Study on Underfill/Solder Adhesion in Flip-Chip Encapsulation

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***Abstract*—Underfill materials are employed in flip-chip assemblies to enhance solder joint reliability performance. The adhesion of underfills with solders is important to the integrity of the flip-chip structure. We have studied the adhesion strength of two underfill samples with tin/lead (Sn/Pb) eutectic solder and tin/copper (Sn/Cu) lead-free solder, benchmarked with a copper surface. It was found that the adhesion of underfills and both solder materials was about 1/3 of the adhesion between underfills and copper. The effect of temperature and humidity aging as well as flux residue on adhesion strength was also investigated. A loss of adhesion was observed after the pressure cooker test, but 85 °C/85% RH aging and flux residue revealed only a slight influence on adhesion strength.**

Surface analysis was performed on solid surfaces including copper, Sn/Pb eutectic solder, Sn/Cu lead-free solder and cured underfills by using the three-liquid-probe three-component surface tension method with a goniometer. The surface tension of liquid underfills was measured by the pendent drop method, and their contact angles on copper, Sn/Pb eutectic solder and Sn/Cu lead-free solder were also measured with a goniometer. The thermodynamic work of adhesion for underfills with copper and solder surfaces of different conditions was then calculated following these two surface analysis approaches. It was found that the thermodynamic work of adhesion was not correlated with the lap shear strength of underfills with copper and solder materials. Thus, the wetting property of an underfill on a substrate is not the determining factor for its practical adhesion strength.

Various possible techniques for improving the adhesion of underfills and solder materials were then considered, and the use of additives in underfill formulations was experimented. However, we have not observed any significant effect of adhesion strength enhancement from any of these additives. Further tests of these additives with the base underfill formulation seemed to reveal a slight possibility to enhance adhesion of underfills and solders by proper manipulation of the underfill and/or flux formulation.

***Index Terms*—Adhesion, flux residue, surface analysis, temperature/humidity aging, thermodynamic work of adhesion, tin/lead and lead-free solder, underfill.**

I. INTRODUCTION

THE flip-chip technology has drawn tremendous attention in electronic packaging over the last few years. The main drive to its ever-increasing applications is the advantages pertaining to the structure, e.g., high I/O capability, short interconnects and good thermal and electrical properties [1], [2]. An underfill material has played an important role in the development of the flip-chip technology [3], [4]. Because of the intrinsic mismatch in the coefficient of thermal expansion (CTE) between the integrated circuit (IC) chip/die and the cost-favored organic substrate (e.g., FR-4 board), a device assembly without an underfill has usually suffered from early failure of the solder joints. An underfill is a polymeric adhesive that serves to reduce the strain of the solder joints between the die and the substrate. Thus, the application of underfill would enhance the reliability performance of flip-chip on board assembly by one to two orders of magnitude over that of a nonunderfilled one.

There are various materials present in the typical structure of a flip-chip assembly, namely, substrate or board, solder mask, flux residue, die passivation layer, solder and underfill, etc. Good adhesion and compatibility between the interfaces of these different components are essential to the expected assembly yield and reliability performance of the flip-chip devices [5]–[9]. In order to enhance the performance of a flip-chip structure, it is necessary to optimize and maintain the adhesion of these interfaces at both as-processed and post-aging stages. Despite their importance, the adhesion and fracture behavior of the underfill interfaces have not been investigated until recently [10]–[21]. There have been a few studies dealing with a single specific interface within a flip-chip structure [22]–[25]. Others have investigated the adhesion based on fracture mechanics [26]–[29].

Since solder mask, flux residue, passivation layer, etc. are all indispensable elements in the flip-chip on board assembly, and are in intimate contact with the underfill material, we have reported adhesion between all these components and underfill encapsulants [30]. In this paper, we will present further adhesion studies on underfill and solder materials, both tin/lead eutectic and lead-free solders. As copper conductive trace is normally beneath the solder mask on a substrate, or beneath the passivation/dielectric layer on a die, or covered with solder joints, an interface of underfill and copper is rarely found within a typical flip-chip assembly. However, due to the shear strength tests employed throughout the study, we have benchmarked the adhesion of underfills and solder materials with that of underfills and copper. In an attempt to understand the observed adhesion behavior, we have resorted to surface analysis for the underfill, copper, and solder materials. This may serve to answer the question whether we can predict the practical adhesion strength by knowing their surface characteristics. And finally, approaches to enhance adhesion of underfills and solder materials were executed and discussed.

