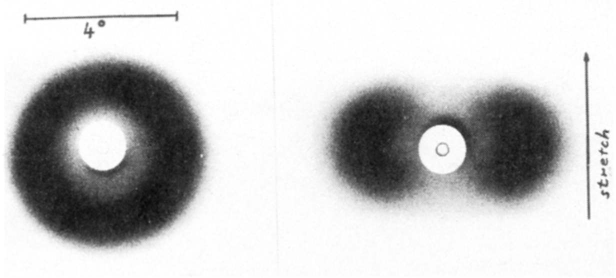

Figure 4. SAXS pattern of a technical grade polybutadiene (CB10 by Chemische Werke Hüls) carrying 10 mol % of **3** (distance sample film, 388 mm; Cu $K\alpha$ radiation; exposure time, 4 h): left, unstrained; right, strained (about 400%).

The experiments reported in this paper show that a multiphase architecture is realized by cooperative structure formation of the polar comonomer units.

This molecular arrangement resembles somehow multiblock copolymers where phase separation occurs between hard and soft segments. This analogy becomes even more striking if the stress–strain behavior of this new material is analyzed.[9]

Presently, no information about the molecular organization of the functional groups into the three-dimensional structure is available. Urazole–urazole and acid–acid interactions might be the basic structural elements, but urazole–acid complexes could also be present. On the basis of molecular models, both a bundlelike and a helical structure formed by **3** are possible. More detailed information about the supramolecular structure is needed to understand in detail the properties of this interesting new class of multiphase materials.

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Surface Modification of PMDA–ODA Polyimide: Surface Structure–Adhesion Relationship

This paper reports on preliminary results of a polyimide surface modification, the characterization of modified polyimide surfaces, and the surface structure–adhesion relationship. The average thickness of the modified layers was studied using a nondestructive measurement technique. It is possible to modify polymer surfaces to obtain the desired surface properties without altering the bulk properties.[1] One of the most desired properties in the electronic industry is adhesion between polymers and other materials such as polymers, metals, and ceramics.[2] There are many techniques for polymer surface modification, but they can be divided into two major categories. One is a dry process in which the polymers are modified with vapor-phase reactive species that are often plasma enhanced.[3] The other is a wet process in which the polymers are modified in chemical solutions.[4,5] In this work we are interested in a wet-process surface modification of polyimides that are employed as insulating layers in the fabrication of chips and chip carriers.[6] It is known that the imide ring can be opened with a base such as an amine or a hydroxide.[7] As shown in Scheme I, a polyimide such as poly(pyromellitic dianhydride–oxydianiline) (PMDA–ODA) reacts with KOH or NaOH to give a polyamate (potassium or sodium salt of polyamic acid), which is subsequently protonated with acid to give the corresponding polyamic acid.[8] Upon curing at 230 °C or higher, the polyamic acid is converted back to polyimide. This reaction can be confined to the film surface by adjusting the reaction conditions and the solvent. It is important to understand the relationship between polymer surface structure and adhesion property and to *nondestructively* measure the thicknesses of the modified layers.

Surface Modification of PMDA–ODA with KOH. PMDA–ODA samples[9] were treated with 1 M KOH aqueous solution at 22 °C for 1–90 min to give the corresponding potassium polyamate. The excess of KOH was removed by washing with water (2 × 3 min). These samples without further washing and drying were used for the protonation reaction (discussed below). To analyze the modified surface by X-ray photoelectron spectroscopy (XPS) and external reflectance infrared (ERIR) spectroscopy, the samples were further washed with isopropyl alcohol (2 × 3 min) and dried under vacuum at ambient temperature for 12 h. The XPS survey spectrum displays a new peak due to potassium. Figure 1 shows the XPS C 1s regions of polyimide and the modified surfaces. The absolute binding energies are shifted due to charging and have not been corrected. We are interested in changes of the characteristic line shapes. There is only one carbonyl carbon peak (highest binding energy peak) of polyimide starting material (Figure 1a) since the polyimide carbonyls have the similar nuclear environments. But the spectrum (Figure 1b) corresponding to potassium polyamate surface exhibits two carbonyl carbon peaks since the binding energies of carboxylate carbon and amide carbon are different. Changes in the O 1s spectra are consistent with the changes in the C 1s region.

