FLUXLESS SOLDERING IN ACTIVATED HYDROGEN ATMOSPHERE

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ABSTRACT
A novel hydrogen activation technology based on activated hydrogen or electron attachment (EA) has been developed for fluxless soldering at ambient pressure and normal soldering temperature. The technology has the potential to be used for several applications in the electronics packaging industry. Recent work from a joint effort between Air Products and Sikama International on beta trials and in-fab trials of a production-scale furnace for flux-free wafer bump reflow based on Electron Attachment (EA) is also discussed, along with current development work in the area of ball drop assembly and flip chip reflow using the EA technology.

KEY WORDS
Fluxless soldering
Activated Hydrogen
Electron Attachment
Solder ball reflow

INTRODUCTION

Packaging technology for electronic devices has advanced rapidly in recent years driven by feature size reduction, new materials development, and increased demand on device functionality. The most fundamental among the advanced packaging technology is the use of wafer bumping and wafer-level chip scale packaging.

In a wafer bumping process, fine-pitch electroplated solder bumps are formed over an entire silicon wafer on which integrated circuits have been built. The wafer is then reflowed at a temperature above the solder's melting point to complete metallic interconnection of the bumps with underneath metal pads and convert the bumps from a deposited shape into a ball shape. After the wafer bumping, the wafer is cut into individual chips, which then go through subsequent packaging processes. In the packaged devices, the formed bumps serve as electrical, mechanical, and mounting connections. The current study is related to the last step of the wafer bumping process ─ wafer bump reflow.

One of the key goals for successful wafer bump reflow is to remove the native oxide layer and prevent additional oxidation on the bump surface.

Any oxide layer on the bump surface will act as a solid skin to constrain the molten solder's flow, which in turn causes a non-qualified bump appearance and non-uniform bump shape across a wafer. This oxide elimination is becoming more critical and difficult as the bump size shrinks since the increased surface to volume ratio, plus the enlarged surface curvature of the solder bump, drives toward a more severe solder oxidation to minimize its surface energy.

Currently, the most common approach is to coat the wafer with a flux and then reflow the wafer in a nitrogen environment. The oxide removal capability is attributed to the organic acids in the fluxes (1).

$$\textit{Metal oxide} + \textit{Acid} \rightarrow \textit{Salt} + \textit{Water} \qquad (1)$$

However, such a flux-containing reflow process is not ideal for all applications, since the decomposition of organic fluxes always leaves residues and generates volatiles, which invariably bring contaminants on the wafer and furnace walls.

Therefore, a post cleaning of the reflowed wafer is always required. A frequent cleaning of furnace interior surfaces is also needed, causing high maintenance costs and potential for a lot of equipment downtime. In addition, special safety precautions must be taken to deal with the hazardous disposal of the flux residues and the unhealthy exposure of the flux vapor. Besides the cost and inconvenience associated with the cleanings, the flux-containing process can directly affect the quality of the reflowed wafer. For example, during reflow the flux can get into the molten solder and create voids inside the bumps, thus degrading mechanical and electrical properties of the solder joints in packaged devices. As the pitch and bump sizes are continually decreasing, the need for process cleanliness increases. This has led to increased use of flux-free processing, which is mainly based on using a reactive gas to replace the organic flux for oxide removal.

However, known flux-free technologies have different problems or limitations. By using formic acid vapor, the process is not completely residue-free and must be operated in a sealed vacuum system. A current hydrogen-based flux-free processing is clean and non-toxic, but high temperature (≥350˚C) and pure hydrogen (flammable) must be applied to activate and hasten the oxide reduction. Plasma-activated hydrogen can make the oxide reduction efficient at low temperatures, but only vacuum plasma appears to be viable, resulting in a batch process.

Therefore, our objective was to develop a novel hydrogen activation technology based on Electron Attachment (EA) for fluxless soldering at ambient pressure and normal soldering temperature using nonflammable mixtures of hydrogen (≤5 vol%) in nitrogen.

ELECTRON ATTACHMENT

Basic Principle

Electron Attachment (EA) is defined as follows: when low-energy electrons, such as below 10 eV, collide with gas molecules, some are captured by gas molecules, producing anions by dissociative or direct attachment [1].

Equation (2) represents the dissociative attachment for hydrogen, where a hydrogen molecule (H_2) combines with an electron (e^-) to give an excited molecular hydrogen anion (H_2^{-*}) which dissociates to give an atomic hydrogen anion (H^-) and a neutral hydrogen atom (H). The neutral hydrogen atom can further capture an electron, forming an excited atomic hydrogen anion (H^{-*}) by direct attachment (3). The excited atomic hydrogen anion can be stabilized by releasing a photon or colliding with a nitrogen molecule. Nitrogen as the dilution gas is inert to EA because its electron affinity is close to zero. Driven by an applied electrical field, the atomic hydrogen anions formed under EA can be directed to the soldering surfaces for oxide reduction. Equation (4) is an example of reducing tin monoxide. As reduction by-products, water vapor can be easily vented out of the furnace and free electrons can be removed properly.

$$H_2 + e^- \rightarrow H_2^{-*} \rightarrow H^- + H \qquad (2)$$
$$H + e^- \rightarrow H^{-*} \qquad (3)$$
$$2H^- + SnO \rightarrow Sn + H_2O + 2e^- \qquad (4)$$

Process Establishment

Fig. 1 shows an example of establishing EA in an open tunnel furnace typically used for reflow soldering. An electron emission apparatus containing a lot of sharp tips is mounted on the top side of the furnace. The furnace is purged with a nonflammable mixture of hydrogen (≤5 vol% in nitrogen). Electronic devices to be soldered are loaded on a transportation system, which continually moves from the entrance to the exit of the furnace. When passing underneath the electron emission apparatus, the electronic devices will be exposed to the EA atmosphere. After EA cleaning of oxides on soldering surfaces, the devices will undergo the normal solder reflow and cooling.

