## FLUXLESS SOLDERING IN ACTIVATED HYDROGEN ATMOSPHERE

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## ABSTRACT

A novel hydrogen activation technology based on electron attachment (EA) is developed for fluxless soldering at ambient pressure and normal soldering temperature. The technology has a potential to be used for a list of applications in the electronics packaging industry.

## INTRODUCTION

The IC packaging trend is moving toward multilayer, three dimensional packaging with increased I/O, increased functionality, and reduced size. With this trend, the interconnections become more challenging. One of the key to ensure a good electrical and mechanical interconnection is to remove oxides on solder and base metal surfaces to be jointed, which is typically done by using organic fluxes. The oxide removal capability is attributed to the organic acids in the fluxes (1).

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

There are many problems associated with the flux containing process, especially flux residues, which are invariably generated and can't be accepted in high reliability applications. With the industrial trend on device miniaturization, cleaning of residues out of tiny gaps around solder joints is almost impossible. Therefore, fluxless soldering has gain more attention in recent years.

Fluxless soldering is mainly based on using a reactive atmosphere for oxide removal. However, existing fluxless technologies all have different problems. For example, formic acid vapor has been used in certain applications, but its mechanism on oxide reduction is the same as that of using organic fluxes (1). Therefore, the residues are only minimized, but not eliminated. The use of hydrogen as a reducing gas is very attractive since the oxide reduction is free of residues and organic volatiles. However, in the normal soldering temperature range, molecular hydrogen is inefficient for oxide removal. Atomic hydrogen formed under a plasma is much more reactive, but such process requires a vacuum since the stability of atomic hydrogen at atmospheric pressure is insufficient. Vacuum operation is not favorable due to the increased cost and inability to fit with the continual production line. Therefore, our objective is 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 (<4 vol%) in nitrogen.

### ELECTRON ATTACHMENT 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<sub>2</sub>) combines with an electron (e<sup>-</sup>) to give an excited molecular hydrogen anion  $(H_2^{-*})$  which dissociates to give an atomic hydrogen anion (H<sup>-</sup>) and a neutral hydrogen atom (H). The neutral hydrogen atom can further capture an electron, forming an excited atomic hydrogen anion (H<sup>-\*</sup>) 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.

$$H_2 + e^- \rightarrow H_2^{-*} \rightarrow H^- + H \qquad (2)$$
  

$$H + e^- \rightarrow H^{-*} \qquad (3)$$
  

$$2H^- + SnO \rightarrow Sn + H_2O + 2e^- \qquad (4)$$

#### **Benefits of EA**

The atomic hydrogen anion formed under EA is a strong reducing agent since it is free of a chemical bond and is a good electron donor for triggering an oxide reduction. Different to the conventional plasma, the charged environment created under EA is singly negative, which makes hydrogen anions repel each other and extends their lifetime at ambient pressure. Comparing with the random diffusion of neutral gas molecules or atoms, the hydrogen anions approaching to soldering surfaces under EA is driven by an electrical field, which is much faster and efficient. In addition, ambient pressure is more favorable than vacuum for forming anions by EA because the increased collisions between electrons and gas molecules, which not only facilitates the formation of low energy electrons but also increases the probability of electrons approaching and attaching to gas molecules. Therefore, EA is considered to be promising for activating hydrogen for fluxless soldering.

#### **Process Establishment**

Figure 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 ( $\leq 4\%$ ) 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 expose to the EA atmosphere. After EA cleaning of oxides on soldering surfaces, the devices will undergo the normal solder reflow and cooling.

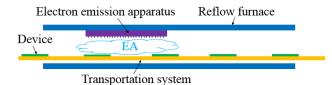


Figure 1: Establishing EA in a reflow furnace

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 commercial available electron emitter that could satisfy the requirements for current application. Therefore, in our research we developed a patented technology for the electron emission apparatus. The apparatus contains 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 a capability to collect free electrons accumulated on the soldering surfaces and still emit electrons.

Figure 2 shows an electron emission module with 3" X 3" in size. A number of such modules can be integrated together to scale up the electron emission. Figure 3 demonstrates a status of electron emission when the module is operated above an electrically insulated glass. By initiating a required electrical power, all the tips on the module are illuminated, which is mainly due to gas molecules surrounding tips are excited. The illuminated tip array is reflected on the glass surface.

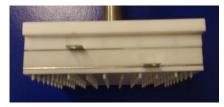


Figure 2: Electron emisison module (3" X 3")



Figure 3: Electron emission above an 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<sub>2</sub>) and deuterium (D<sub>2</sub>) at 280°C. As shown in Figure 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<sub>2</sub> and D<sub>2</sub> intensities. This result confirms the dissociation of H<sub>2</sub> molecules under EA [2].

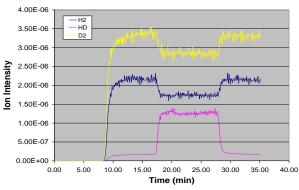


Figure 4: MS spectra showing reactions under EA

### **Solder Wetting**

A fluxless solder preform in a pellet shape was put on a copper plate and heated up in 4 vol%  $H_2$  in  $N_2$  either with or without applying EA. Without applying EA, the molten solder maintained to be 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.

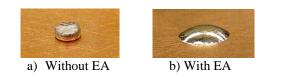


Figure 5: Effect of EA on solder wetting

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 <sub>2</sub> O <sub>3</sub>	20	117	150

Table I. Solder Wetting Temperature under EA

# 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. Figure 6 shows tin-silver bumps on a wafer before and after reflow. In the absence of EA, the reflowed bumps have surface collapses 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 spherical shape, indicating an oxide-free solder surface.

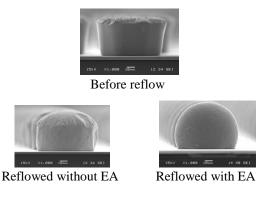


Figure 6: Effect of EA on solder reflow

## **Flip-Chip Bonding**

Two flip chips with tin-lead solder bumps of 100  $\mu$ m in size were manually mounted on a printed circuit board (PCB) having a daisy chain pattern (Fig. 7a). For our demonstration purpose, the end of the daisy chain was grounded to allow charge draining. The PCB was heated to the solder's reflow temperature (220°C) and exposed to EA. After 30 seconds of EA exposure, the daisy chain started to illuminate (Fig. 7b), indicating a formation of a good electrical continuity by a successful solder self-aligning and joint formation.

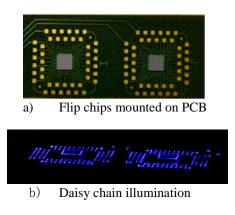
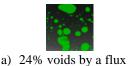


Figure 7: Flip-chip bonding with applying EA

### **Die Attachment**

Die attach is a process during which an individual die containing an integrated circuit is bonded onto a substrate or package base. For high power applications, the bonging is achieved by using a thin layer of solder preform. To satisfy thermal and electrical requirements, a die attach with low voids is highly needed. EA cleaning can eliminate flux vapor, thus reducing void tendency [3]. As shown in Figure 8a, 24% voids were formed for a die with 2 mm X 2 mm in size when it was soldered by a flux. As a comparison, 0% void was achieved for the same size die when it was fluxless soldered by EA (Fig. 8b).





ux b) 0% voids by EA

Figure 8: Effect of EA on void reduciton in die attach

## CONCLUSIONS

Our research demonstrates the efficiency and benefits of a novel fluxless technology based on EA. Its novelty is not only based on the concept of using EA for gas activation, but also based on an apparatus developed for establishing EA. We are working on a prototype development of an EA featured furnace to bring this technology to the market.

## REFERENCES

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