

Infusing inorganics into the subsurface of polymer redistribution layer dielectrics for improved adhesion to metal interconnects

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Abstract—This paper demonstrates a new class of inorganic-organic hybrid dielectric materials to address the requirements for high-temperature reliability of next-generation high-density, high-power packages and electronics in harsh environments for automotive applications. A major concern for reliability is the inadequate adhesion of metals with high-temperature polymers. Adhesion deteriorates further via thermal and oxidative exposure and moisture absorption. In this paper, a novel vapor phase infiltration (VPI) technique is applied to create an organic-inorganic hybrid dielectric surface that improves metal-polymer adhesion. The VPI process infuses inorganic constituents to a depth of at least 3 microns, as revealed by elemental analysis using SEM-EDX and XPS depth profiles. In preliminary testing, Cu/Cr films deposited onto these modified polymer surfaces exhibit 3x higher peel strength than metal films deposited on untreated polymer.

Keywords- High-temperature, dielectrics, Re-Distribution-Layer (RDL), Adhesion, Vapor-Phase-Infiltration (VPI), automotive electronics

I. INTRODUCTION

The increasing electronic functions in modern commercial and military vehicles and avionics drives the need for greater reliability of electronics packaging under extreme conditions [1,2]. These electronics can often be found near the engine or in other harsh-body, high-temperature environments where they can be exposed to increased mechanical stresses, aggressive chemical environments and fatigue-related failures that are not normally associated with consumer electronics.

High temperatures electronic modules used in vehicles fall into two main categories: (1) devices operated at high ambient temperatures and (2) high-power devices operated at high device junction temperatures. In the first case, the external environment determines electronics reliability. In the second case, operating junction temperatures limit reliability. With silicon power-FETs, these operation temperatures are usually limited to ~ 150 °C. However, as wide-band gap semiconductors, which can have junction temperatures well in excess of 150°C, become more widely accepted, new packaging technologies must be developed.

Design of electronic packages that operate at these new conditions should consider various interactions between the

environment and critical material parameters to identify the weak link. High-density high-temperature electronics, which are poised to become a strategic technology for automotive applications, face material and interfacial limitations [3]. Currently, low-temperature cofired ceramic (LTCC) and high-temperature cofired ceramic (HTCC) are used for automotive applications. High T_g laminates such as polyimide and cyanate ester-based laminates are used for fabrication of high-temperature printed wiring boards [4]. However, they pose significant integration challenges as substrate materials if they are to be scaled similar to consumer electronics. Traditional epoxy-based polymer packaging cannot be used beyond 150 °C due to its inherent material limitations. Elevated temperatures in polymers accelerates failure mechanisms such as electromigration and corrosion in addition to inducing phase transitions and degrading mechanical and electrical properties [5]. High T_g polymers such as BCB and polyimide are seen as attractive candidates for taking polymer packaging to high temperatures. Organic laminates with sensor chips are known to fail after high-temperature storage due to material degradation and interfacial delamination and cracking [6]. Thus, improvement to these materials to increase metal-dielectric adhesion and extend long-term reliability is a critical challenge.

Materials and system reliability challenges emerge from the thermal and chemical environment during operation. The harsh conditions are because of high-pressure, vibrations, high-temperature, or in the presence of corrosive media, often requiring long-term continuous operation (>500 hrs). Harsh operating conditions create a plethora of potential failure mechanisms. Mechanical failures such as fatigue cracking, creep, and brittle fracture may occur as a result of thermally cycling joined materials with CTE mismatches. Materials degradation may result from a change in material properties above critical temperatures (e.g., the glass transition temperature). Chemical failures such as corrosion, oxidation, and metal migration can further be exacerbated by aggressive chemical environments [7]. System reliability is influenced by the combination of stresses and thereby, failure mechanisms. A deep understanding of materials properties, effect of processing parameters and operating requirements is required to predict and design for these failure mechanisms.

At elevated temperatures, thermal stresses are induced between the different material systems in the package. The polymer/metal interface constitutes a weak link in the system because of the heterogeneity of the bonding interfaces and the significant differences in coefficient-of-thermal-expansion. The long-term durability of polymer/metal bonds depends strongly upon the chemical nature of those interfacial bonds [8]. Temperature-induced acceleration of chemical reactions at the interface can lead to the formation of a weak boundary layer because of moisture absorption at the interface creating a potent site for delamination. Reference [9] shows that at the same temperature and relative humidity conditions, moisture absorption at the interface is larger than moisture absorption of the bulk, implying that even low moisture absorbing polymers, when subjected to high temperatures and humidities, can delaminate at interfaces due to poor adhesion. Pre-existing cracks at the interface can further accelerate this failure mechanism. Thus, characterization of the polymer/metal interface is important to package reliability at high-temperatures.

