

Cleaning RMA Flux Residues in a High Lead Wafer Bumping Process

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Abstract

During a wafer bump process using high lead (5/95 Sn/Pb) solder, an RMA flux is used for the solder reflow process following solder evaporation. Because the reflow temperatures reach 340-360°C, flux residues can be polymerized and are difficult to remove. A cleaning solvent with high solvency for flux residue is required, yet must not cause pitting or corrosion of the solder bumps. Additionally, the solvent must rinse clean and leave no detrimental residue that would affect the subsequent die-attach process for flip-chip packaging. Finally, it is attractive for the cleaning solvent to be recycled multiple times to prevent excessive amounts of waste. Environmental concerns were also considered during the selection of the cleaning solvent. To reach these goals, a semi-aqueous cleaning solvent combined with a centrifugal batch cleaner has been effective. The solvent is currently recycled through 800 cleaning cycles before being discharged to the wastewater stream.

Introduction

High performance flip-chip packages on ceramic substrates require high lead solder to be used on the chip side due to the hierarchy of subsequent reflow processes. In this process, the high lead solder is deposited sequentially (lead followed by tin) by an evaporative method. A typical RMA rosin-based flux is spun over the entire wafer, and the wafer is reflowed in an IR oven under a hydrogen enriched atmosphere. Subsequently, the wafer must be cleaned to remove the residue left by the flux. In a rosin-based flux the most prevalent compounds are organic acids that convert during high temperature reflow to carboxylic acid. It is important to remove carboxylic acid residues because they are hydroscopic and will contribute to corrosion of the solder. Additionally, during reflow at 340-360°C, the flux is polymerized and the residue can be very difficult to remove. Residue cannot be identified as harmful by a visual inspection, therefore it is best to remove all residues. Post-cleaning processes and properties, including die-attach reflow, underfill adhesion, and long-term reliability may be compromised by the presence of these residues.^{1,2,3} The intent here is to discuss some of the selection criteria used for both the equipment and cleaning chemistry, and also provide some of the data collected during process development and the manufacturing ramp.

Wafer cleanliness must meet the following criteria. 1. No active residues that will cause pitting or corrosion during storage may be present. 2. The solder bumps must reflow and wet the substrate contact pads during the subsequent assembly process. 3. The surface must be clean enough to insure good underfill adhesion. While it is desirable to have shiny silvery bumps in appearance, this objective is not necessary. The presence of color does not necessarily indicate corrosion products, nor does the absence of color prove the lack of corrosion products.⁴ Therefore, the ultimate test of wafer bump cleanliness is the performance of the bumps in subsequent packaging processing and use.

Cleaning Process Selection Criteria

In this application, the cleaning system is multiple use. This objective grew from the desire to minimize initial capital costs and simplify the manufacturing process. Other requirements include adequately cleaned wafers, the chemistry must be environmentally agreeable, hazardous waste must be minimized, safety of the operators must not be compromised, and of course, the cleaning process (including operation, maintenance and process control) must not be cost prohibitive.

As part of the low-cost criterion, a triple-purpose cleaning system is desirable. Not only will this equipment clean wafers, but also flip-chip assemblies and BGA assemblies. Because the single piece of equipment must clean between the die and the substrate in flip-chip manufacturing, in-line aqueous spray cleaners were eliminated from consideration, as they have no method of delivering the cleaning chemistry to the small gap between the die and substrate. To limit the use of stored Class 1 solvents for safety reasons, vapor-degreasing equipment was eliminated from consideration. A batch centrifugal cleaner with different fixtures provides the capability of cleaning several package assembly sizes and both 6" and 8" wafers.

Centrifugal cleaners are an excellent choice to deliver the cleaning chemistry in small gaps and through small channels between solder bumps. Finally, centrifugal cleaning systems are compatible with multiple cleaning chemistry options, including hydrocarbon, semi-aqueous, saponifier, and aqueous cleaning agents. The Accel MicroCeF is the equipment selected for use in this operation. In this equipment the wafers are submersed and rotated in the cleaning solution at 80°C. Following the clean cycle, the wafers are rinsed with DI water at 60°C and dried with 200°C air.

