

Cause and Prevention of Large Void Formation in Flip Chip Solder Connections

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Abstract

X-ray inspection of large die bonded into ceramic packages revealed a high incidence of voids, whose size approached 20 percent of the solder volume. All voids appeared to form on the chip bond pads. Die attachment was performed on a high precision bonder with in-situ reflow under a formic acid atmosphere. The die were bumped with 98.2 tin / 1.8 silver weight percent solder on nickel coated copper pads. The cofired ceramic packages were metallized with electroless gold over nickel. Our investigation determined that the voids were initiated by formation of a gold-nickel-tin intermetallic compound that released hydrogen gas at the solder interface. This compound formed preferentially on the chip pads because after completing reflow, the bonder cooled the assembly by blowing nitrogen on it, which caused the chip to cool faster than the package because of its much lower thermal mass. The propensity for void formation was all but eliminated by reducing the peak reflow temperature, time above reflow, and making modifications to the bonder cooling system to reduce the temperature difference between the chip and its package.

We believe that after the voids nucleated at the solder-intermetallic interface, they continued to grow by release of hydrogen from the molten solder. Our calculations indicate that a concentration of 0.0048% hydrogen atoms in the solder is sufficient to grow voids of the size that we observed. Our hypothesis that release of dissolved hydrogen drives void growth was supported by a hydrogen degassing experiment that we conducted. As-received solder bumped chips were baked under high vacuum for several days, and then bonded to silicon chips with gold/ nickel metallized bond pads. X-ray inspection of these assemblies revealed no voids in contrast to the multiple voids observed in similar samples that were bonded without the hydrogen degassing step.

Key Words:

Flip Chip, Electroplated solder, Hermetic Packaging , Co-Fired Ceramic , Reliability,

Introduction

High I/O flip chip packages for strategic applications are assembled by reflowing solder bumped chips onto pads of a multilayer cofired ceramic substrate in a formic acid environment without the use of

flux [1]. Solder reflow is performed with the package in a shroud that is an integral part of the precision die bonder. The die and package are brought to reflow temperature by low mass electrical heaters in the package nest and die bond collet. Post reflow cooling is accomplished by blowing nitrogen gas through the reflow shroud.

This process was used to attach die with over 900 I/O on a pitch of 205 microns, to ceramic packages; bond pads on both were 90 microns in diameter. The chip pads were metallized with nickel over copper and those on the ceramic were metallized with gold over nickel using an ENIG process. The die were bumped with solder of composition 98.2 wt% Sn / 1.8 wt% Ag. High tin solders are used for flip chip assemblies to enhance temperature-cycle fatigue life [2]. The outer perimeter solder connections on the assembled devices had a standoff height of 54 microns and appeared bright and uniform in shape.

X-ray inspection of these same assemblies revealed the presence of numerous large voids, an example of which appears in Figure 1. Metallographic cross sections and x-ray tomography revealed that the voids covered the chip bond pads as shown by representative images in Figures 2 and 3. Scanning electron microscope (SEM) examination of metallographic cross sections showed that the large voids did indeed terminate on the chip bond pads, but also showed, as in Figure 4, smaller voids in the same solder cross section.

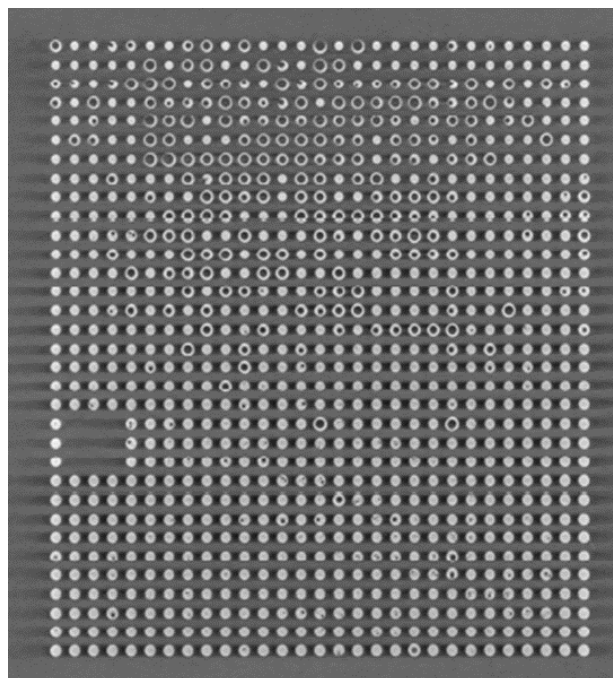


Figure 1. X-ray micrograph of a die flip chip bonded to a cofired ceramic package.

