Wet-process surface modification of dielectric polymers: Adhesion enhancement and metallization

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For many electronic applications, the surface of a dielectric polymer must be modified to obtain the desired surface properties, such as wetting, adhesion, and moisture barrier, without altering the bulk properties. This paper reviews wet-process modifications of dielectric polymer surfaces and also presents unpublished results related to fluorinated polyimides. In a typical wet process, a substrate is immersed in or sprayed with a chemical solution, rinsed with a solvent to remove the excess reagents, and then dried if necessary. Wet processing can provide greatly enhanced adhesion and reliability of the adherate (top) layer to the modified polymer surface (adherend). We discuss a) the wet-process modification of various polymers (e.g., PMDA–ODA, BPDA–PDA, 6FDA–ODA, PTFE, PCTFE); b) polyimide/polyimide and PCTFE/glass adhesion, and c) the surface chemistry and the adhesion at a fluorinated polyimide (6FDA–ODA) surface. Entanglement of polymer chains plays an important role in polyimide/polyimide adhesion, while chemical reactions are the major contributors to PCTFE/glass adhesion strength. The metallization of dielectric substrates often requires surface pretreatments or conditioning by wet processes to sensitize a polymer surface for deposition of a metal seed layer. After seeding, a thick layer of a conducting metal (e.g., Cu) is deposited by electroless or electrolytic plating. Unlike dry or high-vacuum processing of polymer surfaces, the chemistry of a wet-processed polymer surface can be well characterized and often defined at a molecular level. A relationship can be established between a polymer's surface chemical (or morphological) structure and its surface properties such as adhesion and metallization.

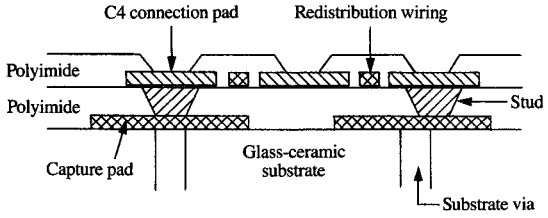


Figure 1

Cross-sectional thin-film structure of ES/9000 processor. Reprinted from *IBM J. Res. Develop.* **36,** 900 (1992).

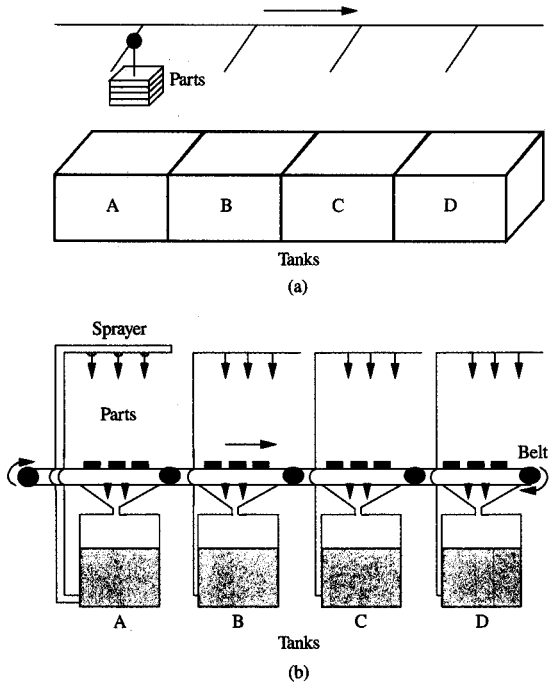


Figure 2

Wet process for manufacturing: (a) batch process; (b) continuous process.

Introduction

Polyimides and fluorinated polyethylenes are employed as dielectric layers in microelectronic applications such as printed circuit boards and multichip modules [1], since they have low dielectric constants, high thermal stability, good mechanical properties, and processability [2]. The key to high-performance packaging in microelectronics is the embedding of high-density wiring in a low-dielectric matrix. The thin-film packaging structure (**Figure 1**) in an IBM Enterprise System/9000™ (ES/9000™) processor consists of the following interfaces: polyimide/glass-ceramic, metal/polyimide, polyimide/metal, and polyimide/polyimide. Reliable adhesion at each of these interfaces is required for high-yield device production and field performance. Adhesion to polyimide materials, which have excellent chemical and mechanical properties, is generally poor. To improve the adhesion of metals or polymers to a substrate polymer film, the substrate surface is usually modified by a dry process such as plasma, corona discharge, X-ray, laser, ion beam, or flame treatments [3]. Recently, interest in wet-process surface modification of polymers has increased because of its simplicity and low cost. In a typical wet-process or immersion treatment for modification of a polymer surface, the polymer substrate is immersed in or sprayed with a chemical solution. The excess reagents are then rinsed off with a solvent, and the substrate is dried if necessary.

For electronics package fabrication, the wet process can increase throughput by continuous processing of large numbers of parts along a belt or robotics handling system, as shown in **Figure 2**. In the batch process [Figure 2(a)], a container holding multiple parts moves through tanks containing chemical formulations. Water and isopropyl alcohol are primarily used as rinsing agents. As the parts move along the belt [Figure 2(b)], the chemical solutions and the rinsing solvents stored in tanks are sprayed onto the parts. The wet parts are blown dry with nitrogen gas or air. These solutions can be replenished and reused, often for weeks or months, since very little of the active components are consumed. The components are replaced and the solutions are filtered to keep them free from contaminants, which can cause irregular surface coatings or corrosion.

Fundamental studies of wet-process surface modifications of polymers have been performed [4–6]. A polymer surface modified by a wet process is readily characterized, and the chemistry can be defined at the molecular level. The reactive species in the wet process are acids (electron acceptors) and bases (electron donors) in solution. Most chemical reactions have been extensively studied in a homogeneous environment. The corresponding reaction at a polymer surface usually follows the mechanism that is operative in a homogeneous environment. Dry processes, on the other hand, are not well understood because of the possibility of multiple reactions at a polymer surface with the radicals and the electrons produced in a dry process. This makes analysis of the products at the molecular level very difficult after dry processing. If the surface chemistry is well defined and

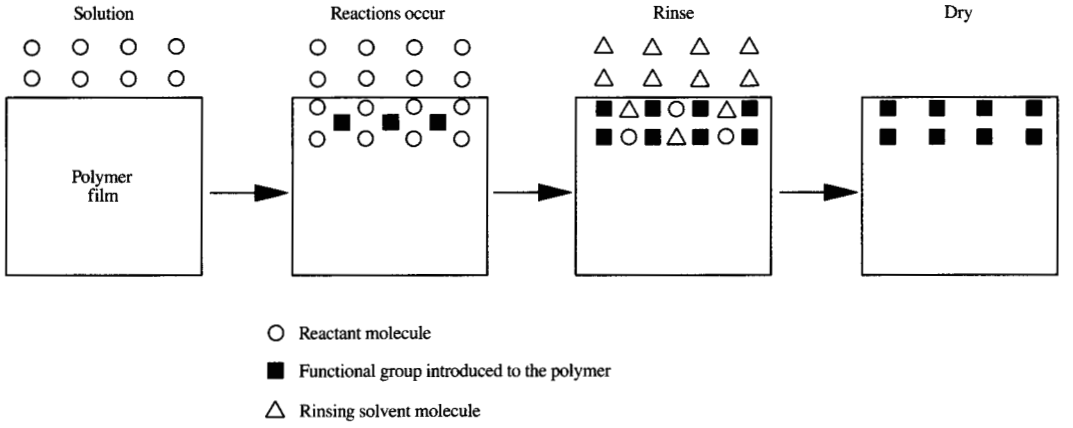


Figure 3

Phenomena at the interface in the wet-process surface modification of polymers.

only one type of functional group is introduced, a surface structure–property relationship can be established. Understanding this relationship is important in the application of surface chemistry for industrial purposes [7].

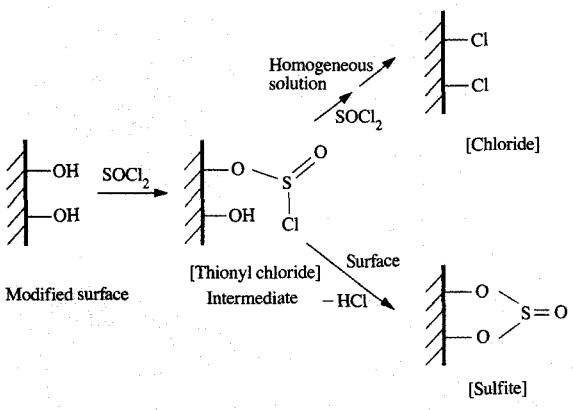
In this paper, adhesion improvements by wet-process surface modification of poly(pyromellitic dianhydride–oxydianiline) (PMDA–ODA), poly(biphenyl dianhydride–*para*–phenylenediamine) (BPDA–PDA), poly (hexafluoroisopropylidene biphenyl dianhydride–oxydianiline) (6FDA–ODA), poly(tetrafluoroethylene) (PTFE), and poly(chlorotrifluoroethylene) (PCTFE) are discussed. Metallization of a PMDA–ODA polyimide film by an immersion redox process is also reviewed.