The primary requirement for the cleaning chemistry is good flux solvency. It also should be free-rinsing and have a low surface tension and low viscosity so that the fluid will go in to small channels and gaps. In the very early phases of the program, five chemistries were selected for beaker-scale testing on flip-chip assemblies. Wafer testing was not performed because it was felt the flip-chip assembly cleaning would be more difficult due to the geometry of the parts. The chemistries evaluated included semi-aqueous, hydrocarbon, aqueous with saponifier, and full aqueous chemistries. Beaker-scale testing eliminated full aqueous and aqueous with saponifier chemistries. Semi-aqueous and hydrocarbon chemistries performed nearly the same in beaker-scale tests. Ionox HC⁶, a semi-aqueous hydrocarbon chemistry, was selected because it had more desirable EHS characteristics than the other chemistries under consideration. This chemistry has a high flux solvency yet very low flammability, a mild odor and is biodegradable.

Results

One of the difficulties in evaluating the cleanliness of wafers is finding an analytical technique. Surface analysis techniques like X-ray spectroscopy for chemical analysis (ESCA) or time-of-flight secondary-ion-mass-spectroscopy (TOF-SIMS) are precise, but are practical only to measure a few solder bumps out of the thousands that are on the wafer. ESCA cannot assign the elemental results to molecules, so it is unknown if the residue is flux or cleaning agent or from another source. Visual techniques, microscopic inspection and scanning electron microscope (SEM) are not quantitative and are also difficult to evaluate over the entire wafer. Gas chromatograph-mass spectroscopy (GC/MS) has the potential to be a valuable tool. The wafer is rinsed with a known quantity of solvent (in this case, acetone). The solvent is collected and analyzed via gas chromatography. The different fractions coming out of the gas chromatograph are analyzed with a mass spectrometer. Theoretically, in this manner one can obtain molecular fragment identification and quantitative comparisons of residue. This method was tried with several product wafers. Unfortunately, the technique is so sensitive that it identifies molecular fragments from photoresist and the polyimide passivation layer, in addition to flux and cleaning residues.

ESCA results presented in Table 1 show that cleaned samples have much less organic contamination than uncleaned samples. All carbon residues are eliminated after a slight sputter on the surface. The uncleaned samples still have a significant amount of carbon present even after a surface sputter.

Table 1. ESCA results for cleaned and uncleaned wafer bumps.

Sample	Carbon	Nitrogen	Oxygen	Tin	Lead
Cleaned	50.8	1.5	30.4	4.6	12.7
Cleaned	45.9	3.0	32.0	2.2	16.8
Cleaned (sputtered 6 nm)	0.0	5.7	18.8	8.3	67.2
Cleaned (sputtered 6 nm)	0.0	6.0	20.5	7.5	66.0
Uncleaned	89.7	0.2	8.8	1.1	0.2
Uncleaned	87.4	0.0	9.2	1.6	1.8
Uncleaned (sputtered 6 nm)	81.8	3.0	1.9	2.3	11.0
Uncleaned (sputtered 6 nm)	46.3	6.5	0.0	5.1	42.1

A similar experiment using GC/Mass spectroscopy confirms these results with the data displayed in Table 2. The wafers used in both the ESCA and GC/MS experiment did not have polyimide passivation on the surface. The polyimide tends to complicate the analysis since it provides a source for organic

contamination. The molecular fragment eluded at 12-14 minutes from the cleaned wafer rinses has been matched with the cleaning chemistry. The amounts displayed in Table 2 for the cleaned wafers represent ion abundance measured by the gas chromatograph and translate to sub-microgram levels of contamination. Many fragments eluded from uncleaned wafer rinses match with RMA flux. Types of flux fragments include aliphatic amides, aliphatic carboxylic acids, and nonylphenol. For clarity, only two of the fragments abundance levels are shown in Table 2. The elution time of 18.5 minutes corresponds to an unsaturated aliphatic acid and 20.7 minutes an aliphatic amide. The amount of residue is quite variable on the uncleaned wafers.

