J Mater Sci (2006) 41:6374–6384
DOI 10.1007/s10853-006-0713-4

Transformation of poly(dimethylsiloxane) into thin surface films of SiO_x by UV/ozone treatment. Part II: segregation and modification of doped polymer blends

L. J. Matienzo · F. D. Egitto

Received: 30 January 2004 / Accepted: 13 July 2005 / Published online: 2 September 2006

Abstract UV/ozone treatment of organic polymers having silicone additives to produce oxidized layers was achieved by doping a host polymer or prepolymer with a silicone additive, poly(dimethylsiloxane) (PDMS). The concentration of PDMS in the host polymer was low, typically in the range of 0.1–2.0% by weight. Host polymers were polyethylene, polyimide, and polyurethane. After film formation, the presence of PDMS was detected on the surface using X-ray photoelectron spectroscopy (XPS), consistent with wetting angle measurements that revealed a hydrophobic surface. The doped blend was then subjected to exposure in a UV/ozone environment such that a thin, stable barrier of SiO_x was formed at the surface of the film. Rate of film modification was monitored by XPS and measurement of advancing contact angle using deionized water. XPS measurements also showed some evidence of modified fragments of the host polymer near the surface. Significant segregation of PDMS and subsequent transformation to silicon oxides has been demonstrated to occur in these doped systems. The stability of the modified glassy surface formed by UV/ozone treatment of a commercially available epoxy formulation containing a silicone additive was shown to be superior to that obtained by other treatment techniques, e.g., oxygen plasma modification.

Introduction

Films of silicon oxides are used extensively, for example, as protective coatings or electrically insulating layers. Films of silicon oxides are required on polymers for a variety of applications. These applications include use as a hermetic seal against diffusion of oxygen and moisture [1–3], coatings for flame retardancy [4], abrasion resistance [5], and layers to promote adhesion to other materials [6]. Methods of forming SiO_x films on substrate surfaces include pyrolitic degradation of high molecular weight PDMS [7], spin-on coatings of sol–gels, e.g., of polysilsesquioxanes [5, 8, 9], sputter deposition [10], 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 SiO_2 [11], plasma-enhanced CVD (PE-CVD) [1, 12, 13], transformation of silicides to SiO_2 using ultraviolet (UV) lamps [14], treatment of monomolecular Langmuir-Blodgett films of silicones using low temperature radio frequency (rf) plasma [15] or UV/ozone [16], and UV/ozone treatment of siloxanes and silazanes to produce an SiO_x overcoat [6, 17].

On a thermodynamic basis, materials present in a mixture tend to orient themselves such that the resulting surface of the system has a minimized energy. If a molecule contains groups with different surface energies, molecular rearrangement or segregation of the lower surface energy component toward the surface is achieved. In a block copolymer whose segments differ in surface energy, block segments having lower surface energy will orient toward the surface [18]. This effect can also be observed in systems containing a polymer and metal atoms. Kovacs et al. [19, 20] studied

---

L. J. Matienzo · F. D. Egitto (✉)
Endicott Interconnect Technologies Inc., 1701 North Street, Endicott, NY 13760, USA
e-mail: egittofd@eitny.com

the deposition of several metal atoms on the surface of a styrene/hexyl-methacrylate copolymer. The results showed that atoms of the metal diffused into the polymer substrate (having lower surface energy) in a manner limited by the viscosity of the polymer. For a film formed as a blend of two polymers, the polymer having the lower surface energy will preferentially migrate to the surface of the film.

When two polymers are blended, the resulting morphology of the mixture depends upon the miscibility of the blend. Speaking very broadly, solubility parameters are a guide to the miscibility of two polymers. Similarity of solubility parameters favors miscibility [21]. However, other factors related to formation of the mixtures will affect miscibility. For example, mixing small volumes of material such that the volume fraction of one polymer in the blend is very small relative to the other is more favorable in terms of miscibility. In a blend of two polymeric materials having different surface energies, prepared such that the mixture is miscible, the material having the lower surface energy will preferentially migrate to the surface of the mixture during film formation. For example, formation of polymer films containing PDMS (surface energy on the order of 24×10^{-3} N/m) and polyimide, PI, (surface energy ca. 40×10^{-3} N/m), if the mixture is miscible, will result in a film surface that is rich in the low surface energy PDMS (Fig. 1a). Surface energies of these and other polymers are listed in Table 1. If the two polymer constituents of a blend are not miscible, or if the Gibbs free energy of a mixture of two polymers increases sufficiently, phase separation may occur, although it is possible for metastable homogeneous systems to exist [22].

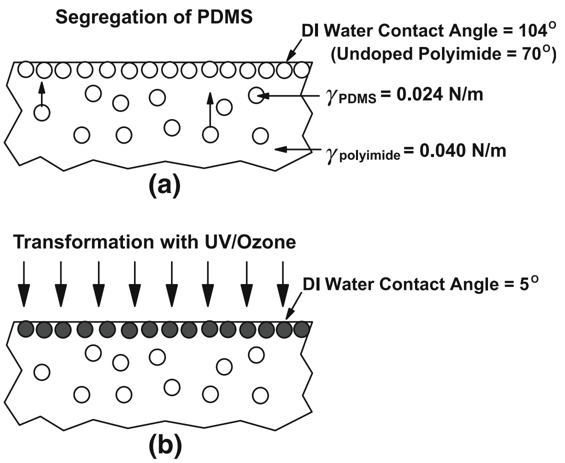

Fig. 1 Simplified schematic representation of segregation of PDMS in a PI matrix (**a**), and subsequent transformation of the siloxane to SiO_x upon exposure to a UV/ozone environment (**b**)

A summary of the various techniques that have been employed to transform the surface of organo-silicon films (like PDMS) to a silicon-oxide is given in ref. [17]. In addition to the use of UV/ozone treatment, other techniques included pyrolytic degradation [7], plasma [25–30], exposure to laser radiation [5, 31] or UV lamps [5, 14]. Ref. [17] addressed, in some detail, the various types of plasma system configurations and how these configurations affect the mode of surface modification. In addition, the authors described UV/ozone treatment apparatus and the gas-phase and gas/surface chemistry leading to modification of organic and organo-silicon polymers on unreactive (gold-coated) substrates.

