

Poly(dimethylsiloxane)-polyimide blends in the formation of thick polyimide films

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Received: 7 June 2005 / Accepted: 10 January 2006 / Published online: 22 December 2006
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Abstract Thick polyimide layers can be formed by using some unique properties of poly(dimethylsiloxane)-polyimide (PDMS/PMDA-ODA) blends followed by surface modification and deposition of a second layer of polyimide precursor chemicals. The method is based on the micro-phase separation characteristics of these blends to yield surfaces that have PDMS-like character. Upon modification with UV/ozone treatment, a surface that is essentially SiO_x and hydrophilic in nature is produced. This surface is amenable to reaction and deposition of a second polyimide layer from polyimide precursors. The thicker polyimide layer has enhanced adhesion between the original layer of the blend and the new polyimide layer and this approach finds extensive applications for products that require thick polymer layers. Changes in surface energy for various blend compositions were monitored by measurement of advancing contact angle with de-ionized water. Contact angle for unmodified polyimide films was on the order of 70° and it increased to about 104° after blending with PDMS and curing. UV/ozone treatment reduced the contact angle of the doped polyimide to less than 5°. X-ray photoelectron spectroscopy (XPS) and angle resolved XPS (ARXPS) measurements were used to monitor the chemical compositions of the various surfaces. High-resolution XPS spectra in the Si2p region confirm the transformation of O-Si-C bonds in PDMS to SiO_x, where *x* is about 2. Scanning electron microscopy (SEM) of some

selected samples shows that the blends contain phase separation of the polymers at the surfaces of the samples. Atomic force microscopy (AFM) of siloxane-free polyimide, and PDMS/PMDA-ODA blends both prior to and after UV/ozone exposure, show that the films are essentially flat at short treatment times (less than 60 min). AFM also reveals the separation of PDMS into micro-domains at the cured film surface and throughout the layer below the surface of the blended films. Adhesion of a subsequently deposited polyimide layer to the modified polyimide surface was found to be greatly improved when compared to the adhesion obtained for deposition onto a pristine polyimide surface.

Introduction

Because of their attractive thermal, mechanical and electrical properties, polyimides are widely used in high-performance military aircraft and spacecraft applications [1] and in microelectronic devices [1, 2]. These properties include high thermal stability, moderate dielectric constant, excellent planarizing characteristics, and high flexibility. As such, polyimide (PI) layers are widely used in the electronics industry to provide protection, electrical insulation, or both. PIs are also good barriers to alpha particles, and are low in alpha particle emission. They are therefore used as an overcoat on integrated circuit (IC) devices as protection from alpha particle radiation that induces soft errors. Thicker PI coatings afford better protection and, therefore, reduction in soft error rates in IC

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devices. The total thickness of PI that can practically be attained in a single layer by spin coating techniques is somewhat limited. If a thicker layer is desired, it is necessary to apply a second layer of PI precursor on top of the first. Typically, the adhesion between the first and second layers of PI is poor.

Adhesion between two surfaces results from a combination of mechanical, chemical and electrostatic contributions. In addition, diffusion characteristics at the mating surfaces of the materials must be considered. Surface micro-roughness can induce mechanical interlocking as well as produce a greater surface area for chemical interactions between the components of the interface. Chemical interactions include acid–base and dipolar effects. Interfacial characteristics are determined primarily by the strength of chemical bonding between the two surfaces in contact.

Pristine PI surfaces are relatively hydrophobic. Fully cured PI films are chemically inert with respect to interaction with subsequently coated layers of PI and inter-diffusion of such films is negligible. Since the fully cured PI surface is smooth (RMS of approximately 1.0–1.3 nm), mechanical contributions to adhesion are understandably insignificant for applications involving multiple coatings of PI from liquid resin precursors. To improve the adhesion between these layers, it is necessary to treat the surface of the first layer before the second layer is deposited [3]. One such chemical treatment involves the hydrolysis of cured PI film with an alkaline solution in a solvent or a mixture of solvents to produce a polyamic acid salt which is transformed to a polyamic acid-containing surface onto which a liquid PI precursor is deposited and subsequently cured [4, 5]. Plasma treatments have also been shown to increase PI/modified PI interaction significantly [6].

Silicon oxide substrates are more amenable to chemical bonding interactions with resin-coated PI than are fully cured PI substrates, and adhesion of PI to SiO₂ is an order of magnitude greater than the adhesion of PI to itself [3]. Films of silicon oxides are used extensively, for example, as protective coatings or electrically insulating layers for inorganic and organic substrates. Some applications for organic substrates include use as a hermetic seal [7–9], flame retardancy [10], abrasion resistance [11], and adhesion promotion [12]. SiO_x films, in general, can be formed by a variety of techniques. These include pyrolytic degradation of high molecular weight poly(dimethylsiloxane) (PDMS) [13], spin-on coatings of sol-gels, e.g., of polysilsesquioxanes [11, 14, 15], sputter deposition [16], chemical vapor deposition (CVD) by use of vacuum ultraviolet (VUV)

radiation to decompose low molecular weight tetraethoxyorthosilicate (TEOS), the decomposition products of which redeposit as SiO₂ [17], plasma-enhanced CVD (PE-CVD) [7, 18, 19], transformation of silicides to SiO₂ using ultraviolet (UV) lamps [20], treatment of monomolecular Langmuir–Blodgett films of silicones using low temperature radiofrequency (rf) plasma [21] or UV/ozone [22], and UV/ozone treatment of siloxanes and silazanes to produce an SiO_x overcoat [12].

It is known that materials with low surface energies tend to segregate to a surface to minimize the overall energy of a system. Hildrebrandt [23] correlated the order of solute solubility with the cohesive properties of solvents. Later on, he proposed the concept of solubility parameters δ to explain the miscibility of a solute into a solvent. Several refinements to this approach have been made to yield some useful concepts that better describe the behavior of a solute in a solvent [24]. For a polymer, δ depends on the chemical structure of the material and δ is also directly related to the square root of its cohesive energy density in the amorphous state at room temperature.

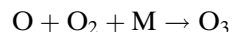
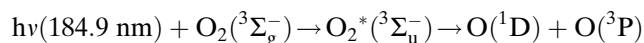
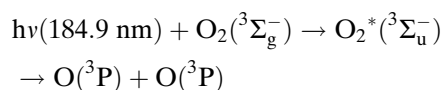
Zisman and co-workers showed that the addition of small amounts of siloxane-containing co-polymers (0.1–2.0% w/w) to the same type of polymer matrix resulted in films that had the same bulk properties of the unmodified materials. However, their surfaces resembled those of PDMS [25]. Other block copolymer systems such as polystyrene-siloxane have also been shown to induce complete surface coverage with PDMS segments [26]. In a more recent approach, Wang and other investigators studied the behavior of film formation of polyurethane-siloxane-co-polymers and demonstrated similar behavior to the systems already described [10, 27]. For example, Wang found that the lower surface energy segments oriented themselves toward the surface of the film and PDMS micro domains were observed in specific ranges of concentration [10].