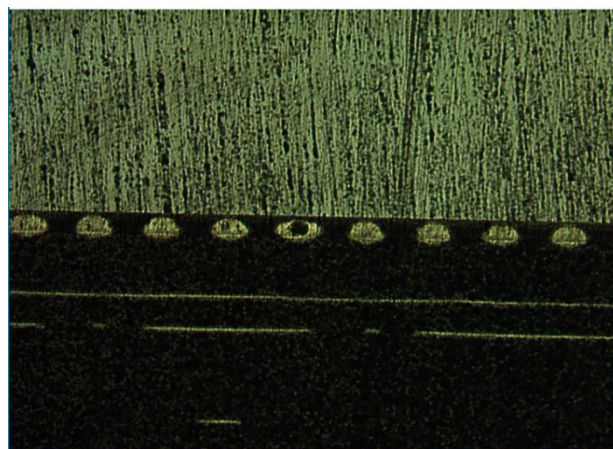


Figure 2. Metallographic cross section that shows a large void in the center solder connection.

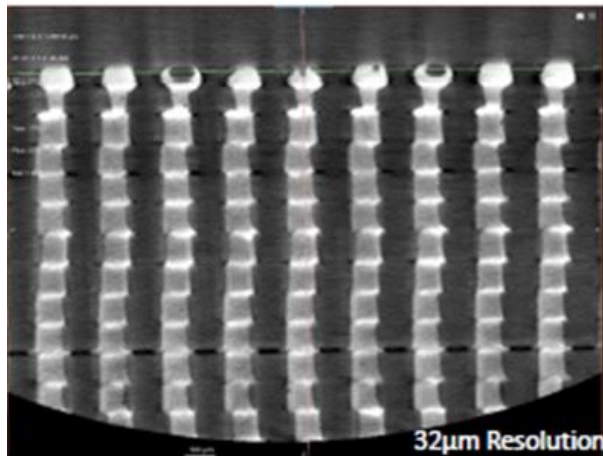


Figure 3. X-ray tomography image showing two large voids at the chip-solder interface.

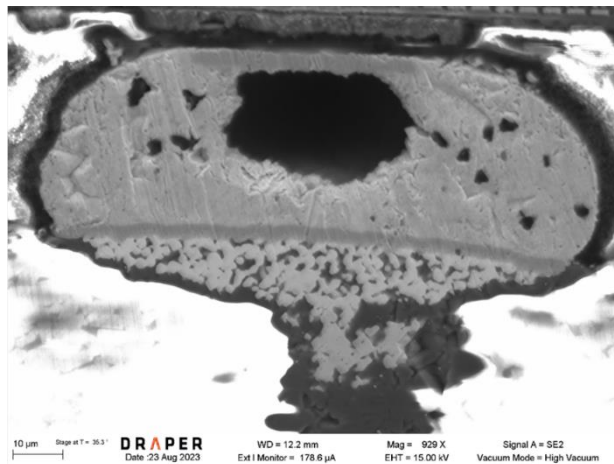


Figure 4. SEM image of a solder connection with a large void that covers the chip bond pad. Several smaller voids are also visible in the solder.

Experimental Investigation

Since the large voids were always associated with chip bond pads, we heated several chips above the solder reflow temperature for extended periods of time to see if something on or within the pads was causing the voids to form. Figure 5 shows x-ray micrographs of chips as received and heated to 270°C for 1, 5 and 60 minutes. We did not observe any voids in these chip samples and

so concluded that void formation was not due to some deficiency of the chip pads. This result directed our attention to the package bond pads, so in our next experiment we bonded die to silicon substrates with thin film bond pads of 500 Å chrome/ 1000 Å platinum/ 5000 Å gold. X-ray examination of these samples revealed numerous large voids as shown in Figure 6. This result was a bit of a surprise and prompted an energy dispersive analytical x-ray examination of solder cross sections. The results of one of these analyses is presented in Figure 7.

