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Adhesion of Dielectric Materials

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Adhesion of Dielectric Materials

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1. Abstract

Silicon oxide, polymers, and epoxy composites are employed as dielectric layers in semiconductor devices. Adhesion of a dielectric layer to another dielectric layer or metal is important to the reliability of electronic packages such as back-end-of-line of a copper chip, a plastic flip chip package, a laminate chip carrier, and a multichip module (MCM) thin film package. Adhesion promoter is often employed to enhance the interface fracture toughness between organic dielectric and inorganic or metallic substrate. A new analytical method has been discovered for silane adhesion promoters by employing X-ray photoelectron spectroscopy (XPS) and reflectance absorbance FTIR. The first monolayer on a conductor surface can be distinguished from the second and upper layers by the charging effect of XPS. Adhesion promoters can also be used as a Cu-capping layer in MCM thin film packages. 8-Azaadenine acted as an adhesion promoter between polyimide and Cu probably because the N-H group reacted with Cu and the NH_2 group reacted with polyimide to form covalent bonds.

2. Introduction

The most advanced packages in which a polymer is employed as dielectric include the back-end-of-line (BEOL) of an ultra-large-scale integrated (ULSI) microprocessor chip, a plastic flip chip package, and a multichip module (MCM) thin film package. SiLK™, an aromatic hydrocarbon thermosetting polymer from Dow Chemical, is used in BEOL in a complementary metal-oxide semiconductor (CMOS). The SEM cross-section of a copper and SiLK™ BEOL is as shown in Figure 1 [1,2].

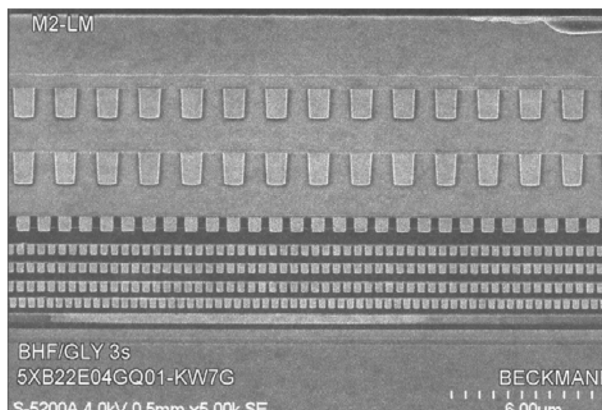


Figure 1. SEM Cross-section of 0.13 µm Copper BEOL with SiLK™ Dielectric. The bottom side is front-end-of-line (FEOL).

BEOL performance improvement requires the reduction of the resistance and the capacitance. Copper and SiLK™ are used as conductor and dielectric, respectively, because of the low resistance of Cu and the low dielectric constant (k=2.62) of SiLK™. CMOS with copper conductor is called as "copper chip". Adhesion of SiLK™ to various substrates is important to the reliability of CMOS chips [3].

In the recent flip chip packages shown in Figure 2 underfill is employed to maintain the structural integrity at the chip-laminate interface. Most underfill materials contain epoxy-based polymers. Adhesion of underfill to chip passivation layer and laminate is one of the most important requirements in a reliable flip chip package with high-density interconnection.

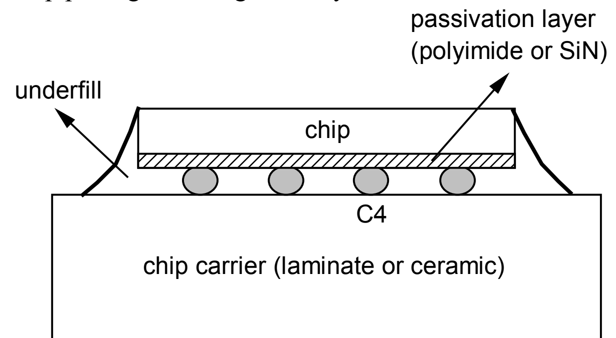


Figure 2. Plastic Flip Chip Package

In high-end MCM thin film packages, copper and polyimide have been used as conductor and dielectric, respectively, over the past two decades. Adhesion of polyimide to ceramic or metal has been extensively studied [4,5,6]. Figure 3 shows a cross-section of IBM's MCM substrate in which the conductor is Cu and the dielectric is polyimide [7].