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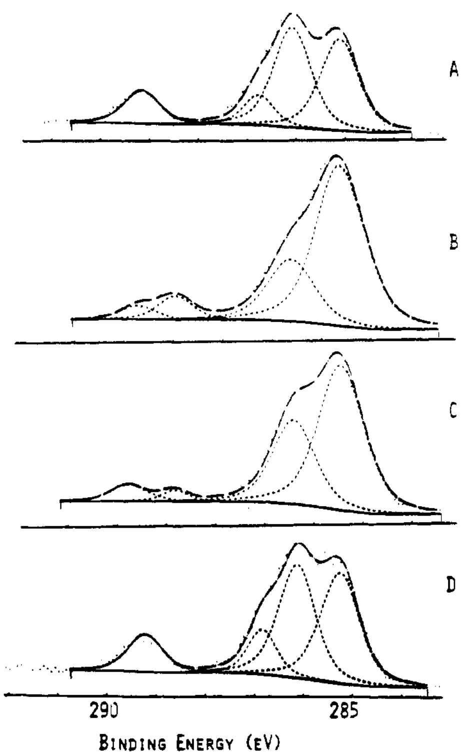
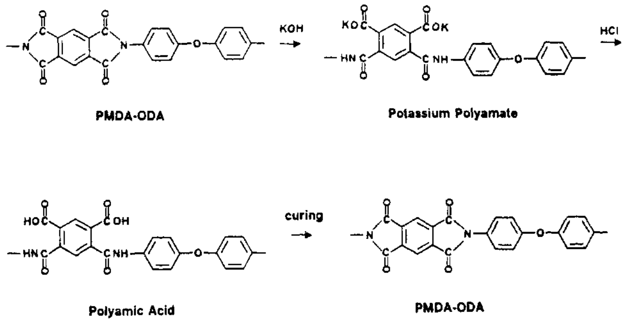


Figure 1. C 1s XPS core-level spectra of (a) PMDA-ODA starting material, (b) potassium polyamate, (c) polyamic acid, and (d) recured polyimide. The takeoff angle of electrons is 35° from the sample surface.

Scheme I



ERIR spectra of thin and uniform layers (100–1000 Å) of polyimide on chromium-coated Si wafers were obtained to analyze the products and to measure the depth of modification (which will be discussed in detail). Figure 2 displays the ERIR spectra of an 870-Å-thick[10] polyimide film and the modified samples. The spectra in the range of 1900–1300 cm^{-1} provide the most useful information for this reaction. The ERIR spectrum of PMDA-ODA[11,12] (Figure 2a) displays the bands at 1778 (w), 1740 (vs), 1726 (w, sh), 1598 (vw), 1512 (m, sh), 1502 (s), and 1381 (m, br) cm^{-1}. The spectral assignment of PMDA-ODA has been reported by other workers.[13] When the whole layer of 870-Å-thick polyimide was modified to obtain a good IR spectrum, as shown in Figure 2b, the imide carbonyl stretching at 1740 cm^{-1} (imide I band) and the imide II band at 1381 cm^{-1} completely disappeared. The peaks corresponding to PMDA-ODA polyamate are located at 1668 (s), 1608 (s), 1540 (m), 1512 (m, sh), 1502 (s), 1411 (m), and 1369 (w) cm^{-1}. The peaks at 1668 and 1540 cm^{-1} correspond to the amide I and amide II bands, respectively. The peaks at 1608 and 1369 cm^{-1} are due to the carboxylate (asymmetric and symmetric stretching).

