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A model system for the optimization of lamination parameters of PTFE-based dielectrics and metal surfaces

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Abstract In microelectronic packaging, organic dielectric materials continue to displace ceramic materials because of cost, reduced weight, and performance advantages. Because thermosetting dielectric composites have long found widespread use in printed wiring board (PWB) fabrication, they have been the components of choice for many organic chip carriers. Conversely, thermoplastic dielectrics, such as fluoropolymer (FP), and in particular poly(tetrafluoroethylene)-based dielectric composites (PTFE composites) have seldom found use in multilayer wiring packages in spite of their attractive electrical properties due to their processing challenges. In this paper, we report the use of a model system comprising pure PTFE film and Cr-coated copper surfaces to optimize the bonding process through lamination conditions for a fluoropolymer composite and chromium-coated copper surfaces and to study both the interface mechanics and its chemistry as a function of processing parameters. The significant finding of the investigation was the linkage between the macroscopic mechanical properties of the interface and the observable chemical alteration of the same under some lamination conditions. The relationship of the interface properties and the processing conditions extend a conceptual framework for the thermodynamics of the metal-polymer interface and the reliability of these electronic packages in their practical designs.

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Introduction

Until recently, the materials of preference for packaging high-end integrated circuits have been ceramic dielectrics. Chosen for their attractive properties such as low moisture uptake, low thermal expansion, and low dielectric loss, ceramics provide a stable package for interconnecting a chip to a circuit card. However, as chips have become more powerful and larger, and economies of scale have continually reduced their cost, more reliable and cost-efficient packaging of chips has been required. To this end, there has been a continued shift toward packaging integrated circuits using organic dielectric composites [1, 2].

A microelectronic package meeting these requirements must be fabricated with a highly optimized material set, including conductors and stiffeners, organic dielectric layers, bonding films, adhesives, underfills and thermal compounds. The design concept of this package is to limit thermally induced stresses that arise from the intrinsic difference in thermal expansion of the chip (3 ppm/°C) and a conventional printed wiring board (17 ppm/°C) [1, 2]. The particular material of interest in our investigation is the base laminate dielectric layer, a thermoplastic organic dielectric composite. Chosen for its low effective stiffness, low thermal expansion, low moisture absorption, and excellent electrical properties, it is a composite of PTFE filled with silica particles.

Due to the cyclic stresses that occur during intrinsic thermal cycling of electronic components in their expected service life, accelerated thermal cycling is used to study failure modes and lifetime statistics, and reliability modeling is used to predict real-world fatigue performance. As is true in a wide array of materials and especially in composites, measures such as tensile strength, fracture toughness, and interfacial adhesion are not necessarily

predictive of fatigue performance. Noting that reliability testing can be time consuming and expensive, it is in the interest of rapid and efficient product development cycles to gain fundamental understanding of the relationship between manufacturing processing conditions and resulting fatigue and damage mechanisms in materials.

Unlike more conventional thermosetting dielectric materials that are widely used in the printed wiring board industry, PTFE-based dielectrics generally require high melt processing temperatures (>327 °C for PTFE), and they must be processed at temperatures beyond their melt. Further, because of their dramatically different rheology and reactivity, compared to thermosetting materials, substantially higher pressures are required during lamination. Electronic packaging applications also contain layers of conducting metals such as copper. However, this complex mixture of materials can develop stresses that affect the electrical and mechanical performance of a package. This is further complicated by the poor reactivity of copper surfaces with fluoropolymers as compared with chromium and other metals under typical lamination conditions [3]. Thus, in the case of a highly stressed interface between copper and PTFE, the strength and reliability are enhanced by sputtering a thin chromium layer on the copper surface prior to lamination [4]. Beyond strength and reliability, other characterization techniques that provide a description of the interfacial region between the dielectric material and the metal are required to provide fundamental understanding of subsequent processing steps. X-ray photoelectron spectroscopy (XPS) has been extensively used to determine surface compositions as well as surface behavior of materials subjected to various fabrication and modification processes. For example, Egitto and Matienzo have used XPS and complementary techniques to follow the evolution of PTFE and PE (polyethylene) surfaces treated downstream from microwave plasmas to understand the interactions of these surface-modified polymers [5]. Other examples of XPS complementing the measurement of mechanical properties of materials can be found elsewhere [6–8].

The above-mentioned approaches are even more critical in the understanding of more complex systems such as those provided by the interfaces that contain a polymeric composite and a metal. Composite materials contain, in addition to the polymer matrix, fillers, coupling agents [9], surfactants [10], surface modified layers, and impurities. Matienzo and Shah have used a combination of XPS and DRIFT (diffuse reflectance IR spectroscopy) to optimize the mechanical properties of surface-treated phlogopite particles in organic composite applications [11]. In the case of fluoropolymers, experimental conditions to perform XPS measurements need to be carefully selected to avoid material degradation during the analysis leading to erroneous results. Thus, previously determined conditions for XPS that minimize material degradation are required [12].

While a thin layer of chromium was proven to be effective in increasing the copper-to-PTFE adhesion strength, high cycle reliability testing revealed a previously unforeseen failure mechanism along the PTFE composite/chromium interface. However, the failures could not be reproduced in mechanical testing of coupons fabricated under a range of lamination temperatures and material lots. Both adhesion strength and FP dielectric fatigue life diminished with increasing time and temperature as expected, but the failure mechanisms were unchanged. Peel tests always revealed visually cohesive fractures in the PTFE dielectric material, whereas the reliability failures in temperature cycling were visually adhesive (although surface analysis revealed an extremely thin residue of PTFE-silica on the chromium surface).

The approach to understanding the long-term thermal cycling failures of the package was to reproduce the failure mechanism in short-term mechanical testing of coupons and to link the occurrence of the failures to process conditions. The present work uses a model system comprising pure PTFE (free of filler particles) and a chromium-treated copper surface subjected to various processing temperatures to understand the critical interactions in the optimization of lamination parameters. Preliminary work on the metallization of PTFE and a fluoropolymer composite with chromium atoms has shown that similar chemical interactions developed on both types of fluorinated surfaces [13]. These results are then applied to optimize the durability of the interfaces of a fluoropolymer composite under simulated stress conditions. The model system enabled a detailed study of the effect of processing on the adhesive strength because it duplicated the visually adhesive failure mode previously only seen in fatigue testing. Further, results were verified by stress testing of the optimized conditions with prototypes produced at various lamination temperatures.

