Characterization of a Novel Fluxless Surface Preparation Process for Die Interconnect Bonding

Eric F. Schulte1, Keith A. Cooper1, Matthew Phillips1, Subhash L. Shinde2
1SET North America
343 Meadow Fox Lane, Chester, NH 03036
2Sandia National Laboratory
MS 1084, Box 5800, Albuquerque, NM, 87185
ericfschulte@yahoo.com
kcooper@set-na.com

Abstract

For applications such as 3D integration, flip chip, and other die interconnection processes, a variety of metals is used to form an electrical and mechanical bond between the two components. Native oxides, however, quickly form on many of the common bond materials, hindering the integrity of the joint and adversely affecting long-term reliability. A new method has been developed to reduce these surface oxides and passivate the exposed metal surfaces against re-oxidation. Avoiding the use of acids or the possible exposure to hot electrons, ions and highly energetic atoms of conventional vacuum plasma, the developed and tested processing is carried out in atmospheric ambient to remove native oxides from solders and contact metals, enabling consistent bonding at modest temperatures and bond forces.

The processing approach has been applied to a variety of metal and alloy surfaces, with bonding pursued over a range of forces and temperatures. Analysis of treated and untreated surfaces will also be presented, including SEM images and surface analysis techniques such as laser ellipsometry. Finally, physical bonding results will demonstrate the efficacy of the proposed atmospheric surface preparation approach, lowering the temperatures and bond forces required to achieve effective joining between component parts.

Introduction

In the push to reduce the footprint and power consumption of electronic components while maximizing their performance, technologists have pursued a variety of chip packaging techniques, including flip chip (FC), wafer-level packaging (WLP), and 3-dimensional integration (3DIC). While the first two have already been widely implemented for consumer devices, the third technique, 3DIC, holds the highest prospects for improvements, but also represents the highest challenges in technical implementation before adoption for widespread use in high-volume manufacturing.

Key to any leading-edge packaging technique is the choice of interconnect materials and bonding method, particularly the case for 3DIC. Chosen materials must exhibit strong adhesion to underlying surfaces, deliver excellent electrical and mechanical bonds, and be scalable to small dimensions, all within cost limits. Many interconnect materials are under consideration for filling through-silicon vias (TSV’s) or creating microbumps, with Cu, Ni and various solder compositions including SnAg and SnAgCu receiving a great deal of attention. [1-6.] Cu and its alloys seem to have taken pole position as interconnect material of choice, while Indium interconnects are also a good candidate and have been used widely in IR detectors, an early adopter of heterogeneous 3D integration.

Metal bonding surfaces typically have native oxides present which can compromise the effectiveness of the bonding process, and represent a persistent problem in device bonding. Because oxides generally adhere poorly to other metals or oxides, the bonding processes must break through surface oxides to establish metal-to-metal cohesion. Not only does this increase the required bonding force, but the oxides may also raise the electrical resistance of the formed joint. Even after bonding, the oxides may provide a convenient site for further oxidation, leading to reliability and performance problems. [7, 8].

The requirements for an oxide removal process have been previously outlined [9] and include:

- Fast, effective removal of native oxides
- Benign to other surfaces
- Minimal or non-existent residue
- EHS compliant
- Long-lasting
- Cost Effective

Historical methods for removing oxides have included mechanical scrubbing during bonding, use of an acid dip prior to bonding, or using oxide-removing flux during bonding. Though effective for previous generations of devices with larger bump sizes and less stringent operating conditions, they are insufficient for small feature sizes with tight alignment tolerances, small bond gaps, and tight performance specifications.

Conventional solder joints have long used either liquid or paste fluxes to remove surface oxides during bonding, but these fluxes must be thoroughly removed after the joining process lest the residual flux continue to attack metal surfaces and cause reliability problems. Numerous rinsing techniques and solutions (organic or aqueous) have been developed to remove flux residues, but the combination of smaller bump sizes, smaller bond gaps, and more rigorous reliability standards have driven the need for bonding without these liquid or paste fluxes. Similarly, an acid dip prior to bonding may have difficulty in wetting small bumps and gaps, will also require removal prior to bonding, and begins to re-oxidize immediately.

The need for fluxless bonding has been highlighted by numerous OEM’s and research organizations. [6,10] To avoid the use of liquid or paste fluxes, some have proposed
the use of an in-situ gaseous reducing environment surrounding the bond chamber, or a vacuum plasma treatment prior to bonding. While these may be effective at removing oxides and possibly other undesirable surface materials, they can add substantial capital expenditure or cycle time to the bonding process. For each of these methods, native oxides will re-form, necessitating additional hardware around the bonding area, or storing the prepared parts in an inert or reducing environment until bonding. In the case of vacuum plasma treatment, there is an additional risk of damage from ion bombardment or charge build-up which can harm sensitive CMOS components.

