Reworkable No-Flow Underfills for Flip Chip Applications
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Abstract—Underfill is a polymeric material used in the flip-chip devices that fills the gap between the integrated circuit (IC) chip and the substrate (especially on the organic printed circuit board), and encapsulates the solder interconnects. This underfill can dramatically enhance the reliability of the flip-chip devices as compared to the nonunderfilled devices. No-flow (compress-flow) underfill is a new type of underfill that allows simultaneous solder bump reflow and underfill cure, which leads to a more efficient no-flow underfilling process as compared to the standard capillary-flow underfilling process. Reworkable underfill is another type of underfill that allows the faulty chips to be replaced individually. It is the key material to address the nonreworkability issue of the current flip-chip devices. Reworkability is especially important to the no-flow underfill because electrical test of the assembled chips can only be done at the end of the no-flow underfilling process. The goal of this study is to demonstrate the feasibility of a no-flow reworkable underfill. Two approaches are taken to develop this new type of underfill. The first one is to add a special additive into a standard no-flow underfill formulation (underfill 0) to make it reworkable, called underfill 1. The second approach is to develop a no-flow underfill based on a new thermally degradable epoxy resin that decomposes around 240 °C, called underfill 2. Comparing to underfill 0, these two underfills have similar properties including glass transition temperature (T_g), coefficient of thermal expansion (CTE) and modulus. Underfill 1 has similar curing and fluxing capability as to underfill 0. Underfill 2 cures faster than underfill 0, and it has slightly weaker fluxing capability than underfill 0, but it still allows 100% of solder bumps wetting and collapsing on the copper board. Moreover, underfill 1 and underfill 2 allow the flip chips to be reworked using a developed rework process while underfill 0 does not.

Index Terms—Compress-flow underfill, flip chip, flux underfill, no-flow underfill, reworkable underfill.

I. INTRODUCTION

FLIP-CHIP technology has received a great deal of attention in the electronic packaging area within the past several years due to the following advantages: high input/output (I/O) capability, short interconnects, and high performance [1]. While the flip-chip technique becomes increasingly popular, the problem of coefficient of thermal expansion (CTE) mismatch between the integrated circuit (IC) chip and the organic substrate becomes critical. Due to the CTE mismatch between silicon IC chips (2.5 ppm/°C) and printed circuit board (18–24 ppm/°C), temperature cycle excursions experienced by the device generate thermo-mechanical stresses at the solder joints which subsequently result in early failure of the device. Underfill is an adhesive that serves to reduce the strain in the solder joints by transforming some of the strain energy into the underfill layer. The underfill provides not only drastic enhancement on solder fatigue life, but also corrosion protection to the IC chip, resulting in ten to one hundred folds improvement in fatigue life as compared to an un-encapsulated package [2], [3]. Due to these attractive traits, this new underfill technology has been gaining acceptance in the chip-to-substrate attachment process.

A. No-Flow Underfill

Conventionally, the underfill is dispensed after formation of the solder joints and it is drawn through the gap between the chip and the substrate by capillary force. Compared to a standard surface mount technology (SMT) process, this conventional capillary-flow underfilling process requires additional steps of underfill dispensing and curing. Therefore, it is a more expensive process. Another concern is that when the flip-chip technology is going toward larger chip and lower solder joint stand-off, capillary force may not be sufficient to draw the underfill through the gap, resulting in incomplete underfilling. Furthermore, it will drastically increase the underfilling time thus assembly cost.

To overcome the disadvantages of the capillary-flow underfilling process, a no-flow underfilling process was proposed. Compared to the capillary-flow underfilling process, this no-flow process dispenses the underfill material before solder reflow, eliminates the flux dispensing and cleaning steps, eliminates underfilling time, and combines the solder reflow and underfill curing into a single step. Therefore, the no-flow underfilling process is a much better process than the conventional capillary-flow underfilling process. However, none of the conventional underfills can be used in the no-flow underfilling process as this process requires a new type of underfill with the following properties.

