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# Cleaning and Reflow of Pb-Sn C4 Solder Bumps

*The Pb/Sn electroplating process for C4 technology requires the ability to etch Ball Limiting Metallurgy (BLM) in the presence of the Pb/Sn bumps. Upon etching, a surface corrosion layer is formed and an appropriate cleaning acid must be used to remove this layer prior to solder reflow of the bumps. It was found that the morphology of the surface layer formed upon etching on the Pb/Sn solder bumps is critically dependent on the concentration of the etchant. Using a gravimetric test, XPS and AES analysis, PbO containing small amounts of Sn and S, was identified to be the primary component of the surface. The thickness morphology, composition and the growth rate of the layer are critically dependent on the sulfur from the etchant. In $H_2O_2$-rich solutions, the surface appears to be loosely packed and the growth rate on the surface of the bump was found to be reaction-rate limited; whereas, in $H_2SO_4$-rich solutions, the diffusion rate is the controlling step in forming the surface layer on the solder bumps, thus producing a thin and dense layer.*

## Introduction

Controlled Collapse Chip Connection (C4) is a technology where a semiconductor chip is interconnected to its package by an array of solder bumps. This solder-bump interconnection was originated by IBM in the early 1960s to remove several problems of manual wirebonding (WB). C4 has several potential advantages over Tape Automated Bonding (TAB) and WB. First, C4 offers a high input/output density by placing solder bumps anywhere on the chip. Second, interconnection by very small solder bumps lowers inductance, thus enhancing the overall electrical performance. Finally, C4 allows for lower process complexity due to the relaxation of pitch separation requirements between bumps and the self-aligning property of C4 die attach (Tummala and Rymaszewski, 1989, pp. 1151–1154).

This study focuses on C4 solder bumps to understand the Pb/Sn surface layer formation kinetics, as well as analysis of layer composition and morphology of C4 bumps after etching the base metal. In addition, the effect of using etchants for removing the surface layer to improve the solderability of solder bumps, and the etch rates and mechanism of the Ball Limiting Metallurgy (BLM) layer which typically consists of a proprietary mix of reactive and refractory metals, were studied.

Specifically, C4 was studied from three view points. First, the kinetics of reaction of the surface layer of the Pb/Sn and the BLM with sulfuric acid and $H_2O_2$ were studied in depth. The thickness variation of the surface layer, its composition, and the rate of growth of the surface layer were the primary features studied. A model was developed to examine the rate limiting step in the formation of these layers. The composition and morphology of those layers were also analyzed using XPS, AES, and SEM. Solubility testing was performed to confirm the spectroscopy data results. From these data, the optimal etchant composition which results in the thinnest surface layer and most efficient etch of the BLM layer, and its etch time was determined.

Second, removing the surface layer of the Pb/Sn before reflow, using the correct acid, is the most important step for good reflow of the solder bumps. The selection of acid can be determined using electrochemical properties of Pb/Sn solders and using the Pourbaix diagram for Pb compounds. The pH change of the acid was studied extensively and the solubility of the surface layer was determined (Pourbaix, 1974).

Finally, the BLM layer etch rate in the lateral and vertical directions was studied to determine optimal etchant composition. Forming a thin layer on the surface of the Pb/Sn using the correct composition of etchant is important, but it is equally important that the acid completely etches the BLM layer around the bumps.

## Experimental Procedures

**2.1 Thickness Morphology and Composition of the Surface Layer of Solder Bumps.** Blanket layers of the proprietary substrate metal or Ball Limiting Metallurgy (BLM) were deposited by Physical Vapor Deposition (PVD) on the wafer. Photoresist was then applied and patterned on the wafer using photolithography. The wafer was then subjected to electroplating of Pb/Sn bumps which were formed in areas not covered by resist as shown in Figure 1. After the plated wafer was prepared, the wafer was cut into dice to perform the experiments for the morphology and composition studies. A BLM etch batch of $H_2O_2$ and $H_2SO_4$ was prepared; the dice with Pb/Sn solder bumps were put in the bath and were agitated to etch the BLM layer; During the etch, a surface oxide layer was formed on the Pb/Sn bump. The concentration of $H_2O_2$ and $H_2SO_4$ was varied as well as the etch time to study the surface layer as a function of concentration variation in BLM etchant. Scanning Electron Microscopy (SEM) was used to study the thickness, the morphology of the surface layer and the etch rates of the BLM layer.