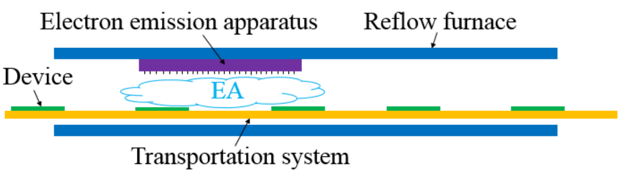


Fig. 1. Establishing EA in a reflow furnace

A major challenge for achieving the proposed fluxless approach with EA was to generate a large quantity of low energy electrons under ambient pressure. There was no commercially available electron emitter that could satisfy the requirements for the current application. Therefore, in our research we developed a patented technology for the electron emission apparatus. The apparatus contains its own anode and cathode. With applying a pulsed DC (direct current) voltage in a range of 2 to 3 kV, electrons can be emitted out of the apparatus independently. In the case that soldering surfaces underneath the apparatus are isolated with ground and not able to drain charges, the apparatus has the capability to collect free electrons that accumulate on the soldering surfaces and still emit electrons.

Fig. 2 shows an electron emission module that is 3" x 3" in size. A number of such modules can be integrated together to scale up the electron emission.

Fig. 3 demonstrates a status of electron emission when the module is operated above an electrically insulated glass. By initiating the required electrical power, all the tips on the module are illuminated, which is mainly due to excited gas molecules surrounding the tips. The illuminated tip array is reflected on the glass surface.

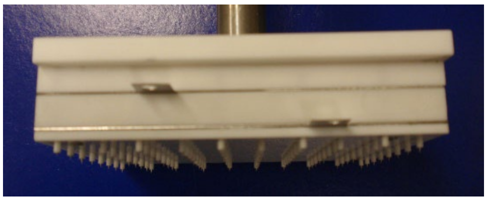


Fig. 2. Electron emisison module (3" x 3")

Fig. 3. Electron emission on insulated glass

PROOF OF CONCEPT

Hydrogen Dissociation

The most fundamental theory of using EA to activate hydrogen is the dissociation reaction that forms atomic hydrogen anions [2]. We investigated this by using a mass spectrometer (MS) to detect hydrogen-deuterium (HD) formation in a furnace environment containing hydrogen (H_2) and deuterium (D_2) at 280˚C. As shown in Fig. 4, the HD intensity increased when EA was applied at t = 15 min, and returned to its original level after EA was stopped at t = 25 min. There were also corresponding changes for H_2 and D_2 intensities. This result confirms the dissociation of H_2 molecules under EA [2].

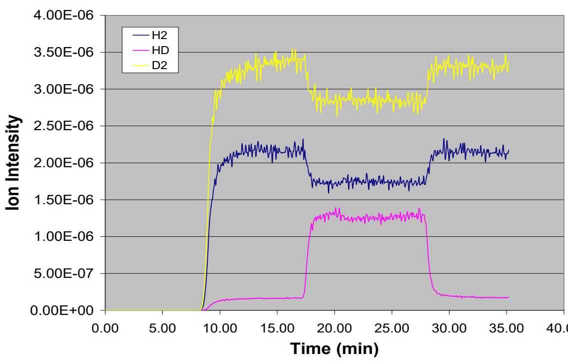


Fig. 4. MS spectra showing reactions under EA and confirming dissociation of H2 molecules.

Solder Wetting

A fluxless solder preform in a pellet shape was put on a copper plate and heated up in 5 vol% H_2 in N_2 either with or without applying EA. Without applying EA, the molten solder remained in the pellet shape (Fig. 5a). When EA was applied during heating, the solder spread out with a shiny surface (Fig. 5b). This experiment was repeated for different solders listed in Table I. In most cases, the temperature for each solder to wet was quite close to its melting point, thus demonstrating the efficiency of EA.

a) Without EA b) With EA

Fig. 5. Effect of EA on solder wetting

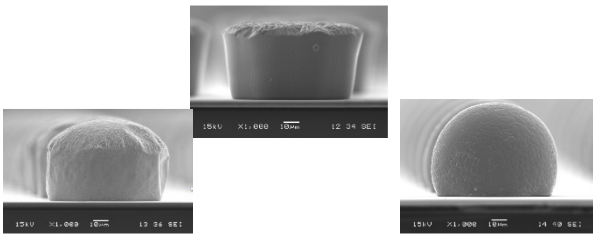
Table I. Solder Wetting Temperature under EA

Solder Composition (wt%)	Dominant Surface Oxides	Oxide Thickness (Å)	Melting Point (°C)	Wetting Temperature (°C)
63Sn/37Pb	SnO	30	183	197
90Pb/10Sn	SnO	30	305	306
96.5Sn/3.5 Ag	SnO	30	221	226
99.3Sn/0.7Cu	SnO	20	227	228
95Sn/5Sb	SnO	20	240	242
48Sn/52In	In_2O_3	20	117	150

APPLICATION DEMONSTRATION

Wafer Bumping

Wafer bumping is used to form solder bumps over an entire silicon wafer before cutting it into chips. The formed bumps serve as electrical, mechanical, and mounting connections for flip-chip assemblies. A reflow process is used to metallically connect the deposited solder bumps with the solder pads and convert the deposited bumps into a spherical shape. Fig. 6 shows tin-silver bumps on a wafer before and after reflowing. In the absence of EA, the reflowed bumps have surface collapse and uncompleted shape conversions due to a restriction of the oxide skin on the molten solder. Solder bumps reflowed under EA have a very smooth surface and a spherical shape, indicating an oxide-free solder surface.



