Engineering Surfaces in Ceramic Pin Grid Array Packaging to Inhibit Epoxy Bleeding

Ningxia Tan
Kenneth H. H. Lim
Bernard Chin
Anthony J. Bourdillon

Bleeding of epoxy resin around surfaces undergoing bonding during electronic packaging assembly has long caused sporadic yield loss. Previously, it was thought that vacuum baking reduced the yield loss resulting from surface contaminants. Although vacuum baking inhibits epoxy resin bleeding, it also produces coatings of hydrocarbons, which affect surface wettability and surface energy. Surfactant coating results in a surface chemistry similar to vacuumbaked substrates but is a better alternative because of its controllability.

Epoxy bleeding is commonly observed in electronic packages around silicon chips attached with epoxy resin to substrates having gold or other metal surfaces. In severe cases, the bleeding contaminates the wire bond pads, causing failure. The effects of bleeding are often critical in advanced packaging components such as ceramic pin grid array (CPGA) substrates. In particular, when there is very little clearance between a bond finger tier and the die, minor resin bleedout can interfere with wire bondability.

During the time that CPGA technology has been used here at HP's Integrated Circuit Business Division in Singapore, we have experienced sporadic yield loss caused by epoxy bleeding. This is known to be an industry-wide problem. For several years the cause of the yield loss was unresolved. With increasing pin count and decreasing clearance between the die and the substrate cavity, resolving the problem has become more urgent.

Earlier studies¹ led us to resort to countermeasures like vacuum baking to reduce yield losses. However, the studies were not comprehensive enough to verify the effectiveness of vacuum baking, and yield losses have continued to occur from time to time for no apparent reason. We had not yet investigated the possibility that surface contamination, resulting from vacuum baking, can have







the positive effect of reducing epoxy bleeding during die attachment.

In this article we describe how we used surface analysis and contact angle measurements to investigate the effects of vacuum baking on yield loss caused by epoxy bleeding. The same analysis techniques were employed to investigate the possibility of using surfactant-coated substrates to reduce epoxy bleeding.

For our analysis we used a CPGA (ceramic pin grid array) substrate² from one of our typical applications (see **Figure 1**). It consisted of a Cu-W heat slug onto which was electroplated a film of Ni (10 μ m thick) followed by Au (typically 1.2 μ m thick). The surface was cleaned and vapor dried with isopropyl alcohol. When the thickness of the surface gold film was varied from 1 μ m to 2 μ m on different specimens, the wettability was found to be independent of the gold thickness. The schematic in **Figure 1** shows the substrate after die attachment but before wire bonding.

Analysis of Vacuum-Baked Substrates

Investigations into the effects of vacuum baking focused on two areas: Auger analysis and wettability.

Auger Analysis. Auger analysis is an analytical technique that uses electron spectroscopy to examine the elemental

composition of the outer atomic layer of a solid material (see "Auger Analysis" on page 83). Examining the elemental composition of surface contaminants on a solid is one application of this technique. Our analysis was performed on a JEOL JAMP- 7100E Auger analyzer. The accelerating voltage was 5 kV, and the probe current was 1.52×10^{-7} A. Argon ion etching was applied with an etching speed estimated at 1.25 nm every 10 seconds on a silicon surface.

The analysis was carried out on substrates prepared for die attachment. **Figure 2** shows the discoloration caused by bleeding around a bonding pad. Auger spectra were recorded from the die attach pads (heat slugs), which consist of Cu electroplated with Ni and Au. Comparisons were made between samples in a vacuum at two stages during the process: before baking and after baking. The purpose of this was to monitor the contamination that results from baking. The samples consisted of the following:

- A raw CPGA substrate
- A CPGA substrate that was baked at 235°C for six hours in a conventional vacuum oven at a pressure of 0.1 mbar
- A CPGA substrate that was baked in an air convection oven at 235°C for six hours.

Figure 2

Photographic image of the die showing attached wires and edge discoloration (see arrow) caused by epoxy bleeding.