1) The underfill must have fluxing capability during solder reflow to allow the formation of solder joints.
2) The no-flow underfill must have latency that allows the solder joints to form prior to the underfill cure.
3) The underfill can either be fully cured on-line when it goes through the reflow oven, or be fully cured off-line at a temperature below 175 °C.

This new type of underfill is called no-flow underfill. A no-flow underfill formulation has been successfully developed by Wong.
et al. in our group which allows simultaneous solder reflow and underfill curing, and provides sufficient reliability to the flip-chip devices [4]–[8].

B. Reworkable Underfill

Besides processability, reworkability is another big issue to the underfill technology. Current flip-chip devices contain many IC chips and discrete components onto a multilayer printed wiring board. The possibility of packaging defects and unknown bad die (opposite to known good die) always exists. The inability to replace one defective component would render the whole board useless after assembly. Reworking of nonunderfilled flip-chip devices is quite similar to other solder interconnected devices such as ball grid array (BGA) and chip scale package (CSP). By using the modern rework station, BGAs, CSPs, and nonunderfilled flip-chip devices can be reworked. However, due to the thermosetting nature of the epoxy underfill after curing, the existence of the underfill in the flip-chip devices makes flip-chip rework very difficult or even impossible. This nonreworkability of the underfill is a severe limitation to the flip-chip technology.

There have been a lot of research studies conducted trying to make the flip-chip devices reworkable. These studies can generally be categorized into two groups depending on whether they are based on the development of reworkable underfills. The first group of studies includes mechanical chip removal using chip-grinding by Tsukada et al. [9] at IBM and the usage of a mold release layer (parylene) on all surfaces as an intermediate of the chip and the substrate for the purpose of removing the chip without damage to the device or to the bumps [10]. However, each method has its own problem. Chip-grinding approach is for chips with high lead solder joints, so it is not applicable to the general eutectic solder bumped flip-chip devices. For the method using parylene, although the chips would come out clean from the underfill with all bumps recovered, the exposed epoxy underfill and parylene required cleaning using depotting solvents. This process is also tedious and expensive [11].

The above-mentioned two methods indicate that the key to addressing the nonreworkability of the flip-chip devices is to develop reworkable underfills; that is, to make the underfills removable under certain conditions. This describes the second approach to developing reworkable flip-chip devices. Presently, the materials that are undergoing development can be classified into two categories: chemically reworkable underfills and thermally reworkable underfills.

Buchwalter et al. [12]–[14] at IBM pioneered the work on reworkable epoxy underfills by developing epoxy compositions that are soluble in an organic acid after curing, which fits into the chemically reworkable category. Unfortunately, it was very time-consuming for the acid to penetrate through the chip-substrate gap and to dissolve the underfill, and usage of solvents makes localized rework difficult [11].

Contrary to the chemically reworkable underfills, thermally reworkable underfills offer the possibility of a quick, clean, and localized rework process. Proposed thermally reworkable underfills include the thermally degradable epoxies by Ober et al. at Cornell [15], [16], a polymer system utilizing the reversibility of Diels-Alder reaction by Iyer et al. at Shell [17], [18], and thermalplastic materials by Ma et al. of National Starch & Chemicals [19]–[21]. Additionally, the authors’ group at Georgia Tech took a two-sided approach to develop the thermally reworkable epoxy underfills [22]–[27]. The first one is to incorporate some special additives into the epoxies to make them reworkable. These special additives are a group of gas emitting chemicals. When incorporated into the epoxy formulation, these additives are stable during epoxy curing and thermal cycling. But when the temperature reaches eutectic solder reflow temperature, they start to decompose and emit large amount of gasses causing a mini-explosion within the epoxy matrix. This makes the chip that initially bonded strongly to the substrate much easier to be removed. The second approach is to develop reworkable underfills based on newly synthesized epoxies that are thermally degradable around solder reflow temperature. This concept is similar to the approach by Ober et al., but the thermally labile groups used are different.

C. No-Flow Reworkable Underfill

In the capillary-flow underfilling process the underfill is dispensed after the solder joints are formed. It is possible to perform electric test on the assembled chips and rework the faulty chips before the underfill is applied, although this is not preferred because it affects the throughput of the assembly. On the other hand, the formation of the solder joints and the curing of the underfill are combined into one single step in the no-flow underfilling process, so the assembled chips can only be tested after they go through the whole process. Therefore, reworkability is even more important to the no-flow underfills than the capillary-flow underfills.