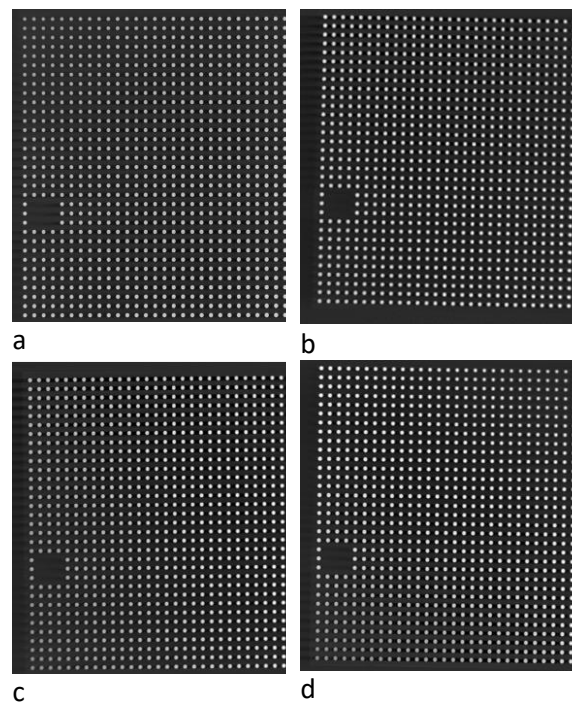


Figure 5. X-ray images of solder bumped die (a) as received, (b) 1 minute at 270°C, (c) 5 minutes at 270°C, (d) 60 minutes at 270°C.

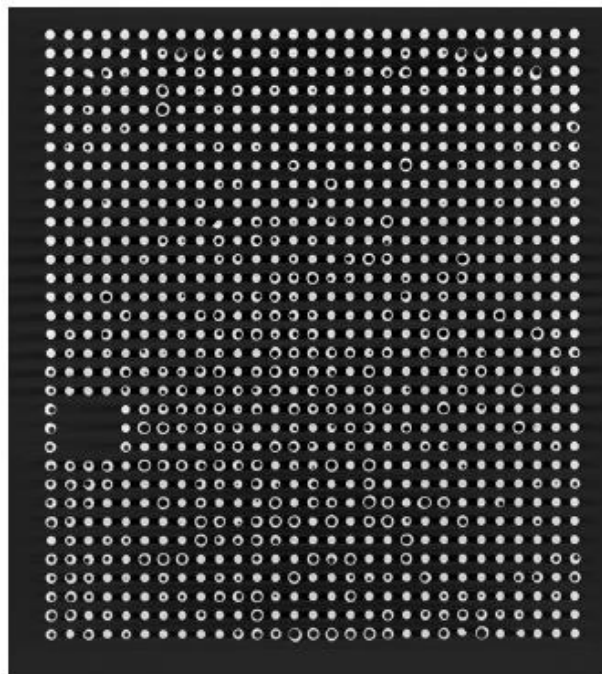
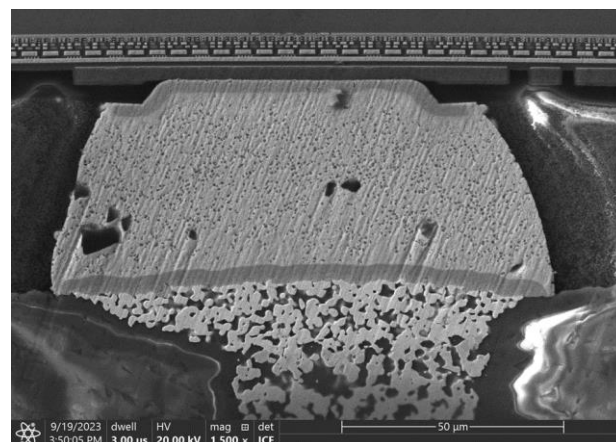
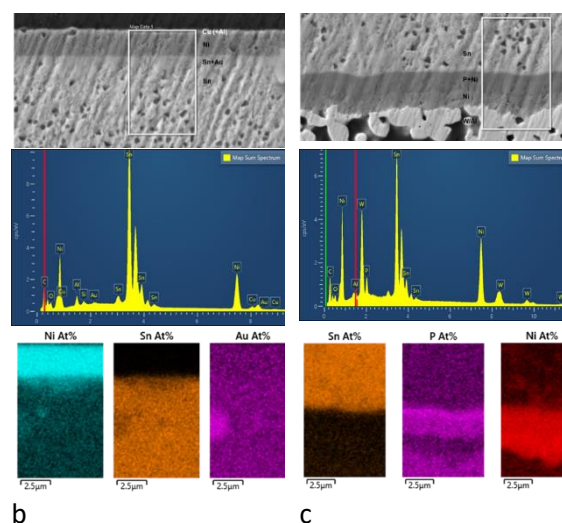