Experimental

Copper foils and PTFE film

A cladded 50-μm Cu-Invar-Cu foil (25% Cu-75% Invar w/w, Invar 36 alloy) was used as the base material. The surface of the copper foil was sputter coated with a layer of chromium that had a thickness of 80 nm. PTFE film (General Electric Corp., part number 80103109) with a thickness of 102 μm and an $M_n > 5 \times 10^6$ D was used without any previous treatment. In some cases, for comparative purposes, experiments were performed with a

commercial fluoropolymer/silica composite (Rogers RO-2800 from Rogers Corp., Rogers, CT, USA).

Lamination conditions

PTFE films and chromium-coated Cu-Invar-Cu foils were laminated using a programmable PHI Model F75R lab press at 3.447 MPa with a 10-h. dwell time. The experimental details obtained with the PHI press are equivalent to three lamination cycles used in conventional processing but with lower lamination pressures than those typically desired in a fabrication process. The selected range of temperatures in the described study included samples produced at 354 °C (670 °F), 366 °C (690 °F), and 379 °C (715 °F). Similarly RO-2800 composite films were laminated against metal to provide comparative samples for the mechanical tests. Effort is made here to include contrasts between samples produced using the latter two temperatures since preliminary experimental results had suggested noticeable changes in reliability results for these conditions.

The reason so much emphasis is placed on a detailed characterization of the system that includes PTFE film rather than a typical fluoropolymer composite (for example, Rogers RO-2800) is to replicate the appearance of the fractured interfaces seen in thermal cycling testing and explain the subtle changes that develop in the selected temperature range of the lamination conditions of the true composite.

Mechanical testing of composite films

Sheets having dimensions of 0.25 m by 0.300 m were laminated in an electric press (PHI press). Temperature was controlled to ±1.5 °C across the entire sample. Densification was monitored for each sample by the shrinkage of pre-drilled holes (initial diameter = 600 μm) in a polymer sheet. Samples for adhesion and tensile tests were identified and cut into strips.

Peel tests were performed on laminated samples of the fluoropolymer-metal composite strips with a minimal length of 0.20 m and a width of 0.0254 m. An Instron model 1123 was used to perform the measurements, peeling at 180° using a peel rate of 0.01 m/min after initiating the peel manually. In a preliminary evaluation, the peel tests were found to be insensitive to speeds of 0.005–0.05 m/min. Elongation measurements were performed on similar samples after metal foil removal by chemical etching using the same instrumentation and displacement rates of 0.01 m/min. The specimens were dog bone in shape with a gauge length of 0.05 m and a width of 0.01 m.

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 and a tilting angle of 65° degrees relative to the analyzer. Survey and high-resolution spectra were collected with pass energies of 158 and 11.8 eV, respectively. Samples from the fractured interfaces were selected, and mating sides of the same were analyzed under conditions that did not affect the fluoropolymer layers (270 W and 12.5 keV). Preliminary experiments with a mass spectrometer in the XPS system were used to optimize these conditions. Binding energies were referenced to the C1s photoemission line of a –CF_2– group at 292.4 eV [14]. The linearity of the binding energy scale was determined by measuring the positions of a dual sample of the most intense lines for copper and gold prior to the experiments described here. High-resolution XPS spectra in the C1s, O1s, and F1s regions were used to determine the contributions from different chemical environments, and to follow them as a function of lamination conditions or after subsequent metal removal. In a parallel experiment, depth profiling with a second spectrometer (AES, PHI 660) was used to verify surface composition and the thickness of the sputter-deposited chromium layers. The estimated thickness of the chromium layer was 80 nm. Ultramicrotomy was also used on the polymer side of a fractured surface laminated with the highest temperature to prepare an area with varying depth. The purpose of this experiment was to determine via XPS the approximate depth of damage induced by the lamination process. Confocal laser scanning microscopy (CLSM) was used to measure the depth of the prepared surface after metal removal. Successive high-resolution XPS scans of the C1s region of this surface were taken after stepping (moving the probe) over the sample with a spot size of 120 μm.

Scanning electron microscopy (SEM)

A Leo1550 FE-SEM-STEM microscope operating at a voltage of 15 keV in the in-lens mode, 30° 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 up to 100,000× were used to observe the surfaces of some selected samples and images were collected in the secondary electron imaging mode.

Microtome and sample preparation

An Ultracut E Reichert-Jung microtome was used to prepare a sample for line scans on a specimen amenable to

step profiling. A section of the fluoropolymer layer from a laminated sample at 379 °C was initially etched to remove the metal layers. The sample was mounted in epoxy potting compound and allowed to cure overnight. The slice on the horizontal surface was produced using the microtome and a diamond blade to minimize contamination.

Confocal laser scanning microscopy

A Zeiss Microsystems LSM 210 was used to image the microtomed section along its *x*–*z* plane. This allowed measurement of the angle of the microtome cut and the area of the slice to be used for a line scan with the stepping motors of the stage in the XPS spectrometer.

Results and discussion

The samples for the PTFE-metal set laminated at various temperatures yielded peel strengths that were more or less constant for the two lower temperatures, but they decreased in value for the highest lamination temperature used in this study. Composite samples were selected in regions of uniform flow and their mechanical responses were also measured. Surfaces resulting from peel tests for these two sets of samples are shown in Fig. 1. The typical FP/silica composite appears to fail cohesively in the polymer layer, while the silica-free material visually appears to have failed adhesively on the metal surface.