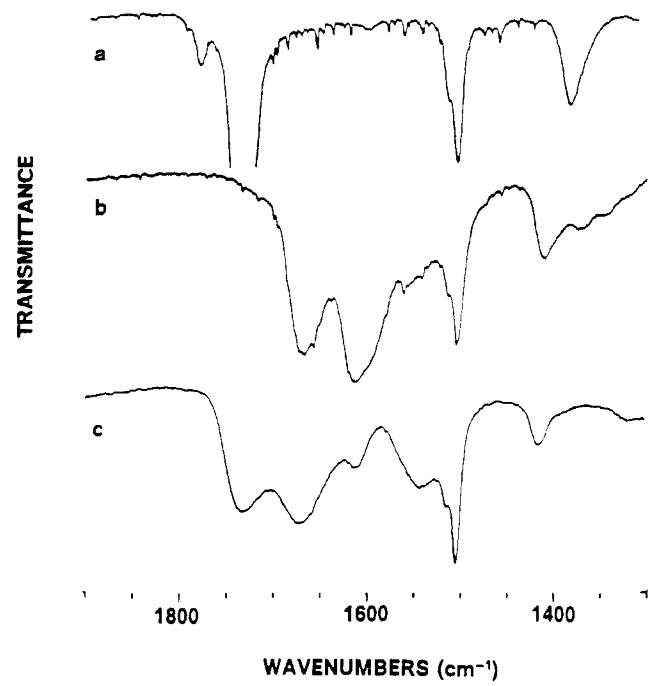


Figure 2. External reflectance IR spectra of (a) PMDA-ODA polyimide, (b) potassium polyamate, and (c) polyamic acid. The starting polyimide is 870 Å thick, and the whole layer is modified. The angle of IR incidence is 37° from the sample surface.

Reaction of Potassium PMDA-ODA Polyamate with Hydrochloric Acid. The samples treated with KOH and washed with water were protonated by treating with 0.2 M HCl aqueous solution at 22 °C for 5 min to yield a polyamic acid surface. The samples were washed with water (2 × 3 min) and isopropyl alcohol (2 × 3 min) and dried under vacuum at ambient temperature for 12 h. The potassium peak in the XPS survey spectrum disappears, and the shape of the XPS C 1s spectrum (Figure 1c) is similar to that of polyamate and consistent with that of polyamic acid as is the O 1s spectrum. The ERIR spectrum (Figure 2c) exhibits the bands at 1727 (s), 1668 (s), 1608 (m), 1540 (m), 1512 (m, sh), 1502 (s), and 1414 (m) cm^{-1}. The bands due to the carboxylate (1608 (s) and 1369 (w) cm^{-1}) disappeared, and the band at 1727 cm^{-1} corresponding to the carbonyl stretching of carboxylic acid has appeared. The peaks at 1668 and 1540 cm^{-1}, which are also observed with polyamate, correspond to amide I band (carbonyl stretching) and amide II band (coupling of C–N stretch and N–H deformation), respectively. The bands at 1608, 1512, and 1502 cm^{-1}, which also appear in the spectra of polyimide and polyamate, are probably due to the phenyl groups. The C–O–C stretching of ODA has the similar wavenumber (1245–1248 cm^{-1}; not shown in the figures) for polyimide, polyamate, and polyamic acid.

These surface-modified films were employed to study polyimide-to-polyimide adhesion. Contact angle measurements were used to investigate wettability, a factor in adhesion strength. The water contact angles decrease from 85°/38° (advancing contact angle/receding contact angle) on PMDA-ODA to 56°/8°, indicating that the modified surface has become more hydrophilic and wettable than the PMDA-ODA surface. Thus better adhesion on the modified film is expected. It is important to control the film thicknesses in microelectronic applications. To measure the thickness change, the films were modified with KOH, acidified, and recured to polyimide. Only the reaction with KOH affects the film thickness. The thicknesses of the films are 4.87, 4.87, 4.82, 4.77, and 4.76 μm for control, 10, 30, 60, and 240 min reaction with KOH, respectively.

Surface Modification of PMDA–ODA with NaOH and Acetic Acid. PMDA–ODA samples were treated with a 1.25 M NaOH aqueous solution at 22 °C for 1–10 min followed by protonating with 0.1 M acetic acid. The samples were washed and dried as previously described. Water contact angles and XPS spectra of the modified surfaces are typical of a polyamic acid surface, indicating that the reaction proceeds in the same way as described above. Upon curing the polyamic acid surface, the starting polyimide surface is produced. Contact angles and XPS C 1s spectrum (Figure 1d) of the recured surface are exactly the same as those of the starting polyimide.