Figure 6. Die bonded to silicon chip with Cr/Pt/Au metallization.

The cross section in Figure 7 does not contain a large central void, but several small voids are visible in the solder. The EDAX analysis on the chip pad of this sample, presented in Figure 7b, shows sharp interfaces of Ni/ Sn + Au/ Sn. By contrast, EDAX analysis of the substrate pad, shown in Figure 7c, reveals sharp interfaces of Ni/ Ni + P/ Sn, with no detectable gold. Our interpretation of this result is that the gold completely dissolves in the solder during reflow and then precipitates out as a gold-tin intermetallic at the chip interface when nitrogen gas impinges on the chip at the end of the bond cycle.



a



b

c

Figure 7. Cross section of reflowed solder connection between chip and package bond pad (a), Elemental mappings of Chip (b) and (c) package interfaces

Analytical Modeling

The formation of gold-tin-nickel intermetallic compounds has been investigated extensively and there is some evidence to suggest that solder adhesion to them is reduced from that of solder to nickel [3], [4], [5]. This inspired our first hypothesis for void formation which was that the formation of the intermetallic reduced the adhesion of the solder to the bond pad and a void formed as the solder tried to minimize its contact area on the pad.

This hypothesis was tested by using the Surface Evolver software to model a solder connection with a void and then allowing the program to evolve the shape to the equilibrium configuration [6]. The initial geometry is shown in Figure 8a. A wetting angle induced line tension is applied in the plane of the bond pad along the edges of the bubble. For the case in which the solder readily wets the bond pad, the solder moves across the interface rapidly collapsing the void. This condition is shown in Figure 8b for a wetting angle of 20° . A wetting angle of 170° causes the solder to move toward the edge of the pad, while pulling the solder surface of the void down in contact with the pad as shown in Figure 8c. These results demonstrated that a dewetting mechanism could not generate the large voids that were observed in solder connections.

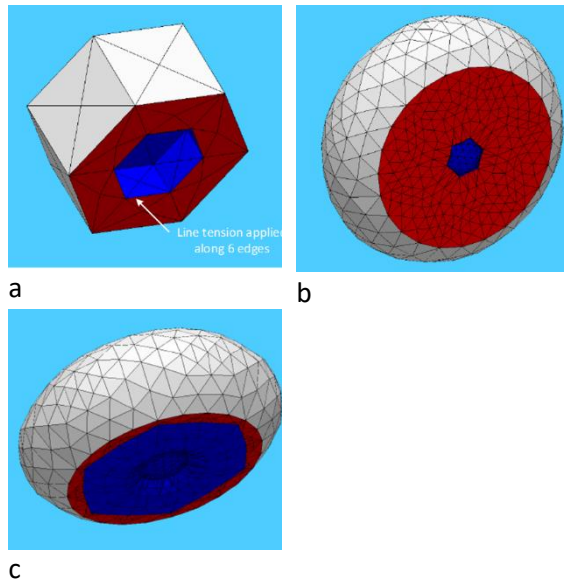


Figure 8. Model of a solder connection with a void. (a) Initial configuration with a wetting angle dependent line tension applied in the bottom surface along the void edges (b) A wetting angle of 20° causes the solder to cover the bond pad rapidly collapse the void. (c) A wetting angle of 170° causes the solder to move toward the edge of the pad,

while pulling the solder surface of the void down in contact with the pad.

