Fluxless Die Attach by Activated Forming Gas

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Abstract
Eutectic gold-tin (Au80Sn20) is widely used as the die-attach material for making radio-frequency (RF) and microwave devices. The metallic bonding is typically achieved by soldering using a gold-tin preform in a forming gas containing hydrogen (H2) and nitrogen (N2) to a peak temperature at 300˚C. The performance and reliability of the devices are strongly dependent on the quality of the die-attach layers. It is always expected to make the die-attach layers as free of voids as possible since the voids are poor thermal and electrical conductors and also are stress concentration centers. There are three major causes for void formation, which include poor solder wetting due to surface oxides, vapor out-gassing by flux decomposition, and gas entrapment from preform melting. It is known that the gas entrapment is more significant for larger dies and can be managed by gas evacuation before the melting of the solder. However, a good fluxless and oxide-free technology for metal die attach is still lacking. The organic fluxes used in conventional soldering not only induce void formation but also leave residues, which contaminate the dies and are corrosive. In addition to being costly and inconvenient to clean, the residues at the bonding interfaces of the die-attach layer are trapped, thus degrading interfacial bonding over time. The current study introduces a novel technology of using electron attachment (EA) to activate H2 diluted with N2 for fluxless die attach. EA is a new concept for ambient-pressure gas activation, which brings several advantages compared with plasma-based gas activation. Results obtained in this study demonstrate that solder oxides and organic contaminations on the surfaces to be bonded can be effectively removed by EA-activated forming gas, which leads to better solder wetting compared to flux-based process. The EA technology also shows a feasibility of reducing peak temperature of die attach from 300˚C to 290˚C, thus minimizing high-temperature induced damages. These advantages are believed to be attributed to the higher surface tension of the oxide-free molten solder compared with that of an organic flux, thus leading to a larger wetting force. As demonstrated in the study, the fluxless and oxide-free technology using EA has made it possible to achieve a high quality die attach with zero or near-zero (∼5%) voids.

Introduction
Radio-frequency (RF) and microwave devices are widely used in aerospace and defense industries for telecommunications. In these applications, a significant power at RF and microwave frequencies is generated and the devices are typically operated in some of the toughest and most demanding environments. Therefore, these devices have to be manufactured with proven reliability and performance. The core of the devices is made of semiconductor dies. Currently, gallium arsenide (GaAs) and silicon (Si) are most popularly used as the semiconductor dies in building RF and microwave devices. When RF and microwave devices are in an operating state, heat will be generated from the active region of each die, which results in a rise in temperature. As the temperature of a die increases, its performance and reliability will both degrade. To promote heat dissipation, the overall device thermal resistance needs to be minimized. One contribution is from the semiconductor die itself. For this reason, the thickness of the dies used for RF and microwave devices is especially thin.

To prevent damage of the delicate dies with sensitive structures on their top surfaces, each die is mounted and fixed on a substrate or package base. This manufacturing step during assembly of devices is named as “die attach”. The performance and reliability of a RF and microwave device are strongly dependent on the quality of the die-attach layer. The die-attach layer needs to provide a good thermal dissipation path and electric contact between the die and the package base. It also has to withstand the thermal stresses when the device is subjected to power and temperature cycling during its operation. Because of the need for low thermal and electrical resistances in the die-attach layer, the dies used in RF and microwave devices are metallically bonded onto the package base by using a solder material to form a very thin bond layer. The backside of each die and its bond pad on the package base are typically terminated with a layer of gold (Au) as a thermal and electrical interface and a layer of nickel (Ni) underneath the gold as a diffusion barrier.