So far, all of the developed reworkable underfills are for the capillary-flow underfilling process or the newly proposed wafer-level-packaging; no attempt has been made to develop the no-flow reworkable underfill—a reworkable underfill for the no-flow underfilling process. The objective of this work is to demonstrate the feasibility of such an underfill.

The reworkable underfills for the capillary-flow underfilling process do not experience the reflow step so they are normally
designed to be reworked at the solder reflow temperature (~220°C). However, the rework temperature for a no-flow reworkable underfill has to be higher than the solder reflow temperature because the underfill has to go through the reflow step once. A desirable rework temperature in this case would therefore be in the range of 240 to 250°C.

II. EXPERIMENTAL

A. Underfill Material

Three underfills were included in the study. Underfill 0 is the underfill formulation that was developed and extensively studied by our group. It is a nonreworkable formulation and used as the reference. The formulation of underfill 0 consists of a commercial epoxy resin, a hardener, a catalyst and a fluxing agent. The commercial epoxy resin was 3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexyl carboxylate which was provided by Union Carbide under the trade name ERL4221. The hardener is hexahydro-4-methylphthalic anhydride (HHMPA), the catalyst is cobalt (II) acetateacetate, and the fluxing agent is glycerol. All of these three chemicals were purchased from Aldrich Chemical Company, Inc. and used as received.

Underfill 0 was prepared by mixing ERL4221 with HHMPA in a mole ratio of 1:0.8, followed by adding 0.4 wt% of cobalt (II) acetateacetate and 2.5 wt% of glycerol into the mixture. Table I shows the structure of the chemicals used to formulate underfill 0 [5]–[7].

Underfill 1 is a formulation based on underfill 0 but it also contains 5 wt% of a special additive. This special additive is a gas emitting agent having a decomposition temperature range from 270 to 300°C.

Underfill 2 is a formulation similar to underfill 0 but it used a new degradable diepoxide to replace the commercial diepoxide ERL4221. After cured with HHMPA, the onset decomposition temperature of the new diepoxide is around 240°C (measured by the Td decrease) and it starts to lose weight around 270°C (measured by Thermo-Gravemetric Analyzer). In comparison, ERL4221 does not lose weight until 350°C.

B. Measurement Method

To study the curing profile, Tg and degree of curing of the underfill formulations, a modulated dynamic scanning calorimeter (DSC, by TA Instruments, Model 2920) was used. A sample of ~10 mg of an underfill was placed into a hermetic DSC sample pan. The sample was then heated in the DSC cell at 5°C/min from 25°C to 250°C to obtain the curing profile. To obtain the Tg of the sample, the cured sample was left in the DSC cell and cooled down to 25°C at 5°C/min. Then the sample was reheated to 250°C at 5°C/min to obtain the Tg of the cured sample. The degree of curing of the underfill formulations after going through the reflow step was obtained using the following procedure:

a) obtain the total curing enthalpy of an uncured underfill by analyzing its DSC curing profile;

b) run DSC dynamic scan of the same underfill after it went through the reflow process, and obtain the curing enthalpy of this partially cured sample by analyzing its DSC curing profile;

c) calculate the degree of curing of this underfill after going through the reflow step by using the curing enthalpy from Step b divided by the enthalpy from Step a.

Measurement of CTE of a cured formulation was performed on a thermo-mechanical analyzer (TMA, by TA Instruments, Model 2940). A specimen for TMA testing was made by placing a liquid underfill formulation into an aluminum pan (3.75 cm diameter), transferring the pan into an 80°C preheated convection oven, and then heating the oven to 250°C at 3°C/min. The sample was isothermally cured in the oven at 250°C for additional 15 min. The sample was then removed from the oven and cooled down to room temperature. A diamond saw was used to cut the cured sample into strips with dimensions of about 5 x 5 x 2 mm. The specimen was placed onto TMA, and ramped from 25°C to 250°C at a rate of 5°C/min. The CTE of the specimen was obtained from the thermal displacement versus temperature curve.