XPS analysis was performed on the fractured surfaces of the PTFE/metal samples, identified as metal side of the fracture (M) and fluoropolymer (FP) side of the same. The metal side of the fracture corresponds to the surface that visually appears to be metal, and the polymer side of the fracture corresponds to the side that contains the bulk of the polymer film. The surface compositions for these samples as a function of temperature and side of the examined fracture are listed in Table 1. The results show that at lower temperatures, the fractured interfaces appear to retain their PTFE character, i.e., C-to-F ratios of 1-to-2. At 379 °C, the FP side of the interface has lost some fluorine, while the metal side of the fracture contains the expected composition of PTFE. At first glance, the fractures appear to be cohesive with low amounts of exposed metal, if any. It is possible that the overlayer of PTFE over the metal side of the interfaces is extremely thin and within the sampling depth of XPS; thus, some underlying chromium may be visible. The value of λ (inelastic mean-free path of a photoelectron) for carbon (C1s) in a C–F environment using monochromatized Kα Al radiation has been reported by Cumpson to be about 3 nm [15]. Since the angle of the sample to the analyzer is known, one can estimate the average thickness of the overlayer. This calculation yields a depth of about 8.2 nm for the residual FP overlayer on the metal surface. However, it is more reasonable to think that because the metal surface has some microroughness, the coverage of the thin layer of PTFE is not completely uniform and some metal is visible in some areas. The same argument can be derived by the AES characterization of the metal sides from these samples. Depth profiling of these three surfaces indicated that the chromium layers were in the expected ranges of thickness; therefore, the peel values were not the result of differences in chromium thickness among the peeled strips but effects introduced by the polymer phase and its thermal behavior. This hypothesis is reinforced by the SEM analysis described below.

In contrast, the XPS analytical results for metal laminated against the fluoropolymer composite appear to yield cohesive fractures at all the temperature ranges examined in this work. Table 1 also includes the results obtained for peeled interfaces of samples produced at 366 and 379 °C. In these cases since the two sides of the fractured interfaces appear to be similar to each other, they are labeled as sides 1 and 2, respectively. For all purposes, both sides of these interfaces are very similar in composition and the presence

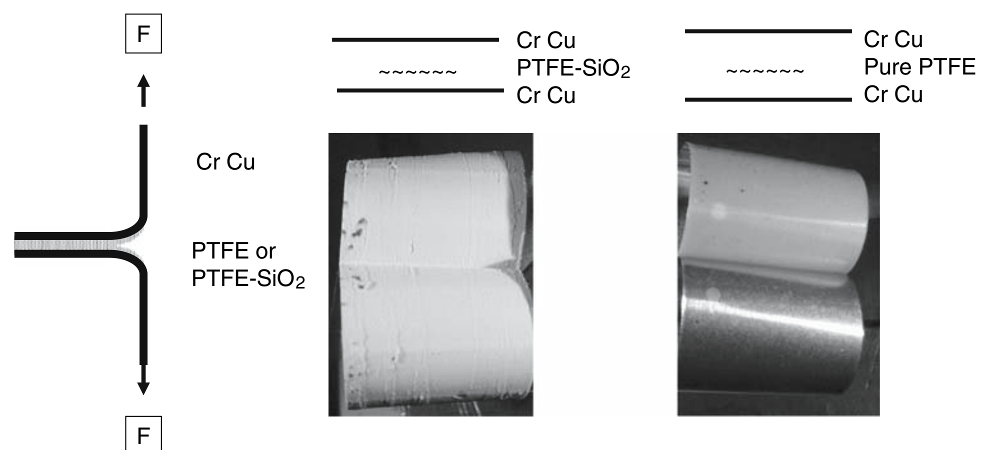


Fig. 1 Schematic representation of 180° peel tests and optical images of fractured interfaces for a fluoropolymer-silica composite and the model fluoropolymer film laminated against metal foils

Table 1 Surface compositions of fractured interfaces as a function of fracture side (results reported as atomic percentages)

Sample	%C	%O	%F	%Cr	%Si
354 °C/FP	31.7		68.1		
354 °C/M	31.7	2.6	63.7	2.0	
366 °C/FP	30.7	0.04	69.2		
366 °C/M	32.5	2.7	63.2	1.6	
379 °C/FP	45.1	3.2	51.7		
379 °C/M	32.1	0.5	67.1	0.4	
366 °C/side 1	28.5	11.5	53.8		6.2
366 °C/side 2	27.9	12.3	53.5		6.4
379 °C/side 1	28.9	9.1	57.2		4.8
379 °C/side 2	28.3	9.4	57.5		4.9

of silicon (as silica filler and coupling agent) is evident. It is relevant to notice the slight decrease in silicon concentration with increasing lamination temperature for these samples.

SEM characterization of fractured interfaces of FP-metal film composites is presented in Fig. 2 for the lowest and highest temperature sides of each examined interface. The top images represent the fractured surfaces at the lowest temperature with the image on the left side showing the metal side of the interface, and the image on its right side, the polymer side of the same. The lower set of images displays those obtained for the highest temperature used in this study. These images clearly show that fibrils of polymer exist over the metal surface at any condition, and as the lamination temperature increases, the morphological characteristics of the overlayers appear to change. In all cases, the metal sides of these fractures look visually metallic, but they contain fluoropolymer material. It is also relevant to point out the difference in appearance, especially for the metal side of the sample laminated at 379 °C, where more fibrils of fluoropolymer are visible than in the case of the 357 °C lamination. It is perhaps this change in morphology responsible for the variation in surface composition detected on the FP side surface by XPS (see Table 1).