This paper explores a unique technique to modify the subsurface of polymer dielectrics to tailor interfacial properties between the re-distribution layer (RDL) dielectric and metal. It addresses a key challenge of polymer/metal adhesion by tuning the surface characteristics of the polymer to create novel hybrid interfaces with improved adhesion characteristics. Unlike polymer composites that are heterogeneous at the sub-micron or nanoscale, hybrid dielectrics are homogeneous at the atomic scale. This paper describes an innovative process, vapor phase infiltration (VPI), to create such hybrid polymer surfaces. This new processing technique is applied to high-temperature polymers to simultaneously achieve high operating temperatures and strong adhesion to metal layers.

Section II discusses the experimental techniques and material properties used in this study while also describing the key process details for vapor-phase-infiltration. Polymer/metal interfacial adhesion is characterized using peel tests and described in section III. Chemical and surface analysis of the modified surface is reported and initial mechanisms for improved adhesion are discussed.

II. EXPERIMENTAL DETAILS

A. Process Flow

Polymer dielectrics must have low dielectric loss, high elongation to failure, moderate CTE, and low moisture absorption to be considered suitable candidates for RDLs in electronic packaging. Table 1 summarizes the target material properties expected for aRDLs in automotive packaging. Tg is an important indicator for the thermal stability and thermo-mechanical properties of a polymer. A polymer dielectric with a high glass transition temperature was chosen for this study.

Table 1. Target polymer properties for high-temperature dielectrics to be used in RDLs for automotive electronics packaging.

PROPERTIES	BENCHMARK
Tg	> 250 °C
Moisture Absorption	< 0.01 % (200 °C)
Dielectric loss constant (D _i)	tanδ < 0.02
Dielectric Constant (D _k)	< 4
Isothermal weight loss	< 1 % at 250 °C
Young's modulus	> 2 GPa (23 °C)
CTE (at 250 °C)	< 40 ppm/°C
HAST (at 135 °C, 85%, 3.3V)	> 500 hrs
Thickness	< 20 μm

Fig. 1 shows the test structures used to evaluate adhesion strength at the polymer/metal interface. Glass panels (4" x 4") or silicon wafers (3" diameter) were used as the substrate material. Polymer layers were prepared by first spin-casting an adhesion promoter onto the substrate at 3000 rpm for 30s followed by baking at 150 °C for 90s on a hotplate. A vacuum hot-press is then used to laminate the polymer dielectric layer to the substrate. Lamination is completed by first pulling vacuum for 90s and then hot-pressing at 0.6 MPa for 30s at 93 °C. The thin-film polymer dielectric is hard-cured in a nitrogen oven at 250 °C for 60 mins.

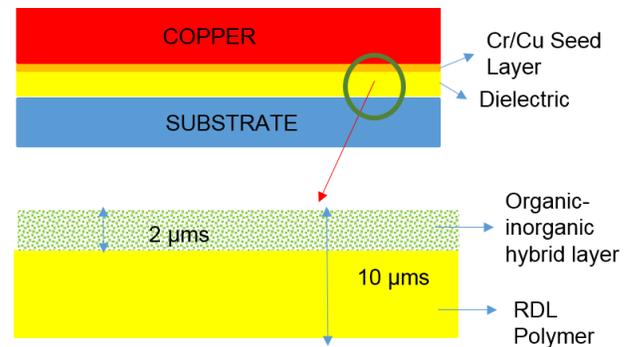


Figure 1. Cross-sectional schematic of test-structures

For test-structures where the sub-surface is chemically modified, VPI was performed after curing the polymer. A thin seed layer of chromium/copper was sputtered onto the samples using DC Sputtering (CVC Inc.). Copper was then electroplated to $\sim 25 \mu\text{m}$ under galvanostatic conditions using Atotech's cupracid BKTM electrolyte solution.

B. Vapor Phase Infiltration (VPI)

VPI exposes the polymeric material to a metal-organic reactant such as trimethyl aluminium (TMA) in a low pressure (~ 1 Torr) heated environment. The reactant then diffuses into the sub-surface of the polymer and becomes entrapped. Fig. 2 depicts this sequence. This process has demonstrated the ability to introduce desirable properties to various polymer substrates such as controlling wetting characteristics, enhancing its mechanical strength, and tailoring material properties for photovoltaics and batteries [10].

In order to investigate the infiltration of TMA into polymer thin films, a Dose/Hold/Water/Hold/Purge = 1s/60 s/1s/8 hrs/90s was followed for two cycles for different temperatures ranging from 100°C to 175°C . This was performed in a custom-built chamber [11].