Eutectic gold-tin (Au80Sn20) is widely used as the die-attach material for making RF and microwave devices due to its superior thermal and mechanical properties, good compatibility with the gold metallization surface, and a relatively high melting temperature (280˚C) to prevent thermal fatigue. For this type of die attach, a preform with a thickness as thin as 25µm is typically used and a general rule for preform size is 90% of the die metallization. The bond formation is usually done at a peak temperature around 300˚C for one minute or less. There is always a desire to reduce the peak temperature if possible to avoid problems such as die degradation by high-temperature exposure and die cracking due to large thermal
stresses. Since the preform-based die-attach layer is so thin, its thermal and electrical resistances are determined not only by the solder material’s intrinsic properties but also by the quality of the formed joint. It is always expected to have a defect-free die attach for building RF and microwave devices. However, the defect-induced die-attach failures may still happen, which are generally localized at the interface of different layers, such as delaminations, cracks, voids, and metal corrosions.

One of the major reasons to cause defects is that the gold-tin preform is easily oxidized, forming a tin-rich oxide layer on its surface. An oxide layer at the bonding interface will adversely affect solder wetting. Defects such as solder de-wetting, delamination, and interfacial voids tend to form, which can largely increase the thermal and electrical resistances of the die-attach layer. A forming gas containing hydrogen (H₂) and nitrogen (N₂) is commonly applied during the preform-based die attach, but the forming gas only can help in preventing solder oxidation at the normal process temperature range up to 300°C. The initial temperature for hydrogen to effectively reduce tin oxides is around 400°C8-11. Therefore, to remove native oxides and help solder wetting, organic fluxes are still required, especially for making high power RF and microwave devices. However, the use of organic fluxes brings other chances of forming defects in the die attach layers. It leaves residues, which not only contaminate dies with unexpected ionic species but also induce corrosion when moisture is present. Therefore, a cleaning step has to be applied after the soldering, which is inconvenient and costly. Besides that, the cleaning cannot remove flux residues left at the interfaces of the die-attach layer, which can degrade the interfacial bonding and cause delamination. In addition, the flux vapor generated by flux decomposition always has a chance to remain in the molten solder or at the bonding interfaces, thus forming voids when the solder is solidified. The amount of flux needed is much less when using a preform compared with using a solder paste12, which is the major reason that preform-based die attach is typically used for high-reliability applications. However, the flux is not the only cause of forming voids when using a preform. This is because when two flat and rigid surfaces touch each other, the true contact area is typically less than 20% of the total interfacial area. Tiny gaps as thin as 0.1 µm at the interface is occupied by gas films12. When the preform is melted, the gas films are wrapped in the molten solder. Since gas diffusion through a molten solder is slow13, the entrapped gas forms voids. The larger the contact area, the greater is the gas entrapment. The voids are very poor thermal and electrical conductors and are stress concentration centers. Therefore, for building high-power RF and microwave devices, there is a high need to make the die attach layers as free of voids as possible. Typically, the acceptable void rate in eutectic die-attach bonds is less than 5% for total voids and less than 1 to 2% for each individual void14.

To pursue a void-free die attach, a process named “pressure variation” or “vacuum release” has been developed12, 15. It applies a vacuum to evacuate gas films at the soldering interfaces before the solder is melted and then release the vacuum to ambient pressure of an inert gas to compress the remaining voids before the solder is solidified. However, the approach still needs an organic flux or formic acid vapor to clean native oxides on the preform surface, and the related issues of corrosive residues remain to be solved. Therefore, to pursue a defect-free solder die attach for high-power and high-reliability applications, there is a need to develop a fluxless and oxide-free process.

The objective of this study was to meet the need by activating a reducing gas to efficiently remove oxides on the soldering surfaces in the normal die-attach temperature range, thus eliminating the use of organic fluxes. A reduction of peak temperature for die attach to minimize the potential of high-temperature induced damages was also evaluated.

Experimental Design

a) Activating hydrogen by electron attachment

The current study proposed using electron attachment (EA) to activate H₂ diluted with N₂ to reduce oxides on the soldering surfaces at a temperature below the solder’s melting point. This is then followed by inert soldering either under ambient pressure or a pressure variation involving vacuum. Hydrogen is selected as a reducing gas since the reduction process is clean and non-toxic. Its only by-product, water, can be easily vented out of the furnace. EA at ambient pressure for gas activation is a new technology developed in recent years. This patented technology is believed to be fundamentally different from the conventional plasma-based gas activation. It has been demonstrated that EA can dissociate hydrogen gas molecules at ambient pressure and temperatures as low as 100°C, thus promoting surface de-oxidation and solder reflow at normal production conditions16-18.