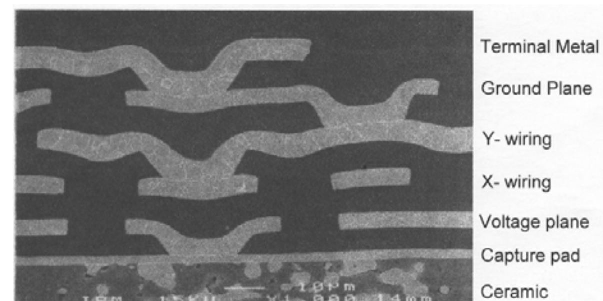


Figure 3. SEM Cross-section of Mulitchip Module Thin Film Package

There are various approaches to enhance adhesion of dielectric polymers in high performance electronic packages for which a specific polymer is chosen on the

basis of other requirements such as electrical and mechanical properties. In case of applying a polymer or a polymer precursor to a substrate, an adhesion promoter is often used to enhance the polymer-substrate interfacial fracture toughness. Two different types of adhesion promoters are reported in this paper. One is a silane coupling agent and the other is a triazole or imidazole type especially on a copper substrate.

Silane couplers have been widely used to enhance adhesion of organic materials to inorganic materials or metals [8,9,10]. Typical silane couplers, X-Si(OR)$_3$, have three alkoxy groups and a functional group. These compounds are hydrolyzed to X-Si(OH)$_3$ prior to their applications. A silanol (Si-OH) group usually reacts with the surface of an inorganic substrate while the X group interacts with an organic polymer such as polyimide and epoxy. Inorganic substrates include glass fiber, silicon oxide, silicon nitride, ceramic, and indium-tin-oxide (ITO). It is generally assumed that two Si-OH groups polymerize to siloxanes and one Si-OH group is bound to a substrate as shown in Figure 4 [8,9].

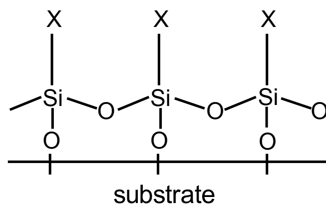


Figure 4

Upon applying a polymer precursor to a substrate with a silane coupler, the X group interacts with an active group(s) of the polymer. Curing at a high temperature often induces covalent bonds between X and an active functional group so that the corresponding adhesion becomes stronger. If X consists of an alkyl chain that forms interpenetrating networks with an organic polymer, the corresponding adhesion can also be enhanced.

Amine end groups (X=aminoalkyl) are most frequently used in industries. As shown in Figure 5, there are two widely used amine-based silane couplers.

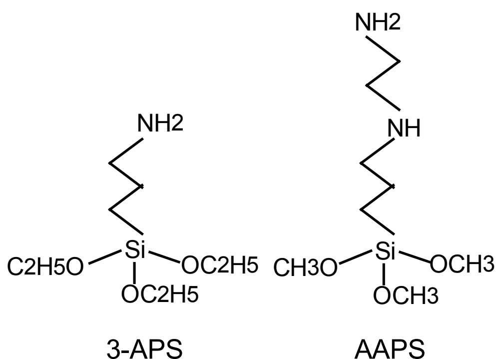
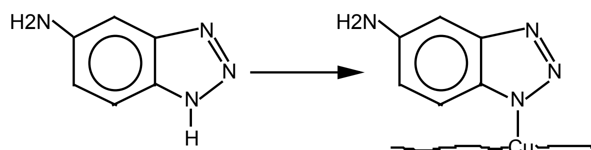


Figure 5. Amine-based silane couplers which are hydrolyzed to silanols prior to use

Since amine is basic, it can interact with acidic metal oxides. The orientation of 3-APS on silicon oxide will be discussed.