No EA With EA

Fig. 6. Effect of EA on solder reflow

CURRENT PROCESS STUDIES

The current study is related to a novel flux-free technology based on Electron Attachment (EA), which can be operated at ambient pressure and normal solder reflow temperatures using non-flammable mixtures of hydrogen (≤5 vol%) in nitrogen. The technology was invented by Air Products in recent years, which involves generating a large quantity of low-energy electrons. Some of the electrons can attach to hydrogen molecules, forming active species for oxide removal. The basic concept and the efficiency for oxide removal have been demonstrated in previous studies [4], [5]. The EA-based technology is completely residue-free and has a potential to be widely used in the electronics packaging industry. This paper presents recent work between Air Products and Sikama International on alpha trials of an EA-enabled prototype furnace for production-scale wafer bump reflow (Fig. 7).

ALPHA TRIAL RESULTS

As shown in Fig. 8, the EA-enabled furnace contains a roller-featured wafer transportation system, which carries wafers through heating and cooling zones at typical production speed. Before entering a reflow zone, wafers are exposed to EA-activated 5 vol% H_2 in N_2 for removing solder oxides (Fig. 9).

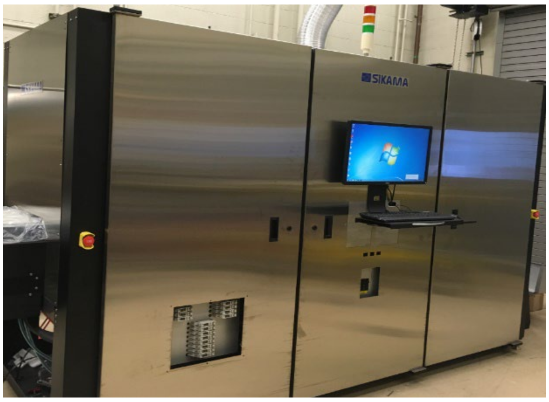


Fig. 7. EA-enabled oven for production-scale wafer bump reflow (EA UP1200 by Sikama)

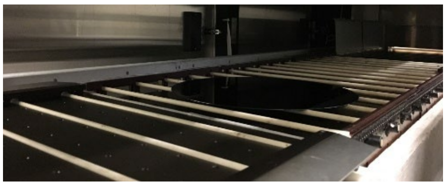


Fig. 8. Roller-featured wafer transportation system

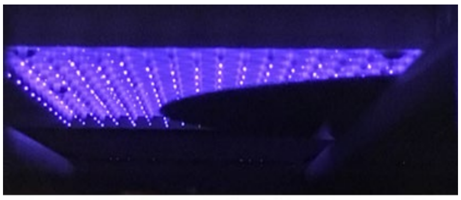


Fig. 9. Wafer entering an EA zone for oxide removal

Various dummy wafers (8" and 12") with as-plated solder bumps were obtained from different customers and processed in the furnace to evaluate bump reflow quality. Fig. 10 shows a cross-section of a reflowed tin-based solder bump plated on nickel. The intermetallic compound (IMC) formation controlled by reflow time and temperature was quite acceptable. The effectiveness of EA on oxide removal has been clearly demonstrated in multiple trials. Fig. 11 compares bump shapes of a lead-free solder on a wafer after undergoing different reflow processes. Before reflowing, electroplated bumps are cylindrically shaped (Fig. 11a). Without applying EA in the H_2 and N_2 mixture, reflowed bumps have a rough surface and an uncompleted shape conversion (Fig. 11b). When applying EA, reflowed bumps have a smooth surface and a spherical shape (Fig. 11c); even better than that of flux-reflowed bumps after cleaning (Fig. 11d). As shown in Fig. 12, the EA-based process can ensure a good bump uniformity across the width of a 12" moving wafer. In addition, the surfaces of the post-reflowed wafers are free of extra solder and foreign materials (Fig. 13).

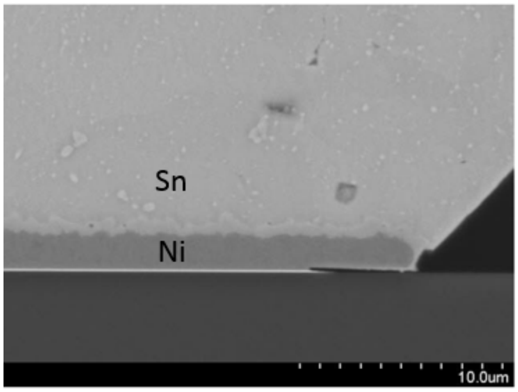
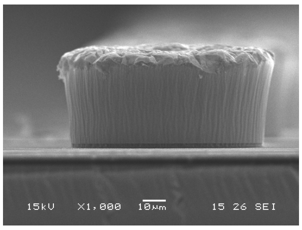
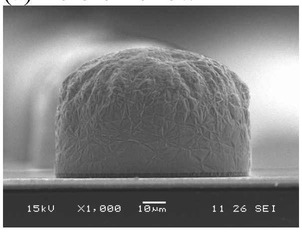