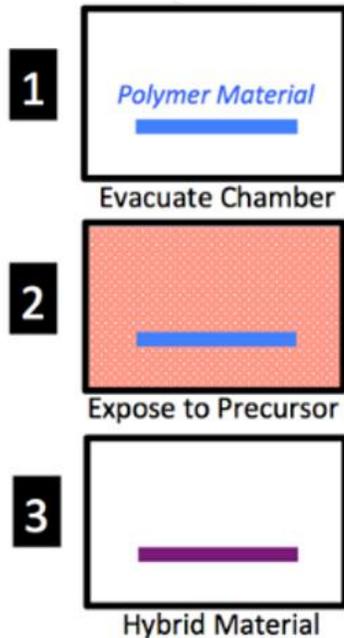


Figure 2. VPI process sequence for creating hybrid organic-inorganic surfaces

C. Chemical & Structural Characterization

X-ray photoelectron spectroscopy (Thermo K-alpha, XPS) was used to characterize the peel surfaces and study the inorganic infusion into the polymer. Depth profiling of the composition was carried out with Ar sputtering at a spot size of $400 \mu\text{m}$ with a 1.2mm raster size on the high current setting. Scanning electron microscopy (Leo 1530 FE-SEM) coupled with energy-dispersive X-ray spectroscopy (EDX)

was used to study polymer sub-surface morphology and composition after infusion.

D. Adhesion test

A 90 degree peel test was used to quantify the interfacial adhesion between the dielectric and the metal seed layer (chromium). A Testing Machines Inc. peel tester was used. Peel tests were performed on 1-cm wide metal strips at a peel rate of 12 inch/min. The substrate was carefully taped onto peel test instrument to ensure that substrate warpage did not influence measured peel strength. The peel strength is dependent on three main factors: the interfacial adhesion, bending of the copper foil and elongation of copper. Controlling the thickness and uniformity of plated copper normalized the external factors and made interfacial adhesion strength comparable from run to run. Prior to testing, the samples were annealed for 1 hour at 120°C to relieve stresses from electroplating.

III. RESULTS AND DISCUSSION

A. Chemical & Structural Analysis

Unlike nanocomposites that are composed of inorganic constituents that are heterogeneously discrete at the sub-micron level, VPI creates hybrid material are homogeneous at the atomic scale. Atomic-scale infusion was confirmed using a combination of SEM and EDX. EDX (Fig. 4) detects ~ 3 wt.% Al near the surface. While no nano-scale inorganic constituents can be seen in electron microscopy (Fig. 3), EDX detects aluminum up to ~ 3 microns in depth from the surface of the film (Fig. 4). Elemental depth profiling by XPS shown in Fig. 5 further supports this infiltration depth.

B. Adhesion measurement

Fig. 6 compares the peel-test adhesion strengths for Cr/Cu layers deposited on RDLs with no VPI treatment to Cr/Cu layers deposited on RDLs exposed to VPI treatments at 100°C , 150°C , and 175°C . For the untreated polymer the peel strength is 200 g/cm . This value is consistent with prior reports for this material. With VPI treatment, the adhesion strength increases for all cases. The maximum adhesion strength measured thus far is 600 g/cm for the samples with VPI conducted at 150°C . This result represents an increase of 3x over the untreated material.

Increased adhesion at metal-polymer interfaces is usually attributed to one of three mechanisms: 1) interfacial roughness that improves the mechanical interlocking between polymer and deposited metal film 2) increased covalent bonding at the interface, or 3) electrostatic interactions that result from charge transfer [12]. Mechanical interlocking requires intimate contact between the deposited film and the substrate, which is usually achieved by providing anchoring points for the metal. Covalent bonding occurs via chemical bonding between adherends and

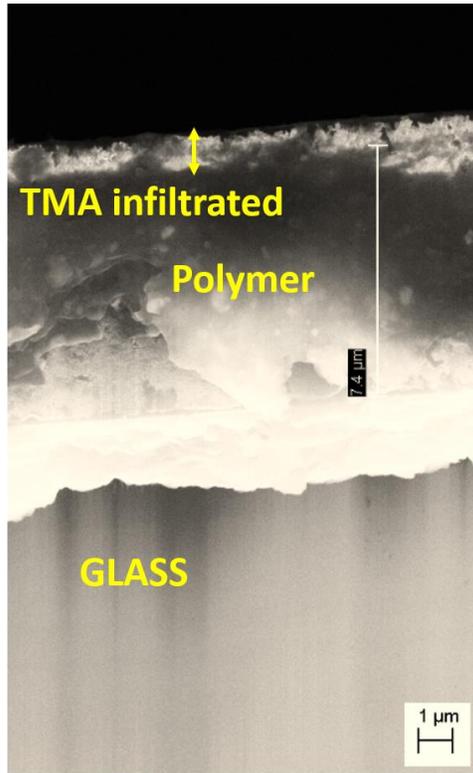


Figure 3. Cross-sectional SEM image of VPI modified RDL dielectric. An organic-inorganic hybrid layer can be seen near the surface.