Silane couplers tend to make more than monolayers on a substrate. Uniform monolayers are probably the optimal case for most applications while a too thick layer can cause adverse effects such as thermal degradation and dielectric loss. Thus it is important to apply an optimum amount of a silane coupler. Here we report on our recent finding in analyzing the amount of silane couplers as well as indentifying monolayers from multilayers with high-resolution X-ray photoelectron spectroscopy (XPS).

Triazoles and imidazoles are known to react with Cu to form a thermally stable complex as shown in Scheme 1 [11]. 5-Aminobenotriazole and 8-azaadenine consist of a triazole group and an amine (NH$_2$) group. The former reacts with Cu and the latter interacts with an active group(s) of a polymer. Thus this type of molecules acts as an adhesion promoter between polymer and copper substrate [5,6,12,13,14]. Adhesion between polyimide and copper using 8-azaadenine adhesion promoter will be discussed [15].



Scheme 1

3. Results and Discussion

Orientation of Amine-Based Silane Couplers

It has been reported that both silanol and amine are in contact with a substrate in case of 3-APS [16,17]. An interesting question was what kind of bonding was formed between primary amine and metal oxide. Two different types of bonding were proposed. One is ionic bonds between amine salt and metal oxide. The other is to form an amine ligand-metal complex as shown in Figure 6 [18].

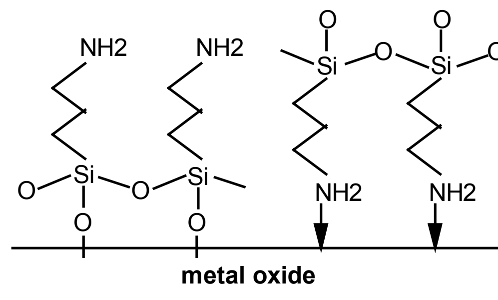


Figure 6. Orientation of 3-APS at the metal oxide surface [18]

3-Aminopropyltriethoxysilane (3-APS) was hydrolyzed in water and then applied onto an ITO substrate followed by baking at 85 ^{o}C for 30 min.

Reflectance absorbance infrared (RAS-IR) spectrum showed siloxane (Si-O-Si) bands but no significant silanol (Si-OH) bands. XPS showed no band due to amine salts ($-NH_3^+$), the band of which appears around 402 eV while the band of amines comes at 399-400 eV. The combination of the published results [16,18] and the results in this work leads to the chemical structure in Figure 6. The primary amine acts as a chelating ligand to form an organometallic complex. Silanols polymerized to poly(siloxane)s at the 3-APS-to-metal oxide interface as well as the 3-APS-to-3APS interface to give more than monolayers.

Quantitative Analysis of Adhesion Promoter with High-Resolution XPS

The chemical structure of [3-(2-aminoethyl)-aminopropyl]trimethoxysilane (AAPS) is shown in Figure 5. AAPS was hydrolyzed in a mixture of 10% water and 90% 2-propanol at room temperature to yield $H_2NCH_2CH_2NHCH_2CH_2CH_2CH_2Si(OH)_3$. The range of its concentration was 0.05% to 3.0%. Stainless steel (SS) was employed as a substrate. SS substrates were cleaned in 5.0M nitric acid and subsequently rinsed with water prior to use. The cleaned surface consists of metal oxides which were analyzed with XPS. The metal components of a cleaned SS surface were Cr (51.7% XPS atomic concentration), Fe (45.7% AC) and Ni (2.6% AC). In a typical experiment, a cleaned SS substrate was immersed into a 0.1% AAPS solution at ambient temperature for 1 min, blow-dried and then baked at 70-120 ^oC for 15-30min.

Atomic concentrations on the AP-coated surface were determined with high-resolution XPS (Table 1).

Table 1. XPS atomic concentrations (ACs) of AAPS on metal oxide substrate containing Cr. The range of the AAPS concentration was 0.05 % to 3.0%.