II. SURFACE ANALYSIS

An underfill encapsulant experiences typical processes in applications, i.e., being dispensed as a liquid to fill the solder

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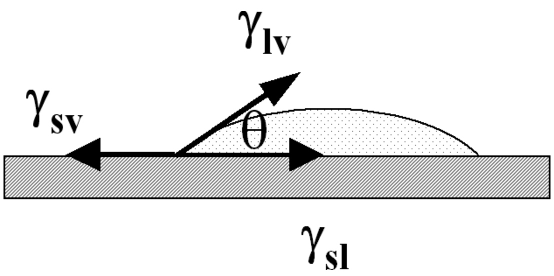

Fig. 1. Contact angle of a liquid on a solid.

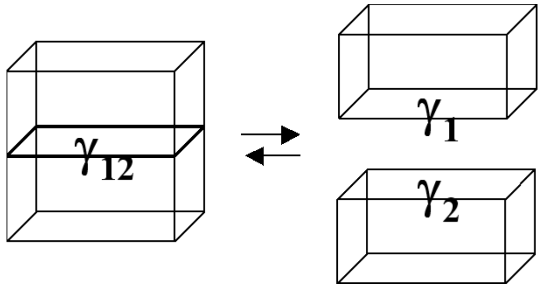

Fig. 2. Thermodynamic work of adhesion.

standoff, and curing into a solid providing solder fatigue enhancement. While curing actually builds up the practical adhesion strength for polymer adhesives, wetting and spontaneous spreading of a liquid on a solid surface, is an important step in dispensing. Wetting can increase the total contact area between the liquid and the solid, and reduce possible voids and defects. Surface tension plays an important role in these interfacial behaviors. The contact angle (θ) of a liquid on a solid is a quantitative measurement of wetting. The smaller contact angle, the better wetting. Contact angle is directly related to the surface tension of the solid surface ($\gamma_{\rm sv}$), the liquid surface ($\gamma_{\rm lv}$), and the interface between solid and liquid ($\gamma_{\rm sl}$). Their relationship is given by the Young's equation, as shown in Fig. 1

$$\gamma_{\rm sv} = \gamma_{\rm sl} + \gamma_{\rm lv}{\rm Cos}(\theta). \tag{1}$$

It was proposed that the surface tension is composed of three components [31], [32]: the Lifshitz-van der Waals component ($\gamma^{\rm lw}$) including electromagnetic interaction, oscillation temporary dipoles interaction, and permanent and induced dipoles interaction, and the polar component (γ^{p}) including the Lewis acid component (γ^{+}) and the Lewis base component (γ^{-}). Their relationship is given by

$$\gamma = \gamma^{\rm lw} + \gamma^{p} = \gamma^{\rm lw} + 2(\gamma^{+}\gamma^{-})^{1/2}. \tag{2}$$

Thermodynamic work of adhesion (Wa, also called physical adhesion) is the reversible work required to separate a unit area of two contacting phases, as in Fig. 2. It is composed of the LW component ($W^{\rm lw}$) and the acid-base (or, the polar) component ($W^{\rm ab}$), and it is directly related to the surface tension. The nongeometric combining rule was suggested [33]

$$\begin{aligned} {\rm Wa} &= W^{\rm lw} + W^{\rm ab} = \gamma_1 + \gamma_2 - \gamma_{12} && (3)\\ W^{\rm lw} &= 2(\gamma_1^{\rm lw}\gamma_2^{\rm lw})^{1/2} && (4)\\ W^{\rm ab} &= 2(\gamma_1^{+}\gamma_2^{-})^{1/2} + 2(\gamma_1^{-}\gamma_2^{+})^{1/2} && (5) \end{aligned}$$

where γ_1 and γ_2 are surface tension of component 1 and component 2, respectively, and γ_{12} is the interfacial tension between the two components.

The three-liquid-probe method was devised to measure the surface tension and its three components of any solid surface [33]–[35]. Water and ethylene glycol can be used as two polar liquids, and diiodomethane is frequently used as the apolar liquid. The surface tension and its three components of these probe liquids are listed in Table I.

TABLE I
SURFACE TENSION AND COMPONENTS OF THREE PROBE LIQUIDS (IN $\mathrm{mJ/m^2}$)

Liquid	γ	$\gamma^{\rm lw}$	γ^{+}	γ^{-}
H_2O	72.8	21.8	25.5	25.5
HOC_2H_4OH	47.9	29.0	1.9	47.0
CH_2I_2	50.8	50.8	0.0	0.0

The work of adhesion between a solid and a liquid can also be expressed by the following equation, deduced from (3) and (1)

$$Wa = \gamma_{\rm lv} + \gamma_{\rm sv} - \gamma_{\rm sl} = \gamma_{\rm lv}(1 + {\rm Cos}(\theta)). \tag{6}$$