Figure 1 describes the basic principle of using EA to activate gaseous hydrogen mixed with nitrogen to clean surface metal oxides on a non-insulated substrate. The substrate with the treating surface facing up is set on a grounded or dischargeable source inside a furnace to act as an anode. The furnace is purged with a forming gas containing H₂ and N₂ at ambient pressure. A specially made field-emission cathode containing an area array of metal tips is mounted above the treating surface. A pulsed direct-current (DC) voltage with a single polarity is applied on the cathode. When the applied voltage is increased to a threshold level, electrons can be emitted from the metal tips by field-emission mechanism. Because of the ambient pressure, the energies of the emitted electrons are much lower than that under vacuum19. These electrons will drift along an electrical field toward the treating surface and drain charges to the ground. During the drifting, some of the electrons can collide with H₂ and N₂ gas molecules. Instead of causing gas ionizations, the low-energy electrons during the
collisions can be captured by \( \text{H}_2 \) molecules since \( \text{H}_2 \) has a positive electron affinity. As shown in equation (1), when a \( \text{H}_2 \) molecule is attached by an electron (\( e^- \)), an excited molecular hydrogen anion (\( \text{H}_2^-\ast \)) can be formed, which has a chance to split into a neutral hydrogen atom (H) and an atomic hydrogen anion (\( \text{H}^- \)) by dissociative attachment. The neutral hydrogen atom can further capture an electron, forming an excited atomic hydrogen anion (\( \text{H}^-\ast \)) by direct attachment (2). The generated atomic hydrogen anions will also drift toward the treating surface driven by the electrical field. At the treating surface, a metal oxide (e.g., a metal monoxide, \( \text{MO} \)) can be reduced to its pure metal (\( \text{M} \)) by the atomic hydrogen anions at an elevated temperature, and water vapor (\( \text{H}_2\text{O} \)) and free electrons are the by-products associated with the reduction process (3). This surface de-oxidation process under EA can be initiated at a temperature significantly lower than that when EA is not applied.

![Field-emission cathode](image)

**Figure 1 — Concept of Forming Atomic Hydrogen Anions (\( \text{H}^- \)) by EA**

| Dissociative attachment: | \( \text{H}_2 + e^- \rightarrow \text{H}_2^-\ast \rightarrow \text{H} + \text{H}^- \) (1) |
| Direct attachment: | \( \text{H} + e^- \rightarrow \text{H}^-\ast \) (2) |
| Surface de-oxidation: | \( 2\text{H}^- + \text{MO} \rightarrow \text{M} + \text{H}_2\text{O} + 2e^- \) (3) |

The effective oxide reduction with EA at low temperatures can be attributed to several factors. Firstly, the atomic hydrogen anion (\( \text{H}^- \)) is a strong reducing agent since it doesn’t contain a covalent bond compared with a hydrogen molecule (\( \text{H}_2 \)) and has an extra electron compared with a neutral hydrogen atom (H), thus acting as a good electron donor to trigger an oxide reduction. Secondly, because of the single-charged environment under EA, the atomic hydrogen anions repel each other, resulting in their relatively long lifetimes. As a comparison, the oppositely-charged particles formed in plasma always attract each other and quickly recombine, especially at ambient pressure. Thirdly, instead of a random diffusion like neutral gas molecules or atoms, the atomic hydrogen anions formed under EA directionally drift toward the treating surface driven by the electrical field, thus largely increasing concentration of the reducing agent at the treating surface. Lastly, nitrogen as a dilution gas is inert to EA because its electron affinity is close to zero, which makes EA for activating hydrogen more efficient. In addition, since nitrogen is a diatomic molecule, it acts as a third body in collision stabilization to absorb the excess energy of the excited atomic hydrogen anions (\( \text{H}^-\ast \)) formed by the direct attachment (2), thus assisting in the formation of atomic hydrogen anions (4).