After the dice were exposed to various etchant baths, each die was cut into four pieces with a scribe. A cover glass with epoxy resin was then placed on the top of the die. This sample was heated on a hot plate till the resin changed to an amber color, and the epoxy resin hardened between the cover glass and the die. Then the sample was polished and mounted using SiC ranging from 400–1200 sequentially. Top view optical microscopy was used to determine when to stop polishing once the center of the bumps was reached. Then, finer alumina oxide papers were used successively for final polishing. Since the Pb/Sn solder bumps are very soft and are easily oxidized, they require very careful polishing. A microscope was used to observe the cross section throughout this polishing process. After making a cross section of the sample, it was put in a gold sputter system to produce a few angstroms of Au which would prevent

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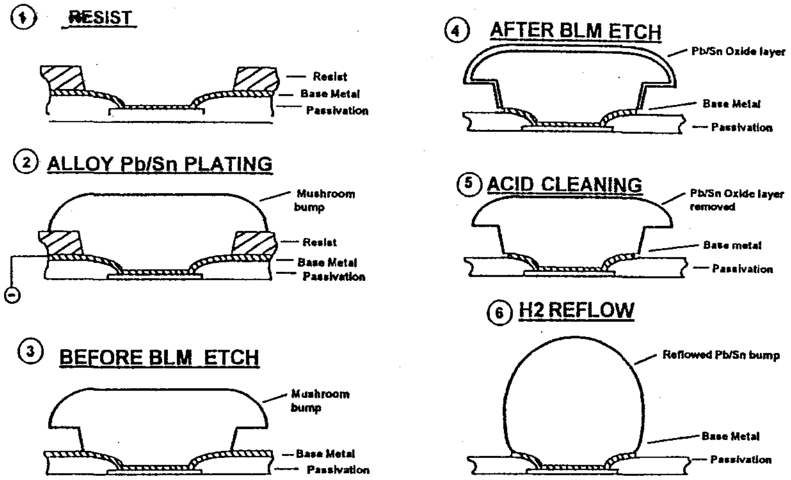

Fig. 1 Electroplating process

charging when using the SEM. The morphology and thickness of the surface layers of the bumps were then studied.

Several spectroscopic techniques were used to analyze the surface of the solder bumps such as Auger Electron Spectroscopy (AES), X-ray Photoemission Spectroscopy (XPS), Secondary Ion Mass Spectroscopy (SIMS), Energy Dispersive X-ray (EDX), X-ray Fluorescence (XRF), Atomic Force Microscopy (AFM), and Rutherford Backscattering Spectroscopy (RBS). AES, XPS, and SEM were the primary techniques.

XPS and AES were performed on Pb/Sn solder bumps before and after BLM etch. From the Auger Analysis data, the percentage of each element in the layer was calculated to determine the dominant compound in the layer. For XPS analysis, since the spot size was larger than the bump size, a blanket wafer plated with Pb/Sn was used. The blanket wafer was agitated in an etch bath at elevated temperature for 10 minutes. The wafer was cleaved to scan across the layer using XPS.

