AIR PRODUCTS

Electron Attachment: A New Approach to H_2 Fluxless Solder Reflow for Wafer Bumping

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Abstract

Wafer bumping, via fluxless solder reflow, can be performed using electron attachment (EA) with nonflammable mixtures of hydrogen (≤4 vol%) in nitrogen. The EA process facilitates dissociation of molecular hydrogen at ambient pressure and a temperature significantly lower than that of thermal dissociation. Our studies suggest that the EA process promotes the formation of atomic hydrogen anions, which reduce solder oxides and facilitate fluxless solder reflows at temperatures close to the solder melting point.

Index Terms—Electric field effects, electron attachment, electron emission, fluxless solder reflow, hydrogen, wafer bumping, wafer-scale integration.

I. Introduction

Wafer bumping is used to form solder bumps over an entire silicon wafer on which integrated circuits have been built. After the wafer bumping process, the wafer is singulated into individual chips (dies) which are "flipped" over for inner lead bonding. Therefore, wafer bumping is a critical step for device packaging. The bumps formed on the wafer serve as electrical, mechanical, and mounting connections for flip-chip assemblies. These bumps must exhibit superior adhesion to the die, minimum electrical resistance, and high planarity. Defects such as residues on the wafer surface, voids in the bumps, and nonuniform bump heights must be prevented or minimized.

The bumps are made by depositing a solder onto metal pads, commonly by electroplating or stencil printing. The deposited solder is then reflowed at a temperature above its melting point to alloy the metals, form a metallic interconnect with the die, and convert from its as-plated form into a spherical shape driven by liquid surface tension.

The deposited solder typically contains a native oxide layer on the surface. When the solder is melted, the oxide layer remains in the solid phase and acts as a skin. This constrains the molten solder surface and prevents the formation of uniform, spherical bumps. Therefore, one of the keys to successful wafer bumping is to remove surface oxides from the deposited solder during the reflow process.

There are numerous methods for removing the initial solder oxides and preventing further oxide formation during reflow. Currently, the most commonly used approach is to incorporate a flux in one of two ways: 1) coat the electroplated solder bumps with a flux before reflow, or 2) mix the flux with the solder paste prior to stencil printing. The flux-coated or flux-containing solder bumps are then reflowed in a nitrogen atmosphere to further minimize the formation of solder oxides.

The flux effectively removes the surface oxide from the solder during reflow. However, this flux-containing reflow can cause problems and inconveniences. For example, volatile materials are generated when organic fluxes decompose during heating. These volatiles can be trapped in the molten solder and form voids, which degrade mechanical and electrical properties, destroy the planarity of the solder-bumped wafer, and affect the subsequent chip bonding process [1]. Flux volatiles also condense and accumulate on the furnace wall, increasing maintenance costs and equipment downtime. The decomposition of organic fluxes always leaves residues [1], [2], which can cause corrosion and degrade the performance of the assembly. In addition, flux residues adversely affect underfill interfacial adhesion in the flip chip assembly process. Flux residues must therefore be removed, which is typically done through post-reflow cleaning. Chlorofluorocarbons (CFCs) were commonly used as the cleaning agents, but their use has been banned to reduce further damage to the earth's protective ozone layer. With no-clean fluxes, which include a small amount of activators to minimize residues, there is a tradeoff between reduced residues and diminished flux performance. Because of the problems associated with organic fluxes, fluxless solder reflow has been of great interest in recent years.

The most attractive among the various fluxless reflow methods is the use of a reactive gas, especially hydrogen, because it is a clean and nontoxic process. Its only by-product, water, can be easily vented out of the furnace. However, the major limitation is the lack of reactivity of molecular hydrogen in the normal solder reflow temperature range (~30°C above the solder melting point). Therefore, high temperatures and pure hydrogen must be applied to activate and hasten the reduction process [3]. This increases the flammability hazard and operating costs compared

with a traditional flux-containing process for wafer bumping. In addition, the high temperature requirement precludes the use of low-melting-point solders due to the coarsening of intermetallic compounds (IMCs).

Because of the limitations of hydrogen fluxless solder reflow, many investigators have pursued various catalytic methods to assist in generating highly reactive hydrogen radicals. One such method, which has been more extensively studied, incorporates the use of plasma. Plasma-activated hydrogen is quite efficient at reducing metal oxides at low temperatures, but such processes often require a vacuum.