Systems that contain blends of two different polymers that are not capable of interacting with each other may offer a different approach to surface modification, provided that their characteristics and concentration ranges are carefully delineated. At present, little information exists on the behavior of siloxane–polyimide systems, thus, these systems merit further investigation. If phase separation is developed, this segregation of one component (PDMS) at low concentrations (designated here as solute) in another one acting as the matrix or solvent (PI), can lead to interesting results. In addition, by controlling the concentration of the segregating material, the blend

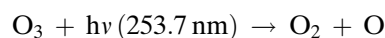
in its solid form is amenable to modification and further applications without alteration of mechanical and chemical properties of the bulk material. This overall approach is graphically illustrated in Fig. 1a for the results presented here.

A summary of the various techniques that have been employed to transform the surface of organo-silicon films (like PDMS) to a silicon-oxide was given by Egitto and Matienzo [28]. In addition to the use of UV/ozone treatment, other techniques included pyrolytic degradation [13], plasma [29–32], exposure to laser radiation [11, 33] or UV lamps [11, 20]. Reference 28 also describes the optimization of a UV/ozone treatment apparatus and the gas-phase and gas/surface chemistry leading to modification of organic and organo-silicon polymers.

In the UV/ozone system used by Egitto and Matienzo [28, 34], a low-pressure mercury vapor lamp with a quartz envelope emits strongly at two wavelengths, 184.9 and 253.7 nm. Oxygen molecules absorb strongly at 184.9 nm and dissociate to form atomic oxygen [35] that reacts with O₂ to form ozone



where M is a third body such as O, O₂, O₃, or N₂ [36–38]. Ozone absorbs at 253.7 nm:



Both atomic oxygen and ozone can react strongly with organic materials [35]. Absorption of UV radiation, common to most polymers and organic compounds, can lead to formation of free radicals, formation of excited molecules, or, if the organic material's ionization potential is low enough, formation of ions. Ultimately, the organic radicals react with atomic oxygen or ozone to form low molecular weight, volatile fragments, like CO₂ and H₂O that can desorb from the surface. As such, UV/ozone processing has been used effectively to remove thin layers of organic contaminants. However, its effectiveness in this regard is somewhat limited to organic materials. In particular, removal of all the components of organo-silicon compounds does not occur. For PDMS, UV/ozone treatment is effective in removing a good portion of the organic components of PDMS while the siloxane component is converted to silicon oxides and carbon-containing residues. This process is illustrated schematically in Fig. 1b. This mechanism is similar to that postulated by Taylor and Wolf (Private communication) for O₂ plasma “anodization” of Si-containing polymers whereby the formation of small Si fragments diffuse to the polymer surface where they are converted to a silicon dioxide etching mask.

For neat films of Kapton polyimide (PMDA-ODA), Sener et al. [39] demonstrated that UV/ozone treatment resulted in a mild chemical degradation of the PI surface. Tape tests were used to evaluate the adhesion of copper that was sputter-coated onto the modified PI surfaces. A decrease in practical adhesion was observed such that a cohesive failure occurred within the modified PI and not at the PI-copper interface. XPS and time of flight secondary ion mass spectrometry (TOF-SIMS) indicated a very thin (ca. 5 nm) weak boundary layer adhering to the Cu.

Matienzo and Egitto [34] have reported on the blending of several polymers, including PI, polyethylene, and polyurethane, with PDMS and the subsequent

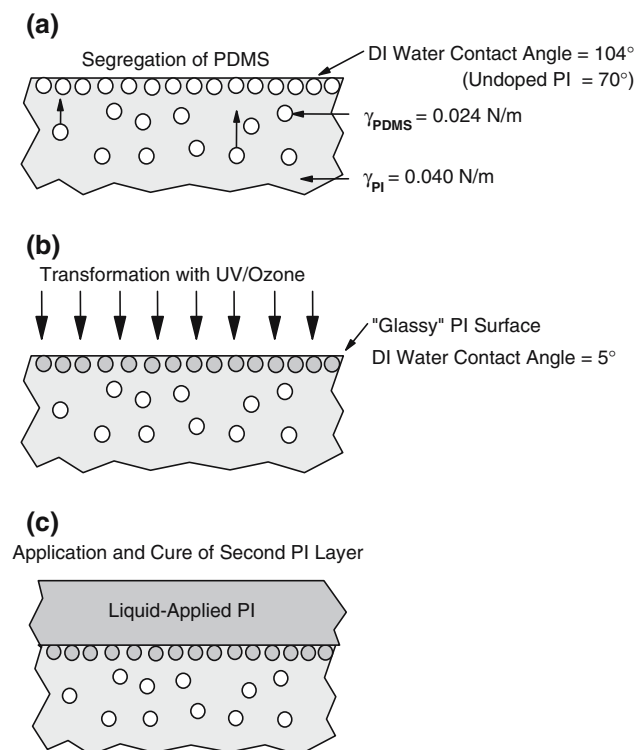


Fig. 1 Simplified schematic representation of segregation of PDMS in a PI matrix (a), subsequent transformation of the siloxane to SiO_x upon exposure to a UV/ozone environment (b), and addition of a second PI layer to the surface-modified initial blend (c)

conversion to silicon-oxides of the PDMS component that segregated to the surface upon treatment with UV/ozone. In the present study, films of SiO_x are formed on the surface of PI films by a process involving: (1) doping of the PI precursor resin with PDMS, (2) preferential segregation of the PDMS to the surface of the polymer blend during film formation, (3) transformation of the siloxane to SiO_x using exposure to UV/ozone treatment, and (4) applying a second layer of PI precursors on the modified surface prior to curing the new polymer layer. Characterization of PDMS/PMDA–ODA blends in which PDMS concentrations were in the range of 0.25–1.4% (w/w) was done by using contact angle measurements, SEM, AFM and variable angle XPS measurements prior to and after treatment by exposure to a UV/ozone atmosphere. Experiments at various concentrations and treatment times were also used to assess the influences of these parameters in surface modification reactions of the blends. Finally, the practical adhesion of the treated interfaces to newly deposited PMDA–ODA is compared to that of films of pure PMDA–ODA deposited over layers of PMDA–ODA without the modification steps.

Experimental

Film formation

Films were formed on polished silicon wafers having a crystalline orientation of (1, 0, 0) so that smaller rectilinear pieces of reproducible size and shape could be obtained by cleaving along orthogonal planes. Samples used for measurement of contact angle were about 0.010 m^2 . Chemical structures for PDMS and the PI investigated in this study are shown in Fig. 2.