High-resolution XPS spectra of the FP-metal film samples are also informative. For example, Fig. 3 shows some spectral regions of the polymer and the mating metal sides of the same fracture for the samples under the three conditions investigated in this work. The spectral traces shown have been normalized to highlight the trends more clearly. In Fig. 3a, the C1s regions of the metal sides contain small contribution of a second component with lower binding energy than the expected $–CF_2–$ signal. The F1s, O1s and Cr2p signals show that the increases in temperature do not appear to affect these chemical environments at all. It is important to notice that the position of the $Cr2p_{3/2}$ signal is indicative of an oxidized chromium environment. This is expected since chromium surfaces oxidize quite readily under normal conditions, and this state of the surface is present even prior to lamination conditions. Similar evaluation of the polymer sides of the fractured interfaces

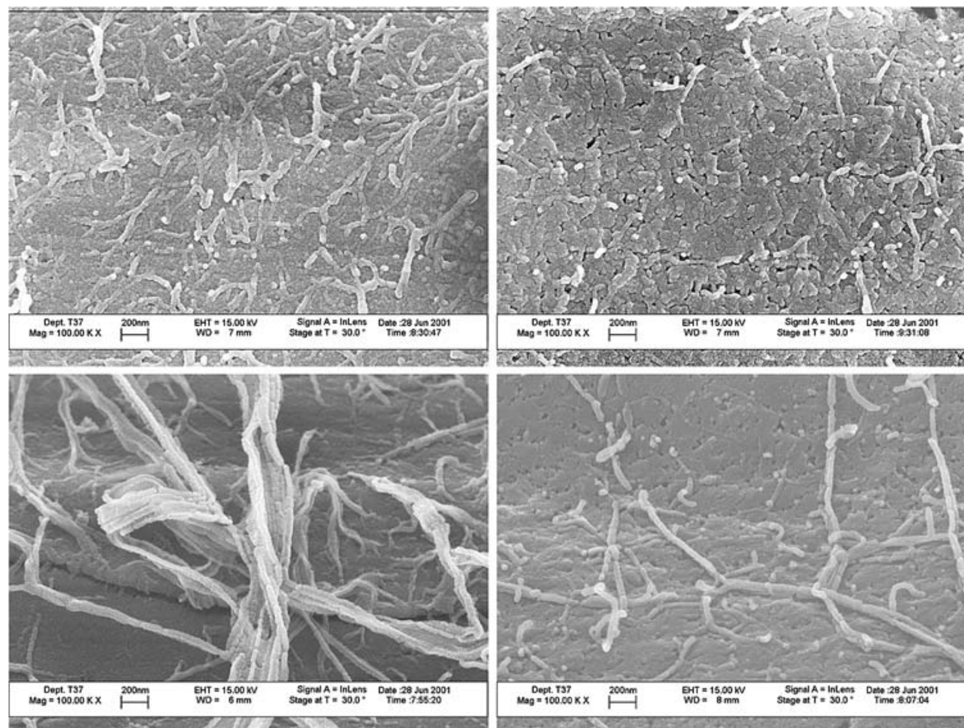


Fig. 2 SEM images for fractured interfaces of a PTFE/metal structure laminated at 354 °C (top images) and at 379 °C (lower set). In each case, the metal sides of the fractures appear on the left side of this figure

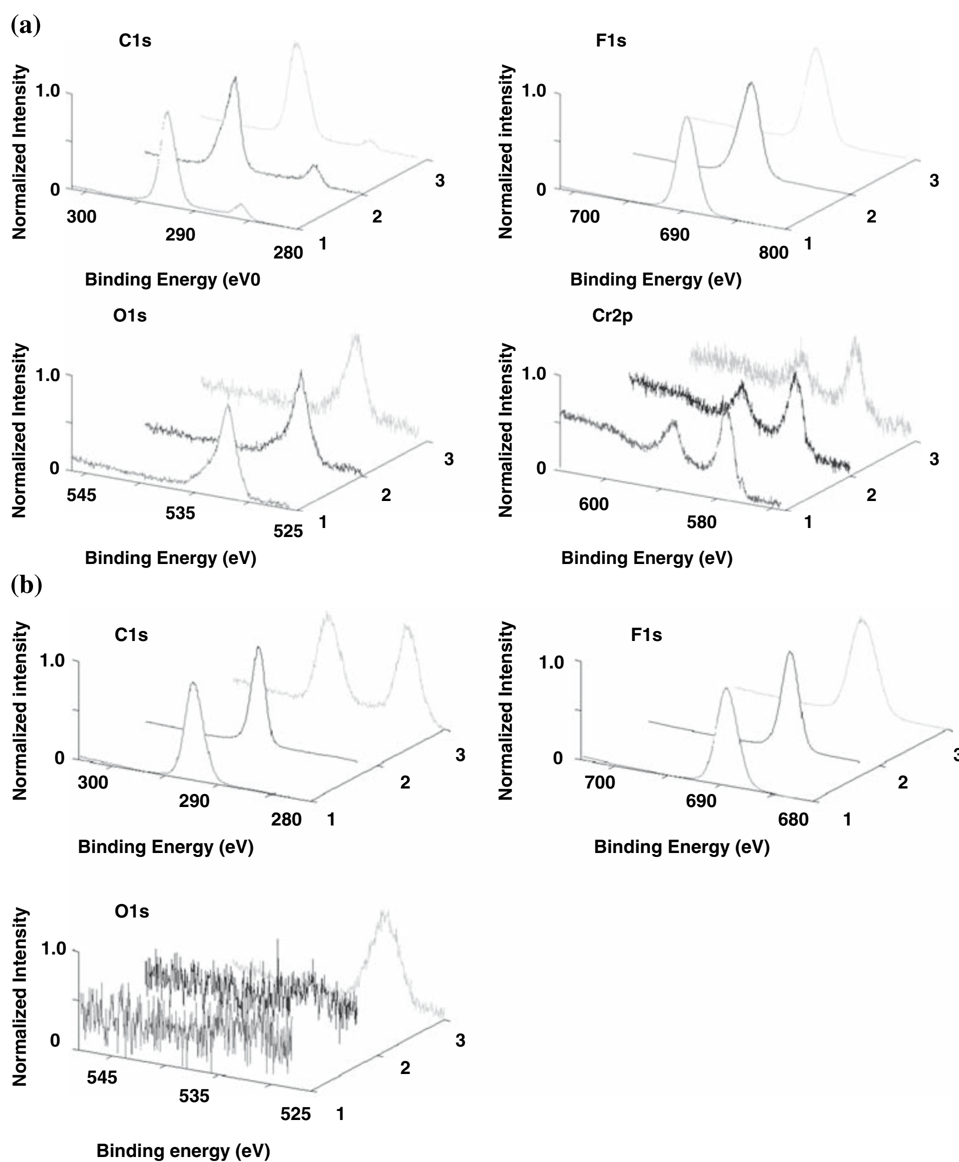


Fig. 3 High-resolution XPS spectra for some selected regions of fractured samples at as function of lamination temperatures. The spectra appear in the order of increasing temperature with the lowest lamination temperature in front. The metal sides of the fractures are presented in (**a**) while the corresponding polymer sides of the fracture appear in (**b**)