Requirements of the wet process

There are a few common requirements for the surface modification of polymers by wet processing. First, a polymer film should be insoluble in most organic solvents. Some swelling of a polymer surface may be desirable. However, if a polymer swells in a process solution at a rate that is faster than the intended reaction, the reaction occurs uniformly throughout the swollen layer and the surface-selective modification cannot be achieved, since bulk properties may be affected. Modification within 1% of the overall film thickness is usually acceptable. It is noteworthy that most dry processes modify the outer layer of a polymer in a thickness range of 1.0–20 nm [8], while the bulk properties of a film 0.1–2.0 (or greater) μm thick remain unchanged. Second, a polymer should in general have excellent chemical resistance except under certain conditions. For example, poly(tetrafluoroethylene) (PTFE) is chemically resistant to most chemicals except strong electron donors. Thus, an electron donor in a solvent is used to modify a PTFE surface. Third, the chemical reagents and reaction byproducts should not remain physically adsorbed onto the polymer surface after the rinse operation. The unreacted reagents should be easily removed with a solvent, as illustrated in **Figure 3**, and only the new chemical functional species or modified layer should remain. Complete removal of reagents and byproducts is necessary in order to monitor and analyze the alteration of the surface. Physically adsorbed compounds or monomers do not typically yield enhanced adhesion; rather, they often lead to adhesion degradation. Fourth, strong bonding should exist between the modified surface layer and the underlying virgin polymer. An inappropriately treated or overly modified polymer surface could fail at the modified surface/virgin polymer interface, and thereby degrade adhesion to the substrate. Finally, the solvents and the chemicals employed in an application of the wet process should be chosen such that they possess low toxicity risks and be environment-friendly.

Surface chemistry vs. solution chemistry

McCarthy and co-workers [5, 9] have extensively studied the surface chemistry of polymers and compared it with solution chemistry. A chemical reaction at a surface between two functional groups usually follows the corresponding reaction in a homogeneous environment. For example, a hydroxyl group at a polymer surface reacts with acid chloride and isocyanate to yield an ester and urethane, respectively. The primary alcohol at the surface is reduced to aldehyde or carboxylic acid with the same



Scheme I

Surface chemistry vs. solution chemistry.

reagents that are used in the homogeneous reactions. Even an S_N2 (bimolecular nucleophilic substitution) reaction can occur at a polymer's outer layer. Lee and McCarthy [5(c)] have reported that a leaving group, *p*-toluenesulfonate, introduced onto a poly(chlorotrifluoroethylene) surface, was replaced by various nucleophiles such as halide and cyanide ions.

A reaction at a polymer surface does not always follow its solution chemistry. If a reagent consists of two or more active sites, then all active sites, up to three, react with the surface functional groups [5(c)]. The reaction of a primary alcohol with thionyl chloride in a homogeneous solution gives the chloride, but the same reaction at the polymer surface yields the sulfite. As shown in **Scheme I**, the chlorosulfite intermediate reacts with an adjacent hydroxyl group to yield the sulfite faster than SO_2 is eliminated to form the chloride. Under homogeneous conditions, the latter reaction has been widely used to chlorinate alcohols.

Surface modification of polyimides

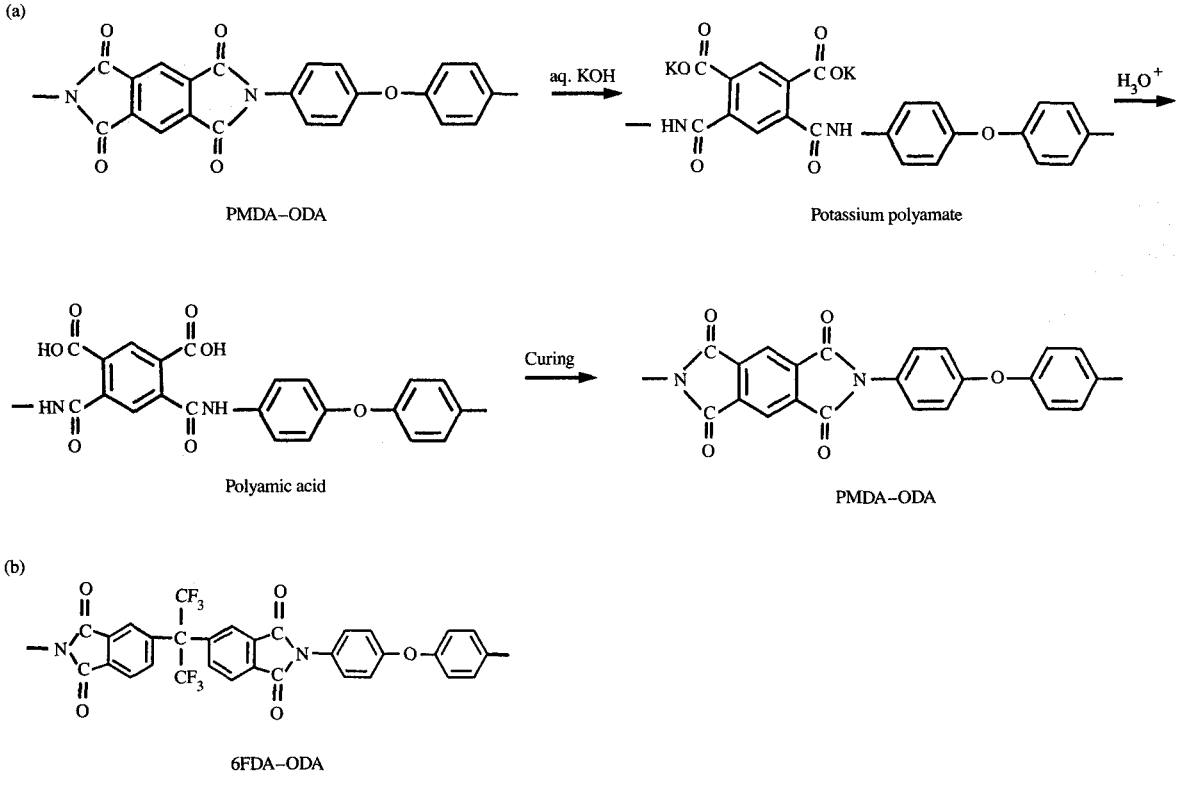
PMDA–ODA, BPDA–PDA, and 6FDA–ODA polyimide films are resistant to most solvents and chemicals, but they react with a strong base or a strong reducing agent. If a polyimide precursor is cured at a temperature of 350°C or higher, the swelling in a solvent under the intended reaction conditions [at 60°C or lower in an aqueous solution for 1–30 min or, in another case, at room temperature in 1–methyl–2–pyrrolidinone (NMP) for 1–5 min] is negligible [2]. If the concentration of a reagent, the reaction temperature, and the time are controlled, the reaction can be surface-selective, and the depth of modification is easily controlled by those reaction conditions.

- *PMDA–ODA chemistry*

The imide functional group reacts with a base to open an imide ring [10]. Polyimides also react with bases such as NaOH, KOH, and NR_4OH (R = H, CH_3, C_2H_5) to open the imide rings to form amides and carboxylate salts [7, 11]. Polyimide films are etched by using a strong base in the electronics industry [12]. The reaction conditions, such as the concentration of a base, the reaction temperature, the reaction time, and the solvent, can be adjusted to limit the hydrolysis to the polyimide surface or to etch the entire film. For instance, treatment of a thermally cured PMDA–ODA film in 1.0 M KOH aqueous solution at 22°C for 10 min gave no significant etching (less than 1.0 nm), while treatment in 9.0 M KOH alcoholic solution at 90°C for 10 min completely etched through a 25-μm-thick film [7, 12]. In the former case, potassium polyamate was formed at the outer 20 nm of the film and then converted to polyamic acid by acidification with 0.2 M HCl aqueous solution at 22°C for 3 min [7]. Heating the polyamic acid surface at 400°C for 30 min gave a fully cured polyimide. The thicknesses of the polyimide films, measured with an ellipsometer, remain unchanged after the surface modification cycle from polyimide, to polyamate, to polyamic acid, and then back to polyimide. These reactions are summarized in **Scheme II(a)**.

- *Surface analyses*

The surfaces were analyzed after each modification by contact angle measurements, X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), ion scattering spectroscopy (ISS), and external reflectance infrared spectroscopy (ERIR). In most instances, a liquid placed on a polymer film does not wet the film, but remains as a drop having a definite angle of contact between the liquid and polymer phases. The dynamic contact angles, which are measured while the liquid drop is spreading (advancing) or withdrawing (receding), are characteristic of the surface energy. The dynamic water contact angles changed from 85°/38° (advancing contact angle/receding contact angle) on virgin PMDA–ODA to 23°/5° on potassium polyamate, and then to 56°/8° on polyamic acid and to 82°/34° on the re-cured polyimide. The observed contact angles are consistent with the assigned chemistry shown in Scheme II(a). The C_{1s} XPS spectra display one carbonyl carbon for polyimide and two carbonyl carbons for polyamate and polyamic acid, since the latter two surfaces have two different carbonyl environments. Lee, Kowalczyk, and Shaw [7] have demonstrated that ERIR spectra are most informative in characterizing surface chemistry at a molecular level. In their experiment, an 87-nm-thick polyimide film was coated



Scheme II

(a) Surface modification of PMDA–ODA. (b) 6FDA–ODA. The chemistry for modification of this fluorinated polyimide follows a similar path.

onto a chromium-coated silicon wafer. As the whole layer of polyimide was modified to potassium polyamate, two imide carbonyl stretching bands at 1778 (w) and 1740 (vs) cm^{-1} disappeared, and peaks corresponding to the carboxylate [1608 (s) and 1369 (w) cm^{-1}] and the amide [1668 (s) and 1540 (m) cm^{-1}] appeared (**Figure 4**). When the polyamate was acidified to polyamic acid, the carboxylate bands disappeared and a peak due to the polyamic acid carbonyl [1727 (s) cm^{-1}] appeared. The re-cured polyimide from the polyamic acid surface gave the same spectrum as that of the virgin polyimide. ISS was used to detect potassium metal ions at the surface of the polyamate and SIMS to detect fragmented ions of modified polymer surfaces [13]. These spectra are consistent with the assigned chemistry, shown in Scheme II(a).