PI layers were formed by cross-linking a solution-deposited PI resin, Pyralin[®] PI-5878 (Pyralin is a registered trademark of E.I. DuPont de Nemours, Inc., Wilmington, DE, USA), containing the PI precursors pyromellitic dianhydride (PMDA) and oxydianiline (ODA). The PI precursor films were thermally cured as described below. Solutions of the organo-silicon material were obtained by mixing equal parts, by weight, of a high molecular weight PDMS grease terminated in hydroxyl groups (SE-30, General Electric) and hexane in a vial. This solution (0.0001, 0.0002, 0.0003, 0.0004, or 0.0006 kg) was mixed with *N*-methyl pyrrolidone (0.0064 kg). The resulting solution was mixed with PI-5878 such that the final solution

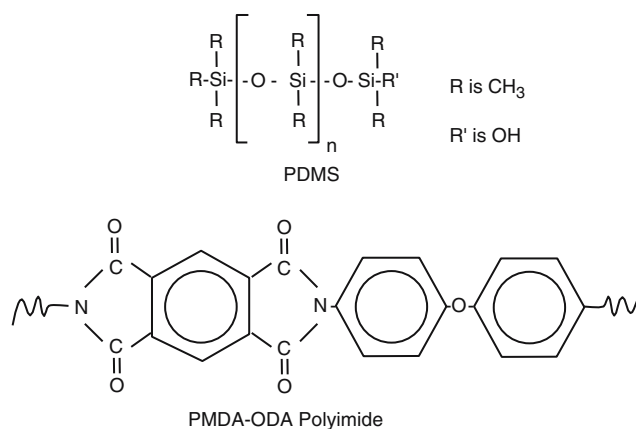


Fig. 2 Chemical structures of polymers used in this investigation

contained 0.021 kg PI-5878 PI precursor, 0.0064 kg *N*-methyl pyrrolidone, and the PDMS–hexane mixture. Hence the concentration of PDMS in PI for these experiments ranged from 0.25% (for the 0.0001 kg PDMS–hexane mixture) to 1.4% (for the 0.0006g PDMS–hexane mixture), wt/wt.

Prior to coating, silicon wafers were prepared with an adhesion promoter solution containing 10 parts Silquest[®] A-1100 (Silquest is a registered trademark of SpecialChem SA, Paris, France) adhesion promoter (3-amino-propyl-tri-ethoxy-silane) with 10 parts methanol and 1 part de-ionized water. The mixture was left standing in a stoppered bottle overnight. Just prior to use, 0.010 kg of this solution was mixed with $4 \times 10^{-4} \text{ m}^3$ of methanol. This solution was spin coated onto silicon wafers at 2,000 rpm for 30 s. The coated wafers were baked for 15 min in air at 110°C .

The PI blend precursor-containing solution was spin-coated onto these wafers at 6,000 rpm for 30 s. The resulting coated wafers were baked (B-staged) in air for 20 min at 110°C . They were then baked in flowing nitrogen gas by ramping from room temperature to 350°C at a rate of $10^\circ\text{C}/\text{min}$, holding at 350°C for 60 min, and cooling to room temperature at a rate of $10^\circ\text{C}/\text{min}$. During this final curing step, the PDMS segregated to the surface of the film coating. Total final thickness of the films was $1.0 \mu\text{m}$. Films of PI were prepared by the same technique, except that none of the PDMS additive solution was added to the PI precursor solution.

To evaluate the adhesion of a second layer of PI to the first layer as prepared above, pristine PI was applied per the technique listed above. When thicker films of the second layer of PI were desired, spin speeds were reduced.

UV/ozone system

UV/ozone treatments were performed in a UVOCS, Inc., model T0606B UV/ozone cleaning system shown schematically in Fig. 3. The UV source is a 0.1524×0.1524 m low-pressure mercury vapor grid lamp with a quartz envelope. The pedestal on which samples were placed was covered with a quartz plate. Samples were placed on the quartz plate such that their surfaces were 0.0057 m from the lamp envelope.

Contact angle measurements

Advancing DI water contact angles on treated and untreated samples were measured with a Rame-Hart, Inc., model A-100 goniometer with optical protractor, using a sessile drop technique and drop volumes between 1×10^{-12} and 2×10^{-12} m³. Measurements were made immediately following treatment. Contact angles were recorded within 30 s from initial application of the drop. Separate samples were used for each data point. Results obtained in this manner were found to be very consistent and reproducible.

X-ray Photoelectron spectroscopy (XPS)

XPS was performed in a modified PHI-5500 Multiprobe spectrometer equipped with a hemispherical analyzer using monochromatized AlK_α rays for excitation with a spot size of 800 μm. Survey and high-resolution spectra were collected with pass energies of 158 and 11.8 eV, respectively. Binding energies were referenced to the hydrocarbon peak at 284.8 eV. The linearity of the binding energy scale was determined by measuring the positions of a dual sample of copper and gold prior to the experiments described here. High-resolution XPS spectra in the C1s, O1s, N1s and Si2p regions were used to determine the contributions due to different chemical environments, and to follow them as a function of UV/ozone treatment. In addition, XPS spectra were collected in the survey and high-resolution modes as a function of tilting angle. The tilting angle is defined here as the angle between the surface

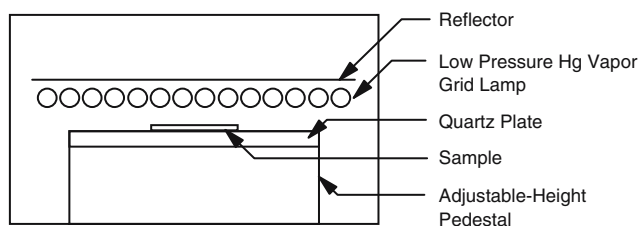


Fig. 3 Schematic illustration of a UV/ozone cleaning system

of the sample and the analyzer. Angles of 65°, 30°, and 15° were taken for all of the analyzed samples.

Scanning electron microscopy (SEM)

A Leo 1550 FE-SEM-STEM microscope operating at a voltage of 5 keV in the in-lens mode, zero angle sample tilt and a working distance of 0.002 m was used to image samples previously coated with a thin layer of carbon, approximately 20 nm thick. Magnifications of 50,000× and 100,000× were used to observe the surfaces of some selected samples and images were collected in the secondary electron imaging mode.

Atomic force microscopy (AFM)

A Nanoscope IIIa (Digital Instruments) atomic force microscope operating in the tapping mode was used to image selected surfaces. The scans were taken in square areas of 0.5, 1 and 5 μm (axial dimensions). The tip frequency was 265.884 kHz with a drive amplitude of 89.4 mV and an amplitude set point of 2.0 V. Software provided with the microscope was used to obtain RMS values of the scanned surfaces for comparative purposes.