Experimental Run	Si AC, %	Si/Cr ratio
1	0	0
2	3.3	0.27
3	5.1	0.42
4	6.3	0.59
5	7.4	1.04
6	8.2	1.39
7	9.2	2.24
8	10.0	3.12
9	11.2	7.47
10	11.6	19.3

There are Si_{2s} and Si_{2p} bands due to AAPS. In these experiments the Si ACs are in the range of 3.3% to 11.6%. If the sample with 6.3% Si AC is compared with that of 11.6% Si AC, the latter has only twice more Si atoms than the former in the XPS sampling depth. But the actual coverage of AAPS on the SS substrate seems much greater. Thus AC does not directly indicate the amount of AAPS adhesion promoter on a substrate while the ratio of Si AC (from adhesion promoter) to Cr AC (from substrate) is a true quantitative measure of the amount of adhesion promoter on an SS substrate. A relatively thick layer of an adhesion promoter on a flat and reflective surface can be measured with ellipsometry [19].

The O_{1s} XPS spectrum of the AAPS-coated SS substrate shows two bands as shown in Figure 7. As the concentration of AAPS increased, the relative

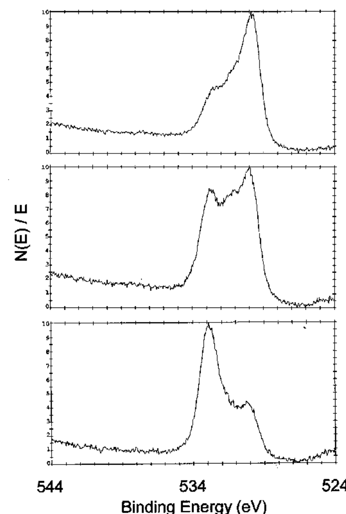


Figure 7. XPS O_{1s} Spectra. As the concentration of silane coupler increased from top to bottom, the intensity of the higher BE peak of AAPS increased

intensity of the higher binding energy (BE) peak increased since the oxygen of AAPS has higher BE in high-resolution XPS than that of metal oxides such as chromium oxide. The area ratio of two peaks which can be obtained by curve-fitting is another quantitative measure of the coverage of an adhesion promoter on metal oxides.

Identification of Monolayers from Multilayers

It is often assumed that adhesion promoters are monolayers on metal oxide substrates when the AP concentration is 0.1% or less. There was no report of distinguishing the first monolayer from the second and upper layers. A new technique was discovered in this work.

In a typical experiment, a hydrolyzed solution of n-octadecyltrimethoxysilane (OTMS) in a mixture of 2-propanol (95%) and water (5%) is spin-coated onto an indium-tin-oxide (ITO) substrate. The 0.1% OTMS solution seems to give mostly monolayers while the 0.5% solution provides multilayers. The ITO surface coated with 0.1% OTMS gave one sharp C_{1s} band in high-resolution XPS while that of 0.5% OTMS showed two C_{1s} bands as shown in Figure 8. The first monolayer on a conductive ITO surface are not expected to have a charging effect during taking XPS since charges are dissipated through the conductive ITO layer, but the second and upper layers are likely to have a charging effect since the first monolayer acts as an insulating layer. Thus the band corresponding to the

second and upper layers could be distinguished from that of the first monolayer since the former is shifted to a higher BE due to charging while the latter appears at a normal BE position (for example, the C_{1s} band appears at 284.5 eV).

The areas of the two bands (284.5 eV and 285.8 eV due to the first monolayer and the second and upper layers of OTMS, respectively) are calculated with a curve-fitting program in the Phi XPS System. The curve-fitted bands are shown in Figure 8 (bottom).