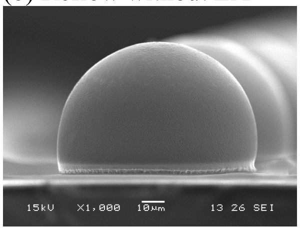
Fig. 10. Cross section of the IMC



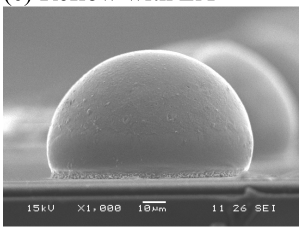
(a) Before Reflow



(b) Reflow without EA



(c) Reflow with EA



(d) Reflow with flux

Fig. 11. Bump shape comparison

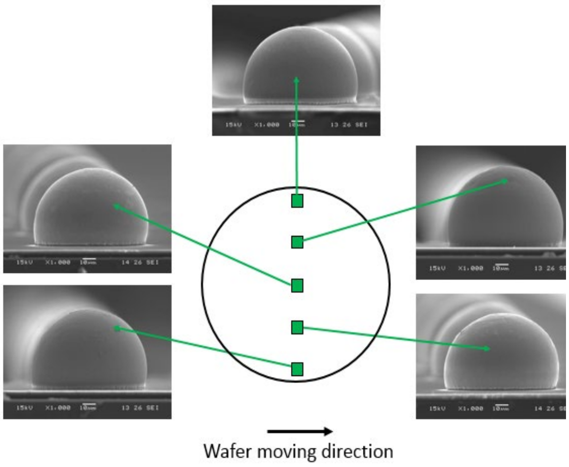


Fig. 12. Uniform bump shape by EA-based process

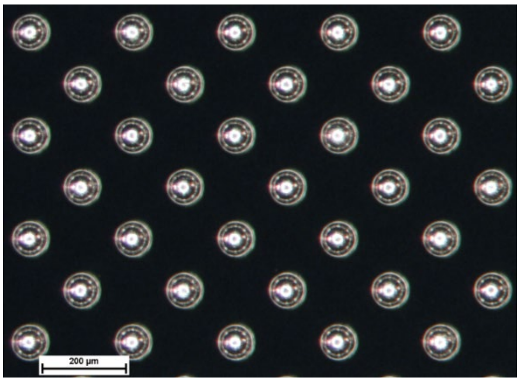


Fig. 13. Clean wafer surface after EA-based reflow

Full dummy wafers reflowed in the EA-enabled furnace were also sent back to corresponding customers for standard quality inspections, such as checking bump shape, bump uniformity, shear strength, failure mode, and bump voids. Results confirm that the wafers reflowed under the EA-based process, indeed, meet all specifications. Fig.14 and Fig.15 represent results of automated optical inspection (AOI), which confirm acceptable bump heights (BH) and bump diameters (BD) across an 8" full wafer. Fig. 16 shows that all shear failures are within solder bumps and, in addition, shear strengths exceed the criterion (> 2 g/mil^2). Fig. 17 is an x-ray image of a die on a reflowed wafer, which demonstrates that the number of bump voids (green) is quite low, and the size of a typical void is 3% of the bump area, which is significantly below the specified upper limit (8% of the bump area). [6]

Spec	62 ± 15 um
AVG BH	59.1um
Max BH	62.8um
Min BH	48.7um
BH Sigma	1.42um

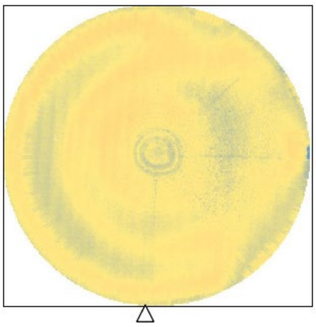


Fig. 14. BH distribution map and data

Spec	88 um +20%/-10%
AVG BD	90.2um
Max BD	91.9um
Min BD	88.0um
BD Sigma	0.47um

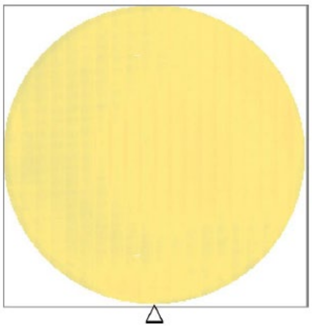
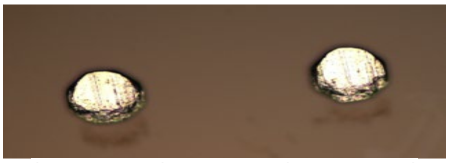


Fig. 15. BD distribution map and data



AVG	Max	Min
3.70	4.11	3.34

Spec>2 g/mil2

Fig. 16. Bump shear failures and data

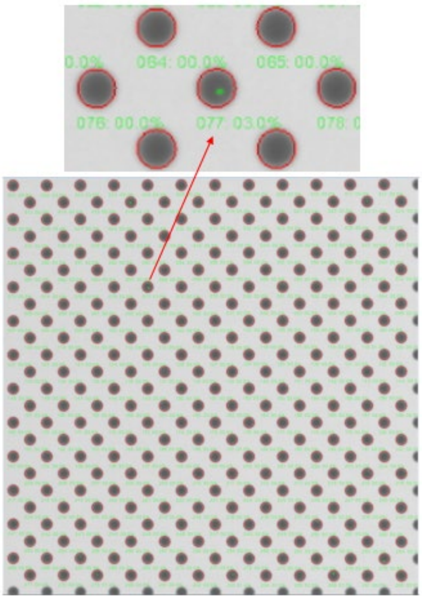


Fig. 17. X-ray image of a die

With integrated circuit packaging geometries being driven lower to accommodate the smaller node dimensions of the semiconductor devices, the interconnects between the integrated circuit and the package are changing to meet this challenge. As seen in Fig. 18, the interconnect scenarios are becoming smaller and are a challenge to reflow the solder bump or the solder cap of a copper pillar (Cu pillar) via flux-based processing.

