The effect of metal oxide on the no-flow underfill fluxing capacity

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Received 24 January 2001; received in revised form 26 March 2001; accepted 5 April 2001

Abstract

In order to investigate the effect of solder pad surface composition on the wetting behavior of solder bumps during reflow using no-flow underfill, the fluxing capability of no-flow underfill material on tin–lead coated and gold plated Cu solder pads were studied. Before reflow, the solder pads were cleaned with dilute HCl and acetone. The X-ray photoelectron spectroscopy (XPS) was then used to examine the cleaned solder pad surface composition. The eutectic solder balls were reflowed to the solder pads using the no-flow underfill as flux agent. By inspecting the wetting angle, it was found that the fluxing capacity of the no-flow underfill on the tin–lead coated pad is much better than that on the gold plated solder pad, but it was susceptible to tin-oxides on the coated surface. Relatively high concentration of tin oxides also gave the wetting angles a wide range of values. The acid cleaning could remove tin-oxides on the coated surface substantially, thus enhancing the no-flow underfill fluxing capacity soundly. For comparison, the fluxing capacity of a no-clean flux paste was also investigated in this work the results showed that the tin-oxides had a negligible effect on the fluxing capacity of the no-clean flux paste. The catalyzing effect of metal salt to the epoxy curing process was used to explain the negative effect of tin oxides to the fluxing capacity of the no-flow underfill. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Flip-chip; No-flow underfill; Fluxing capacity; XPS; Metal oxide; Copper solder pad

1. Introduction

Flip-chip technology provides a solution to the demands of advanced electronic packaging technology, i.e. high I/O density and count, with superior electrical performance and very small size. A challenge in flip-chip technology development is to improve the thermomechanical reliability of the flip-chip assembly. The underlying underfill technology is one of the keys to the challenge [1]. Conventional underfill technology uses capillary flow but it is tedious, expensive, and not transparent to the SMT facilities. To overcome these disadvantages, a more promising no-flow underfill technology has been developed [2].

With no-flow underfill technology, the processes of interconnect soldering and underfill curing are completed in the same reflow process. During reflow, the no-flow underfill materials must be able to flow and act like a flux to let the bumps on the chip be able to penetrate it and solder the solder pads, then cure in a short time period. Proper solder reflow and interconnect formation are related to the no-flow material's flux activity, viscosity and surface tension [3]. The fluxing capability comes from the flux agent in the no-flow underfill, and high flux agent concentration results in low curing onset and peak temperature, consequently hindering the subsequent wetting process. So no-flow underfill is limited by the consideration of the optimum integrated properties [4]. The fluxing capability of the no-flow underfill is often lower than that of normal flux [5]. In order to obtain a good flux effect, consideration of other aspects rather than the no-flow underfill material itself is needed. Research [5,6] has been done studying the effect of copper foil surface composition and reflow profiles on the fluxing effect of the no-flow underfill. It was found that copper oxide (CuO) concentration plays a critical role in solder wetting. However, in practice, the copper pad is covered by a tin–lead coating or is plated with gold film to prevent the formation of copper oxides. In this work, by comparing the solder wetting angle results of no-flow underfill and

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Table 1
Properties of the no-flow underfill materials

<table>
<thead>
<tr>
<th>Property (before cure)</th>
<th>Test method</th>
<th>Unit</th>
<th>Value range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical type</td>
<td>Epoxy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance</td>
<td>Visual</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>ASTM-D-792</td>
<td>g cm$^{-3}$</td>
<td>1.19</td>
</tr>
<tr>
<td>Brookfield viscosity</td>
<td>ASTM-D-2393</td>
<td>Pa s</td>
<td>20</td>
</tr>
<tr>
<td>Property (after cure)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>ASTM-D-2240</td>
<td>Shore D</td>
<td>90 minimum</td>
</tr>
<tr>
<td>Water absorption 24 h boil</td>
<td>ASTM-D-570–81</td>
<td>%</td>
<td>&lt;1.5%</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>ASTM-D-3386</td>
<td>$10^{-6}$ °C</td>
<td>90</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>ASTM-D-3418</td>
<td>°C</td>
<td>100</td>
</tr>
</tbody>
</table>

no-clean flux on the tin–lead coated and gold plated Cu solder pad, the effect of metal oxides on the practical solder pad surfaces to the fluxing capacity of no-flow underfill was studied. The results may contribute to better understanding of fluxing behavior of the no-flow underfill materials, so as to optimize its fluxing capacity.