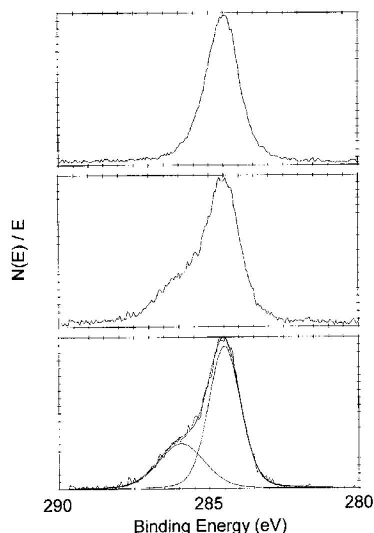


Figure 8. C_{1s} XPS bands of OTMS layers on ITO. 0.1% OTMS (top) and 0.5% OTMS (middle). Curve-fitting of the 0.5% C_{1s} bands (bottom).

The ratio of the two areas is 60/40, indicating that an approximate amount of the first monolayer is 60% of the total OTMS on ITO in case of 0.5% OTMS. This new technique enables us to distinguish organic monolayers on a conductor or semiconductor surface from the second and upper layers.

Adhesion Promoters on Copper Substrate

The N-H group of triazole and imidazole compounds is known to react with Cu to form a N-Cu complex. If a molecule has a triazole or imidazole type group and an amine ($-NH_2$) group that can react with a polymer, it can act as an adhesion promoter molecule. 5-Aminobenzotriazole in Scheme 1 and 8-azaadenine in Figure 9 are such compounds. Thermal stability of adhesion promoters is also important to applications in microelectronics. The decomposition temperature of 8-azaadenine is higher than 300 ^{o}C in air.

A 0.3% solution of 8-azaadenine in NMP is spin-coated onto a copper substrate and baked at 85 ^{o}C for 30 min. A poly(amic ethyl ester) solution, m-Paete™ from Ciba-Geigy, was subsequently spin-coated and then cured to PMDA-ODA polyimide under nitrogen at 400 ^{o}C for 60 min. A peel strength of 420 J/m^2 was obtained by 90° peeling the polyimide film. The same experiment without 8-azzadeine gave 75 J/m^2 [15].

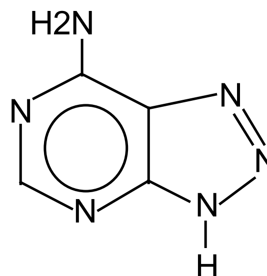


Figure 9. 8-Azaadenine. The secondary amine (=N-H) reacts with Cu surface and the primary amine (-NH2) interacts with active functional groups of a polymer.

Thus the practical adhesion strength increased with 8-azzadenine adhesion promoter. Triazoles and imidazoles are also known to be corrosion inhibitors of Cu since they form organometallic complexes that are stable in ambient.

Cu Capping in MCM Thin Film Packaging

Silane couplers can be used as a Cu capping layer in MCM thin film packages [20]. In a process of depositing a polyimide (PI) dielectric onto copper, a poly(amic acid) (PAA) solution is spin-coated to the Cu surface and subsequently cured at 400 ^{o}C to yield polyimide. Upon curing PAA, Cu reacts with PAA to give Cu_2O which diffuses into the PI layer to leave Cu_2O precipitates that increases the dielectric constant of the cured polyimide [21,22]. To prevent Cu diffusion into the polyimide layer, various metal capping layers have been used over the years such as Cr, Ti, Pd, and CoP. A polymer capping layer has been studied by K.-W Lee, et al. [5,6]. These metal and polymer capping layers also enhance the polyimide-Cu adhesion.

To simplify a capping process in MCM thin film packaging, 3-APS is employed as a capping and adhesive layer. A hydrolyzed solution of 3-APS was applied to a Cu substrate and baked at 85 ^{o}C for 15 min. BPDA-PDA poly(amic acid) was subsequently spin-coated and cured to polyimide under nitrogen at 400 ^{o} C. The peel strength was greater than 750 J/m^2, and the Cu diffusion studied with cross-sectional TEM was negligible. No significant effect of Cu_2O precipitates on the dielectric constant of BPDA-PDA polyimide was found [20]. Triazole and imidazole type compounds can also be employed as a capping layer on Cu substrates.