The present paper presents the results of treatment of PDMS-doped polymers. Treatment of undoped PDMS films was reported as the result of a previous investigation [17]. The present paper focuses on chemical modification of surfaces that result from segregation of PDMS to the surface of the blend, without regard to whether the segregation is driven by thermodynamics (surface energy differences) or phase separation. No attempt was made to fully characterize the bulk morphology of the doped systems. However, results of X-ray photoelectron spectroscopy (XPS) and contact angle analyses suggest the presence of macroscopically homogeneous surfaces before and after modification, possibly due to the inherent limitations in resolution of these techniques.

Studies related to the miscibility of PDMS in blends with any of the polymers used in this investigation, especially at the very low concentrations of PDMS used in this paper, are sparse. In one report by Wang [4], it was reported (not surprisingly) that due to the large difference in solubility parameters between PDMS and urethane, macroscopic phase separation might occur during synthesis of PDMS/polyurethane copolymers and hence solvent selection for synthesis is critical. Wang observed that addition of 15% of PDMS to polyurethane resulted in a complex two phase morphology with the PDMS segment "microphase" separating from the polyurethane segments. In TEM, the spherical PDMS phase exhibited a diameter on the order of 100 nm. Wang proposed that the low surface energy of the PDMS segment tended to migrate to the surface of the polymer where it could be oxidized into a partially silicate-like material upon heating in air.

In contrast to previous investigations by the authors [17], in the present study the substrate underlying the PDMS-rich surface is itself subject to modification by the UV/ozone exposure. Films of SiO_x were formed on the surfaces of various polymers by a process involving (1) doping of the polymer or polymer precursor with poly(dimethylsiloxane) (PDMS), (2) preferential

Table 1 Surface energies for polymers used in this investigation

Polymer	Surface energy ($\times 10^{-3}$ N/m)	Reference
PDMS (dopant)	15–24	[23, 24]
Polyimides	37–41	[23, 24]
Polyethylenes	30–37	[23, 24]
Polyurethanes	36–39	[23]
Epoxies	40–50	[23]

segregation of the PDMS to the surface of the polymer blend during film formation, and (3) transformation of the siloxane to SiO_x using exposure to UV/ozone treatment. Characterization of treated and untreated film surfaces was performed using XPS and measurement of DI water contact angles. The effects of doping concentration of PDMS in the host polymers are also reported. Two examples of the use of this approach in engineering applications are described.

Experimental

Films were formed on polished silicon wafers having a crystalline orientation of (100) so that smaller rectilinear pieces of reproducible size and shape could be obtained by cleaving along orthogonal planes. Unless otherwise indicated, samples used for experiments were about 1.0 cm^2.

Doped polymer preparation

Chemical structures for PDMS and each of the polymers investigated in this study are shown in Fig. 2.

Polyimide

Polyimides have physical properties that make them especially suited for microelectronic applications. These properties include high thermal stability, low dielectric constant, excellent planarization, and high flexibility. As such, polyimide layers are widely used in the electronics industry to provide protection, electrical insulation, or both. Polyimide is also commonly employed as a barrier to alpha radiation in semiconductor devices. Polyimide layers may be formed by cross-linking a solution-deposited polyimide resin such as Pyralin® PI-5878 (®Pyralin is a registered trademark of E.I. DuPont de Nemours, Inc., Wilmington, Del. USA), containing polyimide precursors pyromellitic dianhydride (PMDA) and oxydianaline (ODA), and thermally curing.

A solution of the organo-silicon dopant was formed by mixing equal parts, by weight, of a high molecular weight PDMS grease (General Electric SE30) and hexane in a vial. This solution (0.4 g) was mixed with *N*-methyl pyrrolidone (6.4 g). The resulting solution was mixed with PI-5878 such that the final solution contained 21 g PI-5878 polyimide precursor, 6.4 g *N*-mehtyl pyrrolidone, 0.2 g PDMS, and 0.2 g hexane. For several experiments the amount of dopant solution added to the polyimide precursor was varied such that the final solution contained 0.1 g PDMS and 0.1 g hexane, and 0.3 g PDMS and 0.3 g hexane. Hence the concentration of PDMS in polyimide for these experiments ranged from 0.5% to 1.4% (wt/wt).

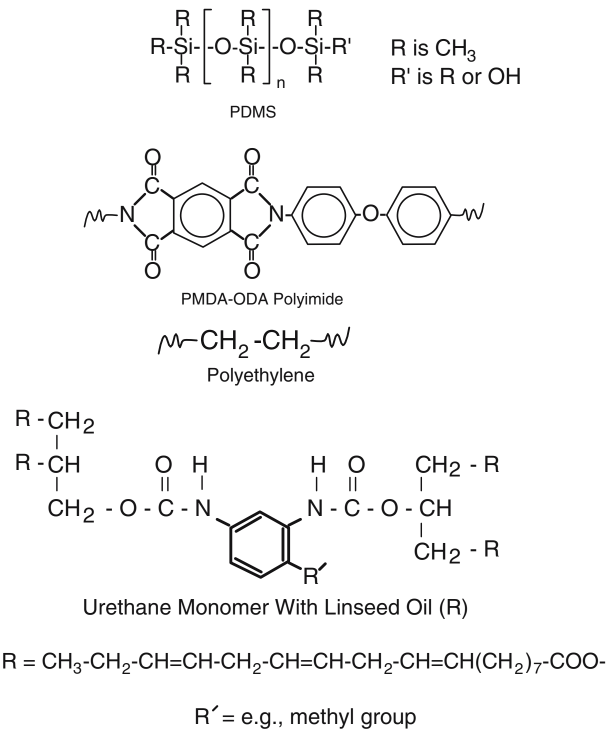

Fig. 2 Chemical structures of polymers used in this investigation

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-triethoxysilane) with 10 parts methanol and one part deionized water. The mixture was left standing in a stoppered bottled overnight. Just prior to use, 10 g of this solution was mixed with 400 ml methanol.

