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Abstract

The undercooling of flip-chip Pb-free solder bumps was investigated by differential scanning calorimetry (DSC) to understand the effects of solder composition and volume, with and without the presence of an Under Bump Metallurgy (UBM). In addition, the solidification of an array of individual solder bumps was monitored in-situ by video imaging technique during both heating up and cooling down cycles. Data obtained by the optical imaging method is used to compliment the DSC thermal measurements. A random solidification of the array of bumps was demonstrated during cooling which also spans a wide temperature range of 40-80°C. In contrast, an almost simultaneous melting of the bumps was observed during heating.

Key Words: Undercooling, Solder bumps, Pb-free, Solidification, DSC

Sn-rich, near eutectic binary and ternary solder alloys, such as Sn-0.7Cu, Sn-3.5Ag and Sn-3.8Ag-0.7Cu, are the leading Pb-free solder candidates to replace Pb-containing solders in electronic assembly applications. To ensure a successful transition and the impacts on solder joint integrity and reliability research studies have been performed to investigate the various issues [1, 2]. Since the compositions of most Pb-free solders are typically more than 90% Sn, their physical, chemical and mechanical properties are heavily influenced by the properties of pure Sn, as opposed to eutectic Sn-Pb which consists of a mixture of Sn-rich and Pb-rich phases. One of the distinct properties of Sn-rich solders is a propensity for large amount of undercooling of β-Sn phase during solidification. The undercooling is defined as the temperature difference between the melting temperature of a solder during heating and the solidification temperature during cooling. Although the undercooling of a bulk sample can be easily measured by differential scanning calorimetry (DSC), it is difficult to measure the undercooling of flip-chip solder bumps because the individual solder bump is too tiny to be handled and the amount of heat associated with melting or solidification is also too small to be detected. The undercooling observed with near-ternary Sn-Ag-Cu solder spheres of a few hundred micrometers in diameter (such as BGA or CSP solder joints) was much larger than high Pb solders or Sn-Pb eutectic solders [3, 4]. The large undercooling is also attributed to the growth of large primary phase such as Ag_3Sn in near-ternary Sn-Ag-Cu solders [3, 5]. It was also reported that the amount of the β-Sn undercooling in Sn-Ag-Cu solders is inversely proportional to sample size, suggesting a larger undercooling in a smaller solder joint (such as flip chip vs. BGA solder joints) [6]. Since the undercooling phenomenon is related to the difficulty of nucleating a solid phase in a liquid state, it can be influenced by many factors, such as alloy composition, solder volume, impurity level, presence of a solderable surface (like UBM or BLM), cooling rate, etc. It was also demonstrated that an addition of minor alloying elements, such as Zn, Fe, Co, Bi, and others could reduce the amount of undercooling of β-Sn phase [7-9]. In this report, a few critical factors affecting the degree of undercooling were examined with Sn-rich solders of flip-chip size: effect of a wettable surface, such as UBM (under bump metallurgy) and solder volume. In addition, the solidification process of flip-chip size solder bumps filled in cavities of glass mold has been directly observed by video imaging the process and later to correlate with the DSC results.

Two types of samples were prepared by the low cost C4NP (Controlled Collapse Chip Connection: New Process) wafer bumping process [10]. The first type uses chips which were deposited with Cu/Ni UBM (100 um pad size on 200 um pitch) with transferred C4NP solder bumps; and the second type uses glass mold first etched with tiny cavities (~100 micrometer in diameter) then filled with solders. Both types of samples were thinned down on its backside to reduce its thermal mass for DSC experiments.