Table 2. GC/MS results from cleaned and uncleaned wafers (without polyimide passivation).

Sample/Elution Time	12.8 (flux)	18.5 (flux)	20.7 (flux)	12-14 (cleaning chemistry)
Cleaned	0	0	0	30,000
Cleaned	0	0	0	14,000
Uncleaned	30,000	290,000	260,000	0
Uncleaned	17,000	0	70,000	0

Finally, SEM photographs shown in Figure 1 and Figure 2 provide a visual illustration of how well the cleaning chemistry removes RMA flux residues. It is clear that the dark residue present on the uncleaned bumps is removed during cleaning. Additionally, some of the small, extraneous solder balls (satellites) surrounding the main solder bump are removed during centrifugal cleaning.

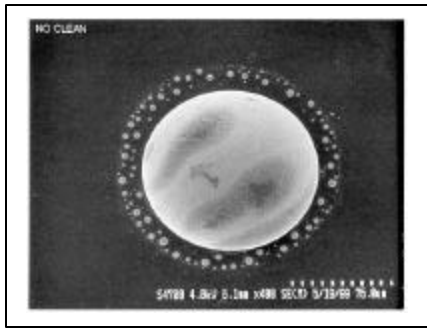


Figure 1. Uncleaned solder bump with satellites.

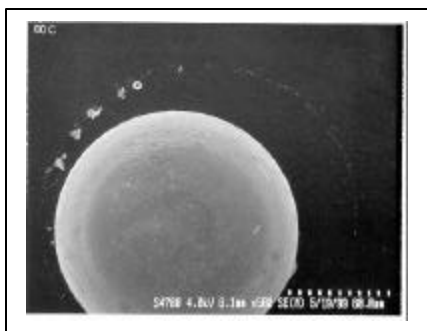


Figure 2. Cleaned solder bump with satellites.

Both ESCA and GC/MS analyses indicate that some of the cleaning chemistry remains on the solder bumps. This observation is confirmed by TOF-SIMS analysis. Several wafers were evaluated using TOF-SIMS in an attempt to identify different types of coloration observed on the surface of the solder balls. While no conclusions were made regarding color, all of the wafers have residue identified as the cleaning

chemistry. Table 3 displays these results. By far the most prevalent contaminants are sulfur, polydimethyl siloxane (PDMS) and dioctylphthalate (DOP). Comparisons with other contaminants found by TOF-SIMS show the cleaning chemistry residue is insignificant. TOF-SIMS is an extremely sensitive tool for surface analysis, but it identifies only the top monolayer of material. Therefore, because tin and lead are by far the most prevalent materials identified in this analysis, we concluded the contamination will have little effect on the performance of the solder bumps. Additionally, no adverse adhesion or voiding has occurred in the underfill reliability testing of the assembled packages.

Table 3 TOF-SIMS analysis of cleaned wafers

Prevalence of Contamination	Wafer 1 (control)	Wafer 2	Wafer 3	Wafer 4
1	Sulfur	PDMS	PDMS	Sulfur
2	PDMS	Sulfur	Sulfur	PDMS
3	DOP	DOP	DOP	Copper
4	Cleaning Chemistry	Cleaning Chemistry	Cleaning Chemistry	Cleaning Chemistry
5	Copper	Copper	Copper	DOP

Cleaning Temperature Effects

As expected, the cleaning chemistry properties change with temperature. The recommended operating temperatures are 50-70°C, where the optimum solvency, free-rinse properties and surface tension occurs. Data supplied by the vendor and presented in Table 4, illustrates temperature effects on the solvent. While surface tension actually increases with temperature, the viscosity and rinse properties are enhanced. Viscosity was measured by a capillary tube method. Rinse time is the amount of time it takes a dye-doped sample of chemistry to be removed by DI water from beneath a 2” die at a 1.5 mil standoff. Time-to-wet is a similar measurement, the time it takes for a dye-doped droplet to travel under the length of a 2” die at a 1.5 mil standoff. Most of the enhancements to performance occur between room temperature and 60°C.