Is the Modification Surface-Selective? To gain insight into the surface modification, kinetic studies were carried out with contact angle measurements, XPS, and ERIR. Contact angle assays the outermost layer (around 5 Å), XPS assays the outer few tens of angstroms, and ERIR assays the entire layer. These experiments distinguish the two possible ways of reaction: a surface-selective reaction (reaction in the contact angle and XPS sampling regions) and a homogeneous reaction (reaction proceeding at an equal rate through the whole layer).[5d]

The surfaces of 260-Å-thick[10] films were modified to polyamic acid by a two-step reaction, first with KOH and then with HCl. Treatment with HCl does not modify the polyimide but acidifies all of potassium polyamate to polyamic acid. Kinetic studies were carried out by only changing the KOH reaction conditions. Analyses by contact angle and XPS were carried out on the polyamic acid surfaces, and IR spectra were taken with the potassium polyamate surfaces to observe the absorbance change of an imide carbonyl band. Contact angles decrease to the lowest value (56°/8°) within 1 min of reaction in KOH solution and by subsequent acidification, indicating that the outermost layer (5 Å) is modified within 1 min. Further reaction up to 90 min does not change the contact angles. To study the reactions of the outer 100-Å layer, the sample was modified with KOH for 2 min and then acidified. The C 1s regions of variable-angle XPS were investigated. The variation of takeoff angle changes the surface sensitivity of XPS.[1,14] The surface-sensitive spectrum recorded at a 5° takeoff angle, which is representative of the outer 8 Å of the film (90% of the photoelectrons measured are ejected from this region[15]), displays the peaks only due to polyamic acid. The less surface-sensitive 35° takeoff angle spectrum, which represents the outer 50 Å of the sample, exhibits the peaks corresponding to both polyimide and polyamic acid. It is noteworthy that the measured modification depth (the method will be discussed) is approximately 40 Å. When the sample was modified for 5 min, the XPS spectrum recorded at a 90° takeoff angle from the sample surface, which represents the outer 90 Å of the sample, only displays the peaks corresponding to polyamic acid. The ERIR spectra show that the intensity of the imide carbonyl band at 1740 cm^{-1} gradually decreases as the reaction proceeds. These results indicate that this method of modification is *surface-selective*.

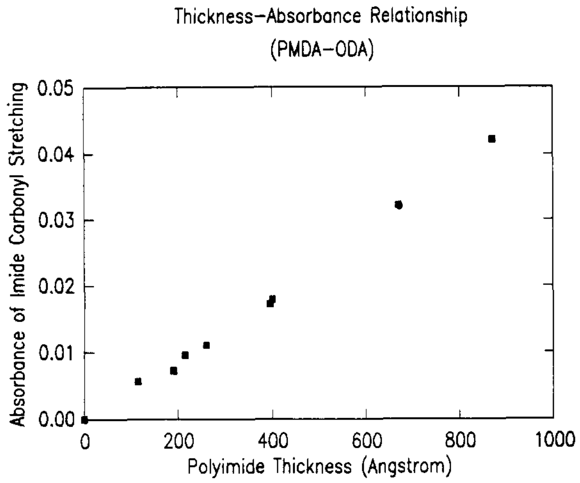


Figure 3. Relationship between PMDA–ODA polyimide thickness and imide carbonyl IR (1740 cm^{-1}) absorbance. The angle of IR incidence is 37° from the sample surface.

Measurement of Thickness of the Modified Layer. The relationship between surface structure and surface property has been poorly understood. Adhesion is one of the most important surface properties in industry. Both chemical structure and thickness of a modified layer are related to adhesion strength. Even though the interface between modified layer and unmodified layer is not sharp, it is useful to obtain an approximate depth of modification to investigate the thickness–adhesion relationship. The average depths of modification have been measured in this work using ellipsometry and ERIR.

Thin and uniform layers (100–1000 Å) of polyimide were prepared on chromium-coated Si wafers (diameter = 2.25 in.), and then the film thicknesses and the absorbances of the imide carbonyl stretching were measured by ellipsometry[10] and ERIR, respectively. As shown in Figure 3, there is a linear relationship between the film thickness and the absorbance of the carbonyl stretching at 1740 cm^{-1}. When this relationship is used, the thickness of the unmodified layer can be calculated by measuring the imide carbonyl absorbance of the modified (to polyamate) film. The average depth of modification can be obtained by subtracting the thickness of unmodified polyimide from the thickness of starting polymer. When a 260-Å-thick PMDA–ODA film was treated with 1 M KOH aqueous solution for 10 min, the absorbance of imide carbonyl (corresponding to unreacted polyimide) is 0.0012, which corresponds to 30 Å in the thickness–absorbance relationship shown in Figure 3. Thus the modification depth for the 10-min reaction is 230 (subtracted 30 from 260) Å. When a thicker film (670 Å) was modified under the same conditions, the absorbance of the imide carbonyl is 0.0190, which corresponds to 420 Å. Thus the modification depth is 250 (subtracted 420 from 670) Å. These results indicate that the modification depth for the 10-min reaction is approximately 230–250 Å. As long as an IR absorbance corresponding to a polymer can be measured, the thickness–absorbance relationship can be established using ellipsometry and ERIR. Thus the average depth of modification can be calculated by measuring the absorbances of starting polymer and modified polymer. An advantage of this method is that the polymer does not decompose during the measurement.[16] We have not found a previous report on measurement of the modification depth by this method.[17]