The adhesion promoter solution was spin coated onto silicon wafers at 2000 rpm for 30 s. The coated wafers were baked for 15 min in air at 110 °C. The doped polyimide precursor-containing solution was spin-coated onto these wafers at 6000 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 °C/min, holding at 350 °C for 60 min, and cooling to room temperature at a rate of 10 °C/min. During this curing step, the PDMS segregated to the surface of the film coating. Total final thickness of the films was 1.0 μm. For comparison, control films of undoped polyimide were prepared by the same technique, except that none of the PDMS dopant solution was added to the polyimide precursor solution.

Polyethylene

Polyethylene films are chemically inert, strong, and transparent. They are commonly used as flexible packaging materials for food products and moisture barriers in construction.

Free-standing films of low density polyethylene, 125 μm thick, were obtained from Northern Petrochemical Co., Des Plaines, IL, USA. The polyethylene was heated until molten in an aluminum tray on a hot plate. A solution containing equal parts of PDMS and hexane was added to the melt while stirring. A film was formed by pressing the molten mixture between flat surfaces. Final concentration of PDMS in polyethylene was on the order of 1% (wt/wt). Several experiments were also performed using the as-received, undoped polyethylene films.

Polyurethane

Thermoplastic polyurethanes exhibit high resilience and resistance to impact, tearing, abrasion and weather. As such, they are used extensively as protective coatings.

A 15% solution (wt/wt) of PDMS in hexane was prepared. Of this solution, 0.75 g was mixed with 40 g of Minwax® Fast-Drying Polyurethane formulation (® Minwax is a Registered Trademark of Minwax Company, Upper Saddle River, NJ, USA) in mineral spirits. The polyurethane/PDMS mixture (labeled ‘‘high concentration’’ below) was spin-coated as described above for the polyimide films. After coating, the films were allowed to dry in air at room temperature. A second mixture having half the concentration of PDMS (labeled ‘‘low concentration’’ below) was prepared in a similar fashion. A third set of undoped polyurethane films was prepared as control samples.

Epoxy

There is a wide variety of uses for epoxies including adhesives, corrosion control, and encapsulation of electronic components. One example of an epoxy used for the last of these applications is Hysol® 4450 (® Hysol is a registered trademark of Loctite, a Henkel Company, Bad Camberg, Germany), an epoxy-based integrated circuit die encapsulant material containing an organosilicon component [32]. It is likely that the organosilicon is added to alter the flow properties of the epoxy. The Hysol 4450 was applied to substrates using manufacturer-recommended procedures.

UV/ozone system

UV/ozone treatments were performed in a Uvocs, Inc., model T0606B UV/ozone cleaning system described in ref. [17]. The UV source is low-pressure mercury vapor grid lamp, in a serpentine pattern, with a quartz envelope. The serpentine lamp covers a square area, 152.4 mm on each side. Samples were placed 5.7 mm from the lamp envelope.

Plasma system

A detailed description of the system, parameters, and procedures used for plasma treatment is given in ref. [17 and 33]. Samples were placed on the RF electrode (cathode) of the reactive ion etching (RIE) system (chemical etching enhanced by bombardment of ions from the plasma). For several experiments, to perform modification in the absence of ion bombardment, a second quartz plate was placed above the sample such that the distance between the quartz-covered cathode and the second plate was less than the thickness of the space-charge sheath. That is, no plasma was sustained in the vicinity of the sample and treatment was due solely to reaction of neutral atomic oxygen.

Surface analytical techniques

A detailed description of the systems, parameters, and procedures used for measurement of advancing DI water contact angles and XPS on treated and untreated samples is given in ref. [17]. XPS analyses were collected with an angle of 65° between the surface of the samples and the analyzer.

Results and discussion

UV/ozone treatment of PDMS-doped PI films

Advancing DI water contact angle is shown as a function of treatment time for neat PI and for two

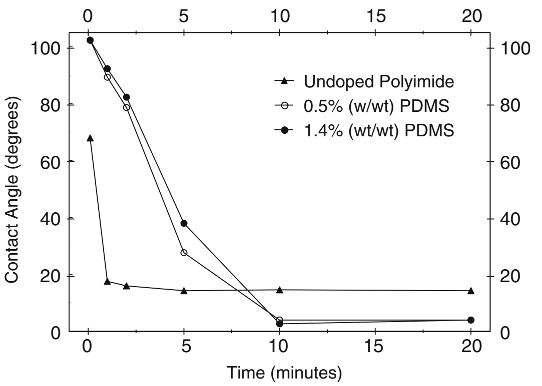

Fig. 3 Advancing DI water contact angle for undoped and PDMS-doped PI films as a function of UV/ozone treatment time

different concentrations of PDMS in PI in Fig. 3. The curves for the doped polymer do not differ significantly from each other. In an earlier investigation using neat PDMS films, Egitto and Matienzo [17] reported that the rate of change in contact angle with UV/ozone treatment decreased as the thickness of the PDMS film increased. One can therefore conclude that doping of the PI at the lower concentration is sufficient to fully modify the surface by migration of PDMS to the surface. Even lower concentrations may likely be adequate for full modification of the surface while preserving the bulk properties of the PI film. Full modification 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 reported in ref. [17]. Contact angle for the undoped and untreated PI is lower than that measured for the untreated doped films. However, extended exposure to UV/ozone results in a doped film surface that is more hydrophilic than that of the treated neat PI film.

High resolution XPS spectra in the Si 2*p* region are shown for PDMS-doped PI, before and after treatment, in Fig. 4a. The peak at 102.3 eV, observed prior to treatment, can be attributed to O–Si–C bonds in the siloxane and the peak at 103.4 eV, observed following treatment, corresponds to contributions from SiO_x, similar to what was observed for neat PDMS films before and after treatment, respectively [17]. That is, upon exposure to the UV/ozone environment, the segregated PDMS behaves in a fashion similar to that observed for transformation of neat PDMS on a gold-coated substrate [17].