Thus, the three components of surface tension of any solid (γ_s) can be obtained by measuring the contact angles (θ_1, θ_2, and θ_3) of the three probe liquids (with known surface tension of γ_1, γ_2, and γ_3 as well as their components) on the solid surface and solving the following three equations deduced from (3)–(6) [36]

$$\begin{aligned} \gamma_1(1 + {\rm Cos}(\theta_1)) &= 2(\gamma_1^{\rm lw}\gamma_s^{\rm lw})^{1/2} + 2(\gamma_1^{+}\gamma_s^{-})^{1/2}\\ &\quad + 2(\gamma_1 - \gamma_s^{+})^{1/2} && (7)\\ \gamma_2(1 + {\rm Cos}(\theta_2)) &= 2(\gamma_2^{\rm lw}\gamma_s^{\rm lw})^{1/2} + 2(\gamma_2^{+}\gamma_s^{-})^{1/2}\\ &\quad + 2(\gamma_2 - \gamma_s^{+})^{1/2} && (8)\\ \gamma_3(1 + {\rm Cos}(\theta_3)) &= 2(\gamma_3^{\rm lw}\gamma_s^{\rm lw})^{1/2} + 2(\gamma_3^{+}\gamma_s^{-})^{1/2}\\ &\quad + 2(\gamma_3 - \gamma_s^{+})^{1/2}. && (9) \end{aligned}$$

The surface tension of a solid surface could then be calculated through (2). In this paper, the three-liquid-probe method was used to obtain the surface tension and its three components for copper and solder surfaces of various conditions as described later. Cured underfill surfaces were also measured using the same procedure. Knowing the surface components of the above solid surfaces, the thermodynamic work of adhesion between underfill and copper or solder could be obtained with (3)-(5).

Noting that the surface tension components of underfill in such a procedure of calculating the work of adhesion are based on cured/solid underfill surface measurement, we are also interested, for comparison purpose, in the calculation of the work of adhesion from the surface tension of liquid underfill. This could be done with (6), where the contact angle is the liquid underfill on copper or solder surface, and the surface tension of a liquid underfill can be measured by the pendent drop method, described later, with a goniometer.

III. EXPERIMENTAL

A. Materials

The copper surface used in the study was a typical copper (Cu) clad FR-4 board with an organic preservative. To investigate the effect of flux residue on surface tension and adhesion, a no-clean flux was applied onto the copper board through a typical reflow profile.

Both tin/lead (Sn63/Pb37) eutectic solder and lead-free solder (Sn/Cu0.7) were used as solder surfaces. They were formed on the copper board from solder pastes (carrying the same no-clean flux component) through appropriate reflow profiles. In some cases, the flux residue was cleaned following recommended procedures to understand the effect of flux residue on surface tension and adhesion.

There were two commercial underfill samples used, namely UF1 and UF2, from the same material supplier. As indicated on the data sheets of the products, they have a filler content of 68% and 50%, a CTE below glass transition temperature of 26 ppm/°C and 45 ppm/°C, and a flexural modulus of 10.3 GPa and 5.6 GPa, respectively. The glass transition temperatures of both underfill samples are 140 °C from thermomechanical analysis (TMA). These two underfill materials are widely used for flip-chip in package and component on board applications.

For cured underfill surfaces, the sample was spin-coated on a wafer, followed by oven curing against air with temperature schedules recommended by the supplier. Both the liquid underfills and the cured/solid underfills were used in surface analysis to obtain the thermodynamic work of adhesion.

The base underfill formulation, an in-house prepared research sample, was obtained with a Bisphenol-A epoxy resin, an acid anhydride hardener and a latent catalyst. In an attempt to improve the adhesion performance, various additives from Aldrich Chemicals were introduced into the commercial underfill samples and the base underfill formulation.

B. Adhesion Strength Measurement

The adhesion strength between underfills and copper or solder materials of different surface conditions was obtained by the lap shear configuration shown in Fig. 3. This shear test is a rather straightforward method compared with those based on fracture mechanics. The FR-4 board of plain Cu, Cu with flux residue, solder paste reflowed, and solder paste reflowed and cleaned, was cut into 5 mm by 50 mm strips, and a lap joint was formed using the underfill being tested. The contact area for two such strips was typically 5 mm by 10 mm for all test specimens. The specimens were oven-cured following the curing schedule recommended by the underfill vendors. The underfill thickness was controlled by mixing glass beads, as spacers, of 75 μm diameter into the underfill sample at 0.5% by weight.

It shall be pointed out that, while experimental data from lap shear strength measurement could be well utilized for the purpose of comparison, cautions must be exercised to observe any difference in test specimen configurations and test parameters employed by different studies.

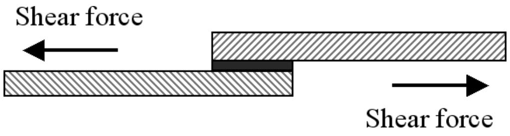

Fig. 3. Schematic of the lap shear strength test.

