Study of wetting reaction between eutectic AuSn and Au foil

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Abstract:

The wetting reactions between eutectic AuSn solder and Au foil have been studied. During the reflowing, Au foil dissolution occurred at the interface of AuSn/Au, which increases with temperature and time. The activation energy for Au dissolution in molten AuSn solder is determined to be 41.7kJ/mol. Au₅Sn is the dominant interfacial compound layer formed at interface. The activation energy for the growth of interfacial Au₅Sn phase layer is obtained to be 54.3kJ/mol over the temperature range 360°C to 440°C.

Wettability of the molten AuSn solder ball is a temperature-dependence process. At 390°C, AuSn solder balls exhibited best wettability among all reflowing cases (wetting angle is about 25°). Kinetics of wetting was proposed to be controlled by the oxidation and Au dissolution rates on the wetting front of spreading molten AuSn solder. Below 390°C, the Au dissolution rate dominates the progression of the wetting front. On other hands, above 390°C, the oxidation rate exceeds Au dissolution rate, thus, wetting was rearded.

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Introduction:

As the signal frequency used in RF (Radio Frequency) devices has approached tens of GHz, flip-chip technology has become increasingly important for the chip assembly of RF devices. This is because the short signal transmission path of the flip-chip structure can alleviate the potential for parasitic inductance and capacitance, which are the main contributions to signal loss.[1,2,3] Beside RF devices, the flip-chip technology also has been applied to other opto-electronic devices, such as, LED (Light Emitting Diode). Flip-chip assembled LED has shown excellent lighting efficiency due to its efficient heat dissipation.[4,5] Most of heat generation from the active layer in LED can be effectively dissipated through the metallic flip-chip bumps, since the metallic bumps have better thermal conductivity than the sapphire substrate of GaN epi-layers.

Currently, flip-chip bumps used for the above opto-electronic devices are either Au plating bump or Au stud bump. Using thermo-compress process, Au bumps on chips are bonded to the Au pads of the substrate. [2,3] Yet, the required compressive forces for the thermo-compression process would potentially damage the devices inside the chips. To solve this issue, C4-type (Controlled Collapse Chip Connection) soldering process is another potential chip-assembly method for Au-bumped chips. However, as the Au bumps reflowing with the substrate solder, some serious issues would occur. For example, serious dissolution of Au in the substrate solders. It is well known that the serious Au dissolution leads to the fast formation of the Au-Sn compound, which results a very brittle joint.[7,8] The current substrate solder is made of eutectic SnPb alloy. Au is reported to have a fast dissolution rate in SnPb solder; the dissolution rate of Au into SnPb is about 255.3µm/min at 25°C.[6] In the near future, SnPb solders would be replaced by Pb-free solders due to the environmental concern. So far, the most promising Pb-free solder candidates often
contain a high percentage of Sn content. For instance, Sn3.5Ag, Sn0.7Cu, and SnAgCu all contain over 95 wt.% of Sn. As Au bump reacting with Sn-rich Pb-free solder, Au bump will be expected to dissolve in solders with much faster rate.[9] The Au embrittlement issue would become worst. Therefore, a compatible substrate solder for the Au stud or Au plating bumps is in serious need for C4-type flip-chip assembly process.

Historically, eutectic AuSn solder is the major solder used for the packaging of opto-electronic chips. Beside Pb-free, one of big advantages for using AuSn solder is that AuSn solder could be soldering with Au bumps or pads with the fluxless process. For opto-electronic packaging, flux is often avoided, because the flux residue would affect the optical performance of optical parts and likely induce corrosion.

Here, we believe that AuSn/Au joint system would fit very well to the assembly process of current opto-electronic chips. Yet, so far, there is no any symmetrical study on the wetting reaction between AuSn solder and Au substrate. In this paper, we study the wetting reaction of eutectic AuSn solder balls on Au foils. The surface oxides on the surface of AuSn solder ball plays an important role on the wetting behavior. XPS (x-ray photoelectron spectroscopy) will be used to examine the oxidation of AuSn solder surface.