The PMDA–ODA polyamic acid surface was also analyzed by measuring contact angles with solutions having different pH values [14]. This analytical method, which has been explored by Whitesides and co-workers [4(a)], is called "contact angle titration." The advancing contact angles of the polyamic acid surface are 55–60° with the liquid of pH ≤ 5 and 20–30° with the liquid of pH ≥ 9. The change in the contact angles from pH = 5–9 follows a trend typical of an acid–base titration curve from which an intrinsic dissociation constant, pK_0, of ~6.5 was determined [14]. The small contact angles with liquids of pH ≥ 9 indicate that an acid–base reaction occurs between the polyamic acid surface and the contact angle liquid (base).

Surface modification of fluorinated polyimide[1]

- *6FDA–ODA chemistry*

The application of fluorinated polyimides for electronic substrates has been extensively investigated, since they have low moisture uptake and low dielectric constants; thus, a relatively thin layer of fluorinated polyimide could be employed to make compact electronic devices [15].

[1] K.-W. Lee et al., unpublished work.

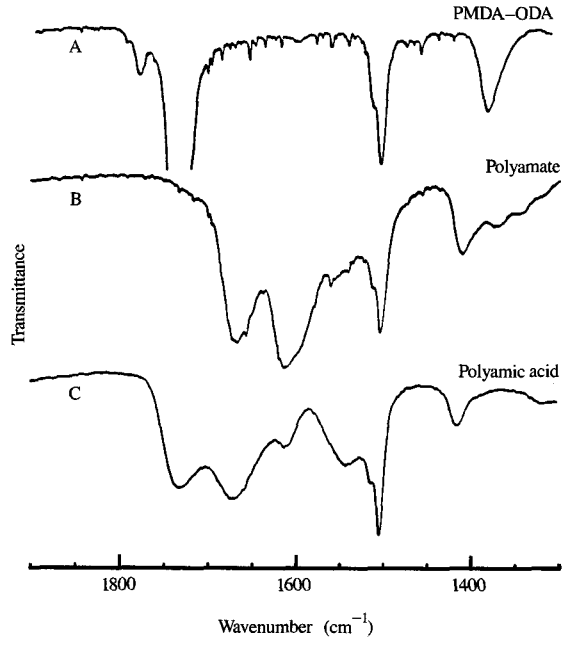


Figure 4

External reflectance IR spectra of PMDA–ODA polyimide (curve A), potassium polyamate (curve B), and polyamic acid (curve C). The angle of IR incidence is 37° from the sample surface. Reprinted with permission from *Macromolecules* **23,** 2097 (1990). Copyright 1990 American Chemical Society.

Poly(4,4′–hexafluoroisopropylidene biphenyl dianhydride–oxydianiline) (6FDA–ODA) amic acid (PI 2566™ from du Pont) was step-cured in a nitrogen ambient at 150°C/30 min, 230°C/30 min, 300°C/30 min, and 400°C/60 min. Negligible reaction occurred between a cured 6FDA–ODA film and 1.0 M KOH at room temperature after 18 h, but proceeded rapidly when the reaction temperature was raised to 60°C. The weak reactivity of 6FDA–ODA compared to PMDA–ODA polyimide is related to a low reactivity of the imide group and a relatively low water uptake. Since the two imide groups of 6FDA are not conjugated, as indicated by the flexibility of the hexafluoroisopropylidene moiety, the effect of electron withdrawal at one imide carbonyl from the adjacent imide carbonyl is minimal. The electron density at the imide carbonyl groups is relatively high, which lowers reactivity at the imide carbonyl group. For polyimides, the decreasing order of imide carbonyl conjugation through the phenyl ring(s) is PMDA–ODA > BPDA–PDA ≅ 6FDA–ODA; the same decreasing order is obtained for reactivity with a base. However, the low reactivity may also be explained by the low rate of penetration of aqueous KOH solution into the polyimide films, which is related to the rate of water uptake. The decreasing order of water uptake [16] and the decreasing order of reactivity in aqueous KOH solution are both PMDA–ODA > BPDA–PDA ≅ 6FDA–ODA.

Table 1 Dynamic water contact angles.

Polyimide	*Advancing/receding angles* (degrees)		
	Virgin PI	*Polyamate*	*Polyamic acid*
6FDA–ODA	87/67	61/8	75/11
BPDA–PDA	79/41	12/4	54/9
PMDA–ODA	85/38	23/5	56/8

- *Analyses*

A sequence of reactions [**Scheme II(b)**] was carried out, and each product was analyzed with contact angle measurements, XPS and ERIR. A 6FDA–ODA film on a Si wafer was treated with 1.0 M KOH aqueous solution at 60°C for 5–60 min to give the corresponding potassium polyamate. Excess KOH was removed by rinsing twice with water for 3 min. These samples, without further washing and drying, were used for a protonation reaction (discussed below). The modified surfaces were analyzed after the samples were rinsed twice with isopropanol for 3 min and dried under vacuum at ambient temperature for 12 h. The polyamate samples were acidified with 1.0 M acetic acid (or 0.2 M HCl) aqueous solution at 22°C for 10 min to yield a polyamic acid surface. The samples were rinsed and dried as previously described. The original polyimide was obtained after curing the polyamic acid at 400°C.

- *Contact angle measurement*

Table 1 shows the dynamic water contact angles on 6FDA–ODA, BPDA–PDA, PMDA–ODA, and their modified surfaces. 6FDA–ODA has a greater receding contact angle than BPDA–PDA and PMDA–ODA, since it contains the nonpolar [$C(CF_3)_2$] unit. Upon modifying the virgin polymer, the advancing/receding water contact angles decreased from 87°/67° on 6FDA–ODA polyimide to 61°/8° on the polyamate. The small receding contact angle is consistent with the carboxylate surface, and the relatively large advancing angle is due to the nonpolar hexafluoroisopropylidene [$C(CF_3)_2$] moiety [17]. The large difference between the advancing and the receding angles, called "hysteresis," indicates that initial wetting is inhibited, but once the surface is wet, it is difficult to de-wet. The large hysteresis is probably due to the heterogeneity of the functional groups at the modified surfaces which consist of polar groups (carboxylate or carboxylic acid) and nonpolar groups [phenyls or $C(CF_3)_2$].

The contact angles on the polyamic acid surface are greater than those on the polyamate surface because the polarity of the carboxylate is greater than that of the carboxylic acid. The contact angles on the 6FDA–ODA film re-cured from polyamic acid are 80°/61°. Small (3–7°) decreases in the magnitude of the contact angles for re-cured polyimide compared to those for the starting polyimide were also observed with other polyimides such as PMDA–ODA and BPDA–PDA (see footnote 1).

• *X-ray photoelectron spectroscopy (XPS)*

After treatment with KOH, the XPS survey spectrum of the potassium polyamate surface displays new peaks at 378.5 eV, 296.5 eV, and 293.6 eV, which correspond to K_{2s}, $K_{2p1/2}$, and $K_{2p3/2}$, respectively. **Figure 5** shows the XPS C_{1s} and K_{2p} regions of polyimide and the modified surfaces. The absolute binding energies are shifted by ~0.5 eV due to charging and have not been corrected. Figure 5(a) displays the spectrum of the starting polyimide. The highest-binding-energy peak at 293.3 eV corresponds to CF_3 carbons. The broad peak at 291.5 eV is due to the $\pi \rightarrow \pi^*$ transition of the phenyl groups. The sharp peak at 288.7 eV corresponds to the carbonyl carbons. Only one carbonyl peak is observed, since the polyimide carbonyls have similar nuclear environments. But the spectrum [Figure 5(b)] corresponding to a potassium polyamate surface exhibits two carbonyl C_{1s} peaks, since the binding energies of carboxylate carbon and amide carbon are different. The two carbonyl C_{1s} peaks can be readily distinguished in the polyamic acid surface. In Figure 5(c), the best fit to the XPS curve occurs when the carbonyl region is deconvoluted into two peaks (289.6 and 288.4 eV). The $K_{2p1/2}$ (296.5 eV) and $K_{2p3/2}$ (293.5 eV, overlapped with CF_3 carbon peak) peaks appear in the spectrum of potassium polyamate and are not detected in that of polyamic acid. **Figure 6** shows the O_{1s} XPS spectra of virgin 6FDA–ODA and the modified surfaces. For all three cases the peak is fitted with two peak components (A, B) as shown in **Table 2.**

The low-binding-energy peak (B) of PI is assigned to carbonyl oxygen and the higher-energy peak (A) to ether as in the case of PMDA–ODA [18]. The ratio of the areas of these peaks (21/79) is close to the stoichiometric ratio (1/4 = 20/80) in the molecular structure. The spectrum of the polyamate [Figure 6(b)] shows an increase of the higher-binding-energy peak which probably corresponds to both the ether oxygen and the carboxylate oxygen with a negative charge. The observed ratio of these two peaks (42/58) matches well with the calculated ratio (3/4 = 43/57) for the molecular structure of a repeat unit. The ratio of two peaks in the case of polyamic acid [Figure 6(c)] increases to 49/51. The calculated ratio for polyamic acid is the same as that for polyamate [Scheme II(b)], but the observed ratio has increased. The XPS atomic

