$

$$Cu^{2+} + 2e^- \leftrightarrow Cu^0 \ (E^0 = 0.340 \text{ V})$$

The onset of the electroless copper deposition is preceded by a non-steady-state period, or an induction period [38]. The major factors that determine the time necessary to reach the rest potential of the reducing agent are the type and the concentration of the ligand present [39]. For the activation of the DMAEMA-*g*-PI surface by the Sn-free process, an approximately 10 min of induction period was needed for the steady copper plating process to commerce. However, for the Q-DMAEMA-*g*-PI and the TMMAC-*g*-PI surfaces with the quaternary amine groups and activated in the same way, 1 min or less was sufficient to initiate the copper plating process. Their surfaces darkened quickly with the evolution of hydrogen bubbles. The plating rate is thus improved substantially in the case of the latter two surfaces. In theory, the electroless plating process is initiated by the reaction of formaldehyde with the hydroxide ions, forming hydrogen with the simultaneous release of electrons [38]. The electrons are transferred across the Pd and used for the decomposition of copper complex into copper metal atom. In the alkaline copper plating bath, the two surfaces with the quaternary amine groups still retain the cationic properties. Thus, the OH^- anions in the plating solution can be adsorbed on these surfaces quickly via electrostatic interaction to facilitate the subsequent electron transfer in the anodic reaction.

3.4.3. Copper absorption on the functionalized PI surfaces

The pristine (un-activated) DMAEMA-*g*-PI, Q-DMAEMA-*g*-PI (DQ ≈ 48%) and TMMAC-*g*-PI films (the latter two involving the NR_4^+ quaternary amine groups) were immersed into a modified copper plating solution, in which no formaldehyde was added, for 30 s. After the reaction, all films were removed and rinsed thoroughly with doubly distilled water before being dried under reduced pressure. The compositions of the resulting surfaces were analyzed by XPS. The Cu 2p and N 1s core-level spectra of the respective surfaces are shown in Fig. 9(a)–(c). The Cu 2p signal is only discernible on the Q-DMAEMA-*g*-PI and TMMAC-*g*-PI surfaces. For the DMAEMA-*g*-PI surface, the N 1s lineshape is still characteristic of that of the tertiary amine groups of the grafted DMAEMA polymer. These results suggest that both the Q-DMAEMA-*g*-PI and the TMMAC-*g*-PI films with the NR_4^+ species on their surfaces have a strong ability to extract copper species from the copper complexes in the plating solution. The results are consistent with those reported in Ref. [40] on the molecular reaction of the NR_4^+ species in the copper complex solution. Nevertheless, the optimum adhesion strength of the electrolessly deposited copper on the TMMAC-*g*-PI surface is far

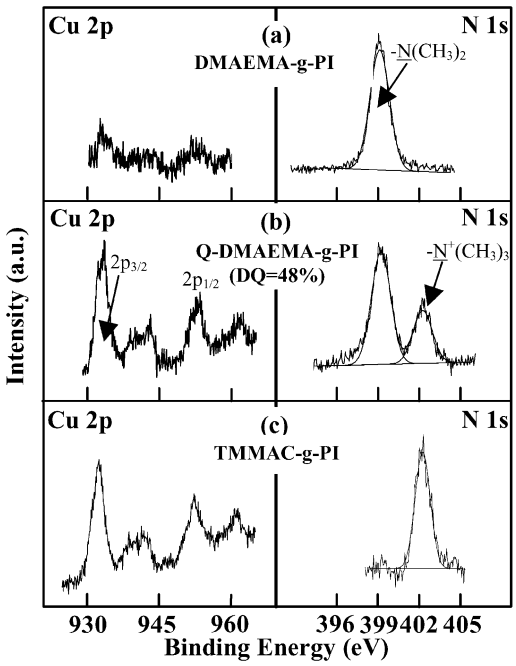

Fig. 9. Cu 2p and N 1s core-level spectra of (a) the DMAEMA-*g*-PI surface, (b) the Q-DMAEMA-*g*-PI (DQ = 48%) surface, and (c) the TMMAC-*g*-PI surface after immersing for 30 s in a modified Cu plating solution, in which no formaldehyde was added.

lower than that of copper on the Q-DMAEMA-*g*-PI surface (see below). Thus, the specific interaction of the NR_4^+ group with Cu(II) ion has only limited contribution to the observed adhesion strength improvement. The enhanced adhesion of electrolessly deposited copper to the Q-DMAEMA-*g*-PI surface, on the other hand, is due to the introduction of the reactive $-NH_2$ in the coupled 3-BPAH (see below).