Fig. 1(a) shows a typical thermal profile obtained from a thinned down Si chip (1.4 mg in weight) with 114 solder bumps of Sn-1.0Ag-0.9Cu (in wt %) transferred on Cu/Ni UBM pads. During heating at the rate of 6°C/min, the onset of melting was observed at 219.5°C followed by two peaks at 220.6°C and 224.7°C, indicating the presence of two phases in this alloy composition. During cooling at 6°C/min, the onset of solidification was observed at 182.4°C, yielding a undercooling of 37.1°C by the onset-to-onset measurement. However, the solidification process was not completed down to 165.5°C, evidenced by the presence of a broad exothermic peak consisting of many small peaks between 181°C and 165.5°C as shown in Fig.1(b), yielding a maximum undercooling of about 55°C. The single large peak at 181.8°C was attributed to the solder bumps melted and solidified together during the DSC run, while the small multiple peaks were attributed to the individually solidifying solder bumps. This was confirmed by examining solder bumps before and after DSC runs as shown in Fig. 2(a) and (b). In the DSC run, a thinned Si chip with solder bumps was placed up side down in an Al sample holder and sealed by pressing an Al cover plate to make a good thermal contact. This pressing action has plastically deformed some solder bumps, as shown in Fig. 2(a), causing melting of some solder bumps to connect together during the DSC run shown in Fig.2(b), which produces a single large peak at a high temperature during solidification while individually solidifying solder bumps are responsible for the broad peak discussed.

Fig.3 (a) and 3(b) show typical thermal profiles obtained from a thinned down glass mold filled with Sn-0.7%Cu (in wt %), (2.8 mg, 165 solder bumps). The onset of melting was observed at 228.7°C during heating at 6°C/min and the peak temperature at 229.2°C, shown in Fig. 2(a), which is quite consistent with the reported value of Sn-Cu eutectic temperature, 227°C [11]. During cooling from 250°C at 6°C/min, many small peaks associated with the solidification of individual solder bumps were observed between 180.4°C and 139.9°C, yielding a maximum undercooling of about 90°C, as shown in Fig. 2(b). No single isolated peak was detected during cooling, indicating solder bumps were well separated in the cavities of a glass mold even it was up side and pressed down during the DSC run.

Fig. 4 displays the sequence of two consecutive solidification processes of about 10 solder bumps sitting in the cavities (100 micrometer in diameter) of a glass mold. The solder bumps were reflowed twice by heating up to 250°C, and then cooling down to room temperature, and repeat. During heating, all solder bumps were simultaneously melted around 227°C, which is in a good agreement with the DSC runs, while during cooling, the first solidification was observed at 195°C, and the last at 126°C, yielding a maximum undercooling of about 100°C. This is in a very good agreement with the DSC results. It is very interesting to note that the solidification sequence of 10 solder bumps under observation is totally random in two repeating solidification processes. This random behavior of the nucleation events within 10 solidifying bumps is consistent with the probabilistic nature of heterogeneous nucleation and growth of the solidification.

In summary, a large amount of the undercooling (as large as 90°C) was observed with Sn-rich, flip-chip solder bumps sitting in a glass mold, while the corresponding undercooling was significantly reduced (to about 55°C) in the presence of a wettable surface such as Cu/Ni UBM. The direct observation of individual solder bumps during their solidification process has revealed the random nature of nucleation events, and confirmed the amount of the undercooling measured with Sn-rich, flip-chip solder bumps by DSC.