Adhesion Tests

There are several different adhesion tests used in industries. They are scotch tape test, peel test, wedge test, modified wedge test, cantilever beam test, 2 or 4 point bending beam test, indentation test, etc. Peel test is most widely employed in industries since it is simple and the test area can be large to check uniformity of adhesion on a large substrate. Another advantage of

the peel test is in easily getting locus of failure with surface sensitive analytical methods such as XPS.

In case of a thin dielectric layer, a peel-backing layer is employed as shown in Figure 10 [23]. A dielectric layer is deposited on a substrate to measure adhesion of dielectric to substrate. Then a thick (~20 um) peel-backing layer that adheres well to the dielectric layer is coated. The peel-backing and dielectric layers are diced together to give 3-5 mm peel width. Then 90° peel strength is measured. Just after peeling, both sides are analyzed with XPS to determine locus of failure within 10 nm of the surface. The combination of peel strength and locus of failure indicates a qualitative practical adhesion strength that can be used to pass or fail a process or a material in applications.

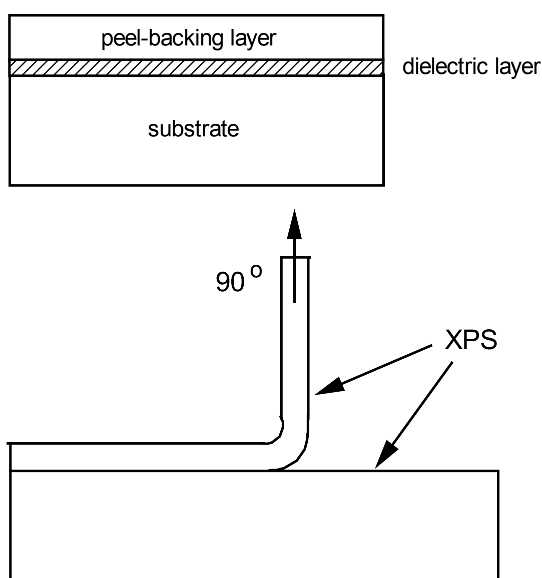


Figure 10. Sample preparation in case of a thin dielectric layer (top) and 90° peel test. XPS is taken on both surfaces to determine locus of failure

4. Summary

Adhesion of dielectric materials in microelectronic devices is one of the most important requirements to qualify processes, materials and eventually products. There are several testing methods and the choice of test depends on processes and materials. The locus of failure usually determined with XPS is indicative of poor or good adhesion.

To enhance adhesion of dielectric to substrate, an adhesion promoter can be employed. Silane couplers are also employed as a capping layer in MCM thin film packages to promoter adhesion as well as to reduce Cu diffusion. An analytical method to determine the amount of adhesion promoter is discovered. The amount of silane couplers such as AAPS and 3-APS on a rough or flat surface of metal oxides could be determined with the ratio of atomic concentrations and/or the ratio of two O_{1s} bands in XPS. Practical adhesion strength is determined by 90° peel test for which a thin (~20 μm) layer of polyimide is employed as a peel-backing layer.

The first monolayer on a conductor surface can be distinguished from the second and upper layers by the charging effect of XPS. 8-Azaadenine acted as an adhesion promoter between polyimide and Cu probably because the N-H group reacted with Cu and the NH_2 group reacted with polyimide to form covalent bonds between Cu and 8-azaadenine and between 8-azzadenine and polyimide.

5. Acknowledgments

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6. References

[1] R.D. Goldblatt et al., “A High Performance 0.13 *u*m Copper BEOL Technology with Low-*k* Dielectric”, *Proceedings of the 2000 Int’l Interconnect Technol. Conf.* pp. 261-263. IEEE Electron Devices Soc. (2000).

[2] J.C. Hedrick, et al. “Low-*k* Dielectric Materials for High Performance Interconnects”, presented at the Amer. Chem. Soc. 233rd Nat’l Meeting; Orlando, FL; April 2002.

[3] J.C. Hedrick, K.-W. Lee, E.G. Liniger, and E. Simonyi, *US Patent*, in press (2002).