3.5. Adhesion of the electrolessly deposited copper on the surface-modified PI films

The ultimate adhesion strength between the metal and the polymer substrate is one of the primary concerns in the actual electronic applications. Fig. 10 shows that the T-peel adhesion strength of the electrolessly deposited copper on the DMAEMA-*g*-PI surface increases with increasing graft concentration on the substrate surface. A maximal T-peel adhesion strength of about 4 N/cm is achieved for the electrolessly deposited copper on the DMAEMA-*g*-PI film, in comparison to 2.5 N/cm on the TMMAC-*g*-PI film at about the same graft concentration. The adhesion strength of the electrolessly deposited copper on the *graft*-modified PI surfaces is thus much higher than that of the electrolessly deposited copper on the pristine PI film (negligible), or that of the electrolessly deposited copper on the argon plasma-treated PI film (0.5 N/cm), via the two-step activation process. The dependence of the T-peel adhesion strength of the electrolessly deposited copper on the DQ of the DMAEMA-*g*-PI surface is also shown in Fig. 10. The adhesion strength increases further

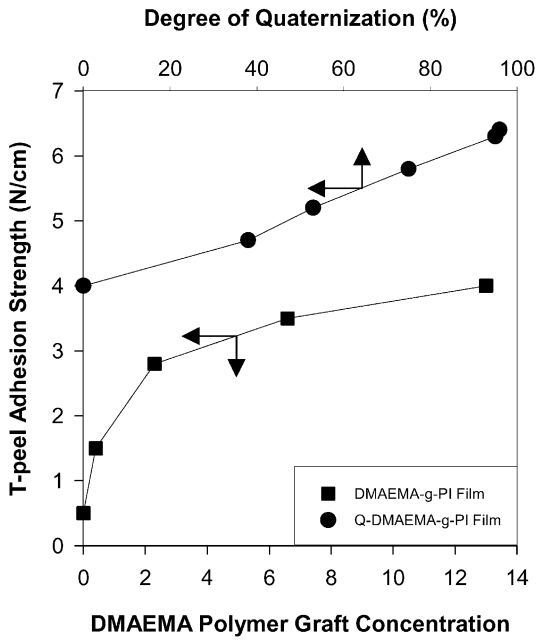

Fig. 10. The dependence of the T-peel adhesion strength of the electrolessly deposited copper on the graft concentration of DMAEMA polymer on the PI surface and on the DQ of the quaternized DMAEMA-*g*-PI surface.

with the DQ. An optimum T-peel adhesion strength of about 6.4 N/cm is achieved for the electrolessly deposited copper on the Q-DMAEMA-*g*-PI (DQ ≈ 95%) surface. The primary amine group introduced by the coupled 3-BPAH can interact actively with the electrolessly deposited copper to form the Cu–N bonds [41]. This interaction accounts, to a large extent, for the enhanced adhesion strength of the electrolessly deposited copper on the Q-DMAEMA-*g*-PI surface. On the other hand, the enhanced adhesion strength generally obtained for the *graft*-modified surface is also attributable to the spatial distribution of the graft chains on the PI film surface and into the metal matrix, as well as the fact that the grafted DMAEMA chains are covalently tethered on the PI surface.