A new method of preparing bonding surfaces is herein proposed which employs a simple hardware set-up with processing performed at atmospheric pressure and temperature with common non-hazardous gasses. The apparatus consists of a compact atmospheric plasma source which is scanned across the surface of a wafer or die. Downstream active chemical species exit the source through a 25mm slit orifice which is translated above the substrate surface. A glow-discharge plasma, confined entirely within the plasma source, creates reactive chemical species which are flowed downstream to the substrate to remove surface oxidation and passivate the surface against subsequent re-oxidation. The downstream flow does not contain ions, hot electrons, or high velocity particles and therefore is safe to use on sensitive electronic components such as CMOS devices or focal plane detectors. Chips can be prepared for bonding in seconds. An 8” wafer is typically completed in less than 2 minutes. Since the system employs a scanning technique and does not require a vacuum chamber, the process is compatible with continuous production throughput.

**Experimental**

1.0 **Surface Treatment and Surface Analysis**

It is first necessary to characterize the effect of atmospheric plasma surface treatment on commonly used contact metals. Silicon wafers were coated with Indium, Aluminum, Titanium, Nickel, or Copper, and then diced into 10mm square coupons. Ellipsometer measurements were taken on the coupons at various stages of processing, and the raw “delta” (\(\Delta\)) angle reading from the ellipsometer was used as a relative indication of the oxidation existing on the coupon’s metal surface. Figure 1 illustrates the change in delta reading on an Indium coupon as it progresses from a freshly wet-etched surface (\(\Delta\) of \(-130.2^\circ\)) to a saturated native oxide surface (\(\Delta\) of \(-126.4^\circ\)) which corresponds to a native oxide thickness of approximately 28Å as determined by XPS profiling. Figure 1 also shows like plots for Aluminum, Titanium, Nickel and Copper.

Next, coupons of the candidate metals were scanned with the atmospheric plasma surface treatment system employing only gasses intended to reduce the native oxides from the surface (no passivation chemistry included). Figure 2, (for the example of Indium) shows a dramatic initial increase in ellipsometer \(\Delta\) corresponding to a removal of native oxide from the surface, followed by a gradual decrease in \(\Delta\) as the Indium surface returns to an oxidized condition in keeping with Indium’s natural oxidation rate.

However, with the passivation chemistry added to the surface treatment, Indium oxide growth is inhibited for many hours, as shown in Figure 3. Note that the treated delta reading for the passivated sample is slightly lower than that for the unpassivated sample. This difference is attributed to the 2-3 monolayers of passivation induced when passivation chemistry is added to the treatment.

![Figure 1. Ellipsometer response to native oxide thickness: as oxide grows thicker, delta decreases.](image1)

![Figure 2. Progression of Indium surface from native oxide, to treated (without passivation), to re-oxidized.](image2)

![Figure 3. When passivation chemistry is added to the surface treatment, Indium re-oxidation is inhibited for many hours.](image3)
Like results, achieved on other contact metal candidates, are summarized in Table 1. The “percent re-oxidation” refers to amount that the ellipsometer Delta value dropped (re-oxidation) over a 24 hour period following treatment, divided by the amount the Delta had risen (oxide reduction) due to the plasma treatment. It should be noted that the passivation parameters were optimized for Indium only, and those parameters were then used “as-is” for the other contact metals. Improving the effectiveness of the passivation for other candidate metals is a topic of ongoing investigation. The dramatic re-oxidation of Copper, even with passivation, may indicate that this surface could prove to be more difficult to passivate. It is theorized that this may have to do with Copper’s ability to continue to oxidize over time, as opposed to most other contact metals which tend to self-limit their native oxidation in the 20-80Å range.

Table 1. Re-oxidation of candidate contact metals after oxide reduction; compare with or without passivation.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Unpassivated: Percent re-oxidation (24h @ R.T.)</th>
<th>Passivated: Percent re-oxidation (24h @ R.T.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>69.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>86.0</td>
<td>13.8*</td>
</tr>
<tr>
<td>Titanium</td>
<td>83.3</td>
<td>8.2*</td>
</tr>
<tr>
<td>Copper</td>
<td>87.0</td>
<td>63.0*</td>
</tr>
<tr>
<td>Aluminum</td>
<td>49.7</td>
<td>25.1*</td>
</tr>
<tr>
<td>SnAg</td>
<td>75.0</td>
<td>2.0*</td>
</tr>
</tbody>
</table>

*Passivation not yet optimized for this metallization.

Figure 4. Oxidation of Indium at 100°C in air for varied surface treatment: i) Atmospheric plasma reduction and passivation; ii) HCl acid strip; iii) No treatment.

Since many interconnect bonding processes utilize elevated temperatures, it is necessary to determine the stability of the passivation at elevated temperatures. Indium coupons were treated with reducing and passivating chemistry and then subjected to 100°C hot plate bakes in air for up to 160 minutes. Figure 4 shows a re-oxidation curve for passivated Indium (solid curve) at 100°C. Also included in figure 4 are oxidation curves under the same conditions for a freshly wet-etched indium surface (dotted curve) and an untreated (as received) indium surface (dashed curve).

