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ORIGINAL CONTRIBUTION

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Electroless deposition of copper on polyimide films modified by surface graft copolymerization with nitrogen-containing vinyl monomers

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Abstract Surface modification of Ar-plasma-pretreated polyimide (PI) films (Kapton® HN films) via UV-induced graft copolymerization with 1-vinylimidazole (VIDz), 4-vinylpyridine (4VP), and 2-vinylpyridine (2VP) under atmospheric conditions was carried out to improve their adhesion with the electrolessly deposited Cu. The surface compositions of the graft-copolymerized PI films were characterized by X-ray photoelectron spectroscopy. The adhesion strength of the electrolessly deposited Cu on the surface-graft-copolymerized PI film was affected by the type of monomers used for graft copolymerization and the graft concentration. T-peel adhesion strengths of about 15, 10, and 6 N/cm were obtained for the Cu/graft-modified PI assemblies involving, respectively, the VIDz, 4VP, and 2VP graft-copolymerized PI films. These adhesion strengths are much higher than those obtained for assemblies involving electrolessly deposited Cu on pristine or on Ar-plasma-treated PI films. The adhesion strengths involving the VIDz and 4VP surface-graft-copolymerized PI films are also higher than those involving PI films modified by chemical etching. The cohesive failure inside the PI substrate of the Cu/graft-modified PI assemblies during delamination suggested that not only were the grafted polymer chains covalently tethered on the PI film, they were also incorporated into the metal matrix during the electroless plating process.

Key words Polyimide · Surface · Graft copolymerization · Electroless plating · Copper

Introduction

Polyimides (PIs) possess many outstanding properties, such as thermoxidative stability, excellent mechanical strength, low dielectric constants, and superior chemical resistance. As a result, they have been widely used as dielectric and packaging materials in the microelectronics industry [1–3]. In microelectronics packaging applications, Cu is the most important metal because of its high conductivity and low electromigratory property [4]. Unfortunately, the adhesion strength of the Cu directly deposited onto PI film is unsatisfactory for many industrial applications. To improve the adhesion strength between the PI film and the Cu metal, numerous methods for modifying the PI surfaces have been developed [5–10].

An organic compound which interacts with Cu to form a stable complex has the potential to serve as an adhesion promotion layer. Xue et al. [11] reported that the imino groups of benzimidazole could interact with Cu metal at zero oxidation state to form a complex. It has also been reported that poly(benzimidazole) and mercaptobenzimidazole coated on Cu form complexes with the latter [12]. PIs containing trizole or imidazole functionalities have also been synthesized to improve the adhesion in PI/Cu and Cu/PI laminates [13]. It has also been shown that the adhesion strength between a PI film and evaporated Cu could be improved by surface modification of the PI film via graft copolymerization with 1-vinylimidazole (VIDz) [14, 15]. Our earlier works [16, 17] have also shown that the adhesion of evaporated Cu or Cu foil to PI film could be enhanced by plasma pretreatment of the PI film, followed by graft copolymerization with VIDz. The imino groups of the grafted VIDz polymer form charge-transfer complexes with the Cu metal, thus enhancing the adhesion strength.

In the present work, surface modification of Ar-plasma-pretreated PI films (Kapton® HN films) was carried out via UV-induced graft copolymerization with VIDz, 4-vinylpyridine (4VP), and 2-vinylpyridine (2VP) to enhance their adhesion with the electrolessly deposited Cu. Physicochemical parameters affecting the adhesion strength between the electrolessly deposited Cu and the surface-graft-copolymerized PI film, such as the type of the monomers used for graft copolymerization and the graft concentration, were investigated.

Experimental

Materials

The PI film used in this study was poly[*N*,*N*′-(oxydiphenylene)pyromellitimide] with the chemical structure shown in Fig. 1a. It was obtained from the Du Pont Chemical Company as Kapton® HN in rolls of 40-mm width and 75-μm thickness. The surfaces of the PI films were cleaned with acetone in an ultrasonic water bath for 45 min before use. The monomers VIDz, 4VP, and 2VP used for surface graft copolymerization were obtained from the Aldrich Chemical Company (Milwaukee, Wis., USA). The chemical structures of these vinyl monomers are shown in Fig. 1b, c, and d, respectively.

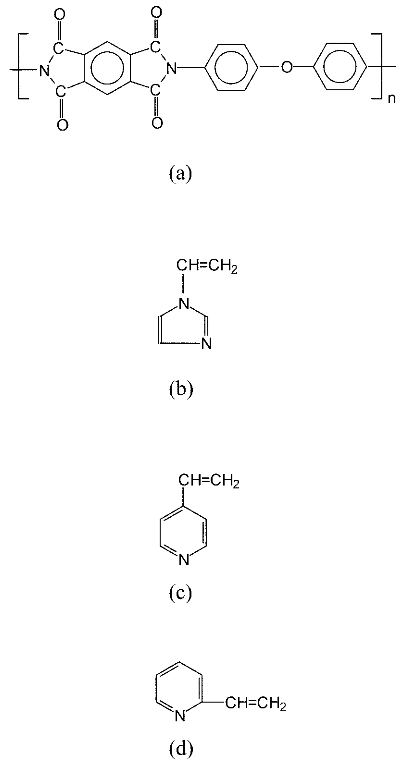

Fig. 1 Chemical structures of **a** poly[*N*,*N*′-(oxydiphenylene)pyromellitimide] (Kapton HN), **b** 1-vinylimidazole (*VIDz*), **c** 4-vinylpyridine (*4VP*), and **d** 2-vinylpyridine (*2VP*)

Ar-plasma treatment and graft copolymerization

The PI films were cut into strips of about 20 × 40 mm in size. They were pretreated with Ar plasma before the UV-induced graft copolymerization. A cylindrical-type glow discharge cell, model SP 100, manufactured by Anatech (Springfield, Va., USA) was used for the plasma treatment. The plasma power applied was kept at 35 W at a radio frequency of 40 kHz. The film was placed between the two parallel plate electrodes and subjected to the glow discharge for a predetermined period of time at an Ar pressure of about 0.5 torr. The Ar-plasma-pretreated polymer films were then exposed to the atmosphere for at least 10 min to facilitate the formation of surface peroxides and hydroperoxides for the subsequent graft copolymerization experiments [18].