This increases both capital and operating costs, and the process must also be divided into discrete, discontinuous batches. Atmospheric plasmas do not appear to be viable because the lifetimes for active species are much shorter than within a vacuum. Therefore, despite continuous advances in fluxless technologies, none have been widely applied. There still remains a need in the microelectronics industry for a fluxless solution that is simple, efficient, cost-effective, and environmentally friendly. The objective of this research was to meet this need by developing a novel technology to activate hydrogen for low-temperature reduction of solder oxides.

II. PROPOSED APPROACH

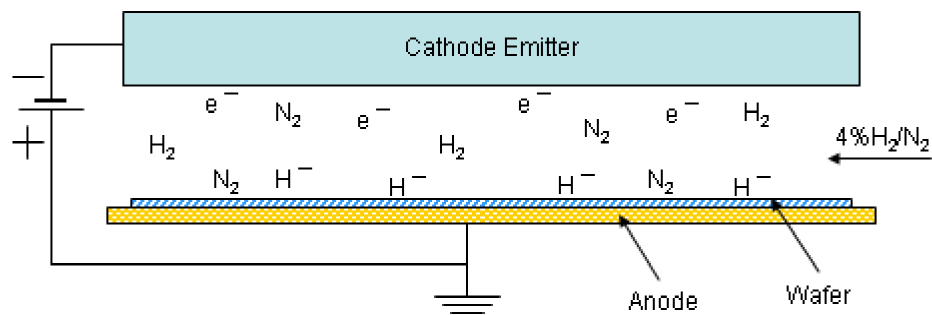
Electron attachment (EA) was identified as a potential ambient-pressure activation process to facilitate dissociation of hydrogen gas molecules. When low-energy electrons (<10 eV) collide with gas molecules, those captured by gas molecules produce negative ions by dissociative or direct attachment, generally defined as "electron attachment" [4]. Because the energy of the incident electrons is low, the gas molecules in EA are not ionized into oppositely charged particles, as occurs in plasma. The charge environment created under EA is singly negative, which is a major distinction between EA and plasma.

Equation 1 describes the major factors for controlling the energy of the electrons emitted from a cathode [5]. The energy (ω_e) is proportional to the field strength (E) applied between the two electrodes because that is the driving force to accelerate an electron within each free path. The energy of the emitted electrons is inversely proportional to gas pressure (P) because an electron will decelerate when colliding with a gas molecule. An increase in pressure will increase the collisions between electrons and gas molecules, not only reducing the electron energy but also increasing the probability of electrons approaching and attaching to gas molecules.

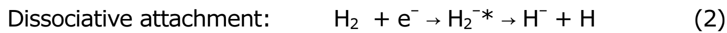
$$\omega_e \propto E/P \qquad (1)$$

Therefore, ambient pressure is much more favorable than a vacuum for generating low-energy electrons and for electron attachment. This is one of the major benefits of using EA for activating hydrogen. Non-vacuum EA has been studied in recent years to remove electro-negative impurities for gas purification [6], [7]. The novelty of this study was using EA in a different application: to dissociate H_2 molecules and promote low-temperature reduction of solder oxides for wafer bumping. The principle of the EA process is illustrated in Figure 1.

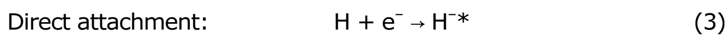
Figure 1. The concept of forming hydrogen ions by electron attachment.



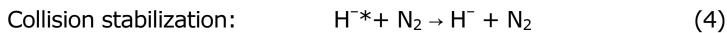
The EA assembly can be mounted inside a furnace. During the reduction process, pure H_2 or a gaseous H_2/N_2 mixture is introduced into the furnace. A nonflammable mixture of H_2 (≤4 vol%) in N_2 is preferred in many cases to ensure safety. Wafers to be reflowed are set inside the furnace on a grounded anode, which can be a belt that moves from one end of the furnace to the other. When a suitable DC voltage is applied to the cathode mounted overhead, low-energy electrons are generated from the cathode and, driven by the electric field, drift toward the anode. Hydrogen molecules can then collide with these electrons, and excited molecular hydrogen anions ($H_2^{-}*$) can be formed. Some of these anions split into neutral hydrogen atoms (H) and atomic hydrogen anions (H^-) by dissociative attachment (2). As seen in (3), additional collisions between the hydrogen atoms and electrons can lead to a direct attachment, forming excited atomic hydrogen anions ($H^{-}*$). During the EA process, N_2 in the gas mixture cannot form negative ions because the electron affinity of N_2 is close to zero. Equation 4 shows how nitrogen can act as a third body in collision stabilization to absorb the excess energy of the excited atomic hydrogen anions ($H^{-}*$) formed by direct attachment. The atomic hydrogen anions (H^-) generated under EA also drifts along the electric field toward the wafer and chemically remove oxides on solder surfaces. Equation 5 describes the solder surface de-oxidation, where the dominant composition of the oxide layer on a tin-based solder surface is believed to be SnO [8]. Water vapor, a by-product of the oxide reduction, can be easily vented from the furnace. Free electrons injected to or generated on the wafer surface are discharged by traveling to the solder bump positions and draining through the silicon matrix to the ground. The neutral hydrogen atoms (H) formed by dissociative attachment (2) are also an active species for oxide removal. However, their role is expected to be much less significant than that of atomic hydrogen anions (H^-) due to the rapid recombination and a slow diffusion of H to the metal surfaces of the wafer.