2. Experiments

2.1. Underfill materials

A commercial no-flow underfill material was used in this study. The main properties of the material are listed in Table 1. The underfill was reflowed by a ‘rapid ramp’ profile as shown in Fig. 1. The underfill cured during the modified reflow cycle, no additional post cure was required.

2.2. Solder wetting studies

The solder pads used in the test were eutectic Sn–Pb solder coated Cu-pads. For comparison, another set of Cu-pads were plated with 15 μm of nickel followed by a less than 1 μm gold flash. The size of pad was large enough for the solder ball wetting on it. Two methods were used to clean the solder pads, one was an ultrasonic wash in solvent grade acetone for ~5 min followed by DI water rinse and compressed air dry; another one was dipping in 50/50 HCl/H$_2$O solution for 30 s followed by DI water rinse and compressed air dry. Before using, the cleaned solder pads were dried in a dry-box for ~6 h. The solder ball used in this study was eutectic Sn–Pb alloy with a 30 mm diameter. At first, an amount of the no-flow underfill material was dispensed by syringe on the solder pad to form a dome-shape, and then a solder ball was placed onto the solder pad. The amount of underfill was sufficient to let the entire solder ball to be immersed in it. Another set of samples were fluxed by no-clean flux paste. The test vehicle then went through the pre-profiled five-zone reflow oven (BTU VIP-70N) in compressed air atmosphere. The time-resolved temperature during reflow in underfill materials was recorded using a wireless profiler (see Fig. 1). The reflored solder ball was then cross-sectioned by a diamond saw. The wetting angle, as defined in Fig. 2, was measured using optical microscopy.

2.3. XPS surface analysis

The tin–lead coated solder pads cleaned with the two methods were examined using X-ray photoelectron spectroscopy (XPS). To prevent charging on the sample surface the PCB surface was coated with gold film except on the solder pad area. The monochromatic AlK$_x$ excitation line (1486.6 eV) was used in this study.
Fig. 3. Wetting angle (maximum, average and minimum value) of the no-flow underfill fluxed solder on Sn–Pb coated and Au plated pads.

Fig. 4. Wetting angle (maximum, average and minimum value) of solder fluxed by the no-clean flux paste on Sn–Pb coated and Au plated pads.

3. Results and discussion

Fig. 3 shows the wetting angle (maximum, average and minimum value) of the no-flow underfill fluxed solder ball on the acid and acetone cleaned solder pads, while Fig. 4 gives the results of no-clean flux paste. There were 15 samples for each kind of test. Figs. 5–8 are the cross-section photos of solder fluxed by the no-flow underfill. Figs. 5 and 6 are cross-section views of the HCl and acetone cleaned Au plated solder pads. Fig. 7 corresponds to the HCl cleaned Sn–Pb coated solder pad. Fig. 8(a and b) gives the left- and right-side views of a cross-section of the acetone cleaned Sn–Pb coated solder pad. Fig. 9(a and b) shows the left- and right-side cross-section views of solder fluxed by the no-clean flux paste on the acetone cleaned Sn–Pb coated solder pad.

From Fig. 3, it can be seen that the fluxing capacity of the no-flow underfill on the tin–lead coated pad is much better than that on the gold plated solder pad. On the other hand, the wetting angle on the acid cleaned Sn–Pb coated solder pad is much smaller than that on the acetone cleaned solder pad, while the influence of clean method to the gold plated solder pad is
not obvious. For the capacity of the no-clean flux paste (see Fig. 4) the difference of wetting angles between the tin–lead coated and gold plated pads is not remarkable, while the effect of clean method to the fluxing capacity is not significant.

For a Sn–Pb–Cu system, it was found [7] that the formation of tin oxides is thermodynamically favored and preferential oxidation of tin would be expected. Table 2 gives the free energies of formation per mole of oxygen consumed for the more stable tin, lead, and copper oxides.