Measurement of dynamic moduli of a cured formulation was performed on a dynamic mechanical analyzer (DMA, by TA Instruments, Model 2980). Specimen preparation for DMA is similar to TMA except that the size of the sample strips was larger (approximately 32 x 11 x 3 mm). The measurement was performed in single cantilever mode under 1 Hz sinusoidal strain loading while each specimen was heated from 25°C to 250°C at a rate of 3°C/min. Storage modulus G’, loss modulus G”, and loss angle tan δ were obtained.

The decomposition of the cured formulations was studied by using a thermo-gravemetric analyzer (TGA, by TA Instruments, Model 2050). A sample of ~30 mg of cured sample was placed into a platinum TGA sample pan. The sample was then heated in the TGA furnace at 10°C/min from 25°C to 400°C under air purging.

C. Wetting Study

An organic-solder-preservative (OSP) coated copper foil which was laminated on a FR-4 board was used for this study. In the first test, a no-flow underfill was first dispensed on the copper. A eutectic solder ball (used as received) was placed on the underfill droplet and then pressed down to touch the copper surface. The test vehicle went through the pre-programmed five-zone reflow oven (by Electrovert, Model OMNI FLO 5). The reflow profile used was the one proved to work for underfill 0 and is shown by Fig. 1. The spreading of the solder melt on the copper was then visually examined and the wetting angle was measured. In the second test, a quartz chip bumped with solder balls was placed on the underfill droplet and then pressed down to touch the copper surface. Then this test vehicle went through the reflow oven and was visually examined.

D. Rework Test

Rework test was performed using a Conceptronic Freedom HGR 2000 rework station. This rework station is designed to rework SMT components including lead framed parts, BGAs and CSPs. It can also be used to rework nonunderfilled flip chip. It has features including IR pre-heater, top and bottom forced convective heaters, vision system, and multifunction nozzles.

The test vehicle consists of silicon test chips mounted on a FR-4 substrate. The test chips are daisy chained flip chips sup-
plied by Flip Chip Technologies. The chips used are 200 μm pitch perimeter array. The solder bumps have a 120 μm diameter for the perimeter array. Test chips are 5 mm × 5 mm in size and have silicon nitride passivation layer. Each chip has 88 solder bumps. The test boards are made from high temperature FR-4 with a Tg of 180 °C. The test chips were attached to a 0.8 mm thick fine pitch circuit board with a TAIYO liquid photoimageable solder mask. The trace metallization is copper, electroplated nickel, and immersion gold. The boards have twelve chip sites per board, and each chip can be tested individually.

Instead of simultaneously assembling the test boards and applying the underfills onto the board using a no-flow underfilling process, these were done separately just like using a capillary-flow underfilling process [28]. First, the test boards were assembled with the chips using a new flip chip assembly process incorporating a dip flux technique. Then the underfills were applied onto the assembled boards using a CAM/ALOT 1818 Liquid Dispensing System. A 25-gauge needle was used for dispensing, and the substrate temperature was held at 90 °C. The dispensing parameters were varied to ensure that enough underfill was dispensed to fill the chip standoff gap. An I-shaped dispense pattern was used for all underfills. Once the underside of the chip was filled, fillets were dispensed along the other sides of the device. Curing of the underfills after dispensing was done using a convection oven.

The reasons for preparing the test vehicles this way are the following.

1) Test boards assembled with the chips using the flux-dipping flip-chip process were available during the rework test. The underfill dispensing onto these boards was very fast. It would take much more time to develop a no-flow underfilling process for applying these underfills on the board.

2) The way that the underfill was applied onto the board (no-flow versus capillary flow) would not make a difference on the rework test results.

Fig. 2 shows the DSC dynamic curing profiles of these three formulations. Underfill 0 and 1 had quite similar curing profile, indicating that the additive within underfill 1 formulation did not affect its curing. Curing peak of underfill 2 was at a lower temperature than underfill 0, indicating that underfill 2 would have higher degree of curing than underfill 0 going through the same reflow process. This was proven by the degree of curing data of these three formulations after going through the reflow process (see Table II). Therefore, underfill 2 is better than underfill 0 in terms of degree of curing because it requires less post cure. But it also made one suspect whether the faster curing of underfill 2 than underfill 0 would prevent the solder bumps from collapsing onto the bond pads.