reveals that the C1s signals for the lower temperatures are similar to those of PTFE and only contain a single C1s environment (see Fig. 3b). It is only when the sample is subjected to the highest temperature that an additional C1s signal is observed. This signal appears to be associated with C–C bonds formed at the expense of C–F bonds. This transformation is verified by comparing the surface compositions of the polymer side of the interface where the atomic percentage of fluorine atoms decreases with an increase in carbon atom levels. In summary, the highest temperature results indicate degradation of the material just within the fluoropolymer film, and it is likely that the mechanical properties of the composite are affected by this exposure.

If the resulting changes observed on the fluoropolymer surface were only induced by temperature; it would be expected that thermal exposure of PTFE film to the same ranges of temperature should produce detectable effects, especially since the range is above the melting point of PTFE. For this purpose, strips of free-standing PTFE (the same material used in the lamination experiments) were heated in an oven under a nitrogen atmosphere for 3 h. Following this, the surfaces of these films were analyzed to determine any possible changes. Surface compositions of the three materials revealed little change in the C-to-F ratios from the original PTFE. The atomic compositions of these films are presented in Table 2. High-resolution XPS spectra of the C1s regions of the same revealed no detectable chemical changes on these films either (see Fig. 4a). These results are not unexpected since PTFE is known to produce only minimal decomposition products below temperatures of the order of 400 °C after appreciable times in this temperature range [16]. In the temperature range 360–380 °C, hexafluoroethane (C_2F_6)

Table 2 Surface compositions of PTFE films heated to various temperatures for 3 h (results reported as atomic percentages)

Sample (°C)	%C	%O	%F
354	31.8	1.3	67.0
366	31.9	1.3	66.8
379	32.1	1.4	66.6

and octafluorocyclobutane (C_4F_8) have been identified as decomposition products [17]. More recent work on the thermal behavior of PTFE under pressures less than 7 MPa has shown that the decomposition of this material is pressure independent [18]. The C1s XPS spectra for the free-standing PTFE film and that of FP-SiO_2 composites at room temperature are also included (see Fig. 4b). The presence of the additional signal on the FP–SiO_2 film ca. 285 eV on the C1s spectrum of this material is associated with other components of the composite, and this signal will obscure any other signals arising from chemical changes with defluorination reactions during composite processing.

Additional information on the mechanical behavior of the FP-SiO_2 and the free-standing PTFE film was obtained by comparing the unixial tension testing of both materials as a function of lamination temperature. These results are shown in Fig. 5. The PTFE films showed no decrease in elongation, while the FP–SiO_2 composite showed a decrease in failure strain with temperature. Previous reports on the relationship of the mechanical properties and PTFE material as a function of its molecular weight show little variation in the molecular weight range of the film used here [19]. The elongation results indicate that in the