**Experimentals:**

100 µm thick Au foils and eutectic Au80Sn20 foils were purchased from Alfa AESAR Inc. Au foil was cut into 5x5 mm square pieces as the wetting substrates. AuSn foils were cut into 1.4mg pieces, then reflowed in the flux ambient at 300 °C to form spherical AuSn solder balls. After cooling to the room temperature in air, the solder balls were collected and ultrasonically cleaned in ethanol. For the sessile drop
experiments, 5x5 mm Au foil was cleaned in acetone and followed by IPA and ethanol cleaning. Au foil was placed on a hot plate of the constant temperatures of 300 °C, 360 °C, 390 °C, and 440 °C. Then, AuSn solder ball was dropped on the top of the Au foil. After a certain reflowing time, the Au foil was lifted off from the hot plate and cooled in air. In this study, we would like to emphasize that the wetting reaction of AuSn solder balls on the Au foils were carried out under the fluxless process (no flux will be used). The oxidation level of the AuSn solder surface and the wetting tips was analyzed by XPS. Then, samples were mounted in epoxy resin for SEM cross-sectional examination. The epoxy-mounted samples were first abraded by coarse sandpapers then finished by the fine polishing of 0.3μm Al₂O₃ powder. To obtain true and meaningful information on the wetting reaction and wetting angle, the cross-section was controlled at the middle of the AuSn solder ball reflowed on the Au foil.

**Results and Discussions:**

**(1) Dissolution of Au foil in eutectic AuSn**

Fig.1 shows SEM cross-sectional images of AuSn solder balls reflowed on Au foils for different reflowing times and temperatures. For the case of 300 °C, no reaction occurred at the AuSn/Au interface after 2-minutes reflowing, as shown in Fig.1. After 10-minutes reflowing, the interfacial reaction was observed at the contact point between the AuSn ball and the Au foil. As shown in the 10-minutes case in Fig. 1(a), small amount of Au foil underneath the contact point had dissolved into the molten AuSn solder. It is of interesting that an incubation time was required for the Au dissolution to initiate. We tend to believe that a native oxide layer pre-existed on the surface of AuSn solder ball, which prevented the molten AuSn solder reacting with the Au foil simultaneously. The surface oxide layer took over 2
minutes to be broken or decomposed. The mechanism of the decomposition of the surface oxide is a very critical issue for the wetting behavior of AuSn solder ball on the Au foil. We will discuss this in the following section. At the higher reflowing temperature, 360°C, we found that the interfacial reaction occurred earlier. After short 30-seconds reflowing, the dissolution of Au foil can be observed, as seen in Fig.1 (b). With prolonged reflowing time, the Au foil increasingly dissolved into molten AuSn solder. Unlike the case of 300°C, no incubation time was taken for the interfacial reaction. It implies that the surface oxide would be broken quickly at a higher reflowing temperature. For the 390°C reflowing temperature case, more intensive interfacial reaction occurred at the interface, as seen in Fig.1 (c). As reflowing AuSn solder ball on the Au foil at 440°C, the 100 μm Au foil was nearly consumed after one minute reflowing, as seen in Fig.1(d). After 2 minutes reflowing, the molten AuSn had penetrated through the Au foil.

Fig. 2 shows the consumed Au foil thickness against the reflowing time for three reflowing temperatures. We found that the initial dissolution is linear with the reflowing time, yet, it decreases and deviates from the linear relation with time in the late stage of reflowing. Fig. 3 is the partial Au-Sn phase diagram at Au-rich side. At a certain reflowing temperature indicated as a horizontal dash tie-line in Fig. 3, during the reflowing process, the composition of the molten AuSn solder would move toward to the two-phase region (solid Au5Sn and liquid AuSn) along the tie-line due to the Au dissolution. The distance, $\mathcal{P}_-$ between the eutectic AuSn composition and the liquidus line of the two-phase region implies the degree of the driving force for the Au dissolution. Clearly, from Au-Sn phase diagram, we note that the driving force for Au dissolution($\mathcal{P}_-$) increases with temperature. This explains our experimental results that at the higher reflowing temperature, the faster Au dissolution occurred.
In the initial reflowing, the amount of dissolved Au in the molten AuSn is very small that its effect on the Au dissolution rate can be neglected. As the molten AuSn solder was saturating with Au and closing to the two-phase region, where the saturation of Au in AuSn establishes, the driving force of Au dissolution would be greatly reducing. So, as seen in Fig. 2, we can observe that the Au dissolution rate deviated from the linear curve in the late stage of reflowing. At higher reflowing temperature, faster Au dissolution resulted in an earlier deviation for dissolution rate. Once molten AuSn reaches the two-phase region, the Au dissolution would depend on the growth of Au$_5$Sn phase in the molten AuSn solder, which would be a slow process. We realize that the dissolution rates in the initial 2 to 5 minutes reflowing are more meaningful for the kinetics of Au dissolution in molten AuSn solder. Here, we use the initial dissolution rates (k) to plot Arrhenius curve, as shown in Fig. 4. Then, the activation energy of Au dissolution in molten AuSn solder was determined to be 42 kJ/mol.