Next, we examined what pressure would be required to generate a bubble at the solder pad interface. We created a Surface Evolver model in which we applied a uniform pressure on the solder across the entire bond pad. The pressure is resisted by the surface tension of the solder. A value of 548 dyne/cm was used for the surface of tin at 523 K [7]. Figure 9a shows the solder model. The bottom surface is fixed while pressure is applied to the top face. Perspective views of solder deflection resulting from applied pressures of 1000, 5000, and 10000 dynes/cm² are shown in Figures 9b through 9d, respectively.

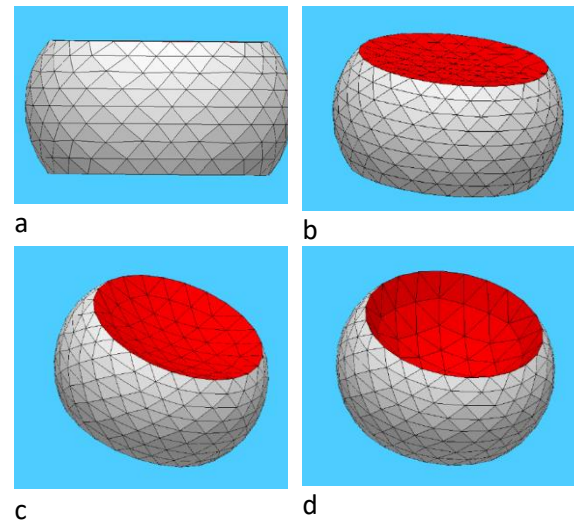
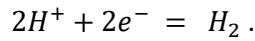
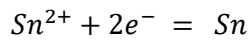


Figure 9. (a) Side view of solder connection. Bottom surface is fixed while pressure is applied to the top face. A surface tension of 548 dyne/cm is applied over the exterior solder surface. Perspective views of solder deflection resulting from applied pressures of (b) 1000, (c) 5000, and (d) 10000 dynes/cm².

Gas Model

Hydrogen gas can be entrapped in electroplated tin when the mass transfer rate is lower than the deposition rate. An increase in current density along with a decrease in stannous concentration promotes hydrogen formation [8]. This was identified as an issue by Tatsumi et. al. when plating solder bumps in cut outs in thick dry film resist, which constrains the flow of plating solution [9]. The two competing reactions are:



For a void or bubble to form, the internal gas pressure must overcome the pressure exerted by the solder, which is given by the Gibbs-Thompson equation [10] [11],

$$P = \gamma\kappa \quad (1)$$

In which γ is the surface tension of the solder and κ is the curvature of the solder connection. The surface tension of tin, γ_{Sn} at 523K is 0.548 N/m [7]. We assume that the solder connection is a truncated spheroid of height, $h = 75 \mu m$, that is attached to bond pads of radius $r_p = 45 \mu m$, so from the construction of Figure 10, the spheroid radius, R , is,

$$R = \sqrt{(r_p)^2 + (h/2)^2} = 58.77 \mu m, \quad (2)$$

and the solder volume, V_s , is,

$$V_s = 2\pi \int_0^{h/2} (R^2 - z^2) dz = \pi h \left(R^2 - \frac{1}{12} h^2 \right) = 6.98e5 \mu m^3 . \quad (3)$$

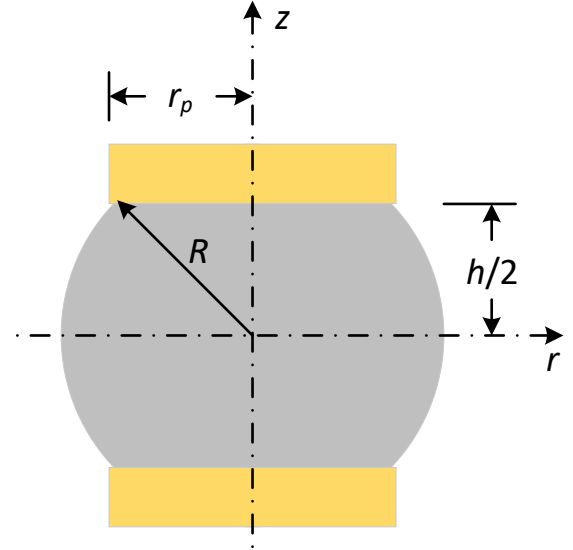


Figure 10. Construction used to calculate solder volume.