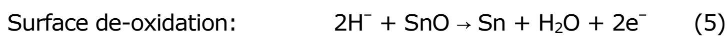
Dissociative attachment: $H_2 + e^- \rightarrow H_2^{-}* \rightarrow H^- + H$ (2)



Direct attachment: $H + e^- \rightarrow H^{-}*$ (3)



Collision stabilization: $H^{-}* + N_2 \rightarrow H^- + N_2$ (4)



Surface de-oxidation: $2H^- + SnO \rightarrow Sn + H_2O + 2e^-$ (5)

It is anticipated that EA-assisted H_2 reduction of solder oxides could provide the following benefits:

- High-efficiency hydrogen reductions at low temperatures due to the dissociation of H_2 molecules under EA.
- The ability to use safer, nonflammable H_2/N_2 concentrations (e.g., ≤4 vol% H_2 in N_2) to achieve the expected reduction rate, which is feasible because the electrical field drives the active species (H^-) to the surface to be treated.
- Ambient-pressure conditions for EA, much more favorable than under a vacuum, making the process simple and suitable for use on an open, continual production line.
- Creation of a single-charge environment in which the hydrogen anions (H^-) repel each other, resulting in a relatively long lifetime of the active species.
- Relatively high energy efficiency, since N_2 as a dilution gas is inert to EA because its electron affinity is close to zero.