C. Contact Angle Measurement

For the three-liquid-probe surface analysis, deionized water, ethylene glycol (99 + %) and diiodomethane (99%), all purchased from Aldrich Chemicals, were used as standard liquid probes for contact angle measurements. The solid surfaces studied include copper and solders of different surface conditions as well as cured underfills on a wafer.

A goniometer (Model 102–00, from Rame-hart, Inc.) was used to measure the contact angles. A substrate was placed on the sample stage of the goniometer, and a micro syringe was used to deposit a liquid drop of 2-3 μL on the substrate surface. The steady-state contact angle was recorded within 30 s after the formation of the sessile drop. Five readings were taken, and the average was reported.

Contact angles of liquid underfills on copper and solders of different surface conditions were also measured with the goniometer following the same procedure.

D. Pendant Drop Method

The pendant drop method was used to determine the surface tension of un-cured liquid underfill samples. A stable pendant drop of underfill material was created by dispensing the liquid underfill through a polytetrafluroethylene needle (18 gauge) at room temperature. The profile of the pendant drop was captured by the imaging system of the goniometer, and analyzed to give the surface tension. Five readings were obtained for each sample, and the average was reported.

IV. RESULTS AND DISCUSSIONS

A. Underfill and Copper Surface, & Effect of Flux Residue

The lap shear strength of the two underfill samples with copper and the influence of temperature and humidity aging are shown in Figs. 4 and 5. The two underfills, as-cured, displayed very similar adhesion toward copper. The adhesion strength decreased with the pressure cooker test (PCT at 121 °C and 100% RH under 2 atmosphere) aging time; however, the UF2 underfill always gave higher adhesion retention than UF1. It seems that 85 °C/85% RH aging had a very limited effect on the adhesion, regardless of the test time frame (up to 1000 h). The fracture surface from lap shear test was always along the interface of underfill and copper.

The glass transition temperatures of both the cured underfill samples were about 140 °C. During the 85 °C/85% RH aging test, the underfill adhesive was well in its glassy state with very restricted chain mobility, which limited the moisture diffusion through the underfill volume. Furthermore, the constitutional surface-active additives in their formulations could effectively minimize degradation of the interface of underfill and copper.

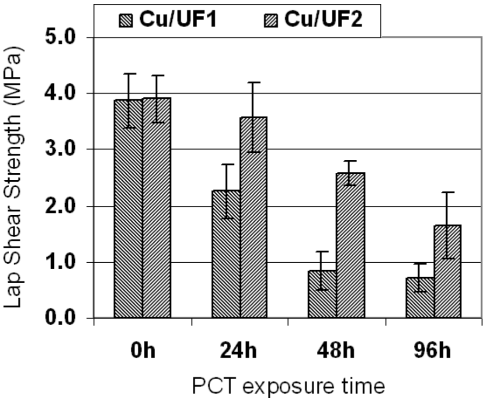

Fig. 4. Effect of PCT aging on lap shear strength for underfill and copper.

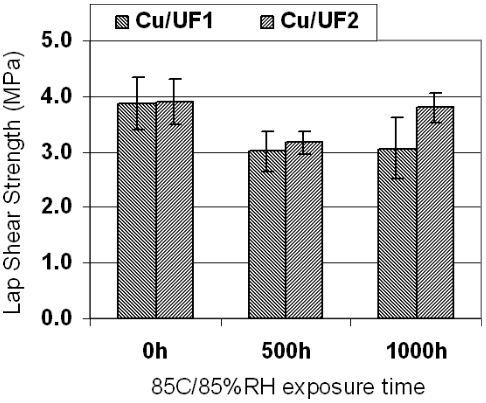

Fig. 5. Effect of 85 °C/85% RH aging on lap shear strength for underfill and copper.

Thus, the adhesion strength was not greatly affected by 85 °C/85% RH aging. However, because of the much higher temperature, pressure and humidity level in PCT aging, the moisture may have penetrated more easily across the interface of underfill and copper as well as through the bulk of underfill, which resulted in gradual deterioration of the adhesion.

The higher adhesion retention of UF2 than UF1 may be attributed to its higher organic matrix content and the surface-active (toward copper) components present in the formulation.

During a typical reflow assembly process, flux is used to promote solder joint yield by removing the oxide layer on solder bumps/balls and the contact pads on the substrate. Conventional flux normally requires cleaning after reflow and before underfill dispensing. No-clean flux has been introduced to improve assembly efficiency, and we are interested in the effect of flux residue on adhesion of underfill and copper. Fig. 6 indicates that the no-clean flux residue could slightly increase the adhesion of underfill samples toward copper. The no-clean flux residue may, on one hand, possess more anchoring sites toward copper, and on the other hand, be compatible with the underfill materials, and thus gave enhancement in adhesion strength.