[4] L.P. Buchwalter, “Adhesion of Polyimides to Various Substrates”, in *Polyimides: Fundamentals and Applications* (M.K. Ghosh and K.L. Mittal Eds.), pp. 587-628. Marcel Dekker, NY, NY (1996).

[5] K.-W. Lee, G.F. Walker, and A. Viehbeck, *J. Adhesion Sci. Technol.* **8**, 1125-1141 (1995).

[6] K.-W. Lee, A. Viehbeck, G.F. Walker, S. Cohen, P. Zucco, R. Chen, and M. Ree, *J. Adhesion Sci. Technol.* **9**, 807-821 (1996).

[7] D. McHerron, K. Patel, E. Perfecto, and T. Redmond, “Application of Polyimide in Thin Film Packaging at IBM”, *Symp. on Polym. for Microelectronics*. Wilmington, DE. (May 2000).

[8] E.P. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York (1982).

[9] *Silanes and Other Coupling Agents*, K.L. Mittal, Ed., VSP, Zeist, The Netherlands (1993).

[10] H.G. Linde and R.A. Previti-Kelly, *US Patent 5114757* (1992).

[11] G. Xue, J. Dong, and J. Zhang, *Macromolecules* **24**, 4195 (1991).

[12] F.P. Eng and H. Ishida, *J. Mater. Sci*. **21**, 1561 (1986).

[13] H. Ishida and K. Kelly, *J. Adhesion 36*, 177 (1991).

[14] S.M. Song, C.E. Park, H.K. Yun, C.S. Hwang, S.Y. Oh, and J.M. Park, *J. Adhesion Sci. Technol.* **12**, 541-561 (1998).

[15] K.-W. Lee, M. Ree, J.M. Shaw, and A. Viehbeck, "High-Temperature Stable Adhesion Promoter for Polymer-to-Copper Interface: Organic Compounds Containing Triazole or Imidazole*", IBM Technical Disclosure Bulletin*, **37**, No. 5, May 1994.

[16] W.J. van Ooij and A. Sabata, *J. Adhesion Sci. Technol.* **5**, 843-863 (1991).

[17] W.J. van Ooij and A. Sabata, in *Polymer/Metal Interfaces* (R.L. Opila, F.J. Boerio and A.W. Czanderna, Eds.), pp. 155-160. Mater. Res. Soc., Pittburgh, PA (1993).

[18] B.N. Eldridge, L.P. Buchwalter, C.A. Chess, M.J. Goldberg, R.D. Goldblatt and F.P. Novak, , *J. Adhesion Sci. Technol.* **6**, 109-125 (1992).

[19] D.I. Kong, C.E. Park, S.T. Hong, H.C. Yang amd K.T. Kim, *J. Adhesion Sci. Technol.* **13**, 805-818 (1999).

[20] E. Perfecto, K.-W. Lee, H. Hamel, T. Wassick, C. Cline, M. Oonk, C. Feger, and D. McHerron, "Evaluation of Cu Capping Alternatives for Polyimide-Cu MCM-D," *IEEE 51st ECTC Proceedings,* Orlando, FL (May 2001).

[21] Y.-H. Kim, G.F. Walker, J. Kim, and J. Park, , *J. Adhesion Sci. Technol.* **2**, 95-105 (1988).

[22] D.Y. Shih, J. Paraszcak, N. Klymko, R. Flitsch, S. Nunes, L. Lewis, C. Yang, J. Cataldo, R. McGouey, W. Graham, R. Serino, and E. Galligan, *J. Vac. Sci. Techonol. A* **7**, 1402 (1989).

[23] J. Kim, L.P. Buchwalter, H. Clearfield, P. Lauro, K.-W. Lee, S. Nunes, J. Paraszcak, S. Purushothaman, A. Viehbeck, D.-Y. Shih, M. Anschel, S. Kamath, R. Lacomb, C. Lund, M. Plat, H. Souleotis, and C. Czornyj, "Adhesion Test Standardization for MCM Packages", *Proceedings of 45th Electronic Components and Technol. Conf.*, pp. 884-888 (1995).