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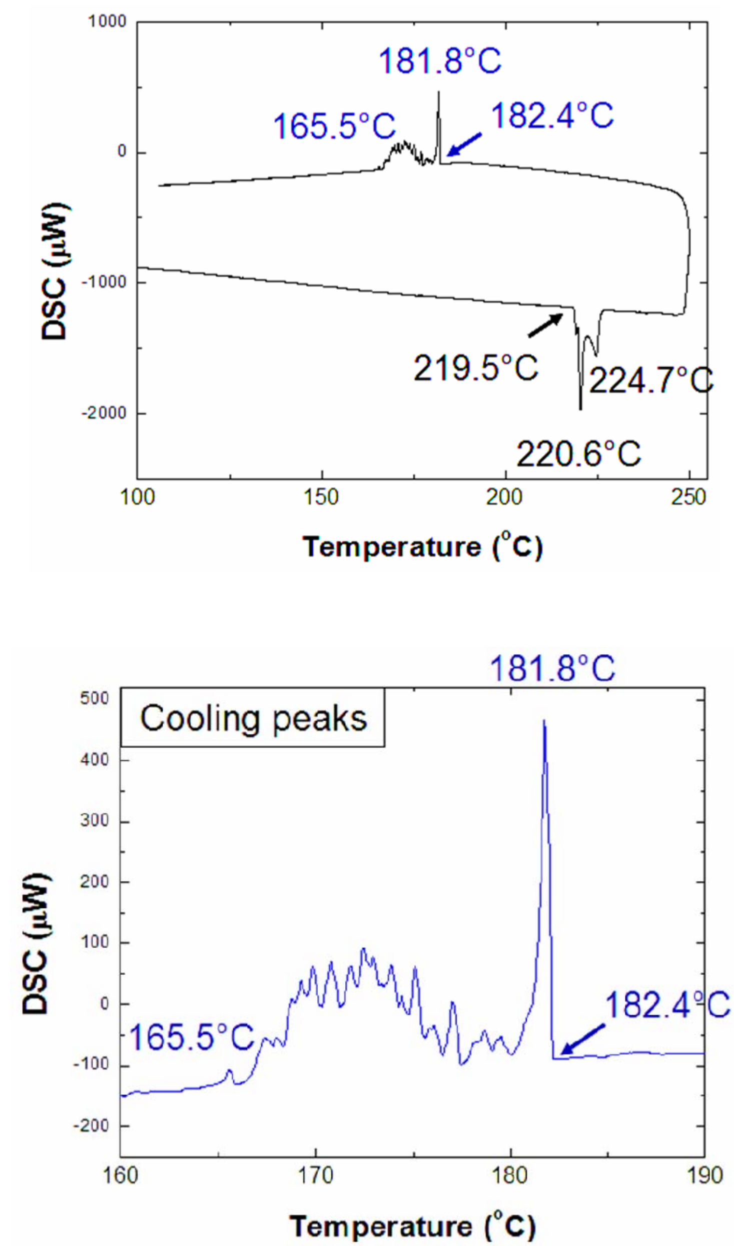


Figure 1. Typical DSC profiles obtained from a thinned Si chip with more than 100 solder bumps of Sn-1.0 wt % Ag-0.9 wt % Cu with the UBM of Cu/Ni: (a) a heating curve from room temperature to 250°C, holding for 10 min at 250°C, and cooled down to room temperature, and (b) an enlarged view of cooling curve between 150°C and 190°C.