3.6. Failure mode of the Cu/Q-DMAEMA-g-PI assembly

In the investigation of metal/polymer adhesion, a study of the locus of adhesion failure is expected to be informative. The adhesion failure mode of the electrolessly deposited copper on the DMAEMA-*g*-PI surface and its quaternized surface via the Sn-free activation process was briefly investigated by XPS. Fig. 11 shows the Cu 2p and N 1s spectra of the delaminated Cu (part (a)) and PI (part (b)) surfaces from an assembly involving the electrolessly deposited copper on the DMAEMA-*g*-PI film (graft copolymerization time = 30 min) and having a T-peel adhesion strength of about 4 N/cm. Copper signal is detected on both of the delaminated surfaces, although its intensity is comparatively lower on the PI surface. Fair amounts of DMAEMA polymer are also detected on both of the delaminated surfaces, as indicated by the presence of the tertiary amine nitrogen signals on both surfaces. These results suggest that the adhesion failure mode must have involved the fracture of the graft chains at the interphase consisting of the electrolessly deposited copper and the grafted DMAEMA polymer. Thus, the failure mode is adhesional in nature. A similar failure mechanism is also observed for the corresponding assemblies involving the Q-DMAEMA-*g*-PI surface and having a T-peel adhesion strength in the range 4–6.4 N/cm.

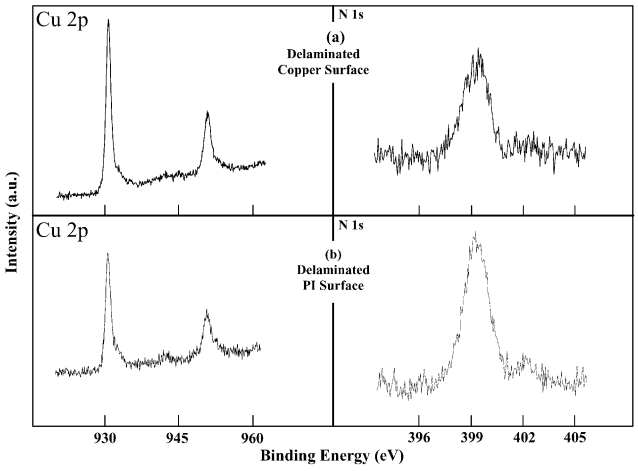

Fig. 11. Cu 2p and N 1s XPS core-level spectra of the delaminated (a) copper and (b) PI surfaces from an assembly involving electrolessly deposited copper on the DMAEMA-*g*-PI film and having a T-peel adhesion strength of about 4 N/cm.

4. Conclusions

Introduction of tertiary and quaternary amine groups onto PI films was carried out via UV-induced graft copolymerization with DMAEMA (the DMAEMA-*g*-PI film) and TMMAC, respectively. Quaternization of the DMAEMA-*g*-PI film with 3-BPAH (the Q-DMAEMA-*g*-PI film) had also been carried out. The DQ was affected by the quaternization time and the reaction temperature. Palladium complex formation on the DMAEMA-*g*-PI, its quaternized counterpart and the TMMAC-*g*-PI surfaces was achieved in the absence of prior sensitization by $SnCl_2$. A rather short induction time (<1 min) was sufficient to initiate the electroless plating of copper on the palladium complex-activated Q-DMAEMA-*g*-PI and the TMMAC-*g*-PI surfaces. The T-peel adhesion strength of the electrolessly deposited copper on the DMAEMA-*g*-PI film was enhanced by quaternization. An optimum T-peel adhesion strength of about 6.4 N/cm was achieved for the electrolessly deposited copper on the Q-DMAEMA-*g*-PI surface. The strong adhesion of the electrolessly deposited copper to the Q-DMAEMA-*g*-PI film was attributed to the strong interaction of the various nitrogen species on the quaternized surface with palladium and copper, and to the spatial distribution of the graft chains on the PI surface and into the metal matrix.