Results and discussion

High-resolution XPS analyses of the C1s region of pristine PMDA-ODA before and after the addition and curing of blends containing 0.25 and 0.75% PDMS are shown in Fig. 4. Notice that the incorporation of the siloxane essentially makes the broad and weak π - π^* transition in the C1s region of PMDA-ODA, ca. 292 eV, disappear due to the enrichment of

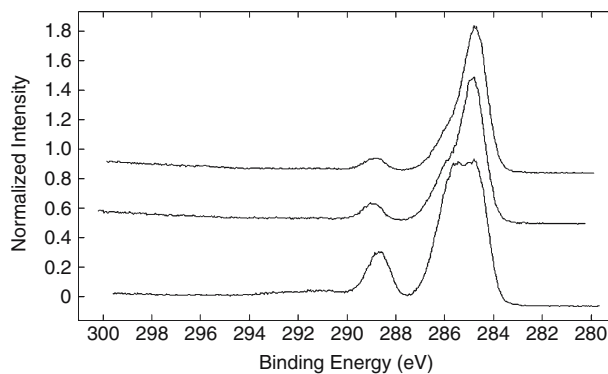


Fig. 4 High-resolution C1s XPS spectra ($\Theta = 65^\circ$) for PMDA-ODA film and two PMDS-PI blends. Sequence of spectra show PMDA-ODA at bottom, 0.25% PDMS addition at center and 0.75% PDMS, top spectrum

the surface layers of the blended films with PDMS material. Further verification of this occurrence is found by examining the PDMS–PI films by means of ARXPS. Figure 5 presents the data obtained for the C1s regions of films containing 0.25% and 0.75% PDMS. Notice that in these cases, the higher concentration mixture shows a complete coverage of the film surface with a hydrocarbon environment, such as that found in PDMS. Similarly, the same conclusion can be reached by examining the N1s spectra as a function of tilting angle for the same film (see Fig. 6). The data for the lowest concentration of PDMS investigated in this work (0.25%), show practically complete coverage of the PI in the C1s and N1s environments of this sample.

The atomic composition of the pristine PI is known, and the presence of PDMS on the blended films will attenuate the signals of the original PI substrate. Then, it is possible to estimate the thickness of the PDMS overlayer in a blended film. The film thickness of PDMS in the blend can be calculated if one knows the inelastic mean free path (λ) of an

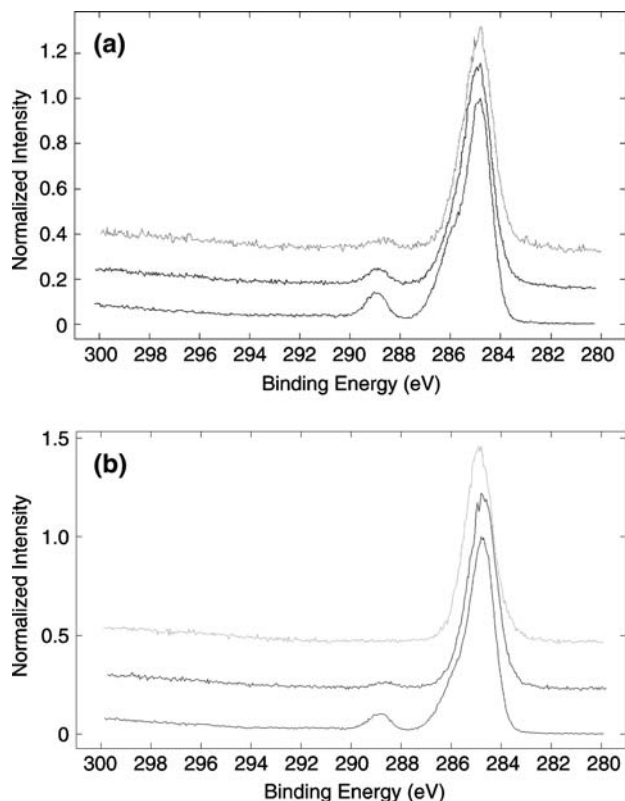


Fig. 5 High-resolution variable angle C1s XPS spectra for the 0.25% PDMS (PDMS–PI) blend (a) and 0.75% PDMS (PDMS–PI) blend (b). Sequence of spectra show Θ values of 65° (bottom), 30° (center) and 15° (top)

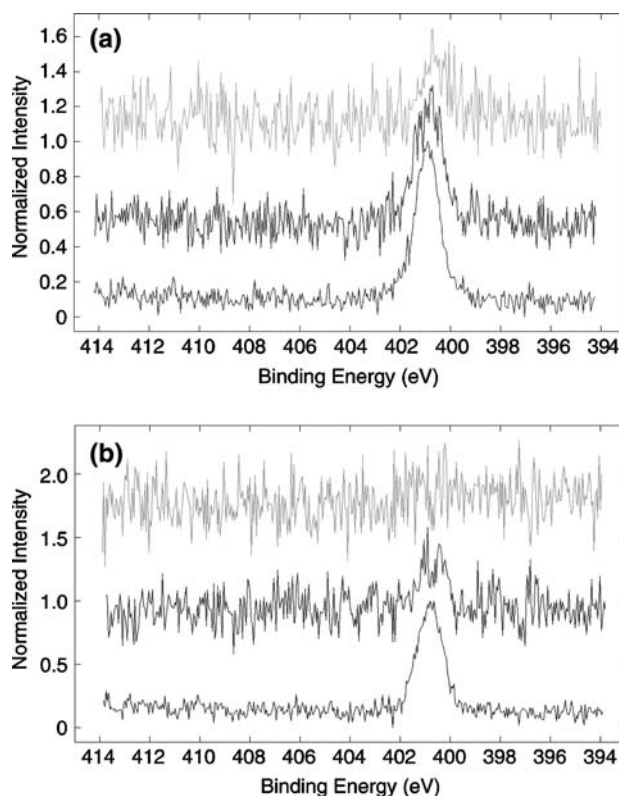


Fig. 6 High-resolution variable angle N1s XPS spectra for the 0.25% PDMS (PDMS–PI) blend (a) and 0.75% PDMS (PDMS–PI) blend (b). Sequence of spectra show Θ values of 65° (bottom), 30° (center) and 15° (top) for both sets of data

element of interest at a given energy and a given angle between the surface and the detector in the spectrometer [40]. The value of λ for the N1s in long chain amides has been reported by Zhang et al. [41] to be 2.84 nm. The concentrations of nitrogen in the pristine PI and the 0.25% PDMS–PI film are 6.4 and 2.3% at., respectively when the sampling angle between the surface and the detector is 65°. This first approximation yields a film thickness of PDMS on the order of 1.8 nm. Also, it is estimated that the sampling depth by XPS at this given angle for PI is on the order of 7.7 nm. Similar analyses for the 0.75% PDMS blend yield an approximate PDMS thickness of 2.0 nm, although it is unlikely that there is a discrete boundary between the segregated PDMS surface region and the underlying PDMS–PI blend.

Contact angle measurements with de-ionized water were used to determine the changes in wettability with incorporation of PDMS to PI films. The initial value of 70° for pure PMDA–ODA increased to a value of 104° for films of the PDMS–PI blends. These results are indicative of the preferential segregation of PDMS to the surface of the films.

Advancing DI water contact angle is shown as a function of treatment time for two different concentrations of PDMS in PI (0.25 and 0.75% w/w) in Fig. 7. Egitto and Matienzo [28] observed for neat PDMS films that the rate of change in contact angle with treatment in UV/ozone depended on the thickness of the PDMS such that thicker films required longer exposure to reach a steady state minimum value of contact angle. The two experiments plotted in Fig. 7 do not differ greatly and they are in agreement with the estimates made above from XPS data. Then, one can conclude that the lower concentration doping is sufficient to fully modify the surface by migration of PDMS. Even lower concentrations may be adequate for full modification of the surface while preserving the bulk properties of the PI film. Full modification of the PDMS–PI films by the UV/ozone treatment was achieved at a time between 5 and 10 min, comparable to times required to fully modify neat PDMS films as shown by Egitto and Matienzo [28].