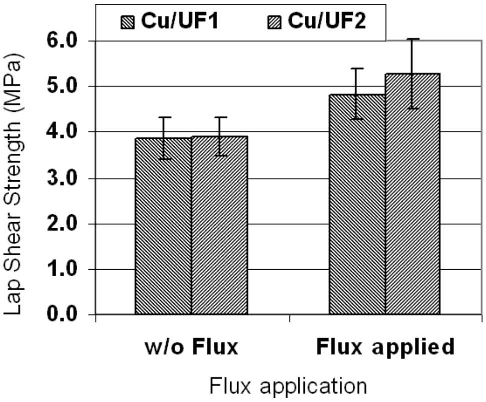

Fig. 6. Effect of no-clean flux application on lap shear strength for underfill and copper.

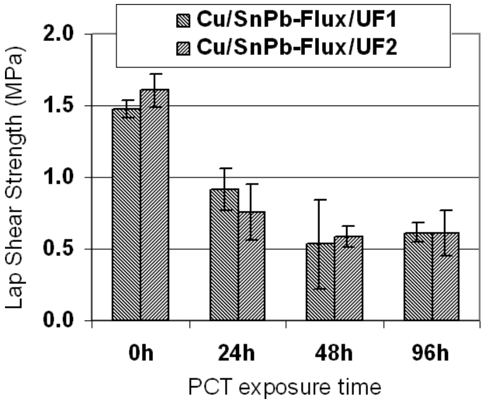

Fig. 7. Effect of PCT aging on lap shear strength for underfill and Sn/Pb eutectic solder.

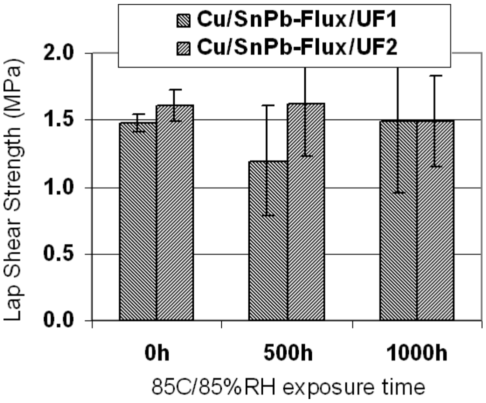

Fig. 8. Effect of 85 °C/85% RH aging on lap shear strength for underfill and Sn/Pb solder.

B. Adhesion of Underfill and Sn/Pb Eutectic Solder

Figs. 7 and 8 show the lap shear strength of the two underfill samples with Sn/Pb eutectic solder surface from solder paste reflow. Again the fracture surface from lap shear test was along the interface of underfill and solder. Although the adhesion strength decreased with PCT aging time, the two underfill samples revealed very similar behavior. This may imply that the interfaces between both underfills and Sn/Pb solder were more susceptible to moisture attack, compared with the case of underfill and copper. For 85 °C/85% RH aging, there was a nearly negligible effect on adhesion.

The Sn/Pb eutectic solder surface was made available from the reflow of the corresponding solder paste, which contains no-clean flux to favor the reflow process. The flux residue was not cleaned for previous tests, and Fig. 9 exhibits that cleaning

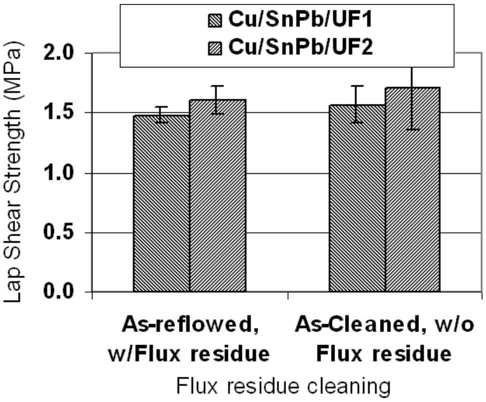

Fig. 9. Effect of cleaning flux residue on lap shear strength for underfill and Sn/Pb solder.

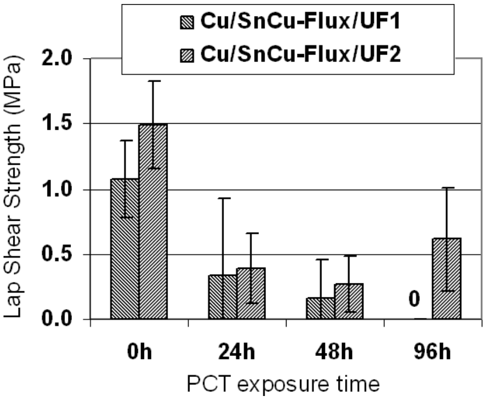

Fig. 10. Effect of PCT aging on lap shear strength for underfill and Sn/Cu lead-free solder (where ’0’ indicates no measurable strength).

of the flux residue only gave a very slight increase in adhesion between underfill and Sn/Pb eutectic solder.