**2.2 Gravimetric Test of Pb Compounds.** Dissolution in the etching acids was used to study the solubility of different compounds. First, each beaker was filled with 120 ml of diluted 10 percent acid and the initial pH of the solution was measured using a pH meter. Then bulk samples of 100 PbO, 97.4 $PbO_2$, 96.6 $Pb_3O_4$, 100 $PbSO_4$, and 99.9 percent SnO were weighed and were dissolved in separate beakers. After the solution was agitated for approximately five minutes, the solution was filtered using a funnel. Then the final mass left on the filter paper was weighted and the solubility was calculated. Diluted 10 percent acid was buffered to a different pH to study the solubility of Pb compounds in the acid as a function of pH. These results were compared to the Pourbaix diagram.

**2.3 BLM Layer Etch Rate Study.** To measure the etch rate of the BLM layer in a lateral direction, a high sulfuric acid concentration of the BLM etch bath was prepared at an elevated temperature in an 8 gallon bath. The dice were agitated in the bath for times ranging from 30 seconds to 5 minutes. A precision cross section of the corner of each die at different time intervals was performed through the middle of the bump to view the overetch of the BLM layer using the SEM. This measured the undercut of the BLM layer underneath the bumps.

To obtain the etch rate in the vertical direction, blanket BLM layer deposited wafers were used. The wafers were premeasured on a RS55/tc Omnimap to obtain initial thickness. The thickness of the blanket wafers were approximately 8000A. Then each wafer was agitated in the same bath as above for times ranging from 5 seconds to 2 minutes. The final thickness was measured using the Omnimap, and the difference between initial and final thicknesses was calculated.

## Results and Discussion

**3.1 Thickness Morphology and Composition of the Surface Layer of Solder Bumps.** Precision SEM cross sections were performed to identify the thickness and morphology of the surface layer on the Pb/Sn solder bumps. It was found that the morphology of the layer is critically dependent on the etchant concentration. $H_2O_2$-rich solutions created a very thin and dense surface layer as shown in Figure 2. However, as the concentration of $H_2O_2$ relative to $H_2SO_4$ increased, the layer appeared to be more loosely packed and thicker as shown in Figures 3. The morphology was independent of the etch time although the thickness increased with time.

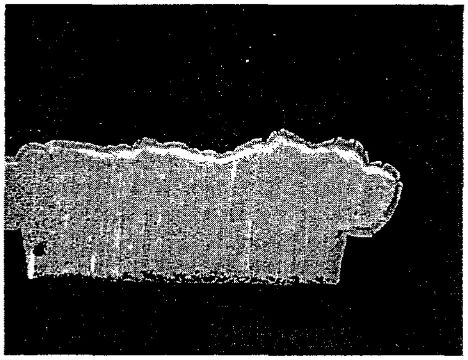

Fig. 2 Cross section of Pb/Sn solder bumps after 33% $H_2SO_4$ bath (4 min. etch)

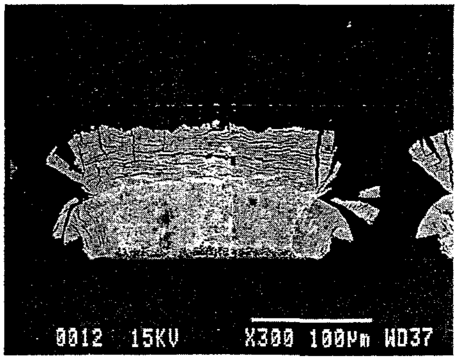

Fig. 3 Cross section of Pb/Sn solder bumps after 90% $H_2O_2$ bath (4 min etch)