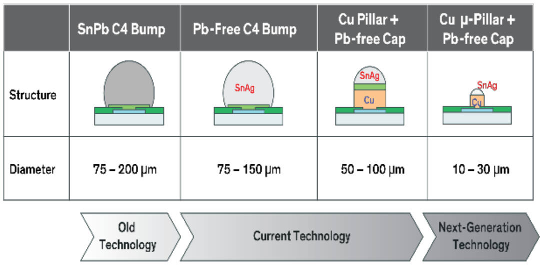


Fig.18. Interconnect geometries (Courtesy of DuPont)

In flux-based reflow processing with smaller geometries as seen in Fig. 19, the flux can be trapped between the Cu pillars and post reflow cleaning will be extremely difficult. With the Electron Attachment reflow technology, the reflow of the solder caps is uniform and there is no need for post reflow cleaning.

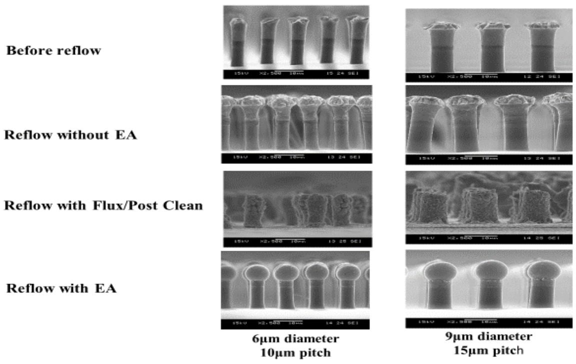


Fig. 19. Electron attachment reflow of Cu pillars

ELECTRICAL EFFECTS

The use of low energy electrons to activate the hydrogen molecule to form hydrogen anions has been a subject of debate regarding possible damage to a functional device or wafer.

With our generation of these low energy electrons from the emitter systems, the key to reduce the buildup of charge on the isolated, non-grounded wafer is eliminated by the emitters' capability to pull back the electrons off the surface of the wafer. To demonstrate that this pull back of the electrons by the emitters was in fact occurring, several tests with active wafers, first level integrated circuits, and Known Good Die (KGD) were conducted.

The initial test group were thirty (30) TI OPA 2333 CMOS operational amplifier Known Good Dies (KGD) purchased from Micross, who also provided the post testing analysis. Fig. 20 shows the KGD as received.

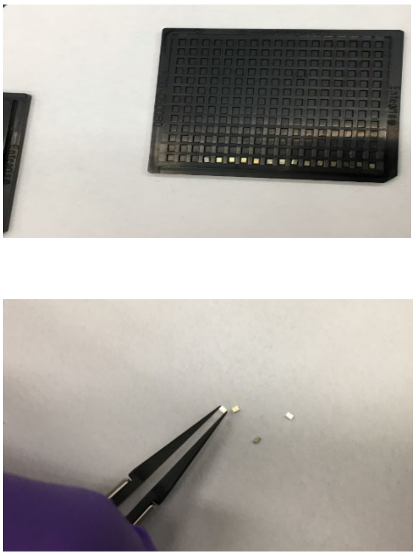


Fig. 20. TI OPA 2333 KGD

The KGD were placed onto a blank silicon wafer that was machined to hold the dies in place as they were passed through the EA reflow furnace. The 30 KGD were exposed to the low energy electrons based on the process parameters used for the bump and copper pillar reflow test as above.
The KGD were sent back to Micross for post EA analysis and their final analytical report concluded that there was no damage to the functionality of the Known Good Dies.

The second test group was done at the transistor level and was a SRAM chip at the 28 nm mode, provided by an integrated circuit foundry house. Fig. 21 shows the first device at the contact level.

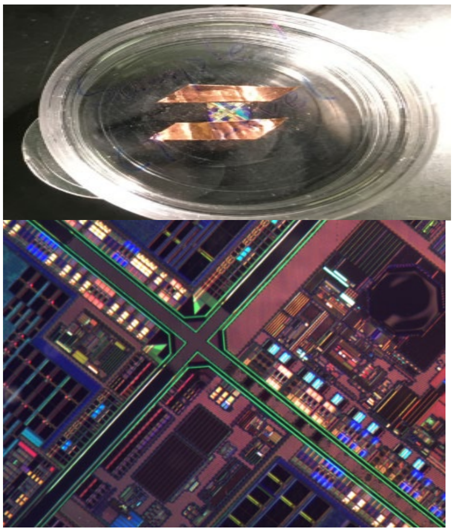


Fig. 21. Die 1 at Contact Level

A device at the metal level was also tested as shown in Fig. 22.