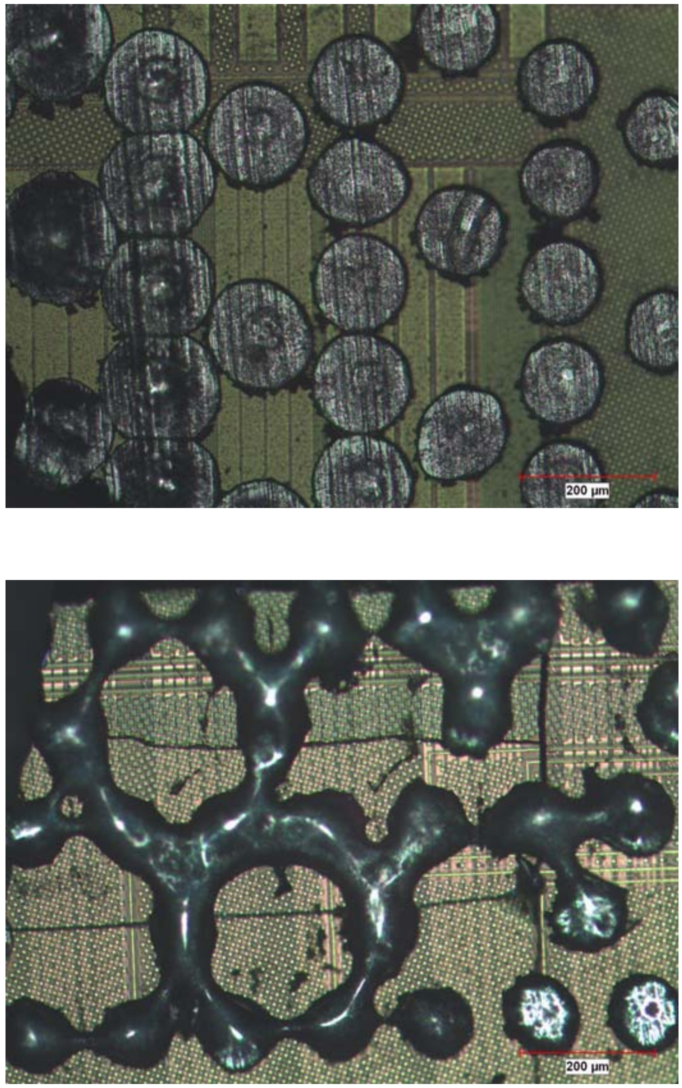
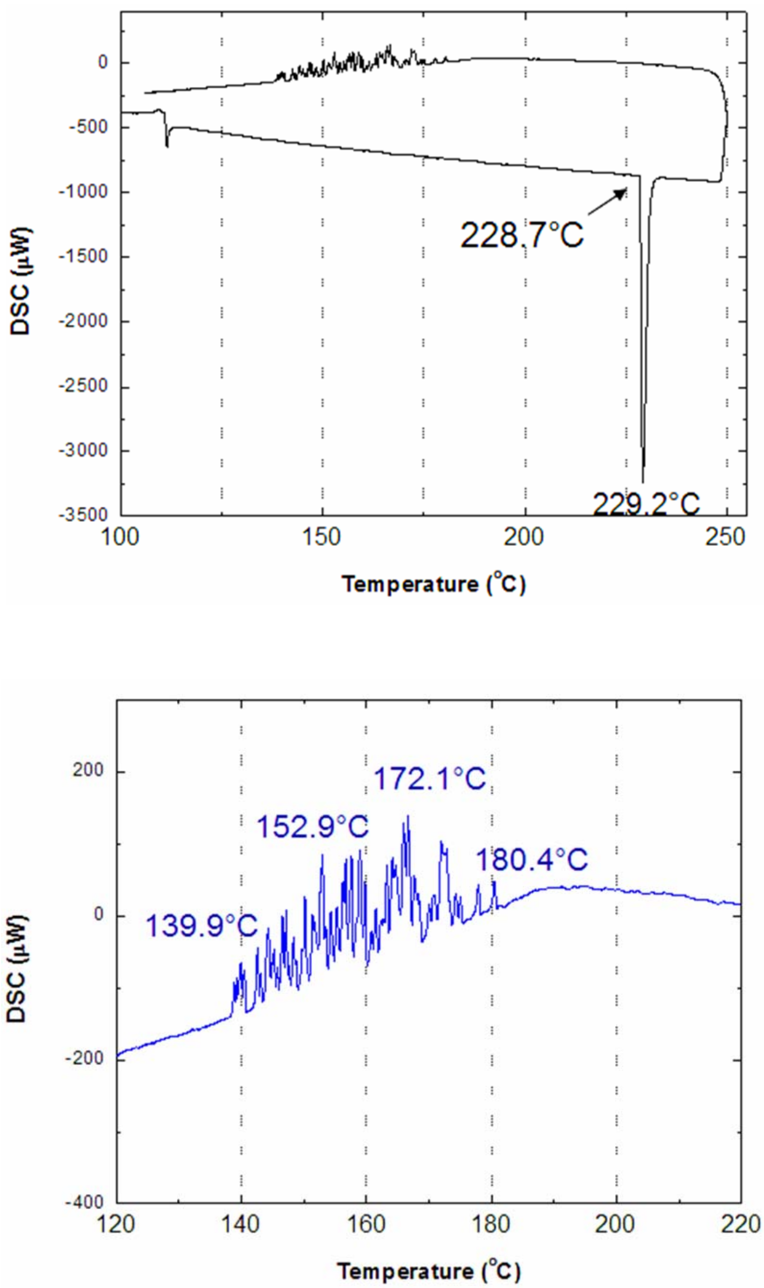


Figure 2. Optical micrographs of flip chip solder bumps of Sn-1.0%Ag-0.9%Cu, (a) before, and (b) after DSC run.



Fgure 3. Typical DSC profiles obtained from Sn-0.7%Cu solder balls of about 100 micrometer in diameter sitting in cavities of a glass mold: (a) a heating and cooling curve at 6°C/min and holding for 10 min at 250°C, and (b) an enlarged portion of the cooling curve between 120°C and 220°C.