Prior to the UV-induced graft copolymerization experiment, a drop of pure 4VP, 2VP, or VIDz monomer was introduced onto the surface of the plasma-pretreated PI film. The film was then sandwiched between two quartz plates. The assembly was subjected to UV irradiation in a Riko RH 400–10 W rotary photochemical reactor (Riko Denki Kogyo, Chiba, Japan). The reactor was equipped with a 1000-W high-pressure Hg lamp and a constant temperature bath. All UV-induced graft copolymerizations were carried out under atmospheric conditions at a constant temperature of 28 °C. After the grafting experiment, the VIDz graft-copolymerized PI film (VIDz-*g*-PI film) was washed thoroughly with doubly distilled water. The 4VP and 2VP graft-copolymerized PI films (4VP-*g*-PI and 2VP-*g*-PI films, respectively), on the other hand, were washed thoroughly with copious amounts of ethanol to remove the residual monomers and physically adsorbed homopolymers.

Surface characterization

X-ray photoelectron spectroscopy (XPS) was used to determine the surface composition of the samples. The XPS measurements were made using an AXI HSi spectrometer (Kratos Analytical, UK) with an Mg Kα X-ray source (1253.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage was 15 kV; the anode current was 15 mA. The pressure in the analysis chamber was maintained at 5.0×10^{-8} torr or lower during each measurement. The samples were mounted on the standard sample stubs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron takeoff angle of 90° (with respect to the sample surface). All binding energies (BEs) were referenced to the C 1*s* hydrocarbon peak at 284.6 eV. In peak synthesis, the linewidth (full width at half maximum) 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 $\pm 5\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries. The surface morphology of the PI film was characterized using a Nanoscope IIIa atomic force microscope (AFM). All images were obtained in air using the tapping mode under a constant force (scan size: 10 × 10 μm, set point: 3.34 μV, scan rate: 1.0 Hz).

Electroless plating of Cu on the graft-copolymerized PI films

The pristine and surface-modified PI films were activated by a two-step process to immobilize the Pd catalyst for the electroless deposition of Cu [19]. The film surface was first sensitized by soaking in a solution containing 0.3 wt% $SnCl_2$ and 2.5 wt% HCl (37%) for 1 min, followed by rinsing with distilled water. It was then immersed in a solution containing 0.1 wt% $PdCl_2$ and 1.0 wt% HCl (37%) for 5 min, followed by rinsing thoroughly with distilled water. The surface-activated PI film was then placed in an electroless Cu plating bath for about 5–20 min to allow the deposition of a Cu layer of about 200-nm thickness. The composition of the solution in the plating bath was as follows: 0.7 wt% $CuSO_4 \cdot 5H_2O$, 2.5 wt% potassium sodium tartrate, 0.4 wt% sodium hydroxide, and 0.4 wt% formaldehyde [19]. The Cu-deposited PI film was rinsed thoroughly with copious amounts of distilled water. It was then subjected to postthermal treatment in a vacuum oven at 140 °C for about 3 h. The thermally treated sample was allowed to cool slowly to room temperature in the vacuum oven over a period of about 4 h to minimize the stress at the metal–polymer interface. The metallized surface of the film was subsequently electroplated with a Cu layer of about 50-μm thickness. This additional Cu layer served as an anchoring layer for peeling the underlying electrolessly deposited Cu. The electroplating was carried out in a standard plating solution containing copper (II) sulfate (0.75 M), sulfuric acid (0.6 M), and glucose (0.2 M), at the temperature of about 25 °C. The current density was maintained at about 2 A/dm^2. The electroplated assembly was rinsed thoroughly with copious amount of doubly distilled water and was dried under reduced pressure.

Adhesion strength measurement

The adhesion strength was determined by measuring the T-peel adhesion strength with an Instron model 5544 tensile tester from the Instron Corporation, USA. All the measurements were carried out at a crosshead speed of 1.0 cm/min. Each adhesion strength reported was the average of at least three sample measurements. The adhesion strengths among these samples usually did not vary by more than ±0.5 N/cm.

Results and discussion

The processes of Ar plasma pretreatment, UV-induced graft copolymerization, surface activation, and electroless plating of Cu on the PI surface are shown schematically in Fig. 2. The details for each process are described in the following.