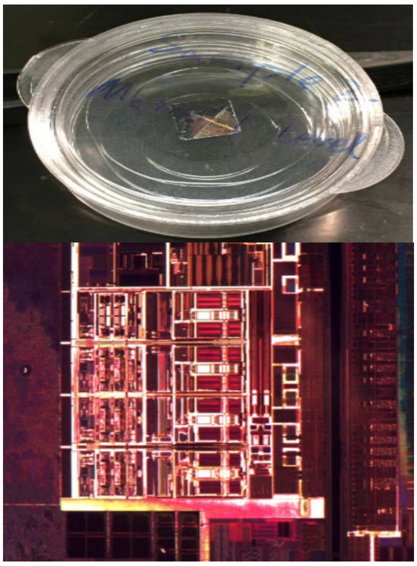


Fig. 22. Die 2 at Metal Level

These functional level devices were run through the EA reflow furnace based on typical process parameters used for the bump and copper pillar reflow tests.
As shown in Fig. 23 and Fig.24, the IV curves (Id – Iv), the overlay of the pre- and post-EA curves are closely matched. For both the PMOS and NMOS, the average change in the Id-lin, Id-sat, Vt-lin and the Vt-sat parameters are within 5% for all the transistors tested. These were acceptable results as tested, which was concluded by the foundry that supplied the devices.

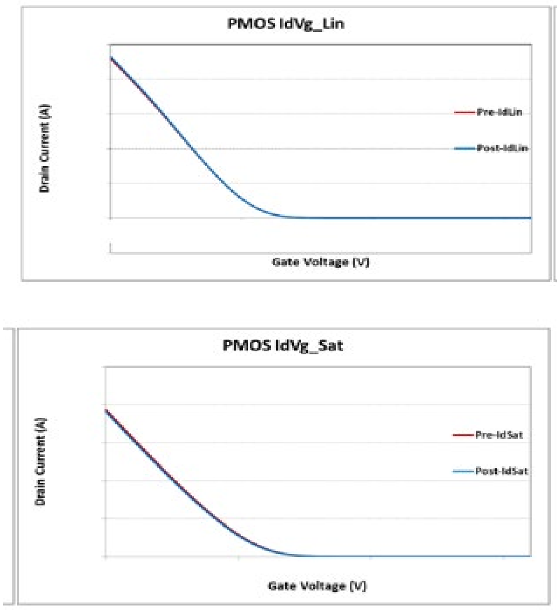


Fig. 23. PMOS Curves

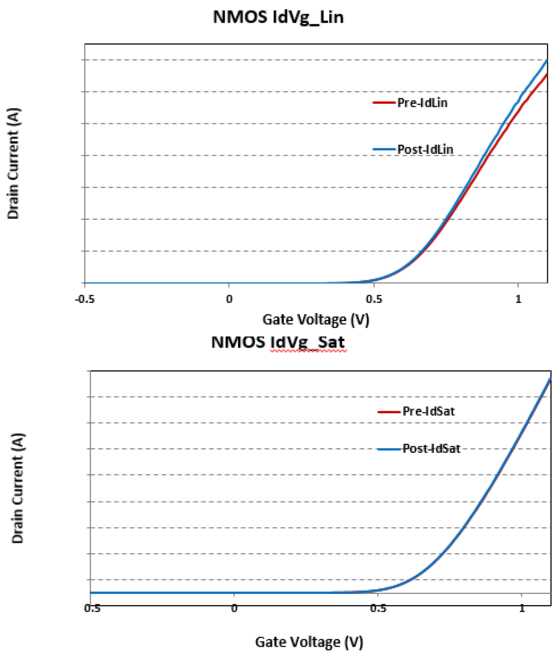


Fig. 24. NMOS Curves

The final test group involved fully functional eight-inch (200 mm) CMOS wafers from a major semiconductor company. Two probed wafers were processed in the EA activated hydrogen reflow system with the same parameters as the previous tests. Pre- and post-probe wafer testing was completed by the major semiconductor company that supplied the wafers. Post-EA processed probe testing showed insignificant changes to the device characteristics as compared to the pre-EA process data.

From the three test programs above, we can conclude that the EA activated hydrogen process had no adverse effect on the electrical characteristics or functionality of the devices on the wafers.

SOLDER BALL DROP STUDY FOR ACTIVATED HYDROGEN ELECTRON ATTACHMENT FLUXLESS REFLOW TECHNOLOGY

An important process step for integrated circuit packages or substrates is to reflow solder balls to the interconnection pads. This process is currently accomplished by printing flux onto the package or substrates contact pads, then placing the solder balls in their correct position. Once this placement of the solder balls is completed, the substrate is sent through a reflow with a nitrogen atmosphere. Post reflow cleaning is required to remove the flux residue.
With the drive towards miniaturization of integrated circuit packaging to accommodate the latest semiconductor node and heterogenous integration, the need to develop improved solder reflow processes is required. This includes a flux free process that will eliminate the need for post reflow cleaning.
The activated hydrogen Electron Attachment (EA) fluxless reflow technology is an alternative process to fluxed based solder ball drop processing. To investigate if the activated hydrogen reflow process works, a design of experiment was developed to explore lead free (SnAg2.6Cu0.6) solder balls. A copper substrate is used to place the solder balls. (Fig. 25)

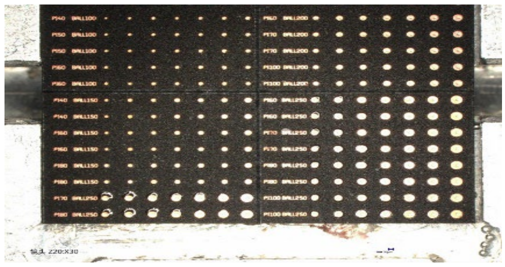


Fig. 25. Copper Substrate

To hold the solder balls onto the substrate, we used Indium NC 702 tacky material. This material was recently developed by Indium to leave a basically residue free post-reflow on the substrate and solder balls.
Using the EA UP 1200 reflow system (as introduced earlier), the experimental design included precleaning of the substrates and no precleaning of the substrates. The parameters used for the EA system on temperature for the EA zones and the reflow zones for the lead-free solder balls is as follows:

EA Zones: 216 deg. C for SnAg2.6Cu0.6
Reflow Zone: 255 deg. C

The precleaning process via the activated hydrogen EA fluxless reflow was used to remove any copper oxide on the pads of the substrate. Post precleaning, the Indium NC 702 was printed onto the substrate, then the solder balls were placed. The solder ball – substrate was sent through the EA UP 1200 system and reflowed at three different wafer transport speeds (20 wafers per hour, 40 wafers per hour and 60 wafers per hour). In Figs. 26 and 27 are the results of the reflow without precleaning of the substrate. The results show that without the removal of the copper oxide, the solder balls did not wet to the copper pads and were easily removed, even with the lower wafer transport speed which increased the exposure to the activated hydrogen EA technology condition.