III. EXPERIMENTS, RESULTS, AND DISCUSSION

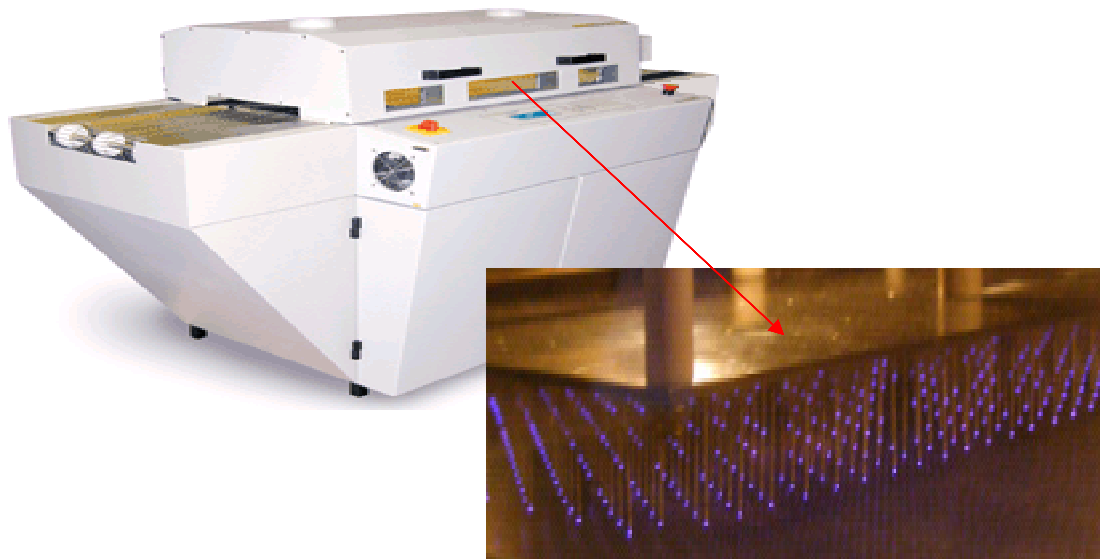
A. Electron Emission

The major challenge to establishing the EA process described in Figure 1 was having a cathode that 1) can generate electrons efficiently and uniformly above the wafer surface, 2) has a long lifetime under normal processing conditions, and 3) has a low manufacturing cost. Since no commercially available cathode was able to meet these requirements, a novel cathode had to be developed especially for this application. After exploring many cathode geometries and emission mechanisms, we finally selected a cathode composed of a metal plate with distributed emission pins. To maximize the electric field, each emission pin (0.025" diameter wire made of a Ni/Cr/Fe alloy) was machined to have a sharp tip with a 10° angle protruding 1.5 cm out of the metal plate surface. The tips of the emission pins were set 1 cm above the wafer surface per an industrial regulation for clearance above a wafer during reflow. Optimal pin spacing was determined to 1 cm, based on a trade-off between minimized interference of electric fields among adjacent pins and maximized surface coverage for electron emission.

Figure 2 shows a production-scale moving belt furnace retrofitted for EA capability. The moving part of the furnace is 12” wide and 6’ long. A cathode containing over 1,000 pins for emitting electrons is mounted inside the furnace. The electron emission can be observed through the window. As seen in Figure 2, a single-polarity, pulsed DC voltage

(frequency 10 KHz, amplitude 2-3 KV) applied to the cathode created a stable and uniform electron emission in a gas mixture of H_2 and N_2. The voltage was pulsed to minimize arcing, since the time required for effecting electron emission near the emission tips was known to be shorter than that necessary for effecting complete dielectric breakdown of the gas phase [9]. The emission current could be varied from 0.1 to 0.5 mA/pin by using the current control capability of a power source (made by Spellman). Figure 2 also demonstrates that the gas phase being activated was visually clear throughout the EA process, indicating that there was no plasma formation.

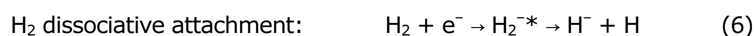
Figure 2. A moving belt furnace retrofitted with EA capability.



The cathode has a simple structure and thus a low manufacturing cost. It also proved to have a long lifetime of operation. This is attributed to the special nature of EA and the fact it forms negatively-charged ions, largely minimizing a "blasting" effect on the cathode by positive ions.

B. Proving the Concept

The most fundamental theory of using EA to activate H_2 is the dissociative attachment of hydrogen molecules and the generation of atomic hydrogen anions (H^-) as the major active species (2). It would be ideal to directly measure atomic hydrogen (H) with mass spectrometry (MS) to demonstrate the occurrence of the dissociative attachment. However, the mass spectrometer could not detect atomic hydrogen because of its low mass and rapid recombination. Therefore, an alternative method was developed to monitor H_2 dissociation: measuring hydrogen – deuterium (HD) exchange in a gas environment containing H_2 and D_2. HD exchange is a chemical reaction in which a covalently bonded hydrogen atom is replaced by a deuterium atom, or vice versa. An increase in HD intensity when EA was applied would indicate that dissociative attachments were taking place for both H_2 and D_2 molecules, confirming the creation of the corresponding atomic anions (6)-(8). This phenomenon was indeed observed experimentally.



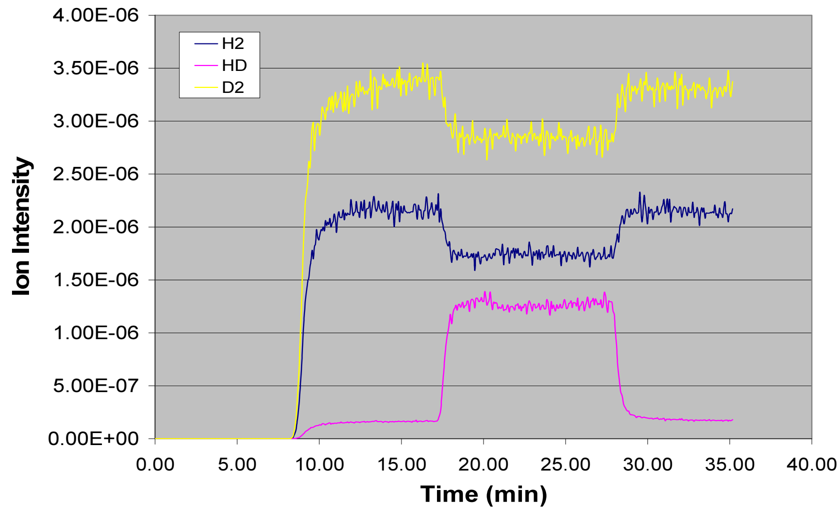
H_2 dissociative attachment: $H_2 + e^- \rightarrow H_2^{-*} \rightarrow H^- + H$ (6)