Electroless seposition of Cu on PI film modified by Ar plasma treatment: the Cu/PI assembly

The respective C 1*s*, O 1*s*, and N 1*s* core-level spectra of the pristine and a 60-s Ar-plasma-treated PI (Kapton® HN) film are shown in Fig. 3a and b. The C 1*s* 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 CH species, the CH–N and CH–C(O) species, the C–O species, the N–C = O species and the π–π* shakeup satellite, respectively [20, 21], as shown in Fig. 3a. Surface modification of PI film by Ar plasma treatment, followed by air exposure, results in the enhancement of the C–O species at a BE of 286.2 eV and the formation of two additional carbon species at BEs of about 287.4 and 289.3 eV. These two peak components are attributable, respectively, to the carbonyl species, which differs from the carbonyl of the imide group in the pyromellitic dianhydride chain, and to the carboxyl species [22], as shown in Fig. 3b. The [O]/[C] and [N]/[C] ratios of the pristine and Ar-plasma-treated PI films, as determined from the C 1*s*, O 1*s*, and N 1*s* core-level spectral peak area ratios, are summarized in Table 1. The [O]/[C] and [N]/[C] ratios of the pristine PI film are about 0.22 and 0.09. These values are comparable to the theoretical ratios of 0.23 and 0.09 for the PI (Kapton® HN) film. The corresponding ratios increase to about 0.35 and 0.1 after 60 s of Ar plasma treatment, in agreement with the results generally reported in the literature [20, 23].

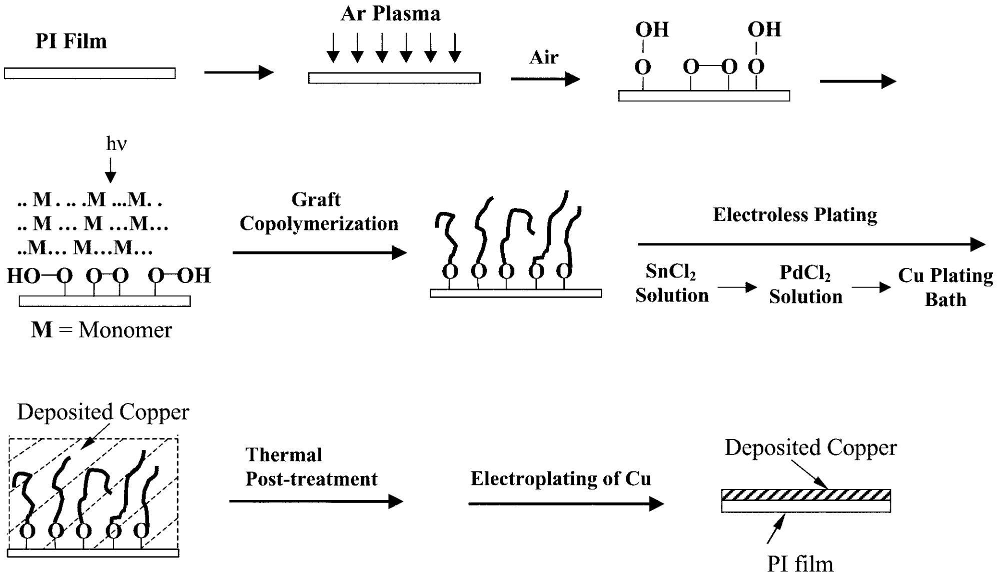

Fig. 2 Schematic diagram illustrating the processes of Ar plasma pretreatment, UV graft copolymerization, and the electroless metallization of the modified polyimide (*PI*) film

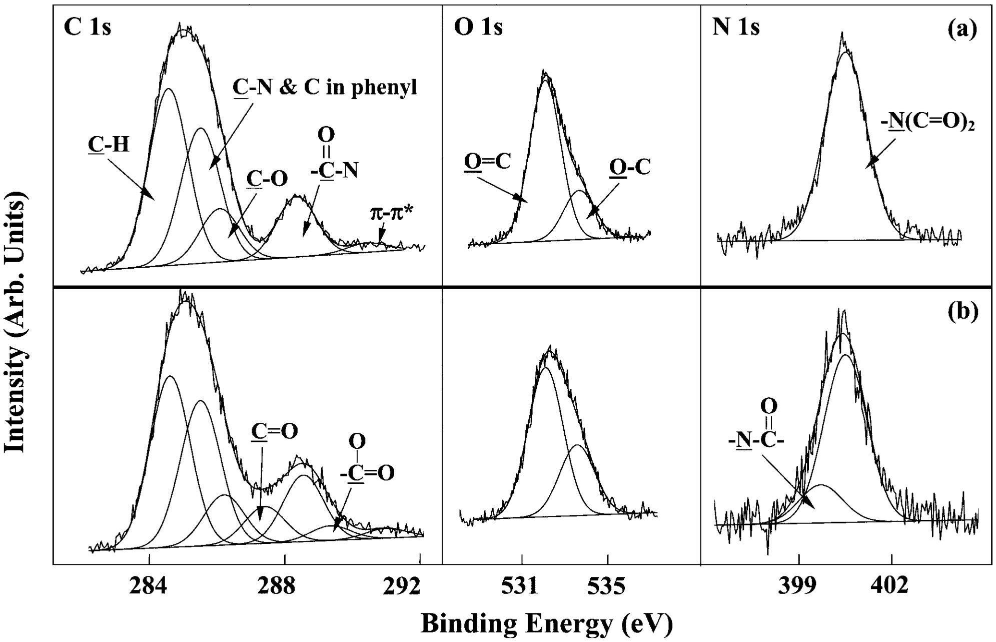

Fig. 3 C 1*s*, O 1*s*, and N 1*s* core-level spectra of **a** the pristine PI film and **b** the 60-s Ar-plasma-treated PI film

Table 1 Effect of Ar plasma treatment on the surface composition of the polyimide (*PI*) film and on the T-peel adhesion strength of the corresponding Cu/PI assembly from electroless deposition of Cu