The effect of varying treatment time in UV/ozone was also investigated by high resolution ARXPS for various blends. For example, Fig. 8 shows the effect of treatment times between 0 and 60 min for a film of the 0.25% PDMS blend in PI in which the tilting angle is 65°. It is relevant to notice that some broadening is detected on the C1s region with a change in the spectra in the region ca. 288 eV. The Si2p regions of the spectra for the same sample show broadening and a shift to a higher binding energy with treatment time (see Fig. 9). The transformation of the siloxane to SiO_x appears to proceed rapidly as shown by the contact angle measurements and the high resolution Si2p spectra for the 0.25% PDMS–PI mixture. The nitrogen N1s region of the spectra indicates that longer

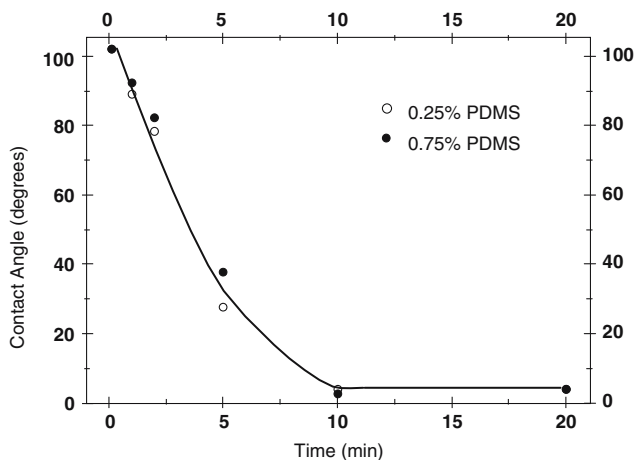


Fig. 7 Advancing DI water contact angle for PDMS–PI films (0.25 and 0.75% PDMS) as a function of UV/ozone treatment time

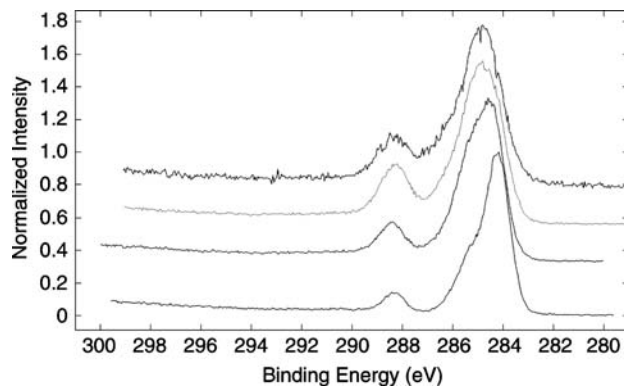


Fig. 8 High-resolution C1s XPS spectra ($\Theta = 65^\circ$) for the 0.25%PDMS (PDMS–PI) blend as a function of UV/ozone treatment time. Spectra are shown in the sequence: no treatment, 5, 20, and 60 min from bottom to top spectrum, respectively

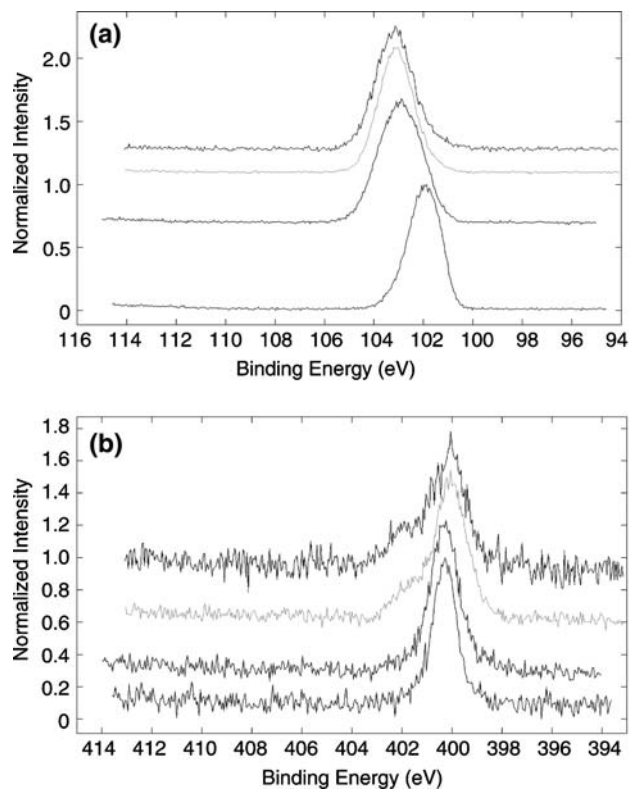


Fig. 9 High-resolution Si2p XPS spectra ($\Theta = 65^\circ$) for the 0.25%PDMS (PDMS–PI) blend as a function of UV/ozone treatment time (a). Complementary high-resolution N1s XPS for the same sample (b). Spectra are shown in the sequence: no treatment, 5, 20, and 60 min from bottom to top spectrum, respectively

treatment times than 5 min appear to induce some alteration of the original N1s environments found in PI (see Fig. 9). This is in agreement with the expected effects of UV radiation on PIs [42].

In order to separate the possible contributions of UV/ozone on the substrate film, samples of PMDA–ODA were compared before and after 5 and 60 min of treatment in UV/ozone. Figure 10 presents the high-resolution C1s and N1s regions of the spectra for these samples. Notice that treatment time in UV/ozone induces oxygen incorporation and the formation of more C = O and R'–O–C(O)–R groups (binding energies of 288.6 and 287.5 eV, respectively) [43]. The initial step is imide ring opening and the formation of more –C = O groups. The N1s region of the spectra also shows the appearance of an oxidized nitrogen-containing species at 402.1 eV (see also Fig. 10). This new signal is identified as a quaternary nitrogen ion environment [43]. These results indicate that during the transformation reactions for PDMS, the PI undergoes modification as well.

The morphologies of the films developed by blending and also following treatment were initially studied by means of high-resolution FE-SEM. Figure 11 presents some images of PDMS–PI films before (for 0.25% PDMS) and after 5 min of treatment in UV/

ozone (for 0.25% and 0.75% PDMS). Notice that globules with an approximate diameter of 100 nm can be found on a very flat surface. These globules are micro phase separated PDMS-rich domains. These dimensions are in agreement with the behavior of PDMS segments present in polyurethane–PDMS copolymers as reported by Wang for siloxane concentrations of 15% and 55% PDMS [10].

Further analyses of PI films, and PDMS–PI films before and after UV/ozone treatment, were conducted using AFM in a tapping mode for data collection. Figure 12 presents isometric views of films of PI, PDMS–PI with 0.25% PDMS (no UV/ozone treatment), and 0.25% PDMS films treated for 5 and 60 min, respectively. The RMS values measured on these films are summarized in Table 1 below. Notice that the morphology of the spin-coated PI film changes once the PDMS phase is incorporated into the film. Spherical domains with an average size of 60 nm are detected. No difference in RMS values was detected for films of PMDA–ODA containing PDMS as compared to pure films. Upon a short treatment time, the morphology and the average surface roughness of the film remain unchanged. It is only after extended treatment times that the surface of the film appears to change in appearance and roughness. Further examination of the blend containing 0.25% PDMS by AFM clearly illustrates the profile of this blended film. Some of the isolated phase-separated domains appear to protrude from the film surface and they reach approximate heights of 3.2 nm (see Fig. 13).