D_2 dissociative attachment: $D_2 + e^- \rightarrow D_2^{-*} \rightarrow D^- + D$ (7)

HD formation: $H + D \rightarrow HD$ (8)

Figure 3 shows results of MS analysis of gas from the outlet of the furnace at 280 °C. Five minutes after data acquisition began (t=5 min), the gas inlet was switched from N_2 to a gas mixture of H_2/D_2 at a 1:1 volume ratio. EA was then applied from t=15 min to t=25 min. As shown in Figure 3, the HD intensity increased when EA was applied, and returned to its original level after EA was stopped. There were also corresponding changes for H_2 and D_2 intensities. These results confirm the dissociation of H_2 gas molecules under EA.

Figure 3. MS spectra showing intensity changes of HD, H_2, and D_2 when EA applied at 280 °C.



This same isothermal experiment was repeated at various temperatures. It was found that as process temperature increased, the peak HD intensity also increased (Figure 4). This result is reasonable, since dissociative attachment is known to be an endothermic reaction [10]. To better assess temperature effects, the HD peak values in Figure 4 were then plotted as a function of furnace temperature. As shown in Figure 5, HD exchange under EA initially occurs at ~100 °C; the HD peak values then stabilize at higher temperatures. It is known that thermal dissociation of hydrogen molecules is more effective at high temperatures. This result indicates that the initial temperature for dissociating hydrogen gas molecules under EA is indeed much lower than that of thermal dissociation.

Figure 4. MS spectra showing the effect of temperature on HD formation under EA.

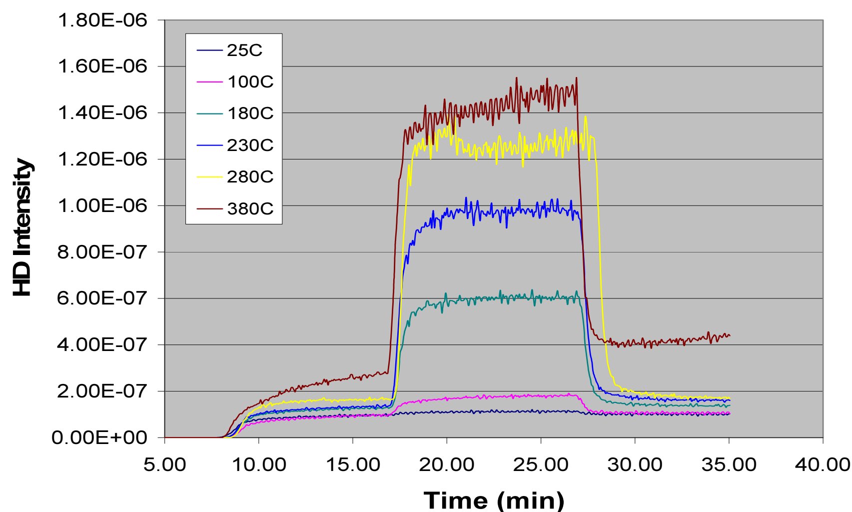


Figure 5. HD peak intensity versus temperature.