Collision stabilization: \( \text{H}^-\ast + \text{N}_2 \rightarrow \text{H}^- + \text{N}_2 \) (4)

**b) EA for preform-based die attach**

For the preform-based die attach, the metal oxides at the soldering interfaces are not fully exposed, and each die-attach assembly typically contains multilayered components with different sizes and made of different materials, including electrically insulated ceramics. Therefore, each surface to be deoxidized can no longer act as anode. Technical challenges related with applying EA include emitting electrons, allowing \( \text{H}^- \) contacting with soldering surfaces, and discharging of free electrons.

Figure 2 shows the proposed approach for solving these challenges. It was proposed to develop an electron-emission device with a self-containing anode and cathode structure, thus being able to decouple with the treating surface for emitting electrons. A modified ceramic plate involving a novel discharging approach was also designed. It was proposed to load die-attach assemblies on the ceramic plate, set on an electrically dischargeable surface inside the soldering chamber. Under EA condition, atomic hydrogen anions (\( \text{H}^- \)) when reaching any surface spot on a die-attach assembly cannot directly discharge by passing electrons across its thickness because of the non-conductive ceramic plate underneath it. Those atomic hydrogen anions will then automatically spread out along the surface and penetrate into the interfacial gaps of the preform layer driven by a tendency for spontaneously minimizing electrical potential. Metal oxides at the non-exposed surfaces can thus be reduced by the atomic hydrogen anions. During the oxide reduction under EA, free electrons injected on or generated at the surfaces of the die-attach assembly will be drained by migrating to the assembly’s edges and then to the specially made ceramic plate for discharging.
**Experimental Results and Discussions**

a) Establishing EA

Figure 3 shows a glass jar soldering unit retrofitted with EA. The unit is commonly used for die attach in production lines. The size of the glass jar is about 5 cm in diameter. The field-emission device with self-containing anode and cathode is installed on the top of the glass jar. The specially made ceramic plate is set on top of a graphite heater. The graphite heater is powered by an alternating current (AC), which acts as a dischargeable source. Die-attach assemblies to be solder bonded can be randomly located anywhere on the ceramic plate, which is about 2” X 2” in size. During EA process, a forming gas contains 15 % H₂ in N₂ was flowed into the soldering unit and the temperature used for pre-cleaning oxides on soldering surfaces was at 250°C. As demonstrated in Figure 4, when a pulsed (10 KHz) DC voltage with a single polarity was applied on the field-emission device, a successful EA condition was established. Figure 4 also shows that emitter tips were illuminated during emitting electrons. The illumination is because of gas excitations around each sharp tip. The gas environment between the emitter tips and the ceramic plate was visually clear, which demonstrates that the gas phase is not ionized under EA.

b) Oxide removal and associated solder wetting

To demonstrate the concept of oxide removal and associated solder wetting by EA activated forming gas, capillary wetting experiments were conducted. A ceramic plate and a metal plate, each coated with a layer of gold and a layer of nickel underneath the gold, were used to simulate a die and a bond pad to be attached with each other, which were in a size of 3 mm X 6 mm. The gold and nickel coatings were done by industry standard. Auger electron spectroscopy (AES) analysis was performed to investigate the state of the coated surface. The result shows an oxygen-containing film on the coated surface, which was less than 5 Å thick. To further understand the chemical composition of the film, x-ray photoelectron spectroscopy
(XPS) in conjunction with electron spectroscopy for chemical analysis (ESCA) was also conducted. It indicates that the oxygen-containing film consisted of organic compound(s) having C-C, C-O and O-C=O bonds. Eutectic gold-tin preform with a thickness of 25 μm was used as the solder. Auger analysis was also applied to check the native oxide on the preform surface. It shows a 15 Å thick tin-rich oxide layer. To facilitate the investigation of capillary wetting, three layers of the preform instead of one layer, were piled up to occupy two-thirds of the gap between the ceramic plate and the metal plate (Figure 5). The other one-third of the gap was empty which was preserved for capillary wetting after the solder’s melting. As shown in equation 5, capillary pressure (ΔP), as the driving force of capillary wetting, is proportional to the surface tension of the molten solder (γ) and inversely proportional to the radius of the surface curvature of the molten solder (r). A high surface tension of a molten solder is always linked with an oxide-free state of its surface. Therefore, the better the oxide removal, the better will be the capillary wetting and the associated solder filling (h in Figure 5). The oxide removal was done by a pre-cleaning step under EA at 250°C in 15% H₂ in N₂ for ten minutes, which was then followed by capillary wetting at 290°C for one minute.