Fig. 10(a and b) are the survey XPS spectrum of the acid and acetone cleaned Sn–Pb coated solder pad surface, respectively. The survey XPS spectrum indicates that the solder pad surface contains mainly carbon, oxygen, tin and lead. Since the metal oxide concentration plays a critical role in solder wetting [6] and the formation of tin oxides is thermodynamically favored, Fig. 11(a and b) gives the high resolution XPS spectrum of tin on the acid and acetone cleaned Sn–Pb coated solder pad surfaces. The tables in Fig. 11(a and b) list the relative concentration of tin and tin oxides. The binding energy in Fig. 11(a and b) for tin and tin oxides (SnO or SnO$_2$) is ~485 eV and 486–487 eV, respectively. The relative concentration of tin oxides on the acetone cleaned pad surface is as high as 94.8%.

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**Table 2**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$ (KJ mole$^{-1}$)</th>
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<tbody>
<tr>
<td>$4Cu + O_2 \rightarrow 2Cu_2O$</td>
<td>$-292.9$</td>
</tr>
<tr>
<td>$2Cu + O_2 \rightarrow 2CuO$</td>
<td>$-254.6$</td>
</tr>
<tr>
<td>$2Pb + O_2 \rightarrow 2PbO$ (orthorhombic)</td>
<td>$-378.9$</td>
</tr>
<tr>
<td>$2Sn + O_2 \rightarrow 2SnO$</td>
<td>$-515.0$</td>
</tr>
<tr>
<td>$Sn + O_2 \rightarrow SnO_2$</td>
<td>$-515.8$</td>
</tr>
</tbody>
</table>
solder coating generally have a relatively small effect on solderability [8]. In this study, it was found that clean methods have little influence to the fluxing capacity of no-clean flux paste on the Sn–Pb coated pad. The average wetting angles on HCl and acetone cleaned Sn–Pb coated pads are ~ 7.2 and 9.0°, respectively, (see Fig. 4) which means that the tin oxide has very little effect on the fluxing capacity of no-clean flux paste, so our results are consistent with earlier conclusions.

However, the situation for the fluxing capacity of no-flow underfill on the tin–lead coated solder pad is significantly different, the average wetting angles on HCl and acetone cleaned tin–lead coated solder pads are ~ 7.5 and 22.0°, respectively, (see Fig. 5) and tin oxides impaired the fluxing capacity of no-flow underfill substantially. How can this phenomenon be explained? With no-flow underfill technology, the processes of interconnect soldering and underfill curing are completed in the same reflow process. The viscosity of the underfill is thought to be an important factor for proper reflow of solder and collapse of IC chip. The idea is that the underfill should have low viscosity before interconnect soldering and a rapid increase in viscosity should occur shortly after reflow. Due to the dissolution of oxides from the solder pad metallization, metal salts are formed during the fluxing action, especially with eutectic Sn–Pb alloys. The metal salts have the effect of catalyzing the epoxy curing process [9]. When the curing process occurs, the viscosity of the underfill becomes very high, and wetting and spreading of solder ball will not occur. Thus, the effect of catalyzing the curing process reduces the effectiveness of the fluxing action. Furthermore, it was also found [9] that Pb-rich flip chip bumps, when used with a HASL finished PCB, did not give rise to appreciable amounts of catalyzing metal salts, due to the presence of low level Sn oxides. Thus for the Sn–Pb–Cu system, tin oxide is the main cause of the catalyzing effect of the metal salt.

while acid cleaning significantly reduced the tin oxide relative concentration to 79.8%. In general, acetone could clean the organic contamination, while the acid could reduce the metal oxide on the solder pad surface [6].

Although the formation of tin oxides is thermodynamically favored, in practice, the eutectic Sn–Pb solder coating is widely used to protect PCB Cu-pad from oxidation that can lead to loss of solderability. Unlike copper oxide, the tin oxide films formed on the tin-rich solder coating generally have a relatively small effect on solderability [8]. In this study, it was found that clean methods have little influence to the fluxing capacity of no-clean flux paste on the Sn–Pb coated pad. The average wetting angles on HCl and acetone cleaned Sn–Pb coated pads are ~ 7.2 and 9.0°, respectively, (see Fig. 4) which means that the tin oxide has very little effect on the fluxing capacity of no-clean flux paste, so our results are consistent with earlier conclusions.