Sample	[O]/[C]	[N]/[C]	T-peel adhesion strength (N/cm)
Pristine PI film	0.22	0.09	0.5 ± 0.5
20-s Ar-plasma-treated PI film	0.28	0.1	2.6 ± 0.5
60-s Ar-plasma-treated PI film	0.35	0.1	3.0 ± 0.5

The O 1*s* core-level spectrum for the pristine PI film can be curve-fitted with two components at BEs of about 532.1 and 533.6 eV, which are assigned to the $O=C$ and O–C species, respectively [15, 23]. The [O–C]/[$O=C$] ratio obtained from the curve-fitted O 1*s* core-level spectrum is 0.3. The corresponding ratio increases to about 0.43 after 60 s of Ar plasma treatment. The interaction of Ar-plasma with saturated hydrocarbons has been extensively reported [14, 24]. Ar plasma treatment generates radicals on the PI film and the subsequent exposure to air results in the formation of various oxygen-containing species, such as peroxides and hydroperoxides. The increases in the relative amount of the C–O species and in the [O]/[C] ratio are consistent with the formation of peroxide or hydroperoxide species. The peroxide species can be utilized to initiate the surface free-radical polymerization in a mechanism generally proposed for UV-induced surface graft copolymerization [18, 24].

It has also been suggested that plasma treatment of the PI film can result in the cleavage of imide linkages and that it gives rise to the formation of carboxyl and secondary amine groups as the main hydrophilic components [25]. The formation of the secondary amine species is discernible in the N 1*s* core-level spectra as a new lower BE component at about 399.7 eV. On the other hand, the N 1*s* core-level spectrum of the pristine PI surface consists of a single peak component at a BE of 400.6 eV, which is attributable to the imide species ($-N-(C=O)_2$) [20, 26].

The effect of Ar plasma treatment of the PI substrate on the T-peel adhesion strength of the electrolessly deposited Cu is summarized in Table 1. Thus, simple Ar plasma treatment of the PI surface can enhance the T-peel adhesion strength of the electrolessly deposited Cu on PI to about 3 N/cm. This adhesion strength is almost 1 order of magnitude higher than that of the assembly obtained from the electroless deposition of Cu on the pristine PI film. The increase in adhesion strength is due to the chemical modification of the PI film surface. Ar plasma treatment of the PI film, followed by exposure to air, results in the formation of carboxyl and secondary amine groups and thus gives rise to a more hydrophilic PI surface [25]. Rozovskis et al. [8] reported that with the increase in O_2 plasma treatment time of the PI film, the relative number of oxygen-containing groups on the PI surface increases. The O_2 plasma treatment also gave rise to the formation of cavities, as well as surface micro- and macroroughness. As a result, the adhesion strength between the electrolessly deposited Cu and PI film was increased. The peel adhesion strength reached 4 N/cm at an O_2 plasma treatment time of 5 min and 6 N/cm at an O_2 plasma treatment of 10 min.

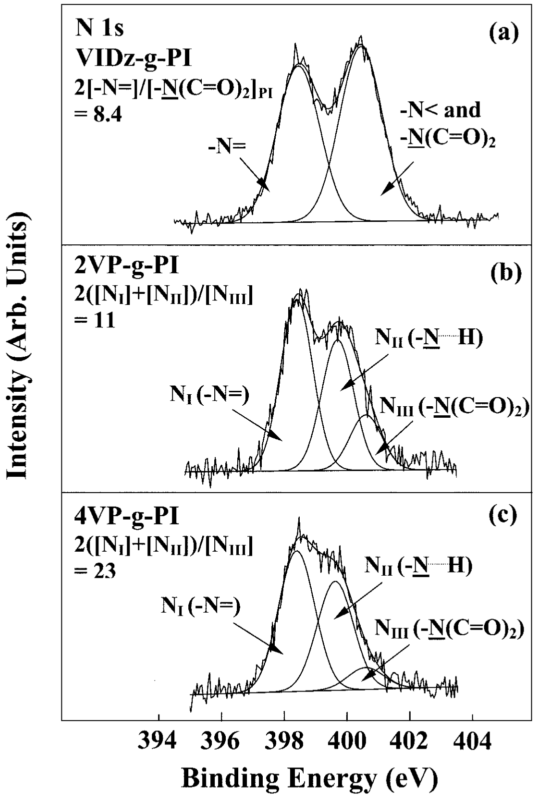

Fig. 4 N 1*s* core-level spectra of Ar-plasma-pretreated PI films after UV-induced graft copolymerization with **a** VIDz, **b** 2VP, and **c** 4VP

Electroless deposition of Cu on PI film modified by surface graft copolymerization with VIDz: the Cu/VIDz-*g*-PI assembly

The N 1*s* core-level spectrum of a 60-s Ar-plasma-pretreated PI surface after having been subjected to UV-induced graft copolymerization with VIDz for 90 min is shown in Fig. 4a. The N 1*s* core-level spectrum for the pristine PI shows only one peak component, at a BE of 400.6 eV (Fig. 3a). The spectrum of the VIDz homopolymer contains two peak components of equal intensity, at BEs of about 398.4 and 400.4 eV, corresponding to the imino (–N =) and the amino (–N <) species, respectively [27]. The presence of the grafted VIDz polymer on the PI surface can thus be deduced from the new imino component which has appeared in the N 1*s* core-level spectrum of the VIDz graft-copolymerized PI film (the VIDz-*g*-PI film). The BEs of the amino (–N <) and imide [–N(C = O)$_2$] species differ by about 0.2 eV and thus cannot be resolved unambiguously. The two species are represented by a single peak component at a BE of about 400.5 eV.