Figure 4b presents a comparison of C 1*s* spectra for an untreated, undoped PI film, doped PI film (0.5% wt/wt of PDMS) after cure, and the same film after 20 min of exposure to UV/ozone. The characteristic C 1*s* region of a PMDA–ODA polyimide contains a distinct

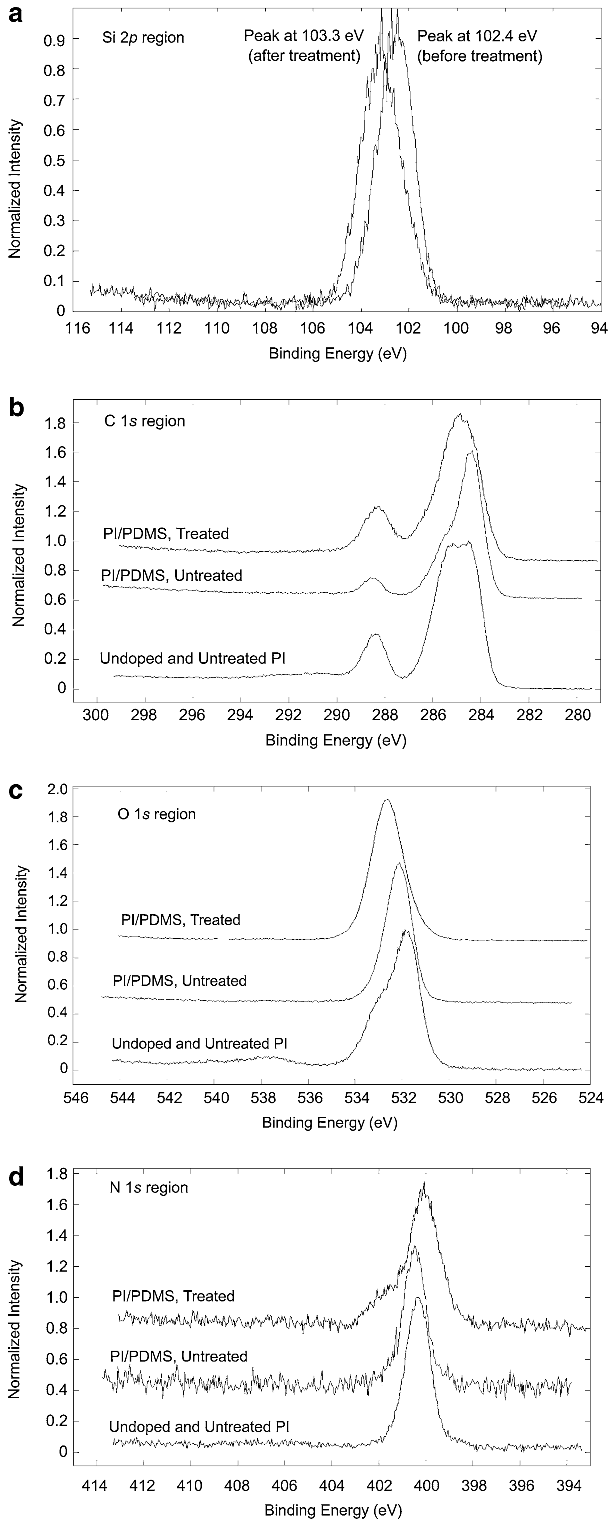

Fig. 4 High resolution XPS spectra in the Si 2*p* region for PI/PDMS (0.5% wt/wt) before and after treatment for 20 min with UV/ozone (**a**). High resolution spectra in the C 1*s* (**b**), O 1*s* (**c**), and N 1*s* (**d**) regions for undoped and untreated PI, PI/PDMS before treatment, and PI/PDMS after treatment for 20 min

separation between the carbonyl groups located ca. 289 eV and two intense signals ca. 284.8 eV and 285.4 eV. Detailed explanations of the spectrum for the untreated PI film are abundant in the literature [34, 35, and references therein]. Notice that in the region intermediate to these binding energies, the envelope reaches the baseline of the spectrum. After the film is cured and PDMS migrates to the surface, the spectrum exhibits the dominance of a hydrocarbon signal and decreased intensity of the carbonyl band. In other words, the PDMS is efficiently covering the surface of the polymer. Following treatment in UV/ozone, the carbonyl region is not as intense as for polyimide and it is likely associated with the appearance of oxidized groups on the polyimide. In essence, the resulting film contains the oxidation products of PDMS, but because the segregated and modified film is thin, some oxidation of the underlying PI is also detected and this appears to be unavoidable.

Analysis of the O 1*s* region of the XPS spectra is presented for the same three samples in Fig. 4c. The main O 1*s* signal of polyimide associated with the imide ring appears at 532.1 eV (C=O) with a second contribution at 533.0 (C–O–C). PDMS segregation and transformation yields a single signal at 532.9 eV. The position of this signal is in agreement with the reported binding energy for SiO_2 [36]. Figure 4d shows the N 1*s* spectra of the three samples. The doped polyimide sample still contains a single N 1*s* signal coincident with the location of the same in undoped polyimide. It is only after UV/ozone oxidation that a second small signal at 402.1 eV is detected. The intensity of the nitrogen peak is diminished compared to the undoped control sample. Detection of nitrogen in the doped material suggests that the PDMS-segregated layer is thin, certainly less than 10 nm. The possibility of detection of nitrogen by virtue of a discontinuous PDMS layer is not likely per the discussion of the C 1*s* spectra above. A slight shift of about 0.7 eV to a higher binding energy value is detected on the doped and treated films, relative to the control film. It is possible that the shift in binding energy that occurs with doping may be due to interaction of the nitrogen in the polyimide with hydrogen atoms in the terminal silanol groups of the PDMS. No further binding energy shift is detected upon UV/ozone treatment. This is not surprising since (1) the polyimide is sufficiently covered with PDMS, and (2) nitrogen atoms do not oxidize upon UV/ozone treatment, a result that has been reported for treatment of other organic polymers containing both oxygen and nitrogen atoms [2].

UV/ozone treatment of PDMS-doped PE films

Advancing DI water contact angle is shown as a function of UV/ozone treatment time in Fig. 5. Data are shown for treatment of both front and back sides of the free-standing film. As one might expect, behavior is the same for both sides. Even for treatment times as long as 50 min, an equilibrium value for contact angle was not achieved. For comparison, the contact angle for undoped and untreated PE is 95° and is shown by the dashed line in the figure.