C. Adhesion of Underfill and Lead-Free Solder

The case of Sn/Cu lead-free solder was very similar to that of Sn/Pb solder, as demonstrated in Figs. 10–12. The adhesion of both underfills and Sn/Cu solder surface revealed rather rapid degradation with PCT aging time (within 24 h), which leveled off with further aging time. The 85 °C/85% RH aging condition and cleaning of the flux residue did not contribute any significant change to the adhesion strength. The fracture surface from lap shear test was also along the interface of underfill and solder surface.

D. Comparison of Adhesion Strength

As can be seen, the adhesion (in terms of lap shear strength) of as-cured underfill samples and Sn/Pb eutectic as well as Sn/Cu lead-free solder was about one third the adhesion strength of underfills and copper. The experimental ratio found was from about 28% to 42%, which is shown in Fig. 13.

E. Determination of the Three Components of Surface Tension for Copper, Solders and Cured Underfills

Table II lists the contact angles of water, ethylene glycol and diiodomethane on copper, Sn/Pb eutectic and Sn/Cu lead-free solder of different surface conditions. Also included in the table are the contact angles of the probe liquids on the two oven-cured underfills.

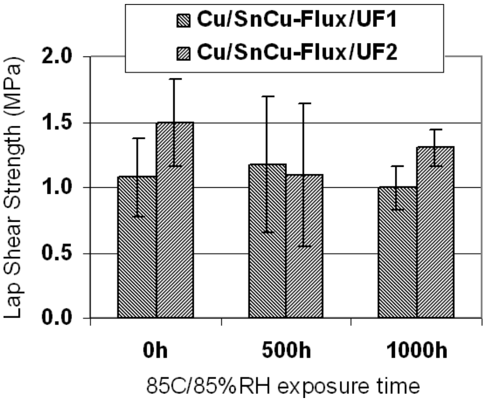

Fig. 11. Effect of 85 °C/85% RH aging on lap shear strength for underfill and Sn/Cu solder.

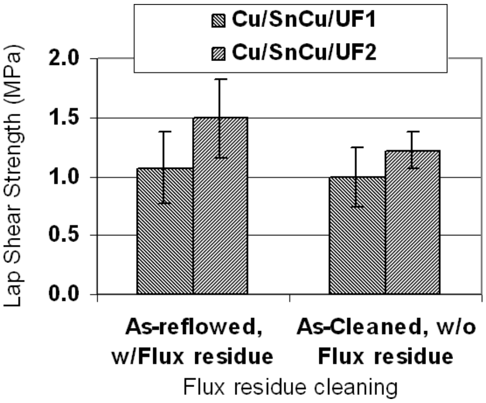

Fig. 12. Effect of cleaning flux residue on lap shear strength for underfill and Sn/Cu solder.

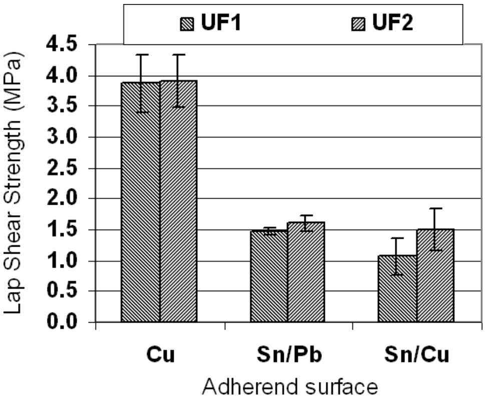

Fig. 13. Comparison of lap shear strength of underfill with copper and Sn/Pb, Sn/Cu solders.

From (7) through (9), the total surface tension (γ) and their three components for these solid surfaces are calculated and summarized in Table III. Among the three components of surface tension, the γ^{lw} component contributed the most to the total surface tension, i.e., the ratio of the polar components (γ^{p}) and the total surface tension was typically less than 0.20. Applying no-clean flux on copper increased the surface tension of organic passivated copper from 39.5 $\mathrm{mJ/m^2}$ to 59.8 $\mathrm{mJ/m^2}$, which was mostly attributed to an increase in the γ^{lw} component because

TABLE II
CONTACT ANGLES (IN DEGREE) OF THREE PROBE LIQUIDS ON SOLID SURFACES

Solid surface	H_2O	HOC_2H_4OH	CH_2I_2
Copper (w/OSP)	57.6	61.7	54.0
Copper, w/Flux	50.0	47.9	17.7
Sn/Pb solder, reflowed	58.7	50.5	37.4
Sn/Pb solder, cleaned	48.4	45.4	33.9
Sn/Cu solder, reflowed	59.5	42.3	33.2
Sn/Cu solder, cleaned	51.9	43.3	34.6
UF1, oven-cured	59.9	53.2	31.6
UF2, oven-cured	63.0	46.3	33.1