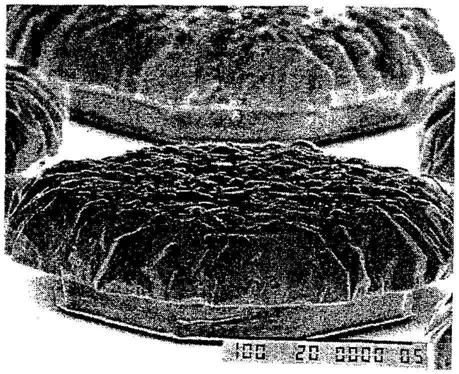

Fig. 4 Solder bumps before BLM etch

Fig. 5 Solder bumps after BLM etch

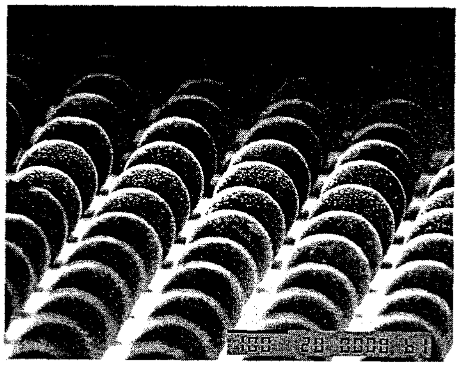

Fig. 6 Solder bumps after acid cleaning and after reflow

Auger Analysis was performed on bumps that were dipped in the $H_2O_2$-rich solution of the BLM etch bath for three minutes. These were reflowed in the furnace. SEM pictures of bumps are shown sequentially before dipping in the etch bath, after dipping in the bath, and after acid cleaning and reflow (see Figs. 4–6). After exposure to the BLM etchant, S, Sn, Pb and O were found as shown in Table 1. The percentage of Pb increased after acid cleaning indicating that as the surface of the bump was cleaned by the acid, fresh Pb was exposed. The level of Sn on the surface decreased after acid cleaning and reflow, due to formation of an intermetallic layer with the BLM. To find out about the bonding states of compounds, XPS was performed on the Pb/Sn plated blanket wafer with the same conditions as with the AES analysis. The limitation with XPS is that the difference in binding energy between $Pb^{2+}$ and $Pb^{4+}$ is less than 1eV. In addition, the charging effect causes peak shifts which make it harder to distinguish which peak corresponds to the surface layer. The binding energy peak on the surface layer produced with the 86 percent $H_2SO_4$ etchant bath was close to the binding energy peak for $PbO_2$. Moreover, the atomic concentrations of each element, before and after agitating in an etchant bath, are shown in Table 2. From these results, it is seen that the concentration of sulfur on the surface of the bumps after dipping in the BLM etch bath appear to be elevated. Also, the percentage of sulfur on the surface of the bumps was 10 percent higher after exposure to the high sulfuric concentration bath as compared to the low sulfuric acid bath. This higher percentage of sulfur could be the reason for the difference in morphology of the surface layer as a function of acid concentration by Auger analysis. Also, the concentration of sulfur was found to be higher at the top of the surface layer.

**Table 1 Percentage composition of surface analysis using AES**

| Element/ % composition | Before BLM etch (%) | After BLM etch (%) | After acid cleaning and reflow (%) |
|---|---|---|---|
| Pb | 38.50 | 40.20 | 54.50 |
| Sn | 15.80 | 3.01 | 8.47 |
| S | 15.20 | 17.20 | 17.60 |
| O | 17.00 | 27.60 | 19.39 |
| C | 13.40 | 12.00 | 0.04 |

**Table 2 Percentage composition of surface analysis using XPS**

| Sample/% composition | Pb | C | S | O | Sn |
|---|---|---|---|---|---|
| Pb/Sn bumps before BLM etch bath | 28.1 | 20.6 | 0 | 47.9 | 3.4 |
| Pb/Sn bumps after BLM etch bath | 19.4 | 2.3 | 28.9 | 49.2 | 0.2 |

According to the XPS results, the binding energy peak for the sample was 135.5 eV while the energy peak for $PbO_2$ is 136.3 eV; for PbO, it is 142.4 eV and for $Pb_3O_4$, it is 143.0 eV. Therefore, the peak that is the closest to the peak of the sample is $PbO_2$ although the peak value is not within the given range as determined from the National Institute of Standards and Technology (NIST) data. Since peak shifts occur due to charging and due to the experimental environment. By looking at graphs of standardized peaks for Pb compounds, the C peak was found to be shifted more than 1 eV; so, a gravimetric test was then performed to verify these results.