Glossary

Auger Analysis

Auger (pronounced o-jay) analysis is a widely used electron spectroscopic method that is capable of providing information about the elemental composition of the outermost atomic layer of a solid. This technique examines the surface chemistry and interactions of elements on the surface of materials such as metals, ceramics, and organic matter. Auger analysis is named after its discoverer Pierre Auger.

The Auger process involves using a finely focused electron beam to bombard atoms on the surface of the sample being analyzed. When an atom on the sample is struck by a highenergy electron, there is a probability that a core-level electron will be emitted (**Figure 1a**). This collision puts the atom into an energetic ionic state with an electron missing from the core level. The atom can relax into a lower-energy state when another electron from the same atom falls from a higher-energy level to fill the core-level hole, releasing enough energy to eject a second electron—the Auger electron (**Figure 1b**). The state shown in **Figure 1c** is still excited and decay continues radiatively by another Auger process. Auger electrons will have an energy characteristic of the parent element. An energy spectrum of detected electrons shows peaks assignable to the elements present in the sample.



The ratios of the intensities of Auger electron peaks can provide quantitative information about the surface composition of a sample (for example, see **Figure 3** of the main article).

Surfactant

Some chemical materials have a special propensity to locate (adsorb) at interfaces or to form colloidal aggregates in solution at very low molar concentrations. Such materials are called surface-active agents, or surfactants. Surfactants are used to modify the wettability of solid surfaces.

Wettability

When a drop of liquid is placed on a solid surface, the liquid either spreads to form a thin film on the surface as in **Figures 2a** and **2c**, or remains a discrete drop as in **Figure 2b**. The measure of the degree of wetting is the *contact angle* (see **Figure 2a**). The contact angle is the angle made by the tangent to a droplet at the solid surface interface. High wettability is indicated by a small angle (**Figure 2c**). The extreme case of no wettability is shown in **Figure 2b**.



Measurements were taken from several specimens of each type and found to be consistent. For comparison, additional measurements were taken from a second specimen (specimen B in **Table I**) which was subjected to evacuation at room temperature, without baking.

Wettability, Contact Angle, and Surface Energy. A liquid that spreads easily on a solid because of high surface energy has high wettability. This is quantified by measuring the angle that the liquid surface makes at the interface with the solid surface. Such wettability contact angles were measured through the sessile drop method³ on a face contact anglemeter, model CA-A from Kyowa Interface Science Company.

Media used for calculating surface energies were deionized water and methylene iodide. Contact angle measurements were performed on raw substrates and on substrates after vacuum baking. To measure contact angles, the die pad area of a package was separated from the corresponding ceramic substrate by chipping away the side walls. A horizontal profile projector, at $20 \times$ magnification, was used to measure the equilibrium contact angle.

Repeated measurements from several specimens of each type of substrate were found to be consistent to within three degrees. The computation for the surface energy, r_{S} , is based on the method described by Wu and Brzozowski.⁴ The surface energy of the solid is the sum of the surface

dipole component, r_S^p , and the surface dispersion component, r_S^d . These components are related to the contact angle θ by the formula:

$$1 + (\cos \theta) r_{\rm L} = 4 \left(\frac{r_{\rm L}^{\rm d} r_{\rm S}^{\rm d}}{r_{\rm L}^{\rm d} + r_{\rm S}^{\rm d}} + \frac{r_{\rm L}^{\rm p} r_{\rm S}^{\rm p}}{r_{\rm L}^{\rm p} + r_{\rm S}^{\rm p}} \right)$$
(1)

where r_L is the surface tension of the liquid used in wetting and consists of the sum of the dispersion and polar components. If all of the components of r_L are known for two liquids, then two corresponding measurements of the contact angle will make it possible to solve for r_S^d , r_S^p , and so on by solving the quadratic equation derived from equation 1.

Preliminary Results

Our quantitative analysis focused on Auger analysis as well as contact angle measurement and surface energy computation.