High resolution XPS spectra in the C 1*s* region are shown for treated and untreated PE/PDMS films in Fig. 6. The spectrum for the untreated film is for all practical purposes indistinguishable from that of either neat PDMS or undoped PE. Upon treatment, a little broadening occurs, indicative of a slight degree of oxidation of the carbon-containing chains. Si 2*p* spectra after UV/ozone treatment (not shown here) reveal similar results to those observed for PI/PDMS, i.e., transformation of the segregated PDMS to SiO_2.

UV/ozone treatment of PDMS-doped PU films

Advancing DI water contact angle is shown as a function of treatment time for neat PU and for two different concentrations of PDMS in PU in Fig. 7. As was observed for PI/PDMS, the curves for the doped films do not differ significantly from each other. One can therefore conclude that doping at the lower concentration is sufficient to fully modify the surface by migration of PDMS to the surface and doping at even lower concentrations would likely be adequate for full modification of the surface while preserving the bulk properties of the PU film. An equilibrium value for contact angle was not achieved until treatment times

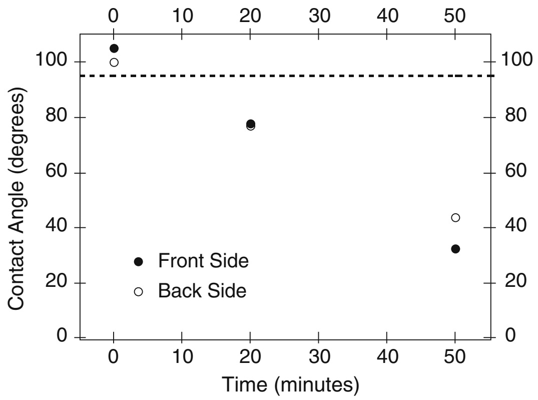

Fig. 5 Advancing DI water contact angle for PDMS-doped PE films as a function of UV/ozone treatment time. The dashed line indicates the value for undoped and untreated PE (95°)

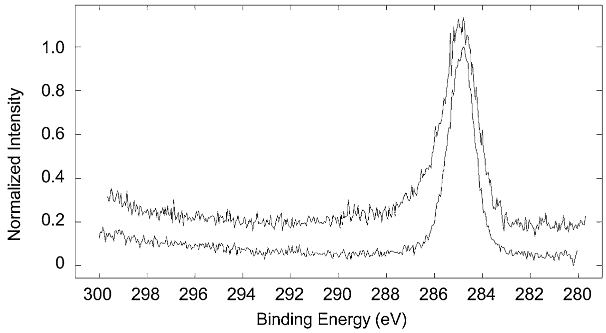

Fig. 6 High resolution XPS spectra in the C 1*s* region for PDMS-doped PE before (lower trace) and after (upper trace) treatment for 14 min with UV/ozone

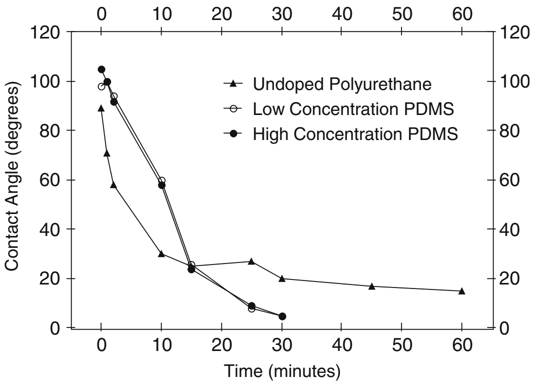

Fig. 7 Advancing DI water contact angle for PDMS-doped PU films as a function of UV/ozone treatment time

were greater than or equal to 30 min. Contact angle for the undoped and untreated PU is lower than that measured for the untreated doped films. However, extended exposure to UV/ozone results in a doped film surface that is more hydrophilic than that of the treated neat PU film. The comparative contact angle behavior of the doped and undoped PU films is similar to that observed for doped and undoped PI films (Fig. 3).

High resolution XPS spectra in the C 1*s* region are shown for treated and untreated PU/PDMS films in Fig. 8. The spectrum for the untreated film is very much similar to that shown for PU in ref. [37]. The strongest contribution is due to aliphatic and aromatic hydrocarbons with a shoulder around 286 eV due to C–O– linkages. A contribution from the carbon in the urethane group is detected around 289 eV. For the treated PU/PDMS, a much higher degree of oxidation of the carbon occurs than was observed for either PI/PDMS or PE/PDMS treatments.

Treatment of silicone-containing epoxy-based materials

Samples of a commercially available epoxy-based encapsulant (Hysol 4450) containing some silicone and other inorganic (silica) fillers were exposed to UV/ozone and oxygen plasma treatments for various durations. As shown in Fig. 9, advancing DI water contact angles on the Hysol surfaces were reduced from initial average values greater than 100° to a values less than 10° for UV/ozone and plasma treatments. Contact angles were then monitored as a function of time during storage in lab ambient conditions. As Fig. 9 shows, the UV/ozone treated surface maintained its high degree of hydrophilic character, while the plasma-treated surfaces reverted back to a more hydrophobic character.

High resolution XPS in the Si 2*p* region suggests that during UV/ozone and plasma treatments of the Hysol material, O–Si–C bonds in the siloxane, observed prior to treatment, are converted to SiO_x, where x is between 1.6 and 2. This is illustrated in Fig. 10 which shows high resolution XPS spectra in the Si 2*p* region for silicone samples before treatment (a), after 2 min of O_2 plasma treatment (b), and after 50 min of UV/ozone exposure (c). The spectrum of the untreated sample (a) contains contributions from the silicon containing polymer (low binding energy) and silica filler (higher binding energy). After treatment (b and c), the silicone is transformed into a glassy surface (higher binding energy). Because of the results observed with the polymer systems that are not silica-filled (above), it is believed that the signals in Fig. 10, curves **b** and **c**, are the result of transformation to SiO_x and not exposure of underlying silica-filler particles.