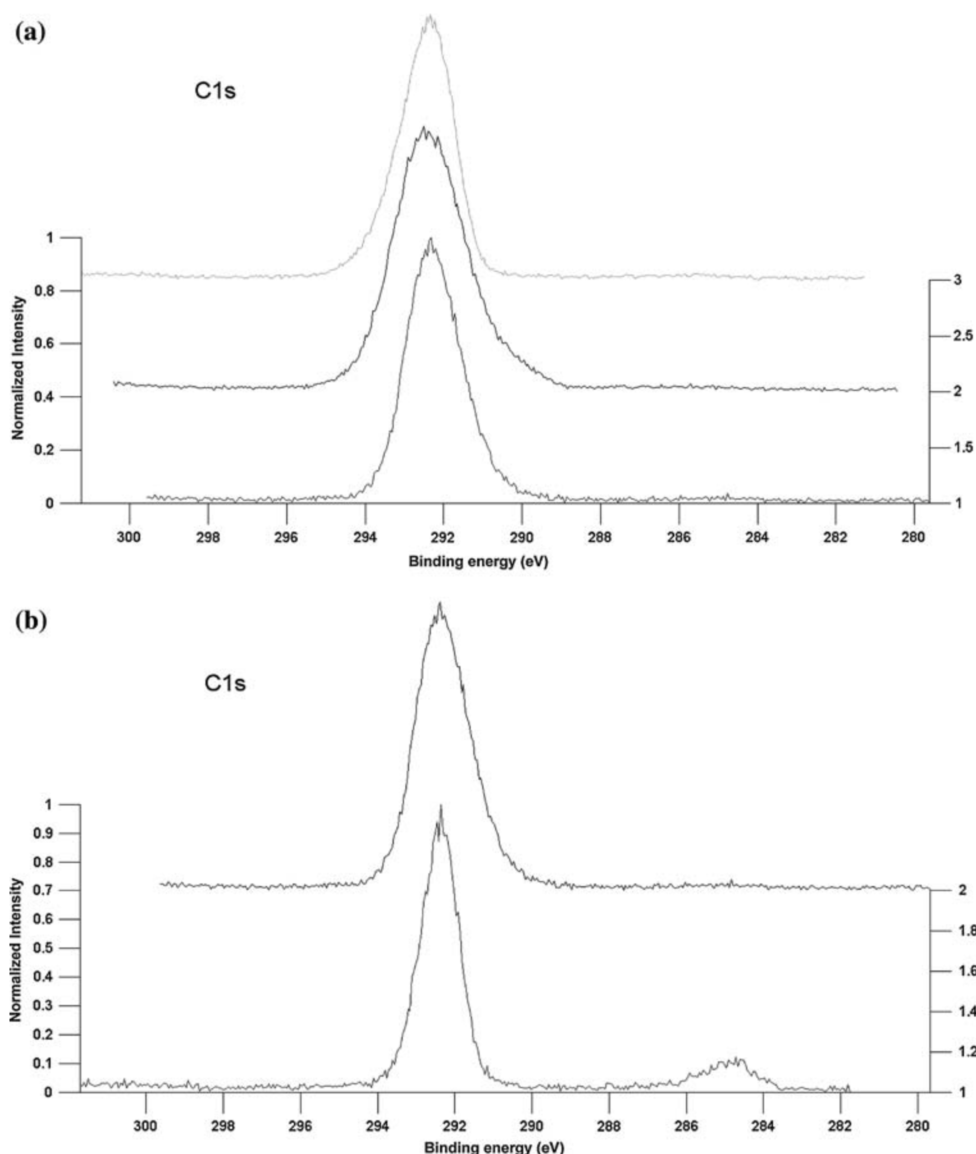


Fig. 4 High-resolution C1s XPS spectra of: (**a**) Free-standing PTFE films heated at the various temperatures from this experiment (lower temperature at bottom of series) and (**b**) signatures of PTFE film and a fluoropolymer composite film at room temperature

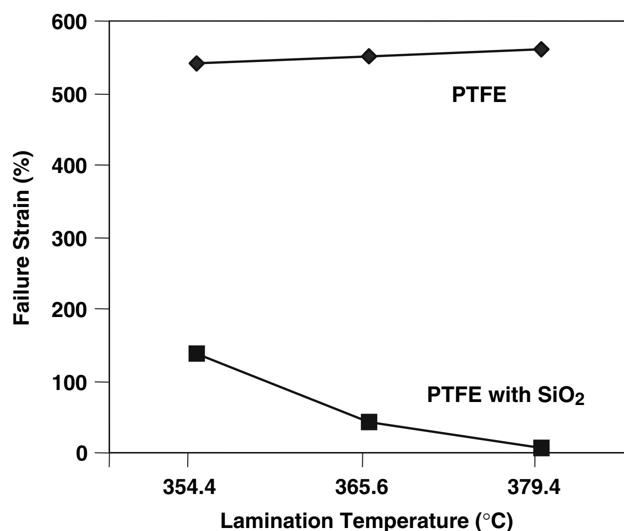


Fig. 5 Uniaxial tension results for composites of PTFE/metal and PTFE/SiO_2-metal laminated at various temperatures

selected temperature range, the PTFE film behaves as expected.

Previous work on the nature of the interaction between fluoropolymer materials and chromium films has been able to show surface reactions between a fluoropolymer layer and an oxidized chromium surface [3]. Reactive metals such as chromium and zinc tend to thermodynamically favor this reaction. However, metals such as copper cannot favorably react with these materials [20]. The resulting adhesion at the created interface is mainly mechanical in character with some chemical component induced by interfacial reactions between the metal oxide and the fluoropolymer layer. Adamczyk et al. have reported the reactions of fluorine-modified chromium oxide in heterogeneously catalyzed fluorination reactions [21]. These investigators have shown that some small replacement of oxygen atoms in Cr_2O_3 by fluorine atoms yields acidic sites that enhance catalytic activity. Since PTFE can lose some volatile fluorinated compounds during lamination, this fluorination step of the metal oxide is possible. Subsequent reactions that yield fluorine loss from PTFE during lamination can occur with the formation of a layer attached to the metal surface. More recently, a more precise evaluation of the reactivity of PTFE with various other materials has shown that a stainless steel alloy (SUS316L-EP) has more reactivity than other metals and their compounds [22]. In this case, the lower degradation temperature of the fluoropolymer is achieved by the presence of chromium atoms in the alloy.

A means of observing the metal/FP interface is ion beam depth profiling with simultaneous XPS analysis. The ion beam profiling can be performed frontally (from the polymer side of the interface) or from the metal side of the interface and toward the fluoropolymer region. Because the ion beam technique induces damage of the fluoropolymer with appreciable defluorination, interfacial information is readily lost. An alternative approach that can be used to study the fluoropolymer side of the interface is by chemically etching the metal layer before XPS analysis. For example, Park et al. [3] have shown that $FeCl_3$ was successfully useful in removing copper from a fluoropolymer layer laminated to a copper film treated with an extremely thin layer of chromium. Since the metal film is more complex in the present study, a series of chemical etches were used to remove copper, invar, copper, and chromium before reaching the polymer film. The chromium layer was removed with a potassium permanganate solution. The only drawback of the approach is the introduction of small amounts of manganese oxides on the polymer surface. After metal etching a final rinsing with de-ionized water and UHV drying were performed. The free-standing surfaces were analyzed by SEM and XPS. The SEM results reveal a polymer surface that replicates the metal film morphology of the copper grains under the chromium surface (see Fig. 6). Surface compositions for the three samples that were analyzed by XPS are presented in Table 3. The presence of manganese is related to the remnant of chromium removal from the polymer layer.

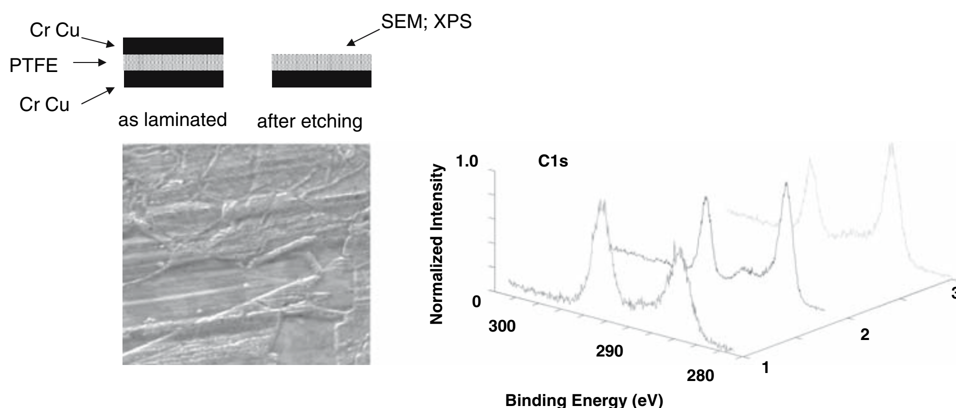


Fig. 6 SEM image of PTFE film after chemical removal of metal layers and isometric view of the C1s XPS spectra for the resulting surfaces. The spectrum up front is the one obtained for the sample laminated at 354 °C