TABLE III
SURFACE TENSION (mJ/m^2) OF SOLID SURFACES

Solid surface	γ^{lw}	γ^{+}	γ^{-}	γ	γ^{p}	γ^{p}/γ
Copper (w/OSP)	32.00	0.34	41.30	39.5	7.53	0.19
Copper, w/Flux	48.43	0.81	39.81	59.8	11.36	0.19
Sn/Pb solder, reflowed	40.88	0.16	29.54	45.2	4.32	0.10
Sn/Pb solder, cleaned	42.53	0.22	41.40	48.6	6.07	0.12
Sn/Cu solder, reflowed	42.85	0.002	23.58	43.2	0.38	0.009
Sn/Cu solder, cleaned	42.23	0.07	34.90	45.3	3.03	0.07
UF1, oven-cured	43.54	0.47	29.23	50.9	7.40	0.15
UF2, oven-cured	42.91	0.03	21.06	44.4	1.50	0.03

of the organic flux residues; at the same time, there was an increase in the acid component and a decrease in the base component. Cleaning of the reflowed solder surface also exhibited a slight increase in surface tension as well as the polar components. It shall be noted that there seemed much difference in the total surface tension and the polar component for the two cured underfill samples.

F. Determination of Surface Tension of Un-Cured Underfills, and Contact Angle of Liquid Underfills on Copper and Solder Surfaces

The liquid underfill surface tension was determined by the pendant drop method, and the results are listed in Table IV. The surface tension of the underfill materials was about 20 mJ/m^2, which was quite low when compared to those from the oven-cured underfills. This could be attributed to the highly effective surface-active agents present in the liquid underfill formulations, which have been consumed/transformed during curing.

The contact angles of both liquid underfill samples on the various metal surfaces were also measured and summarized in Table IV. Generally the underfill samples showed good wetting on all metal surfaces.

G. Work of Adhesion for Underfills With Copper and Solders

Utilizing the data obtained so far, we could calculate the thermodynamic work of adhesion via two different methods, i.e., from the three components of surface tension (solid metal surface and cured underfill), and from the liquid drop of underfill on solid metal surface. The results are listed in Table V, and it can be seen that the values of thermodynamic work of adhesion calculated are quite different for these two surface analysis methods, in the range of 80 to 110 mJ/m^2 and of 30 to 50 mJ/m^2, respectively. These differences can again be attributed to the underfill curing process.

TABLE IV
SURFACE TENSION (mJ/m^2) OF LIQUID UNDERFILLS AND THEIR CONTACT ANGLES ON METALS

Underfill	UF1	UF2
Surface tension by pendent drop	18.3	23.4
Contact angle (in degree)	UF1	UF2
Copper (w/OSP)	44.8	55.5
Copper, w/Flux	51.1	51.9
Sn/Pb solder, reflowed	25.4	19.2
Sn/Pb solder, cleaned	27.2	15.0
Sn/Cu solder, reflowed	25.3	19.1
Sn/Cu solder, cleaned	22.6	19.0

TABLE V
WORK OF ADHESION (mJ/m^2) FROM DIFFERENT SURFACE ANALYSIS APPROACHES

Calculation approach	Three-liquid-probe Three-component		Pendent drop method	
Work of adhesion	UF1	UF2	UF1	UF2
Copper (w/OSP)	89.8	81.6	31.3	36.7
Copper, w/Flux	110.2	101.5	29.8	37.8
Sn/Pb solder, reflowed	96.1	89.2	34.8	45.5
Sn/Pb solder, cleaned	100.0	91.9	34.6	46.0
Sn/Cu solder, reflowed	93.5	87.7	34.8	45.5
Sn/Cu solder, cleaned	96.6	89.4	35.2	45.5

Comparing the adhesion strength data from the lap shear test with the calculated thermodynamic work of adhesion, it is obvious that the work of adhesion calculated from either of the discussed surface analysis approaches was not correlated with the lap shear strength of underfill materials on copper and solders. While the lap shear strength for underfills with both Sn/Pb eutectic solder and Sn/Cu lead-free solder was about one third that of underfills toward copper, the work of adhesion calculated seemed not to vary much between copper and solder materials by either surface analysis approach. In other words, the wetting property of an underfill on a substrate is not the determining factor for its adhesion in terms of lap shear strength. During the underfill curing process, chemical bonding can be introduced at the interface between underfills and adherends, increasing the interfacial adhesion and the lap shear strength. The thermodynamic work of adhesion does not account for very strong interaction such as chemical bonding at the interface, thus they may not be well suited for prediction of adhesion with very strong interfacial interaction. It was reported, however, that some correlation was found between fracture toughness and the thermodynamic work of adhesion [36].