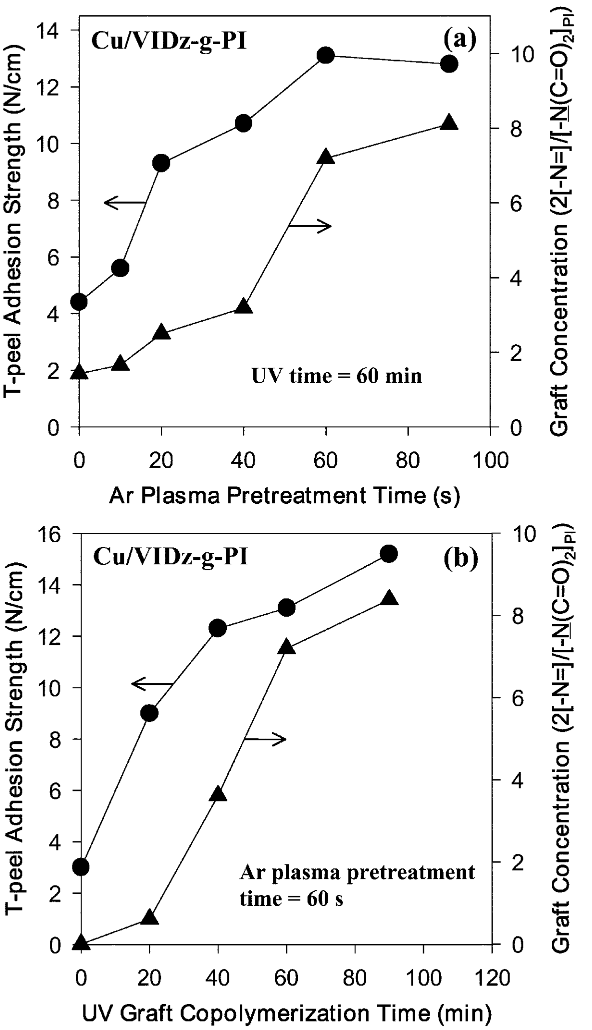

Fig. 5 The dependence of the graft concentration and the T-peel adhesion strength of the corresponding Cu/VIDz-*g*-PI assembly on **a** the Ar-plasma-pretreatment time of the PI film and **b** the UV-graft-copolymerization time

The dependences of the VIDz polymer graft concentration on the Ar plasma pretreatment time of the PI film and the UV graft copolymerization time are shown in Fig. 5a and b, respectively. The surface graft concentration is defined as the number of repeat units of the graft chain per repeat unit of the substrate chain. Thus, the surface graft concentrations are determined from the curve-fitted N 1*s* peak area ratios of the imine (–N =) and imide [–N(C = O)$_2$] components, associated, respectively, with the graft and the substrate polymers. The concentration of the surface-grafted VIDz polymer is thus expressed as the 2[–N =]/[–N(C = O)$_2$]$_{PI}$ ratio. The 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. The number of [–N(C = O)$_2$] species contributed by the PI substrate is deduced from the N 1*s* spectrum by subtracting the area of the imine species (–N =) of the grafted VIDz polymer from the area of the peak component arising from the combined contribution of the $–N(C=O)_2$ and –N < species, as each VIDz unit contains equal numbers of the –N = and –N < species. It can be observed that the graft concentration increases rapidly with both the Ar-plasma-pretreatment time and the UV-graft-copolymerization time.

Figure 5 also shows the T-peel adhesion strength of the Cu/VIDz-*g*-PI assembly, prepared from the electroless deposition of Cu on the VIDz-*g*-PI surface, as a function of the Ar-plasma-pretreatment time of the PI film and as a function of the UV-graft-copolymerization time. The adhesion strength reaches about 15 N/cm at an Ar-plasma-pretreatment time of about 60 s and a UV-graft-copolymerization time of about 90 min. This T-peel adhesion strength is much higher than that obtained for the electrolessly deposited Cu on the pristine PI film or on the 60-s Ar-plasma-treated PI film. Thus, the effective contribution of the grafted VIDz polymer in improving the adhesion of the electrolessly deposited Cu on the PI film is ascertained. The fact that the increase in adhesion strength coincides approximately with the increase in surface graft concentration suggests that a graft chain-induced adhesion mechanism is operative. The adhesion of the electrolessly deposited Cu on the graft-modified PI surface can be described in terms of the microscopic interactions at the metal/polymer interface and interphase, and is related to the sum of all the intermolecular interactions [28, 29]. The imidazole rings of the grafted VIDz chain on the PI film undergo charge transfer interaction with the electrolessly deposited Cu [15, 30]. The spatial distribution of the graft chains, and thus the imidazole rings, on the PI film surface dictates the formation of an interphase consisting of an interpenetrating network of the graft chains in the metal matrix (Fig. 2).

In the earlier work of Vorobyova [10], PI films were treated with acidic, alkaline, or neutral solutions. The adhesion strength of the electrolessly deposited Cu on the so-modified PI films varied between 3 and 9 N/cm. The highest adhesion strength was achieved if an etchant with a high alkaline content (up to 10 mol/l) and with nitrogen-containing additives was used. The formation of chemical bonds between the metal atoms and the oxygen atoms of carboxyl groups or the nitrogen atoms of amide groups, which appeared as a result of the chemical etching of the PI film, played an important role in the observed metal/polymer adhesion. In the work of Rozovskis et al. [8], on the other hand, O_2 plasma treatment and chemical etching of the PI films were carried out. The 90°-peel adhesion strength between the electrolessly deposited Cu and the PI film reached about 6 N/cm for both treatment methods.