(2) Wetting behaviors of AuSn on Au substrate

Wettability of molten solder on metal substrates is a very important subject for the assembly process of the flip-chip packaging technology.[10] From the SEM cross-sectional images in Fig.1, the wettability of AuSn solder balls on Au foils can be analyzed. A unique feature was observed from the morphology of AuSn solder balls reflowed on Au foils is that the top portions of AuSn solder balls maintained spherical shape for all the reflowing cases. Here, we tend to believe that the surface oxide should play a key role on this behavior. XPS (X-ray Photoelectron Spectroscopy) was used to analyze the atomic depth profile on the surface of the AuSn solder ball before using for the sessile drop experiment. Hence, we should note that the AuSn solder ball was produced by re-melting in the flux ambient and followed by alcohol
cleaning. According to XPS result, an initial 40 Å SnO oxide layer formed on the AuSn surface. As the AuSn solder ball being reflowed on the Au foil, the initial 40 Å SnO oxide layer was found to transform to SnO$_2$ oxide phase. XPS analysis was performed on the top surface of the AuSn ball reflowed on Au foil for 1 minute. As seen XPS result in Fig. 5, the most outer layer is SnO$_2$ phase, which is over 45 Å thick. SnO$_2$ oxidation layer is known to be very protective and tough, so that the formation of SnO$_2$ layer on the surface of the molten AuSn ball should be the key to hold the molten AuSn solder ball as spherical shape.

In above, we explained that the surface SnO$_2$ layer kept the molten AuSn ball maintaining spherical shape. Yet, the formation of the SnO$_2$ surface oxide did not restrict the wetting of the molten AuSn solder ball on Au foils. We found that the very bottom of molten AuSn solder balls could, somehow, perform wetting on Au foils. Here, we evaluate wettability of molten AuSn solder balls on Au foils in term of the spreading area. For the 300°C case, since no interfacial reaction occurred at the AuSn/Au interface, the molten AuSn solder ball did not wet on the Au foil, as seen in Fig.1 (a). After prolonged 10-minutes reflowing, the interfacial reaction occurred, nevertheless, it seems that the interfacial reaction did not have any enhancement effect on the wetting of molten AuSn solder balls. The molten AuSn solder ball only contacted the with Au foil in a small area. For the 360°C case, molten AuSn balls have larger spreading area on Au foils than those of the 300°C case. As reflowing AuSn solder ball at 390°C, we found that the molten AuSn solder ball exhibited a fair wetting on the Au foil. As shown in Fig.1 (c), after 10 minutes reflowing, the top molten AuSn cap still maintained semispherical shape, the bottom molten AuSn wet fairly well on the Au foil. The wetting angle between the molten AuSn solder and the Au foil was estimated to be as small as 25°. Compared to two previous temperature cases, the molten AuSn solder ball has the largest spreading area at 390°C.
Yet, at the higher reflowing temperature, 440 °C, the molten AuSn solder balled up on the Au foil (non-wet) like the cases of 300 °C.

Based on the previous observations, we note that the wettability of the molten AuSn solder ball has a dependence on the reflowing temperature. In the temperature range between 300 °C to 390 °C, wettability increases with temperature. Over 390 °C, wettability decreases. At 440 °C, non-wet was shown. In the most of reactive wetting cases, the interfacial reaction could provide an additional driving force to enhance wetting.[11, 12] In the temperature range between 300 °C to 390 °C, we tend to believe that the increasing wettability corresponds to the increasing interfacial dissolution with reflowing temperature. In the thermodynamics point of view, the interfacial dissolution results in a decrease in entropy; this represents a drop in the free energy of the melting system. So, the interfacial dissolution would be a part of the driving force for wetting beside the balance of surface energies of liquid AuSn, and solid Au foil.

In additional to the free energy drop due to the interfacial dissolution, another mechanism of the wetting improvement by the interfacial Au dissolution was proposed. Here, we take 390 °C as an example. During the reflowing, we have confirmed that the surface SnO on AuSn solder ball would transform to SnO₂. This SnO₂ oxide surface layer maintained the molten AuS solder ball in spherical shape. Yet, as observed earlier, the very bottom of the molten AuSn solder ball could actually wet on the Au foil. This implies that, under the presence of Au, the Sn oxide layer (either SnO or SnO₂) in contact with the Au foil would be broken or decompose. Only if the Sn oxide layer, in contact with Au foil, was broken, the fresh AuSn molten solder could start to spread out and wet on the Au foil.