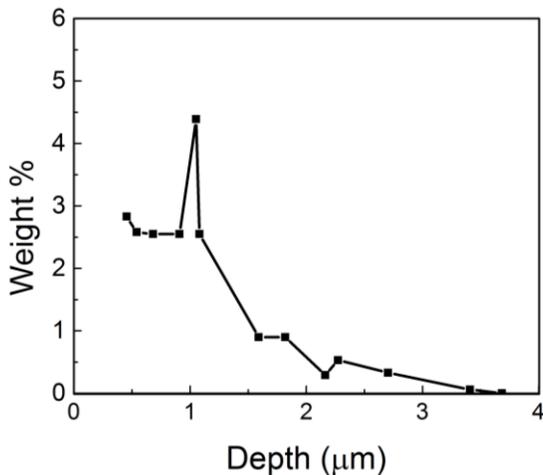


Figure 4. SEM-EDX elemental analysis of infiltrated alumina in polymer

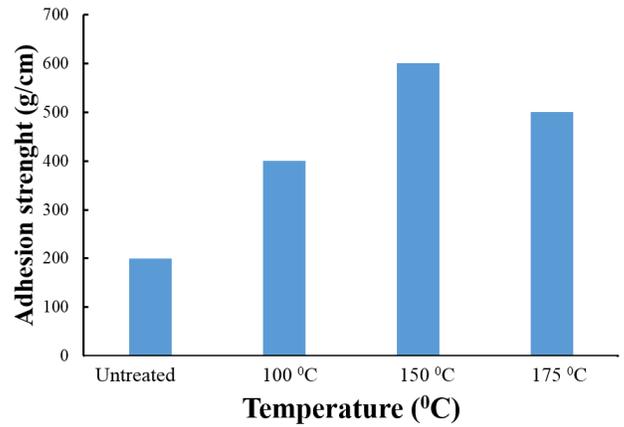


Figure 6. Peel test measurements of adhesion strength between copper and polymer for both treated and untreated polymer conducted at three different temperatures

IV. CONCLUSION

In this paper, the novel processing method of vapor phase infiltration was demonstrated to dramatically improve the metal/polymer interfacial adhesion strength in RDLs by at least a factor of 3x. This process infuses the polymer with inorganic constituents to a depth of at least two microns. Most importantly, strong covalent bonds are formed between the organic and inorganic components enabling greater adhesion to the metal layers. These improvements to RDL polymers are critical in emerging high-temperature electronics packaging applications where thermal stability beyond 200 °C is necessary. While some promising properties are shown here, further testing is required to fully understand the interfacial stability. If stable in high-humidity conditions and under mechanical vibrations, this technology

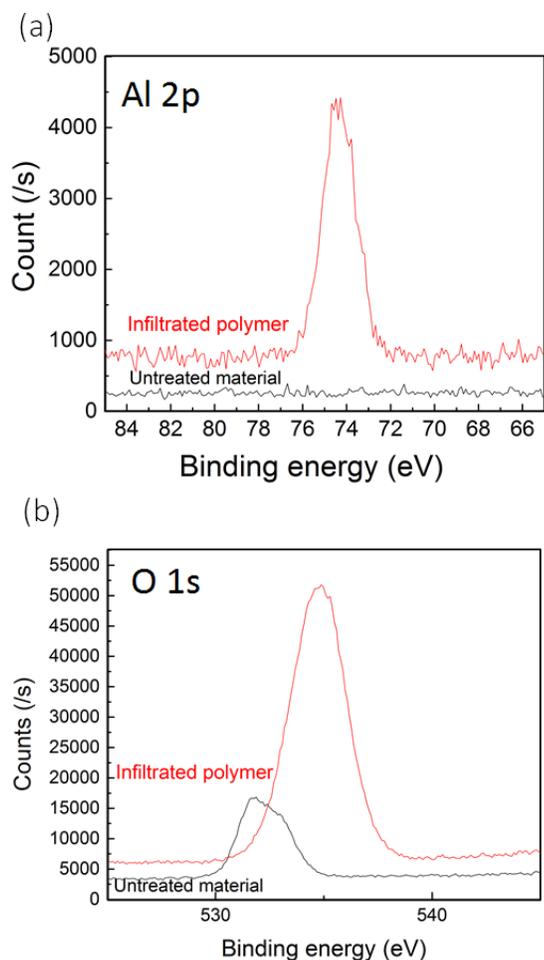


Figure 7. High-resolution XPS scans of the (a) Al 2p surface chemistry of the polymer RDL (a) before and (b) after comparison of treated and untreated polymer

has the potential to enable high-temperature high-density packages to be used in consumer, automotive or high-power electronic packages.

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