Table 3 Surface compositions of fluoropolymer surfaces laminated at various temperatures and after chromium removal (results reported as atomic percentages)

Sample (°C)	%C	%N	%O	%F	%Mn	%Cl	%Na
354	47.6	0.6	12.5	36.9	2.3		
366	55.1	1.7	16.1	23.7	2.4	0.4	0.7
379	51.2	0.4	17.9	22.8	7.4	0.3	

Although these surface compositions may not be accurate, the lower concentration of fluorine is consistent with polymer defluorination on the oxide surface originally present at the fluoropolymer/metal interface.

High-resolution C1s XPS spectra for the chemically stripped surfaces are also presented in Fig. 6. The lowest temperature film contains contributions from the $–CF_2–$ and –C–C– environments that represent about 45% and 43% of the total carbon area envelope, respectively. At the intermediate and highest temperatures, the envelopes can be almost superimposed and the areas of the $–CF_2–$ and –C–C– bands are approximately 30% and 58% of their total C1s area, respectively. It is important to notice a small contribution from another band intermediate between the major ones. The exact position of this band is 288.8 eV and it is identified as that induced by a carbon atom in a –O–C(O)– group [23]. The relative concentration of this other component is about 12% of the total C1s envelope area, and it does not appear to change with temperature. These results indicate that the reaction of the chromium oxide surface and PTFE occurs even at all the temperatures used in these experiments. In addition, a notable degree of polymer alteration, as measured by the enhancement of the band ca 285 eV, after the temperature reaches 366 °C, can be noticed.

Because monochromatized XPS at 65° samples a specimen to an approximate depth of 8.2 nm, it is important to determine if the changes in surface composition observed here affect the polymer side of the interface beyond this depth and if they can influence practical adhesion values. A measurement of the thickness of the polymer layers from these surfaces after metal removal by successive chemical etching indicated that the films were 109-μm thick, in agreement with the estimated initial thickness values for the material. Figure 7 shows a diagrammatic view of the polymer side of the fracture for a sample processed at 379 °C after dry microtome cutting with a diamond knife. Measurement of the depth of the cut (straight line side of cut) by CLSM indicated that it was 9 μm. The length of the cut also was measured to provide the calculation of the angle at the opposite end to allow the estimation of depth at a given position. XPS spectra were taken for the C1s region of each selected point with a spot of 120 μm after stepping known distances. Some of the resulting XPS spectra for this experiment are also incorporated in Fig. 7. The surface at which modification does not proceed is expected to contain only or predominately $–CF_2–$ groups. These effects take place roughly at spot number 4 which has a depth of 4 μm. This measurement corresponds to about 4% of the PTFE film thickness. As indicated here, the depth of material alteration appears to be a function of lamination temperature, and it is only a small percentage of the total film thickness.

As described earlier, comparison of 180° peel strengths for the model system and actual FP-SiO_2 composites laminated at the same temperatures is presented in Fig. 8. For each condition, four individual samples were used. The peel strengths of PTFE films laminated against the cladded metal layers drop significantly at the highest lamination temperature even though a drop in failure strain was not observed in the uniaxial testing (see Fig. 8a). In contrast, the results for the FP-SiO_2 composites drop with increasing lamination temperature (see Fig. 8b). The observed failure was cohesive in the dielectric material layer and a decrease in strength with temperature was consistent with the decrease in failure strain in uniaxial testing. The depth of damage observed for the PTFE-metal model composite is noticeable at the highest temperature, and the behavior observed for the FP-SiO_2 composite cannot only be

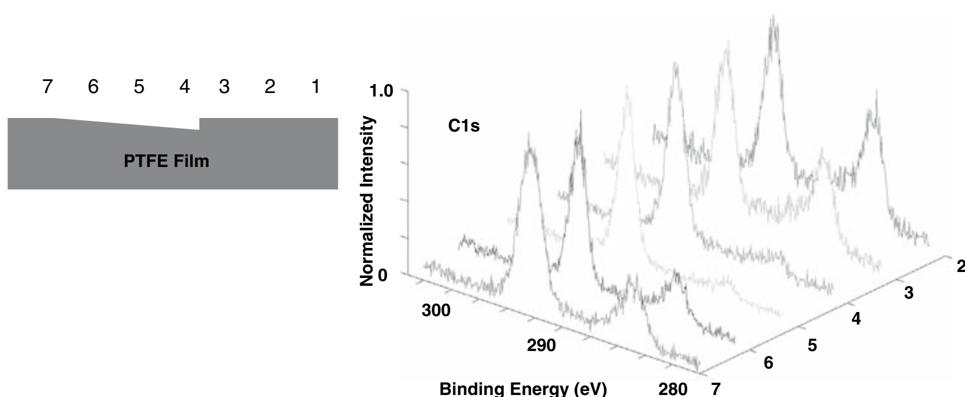


Fig. 7 Schematic representation of microtome slice and its sampling points for XPS measurements. The resulting C1s XPS spectra correspond to the points shown in the diagram