H. Effect of Additives on Adhesion Strength

There are a few approaches commonly practiced to improve the adhesion of organic matrix and metal surface/finish, e.g., mechanical pre-treatment for roughness and anchoring, no use of inorganic filler, more acid component in adhesive, etc. However, none of these are readily applicable to solder interconnects and underfills as in flip-chip structure. The surface tension of solder, which is responsible for self-alignment phenom-

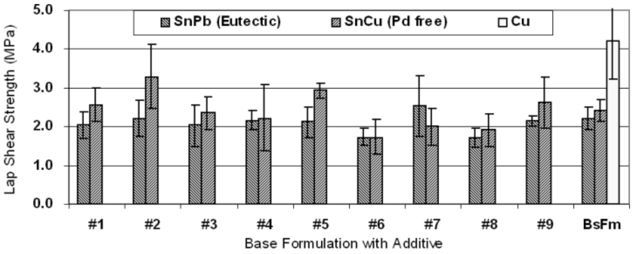

Fig. 14. Effect of additives on lap shear strength of the base underfill formulation with solder materials.

enon, would render the solder joints rather smooth, and it is nearly impossible for mechanical roughing within the flip-chip standoff. Eliminating filler from the underfill formulation would adversely affect the CTE of underfill and thus the reliability enhancement capability. Overloaded acid component in underfill would interfere with its curing and moisture stability. Also, as a matter of fact, the no-clean flux residue, containing a high percentage of acid component for fluxing purpose, did not exert significant influence on the adhesion strength, as described earlier.

UV/Ozone and plasma treatment are another category extensively employed in microelectronic and optoelectronic industries for surface modification/activation, contamination removal and deposition of various materials, etc. They could be adapted to flip-chip assembly before underfill dispensing; Nevertheless, surface treatments with UV/Ozone and plasma did not increase the adhesion strength significantly either [37], [38]. Thus, the options left for us in an attempt to improve the adhesion of underfill and solder would be underfill and/or flux formulation adjustment.

We have introduced different additives (coupling agents, primers and hetero-ring active chemicals, etc.) into the UF2 underfill sample. Unfortunately, however, we have not observed any positive effect of adhesion strength enhancement from any of these additives. Some of the additives even revealed negative influence on the adhesion performance of the materials studied.

To avoid the possible interference of the additives with the ingredients present in the UF2 underfill sample (a commercial one), we then used an in-house prepared base underfill formulation. The adhesion of the base underfill formulation and solder surfaces, both Sn/Pb eutectic and lead-free solder, as shown in Fig. 14, was much lower than that with copper surface. This was in line with the experimental observations made earlier with commercial underfill samples. The additives studied did not show any obvious enhancement in adhesion of the base underfill toward Sn/Pb eutectic solder; while two of the additives (#2 and #5) appeared to show a very limited, though not statistically significant, increase in adhesion for underfill and Sn/Cu lead-free solder. It is known that some alloy components commonly found in lead-free solders, e.g., silver, copper, etc., may undergo certain chemical bonding with chemical functionalities such as carboxy, mercapto, amino, etc. These active ingredients may be readily present in underfill and/or flux formulation, or may be introduced into the system via various additives. This might represent a possibility, slight or not, to improve the adhesion of underfill and solders, especially lead-free solders, by proper formulation manipulation.

V. CONCLUSION

We have studied the adhesion strength of two underfill samples with Sn/Pb eutectic solder and Sn/Cu lead-free solder, benchmarked with copper surface. It has been found that the adhesion of underfills and both solder materials was about 1/3 the adhesion of underfills and copper. A loss of adhesion was observed with pressure cooker test, but 85 °C/85% RH aging and flux residue revealed only a slight influence on adhesion strength.

Surface analysis was performed on copper, Sn/Pb eutectic solder, Sn/Cu lead-free solder and the cured underfills by using the three-liquid-probe three-component surface tension method. The surface tension of liquid underfills was measured by the pendent drop method, and their contact angles on copper, Sn/Pb eutectic solder and Sn/Cu lead-free solder were also measured with a goniometer. The thermodynamic work of adhesion for underfills with copper and solder surfaces was calculated. It was found that, because of the strong interfacial interactions including chemical bonding established during underfill curing process, the thermodynamic work of adhesion calculated from either surface analysis approach was not correlated with the lap shear strength of underfills on copper and solder materials. Thus, the wetting property of an underfill on a substrate is not the controlling factor for its practical adhesion strength.

There were very limited approaches to feasibly and practically enhancing the adhesion of underfill and solder materials, e.g., by judicious formulation manipulation of the underfill and/or flux system. Enhancing interfacial chemical interactions between underfill and solder, especially lead-free solder, could potentially improve the adhesion.

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