**3.2 Gravimetric Test.** The Pourbaix diagram for Pb (figure 7) indicates that there are different regimes for Pb oxides, depending on the pH and the electrode potential of the solution. A gravimetric test was performed to identify the surface layer and also to confirm the XPS results. With a detection limit of 0.1 g/l, this gravimetric test was performed by dissolving several chemicals, such as PbO, $PbO_2$, $PbSO_4$, $Pb_3O_4$, and SnO, in the diluted 10 percent acid. The pH of the acid before dissolving any oxide was approximately −0.53. No chemical except PbO seemed to be very soluble in the acid. Table 4 indicates the pH before and after these Pb compounds were dissolved in the acid. From this table, the PbO showed a dramatic pH change whereas the other compounds showed slight

**Table 3 Binding energy of Pb compounds according to NIST data**

| Compounds | Binding Energy (eV) |
|---|---|
| Pb | 136.4–136.9 |
| PbO | 137.7–138.2 |
| $PbO_2$ | 136.8–137.6 |
| $PbSO_3$ | 138.6 |
| $PbSO_4$ | 139.4–139.5 |

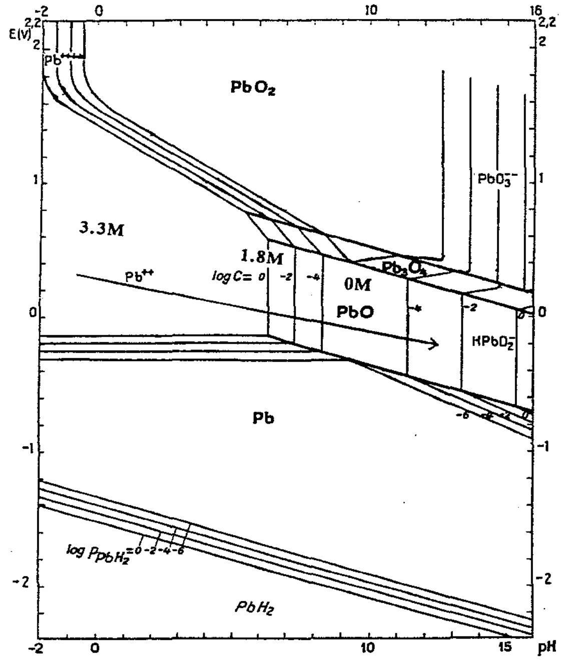

FIG. 1. Potential-pH equilibrium diagram for the system lead-water, at 25°C.

Fig. 7 The trend of solubility of PbO in the Pourbaix Diagram for Pb compound

pH changes, indicating that only PbO reacted with the acid, whereas the other Pb compounds did not. Pb compounds, except PbO, just remained in the bottom of the beaker giving a clear liquid on the top and the reaction temperature did not change. However, PbO showed very high solubility, forming bubbles initially, changing color of the solution to light yellow and finally increasing the temperature to 45°C. When the solution was filtered, the solubility was found to be approximately 405.6 g/l which is 1.82 M. After the solution saturated, the pH was about 6.03 whereas the initial pH of the solution without PbO was −0.53. In the PbO region of the Pourbaix Diagram, 1 M solution of PbO is in the aqueous state with a pH close to 6.5 which matches closely with the experimental values. Moreover, the graph indicates a decrease in concentration of dissolved PbO as the final pH becomes greater than 6.5. To demonstrate whether this is consistent with the experimental values or not, the acid solution was buffered to an initial pH of 13.0. At final pH of 6.67 in the saturated solution, the solubility of PbO was 0.032 M. This result is consistent with the Pourbaix diagram in that an order of magnitude change in concentration of PbO resulted as the pH increased by 0.5. As the final pH is less than 6.50, there is an increase in solubility when using the acid. From these results, we conclude that the bulk gravimetric test indicates the surface layer of Pb/Sn solder bumps is composed of PbO, having a solubility of 3.35 M at a final pH of −1.02 at saturation using gravimetric test and pH meter. The solubility of PbO is favorable until the final pH reaches 6.03 with a saturated concentration of 1.82 M. The solubility of PbO with different pH is summarized in Table 5.