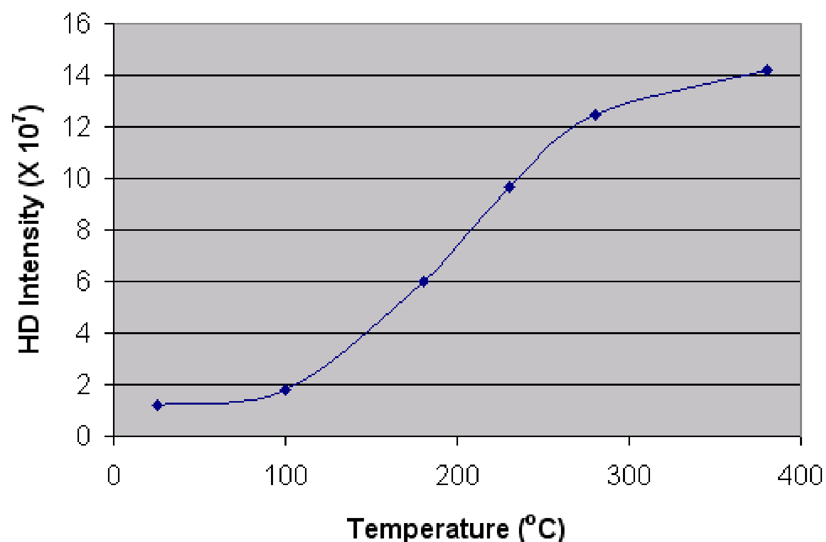
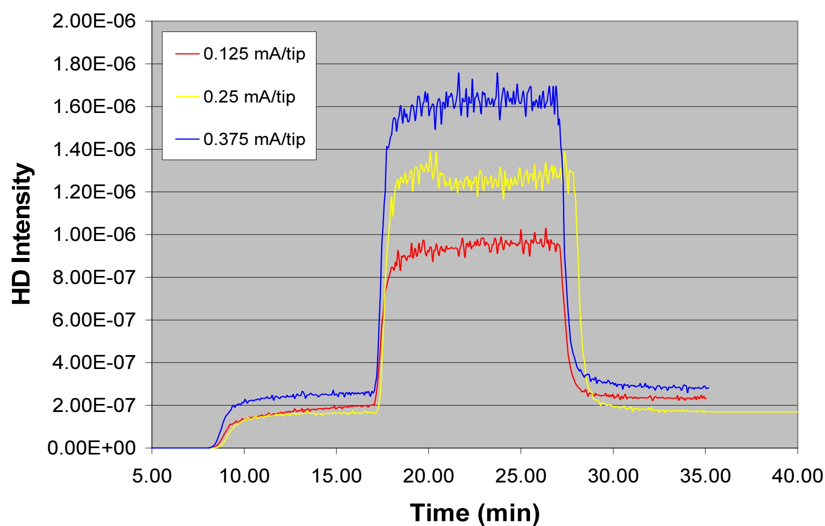


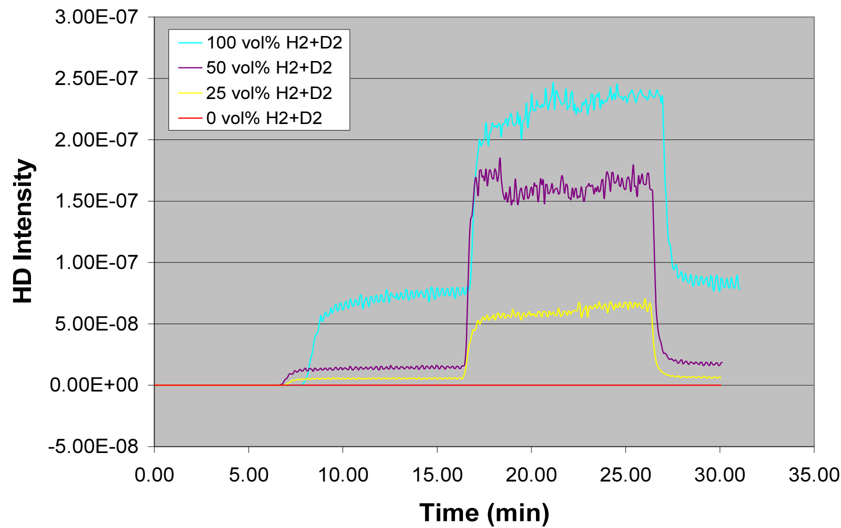
Figure 6 illustrates the effect of emission current on HD exchange at 280 °C. The conditions and procedures for this experiment were maintained as discussed previously, except the emission current was varied from 0.125 to 0.375 mA/tip. The HD intensity peak significantly increased as the emission current was raised. This result confirms that dissociative attachment depends upon the number of electrons emitted from the cathode.

Figure 6. MS spectra showing the effect of emission current on HD formation.



Further testing was conducted to determine the effect of N_2 dilution on HD exchange at ambient pressure and 280 °C. In the gas mixtures tested, the H_2/D_2 volume ratio was maintained at 1:1, and N_2 was varied from 0 to 100 vol%. As anticipated, the peak HD intensity decreased with increasing N_2 dilution (Figure 7).

Figure 7. MS spectra showing the effect of N_2 dilution on HD formation at 280 °C.



In addition to the observed effect of N_2 dilution on HD exchange, no NH_3 peak was detected when EA was applied in the gas mixtures. It is known that 1) the ionization energy of H_2 is quite close to that of N_2, and 2) H_2 and N_2 ionizations, whether under high field strength or by collision with high-energy electrons, will cause NH_3 formation. The lack of an NH_3 peak further proves that the above-demonstrated H_2 and D_2 dissociations were indeed induced by dissociative attachment rather than by gas ionization.