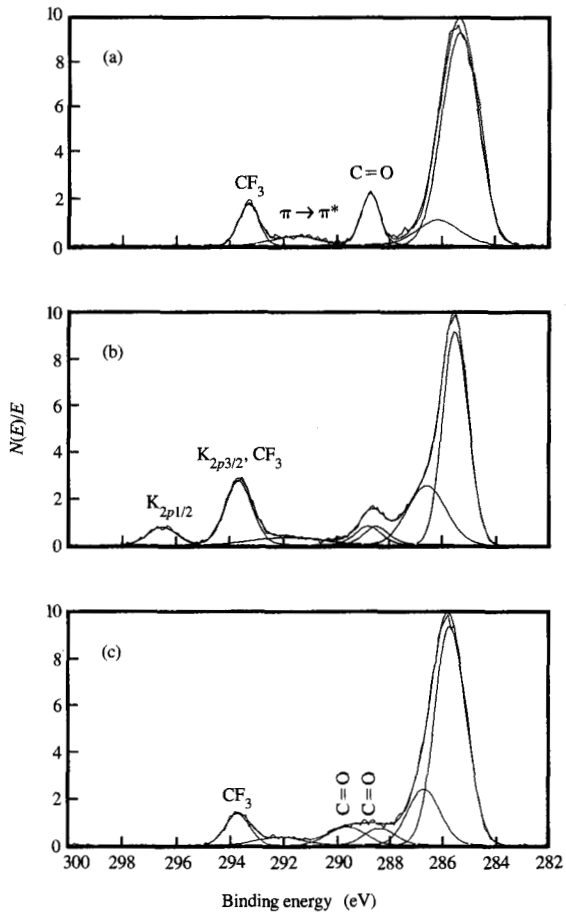


Figure 5

C_{1s} XPS core-level spectra of (a) 6FDA–ODA starting material, (b) potassium polyamate (surface after reaction with KOH), and (c) polyamic acid (after acidification). The take-off angle of electrons from the sample surface is 45°. Photoemitted electrons are detected at an angle of 45° to the sample surface. Potassium binding energies overlap the C_{1s} XPS peaks.

compositions and O_{1s} curve fittings indicate that a portion of the carbonyl peaks of the lower O_{1s} binding energy is shifted to the higher-binding-energy peak, while the total amount of oxygen remains unchanged in comparison to the polyamate (the same atomic ratios of O:N = 7:2 for the polyamate and the polyamic acid surfaces were observed). The shifted portion probably corresponds to carbonyl groups which form hydrogen bonds with neighboring carboxylic acids.

• *External reflectance infrared spectroscopy (ERIR)*

ERIR spectra of thin and uniform layers (50 nm) of polyimide on chromium-coated Si wafers were obtained.

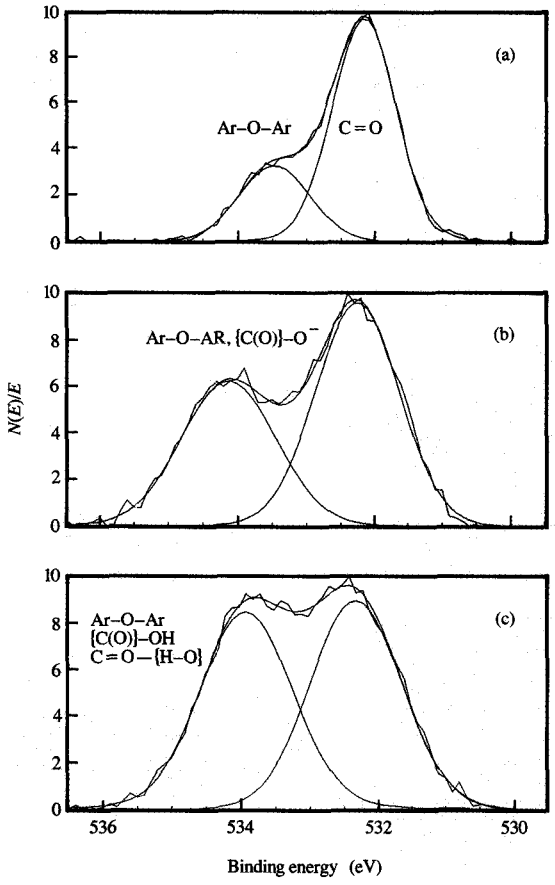


Figure 6

O_{1s} XPS core-level spectra of (a) 6FDA–ODA starting material, (b) potassium polyamate (surface after reaction with KOH), and (c) polyamic acid (after acidification). The take-off angle of electrons is 45°. The lower-binding-energy peaks correspond to carbonyls and the higher-binding-energy peaks to ether, carboxylate, and carboxylic acid. (Ar: aromatic group such as phenyl.)

Figure 7 displays the ERIR spectra of a virgin 6FDA–ODA polyimide film and of the modified samples. The spectra of samples in the range of 1900–1000 cm^{-1} provide the most useful information for these reactions. The important bands are listed in **Table 3**.

The bands at 1787 and 1738 cm^{-1} in Figure 7(a) correspond to the imide carbonyls. The peaks at 1513 and 1505 cm^{-1} are due to 6FDA and ODA phenyl groups, respectively. The imide II band at 1385 cm^{-1} is related to C–N stretching vibrations. When the whole layer of the polyimide film reacted with KOH to obtain an IR spectrum, as shown in Figure 7(b), the imide carbonyl stretching vibration at 1788 and 1738 cm^{-1} completely disappeared. The peak at 1667 cm^{-1} corresponds to the amide I band. The peaks at 1601 and 1381 cm^{-1} are due to the carboxylate asymmetric and symmetric stretchings. The strong band around 1260 cm^{-1} from 6FDA–ODA and modified polymers corresponds to a C–O–C (ODA) stretching vibration.

Table 2 O_{1s} XPS data.

6FDA–ODA surface	*B.E. (eV)*		*Observed ratio*	*Calculated ratio*
	$O_{1s}(A)$	$O_{1s}(B)$	$O_{1s}(A)/O_{1s}(B)$	$O_{1s}(A)/O_{1s}(B)$
Polyimide	533.5	532.1	21/79	20/80
Polyamate	533.6	531.8	42/58	43/57
Polyamic acid	533.9	532.3	49/51	43/57*

$O_{1s}(A)$: oxygens of ether, carboxylate, and carboxylic acid.
$O_{1s}(B)$: oxygens of carbonyl.
*Calculated ratio without consideration of hydrogen bonding.

After acidification of the potassium polyamate surface, the bands due to the carboxylate [1601 (s) and 1381 (s) cm^{-1}] disappeared, and the band at 1736 cm^{-1} corresponding to the carbonyl stretching of carboxylic acid appeared. The peaks at 1676 and 1540 cm^{-1} correspond respectively to the amide I band (carbonyl stretching) and the amide II band (coupling of C–N stretching and N–H deformation). The band at 1414 cm^{-1} corresponds to the C–N stretching.

Upon curing the polyamic acid surface, the starting polyimide surface was reproduced. Contact angles, C_{1s} XPS spectrum, and ERIR spectrum of the re-cured surface are indistinguishable from those of the starting polyimide.

Polyimide–polyimide adhesion and locus of failure

The durability of adhesion at a polyimide–polyimide interface is important for multilevel thin-film packaging [1]. PMDA–ODA/PMDA–ODA and BPDA–PDA/BPDA–PDA adhesion has been reported by Lee, Kowalczyk, and Shaw [7]. A 20-nm-thick PMDA–ODA surface was modified to polyamic acid, and then PMDA–ODA polyamic acid was coated onto the modified surface followed by curing at 400°C. The 90° peel strength, which was measured as illustrated in **Figure 8**, showed a significant increase from 30 J/m^2 to 1240 J/m^2 (see footnote 2). The corresponding experiment with BPDA–PDA gave peel strengths of 23 J/m^2 in the absence of surface modification and of 950 J/m^2 for a 22.5-nm-deep modification.

It is critical to understand the interfacial behavior by identifying the locus of failure in the adhesion test. In the cases of adhesion of PMDA–ODA to PMDA–ODA and BPDA–PDA to BPDA–PDA, both sides of the interfaces are identical and therefore have the same elemental and

[2] The unit employed here is joules/m^2. The unit g/mm is often used in industry (1 joule/m^2 = 0.102 g/mm).

Table 3 External reflectance infrared spectral data.

6FDA–ODA	*Wavenumber* (cm^{-1})
Polyimide Figure 7(a)	1787 (w), 1738 (vs), 1513 (m, sh), 1505 (vs), 1438 (w), 1385 (s), 1260 (vs)
Polyamate Figure 7(b)	1667 (s), 1616 (m, sh), 1601 (s), 1562 (w), 1512 (m, sh), 1503 (vs), 1413 (m), 1381 (s), 1262 (vs)
Polyamic acid Figure 7(c)	1736 (s), 1676 (m), 1609 (w), 1540 (m), 1513 (sh), 1505 (s), 1414 (m), 1262 (vs)

chemical composition regardless of the locus of failure. It is not possible to identify the exact locus of failure in this system with XPS or any other analytical technique. If an adherate contains an element such as F which does not exist in the adherend, that element can be detected with XPS, which makes analysis of the locus of failure possible.