![Figure 5 — Sample Preparation for Capillary Wetting Experiments](image)

Capillary pressure: \[ ΔP = \frac{2γ}{r} \] (5)

Figures 6a to 6f summarize test results of the capillary wetting experiments. Without the pre-cleaning step, capillary wetting was not completed at the side of a sample which initially contained the empty gap (Figure 6a), and the solder de-wetted at another side of the sample which initially filled with the solder (Figure 6b). When EA-assisted pre-cleaning was applied, a good solder filling and wetting were obtained (Figures 6c and 6d). As a comparison, a flux typically used in the existing die-attach process was covered on the sandwich structure of a sample, which was then heated in 15% H₂ in N₂ to 290°C by using a recommended heating profile. As shown in Figure 6e, the solder filling was not completed on the side of the sample that initially contained the empty gap. This is because of the low surface tension of the flux covering on the molten solder surface, thus leading to a low capillary force. It was also found that there were flux residues left between layers (Figure 6f). As mentioned previously, flux residues are another drawback of using fluxes. The above results demonstrate that the EA-activated forming gas can effectively clean the soldering surfaces without leaving residues, which results in an even better wetting than that of flux-based soldering. The developed technology also shows a feasibility of reducing peak temperature of die attach from 300°C to 290°C. These advantages are attributed to the higher surface tension of the oxide-free molten solder compared with that of an organic flux, thus leading to a larger wetting force.

![Image a) Unfilled gap for a sample without EA-assisted pre-cleaning](image)

![Image b) Solder de-wetting for the sample without EA-assisted pre-cleaning](image)

![Image c) Completed gap filling for a sample with EA-assisted pre-cleaning](image)

![Image d) Good wetting for the sample with EA-assisted pre-cleaning](image)
c) Void reduction

Experiments were also conducted to evaluate the benefits of EA-assisted pre-cleaning on void reduction of the preform-based die attach. As in previous tests, the gold-tin solder preform used in this study was 25 µm thick, and the standard gold and nickel coatings were applied on die-attach components and metal substrates. To hold each die-attach sample during handling to the furnace when a flux was absent, a liquid solvent with a low boiling point such as acetone or isopropyl alcohol was used. When EA-assisted pre-cleaning was applied, it was done at 250°C in 15% H₂ diluted with N₂ for ten minutes. The solder bonding was conducted at a peak temperature of 290°C in N₂ for one minute either under ambient pressure or a pressure variation involving vacuum. After forming the metallic bonds, x-ray analysis was used to diagnose void formation in the die-attach layer of each sample. It was noticed that through-layer voids were common if the void level was relatively high. However, when the amount of voids was relatively low, they always had a tendency to stay at the bonding interfaces, resulting in two-layer overlapped voids. Those interfacial voids were found to be much thinner than the bond layer. It is known that x-ray analysis is based on the total cast area of the voids in the die attach layer. Therefore, each estimated result by x-ray analysis should be regarded as an upper limit of the formed voids, especially for the case with a trace amount of voids.

Figures 7a to 7c compare void formations of ambient pressure bonded dies using the flux-based cleaning versus using EA-assisted pre-cleaning. As shown in Figure 7a, voids were formed for all sized dies soldered in a production line by using the conventional flux-based approach. More specifically, there were 24% voids for a die with 2 mm X 2 mm in size (Figure 7b). As a comparison, 0% void was achieved for the same sized die when EA-assisted pre-cleaning was applied (Figure 7c). This result demonstrates the advantage of the EA-assisted die attach, which eliminates the flux-vapor induced voids. Because of the strong wetting resulting from the efficient pre-cleaning under EA plus the relatively small dimension of the die (2 mm X 2 mm), entrapped gas can be squeezed out, thus resulting in a void-free metal die attach.