The findings on the UV/ozone surface modification behavior of PDMS–PI blends was applied to the preparation of thick, multi-layer PI films. Films of PDMS–PI (0.5% PDMS), 1.0 μm thick, were prepared on silicon wafers as described above. These films were then treated in a UV/ozone system for 60 min to convert the organo-silicon compounds that had segregated to the surface to a silicon-oxide. Films of the PI were similarly coated onto silicon wafers using the same parameters of spinning and baking as for the doped PI films. Each of the two groups of wafers, i.e., those coated with the blend and UV/ozone-treated, and those coated with the PI, were coated again with the uncrosslinked PI precursor solution. The thickness of the latter PI coating was adjusted by varying the spin speed to form a thick top layer and a thin top layer. Final test structures are shown schematically in cross-section in Fig. 14.

Two techniques were employed to measure the practical adhesion of the top PI film to the PDMS–PI blend with UV/ozone treatment and compare it to that obtained when the PI was applied to layers of

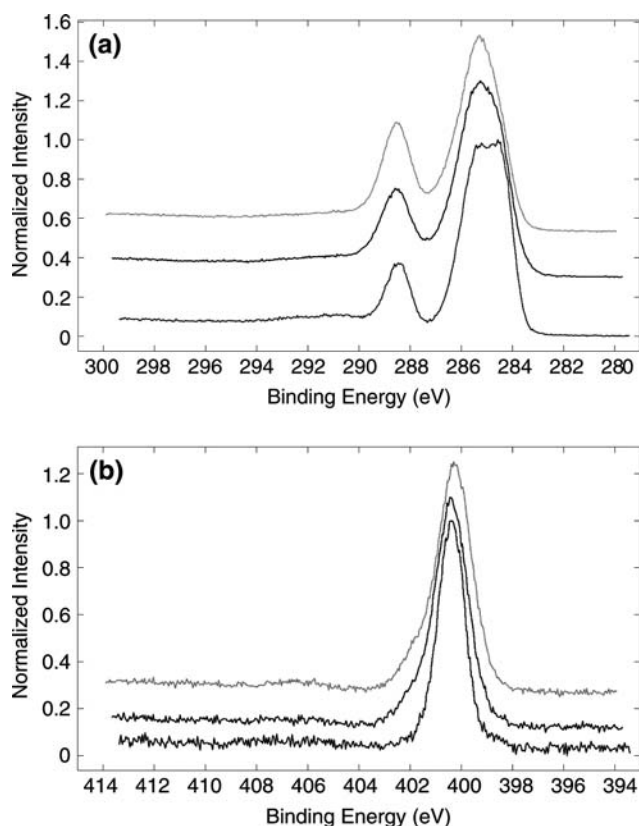


Fig. 10 High-resolution C1s XPS spectra ($\Theta = 65^\circ$) for the PMDA–ODA as a function of UV/ozone treatment time (a) and similar data for the N1s region of the same sample (b). Spectra are shown in the sequence: no treatment, 5, and 60 min from bottom to top image

Fig. 11 SEM images of the 0.25% PDMS blend before (left), after 5 min under UV/ozone irradiation (center) and the 0.75% PDMS blend after the same treatment time (right). The white area on the first sample is a mechanical defect on the PI film

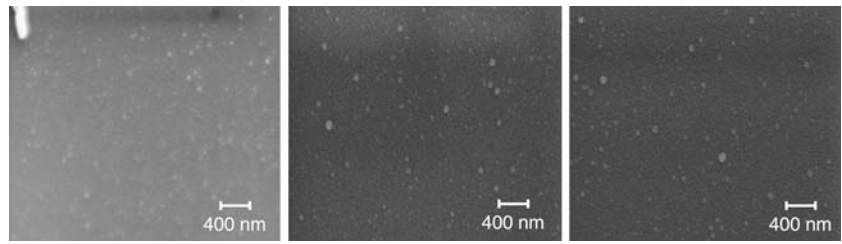
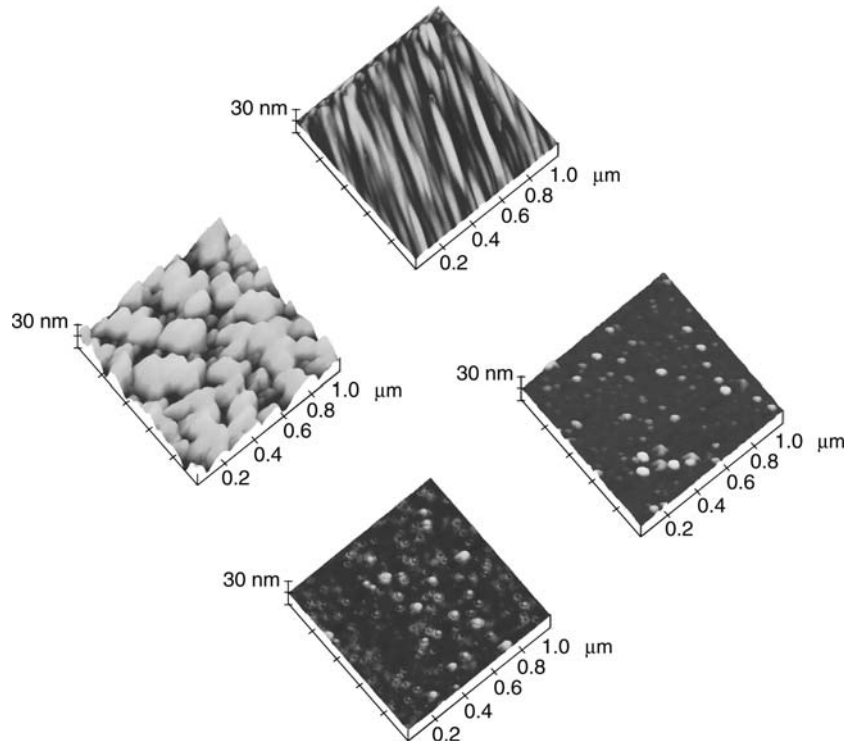


Fig. 12 Isometric views (clockwise from top) of PMDA–ODA film, 0.25% (w/w) PDMS (PDMS–PI) blend before UV/ozone treatment, same blend after 5 min of treatment, and a sample after 60 min of UV/ozone treatment



unmodified PI. For thick films, a strip was defined by scribing a feature in the film as shown in Fig. 15a. Separate wafers were used for each experiment, with