If a hemispherical-void forms that covers the bond pad, as shown in Figure 11, its volume, V_v is,

$$V_v = \frac{2}{3}\pi(r_p)^3 = 1.91e5 \mu m^3. \quad (4)$$

The curvature, κ_v of the void is,

$$\kappa_v = \frac{2}{r_p} = 4.44e4 [m^{-1}], \quad (5)$$

and from equation 1, its internal pressure is,

$$P_v = \gamma_{Sn}\kappa_v = 2.44e4 [Pa] . \quad (6)$$

The moles of gas, n in the void can be estimated using the perfect gas law,

$$n = P_v V_v / RT = 1.05e-12 \text{ moles}, \quad (7)$$

In which R is the gas constant with a value of $R = 8.314472 [m^3 Pa K^{-1} mol^{-1}]$ and T is the absolute temperature with a value of $T = 533 K$. The density of tin is $7.29 [gm/cc]$ so the mass of the solder connection is,

$$mass_{Sn} = \rho_{Sn} V_s = 5.09e-6 [g] . \quad (8)$$

The molar mass of tin, AtW_{Sn} is 118.71 [g], so the mole of tin, n_{Sn} in the solder connection is,

$$n_{Sn} = mass_{Sn}/AtW_{Sn} = 4.29e - 8 \text{ [moles]}. \quad (9)$$

The change in gas concentration, Δc in the solder needed to fill the void is,

$$\Delta c = 100 \times n/(n + n_{Sn}) = 2.45e - 3 \text{ [\%]}. \quad (10)$$

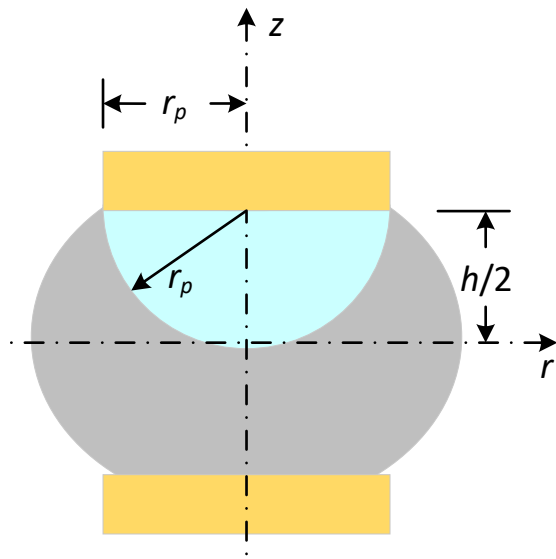


Figure 11. Solder connection with a hemispherical void that covers the bond pad.

Presumably, if the gas species in the void is hydrogen, it would be dissolved in the solder as atomic hydrogen so that twice the number of gas molecules in the void would be extracted from the solder. Thus $\Delta c_H = 2\Delta c_{H_2} = 4.8e - 3 \text{ \%}$.

A second source of gas at the solder bond pad interface is from contaminants in the nickel plating. Studies by Lei, Borgesen and Dimitrov suggest that $Ni(OH)_2$ and $NiOOH$ form during nickel electroplating and then decompose when exposed to temperatures

above 280°C [12], [13]. Their investigation concluded that it is impractical to avoid deposition of these impurities in commercial electroplating and focused on post plating heat treatments to remove them. Their experiments demonstrated that a significant reduction in voiding of solder connections was realized by heat treating plated nickel prior to deposition and reflow of solder.

Metallographic cross sections of solder connections without large voids suggest that gas is evolved at the pad-solder interface. The focused ion beam (FIB) image in Figure 12 shows a number of small voids at the interface, but none in the solder volume. A FIB image of a solder connection with a single large void appears in Figure 13, but as in Figure 12, no small voids are visible in the solder volume. Our interpretation of these results is that it is difficult to nucleate voids, but once formed, hydrogen diffuses out of the bulk solder to grow the void. The sample shown in Figure 12 was treated to remove hydrogen from the solder prior to reflow.