Auger Analysis. Figure 3a shows typical Auger spectra taken from a raw substrate. The etching times were zero seconds and five seconds. The elements detected on the surface were Au, S, C, and N. After five seconds of etching (**Figure 3b**), two of the contaminants, C and N, disappeared. A trace of S on the subsurface was estimated to be at a mean depth of 1.25 nm below the original surface.



Figure 4



Auger spectra generated from the die attach pad of a CPGA substrate after vacuum baking and after etching times of (a) 0 seconds, (b) 10 seconds, and (c) 20 seconds.

Figure 4 shows the Auger spectra taken on a substrate after vacuum baking. Etching times of zero seconds, ten seconds, and twenty seconds were used. Notice that, compared with the raw substrates, the C contamination is much greater. Even after a 20-second etching time (equivalent to an etching depth of about 5 nm), C continues to be observed, showing that the thickness of the carbon film is greatly increased by the baking procedure.

Auger spectra were taken on the substrate after baking in air only. Etching times of zero, five, and ten seconds were applied (see **Figure 5**). Notice that after five seconds of etching, C contamination was gone. The C contamination level is comparable with spectra for the raw substrate shown in **Figure 3b**. Although they were etched away before the plot in **Figure 5b** was made, traces of Ni and O were detected on the surface. These traces apparently result from diffusion of subsurface Ni during baking and from its oxidation by air.

Table I lists the results of the quantitative analysis. The results from specimen 2 show that evacuation at room temperature is not contaminating by itself. Some of the contamination comes from a dynamic process in which a cold specimen is immersed in a hot oven containing back-stream oil vapor.

Contact Angle Measurement and Surface Energy Computation. The measurement and computational results⁴ from a raw substrate before vacuum baking and after vacuum baking are listed in **Table II**. In these measurements, possible variations related to surface morphology were minimized by comparing measurements from specimens of the same lot. Furthermore, gold-plated surfaces are sufficiently dense to allow us to ignore surface morphology.

As described earlier, a significant increase in the carbon signal is observed after baking. At the same time, the solid surface energy decreases, especially the polar component. The observed decrease in surface energy is consistent with known surface energies from typical hydrocarbons, such as paraffin tetradecane (25.6 milliJoules per square meter, or mJ/m²), so that the surface energy of the contaminated surface (33.6 mJ/m²) lies between that value and the surface energy of the raw surface (41.1 mJ/m²). Thus, the effective polarity of the substrate is reduced by the separation from the liquid drop provided by the insulating hydrocarbon film. This is also consistent with the knowledge that hydrocarbons prevent the spreading

Figure 5

Auger spectra generated from the die attach pad of a CPGA substrate after baking only in air and after etching times of (a) 0 seconds and (b) 5 seconds. After etching for 10 seconds, the spectrum was similar to (b).



Table I

Elemental Analysis of CPGA Surface from Auger Spectra

	Etching Time	Etched Thickness	Chemical Concentration (Atomic %)					
	(s)	(nm)	Au	0	С	S	Ν	Ni
Specimen A								
Raw Substrate	0		58		34	4	4	
	5	1.25	100					
Vacuum Baked	0		33	4	57	1	5	
	10	2.5	66		34			
	20	5.0	76		24			
Baked in Air	0		45	20	27	2	2	4
	5	1.25	100					
	10	2.5	100					
Specimen B								
Raw Substrate	0		45		51	1	3	
	5	1.25	100					
	10	2.5	100					
Ambient Evacuated	0		45		51	2	2	
	5	1.25	100					
	10	2.5	100					

Table II Measured Equilibrium Contact Angles and Computed Surface Energies											
	Contac	t Angle (Degrees)	Sur	Surface Energy (mJ/m ²)*							
CPGA Substrate	Water	Methylene lodide	rgd	r ^p S	r _S	Polarity**					
Raw substrate	76.3	44.8	28.6	12.5	41.1	0.30					
Vacuum baked	92.4	54.1	27.9	5.7	33.6	0.17					
Surfactant coated	94.4	49.3	31.7	4.1	35.8	0.11					

* The surface energy \mathbf{r}_S is the sum of the dispersion component \mathbf{r}_S^d and the polar component \mathbf{r}_S^p .