C. Solder Surface Deoxidation and Reflow

To investigate fluxless solder reflow on a copper substrate under EA-activated H_2, tests were conducted on fluxless lead-containing and lead-free solder preforms which were made into pellet shapes (2 mm in diameter, 1 mm thick). Auger Electron Spectroscopy (AES) was used to measure the composition and thickness of the native oxide layer on the surface of each solder preform. For each test, a selected solder preform was placed on a copper plate (1 cm × 1 cm), which was set on the grounded anode inside the furnace. The furnace was heated under a gas flow of 4 vol% H_2 in N_2. EA was applied for ~10 minutes during heating, and the dynamic behavior of the melted solder was closely observed. It is known that when the native oxide layer on the solder surface is efficiently removed, the pellet-shaped solder preform normally bulges into a ball after reaching its melting point, then spreads out on the copper surface. These reactions are known as solder ball formation and solder wetting, respectively.

Table I shows the experimental results. The native oxide layers of most tin-based solders are tin-dominated, with a typical thickness of ~20–30 Å. These fluxless solders were successfully reflowed (including ball formation and wetting) by applying EA, in most cases at temperatures near the melting points of the solders. Without EA, however, wetting could not be attained at such low temperatures, even in pure H_2 [11].

Additional trials were performed using flip chips with electroplated solder bumps (90Pb/10Sn, 40 μm diameter) to demonstrate the feasibility of reflowing fluxless solder bumps under EA-activated H_2. During each reflow, either with or without applying EA, the test chip was set on the grounded anode with the solder bumps facing up, and heated from ambient temperature to 310 °C (slightly above the 305 °C solder melting point) in a gas mixture of 4 vol% H_2 in N_2. When the peak temperature was reached, the furnace was immediately cooled down under an N_2 flow. For trials including EA, it was applied during heating from 250 °C to 310 °C, with an EA exposure time of ~6 minutes.

Table I. Fluxless solder reflow in 4% H_2 balanced with N_2 under electron attachment

Solder Composition	Dominant Surface Oxides	Thickness (Å) of Surface Oxides	Std. Melting Point (°C)	Ball Formation Temp. (°C)	Wetting Temperature (°C)
63Sn/37Pb	SnO	30	183	181	197
90Pb/10Sn	SnO	30	305	305	306
96.5Sn/3.5Ag	SnO	30	221	226	226
99.3Sn/0.7Cu	SnO	20	227	226	228
95Sn/5Sb	SnO	20	240	237	242
48Sn/52In	In_2O_3	20	117	150	150

Figs. 8 to 10 are scanning electron microscope (SEM) micrographs of the initial mushroom shape of the electroplated bumps (Figure 8), and reflowed bumps without (Figure 9) and with (Figure 10) application of EA. In the absence of EA, the solder bump surfaces are quite wrinkled, and the bump height is small due to the oxide skin on the molten solder during reflow. Solder bumps reflowed under EA, however, have a very smooth surface and spherical shape, indicating an oxide-free solder surface.

Figure 8. SEM micrograph of electroplated solder bumps.

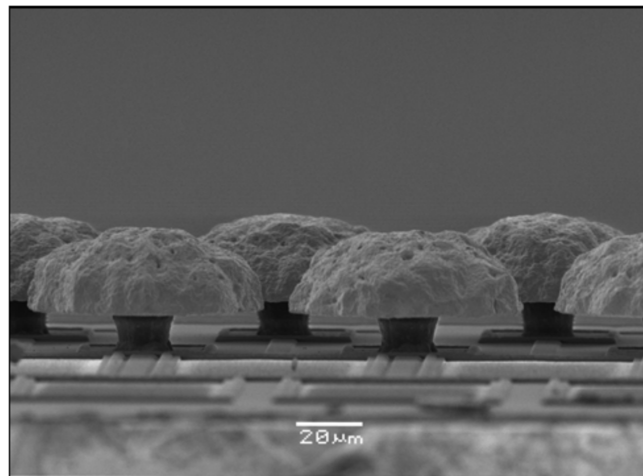


Figure 9. SEM micrograph of the reflowed bumps without applying EA.