References

[1] Ressano DSM, Wu SY, Denice DD. In: Ghosh MK, Mittal KL, editors. Polyimides: fundamentals and applications. New York: Marcel Dekker, 1996. Chapter 12.
[2] Nishi Y, Doering R, editors. Handbook of semiconductor manufacturing technology. New York: Marcel Dekker, 2000. p. 377.
[3] Lee KW, Kowalczyk SP, Shaw JM. Langmuir 1991;7:2450.
[4] Inagaki N, Tasaka S, Hibi K. J Polym Sci, Polym Chem 1992;30:1425.
[5] Rozovskis G, Vinkevicius J, Jaciauskiene J. J Adhes Sci Technol 1996;10:399.
[6] Zhang JY, Esrom H, Kogelschatz U, Emig G. J Adhes Sci Technol 1994;8:1179.
[7] Celina M, Kudoh H, Renk TJ, Gillen KT, Clough RL. Radiat Phys Chem 1998;51:191.
[8] Inagaki N, Tasaka S, Ohmori H, Mibu S. J Adhes Sci Technol 1996;10:243.
[9] Inagaki N, Tasaka S, Masumoto M. Macromolecules 1996;29:1642.
[10] Charbonnier M, Romand M, Esrom H, Seebock R. J Adhes 2001;75:381.
[11] Shafeev G, Hoffmann P. Appl Surf Sci 1999;139:455.
[12] Baumgartner C, Scott L. J Adhes Sci Technol 1995;9:789.
[13] Lee KW, Viehbeck A. IBM J Res Dev 1994;38:457.
[14] Esrom H, Seebock R, Charbonnier M, Romand M. Surf Coat Technol 2000;125:19.
[15] Viehbeck A, Kovac CA, Buchwalter SL, Goldberg MJ, Tisdale SL. ACS Symp Ser 1990;440:394.
[16] Yang GH, Kang ET, Neoh KG, Zhang Y, Tan KL. Colloid Polym Sci 2001;279:745.
[17] Rye RR, Ricco AJ. In: Mittal KL, editor. Metallized plastics: fundamentals and application. New York: Marcel Dekker, 1998. p. 15.
[18] Mittal KL. Polyimides and other high temperature polymers: synthesis, characterization and applications. The Netherlands: VSP, 2001. Chapter 1.
[19] Robert MG, William TM. In: Yoshio N, Robert D, editors. Handbook of semiconductor manufacturing technology. New York: Marcel Dekker, 2000. p. 377.
[20] Pearlstein F. Metal Fin 1955;53:59.
[21] Sard S. J Electrochem Soc 1970;117:864.
[22] Meek RL. J Electrochem Soc 1975;122:1478.
[23] Osaka T, Takematsu H, Nihei K. J Electrochem Soc 1980;127:1021.
[24] Jackson RL. J Electrochem Soc 1990;137:95.
[25] Kang ET, Neoh KG, Shi JL, Tan KL, Liaw DJ. Polym Adv Technol 1999;10:20.
[26] Loh FC, Lau CB, Tan KL, Kang ET. J Appl Polym Sci 1995;56:1707.
[27] Beamson G, Briggs D. High resolution XPS of organic polymers: the Scienta ESCA300 database. New York: Wiley, 1992. p. 214.
[28] Beamson G, Briggs D. High resolution XPS of organic polymers: the Scienta ESCA300 database. New York: Wiley, 1992. p. 210.
[29] Inagaki N, Tasaka S, Onodera A. J Appl Polym Sci 1999;73:1645.
[30] Zhang Y, Tan KL, Liaw BY, Liaw DJ, Kang ET. Thin Solid Films 2000;374:70.
[31] Muilenberg GE, editor. Handbook of X-ray photoelectron spectroscopy. MN: Perkin–Elmer, 1978. p. 228.
[32] Tan KL, Woon LL, Wong HK, Kang ET, Neoh KG. Macromolecules 1993;26:2832.
[33] Zhang Y, Tan KL, Yang GY, Kang ET, Neoh KG. J Electrochem Soc 2001;148:C574.
[34] Ingold CK. Structure and mechanism in organic chemistry. New York: Cornell University Press, 1953. p. 322.
[35] Avci D. Polym Bull 2000;44:469.
[36] Se K, Kijima M, Ohtomo R, Fujimoto T. J Polym Sci, Polym Chem 1997;35:1219.
[37] Dressick WJ, Dulcey CS, George JH, Calabrese GS, Calvert JM. J Electrochem Soc 1994;141:210.
[38] Paunovic M, Schlesinger M. Fundamentals of electrochemical deposition. New York: Wiley, 1999. p. 133.
[39] Paunovic M, Schlesinger M. Fundamentals of electrochemical deposition. New York: Wiley, 1999. p. 151.
[40] Juang RS, Huang IP. Sep Sci Technol 2000;35:869.
[41] Lyons AM, Vasile MJ, Pearce EM, Waszeza JV. Macromolecules 1988;21:305.