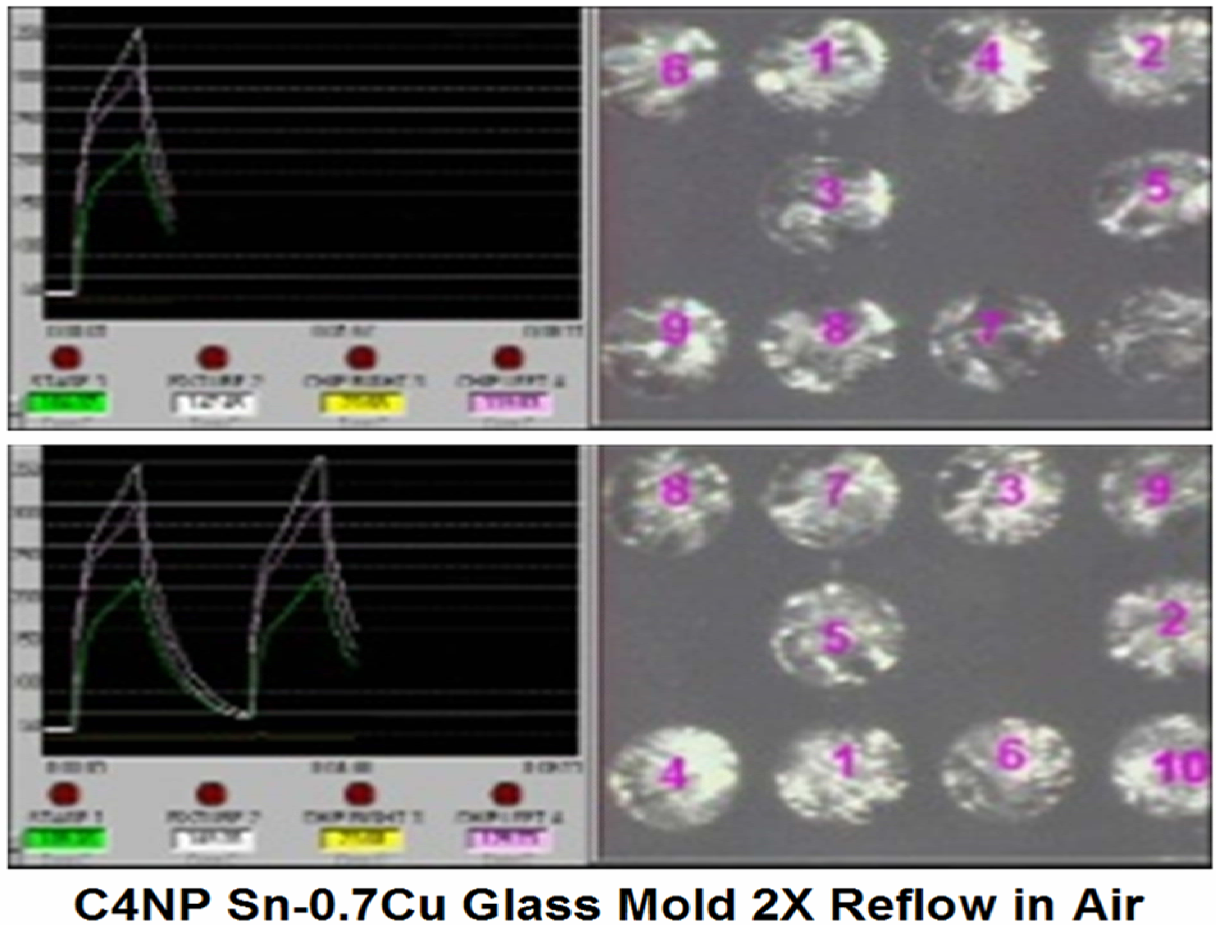


Fig. 4. Two video images of the solidification sequence of 10 solder bumps of Sn-0.7%Cu, sitting in the cavities of a glass mold. The solder bumps were reflowed twice in sequence by heating up to 250°C, and then cooling down. During cooling down, 10 individual bumps were examined to find out the solidification sequence of them. The number written on each bump tells the order of the solidification sequence, which occurred randomly in two consecutive solidification processes.