A 6FDA–ODA polyimide surface was modified in 1.0 M KOH aqueous solution at 60°C for 10 min followed by acidification, rinsing, and drying (as described in detail above). A BPDA–PDA polyamic acid was then spin-coated onto the modified 6FDA–ODA surface, and the sample was cured at 400°C for 60 min. The BPDA–PDA layer was peeled, and both sides were analyzed (Figure 8). **Figures 9** and **10** respectively display the XPS spectra of the peeled BPDA–PDA side and the 6FDA–ODA substrate side. The BPDA–PDA side contains a small amount of F [Figures 9(a) and 9(b)]. The BPDA–PDA side in the spectrum taken at a 90° electron take-off angle [Figure 9(c)], which probes deeper into the surface layer, is similar to a virgin BPDA–PDA layer (control) shown in Figure 9(d). The atomic composition data indicate that BPDA–PDA is still the major compound at the surface of the peeled BPDA–PDA side. The 6FDA–ODA substrate side [Figure 10(a)] shows that at the very outer surface region (~1.5 nm) the intensity of the F_{1s} peak is similar to the F_{1s} peak intensity at the surface of the peeled BPDA–PDA side [Figure 9(a)]. The XPS spectrum at a greater electron take-off angle has a more intense F_{1s} peak [Figures 10(b) and 10(c)]. The average concentration of the 6FDA–ODA polyimide has increased in the outer 7.0-nm layer in comparison with the top 1.5-nm layer. However, when compared with the 6FDA–ODA control [Figure 10(d)], it is clear that the major component at the outer layer is BPDA–PDA.

These results lead us to postulate the following interface mechanism when two polymers adhere to each other. First, the incoming BPDA–PDA polyamic acid diffuses into the modified 6FDA–ODA surface layer. At the outer layer

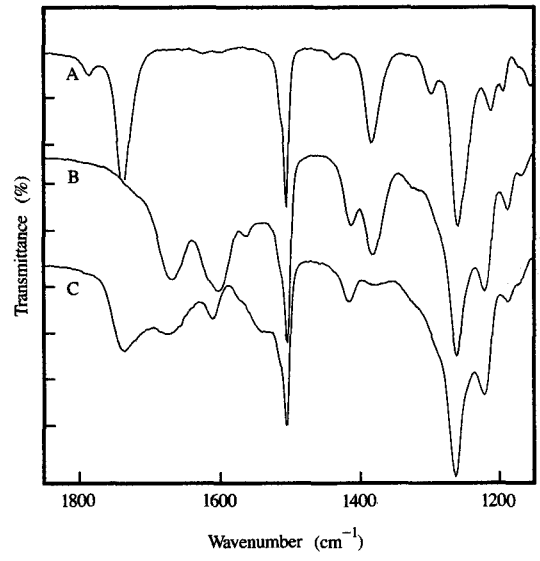


Figure 7

External reflectance IR spectra of 6FDA–ODA polyimide (curve A), potassium polyamate (surface after reaction with KOH, curve B), and polyamic acid (after acidification, curve C). The starting polyimide is 80 nm thick, and the whole layer is modified. The angle of IR incidence is 15° from the sample surface.

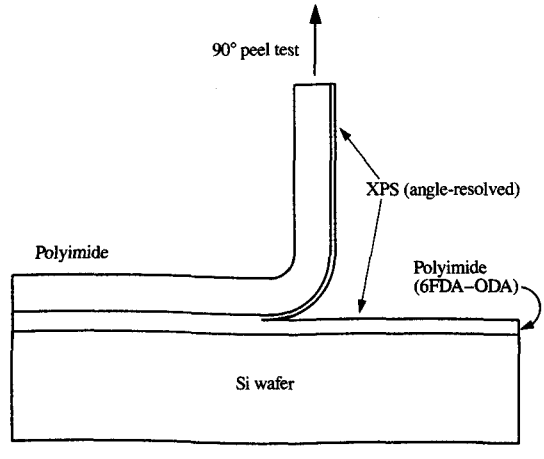


Figure 8

Measurement of 90° peel strengths. Analyses of both surfaces after peeling with angle-resolved XPS technique can determine the locus of failure.

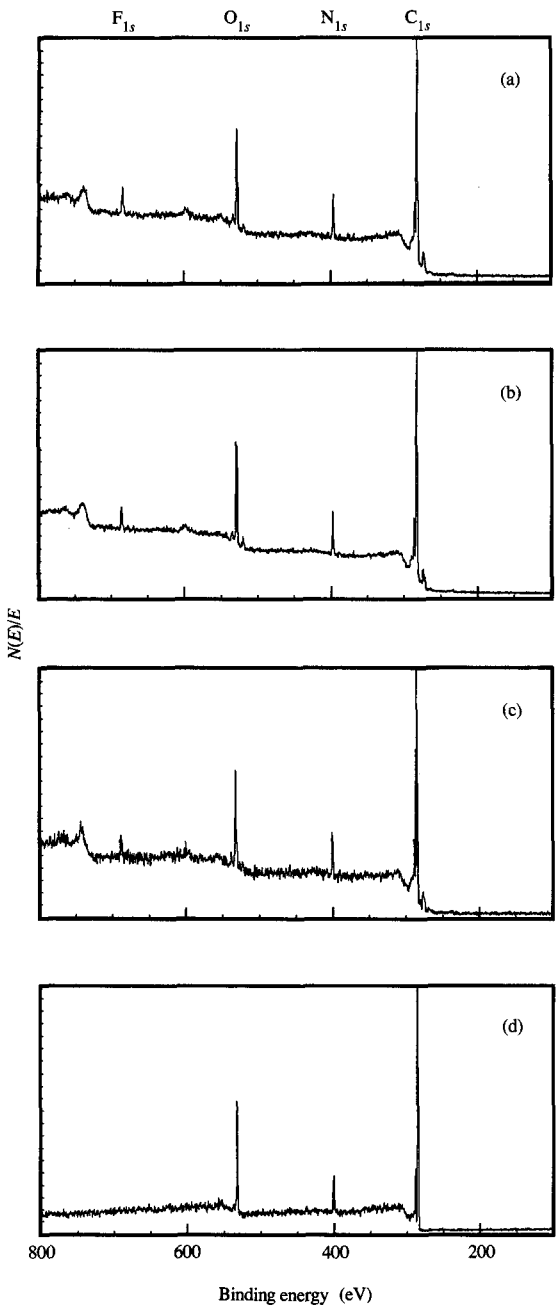


Figure 9

XPS survey spectra of the peeled BPDA–PDA side of the BPDA–PDA/6FDA–ODA system: (a) 15° electron take-off angle from the sample surface, (b) 45°, (c) 90°, and (d) BPDA–PDA.

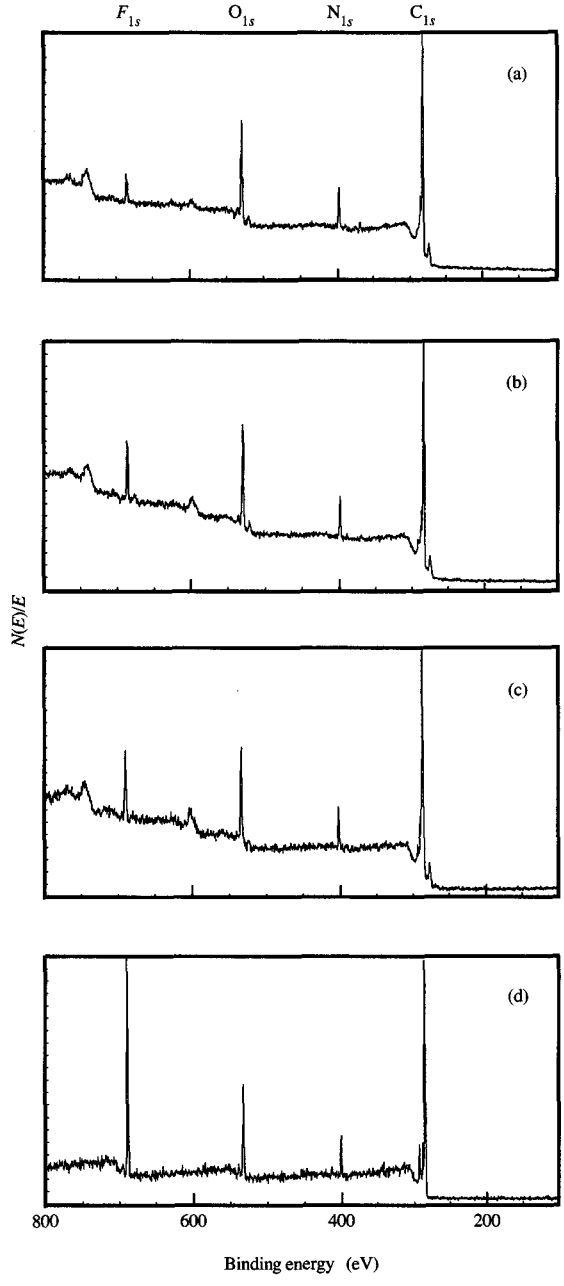


Figure 10

XPS survey spectra of the 6FDA–ODA substrate side after peeling off the BPDA–PDA layer of the BPDA–PDA/6FDA–ODA system: (a) 15° electron take-off angle from the sample surface, (b) 45°, (c) 90°, and (d) 6FDA–ODA.

of the underlying polyimide substrate, the incoming BPDA–PDA molecules are dominant. Upon curing, the two polymers become interlocked (as discussed below). When the top layer (BPDA–PDA) is peeled off, the surfaces of both sides contain more BPDA–PDA than 6FDA–ODA. The amount of 6FDA–ODA left on the BPDA–PDA side is very small at a depth of ≤3 nm. The depth of penetration (interdiffusion) of BPDA–PDA into

the 6FDA–ODA substrate is greater than 10 nm, and the concentration of BPDA–PDA gradually decreases within the XPS sampling depth.