XPS examination of surfaces aged for greater than 40 days revealed that the UV/ozone-treated and plasma-treated surfaces retained a strong SiO_x contribution. The increase in contact angle with time after treatment for plasma-treated parts is due primarily to a combination of several phenomena; (1) some diffusion of silicone material from the bulk of the encapsulant to the surface, (2) changes in surface groups, e.g., decrease in carbon–oxygen groups, perhaps by some reorientation, and (3) adsorption of adventitious carbon. All of these factors influence the surface wetting properties. In addition, the observation that the UV/ozone-treated surface maintains a highly hydrophilic nature indicates that in addition to resisting diffusion, the UV/ozone-treated surface is resistant to contamination from the environment. Niwano et al. [38, 39] have reported oxidation of monocrystalline silicon in UV/ozone ambients and suggested that this oxide film functions as a protective layer for adsorption of adventitious carbon impurities onto the Si substrate upon exposure to air. Although the exact mechanisms leading to these differences in the surface properties resulting from each of the treatments are unknown at

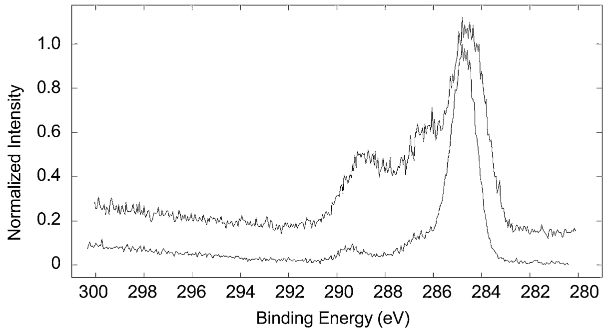

Fig. 8 High resolution XPS spectra in the C 1*s* region for PDMS-doped PU before (lower trace) and after (upper trace) treatment for 6 min with UV/ozone

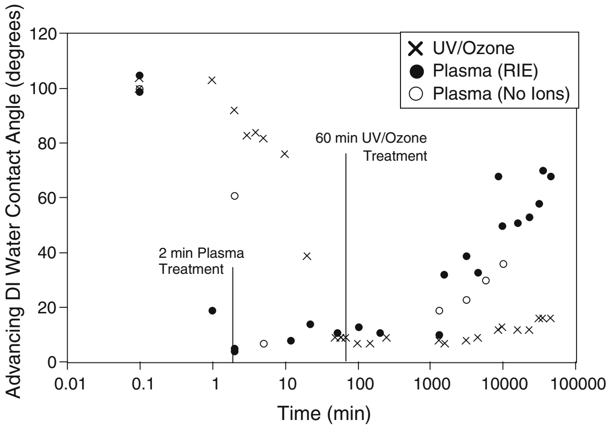

Fig. 9 Advancing DI water contact angle as a function of duration in UV/ozone and oxygen plasma treatments. Contact angles were also measured as a function of time following treatment

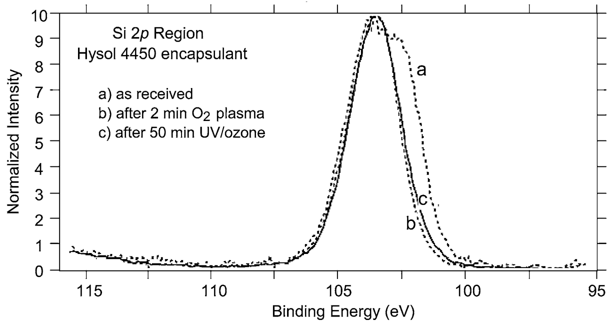

Fig. 10 High resolution XPS spectra in the Si 2*p* region for samples of Hysol 4450 encapsulant material before treatment (**a**), after 2 min of O_2 plasma treatment (**b**), and after 50 min of UV/ozone exposure (**c**)

this time, one might suspect that the presence of the intense UV exposure and/or the absence of bombardment by kinetically energetic particles in the UV/ozone system may impart such favorable properties. In addition, since under the conditions employed in this study material removal is more pronounced in the plasma system, the formation of the protective barrier may be less effective than that produced using UV/ozone treatment.

Comparison of XPS analyses for various polymer systems

Atomic concentrations from XPS are given in Table 2. For untreated PDMS, atomic ratios are consistent with the molecular structure shown in Fig. 2. After treatment, the ratio Si/O is on the order of 1/2 [17].

For doped PE, segregation of PDMS to the surface results in atomic ratios that are consistent with neat PDMS. PI/PDMS film curing induces enrichment of oxygen and silicon and the surface compositions also resemble those of a pure PDMS film. Spectra for doped PI show some contribution from the PI matrix below the segregated PDMS surface (0.4% N). However, as for PDMS and doped-PE, upon treatment Si/O goes to 1/2, i.e., following the UV/ozone treatment, the film is mainly silicon dioxide. The presence of nitrogen in the spectra for both the treated and untreated PI/PDMS films suggests that the thickness of the segregated layer and the resulting modified glassy surface layer are thin, less than 10 nm. This estimate is based on the escape depth of C1*s* photoelectrons in polyimide, calculated to be 8.8 nm for electron energies of 1200 eV, using a value of the inelastic mean free path of 3.25 nm as reported by Tanuma et al. [40] and an angle of the sample to the analyzer of 65°. In addition, the concentration of nitrogen remains unchanged with treatment. This is not surprising since even for neat PI, degradation of the PI would occur primarily at the imide ring without nitrogen loss [34]. For PU/PDMS, elemental analysis indicates an increase (about 2×) in concentration of N and an enhancement of the contribution at 289 eV upon treatment of the PU/PDMS film (Fig. 8). This is in agreement with the results of Yang et al. [41] for neat PU exposed to UV (340 nm) and moisture. Fourier transform infrared (FTIR) spectroscopy results provided strong evidence for the formation of hydrophilic degradation products such as polyurea. For untreated PU/PDMS, Si/O is not 1/1, but is very nearly 1/2. This may be due to the inclusion of oils (e.g., linseed oil) attached as branches in the polyurethane coating used in this experiment [42]. The surface tension of linseed oil is 25×10^{-3} N/m [43], on the order of that for PDMS. These low surface energy oil segments likely take on an orientation toward the surface, competing for space with the segregated PDMS. Hence, higher carbon content is observed (64.3%). Evidence for this preferential orientation is

Table 2 Atomic compositions obtained from XPS survey spectra for surfaces of PDMS, and for polymer blends of PDMS with PI, PE, and PU