Although there is a slight slope to the atmospheric plasma-treated surface indicating a slight amount of Indium oxidation, it retains a significant advantage over a wet-etched surface or untreated surface. This reduced oxide level has been empirically shown to produce excellent Indium-to-Indium bump bonds at room temperature. The authors intend to develop like data for the other candidate metals in this ongoing investigation.

2.0 Empirical Bump Bonding Results and Discussion

As described in the introduction, native oxides on the surface of the bonding materials inhibit effective bonding. For many materials, this would be observed as a flattening or “coining” of bumps surfaces when bonds are attempted at low temperature or force. In these cases, a weak or non-existent bond would result, leaving a cold solder joint with little or no mechanical or electrical integrity.

Figure 5 – 70um Indium bumps with no surface treatment. The post-bond bump surface was compressed, but exhibited zero bond strength due to oxide interference.

Figure 6 – Indium bump with Atmospheric plasma treatment shows ideal shear within the Indium bulk, indicating a strong metallurgical bond at low force and room temperature (no reflow).

This effect is shown in Figure 5, where In was deposited in 70um diameter bumps on a test sample, then compressed against opposing In bumps with 1g/bump of bonding force at
room temperature. The bumps were compressed but the sample exhibited effectively zero bond strength.

Identical Indium bumps were treated with the proposed surface preparation, then bonded under identical conditions. After shearing, the SEM in Figure 6 shows tensile rupture within the Indium bulk itself, indicating that the bond strength is greater than the shear strength of the Indium.

A similar behavior employing atmospheric plasma treatment was observed with single-sided Indium bumps from a different source, where as-plated Indium bumps Figure 7 (upper) were bonded at 27°C and low force to a treated blanket Copper surface (Figure 7 Lower). Following shear testing, SEM analysis of bump and substrate show transfer of Indium bump material to the Copper substrate - a successful bond at room temperature with minimal compression.

Figure 7 – Shear test of Indium bump bonded to Copper. Both surfaces received atmospheric plasma treatment and then were bonded at room temperature (no reflow). Indium transfer to Copper sheet confirms metallurgical bond.

Likewise, the atmospheric plasma surface preparation was performed on single-sided SnAg bumps against a Copper substrate. Tack bond was performed at 185°C, then reflowed in air at 255°C. Untreated samples exhibited no adhesion, whereas treated samples showed good transfer of SnAg material from bump to substrate, as shown in Figure 8.

Figure 8 – Following Atmospheric Plasma treatment, SnAg cap on Copper pillar was tack-bonded to opposing Copper pad at 185°C in air, then reflowed at 255°C in air. Shear test shows SnAg remnants adhered to Copper pad.

An unexpected bonding benefit was discovered while bonding Gold pads to Gold pads for a Detector/Readout flip-chip configuration. Room-temperature bonding without plasma treatment had yielded very poor adhesion between Gold pads, even though there was significant visual pad-to-pad compression (Figure 9).

Figure 9 – Untreated Gold pads show adequate compression, but nearly zero adhesion following room temperature compression bonding and pull test.

Sister die were treated with the atmospheric plasma process and then bonded under identical conditions, yielding remarkable Gold-to-Gold adhesion. Pull-apart tests showed tensile rupture within the Gold bulk and adhesion was so good that many Gold bondpads were ripped away from the substrate, taking chunks of underlying Silicon with them (Figure 10).

While this was certainly a gratifying empirical result, we are still working to understand the effect that the plasma had on the Gold surfaces to enable the very high adhesion. We theorize that there may have been some form of hydroxide, adsorbed water, or organic on the surface following the Gold liftoff process, and that the plasma was able to remove this layer either by chemical reaction with the reducing chemistry, or by desorption due to the modest thermal energy of the downstream gas flow. We plan follow-on experiments to attempt to quantify this effect.
Figure 10 – Room temperature Gold-to-Gold bonding after atmospheric plasma treatment showed exceptional adhesion – enough to rip the underlying Silicon apart at pull-test.

Conclusions

Atmospheric plasma has been demonstrated to reduce surface oxides and enable low-temperature, low-force bonding of conventional interconnect bonding materials. The process eliminates the need for flux, acid etching, or a vacuum preparation chamber. The apparatus is relatively simple and is capable of rapid continuous throughput while employing non-hazardous chemistry.

Effective bonding at room temperature and low force has been demonstrated for Indium-to-Indium, and Indium-to-metal pad (such as Copper, Nickel or Titanium) and Gold-to-Gold. SnAg-to-Copper bonding has been demonstrated employing a 185°C tack followed by 255°C reflow.

We will continue to explore the surface chemistry of the atmospheric plasma process and to characterize its effect on a broad sampling of interconnect metals. Our near-term goal is to optimize process parameters to achieve substantial reductions in required force and temperature for a variety of conventional chip interconnect systems. Our long-term goal is to develop a reliable fine pitch chip-to-chip interconnect system enabling room-temperature assembly of multi-layer 3DIC structures.

References