Relationship between modification depth and adhesion

Even though adhesion is one of the most important surface properties in industry, the relationship between surface structure and adhesion is poorly understood. Lee and co-workers [7, 13] have explored the relationship between the modification depth of a polyimide surface and adhesion strength. They have also developed a method to nondestructively measure the average depth of modification using ellipsometry and ERIR techniques. As shown in **Figure 11**, a linear relationship was obtained between the absorbance of the imide carbonyl stretching vibration at 1739 cm^{-1} and the film thickness (for films less than 100 nm). Once a polyimide surface is modified under conditions which do not etch the polyimide film, the thickness of the unmodified layer can be calculated by measuring the imide carbonyl absorbance of the polyamate film. The average depth of modification can be obtained by subtracting the thickness of unmodified polyimide film from the thickness of a starting polymer. In a real application, the polymer thickness is in the range of 1.0–25 μm, but it is reasonable to assume that the rate of reaction from the outer layer should not depend significantly on the film thickness; thus, the modification depth of thick and thin films should be approximately the same.

The relationship between depths of modification and peel strengths for PMDA–ODA/PMDA–ODA and BPDA–PDA/BPDA–PDA systems are summarized in **Table 4**. These results show that the deeper the modification depth, the greater is the peel strength. If the PMDA–ODA surface was modified to depths greater than 25 nm, the ultimate tensile strength of the PMDA–ODA peel layer was exceeded by the interfacial adhesion strength. However, if the BPDA–PDA polyimide was employed as a peel layer, the adhesion strength did not exceed the tensile strength of the BPDA–PDA polyimide, because the BPDA–PDA polyimide film has a greater tensile strength at break (300 MPa) than PMDA–ODA (140 MPa).

The mechanism which enhances polyimide/polyimide adhesion by the wet process is quite different from those for a dry process, such as plasma treatment, in which an interfacial chemical reaction is the most important factor. For the wet process, a transamidization reaction between incoming polyamic acid and a polyamic acid surface (substrate) would enhance the adhesion strength. If a polyamic acid surface is imidized to an amorphous polyimide, an interfacial chemical reaction between incoming polyamic acid and the amorphous polyimide surface does not occur. The peel strengths in the two cases are exactly the same. From this result, an interfacial chemical reaction can be excluded from contributing to strong adhesion. Interdiffusion of incoming polyamic acid into the underlying modified surface and subsequent mechanical interlocking upon curing are the most probable adhesion mechanisms for the wet-processed interfaces. The extent of interlocking between two polymers is greater for the more deeply modified surface, as indicated in Table 4.

A polyimide film can be etched in a concentrated base solution especially at a high temperature, and thus the surface topography of the extensively etched film can be changed. For some applications in which a thin film is employed, it is necessary to modify a polymer surface sufficiently deep while maintaining the surface topography to achieve good adhesion without significant depletion of the bulk polymer. When PMDA–ODA polyimide films (5 μm or 22.3 nm thick) were treated with 1 M KOH

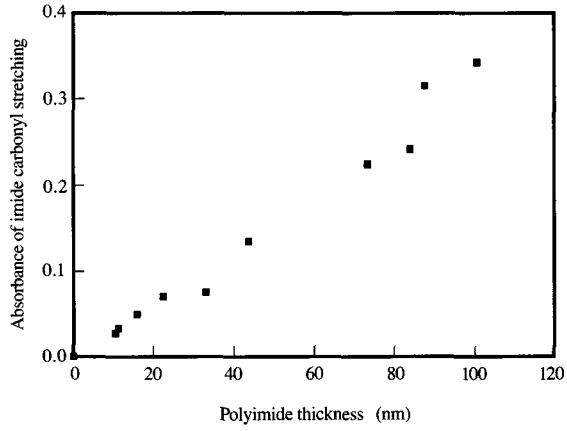


Figure 11

Relationship between imide carbonyl IR (1739 cm^{-1}) absorbance and BPDA–PDA polyimide thickness. The angle of IR incidence is 75° from the sample surface. Reprinted with permission from *Langmuir* **7**, 2450 (1991). Copyright 1991 American Chemical Society.

Table 4 Relationship between surface modification depths and peel strengths.

PMDA–ODA		*BPDA–PDA*	
Depth (nm)	*Peel strength* (J/m^2)	*Depth* (nm)	*Peel strength* (J/m^2)
0	40	0	30
0.5–2.0	400	1.7	160
10	850	16	680
20	1250	22	900
>25	cnp		

cnp: cannot peel without tearing the peel layer.

aqueous solution at 22°C for 10 min, both the thickness (within 1 nm of the polyimide surface) and the topography of the modified surface remained unchanged. However, the polyimide/polyimide adhesion strength was greatly increased.

Modification of polyimide surface morphology [13]

Polymers are generally either semicrystalline or amorphous [19]. These categories are used to describe the degree of ordering of the polymer molecules. Amorphous polymers consist of randomly ordered tangled chains; i.e., amorphous polymers are highly disordered and intertwined with other molecules. Semicrystalline polymers consist of a mixture of amorphous regions and crystalline regions. The crystalline regions are more ordered, and segments of the chains actually pack in crystalline lattices. Some crystalline regions are more ordered than others. If crystalline regions are heated above the melting temperature of the polymer, the molecules become less ordered, or more random. If cooled rapidly, this less ordered feature is frozen in place, and the resulting polymer is amorphous. If cooled slowly, these molecules can repack to form crystalline regions, and the polymer is crystalline.

One possible way to enhance adhesion without introducing foreign materials to the interface is to change the morphology of the polyimide surface, then coat with the next layer (metal or polyimide), and then convert the modified morphology back to the original state. A semicrystalline polyimide consists of some amorphous polyimide regions, whereas an amorphous polyimide contains a small amount of crystalline polyimide regions. However, the mechanical properties of the two materials are very different. The rate of water diffusion in an amorphous polyimide is three times as fast as that in a semicrystalline polyimide [16]. Adhesion of a polymer is related to its surface properties. The morphology of a polyimide surface can be altered without changing the bulk morphology, and thus the mechanical properties of the polymer remain unchanged. Saenger, Tong, and Haynes [20] reported that the polyimide/polyimide adhesion strength could be enhanced by swelling the adherend (bottom) layer of a cured PMDA–ODA in NMP. However, a poly(biphenyldianhydride–*p*–phenylene diamine) (BPDA–PDA) film did not swell in NMP at ambient temperature to give enhanced polyimide/polyimide adhesion.[3] The swelling method, even though it improves adhesion, cannot be employed in a multilevel thin-film package, since the swelling destroys the overall structural integrity. Brown and co-workers [21] have studied the adhesion of a polyimide layer to a partially cured polyimide which is often a mixture of disordered polyimide and polyamic acid. However, in a manufacturing process of a multilevel package, the adherend layer is fully cured at high temperature (usually 350–400°C) followed by metallization, and then coated with the polyimide for the next layer. Thus, modification of a polyimide surface without changing the bulk properties is important to multilevel thin-film packaging technology.

Lee [13] reported that re-curing a polyamic acid surface at only 230°C for 30 min gave an amorphous polyimide surface layer. Adhesion strengths of polyimides to the amorphous polyimides were the same as the corresponding adhesion to the polyamic acid surface, indicating that interdiffusion of the incoming polyamic acid solution into the modified amorphous layer and subsequent mechanical interlocking between two polymers are the major factors in promoting strong adhesion. Chemical reactions and wettability are not significant factors in the adhesion of this system.

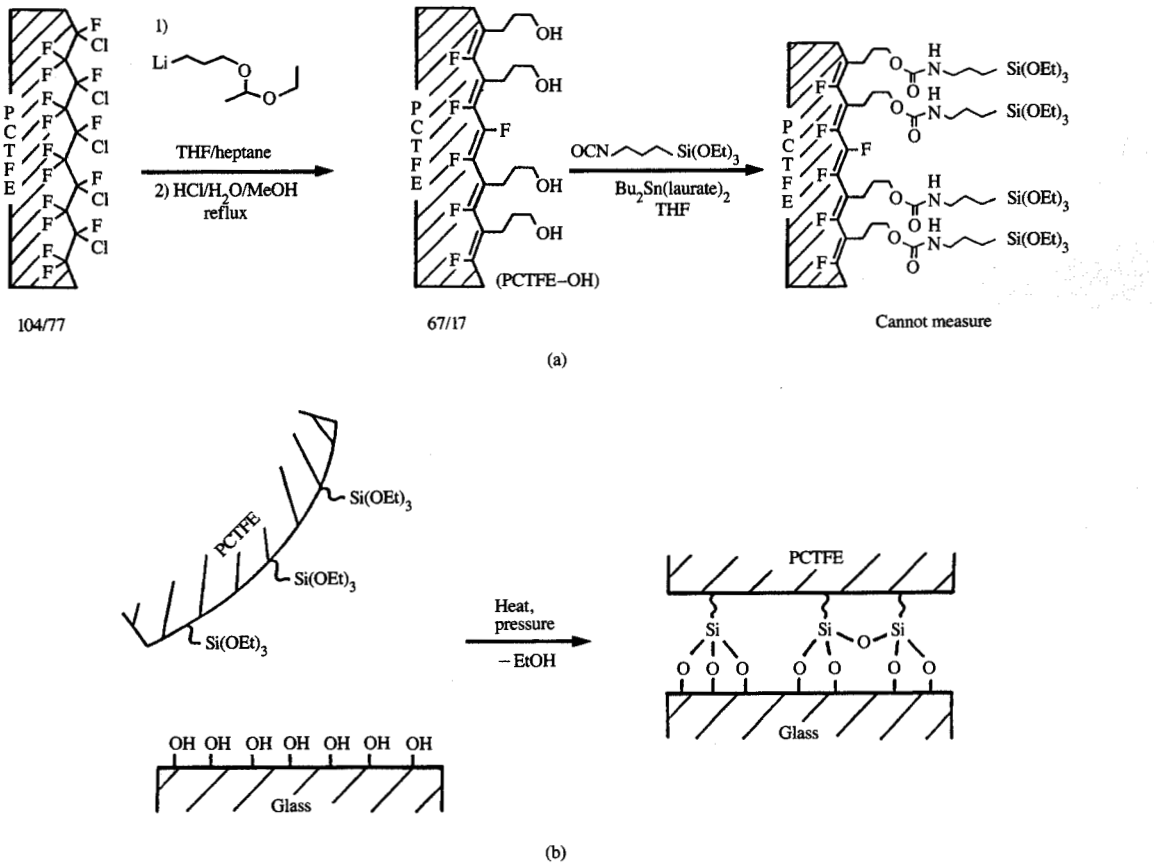
Surface modification of poly(fluorinated ethylene)