Sample	C	O	Si	N
PDMS (theoretical)	50.0	25.0	25.0	-
PDMS (48 nm), Untreated	50.0	25.5	24.5	-
PDMS (48 nm), 13 min UV/Ozone [17]	22.5	54.0	23.5	-
PE (theoretical)	100.0	-	-	-
PE/PDMS (1% wt/wt), Untreated	52.0	24.2	23.8	-
PE/PDMS, 80 min UV/Ozone	34.3	43.4	22.3	-
PI (theoretical)	75.9	17.2	-	6.5
PI, Untreated	76.7	16.0	-	7.6
PI/PDMS (1.4% sample), Untreated	47.3	29.5	22.5	0.7
PI/PDMS (1.4% sample), 20 min UV/Ozone	17.7	55.3	26.1	0.9
PU/PDMS (High), Untreated	64.3	22.9	11.7	1.1
PU/PDMS (High), 30 min UV/Ozone	35.8	48.2	13.5	2.5

given by the relatively greater wetting angles (ca. 90°) measured for the undoped PU films. As observed for PI/PDMS, the presence of N in the doped PU film indicates that the segregated PDMS layer is thin. In addition, unlike treated PI/PDMS and PE/PDMS systems for which Si/O is 1/2, for the treated PU/PDMS film surface Si/O is about 1/3.6.

Not all oxygen observed on the treated surfaces is bound as Si–O. For example, high resolution C 1*s* spectra for treated PE/PDMS shows formation of a small amount of oxidized segments. Creation of carbon–oxyen groups occurs to a greater degree for treated PI/PDMS, and to an even greater degree for treated PU/PDMS than for PE/PDMS systems. The imide rings in polyimides are known to be highly reactive and form carboxylic groups upon exposure to UV and/or oxidizing environments [35]. It is possible for the underlying host polymer to be affected by UV irradiation since neither the SiO_2 nor the PDMS absorb well at these wavelengths. Unsaturated groups in the branches of PU are particularly susceptible to oxidation [44], especially for those containing groups that are highly-susceptible to oxidation, such as linseed oils [44].

The carbon in the spectra for treated films results from a combination of contributions from residual carbon in the silica network, carbon from the host polymer (or decomposition products of the host polymer), and environmental surface contamination. Temperatures on the order of 350 °C to 800 °C are required for complete carbon elimination [45]. At the low temperatures (near room temperature) of the experiments in the present study, it is not possible to fully eliminate the presence of carbon in the modified films. Furthermore, the amount of carbon on all UV/ozone-treated surfaces is less than 36%, comparable to levels of adventitious carbon that might be observed on a "clean" Au surface (Table 2).

Differences in behavior among the various doped systems may result from different activities of host polymers in the UV. For example, PE, like PDMS, is relatively more transparent in the UV [46] than PI and PU, both of which possess aromatic chromophores. Also, there are differences in reaction/volatilization in oxidizing environments among the structures of the different host polymers. Cain et al. [47] demonstrated that the etching rate of PE in O_2 RIE plasmas was greater than that observed for PI . Taylor and Wolf [48] showed that, in general, the etching rates of non-aromatic polymers in O_2 plasmas was greater than that observed for aromatic polymers.

Some engineering applications

Adhesion of a polyimide layer deposited onto a PDMS-doped and modified PI surface was found to be greatly improved when compared to the adhesion obtained for deposition onto an undoped and pristine polyimide surface [49]. This suggests that the structural integrity of the polymer blend and underlying host polymer is maintained, and no weak boundary layers are generated during UV/ozone exposure. Therefore, modification of the host polyimide polymer that occurs during exposure is not necessarily problematic. This is not surprising since it is well documented that adhesion to polymer surfaces can improve with treatment by plasma, UV, or UV/ozone [26]. As such, it is possible to obtain thick films of polyimide by multiple applications of the liquid resin polyimide precursors, potentially useful when additional protection against alpha radiation in semiconductor devices is desired. Such radiation can lead to generation of soft errors [50].

A second potential application of the methods described in this paper is formation of a gas diffusion barrier at the surface of a variety of polymers [3].

The stability of the UV/ozone-treated encapsulant surface, described in section 'Treatment of silicone-containing epoxy-based materials' and shown in Fig. 9 above, is indicative of the formation of a thin, protective barrier against diffusion. Park et al. [51] reported that UV/ozone treatment of poly(imide siloxane) copolymers decreased gas permeability for helium, oxygen, nitrogen, and carbon dioxide when compared with the permeability for their non-treated counterparts.

Conclusions

Significant segregation of PDMS has been demonstrated to occur in doped systems for which there is a difference in surface energies between the PDMS and the host polymer. No attempt was made to fully characterize the bulk morphology of the doped systems. Results of XPS and contact angle analyses suggest the presence of macroscopically homogeneous surfaces before and after modification, but a more detailed study of the morphology of PI/PDMS blends is reported in ref. [52]. SiO_2 films have been formed by segregation and UV/ozone treatment for a number of different polymers. The chemical structure of the host polymer affects the composition of the surface films that result from treatment because the segregated PDMS film is thin and transparent at wavelengths above 184.9 nm, allowing for modification of the underlying host polymer. In turn, some of the decomposition products of the host may be found within the sampling depth of the XPS instrument. Measurement of Si/O ratios can therefore differ from the expected ratio of 1/2. UV/ozone generated SiO_x films on epoxies have been demonstrated to be much more stable than SiO_x films generated by other techniques, e.g., plasma oxidation.

Acknowledgments The authors acknowledge Dr. Steven Fuerniss and Sarah Winnacker for assistance with film preparation, Kevin Chartrand for assistance with contact angle measurement, and Bruce Morrison for preparation of silane-doped epoxy samples.