Table 4. Cleaning chemistry property changes with temperature

Temperature (°C)	Viscosity (centipoises)	Time to Rinse (mm:ss)	Time to Wet (sec)	Surface Tension (dynes/cm)
22	9.06	12:30	90	21.2
49	4.60	No data	No data	25.4
60	3.31	3:15	15	26.8
77	2.33	1:14	13	27.5

Due to the nature of the evaporative solder deposition process, small solder balls remain around the main solder bump after reflow. These are referred to as “satellites”. Satellites are formed during reflow from the evaporated solder to a spherical wafer bump. The satellites are not known to be a reliability problem, except for the following hypothesized effects. First, flux residue tends to collect around the base of the satellites, and since this is an active flux, it must be removed entirely to avoid corrosion. Second, satellites form on the passivation layer, and are not adhered as well as the solder bumps to the under bump metalization. Therefore, satellites are a potential underfill failure-mode during long-term use and during thermal excursions.

During initial process development, experiments showed that flux removal was better at 80°C than at 70°C. However, at 80°C the cleaning agent is more aggressive and causes some degradation in fixtures and seals in the cleaning equipment. An evaluation to compare cleaning at these two temperatures was only partially successful. Because the wafer samples had polyimide passivation on the surface, GC/MS results were not conclusive. Organic residues other than flux residue dominated the results. SEM photographs show visually

that the flux removal is approximately the same for the two temperatures. Figures 3 and 4 illustrate visually how satellite removal is much improved at an 80°C cleaning temperature. Therefore, the process conditions remain at 80°C. Remaining satellites are removed during subsequent process steps.

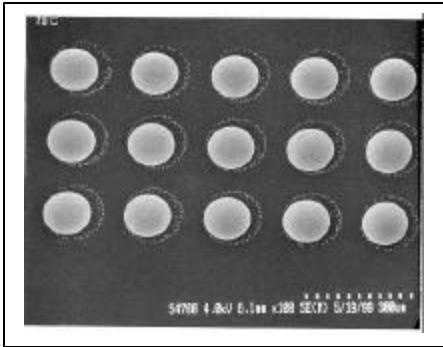


Figure 3. Solder bumps cleaned at 70°C, many satellites remain.

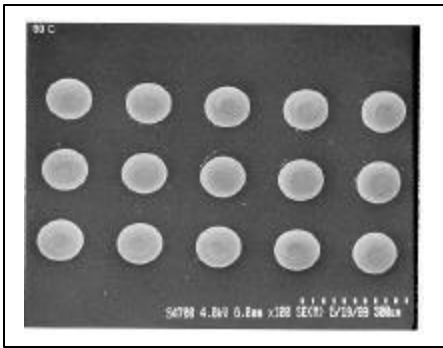


Figure 4. Solder bumps cleaned at 80°C, few satellites remain.

Minimizing Solvent Use and Handling

During development of the manufacturing process, the cleaning solvent was changed every 200 cycles. This was calculated to maintain a flux loading level below 1-2% by volume, as recommended by the manufacturer. Above this loading, the solvency of the cleaning fluid could be compromised. These initial calculations were “worst-case” and based the value on the amount of flux dispensed on the parts, not on the amount of flux remaining after reflow. As manufacturing demands increased, the replacement schedule proved to be a bottleneck. The solvent replacement procedure and subsequent heat-up time was impacting throughput. Additionally, the amount of solvent handled, used, and disposed was excessive. New calculations based on estimated flux residue after reflow indicated the cycles prior to solvent replacement could be increased to at least 800.