Poly(tetrafluoroethylene), PTFE, is of interest in electronic packaging because of its low dielectric constant ($\varepsilon = 2.0$) and high thermal stability. The presence of very stable carbon–fluorine bonds yields a low surface energy in PTFE which, in turn, results in poor adhesion of metals to this material. To obtain good metal-to-PTFE adhesion, a surface pretreatment is necessary to chemically modify the surface. Broader application of PTFE beyond specialty microwave and military circuits could be realized if it were not for the difficulties in processing and metallizing fluoropolymer materials.

Of the variety of methods which yield surface modification, including plasma, ion beam, and electron beam, a wet chemical process is the preferred choice for reliable surface treatment. The C–F bond is susceptible to cleavage under an extreme reducing environment. PTFE treatment with sodium in liquid ammonia or sodium naphthalene in glycol ether leads to both chemical and physical changes at the surface [22]. The increase in surface energy and the introduction of new chemical species at the surface leads to increased metal adhesion.

Costello and McCarthy [23] reported that reaction of a PTFE surface with a benzoin dianion reducing agent in dimethyl sulfoxide produced a polymeric carbon surface. The most obvious change was visible to the eye: The PTFE color changed from white to metallic gold. The UV-visible spectrum exhibited an absorbance with $\lambda_{max} = 540$ nm. The reduction was not surface-selective and was corrosive in nature. The average depth of reaction after 6 h was ~250 nm. Shorter reaction times produced silver-colored films, and longer times rendered more highly

[3] K.-W. Lee, unpublished result.



Scheme III

(a) Chemical reactions at the PCTFE surface. The dynamic water contact angles (advancing/receding) are listed below the chemical structure. (b) Proposed mechanism for fluorinated polymer adhesion to glass.

reduced and gold-colored films; the thickness of a reduced layer can be in the range of 15–2000 nm. The authors have proposed [23] a complex structure (not shown) for this reduced carbonaceous (PTFE–C) layer. It has also been proposed [24] that the reduced PTFE surface contains *trans*–polyacetylene [*trans*–$(CH)_n$] with polyene conjugation lengths of 12–28 units. Formation of reduced and conductive surfaces can be used for metal adhesion enhancement. Poly(tetrafluoroethylene-co-hexafluoropropylene), FEP, was modified with sodium naphthalide in tetrahydrofuran (THF) to an unsaturated surface, and the modification depth, which is controlled by the temperature, was in the range of 25–80 nm [9(b)]. The PTFE surface wettability, which is closely related to adhesion [25], is controlled by the introduction of various polar functional groups [26].

Poly(fluorinated ethylene)s are widely employed as dielectric layers for printed circuit boards. Lamination of these polymers to the substrates (metal, glass, polymer) at a low temperature is important in the fabrication of electronic components. Lamination of poly(chlorotrifluoroethylene) (PCTFE) film to pyrex glass has been studied by Lee and McCarthy [27]. The PCTFE film surface was first hydroxylated and the chemical structure of the modified surface was determined, as summarized in **Scheme III(a)** [5(c)]. The water contact angles listed under the chemical structures are consistent with the assigned chemistry. The depth of surface modification is controlled by the first reaction temperature. For the adhesion study a 5.0-nm-thick outer layer was modified to PCTFE–OH. The reaction of PCTFE–OH with (3–isocyanatopropyl)triethoxysilane in the presence of

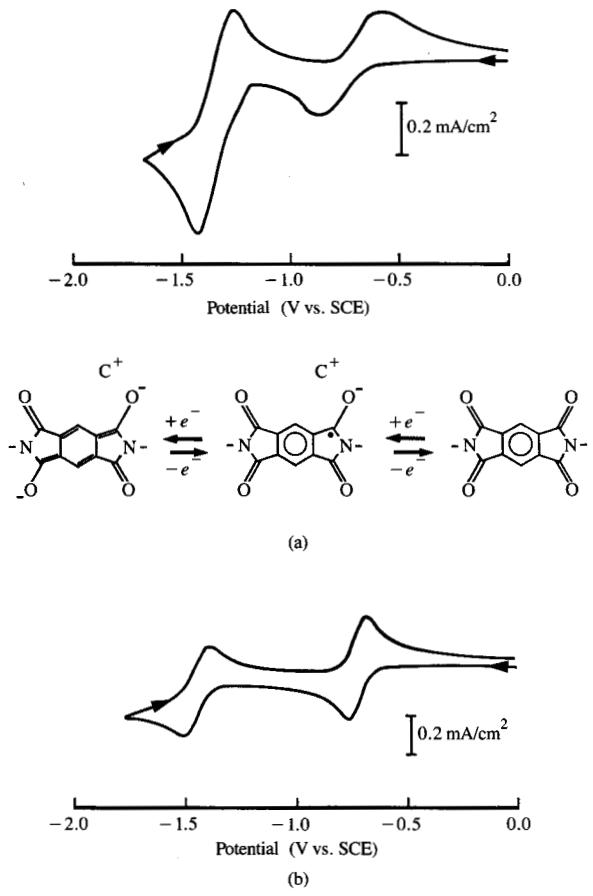


Figure 12

Cyclic voltammograms (a) for a 12.5-μm-thick PMDA–ODA film on a stainless steel electrode and (b) for 5 mM N,N′–di–(n–butyl) pyromellitimide model compound in 0.1 M TBAFB/ACN at a Pt electrode. The voltages were recorded against the saturated calomel electrode (SCE). C^+ is a cation such as tetrabutylammonium ion. Reprinted with permission from *ACS Symposium Series* **440** (1990). Copyright 1990 American Chemical Society.

dibutyltin dilaurate (a urethanation catalyst) in dry THF yielded PCTFE–$OC(O)NH(CH_2)_3Si(OEt)_3$. Water contact angles could not be obtained because the triethoxysilane groups react with water and thus alter the surface chemistry. The urethane was the sole product of this reaction; the triethoxysilane moiety did not condense with surface hydroxyl groups at room temperature for 24 h.

At temperatures from 80 to 120°C for times up to 24 h, PCTFE, PCTFE–OH, and PCTFE–$OC(O)NH(CH_2)_3Si(O)OH$ showed no tendency to adhere to glass. These polymer films spontaneously fell from the glass slide. On the other hand, PCTFE–$OC(O)NH(CH_2)_3Si(OEt)_3$ samples adhered tenaciously to glass when the lamination was carried out at 80°C for 12 h. The film could not be peeled off the glass without a cohesive failure in the polymer film. SEM micrographs of the glass surface after peeling the film indicated that polymer remained bonded to the glass surface. The XPS spectrum of the glass surface displays the C, O, F, and N peaks, indicating that the PCTFE polymers were left on the glass side. Covalent bonding between the hydroxyl groups at the glass surface and triethoxysilane groups at the polymer surface, as shown in **Scheme III(b)**, has been proposed as a cause for the strong adhesion strength.

Metallization at polyimide surfaces

Viehbeck et al. [28] reported on the redox properties of polyimides and deposition of a seed layer for electroless metallization. A redox mechanism has also been proposed for PMDA-derived imides [29, 30]. Polyimides undergo reversible reduction/oxidation reactions at an electrode surface in an electrolyte solution. The cyclic voltammetric responses for a PMDA–ODA film on an electrode surface and for a N,N′–di(*n*–butyl)pyromellitimide model in solution are shown in **Figure 12**. The imide functional group is initially reduced to a radical anion, which is further reduced to a dianion. For example, a 12.5-μm-thick PMDA–ODA film (Kapton®) was partially reduced in 0.05 M benzil (reducing agent) and 0.1 M tetrabutylammonium tetrafluoroborate (TBAFB) (supporting electrolyte) in an anhydrous acetonitrile. The visible absorbance peaks at 724 and 659 nm, as shown in **Figure 13**, correspond to a green colored radical-anion state of PMDA–ODA, and the spectrum is used as an indicator that the reduction reaction has occurred.