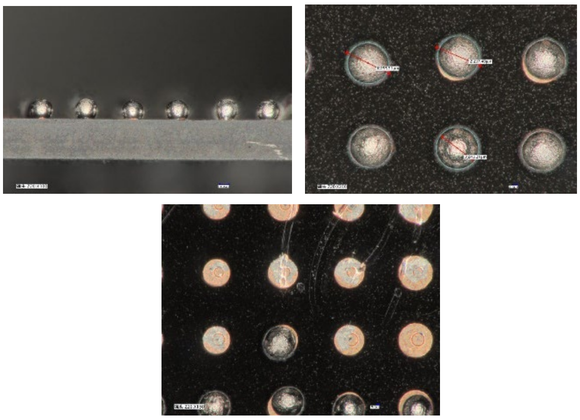


Fig. 26. Without Precleaning, 60 wph EA Fluxless Reflow

The results are different with precleaning of the copper pads on the substrate. In the following figures (28, 29 and 30), the results demonstrate excellent solder ball wetting to the copper pads, and good solder ball adhesion to the copper pads, which is indicated by the fact that either the copper layer is delaminated from the substrate, or the solder ball was broken when it was peeled off from the substrate

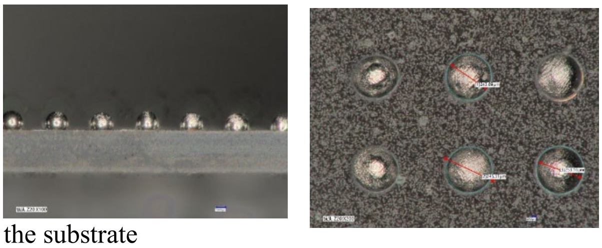
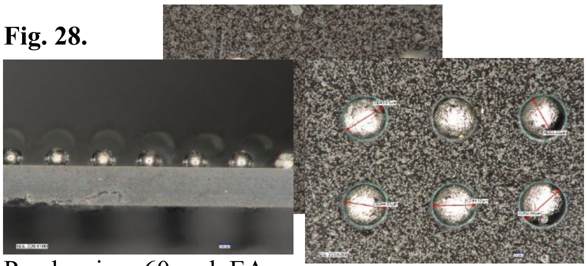


Fig. 28.



Precleaning, 60 wph EA Fluxless Reflow

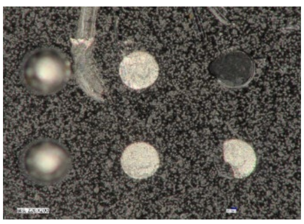
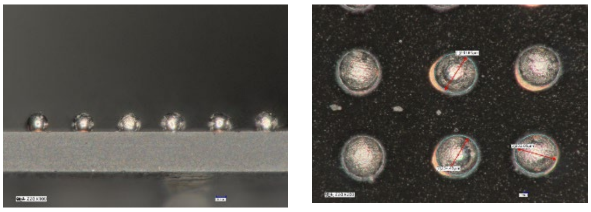
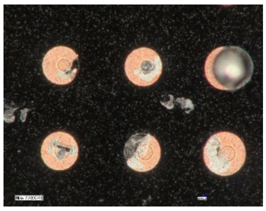


Fig. 30.



20 wph Reflow



Precleaning, EA Fluxless

Fig. 27. Without Precleaning, 20 wph EA Fluxless Reflow

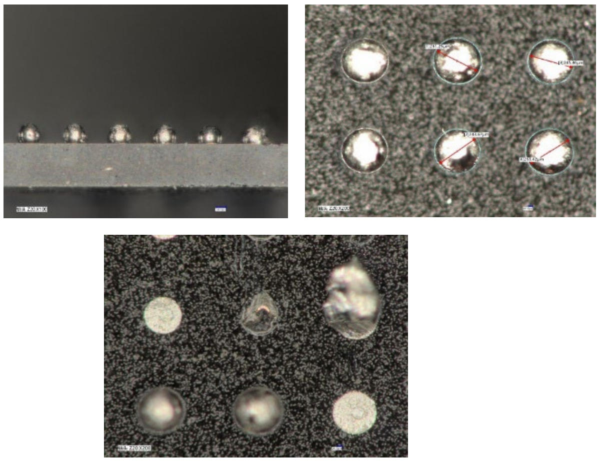


Fig. 29. Precleaning, 40 wph EA Fluxless Reflow

The Indium NC 702 material has the capability to hold the balls in respective positions of chip substrates during EA treatment and thereafter reflow bumping. The preliminary results with Indium NC 702 material on chip substrate demonstrate residue free under optical microscopy after normal temperature processing. The TGA analysis of the Indium NC 702 material is seen below in Fig. 31. Temperature ramp up rate is 50 ºC/min and a 100% weight loss at 280 deg. C to ensure near zero residue.