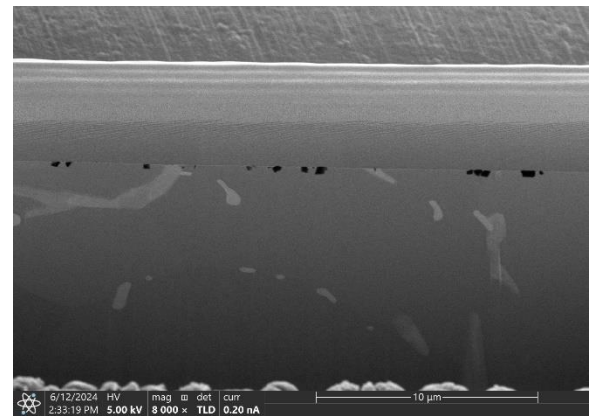


Figure 12. FIB cross section that shows voids at the solder - intermetallic layer.

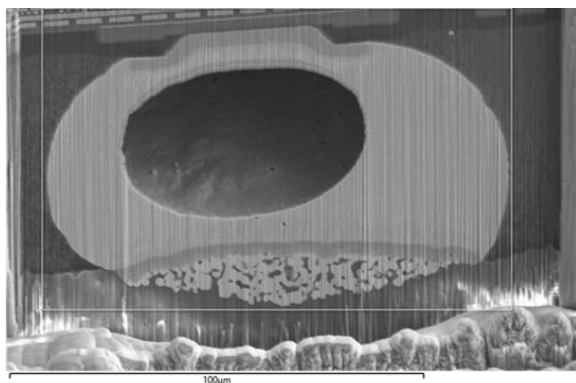


Figure 13. FIB cross section that shows a single large void, but no population of smaller voids.

Hydrogen Degas Experiment

Motivated by our hypothesis that the large voids were being created by gas released from the solder and nickel layer of the chip bond pads, we performed a degas treatment of bumped die prior to bonding. The as received die were placed on a hot plate inside a vacuum chamber maintained at a pressure of 1.0×10^{-6} Torr with the hot plate set at 125°C .

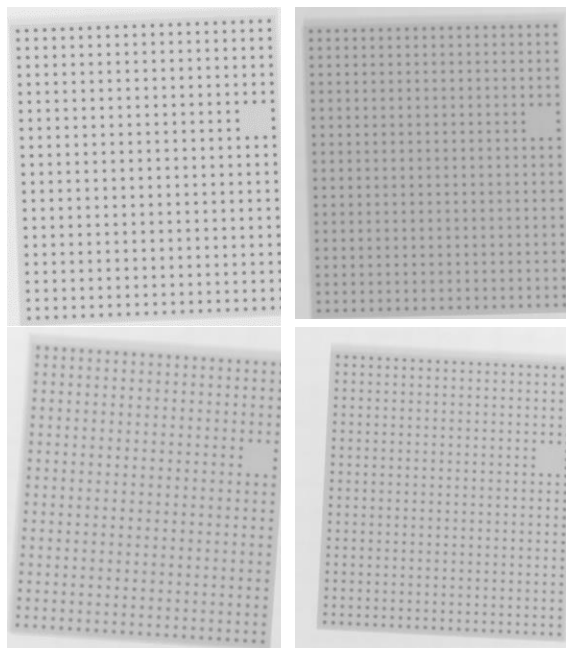


Figure 14. X-ray images of die bonded to a silicon substrate with no large voids.

The chips were degassed under these conditions for 72 hours before bonding to silicon substrates using the same settings that previously generated large voids. Figure 14 shows x-ray images of four assemblies made with the degassed chips. None of the solder connections exhibit large voids in contrast to the x-ray image of Figure 6.

Conclusions

Large voids were observed in 98.2 Sn/ 1.8 Ag solder connections of die that were flip chip bonded to ceramic packages with ENIG pad metallization. Solder reflow was performed on a precision die bonder under a formic acid atmosphere without the use of flux. Large voids were also observed when the same die were bonded to silicon substrates with gold over platinum pads deposited by e-beam evaporation. The incidence of void formation was greatly reduced by lowering both the peak reflow temperature and time above reflow as well as reducing the cooling rate. Heating the unbonded chips to 125°C under high vacuum for several days eliminated void formation when the die were reflowed using the original bonder settings. Finally, we were unable to generate voids in unbonded die when they were held above reflow temperature for up to an hour.