Figures 8a to 8d compare void formations for ambient pressure bonded dies with and without applying EA-assisted pre-cleaning. The dies tested were in a range with an edge length of 3 mm to 5 mm. As shown in Figures 8a and 8b, without EA-assisted pre-cleaning, there were many voids in the die-attach layers of two sized dies. This is quite understandable since
solder wetting will be poor if surface oxides and organic contaminations are present. Poor solder wetting will facilitate gas entrapment at the joining interfaces, thus forming a lot of voids. Figures 8c and 8d provide a comparison for the case when EA-assisted pre-cleaning was applied. As shown, the void levels were significantly reduced for both dies. A void amount as low as 1.32% was obtained for the smaller die with 3 mm X 4 mm in size. As anticipated, the larger die with 5 mm X 5 mm in size had a higher void level since the gas entrapment was aggravated with increased gas diffusion path. Besides the reduced void amount, the voids in the pre-cleaned dies were significantly smaller and elongated. This is believed to be due to a strong wetting of the molten solder on the bonding surfaces resulting from the efficient pre-cleaning, which collapse the entrapped gas pockets.

Figure 8 — A Summary of Void Formations of Ambient Pressure Bonded Dies

To further minimize gas entrapment induced voids, a pressure variation involving vacuum was incorporated, such as applying a vacuum at a temperature below the solder’s melting point and release the vacuum to ambient pressure N₂ before the solder is solidified. During each pressure variation, a house vacuum in a level around 300 mmHg in absolute pressure was applied. Figures 9a to 9d summarize void formations in die-attach layers bonded under the pressure variation either with or without EA-assisted pre-cleaning. As shown in Figures 9a and 9b, with EA-assisted pre-cleaning plus soldering with the pressure variation, 0% voids was obtained for a die with 3 mm X 4 mm in size. Even for a die as big as 10 mm X 10 mm, the void level was only 4.02%. This result demonstrates the effect of applying the pressure variation on minimizing gas entrapment and its associated void. However, when the pressure variation was applied without EA-assisted pre-cleaning, there were a lot of voids for both sized dies due to poor solder wettings (Figures 9c and 9d). This result further confirms the need on removing oxides and organic contaminations at the soldering surfaces.
Conclusions

A novel technology of using EA to activate a forming gas containing H₂ and N₂ for fluxless die attach with eutectic gold-tin preform has been developed. Our study introduces applying the EA-activated forming gas to clean surface oxides and organic contaminations at a temperature below the solder’s melting point. This is then followed by an inert soldering either under ambient pressure or a pressure variation involving vacuum. The results obtained demonstrate that oxides on the preform surface and organic contaminations on the gold termination can be successfully removed by the EA-assisted pre-cleaning. If an inert soldering under ambient pressure is applied after the EA-assisted pre-cleaning, a zero or near-zero (≤ 5%) voids can be achieved for the size of the dies around 3 mm X 4 mm or below. For relatively large dies, the EA-assisted pre-cleaning can be combined with the vacuum contained pressure variation. A result in this study shows that by using the recommended approach, a die-attach layer with a near-zero voids can still be achieved even for the die as big as 10 mm X 10 mm. Comparing with the conventional flux-based die attach, the fluxless and oxide-free technology using EA has the following major advantages: 1) it eliminates the flux-vapor induced voids, 2) it removes the flux-residues related problems, 3) it provides a reduced peak temperature for die attach (e.g. 290°C versus 300°C), and 4) it leads to an even better solder wetting, thus decreasing the overall voiding tendency. Therefore, the developed technology is believed to be a promising solution for achieving high-quality die attach, thus satisfying the needs for applications requiring high reliability.

References
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