** The surface polarity is equal to the ratio $\,r_S^p/r_S\,$.

of water on gold,⁵ even at a coverage of one monolayer. The surface energy, as measured, is much less than the known surface energy of Au (1510 mJ/m²).⁶ The very high surface energy of gold demonstrates the importance of the surface film on wettability. Clearly, the polar interaction of the gold surface is reduced by atmospheric contamination (water vapor and organics). With baking, the nonpolar oil vapor further reduces the polar interaction.

Preliminary Discussion

The Auger results discussed above show that carbon contamination increases dramatically after standard procedures of vacuum baking. Typically, oil from the rotary vacuum pump backstreams to the oven and diffuses pore contaminants in the process. The samples are placed in a hot oven, which is then pumped down to create a vacuum. Because of thermal gradients, hydrocarbon vapor can then preferentially condense on cold substrate surfaces. This likelihood is consistent with the Auger analysis data on substrates that have been vacuum baked. In confirmation, surfaces that are only exposed to a high vacuum at room temperature, but without baking (that is, without thermal gradients) show an insignificant increase in contamination deposition.

Since hydrocarbon contamination inhibits epoxy bleeding, it is not necessarily advantageous to eliminate surface contamination. Hydrocarbon films, deposited on substrates during vacuum baking, have reduced surface energies (**Table II**) compared with clean Au surfaces. Surface energy and contact angle are related as in the Young-Dupré equation:^{7,8}

$$\mathbf{r}_{\mathbf{S}} = \mathbf{r}_{\mathbf{L}} \cos \,\theta + \mathbf{r}_{\mathbf{LS}} \tag{2}$$

where r_{LS} is the interfacial tension. When the surface energy is reduced, $\cos \theta$ is correspondingly reduced, resulting in high contact angles. A high contact angle implies a less wettable surface and therefore inhibits spreading phenomena when an adhesive material is applied to the solid surface. Consequently, the resin bleeding, caused by epoxy applied for die attachment in electronic packaging substrates, will be inhibited by the coatings. Since the electroplated Au surfaces have natural porosity, any degradation in adhesion caused by the coating is not critical. (Further discussion of this adhesion is given later.) Also, the dependence of the coating on various vacuum systems is discussed in reference 9.

The coating on vacuum-baked substrates, whether caused by oil backstreaming or by substrate contaminating residue, cannot be controlled. Neither the source of contamination nor the deposition conditions can be precisely determined. Inconsistency in surface quality explains why the sensitive effects of the contamination result in sporadic yield losses. A technique is needed that is compatible with other required properties, such as adhesion strength, that will result in hydrocarbon film coatings with near optimum contact angle.

Analysis of Surfactant-Coated Substrates

A substrate was coated with a surfactant and subjected to the same Auger and contact angle characterization used on vacuum-baked substrates.

Auger Analysis. Figure 6 shows the presence of carbon on the gold-plated layer. Initially, the carbon concentration is greater than in the vacuum-baked specimen shown in Figure 4. After 10 seconds of etching (Figure 6b),



Auger spectra generated from a surfactant-coated CPGA substrate after etching times of (a) 0 seconds and (b) 10 seconds.



there is still a considerable amount of surface carbon, showing that the film thickness of the hydrocarbon contaminants is greater than 1.2 nm.

As mentioned earlier, vacuum baking inhibits epoxy bleeding because of the hydrocarbon contamination it leaves on the surface of the substrate. Surfactant coating is also meant to contaminate a substrate's surface with a hydrocarbon film. From the results given in **Figures 4** and **6** it would seem that there is no difference between these two processes. However, from our study the shortcoming of the vacuum-baking process is that the hydrocarbon source is not controlled because of the oil backstreaming from the vacuum pump. On the other hand, surfactant coating can be controlled by mixing the right concentration of surfactant with water, forming the hydrocarbon film in the solution.