Table 1 RMS values for various PI and PDMS–PI films as measured by AFM

| Film analyzed | Scan size | RMS roughness |
|---|-----------|---------------|
| PMDA–ODA | 500 nm | 1.20 nm |
| | 1.0 μm | 1.30 nm |
| | 5.0 μm | 1.33 nm |
| 0.25% PDMS (PDMS–PI) 0 min UV/ozone | 500 nm | 0.92 nm |
| | 1.0 μm | 1.02 nm |
| | 5.0 μm | 2.06 nm |
| 0.25% PDMS (PDMS–PI) 5 min UV/ozone | 500 nm | 1.25 nm |
| | 1.0 μm | 1.30 nm |
| | 5.0 μm | 2.10 nm |
| 0.25% PDMS (PDMS–PI) 60 min UV/ozone | 500 nm | 6.4 nm |
| | 1.0 μm | |
| | 5.0 μm | 9.7 nm |

the first layer being either a PDMS–PI blend or undoped PI. It was possible to easily peel the untreated PI overlayer from the underlying siloxane-free PI substrate. However, attempts to peel the PI overlayer from a treated PDMS–PI substrate revealed greater adhesion, resulting in the inability to continuously peel the strip from the substrate. In the latter instance, the strip consistently ripped during the peel. A second test performed on thinner PI overlayers involved scribing a series of orthogonal lines to produce a crosshatched region, shown in Fig. 15b. When an adhesive tape was applied to this region and peeled from the surface, the PI overlayer was removed from the underlying untreated PI over 40% of the area tested. A similar test performed using an underlayer of the treated PDMS–PI blend as a substrate resulted in no removal of the PI overlayer.

Modified polyimide blends can be used as chip passivation layers to enhance adhesion to other

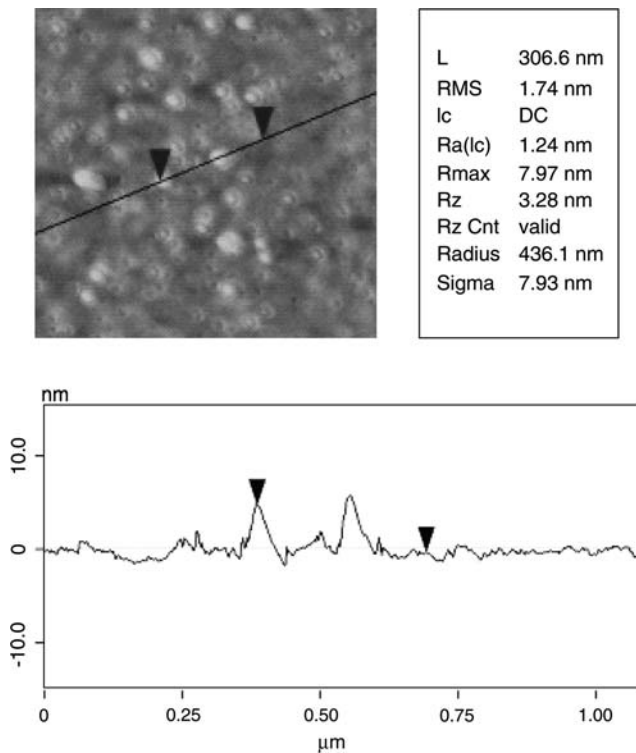


Fig. 13 Cross-sectional view for AFM line scan on a surface containing the 0.25% PDMS (PDMS-PI) blend. The initial surface scan (top left) was done over an area of $1 \times 1 \mu\text{m}$

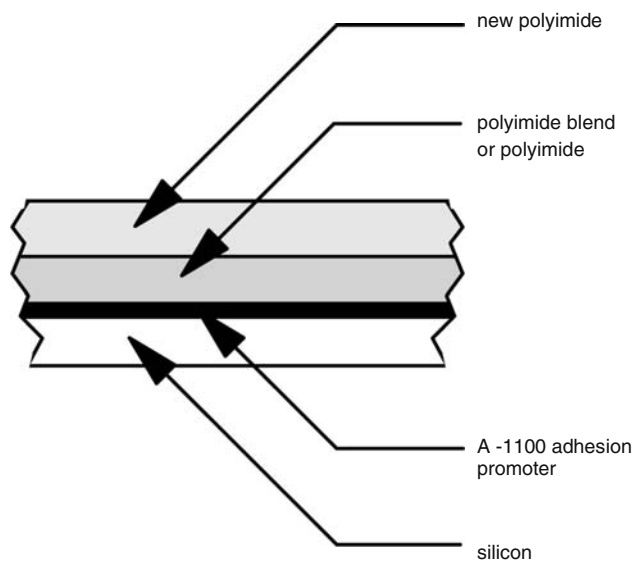


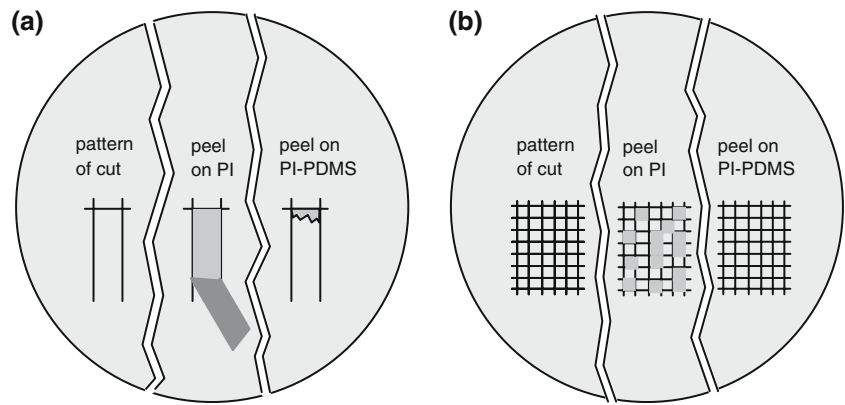
Fig. 14 Schematic drawing of the cross-sectional view of the test structure used to investigate adhesion of a PI layer deposited onto both PDMS-PI and PI films

packaging components, for example, underfill materials for flip-chip packaging configurations or overmold materials for wire-bonded packages. These configurations are widely used and their cross-sectional views

are illustrated in Fig. 16a and b, respectively. Further details of the applications of these packages can be found elsewhere [44, 45]. Because silicon IC devices are sensitive to soft error rates caused by alpha particle emission of some materials, barriers that prevent or decrease these errors are required. Thick PI films are excellent barriers for such applications. The experiments described above indicate the advantages of using polymeric blends for the production of thick PI films.

The concept of solubility parameters when applied to polymeric systems is useful in answering some preliminary questions, if these data are available. Solubility parameters for polymers can be calculated or determined empirically. Typically, δ values for polymers range from 17.4 to 28.6 $\text{MPa}^{1/2}$. Reports of solubility parameters for PIs are scant in the open literature; values for PI P84 and BTDA-TMDA have been reported to be 26.8 and 26.5 $\text{MPa}^{1/2}$, respectively [46, 47]. The solubility parameter for PDMS has been reported as 14.9 $\text{MPa}^{1/2}$ [10]. The squared difference in solubility parameters is essentially related to the enthalpy of mixing, and in a favored system, this value has to be as small as possible in order to obtain a negative free energy of mixing. In the general case of the PDMS-PI blends, this difference is quite large and phase separation is expected, although reports of experiments with PDMS-PI blends are difficult to find. In a recent report, Tiwari et al. [48] studied blends of PMDA-ODA and methylphenylsiloxane (PMPS) subjected to plasma ashing conditions and in the concentration ranges of 4.76–20.0% w/w PMPS in PI. These researchers also reported phase separation of the siloxane component on the cured films as measured by FT-IR microscopy. In additional work by the same group it has reported that siloxane-polyimide mixtures have improved thermal stability [49] and better physico-mechanical properties [50] over neat PI films.