Table III lists Tg, CTE and modulus values of these three formulations. It can be seen that underfill 1 and underfill 2 had quite similar values compared to underfill 0.

### III. RESULTS AND DISCUSSION

#### A. Thermal Analysis

First of all, thermal analysis of two developed formulations was conducted and the results were compared to those of underfill 0. Desirable formulations should have similar curing behavior as underfill 0 but decompose at lower temperature.

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Table III lists Tg, CTE and modulus values of these three formulations. It can be seen that underfill 1 and underfill 2 had quite similar values compared to underfill 0.
Fig. 3. TGA curves of underfill 0, underfill 1, and underfill 2.

Fig. 3 shows the TGA curves of three formulations. It is clear that underfill 2 degraded at a lower temperature than underfill 0. The additive-containing underfill 1 decomposed at a slightly lower temperature than underfill 0.

B. Wetting Study

The wetting appearance of the solder ball on the copper surface for the three underfills can be seen in Fig. 4. These are pictures taken by an optical microscope after the reflow. If the underfill does not have fluxing capability, the solder ball would not wet the copper surface and it would keep its round ball shape. On the other hand, if the underfill has the fluxing capability, the solder ball would then wet the copper surface and collapse on it. Its shape would then change from round to some irregular shape. Fig. 4 shows that the solder ball immersed in any of the three underfills wetted the copper surface and collapsed, indicating that these three underfills all have fluxing capability. This also eliminates the suspicion that underfill 2 might prevent the solder bumps from collapse due to its faster curing profile than underfill 0.

Table IV shows the wetting angle results of these three underfills. Generally, the lower the wetting angles of the solder ball on the copper board, the stronger fluxing capability of the underfill in which the solder ball was immersed. It can be concluded that underfill 0 and underfill 1 had similar fluxing capability, and the fluxing capability of underfill 2 is slightly weaker than the other two formulations.

Fig. 5 shows the wetting appearance of the quartz chip on the copper surface for the three underfills. The solder bumps on the quartz chip encapsulated with underfill 0 and underfill 1 wetted the copper surface and fully collapsed on the copper, which indicates that both underfills provide good fluxing to the solder bumps. Although the solder bumps encapsulated with underfill 2 did not fully collapse on the copper surface, they all wetted the copper surface. These results indicate that the fluxing capability of underfill 1 is similar to underfill 0. Furthermore, although the fluxing of underfill 2 is not as strong as underfill 0, it is enough for 100% wetting of the solder bumps. These results are also consistent with the wetting angle results.

C. Rework Test

Rework process for flip chip on board devices has been studied at Georgia Tech. The whole process includes chip removal, site preparation, and chip replacement.

1) Chip Removal: Chip removal test was conducted on the rework station using assembled and underfilled flip chip test boards. Temperature profile of the board site during chip removal can be obtained by monitoring the actual temperature inside the board during chip removal through a buried thermal couple. Through adjusting various machine parameters and checking the subsequent temperature profiles of the board site, a chip removal profile allowing the board site to reach desired rework temperature without damaging the board was obtained. This chip removal profile was found to loosen the underfill at the peak temperature. The major steps of the profile are listed as follows.

a) Preheat

Top and bottom heater was set at 200 °C. The board is heated until 25 s have passed since the preset temperature is reached.
b) Activate
Top and bottom heater was set at 270 °C. The board was heated until 20 s have passed since the preset temperature is reached.

c) Adjust Head Position.

d) Reflow
Top heater was set at 380 °C while the bottom heater was set to 400 °C. The board was heated until 30 s have passed since the preset temperature is reached.

e) Remove Part
Fig. 6 shows the temperature profile of the board using the established chip removal profile.