Determining contamination at such low levels in the cleaning solvent is difficult. GC/MS proves to be an excellent tool for this type of information, and has been used in a similar investigation.⁷ GC/MS data on the cleaning chemistry after 272 process cycles and 816 process cycles are presented in Figures 5 and 6, respectively. There are no indications that flux is present in the solution at the detection limit of around 0.01%. Figure 7 displays absorbance spectra from fourier transform infrared spectroscopy (FTIR) tests that also show the amount of flux residue in the cleaning solvent does not change the chemistry and is below detection limits.

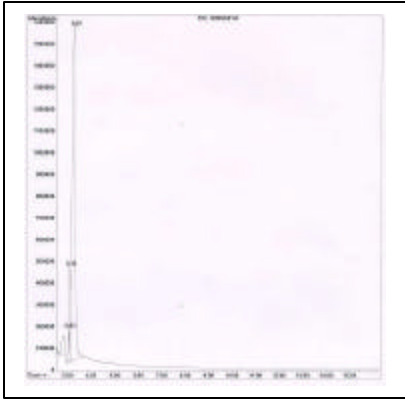


Figure 5. GC/MS of used cleaning chemistry, 272 process cycles.



Figure 6. GC/MS of used cleaning chemistry, 816 process cycles.

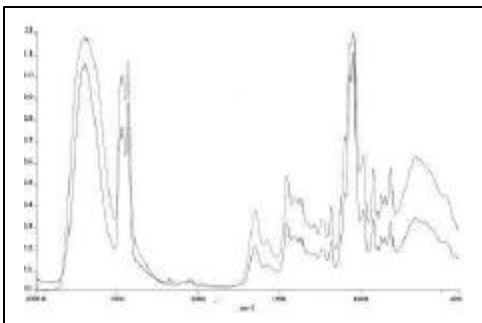


Figure 7. FTIR of fresh cleaning chemistry and used chemistry at approximately 200 cycles.

Process Control

Due to the centrifugal cleaning equipment design and the elevated process temperature, some of the cleaning solution water evaporates during each cleaning cycle. When the water level drops, the cleaning capability decreases so the water content must be carefully controlled. The refractive index is an indication of the amount of water in solution. As the water level drops, the refractive index increases. Therefore, the refractive index is used to indicate when water must be added to the reservoir tank. To maintain process

control, a hand-held refractometer is used once a week to measure the refractive index of the cleaning agent. A process control action limit has been set to indicate when water must be added to the solution. A process control chart for the past year, Figure 8, shows that about once per month the refractive index is out of the action limit (shown as the dashed line).

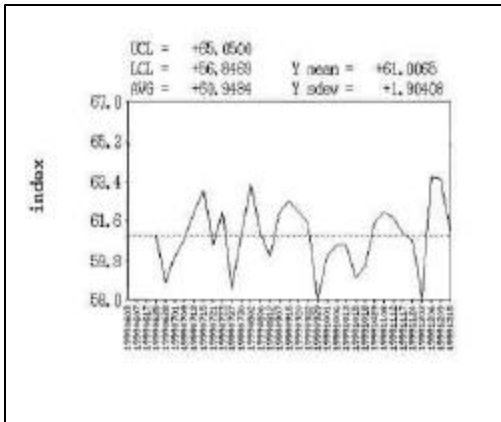


Figure 8. Process control chart for six months of manufacturing.

Conclusion

A batch centrifugal cleaning system combined with a semi-aqueous alcohol based cleaning chemistry has been very effective in cleaning RMA flux from the surface of wafers in a wafer bump/flip-chip assembly line. In two years of production, wafer cleanliness has never been identified as the cause of suspect parts or part failure. Regularly performed pull strengths from assembled packages show excellent wetting of the wafer bump to the substrate pad. Analytical tests and visual inspections indicate flux residues are adequately removed from the solder bumps. Costs have been minimized by using the centrifugal cleaner for multiple cleaning processes, and by increasing the time between cleaning solvent replacement.

Acknowledgements

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