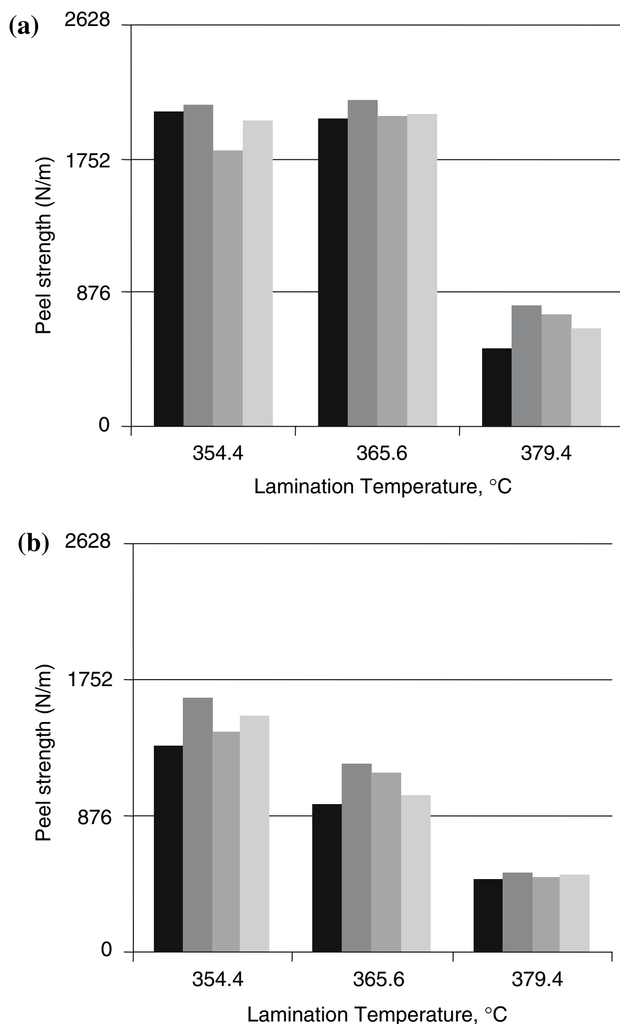
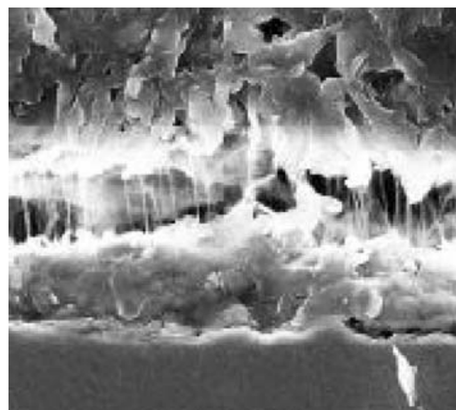


Fig. 8 Peel strengths for (**a**) PTFE/metal and (**b**) FP/SiO_2 samples as a function of processing temperature. For each experiment, four individual measurements were made and they are included in the figures

accounted for by the observations obtained thus far. Then, a second component of significant contribution to mechanical composite failure must be invoked.

To disperse filler particles into organic materials, inorganic particles such as silica must be surface modified to make them compatible with an organic medium. Dispersion of PTFE particles can be done by either incorporating a surfactant agent or organo silane-coupled silica particles. Alkoxy silane-coupling agents have been used for many years to make these inorganic surfaces more compatible with organic media [24]. For non-reactive materials such as PTFE, the modified particle has to rely on mechanical interlocking with the polymer matrix if no chemical surface pretreatment of the polymer that enhances the particle/matrix interactions has been done. Typical materials for such coupling reaction include, for example, phenylmethoxy silanes [25]. Although silicones or siloxanes are considered to be thermally stable, they appear to degrade at temperatures >300 °C [26]. For example, polymethylphenylsiloxane has a range of stability of −55 °C to 290 °C. As it has been described earlier, the formulation of the composite includes other organic materials such as surfactants which may also be sensitive to thermal degradation as well during the lamination cycles. These conditions compromise the particle/polymer interface and some separation can develop, especially at lamination conditions above 366 °C. Fluoropolymer degradation and decomposition of coupler material and surfactants from the composite can lead to laminate cracking during stress cycles. Figure 9 presents a cross-sectional view of a laminate produced at 379 °C which shows the typical cracking observed within the composite. The diagram shown on the right side of the micrograph contains a representation of the actual interface that leads to the type of fractures observed after lamination, weakening of the polymer near the metal interface, and propagation through the composite matrix itself.

From a practical consideration, if the material is prone to cracking, the changes induced in the polymer by the lamination conditions and the breakdown of the interface between the filler and the matrix will result in structures that may not be mechanically and electrically acceptable for microelectronic applications.



Silica particles
-CF2-
-CF2-
-CF2-
-CF2-
-CF2-
-CF2-
-CF2-
-C-O-
-CH-
-CH-
Fractured interface
-CF2-
-CH-
-C-O-
-CF2-
F
F
F
CrxOy
Cr
Cu

Fig. 9 Cross-sectional SEM view of a crack near the metal-to-fluoropolymer composite interface (left) and a schematic representation of an embrittled zone in the filled FP region and defluorinated zone near the metal interface showing a fracture line (right)

Table 4 A comparison of stress testing for an electronic package at test cycles of 0–100 °C

Composite lamination temperature (°C)	Sample size	N_{50} (cycles)	σ	Time to failure (h)
379	60	3,530	0.87	500
366	73	4,559	0.14	3,000

The contribution of the lamination temperature to both fluoropolymer alteration and loss of materials that induce coupling between the filler and the matrix can only be evaluated through reliability measurements. Table 4 presents data that contain information on the number of cycles to failure for fully assembled microelectronic modules including two of the lamination conditions used here. In this example, test vehicles containing a 0.018 m chip were cycled between 0 and 100 °C until failure was detected. The N_{50} value represents the cycle at which 50% of the population showed some failure and σ represents the distribution of the failures. These results showed that the temperature selected for laminate fabrication plays an important role on the reliability of fluoropolymer composites in electronic packing applications.

Conclusions

The characterization of fractured interfaces of PTFE/Cr sputtered onto Cu-Invar-Cu composites has shown that the lamination process at temperatures above 366 °C not only induces surface reactions at the FP-metal interface but can also influence the chemical characteristics of the fluoropolymer material. At the highest investigated temperature (379 °C), the alteration of the fluoropolymer extends to a depth of 4 μm. Concurrent with this, the loss of integrity at the filler/particle interface increases. As a result, the composite structure of filled PTFE-silica and metal layers develops cracks that can propagate through the filled polymer layer during thermal cycling. The model system containing PTFE and metal composites has been successfully used to unravel the complex interactions that occur in composites useful in microelectronic packaging applications.

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