The XPS results reported in the present study indicate the preferential segregation of the PDMS to the surface of the films. ARXPS spectra of films prior to blending, after blending, and following UV/ozone treatment are quite useful in understanding these systems. This set of reactions is considered to be the initial chemical transformation of the blend to yield a surface amenable to further chemical interactions. The exposure of the blend to UV/ozone irradiation not only yields changes in the siloxane part of the blend, but also alters the host polymer to some extent. These effects can be separated by irradiation studies on the individual components of the blend. The behavior of PDMS films on inert substrates has been shown to yield SiO_x and carbonaceous segments [12, 28]. A comparison of C1s spectra for PI films at 0, 5 and

Fig. 15 Adhesion testing methods for PI films

60 min exposure to UV/ozone indicates that some of the changes observed for the blends can be observed in pure PI films. The formation of carboxylated components, higher oxidation products, and oxidized nitrogen atoms occurs during the UV/ozone irradiation process. These results are in agreement with practical adhesion data that report improved adhesion of copper foils on PIs treated by this means of modification [51].

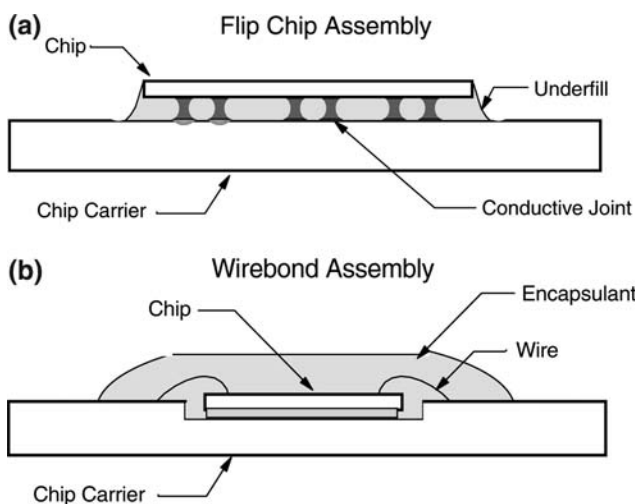
The depth of the siloxane layer has been estimated to be relatively shallow for two of the films used in this study. The transformation of siloxane to SiO_x domains in the mixture occurs with very short treatment times as verified by contact angle and XPS measurements. Since the positions of the two silicon environments present in a film are accurately known, curve-fitting the individual $\text{Si}2p$ envelopes in each experiment is useful

for estimating the concentrations of siloxane and SiO_x after treatment. For example, after 5 min of exposure, the 0.25% PDMS mixture contains 45.2% of silicon as siloxane groups and 54.8% as SiO_x . If the initial concentration of the same untreated film is known at the same sampling angle, the relative signal attenuation of the siloxane groups by the SiO_x can be estimated. The value of λ for silicon in a Si–O environment using monochromatized AlK_α radiation has been reported by Shioji et al. [52] to be 3.81 nm. These parameters can be used to estimate the thickness of the silicon oxide layer after treatment. The calculated values for this sample yield an approximate thickness of 5.3 nm. These results are in the range of previously reported values for siloxane films modified by plasma, UV only, or UV/ozone irradiation [53–55].

The AFM results indicate that the RMS values for films cast from PDMS–PI blends having low levels of PDMS are comparable to those for films cast without PDMS. It is also important to note that the 5-min treatment of the 0.25% PDMS blend preserves the RMS values of the untreated samples (see Table 1). Matienzo and Winnacker [8] have reported that brief treatment by UV/ozone did not significantly alter the roughness of polymer films, whereas plasma treatment of the same polymers increased the RMS roughness.

UV/ozone treatment for 60 min resulted in an increase in nano-roughness of the PDMS–PI blend. These physical changes on the treated surfaces lend themselves to better mechanical interlocking with film-formers from polymer precursors applied onto them to form a second PI layer.

A variety of treatments to produce PI-silica composites have recently been reported in the literature [56, 57]. These treatments have included silicon compounds that have undergone sol-gel reactions or hydrolysis of silicon-containing materials with attachment of the formed silica particles to the polymeric matrix via silane coupling agents. Another

**Fig. 16** Schematic representations of flip-chip (a) and wirebond (b) electronic packages. Device orientations are such that the chip surface (and passivation layer) are facing downward in (a) and upward in (b). Adhesion between the polyimide passivation layers on the surfaces of the IC devices and the underfill or encapsulant materials is critical for maintaining reliability of the package

approach used by Tiwari et al. [48] included oxygen plasma ashing of blends of PI–PMPS for long periods of time (20 h). Their results have shown that lower levels of PMPS addition (at much higher levels than those used here) did not have any influence in the degree of imidization of the PI–PMPS films. The long and extended plasma ashing process induced extensive roughness, and the resulting surfaces, as expected, were much rougher than the ones described here for UV/ozone treatments. However, it is important to mention that these blends showed higher fire resistance and preservation of mechanical properties as compared to the base PI. Based on these findings, it is believed that the lower concentrations of PDMS used in the present investigation preserve the bulk properties of the host PMDA–ODA film.

Conclusions

Significant segregation of PDMS has been demonstrated to occur at low concentration (0.25–1.4% wt/wt) of PDMS in PDMS–PI blended systems. SiO₂ films were formed by segregation and UV/ozone treatment of the blended PI films. The adhesion of a PI layer subsequently deposited onto these blended and modified substrates is greater than obtained between two layers of the pristine PI. As such, thicker films of PI can be obtained by multiple applications of the liquid resin PI precursors.

The chemical transformation of the blended film by UV/ozone treatment causes some degradation of the host polymer. The experiments with PMDA–ODA have shown the formation of C = O, R–C(O)O–R groups and other nitrogen containing species during the oxidation of the basic monomeric unit. These reactions, in combination with the transformation of siloxane groups to silica domains yield a surface layer that can interact favorably with pre-polymer components to form a thicker layer of PI after thermal curing. The contribution from nano-surface roughness induced in PDMS–PI blended films with low concentrations of PDMS and UV/ozone exposure for greater than 5 min, imparts a mechanical component to the adhesion. Both mechanical and chemical effects contribute as the two-layer PI film cures, and improved adhesion of the two-layer system has been demonstrated.

Acknowledgements The authors acknowledge Sarah W. Winnacker for assistance with film preparation and Kevin Chartrand for assistance with contact angle measurement. B.L. Pennington produced excellent SEM images of the films and F.

Ochanda, Binghamton University, was instrumental in helping with the reproducibility of AFM images.

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