The change in surface morphology of the PI film after modification by graft copolymerization with VIDz was studied by AFM. The representative AFM images of the pristine PI surface and the VIDz-*g*-PI surface (graft concentration of 3.6) are shown in Fig. 6a and b, respectively. The root mean square surface roughness (R_a) of the pristine PI surface is about 1.5 nm; however, the R_a value of the VIDz-*g*-PI surface increases to about 4.7 nm. As shown in Fig. 6b, the graft-copolymerized VIDz polymer on the PI surface exists as a distinctive overlayer. The more rugged surface morphology of the VIDz-*g*-PI film has probably also facilitated the spatial interactions with the incoming metal atoms.

Electroless deposition of Cu on PI film modified by surface graft copolymerization with 2VP: the Cu/2VP-*g*-PI assembly

The N 1*s* core-level spectrum of a 10-s Ar-plasma-pretreated PI film after having been subjected to UV-induced graft copolymerization with 2VP for 60 min (the 2VP-*g*-PI film) is shown in Fig. 4b. The presence of the surface-grafted 2VP polymer can be deduced from the N 1*s* peak component at a BE of 398.4 eV, attributable to the –N = species (N_I) of the 2VP polymer [31]. The highest BE peak component, at about 400.6 eV, is assigned to the $–N(C=O)_2$ species (N_{III}) of the PI film. An additional peak component appears ata BE of about 399.6 eV, which may be due to the partially protonated or the hydrogen-bonded nitrogen in the 2VP polymer (N_{II}). The formation of hydrogen bonding

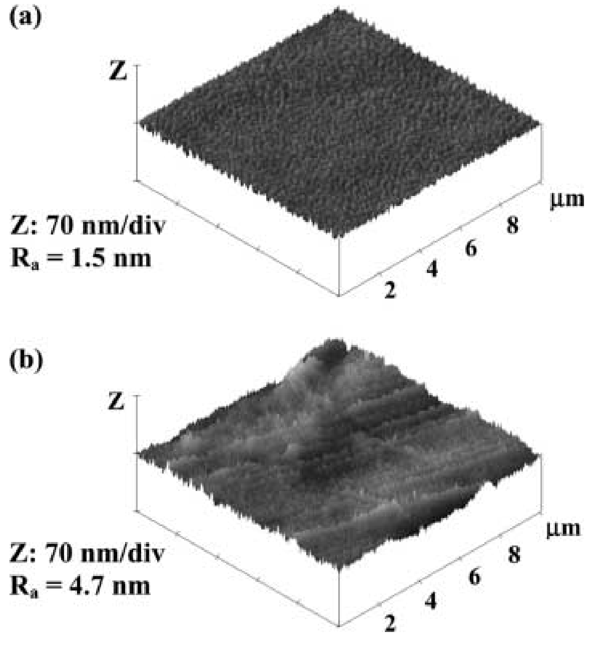

Fig. 6 Atomic force microscope images of **a** the pristine PI surface and **b** the VIDz-*g*-PI surface (plasma pretreatment: 60 s, UV graft copolymerization: 40 min, graft concentration: 3.6)

between the pyridine ring and other polymers has been investigated in detail [32–34].

The dependences of the graft concentration and the T-peel adhesion strength of the corresponding Cu/2VP-*g*-PI assembly on the Ar-plasma-pretreatment time of the PI film and the UV-graft-copolymerization time are shown in Fig. 7. The concentration of the surface-grafted 2VP polymer is expressed as the $2([N_I]+[N_{II}])/[N_{III}]$ ratio, as each 2VP unit contains one –N= group. It can be observed that the graft concentration increases with the increase in both the Ar-plasma-pretreatment time and the UV-graft-copolymerization time. The increase in the T-peel adhesion strength again coincides approximately with the increase in the graft concentration of the 2VP polymer. A T-peel adhesion strength of about 6 N/cm is achieved for the electrolessly deposited Cu on the 2VP-*g*-PI substrate with an Ar-plasma-pretreatment time of about 60 s and a UV-graft-copolymerization time of about 120 min. This adhesion strength is more than that of the assembly involving PI substrate with Ar plasma treatment alone and is comparable to those involving PI substrates modified by chemical etchants [8].

Electroless deposition of Cu on PI film modified by surface graft copolymerization with 4VP: the Cu/4VP-*g*-PI assembly

The N 1*s* core-level spectrum of a 10-s Ar-plasma-pretreated PI film after having been subjected to UV-induced graft copolymerization with 4VP for 60 min (the 4VP-*g*-PI film) is shown in Fig. 4c. The presence of the surface-grafted 4VP polymer can be deduced from the appearance of the new peak components with BEs at