By using this rework profile, no-underfilled chips were found to be easily removed by the vacuum force applied through the nozzle. However, the nozzle could not remove the underfilled chips from the board because the vacuum force was not strong enough. An accessory was then designed, manufactured, and mounted onto the small nozzle for flip chip rework. The schematic of this design is shown in Fig. 7. The idea is to have the accessory holding the chip during the rework. This would allow shearing or twisting force to be applied to the chip.

This accessory was put to test. After the nozzle touched the chip, the frame that held the board was moved in both X and Y directions in order to apply the force on the chip. This was found to not only apply the force to the chip, but also help remove part of the underfill fillet. After that, the chip was lifted up by the nozzle and removed from the board.

2) Site Cleaning:

After chip removal, the underfill residue and solder residue have to be cleaned and the site prepared to accept a new chip. Different cleaning methods were tried and the combination of a gentle mechanical process with solvent cleaning worked best. The mechanical cleaning was done by using a horsehair brush which was attached to a Dremel tool to slowly and carefully sweep away the underfill and solder residues. The debris generated during the mechanical cleaning was then removed by isopropyl alcohol. With this cleaning method the site was cleaned with minimum damage to the solder mask and bump pads on the FR-4 board. Fig. 8 shows the comparison of the IR spectrum of a board after clean versus a clean board. Both spectra match well, indicating that the board was clean after the cleaning step.

3) Chip Replacement:

New chips were assembled on the reworked sites following the same procedure for test vehicle assembly. Inspecting replaced chips using continuity test and x-ray machine found that good solder interconnects were formed. High yield chip replacement was achieved on the replaced chips, which indicated that the cleaning process maintained the integrity of the bump pads.

4) Test Results:

Die removal test showed that the dies encapsulated with underfill 0 were the hardest ones to remove. Sometimes when the die was removed, the board was damaged. Even in the case when the board surface was intact, the underfill residue was very difficult to clean. Fig. 9(a) shows one board site after die removal for underfill 0. A small portion of the solder mask on the board surface (as marked by the arrow) was delaminated from the board during the die removal, which was caused by the force needed to remove the die. Fig. 9(b) shows another board site after board cleaning for underfill 0. It clearly shows that the residue
Fig. 10. Optical microscopy of a board site after die removal and site cleaning for (a) underfill 1 and (b) underfill 2.

Fig. 11. Optical microscopy of bond pads for (a) Before bonding, and after site cleaning for (b) underfill 1 and (c) underfill 2.

of underfill 0 could not be totally cleaned. Based on the above results, underfill 0 was proved to be nonreworkable.

The dies encapsulated with underfill 1 or underfill 2 could be removed from the board. Although there were some underfill residues left on the board site after the die removal, the site remained undamaged. Following die removal, site cleaning was performed to remove the residue. The combination of mechanical and solvent cleaning was found to be effective in removing underfill and solder residue without damaging the board site. Fig. 10 shows the board site before and after cleaning for underfill 1 and underfill 2. Site cleaning appeared to remove all underfill and solder residue and resulted in a clean board site ready for a new chip to mount. Fig. 11 shows the bond pads of the two board sites shown in Fig. 10. For comparison, the clean bond pads before any bonding are also shown. It appeared that cleaning of underfill 1 and underfill 2 were successful, as all underfill residues were removed. Fig. 12 shows higher-resolution pictures of the above bond pads. Before bonding, the bond pad had golden appearance as it is copper finished with Ni/Au. After rework, the appearance changed to silver because there is a thin layer of solder left on the pad surface. But this thin layer of solder does not affect the formation of new solder joints. Moreover, the bond pads and solder mask for underfill 1 and underfill 2 looked undamaged under microscope.

IV. CONCLUSION

Two no-flow reworkable underfills—underfill 1 and underfill 2—have been developed. Compared to underfill 0 (standard no-flow underfill), these two underfills have similar properties including $T_{g}$, CTE and modulus. Underfill 1 has similar curing and fluxing capability as to underfill 0. Underfill 2 cures faster than underfill 0, and it has slightly weaker fluxing capability
than underfill 0, but it still allows 100% of solder bumps wetting and collapsing on the copper board. Moreover, underfill 1 and underfill 2 allow flip chips to be reworked using a developed rework process while underfill 0 does not.

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**REFERENCES**


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