References

1. Brody AL (2003) Food Technol 57:75
2. Matienzo LJ, Winnacker SK (2002) Macromol Mater Eng 287:871
3. Egitto FD, Matienzo LJ, Morrison BO Jr (1997) US Patent 5:693–928
4. Wang F (1998) Doctoral Dissertation. Virginia Polytechnic Institute, Blacksburg, VA, USA
5. Arkles B, Janeiro B, Berry DH, Ezbiansky KA, Composto R (2000) In: Proceedings of silicones in coatings III, Barcelona, Spain, 28–30 March, 2000, (The Paint Research Association, Teddington Middlesex, UK, p 1
6. Egitto FD, Matienzo LJ, Spalik JM, Fuerniss SJ (1995) In Proceedings of the MRS spring meeting: polymer/inorganic interfaces II, 385. MRS, San Francisco, CA, USA, pp 245
7. Seyferth D (1990) Adv Chem Ser 224:565
8. Arkles B, Berry DH, Figge LK, Composto RJ, Chiou T, Colazzo H, Wallace WE (1997) J Sol–Gel Sci Technol 8:465
9. Pan Q, Gonzalez GB, Composto RJ, Wallace WE, Arkles B, Figge LK, Berry DH (1999) Thin Solid Films 345:244
10. Ghate PB (1982) In: Bunshah RF (ed) Deposition technologies for films and coatings. Noyes Publications, Park Ridge, NJ, USA
11. Kurosawa K, Maezono Y, Miyano J, Motoyama Y, Yokotani A (2001) J Phys 11:739
12. Pecheur A, Autran JL, Lazarri JP, Piners P (1999) J Non-Cryst Solids 245:20
13. Hitchman ML, Alexandrov SE (2001) Electrochem Soc Interface 10(2):40
14. Li J, Mayer JW, Matienzo LJ, Emmi F (1992) Mater Chem Phys 32:390
15. Kalachev AA, Mathauer K, Hohne U, Mohwald H, Wegner G (1993) Thin Solid films 228:307
16. Mirley CL, Koberstein JT (1995) Langmuir 11:1049
17. Egitto FD, Matienzo LJ J Mater Sci, this issue
18. Li L, Chan C-M, Liu S, An L, Ng K-M, Weng L-T, Ho K-C (2000) Macromolecules 33:8002
19. Kovacs GJ, Vincent PS, Tremblay C, Dundsack L (1983) Thin Solids Films 101:101
20. Kovacs GJ, Vincent PS (1984) Thin Solids Films 111:65
21. Billmeyer FW Jr (1971) Textbook of Polymer Science, 2edn. John Wiley and Sons, Inc., New York, p 41
22. Barton AFM (1983) Handbook of solubility parameters and other cohesion parameters. CRC Press, Inc., Boca Raton, FL
23. Wu S (1999) In: Brandrup J, Immergut EH, Grulke EA (eds) Polymer handbook, 4th edn. John Wiley and Sons, Inc., NewYork
24. The Sabreen Group, Inc., Plano, TX, USA, Plastics Technical Reference Library, www.sabreen.com/index (2001)
25. Egitto FD, Vukanovic V, Taylor GN (1990) In: Agostino RD' (ed) Plasma deposition, treatment, and etching of polymers, Academic Press, Inc., San Diego, CA, pp 321–422, and references therein
26. Egitto FD, Matienzo LJ (1994) IBM J Res Develop 38(4):423
27. Roberts ED (1973) J Electrochem Soc 120:1716
28. Feneberg P, Krekeler U (1976) US Patent 3:959
29. Owen MJ, Smith PJ (1994) J Adhes Sci Technol 8(10):1063
30. Taylor GN, Wolf TM, private communication
31. Sharma J, Berry DH, Composto RJ, Dai H-L (1999) J Mater Res 14:990
32. Gaynes MA, Morrison BO, Egitto FD, Matienzo LJ, unpublished results
33. Egitto FD, Emmi F, Horwath RS, Vukanovic V (1985) J Vac Sci Technol B 3:893
34. Matienzo LJ, Unertl WN (1996) In: Gosh MK, Mittal KL (eds) Polyimides: fundamentals and applications. Marcel-Dekker, New York, p 659
35. Egitto FD, Matienzo LJ (1996) In: Gosh MK, Mittal KL (eds) Polyimides: fundamentals and applications. Marcel-Dekker, New York, p 419
36. Moulder JF, Stickle WF, Sobol PF, Bomben KD (1992) Handbook of X-ray photoelectron spectroscopy. Perkin-Elmer Corporation, Eden Prairie, MN, USA

37. Beamson G, Briggs D (1992) High resolution XPS of organic polymers: the scienta ESCA300 database. John Wiley & Sons, Chichester, UK p 211
38. Niwano M, Suemitsu M, Ishibashi Y, Takeda Y, Miyamoto N, Honma K (1992) J Vac Sci Technol A 10:3171
39. Niwano M, Kageyama J, Kinashi K, Miyamoto N, Honma K (1992) J Vac Sci Technol A 12(2):465
40. Tanuma S, Powell CJ, Penn DR (1994) Surf Interface Anal 21:165
41. Yang XF, Vang C, Tallman DE, Bierwagen GP, Croll SG, Rohlik S (2001) Polym Degrad Stab 74:341
42. Wells ER (1974) In: Martens CR (ed) Technology of paints, varnishes and laquers. Robert E. Krieger Publishing Company, New York, p 210
43. U.S. Coast Guard, Department of Transportation (1985) CHRIS (Chemical Hazards Response Information System) hazardous chemical data, vol 2. U.S. Coast Guard, Washington, D.C. Volume 2
44. Solomon DH (1967) The chemistry of organic film formers. John Wiley & Sons, Inc., New York
45. Joubert O, Hollinger G, Fiori C, Devine R, Panier P, Pantel RJ (1991) Appl Phys 69(9):6647
46. Partridge RH (1966) J Chem Phys 45:1685
47. Cain SR, Egitto FD, Emmi F (1987) J Vac Sci Technol 5(4):1578
48. Taylor GN, Wolf TM (1979) In: Proceedings of the Reg. Tech. Conf. on Photopolymers, Ellenville, NY, USA (Mid-Hudson Sect., Soc. Plast. Eng., 1979) p 175
49. Egitto FD, Matienzo LJ (2003) US Patent 6:656
50. Flack WW, Kulas S, Franklin C (2001) In: Progler CJ (ed) Proceedings of SPIE conference on optical microlithography XIV, vol 4346. SPIE, Bellingham, WA, p 945
51. Park HB, Han DW, Lee YM (2003) Chem Mater 15(12):2346
52. Matienzo LJ, Egitto FD (2006) J Mater Sci, accepted for publication