Surface Structure–Adhesion Relationship. To study polyimide–polyimide adhesion,[18] a thin layer (200 Å) of gold was sputter-coated onto one side (20% of the toal area) of the polyimide sample to initiate peel (polyimide has a poor adhesion to gold). The surface of the polyimide in the exposed area was modified to the polyamic acid surface, and then PMDA–ODA polyamic acid in 1-methyl-2-pyrrolidinone solvent was spin-coated to the surface-modified (to polyamic acid) polyimide film and subsequently cured at 400 °C under nitrogen. Thickness of the adherend layer (peel layer) after curing is approximately 20 μm, and the width of the peel layers is 5 mm. The peel strengths, which are indicative of adhesion strengths and measured by 90° peel of the top polyimide layer, depend on the time of reaction with KOH but not on the acidifying condition. The peel strengths are 3, 40, 85, and 126 g/mm[19] for control and 1-, 5-, and 10-min reactions with KOH, respectively. Once the outermost layer is modified to polyamic acid (1-min reaction with KOH and acidifying), the peel strength increases by more than 10 times. The deeper the modified layer is, the stronger the adhesion. These results suggest the following polymer surface structure–adhesion relationship. If the modified surface has a similar chemical structure as an incoming polymer (adherend), affinity between two phases is good and thus adhesion is strong. If the modified surface layer is amorphous like the polyamic acid layer in this work, an adherend polymer quickly diffuses into the amorphous layer (modified region) of an adherate. Subsequent curing induces interlocking of the polymer chains of adherend and adherate, and thus a strong adhesion is obtained. Another possible reason why a good adhesion is achieved is that transamidization between two polymers may occur,[20] and thus the polymer chains of adherend and adherate are covalently bonded. But a direct evidence has not been obtained for this chemistry.

For some industrial applications, it is useful to modify the polymer surface deep enough to achieve good adhesion while minimizing the loss of polymer and maintaining the surface topography. When the polyimide films (5 μm or 260 Å thick) were treated with 1 M KOH aqueous solution at 22 °C for 10 min, the thickness of polyimide and topography of modified surface remain unchanged within several angstroms and within the limit of SEM sensitivity, respectively. However, the polyimide–polyimide adhesion strength increases by 40 times.

Summary. A polyimide surface modification with KOH or NaOH aqueous solution is well-defined. The reaction initially gives a potassium or sodium polyamate surface, which is protonated with acid to yield a polyamic acid surface. This modification method is surface-selective. The average depth of modification can be *nondestructively* measured by a method using an absorbance–thickness relationship established with ellipsometry and ERIR. The surface topography and the film thickness can be retained while a strong polyimide–polyimide adhesion is achieved. Relationship between polymer surface structure and polymer surface properties is understood to some extent.

Modification of other polyimides with different properties as well as further reactions of the functional groups in the modified polyimide surface is under investigation.

Acknowledgment. We acknowledge Gareth Hougham and Dr. Steve Molis for helpful discussion.

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(10) The film thicknesses were measured using a Waferscan ellipsometer (from Gaertner Scientific Corp.) equipped with an HeNe laser (λ = 633 nm). The refractive index of PMDA–ODA employed is 1.73, which was obtained by Gareth Hougham at IBM Research with several samples with different thicknesses. The film thickness is quite uniform in the range of 40–1000 Å, and the experimental error is within 5%.

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(20) If the two different polyamic acid solutions were mixed, stored for a few days, and then cured, the glass transition temperatures of the cured polyimides are different from those corresponding to separately cured polyimides. These results are interpreted as transamidization, which gives random copolymer(s). Feger, C. Presented at the Polyimide Symposium, San Diego, January 1990.

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