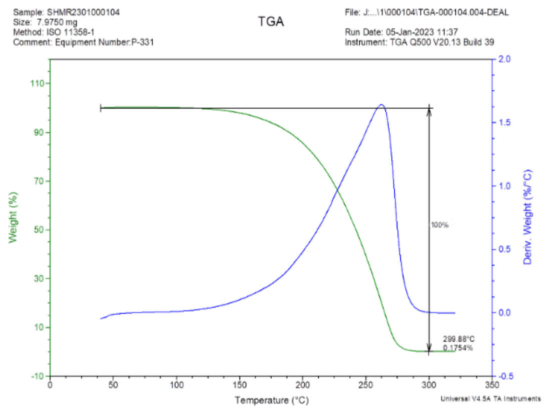


Fig. 31. TGA Analysis

The substrates precleaned by activated hydrogen EA fluxless processing show acceptable wetting, ball formation and bonding, even if the fastest conveyer speed (60wph) shows the promising results. The pads with precleaning after balls were removed indicate that the complete wetting & spread and good bonding could be achieved after appropriate activated hydrogen EA precleaning, while the chip substrates without precleaning show insufficient wetting, ball formation and bonding.

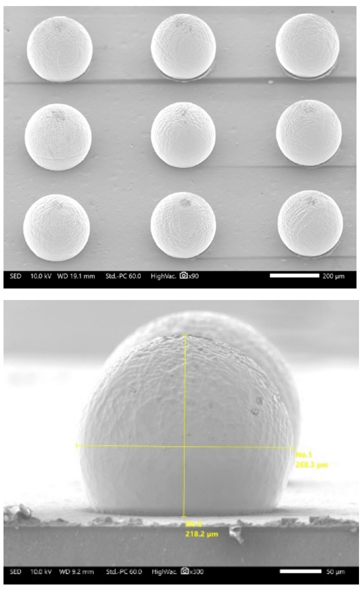


Fig. 32. Ball Shape

Further analysis of the samples processed via SEM morphology showed the following ball shape post activated hydrogen EA reflow in Fig. 32. Cross section studies demonstrated excellent wetting and adhesion to the copper pads. This can be observed in Fig. 33.

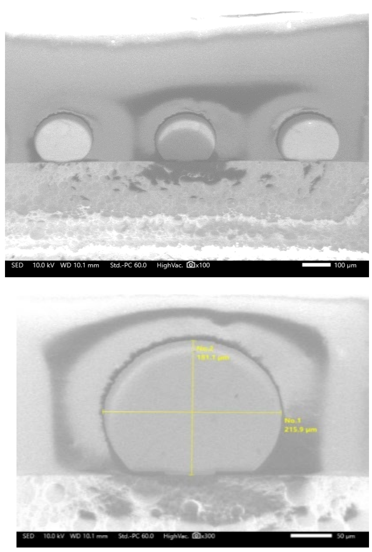


Fig. 33. Wetting to the Substrate

Through EDS mapping we were able to confirm the SEM analysis above. See Fig. 34 a and b for EDS mapping.

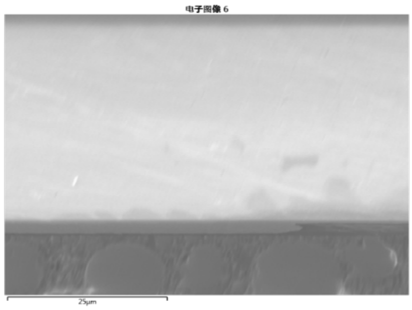


Fig. 34a. IMC Layer of the Cross Section

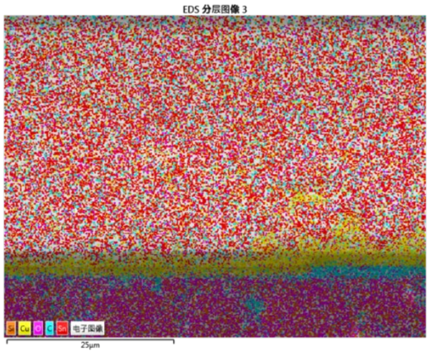


Fig. 34b. Combined picture of Sn, Cu, A & Si EDS mapping

Future studies will use the above information and technology to investigate the use of the Indium NC 702 material in conjunction with the activated hydrogen EA precleaning to remove oxides and fluxless reflow processing for flip chip assembly and to eliminate the need for flux and post reflow cleaning.

CONCLUSIONS

Trial results demonstrate that dummy wafers reflowed in the EA-enabled production-scale oven meet customer specifications. The EA-based technology offers the following benefits for wafer bump reflow: 1) enhanced bump reflow quality because the flux induced solder voids and wafer contaminations naturally disappear, 2) improved productivity by having in-line process capability, eliminating post wafer cleaning, and avoiding furnace down time cleaning, 3) reduced cost of ownership due to eliminated costs associated with cleaning equipment, solution, labor work, and flux, 4) improved safety by eliminating flux exposure and using a non-toxic and non-flammable gas mixture, and 5) no environmental issues by eliminating organic vapors, hazard residues, and CO_2 emissions. Throughout the testing to observe the effects of the low energy electrons, EA activated hydrogen process had no effect on the electrical characteristics or functionality of the devices on the wafers. The use of the activated hydrogen electron attachment fluxless soldering processing has demonstrated the precleaning can effectively remove surface oxidation and allow for solder ball attach and reflow without the need for fluxes. The next step is to utilize our learnings to assemble flip chips without the need for fluxes.

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