Two possible mechanisms for the break-down of Sn oxide layer are provided. Morenot reported that SnO is an unstable phase over 300 °C.[13] SnO, where was in
contact with the Au foil, might not undergo the SnO\textsubscript{2} formation. Instead, SnO could be reduced to Sn and O\textsubscript{2}. Au played the role of a reducing agent. Another possibility is that even if the SnO phase in contact with the Au foil did transform to Sn\textsubscript{2}O layer, Au could dissolve or diffuse into SnO\textsubscript{2} layer and cause the break-down of SnO\textsubscript{2} layer. Taylor reported that Sn\textsubscript{2}O oxide layer on the surface of AuSn alloys will diminish as the increasing of Au content.\textsuperscript{[14]} So, if Au could dissolve into SnO or SnO\textsubscript{2} layer up to a certain amount, the Sn oxide layer would likely be reduced and broken eventually.

As the Sn oxide layer was breaking, fresh molten AuSn solder started to wet on the Au foil and expose to air. There are two reactions would proceed simultaneously: (1) oxidation on the wetting front of the spreading molten AuSn (2) Au dissolution in the wetting front of the spreading molten AuSn. The oxidation on the wetting front of spreading molten AuSn certainly would block the wetting of the molten AuSn solder. Yet, if the rate of Au dissolution is fast enough to keep the very wetting front in a very Au-rich level, the oxidation could be diminished to a minimum, which allows wetting proceeding. To verify the oxidation level in the very wetting front, we performed XPS analysis on the wetting tip of AuSn solder ball reflowed on the Au foil for 1 minute. The area of XPS analysis is indicated by white dash-line in Fig. 6(a). XPS analysis is shown in Fig. 6(b). We can see that the oxygen level in the very wetting front is very low. It indicates that the wetting front has little or no formation of Sn oxide. At 390°C, the Au dissolution was able to keep the wetting front in a very low oxidation level, hence an adequate wetting can be observed. Above 390°C, we believe that the oxidation rate could dramatically increase to a certain rate exceeding the rate of Au dissolution. As a result, the wetting of the molten AuSn was greatly retarded.

According to the above proposed wetting mechanism, couple previous
experimental findings can also be explained: (1) the wetting incubation time at 30°C. At 30°C, a so-called incubation time was spent to enrich the oxide layer with Au, and then cause the break-down of the oxide layer. (2) In the temperature range 300°C~390°C, the wettability increased with reflowing temperature. With increasing temperature, the higher Au dissolution would keep the oxidation level in minimum level in the vicinity of the very wetting front, which enables the progression of wetting.

Fig. 7 is a plot of wetting angle vs. reflowing time for 360°C and 390°C. In general, the wetting angle decreased quickly in the initial reflowing time and stabilized in the late reflowing. This kinetic behavior can also be interpreted by using the previous wetting mechanism. The oxidation and Au dissolution rates control the wetting velocity of the molten AuSn on the Au foil. At a constant reflowing temperature, since the oxidation rate is roughly fixed, the wetting kinetics really depends on the de-oxidation process, i.e., the Au dissolution rate in present case. Therefore, in the initial reflowing stage, the wetting speed was fast due to the quick Au dissolution rate. In the late reflowing stage, the slow Au dissolution caused sluggish wetting.

(3) Interfacial compound formation

Fig. 8 (a)-(c) is the enlarged SEM cross-sectional images of AuSn/Au reaction couples for three reflowing temperatures. An interfacial compound layer formed at interface of AuSn/Au. From EPMA (Electron Probe Microanalysis) analysis, the interfacial compound phase is identified to be Au5Sn. In the previous discussion, we note that the reflowing AuSn solder ball on Au foil would take some time (over at least 5 minutes at 360°C case) to reach the two phase region, i.e., liquid eutectic AuSn and solid Au5Sn phase. It would be expected that no solid Au5Sn phase would exist in the molten AuSn in the initial reflowing (less than 5 minutes). So, we suspect that
the Au₅Sn compound layer precipitated out at the interface during the solidification. During the reflowing, since Au foil continuously dissolved into the molten AuSn solder, the more precipitation of Au₅Sn phase at the interface would be expected. So, that is why we can observe that the interfacial Au₅Sn thickness increases with time.