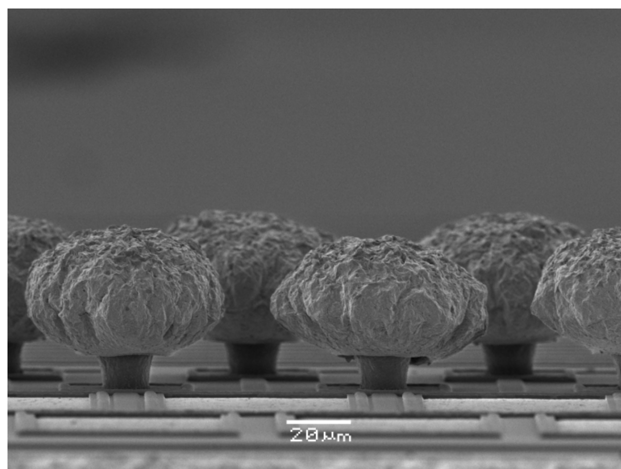
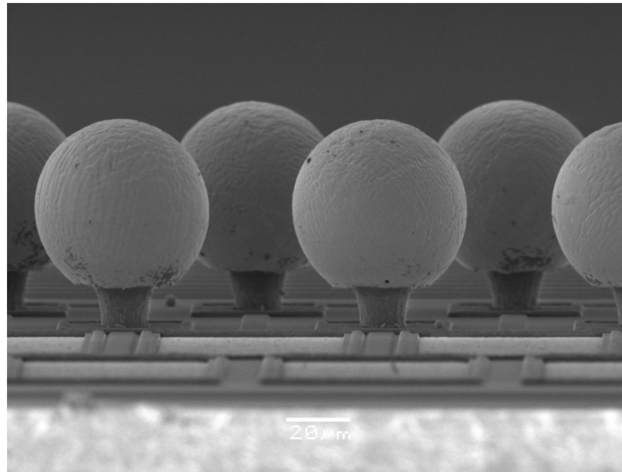
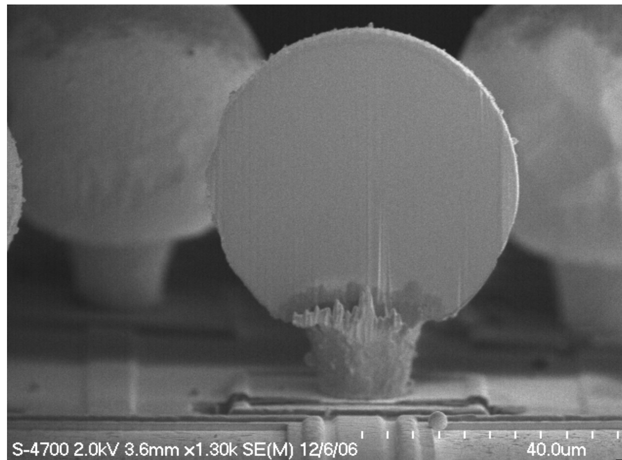


Figure 10. SEM micrograph of solder bumps reflowed by applying EA.



A focused ion beam (FIB) was used to cross-section a solder bump that had been reflowed under EA-activated H_2. Figure 11 shows good uniformity, with no void formation, across the entire diameter of the fluxless reflowed solder bump.Figure 11. SEM micrograph showing a cross section of a bump reflowed under EA.



X-Ray Photoelectron Spectroscopy (XPS) was used to analyze the surfaces of as-received and EA-treated copper plates to determine if any debris from the electron emission pins contaminated the surface of the EA-treated plates. Instead of using small solder bumps for this test, copper plates were used because a flat surface is generally preferred to minimize error of the XPS analysis. The EA treatment was conducted by heating the copper plate in 4 vol% H_2 in N_2 and maintaining the peak temperature of 330 °C for 10 minutes. EA was applied throughout the heating process, resulting in a total EA exposure time of ~20 minutes. As shown in Table II, results for the metals found in the emission pins (Ni, Cr, and Fe) are all "not detected," meaning that they are either not present or below the detection limit (<0.1 atm%).

Table II. XPS analysis of surface composition of copper plates (Atm%)

	Cu	Ni	Cr	Fe	O	C
As-received Cu plate	96.7	ND	ND	ND	0.8	2.5
EA-treated Cu plate	98.2	ND	ND	ND	0.7	1.1

ND = not detected

IV. Conclusions

We have employed a novel, EA-based technology for fluxless solder reflow for wafer bumping applications. This process utilizes EA to produce atomic hydrogen anions. Fluxless solder reflow can be achieved at ambient pressure and normal reflow temperature in a nonflammable concentration of hydrogen ($\leq$ 4 vol%).

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This technical paper provides just an overview of our capabilities for the electronics packaging and assembly industry.

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