**Table 4 pH measurement of Pb compounds using gravimetric test**

| Compounds/pH | Initial pH (pH of 10% acid) | Final pH (after Pb compounds were dissolved) |
|---|---|---|
| PbO | −0.53 | 6.03 |
| $PbO_2$ | −0.53 | −0.39 |
| $PbSO_4$ | −0.53 | −0.28 |
| $Pb_3O_4$ | −0.54 | −0.28 |
| SnO | −0.53 | −0.56 |

**Table 5 Solubility of Pb compounds**

| Initial pH | Final pH | Conc. (M) | Observation |
|---|---|---|---|
| −1.02 | −1.02 | 3.35M | 50% concentrated acid, white dense crystals formed and the temp. was 75°C. |
| −0.53 | 6.03 | 1.82M | Solution turned to ivory yellowish color and the temp. increased to 47°C (10% acid). |
| 0.77 | 6.66 | 0.032M | Solution turned to white color with reaction temperature of 55°C (10% acid). |
| 1.06 | 9.87 | 0 | PbO did not dissolve in the acid, maintaining its orange color at room temperature (10% acid). |
| 13.10 | 13.24 | 0 | same as above except that the color of PbO was heavy orange (10% acid). |

From Table 4, $PbSO_4$ was not soluble which matches with the XPS analysis result; therefore, this test confirms the absence of any significant concentration of $PbSO_4$ in the surface layer. The identification of the surface layer contrasts with the results from XPS in that PbO is the probable surface layer instead of $PbO_2$. Thus the bulk solubility test appears to be more accurate than the XPS analysis. Therefore, PbO, containing small amounts of Sn and S, is believed to be the layer that has formed on solder bumps after reacting with $H_2SO_4$ and $H_2O_2$.

**3.3 Reaction Mechanism for Surface Layer Growth Studies of Solder Bumps.** To study surface layer growth as a function of the concentration of $H_2O_2$ and $H_2SO_4$, the $H_2O_2$ was varied with a constant ratio of $H_2O$ and $H_2SO_4$. The etch time was four minutes for each set of experiments. The thickness of the surface layer was measured by taking a cross section of the die. As shown in Fig. 8, as the concentration of $H_2O_2$ increased, the surface layer thickness increased dramatically, proportional to the concentration level of $H_2O_2$. At a low concentration of $H_2O_2$, the surface layer growth rate did not increase as fast as it did in the 35 percent or higher concentrations of $H_2O_2$. In the regions of 0 to 35 percent $H_2O_2$ solution, with 65–100 percent $H_2SO_4$. The surface oxide layer was thin (less than 5 $\mu$m). In the region of more than 35 percent $H_2O_2$, the thickness of the layer grew at a faster rate, resulting in a very loose layer of up to 45 $\mu$m as shown in Fig. 3. These high $H_2O_2$ solutions are not favorable for further processing even though the BLM is etched rapidly. It is difficult to remove the thick oxide layers and a dramatic volume loss in the bumps resulted. The rapid

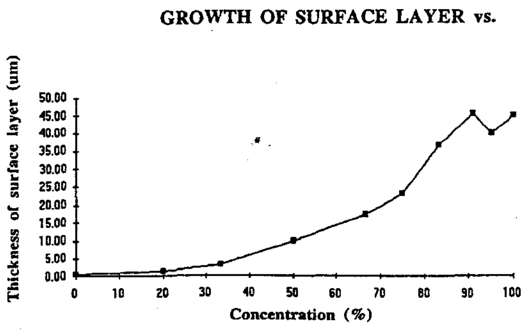

Fig. 8 Growth of surface layer versus concentration of $H_2O_2$ (4 min etch)