The reduced polyimide surface can function as a reducing substrate for subsequent deposition of metal cations from the solution. The reduction potential of the dissolved metal complex must be more positive than the oxidation peak potential of the reduced film (−0.79 V vs. SCE for PMDA–ODA). Various metal complexes such as $PdBr_2$, $PdCl_2$, $AgBF_4$, $CuI(OCH_3)_4$, and $PtBr_2$ have a more positive reduction potential, and thus they can be reduced to metal with the reduced PMDA–ODA film. Redox-mediated metal deposition results in oxidation of the polymer film back to its original neutral state. During metal deposition, the characteristic visible absorbance of reduced films rapidly bleaches on exposure to an appropriate metal complex solution as the film reoxidizes. The redox chemical reactions occur at the outer polymer layer, and the reduced metal is deposited at the outer layer. Rutherford backscattering (RBS) profiles of the PMDA–ODA/$PdCl_2$ system display a Pd signal at the polymer surface. The amount and the thickness of the metal layer can be increased by increasing the initial reduction time and repeating the redox chemistry.

For a practical application of this redox chemistry to electronics device fabrication, a substrate polyimide layer

was patterned with photoresist, as shown in **Scheme IV**. The photoresist, of course, must be inert to the redox chemistry employed for the scheme to work. The exposed polyimide surfaces underwent reduction to the radical-anion form, followed by the reduction of Pd metal onto the film. Subsequently, the area seeded with Pd metal was plated with copper in an electroless plating bath.

Plechaty and Thomas [31] have reported that the Pd seed layer can be introduced to the polyimide surface in the form of palladium polyamate, as shown in **Scheme V**. Reaction of a polyimide film in a NaOH aqueous solution yielded a sodium polyamate surface. The ion exchange reaction of sodium polyamate in a palladium ionic solution gave palladium polyamate. The same palladium polyamate surface was produced by the reaction of a polyamic acid surface with palladium nitrate. Treatment of sodium polyamate with a palladium ionic solution gave palladium polyamate. This Pd-enriched surface acts as a seed layer for electroless Cu plating.

Karas, Foust, and Dumas [32] have reported on adhesion of metal to polyetherimides which were modified by the wet processes. A certain thickness of outer layer was removed with sulfuric acid and hydrolyzed with KOH. A Sn/Pd seed layer was applied, and a thick layer of copper was electrolessly or electrolytically plated. Heat treatments after seeding/electroless plating and final metallization were necessary to obtain a good adhesion strength, greater than 1000 J/m^2.

Mitsubishi researchers [33] studied a wet-process copper plating process on polyimide but did not report on the detailed chemistry. The polyimide surface was activated with an alkaline solution containing Zn ions. The XPS spectrum displayed the Zn peaks, indicating that the Zn polyamate was a probable product. The Zn ions were exchanged with Pd ions to give the same palladium polyamate as in Scheme V. Copper was electrolessly and selectively plated in the Mitsubishi hybrid integrated circuits, which consisted of polyimide dielectrics and copper conductors. While adhesion of copper to untreated polyimide is very poor, the adhesion strength was greatly improved using this approach.

Summary

Several wet processes are described that modify polymer surfaces and improve adhesion of polymers and metals to the modified surfaces. A polyimide film surface can be converted into its precursor in a chemical solution to enhance adhesion. The treatment of a polyimide surface with a base such as NaOH, KOH, NH_4OH, and $(CH_3)_4NOH$ yields a polyamate surface which is then converted to a polyamic acid surface, the polyimide precursor, by acidification. Upon curing the polyamic acid surface, the starting polyimide surface is reproduced. Spin-coating of a polyamic acid solution onto the modified

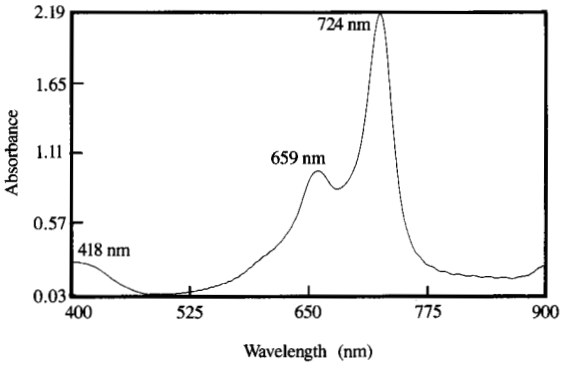
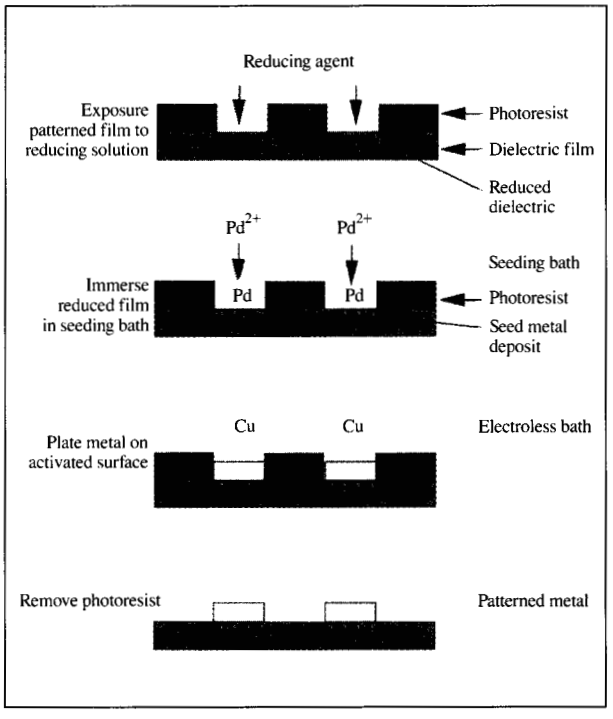


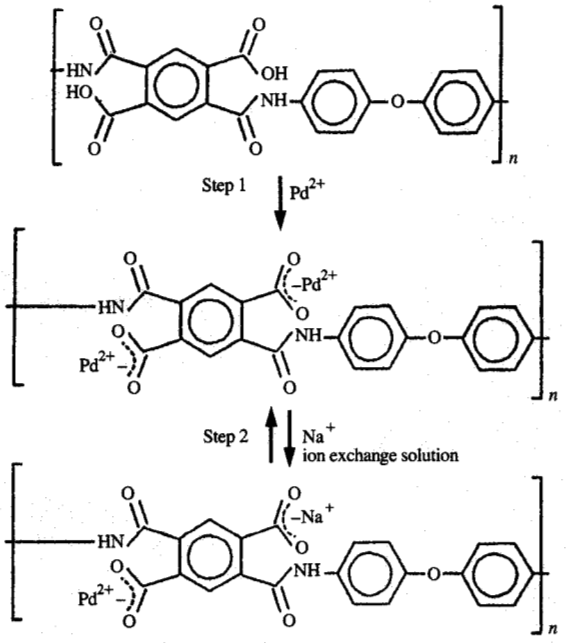
Figure 13

UV–Vis spectra for a 12.5-μm-thick Kapton (PMDA–ODA) film after a 5-s immersion in a solution containing 0.0475 M benzil/0.0025 M benzil radical anion electrochemically generated in 0.1 M TBAFB/ACN solution. The absorbance peaks at 659 and 724 nm indicate that radical anions of PMDA–ODA were formed. Reprinted with permission from *ACS Symposium Series* **440** (1990). Copyright 1990 American Chemical Society.



Scheme IV

Process steps for redox-mediated metallization of polymers. Seeding and electroless metallization approach are illustrated.



Scheme V

Step 1: Ion exchange with Pd^{2+} to form palladium polyamate. Step 2: Sodium ion exchange when contacted with ion exchange solution. Reprinted with permission from *J. Electrochem. Soc.* **139,** 810 (1992). Copyright 1992 Electrochemical Society.

polyimide surface (polyamic acid), followed by curing, greatly enhances adhesion compared to coating directly onto the unmodified polyimide.

The average depth of polyimide surface modification, which is determined by a method established with an absorbance–thickness relationship, is controlled by the reaction temperature and time. A direct relationship exists between modification depth and peel strength. The locus of failure in the case of adhesion of a nonfluorinated polyimide (BPDA–PDA) onto a wet-chemically-modified fluorinated polyimide (6FDA–ODA) surface was investigated by XPS. The probable mechanism by which adhesion between these polymers is enhanced involves diffusion of an adherate polyimide (BPDA–PDA) precursor into the modified polyimide (6FDA–ODA) surface and subsequent entanglement of the chains of both the adherate and the adherend polymers. At the interface, the concentration of the adherate (BPDA–PDA) is greater than that of the adherend (6FDA–ODA) molecules. Upon curing, the two entangled polymers become interlocked. The practical adhesion strength depends on the extent of interlocking as well as the mechanical properties of both polymers.

Other wet processes have been used to deposit a metal onto a polymer surface. A polyimide surface is electrochemically reduced when it is contacted with certain reducing agent solutions. The electroactivity of polyimides was used to mediate electron transfer for depositing metal (e.g., Pd, Pt, Ni, Cu) seeds onto the polymer surface. Subsequently, a thick layer of conducting metal, such as Cu, was deposited onto the surface by electroless or electrolytic plating.

Triethoxysilane functional groups were introduced at the surface of PCTFE by wet chemical reactions. The modified film was then laminated and strongly adhered to a glass surface at a temperature lower than T_g of PCTFE, presumably by a reaction between hydroxyl groups at the glass surface and the triethoxysilane groups at the PCTFE surface.

In contrast to dry processing, the chemistry for the wet-process modification of polymer surfaces can be defined at a molecular level. Analyses by several surface-sensitive techniques such as contact angle measurement, XPS, ERIR, ISS, and SIMS are used to fully characterize the modified polymer surfaces and provide a basis for further understanding of the adhesion mechanisms.

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