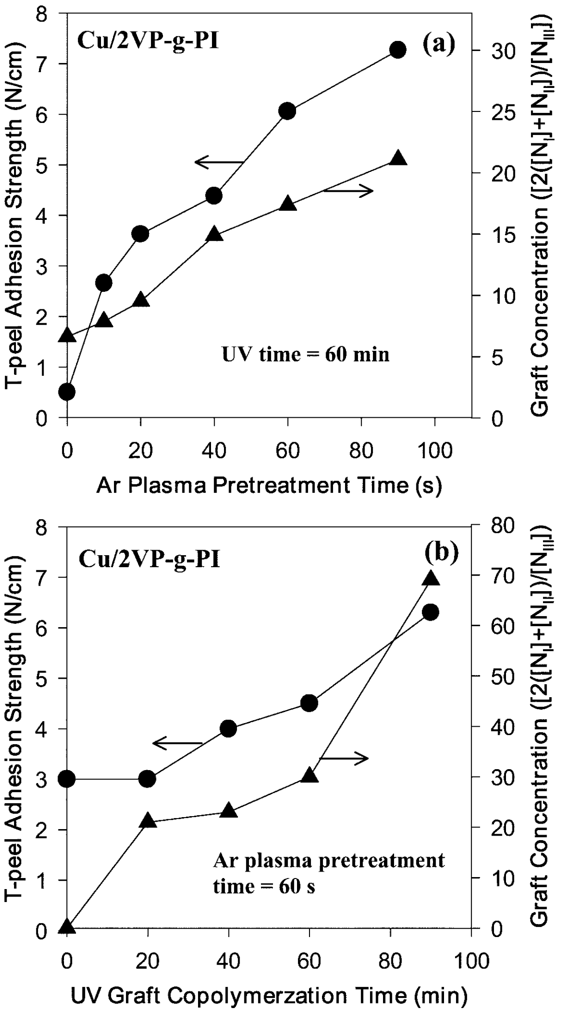

Fig. 7 The dependence of the graft concentration and the T-peel adhesion strength of the corresponding Cu/2VP-*g*-PI assembly on **a** the Ar-plasma-pretreatment time of the PI film and **b** the UV-graft-copolymerization time

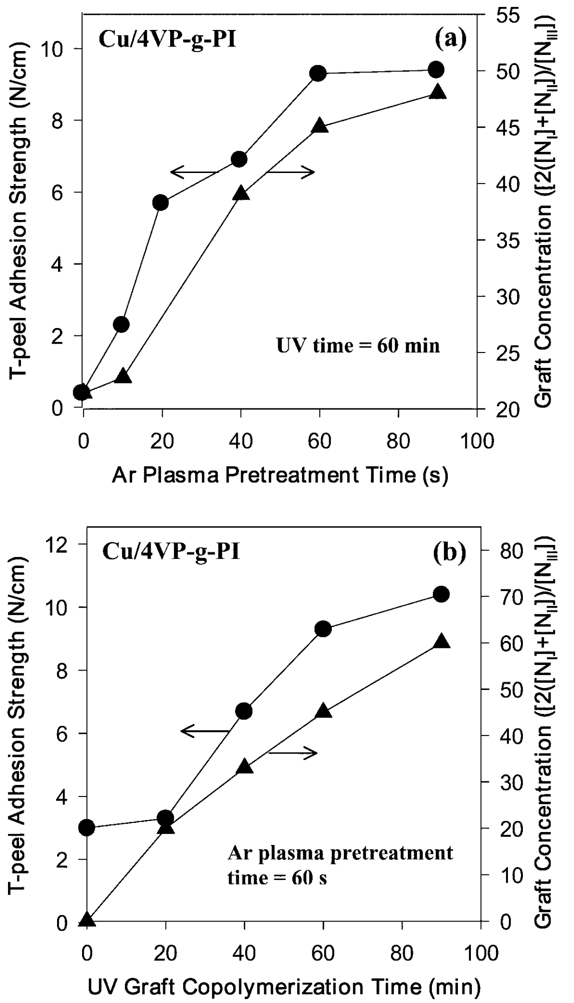

Fig. 8 The dependence of the graft concentration and the T-peel adhesion strength of the corresponding Cu/4VP-*g*-PI assembly on **a** the Ar-plasma-pretreatment time of the PI film and **b** the UV-graft-copolymerization time

about 398.4 and 399.6 eV, associated with the imine species (–N =) and the hydrogen-bonded imine species, respectively, of the 4VP polymer [30]. The presence of only a weak –N(C = O)$_2$ component (N$_{III}$) in the N 1*s* core-level spectra suggests that the surface coverage of the 4VP polymer is approaching the probing depth of the XPS technique (about 7.5 nm for an organic matrix [24]).

The dependences of the graft concentration and the T-peel adhesion strength of the corresponding Cu/4VP-*g*-PI assembly on the Ar-plasma-pretreatment time of the PI film and the UV-graft-copolymerization time are shown in Fig. 8. Similar to the case of the 2VP-*g*-PI surface, the concentration of the surface-grafted 4VP polymer is simply expressed as the $2([N_I]+[N_{II}])/[N_{III}]$ ratio. The increases in graft concentration and T-peel adhesion strength with both the Ar-plasma-pretreatment time and the UV-graft-copolymerization time are also observed. The phenomena are thus similar to those observed for the Cu/VIDz-*g*-PI and 2VP-*g*-PI assemblies. A T-peel adhesion strength above 10 N/cm can be achieved for the electrolessly deposited Cu on the 4VP-*g*-PI substrate with 60 s of Ar plasma pretreatment and 90 min of UV graft copolymerization. A substantially higher adhesion strength is observed for the Cu/4VP-*g*-PI assembly than for the corresponding Cu/2VP-*g*-PI assembly prepared under similar conditions. In the case of the Cu/4VP-*g*-PI assembly, the nitrogen atoms in the pyridine rings of the grafted 4VP polymer can interact more readily with the electrolessly deposited Cu to form Cu–N bonds [35], which account for the stronger adhesion of the metal to the polymer. The nitrogen atoms in the grafted 2VP polymer, on the other hand, are more sterically hindered [31] owing to the presence of the neighboring alkyl backbond. The extent of charge-transfer interaction is thus reduced. As a result, the adhesion strength of the Cu/2VP-*g*-PI assembly is generally lower than that of the corresponding Cu/4VP-*g*-PI assembly. The phenomenon is in general agreement with that observed earlier for surface-graft-copolymerized poly(tetrafluoroethylene) and poly(vinylidene difluoride) films during simultaneous lamination to Cu foils [36, 37]. A similar steric effect on the extent of charge-transfer interaction has also been reported in complexes involving Cu and pyridine polymers [35].