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![Fig. 10. The survey XPS spectrum of (a) HCl cleaned Sn–Pb coated Cu-pad; (b) acetone cleaned Sn–Pb coated Cu-pad.](image1)

![Fig. 11. The high-resolution Sn XPS spectrum of (a) HCl cleaned Sn–Pb coated Cu-pad; (b) acetone cleaned Sn–Pb coated Cu-pad.](image2)
Table 3
Average of the absolute deviations from the mean wetting angle

<table>
<thead>
<tr>
<th></th>
<th>HCl cleaned pad</th>
<th>Acetone cleaned pad</th>
</tr>
</thead>
<tbody>
<tr>
<td>No-flow underfill</td>
<td>1.9°</td>
<td>7.6°</td>
</tr>
<tr>
<td>No-clean flux paste</td>
<td>0.7°</td>
<td>2.0°</td>
</tr>
</tbody>
</table>

Since the negative influence of tin oxide to the fluxing capacity of no-flow underfill is an indirect process, and the underfill curing process is a complex reaction, many other factors can affect curing speed. The degree of dispersion of the no-flow underfill fluxing wetting angles on the acetone cleaned tin–lead coated pads must be very serious. Table 3 gives average values of the absolute deviations of wetting angles from their mean for the Sn–Pb coated solder pad. Compared with other situations, the value for the solder fluxed by no-flow underfill on the acetone-cleaned pad is exceptionally high. The dispersion character can also be reflected by the asymmetry of the cross-section view of the solder on the acetone cleaned Sn–Pb coated solder pad (see Fig. 8 (a and b)). For comparison, Fig. 9 (a and b) gives the left- and right-side views of a cross-section fluxed by the no-clean flux paste. In Fig. 3, the difference between maximum and minimum reveals this feature also.

Comparison of Fig. 3 and Fig. 4 reveals another feature that the fluxing capacity of the no-flow underfill on the gold plated solder pad is much worse than that on the tin–lead coated pad, while for no-clean flux, although the fluxing capacity on the tin–lead coated solder pad is also better than on the gold plated pad, the difference is very small. On the other hand, the effect of acid cleaning on the fluxing capacity of the no-flow underfill on the Au plated pads is negligible. The gold is a noble metal and the formation of metal oxides is negligible.

4. Conclusions

When compared with acetone cleaning, the HCl cleaned tin–lead coated solder pad can improve the fluxing capacity of no-flow underfill substantially, the average wetting angle on the acetone cleaned tin–lead coated solder pad was ~22.0°, while the corresponding value for the HCl cleaned solder pad was only ~7.5°. For the no-clean flux paste, the enhanced effect of HCl cleaning was not obvious. For a Sn–Pb–Cu system, the formation of tin oxides is thermodynamically favored. Due to the dissolution of tin oxides from the solder pad, metal salts are formed during the fluxing action, which have the effect of catalyzing the epoxy curing process, thus increasing the viscosity of underfill and reducing the effectiveness of the no-flow underfill fluxing action. The acid cleaning could remove tin-oxides on the solder pad surface remarkably, thus enhancing the fluxing capacity of no-flow underfill soundly. For the solder fluxed by no-flow underfill, the average values of the absolute deviations of wetting angles from their mean for the acetone cleaned Sn–Pb coated solder pads was ~7.6°, but for the HCl cleaned pad, it was only ~1.9°. Therefore, a relatively high level concentration of tin oxides also resulted in a wide range of wetting angles. The negative effect of tin oxides on the fluxing capacity of no-clean flux paste is not obvious.

The fluxing capacity of the no-flow underfill on the gold plated Cu-pad is much worse than that on the tin–lead coated Cu-pad, the wetting angles on HCl and acetone cleaned gold plated solder pads are ~38.0 and 40.0°, respectively. For the no-clean flux paste, the difference of wetting angles between the tin–lead coated and gold plated solder pads is negligible.

Acknowledgements

The authors would like to thank Edwina Luk of Department of Electronic Engineering, City University of Hong Kong for suggestions and proof reading and thanks to Dr C.S. Lee, M.K. Fung and S.L. Lai of Department of Physics and Materials Science, City University of Hong Kong for their help in doing XPS tests. The authors would also like to acknowledge financial support provided by the Strategic Research Grant (7000955) of the City University of Hong Kong.

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