Using image processing software on SEM cross-sectional images, the thickness of interfacial Au₅Sn phase can be estimated. Fig. 9(a) is a plot of the Au₅Sn thickness versus the square root of reflowing time. Here, we notice that the thickness of interfacial Au₅Sn compound layer increase linearly with square root of reflowing time. Usually, this growth kinetics suggests a diffusion-controlled for the growth of Au₅Sn compound layer. In other words, the Au₅Sn compound layer could grow by the interfacial reaction and controlled by the Au or Sn diffusion in the interfacial Au₅Sn phase during the reflowing process. We should emphasize that this growth mechanism is only valid under the assumption that the growth rate of interfacial Au₅Sn phase is faster than the dissolution rate of Au₅Sn phase in the molten AuSn. Taking the slopes of the linear curves in Fig. 9(a), Arrhenious curve can be plotted, as shown in Fig. 9(b). The activation energy for the growth of interfacial Au₅Sn phase layer is obtained to be 54.3kJ/mol over the temperature range 360°C to 440°C. The growth of Au₅Sn phase under the solid-state aging process (below the 280°C) was investigated by Carney and Kallmayer[15, 16]. Their data points (diffusivity in Au₅Sn phase) were marked in Fig. 9(b) by solid squares and circles, respectively. Interestingly, their data fit fairly well with our measured data by a linear line. This is a strong evidence to support that the growth of the interfacial Au₅Sn phase is due to the interfacial reaction during the reflowing process.

**Summary:**

The kinetics of Au foil dissolution in molten AuSn was studied. The activation
energy for Au dissolution in molten AuSn solder is determined to be 41.7kJ/mol. To start Au dissolution, the surface oxide layer needs to be broken. We believe that the break-down of the Sn oxide layer (either SnO or SnO₂) in contact with the Au foil was assisted with the Au dissolution. Once the Sn oxide layer, in contact with Au foil, was broken, the fresh AuSn molten solder could start to spread out and wet on the Au foil. The subsequent wetting of molten AuSn was controlled the oxidation and Au dissolution rates on the wetting front of spreading molten AuSn solder. Below 390 °C, the Au dissolution rate dominates the progression of the wetting front. On other hands, above 390 °C, the oxidation rate exceeds Au dissolution rate and retards wetting. At 390 °C, AuSn solder balls exhibited best wettability among all reflowing cases (wetting angle is about 25°). At higher temperature, 440 °C, non-wet was shown. While the bottom molten AuSn balls wet on Au foils, the initial surface SnO layer was found to transform to SnO₂. The surface SnO₂ layer is the key to hold the molten AuSn solder ball as the spherical shape.

Au₅Sn is the dominant interfacial compound layer formed at interface. The activation energy for the growth of interfacial Au₅Sn phase layer is obtained to be 54.3kJ/mol over the temperature range 360 °C to 440 °C.

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References:


Captions:

Fig. 1 SEM cross-sectional images for all case.

Fig. 2 (a) the XPS result on the surface of AuSn ball right after remelt in flux ambient and followed by alcohol cleaning. (b) After reflowing AuSn ball on Au for 1 min.

Fig. 3(a) Wetting mechanism of initial wetting reaction and wetting progression in the wetting tip.

Fig. 3(b) The oxygen atomic level in the wetting front.

Fig. 4 wetting angle vs. reflowing time.

Fig. 5(a) the dissolution of Au in eutectic AuSn for 360, 390, and 440 ºC. (b) the Arrhenius plot.

Fig. 6 Growth of $\alpha$-phase, eutectic AuSn beads were reflowed at 360, 390 and 440 ºC for increasing time.

Fig. 7(a) Growth of $\alpha$-phase at 360, 390, and 440 ºC. (b) Arrhenious plot of the diffusion coefficient.
Fig. 1
Fig. 2

Temperature (°C)

Sn atomic (%)

Reflowing time (minutes)

Fig. 3
Fig. 4

\[ \text{E}_a = 42 \text{ kJ/mol} \]
Fig. 5
Fig. 6 (a)

Au substrate

AuSn solder ball

Wetting front

Fig. 6(b)

[Graph showing atomic percentage (%)]

atomic percentage (%)

0 10 20 30 40 50 60 70 80 90 100

depth (Å)

Sn
Au
O
Fig. 7

The graph shows the change in wetting angle with reflowing time for two different temperatures: 390°C and 360°C. The wetting angle decreases with increasing reflowing time, indicating improved wetting of the solder.
Fig. 8
Fig. 9(a)

Fig. 9(b)