Adhesion failure mode of the electrolessly deposited Cu on the graft-modified PI film

The failure mode of the Cu/PI interfaces obtained from the electroless deposition of Cu on the graft-modified PI surfaces was briefly investigated by XPS. The failure mode of the Cu/VIDz-*g*-PI assembly was first investigated. The respective wide-scan, C 1*s*, and N 1*s* spectra of the pristine PI film and of the delaminated PI surface and Cu surface from an assembly having a peel adhesion strength of 10.7 N/cm are shown in Fig. 9a and c. The wide-scan spectra of the delaminated PI surface and Cu surface are grossly similar to that of the pristine PI film (Fig. 9a). No Cu or Pd signal is detected on either of the delaminated surfaces, while a strong nitrogen signal is detected on the delaminated Cu surface. Furthermore, the respective C 1*s* and N 1*s* core-level line shapes of the delaminated Cu and PI surfaces closely resemble those

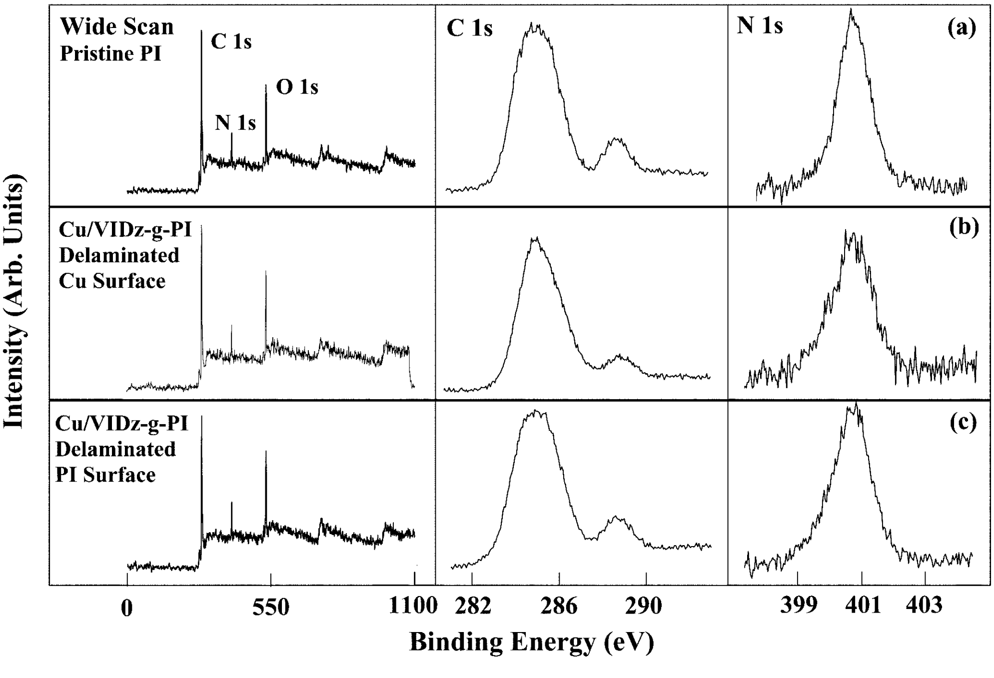

Fig. 9 X-ray photoelectron spectroscopy wide scan and C 1*s* and N 1*s* core-level spectra of **a** the pristine PI film, **b** the delaminated Cu surface, and **c** the delaminated PI surface from a Cu/VIDz-*g*-PI assembly having a T-peel adhesion strength of about 10.7 N/cm

of the pristine PI film. These results readily suggest that the assembly has delaminated by cohesive failure inside the PI substrate.

The failure mode of a Cu/4VP-*g*-PI assembly having a T-peel adhesion strength of about 9.3 N/cm was also investigated by examination of the chemical compositions of the delaminated Cu and PI surfaces. The XPS wide-scan and C 1*s* and N 1*s* core-level spectra of the delaminated Cu and PI surfaces are again grossly similar to those of the pristine PI surface. This observation, as well as the fact that no Cu or Pd signal is detected on either of the delaminated surfaces, again suggests that the metal/polymer assembly must have delaminated by cohesive failure inside the PI substrate.

The distinct failure mode inside the PI substrate testifies to the presence of strong interactions of the Pd catalyst [38] and the electrolessly deposited Cu atoms with the nitrogen moieties of the grafted VIDz and 4VP polymers. The extents of these interactions are further augmented by the spatial distribution of the graft chains on the PI surface and inside the metal matrix.

Conclusion

Ar-plasma-pretreated PI films were subjected to further surface modification via UV-induced graft copolymerization with VIDz, 2VP, and 4VP monomers under atmospheric conditions. The surface compositions of the graft-copolymerized PI film were analyzed by XPS. In all cases, the adhesion strength between the electrolessly deposited Cu and the surface-modified PI film increased with the surface graft concentration. A T-peel adhesion strength of about 15 N/cm was achieved for electrolessly deposited Cu on the VIDz-*g*-PI surface. The mode of adhesion failure of the electrolessly deposited Cu on the graft-modified PI film was cohesive in nature. The strong adhesion could be attributed to the strong interaction of the pyridine and imidazole functional groups of the grafted polymers with Cu, the spatial distribution of the graft chains on the PI surface and into the metal matrix, and the fact that the graft chains were covalently tethered on the PI surface.

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