Based on these observations, we believe the probable root cause of the large solder joint voids is release of hydrogen that is embedded in the nickel bond pads and solder of the bumped die. It is challenging to electroplate tin free of entrapped hydrogen because of its low electro-potential of -0.6 V vs Ag/AgCl relative to any alloying elements. Simple calculations suggest that hydrogen concentrations within the solder of $4.8 \times 10^{-3}\%$ is sufficient to grow large voids.

Nickel is also difficult to electroplate free entrapped hydrates. We propose that void nucleation occurs when gold in solution reacts with the nickel to form a gold-nickel-tin compound that expels and decomposes entrapped hydrates to nucleate micro-voids at the solder-intermetallic interface. As the molten solder cools, the hydrogen dissolved within it forms gas molecules at the interface between the solder and micro-voids, which causes them to grow and eventually coalesce into a large void.

We demonstrated that a hydrogen depletion bake of solder bumped die eliminated void formation. It is recommended that a hydrogen depletion bake be performed prior to bonding solder bumped die to avoid void formation as well as eliminate the potential for moisture formation from flip chip die within hermetic packages.

References

- [1] J. Ramirez Ramos, K. Graham, T. Marinis and D. Hanson, "Assembly of Large Flip Chip Die in Ceramic Packages," in *Proceedings of IMAPS Symposium*, San Diego, CA, 2023.
- [2] S. K. Kang, "Effects of Minor Alloying Additions on the Properties and reliability of Pb-free Solders and Joints," IBM RC25045 (W1009-018), 2010.
- [3] H. Dong, *Design of the Contact Metallizations for Gold-Tin Eutectic Solder-A Thermodynamic-Kinetic Analysis*, PhD Thesis, Aalto University, 2016.
- [4] A. Katz, C. H. Lee and K. L. Tai, "Advanced Metallization Schemes for Bonding of InP-Based Laser Devices to CVD-Diamond Heatsinks," *Materials Chemistry and Physics*, vol. 37, pp. 303-328, 1994.
- [5] H. G. Song, *Microstructural Evolution of Eutectic Au-Sn Solder Joints*, PhD Thesis, University of California, Berkely, 2002.
- [6] K. A. Brakke, "The Surface Evolver," *Experimental Mathematics*, vol. 1, no. 2, pp. 141-165, 1992.
- [7] B. B. Alchagirov, O. I. Kurshev and T. M. Taova, "Surface Tension of Tin and Its Alloys with Lead," *Russian Journal of Physical Chemistry A*, vol. 81, no. 8, pp. 1281-1284, 2007.
- [8] H. Sun, J. Sun, D. Ding, C. Chen, M. Li and Y. He, "Effect of Deposit Microstructure on the Reflow Discoloration of Electroplating Pure Tin," in *International Symposium on Advanced Packaging Materials*, Xiamen, China, 2011.
- [9] K. Tatsumi, A. Sakai, S. Kawai, T. Katase, T. Miyazawa and M. Ishikawa, "Study of Void Formation Mechanism in Electroplated SnAg Solder Bump," in *IMAPS 2016 49th International Symposium on Microelectronics*, Pasadena, CA, 2016.
- [10] M. A. Fortes, "Capillary Forces in Liquid Bridges and Flotation," *Port Quim*, vol. 23, p. 193, 1981.
- [11] I. S. Zavarine, O. Khaselev, Y. Zhang, C. Xu, C. Fan and J. Abys, "Lead-Free Solder Bumping Technologies," in *IPC Printed Circuits Expo*, 2004.
- [12] Z. Lei, P. Borgesen and N. Dimitrov, "Hydrogen Evolution and Thermal Treatments for Removal of Plating Induced Impurities from Ni to Extend Life of Solder Joints," *Colloids and Surfaces A*:

Physicochemical and Engineering Aspects,
vol. 692, p. 133995, 2024.

- [13] Z. Lei, P. Borgesen and N. Dimitrov,
"Electrodeposition Complexity and the
Root Cause of Interfacial Voiding in Solder
Joints with Plated Nickel," *ACS Applied
Electronic Materials*, vol. 6, pp. 457-464,
2024.