Wettability Contact Angle and Surface Energy. Equilibrium contact angles and computed surface energies on a surfactant-coated substrate are shown in **Table II** (last entry). The surface energy is considerably reduced from the raw substrate state and is close to the value calculated from the vacuum-baked substrate.

The coating consistency was evaluated by comparing contact angles of deionized water on 25 substrates sampled from five different lots. For an average measurement of 95°C the standard deviation was 1.9 percent. This deviation of less than 2 percent was about five times lower than was observed in vacuum-baked substrates and illustrates the satisfactory controllability of the surfactant coating process.

The coating stability was also investigated in two ways: by exposure to solvents and by exposure to air. After subjecting the coated substrate to typical cleaning processes, such as soaking in deionized water for 72 hours, Auger analysis showed no significant difference between substrates soaked 72 hours and substrates not soaked at all. Secondly, the contact angle was monitored in coated substrates exposed to a normal air-conditioned environment. With exposures of up to six months, no change was observed. However, at longer exposures, a small reduction in the contact angle was observed (for example, 5° after nine months). Thus, the surfactant coating process is compatible with production needs.

Discussion

Surfactant coating results in a surface chemistry similar to vacuum-baked substrates, but with the benefit of controllability. What effect do surfactants have on adhesion? The adhesion was tested by experiments involving die shear strength. Adhesive strengths greater than 20 kg/cm² were measured, consistent with U.S. military specifications.¹⁰ Thus, although low wettability is generally accompanied by reduced adhesion, we found that the reduction

was not critical and within process margins. In these substrates, capillary effects, chemical bonding, and other factors ensure that the surfaces retain sufficiently strong adhesion, even when the surfaces are altered by the contamination we measured.

Similar tests were performed involving wire bond pull strength. In spite of the surface modification resulting from processing, pull strengths greater than 6 g for 1.2-µm-diameter gold wires were measured. Thus, the coated films were thin enough to have an insignificant effect on wire bond strength. The surfactant coated substrates passed Hewlett-Packard's general semiconductor qualification specification.

Finally, the surface tension is different in various adhesives, including various types of epoxy, polyimides, and similar materials. The selection of an adhesive depends on trade-offs between adhesion strength, curing times, moisture absorption, and other parameters. We have demonstrated that wettability can, in actual practice, be controlled.

Conclusion

This study illustrates the degree of cleanliness appropriate in processing of electronic packages. We had been striving for very clean ceramic surfaces, but that degree of cleanliness produces high surface energies that are susceptible to epoxy bleeding. It is not necessary to provide very clean substrates. On the contrary, it is preferable to engineer surfaces by treatment with a film of high wettability. Vacuum baking is not sufficiently controllable and is therefore not effective. A better alternative is an effective, controllable, simple, and reliable surfactant coating.

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Ningxia Tan A principal engineer at

the HP Integrated Circuit Business Division, Ning-

xia Tan is responsible for new packaging development and package material research. She joined HP in 1994. She received a BSc degree in material science from Chongqing Institute for Architecture and Engineering in 1985 and a PhD in material science from the University of New South Wales in 1991. Born in the Peoples Republic of China, she is married and has two children.



Bernard Chin Bernard Chin joined the

HP Integrated Circuit Business Division in

1990. Bernard is responsible for conducting reliability evaluations and interpreting results from the failure analysis and reliability laboratory. He received a BSEE degree in 1990 from the State University of New York at Buffalo. He has published several articles on failure analysis and reliability.



Kenneth H. H. Lim

Kenneth Lim is a process development engineer at the HP Integrated Circuit

Business Division. He joined HP in 1992. He has a BS degree in mechanical engineering from the National University of Singapore. Ken was born in Singapore, is married, and has two children. He lists jogging and reading as his outside interests.



Anthony J. Bourdillon A professor at the National University of Singapore, Anthony Bourdil-

lon has a Doctorate in physics (1976) from the Oxford University. He assisted HP in performing a theoretical analysis of the ceramic pin grid array components discussed in this article. Electronic materials and characterization are his main professional interests.

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