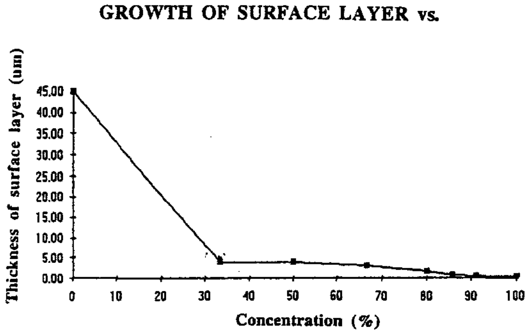

Fig. 9 Growth of surface layer versus concentration of sulfuric acid (4 min etch)

growth of the layers consumes the bump height by oxidation, and a faster growth rate of the surface layer will eventually result in uneven bump height which is not favorable for further processing. The reason for the rapid growth of the layer is that since this high $H_2O_2$ acid forms loose layers when there is no sulfate layer on the top to prevent the layer from growing rapidly, the reaction rate is much slower than the diffusion rate. Therefore, the reaction rate is controlling the growth rate. At 100 percent $H_2O_2$, the surface layer thickness reaches its peak at 50 $\mu$m. The layers remain loose and slough off when no $H_2SO_4$ is present. Many layers got washed away during rinsing, resulting in a 50 $\mu$m bump height reduction. Moreover, pure $H_2O_2$ did not etch the BLM layers at all. Therefore, rich concentrations of $H_2SO_4$ prevent a fast growth rate of surface layer formation on the Pb/Sn bumps while promoting the BLM etch. From Fig. 8, at 95 percent of $H_2O_2$, the thickness of the layer dropped about 5 $\mu$m, resulting in a drop in the bump height.

At 95 percent $H_2O_2$, the layer is very flaky and uneven, and it is difficult to measure accurate thicknesses of the layers. The effect of concentration variation in $H_2SO_4$ by keeping the other ratios constant was studied to further investigate the impact of $H_2SO_4$ on surface layer growth. SEM pictures for cross sections at different concentrations are shown in Figs. 2–3. Keeping these ratios constant, only the ratio of $H_2SO_4$ varied with respect to the other two components. As shown in figure 9, concentrations of 0–30 percent $H_2SO_4$ showed a dramatic decreasing trend in the thickness of the surface layer, resulting in a final thickness of 5 $\mu$m at 30 percent $H_2SO_4$ from an initial thickness of 45 $\mu$m. At 0 percent $H_2SO_4$, only oxidation of Pb/Sn solder bumps takes place. Therefore, $H_2SO_4$ plays a significant role in making layers denser and thinner. At up to 35 percent $H_2SO_4$ concentration, the growth rate of the surface layer of the solder bumps is rapid. This rapid growth is limited by the reaction rate where the thickness growth is proportional to the time. However, at $H_2SO_4$ concentrations more than 30 percent, a very low thickness of the surface layer, results. In this region, because the diffusion rate is the rate-determining step, the growth of the layer is slow. The overall thickness of the surface layer after etching in 35 percent $H_2SO_4$ was approximately 5 $\mu$m. The thickness difference between 30 and 100 percent $H_2SO_4$ was less than 3 $\mu$m as shown in Fig. 10. At 35 percent $H_2SO_4$, the layer decreased from 5 $\mu$m, eventually going down to 1 $\mu$m at 100 percent $H_2SO_4$. From these studies, having a large percentage of $H_2SO_4$ in solution will result in a zero order reaction where the thickness of the surface layer is less than 5 $\mu$m. Also, having a thin layer will make it easier for the acid to remove the layer so that these Pb/Sn bumps can be reflowed.

A combination of $H_2SO_4$ and $H_2O_2$ with a high concentration of $H_2SO_4$ is necessary, not only to produce a thin surface layer, but also for a fast BLM etch. Using these two figures, an optimal BLM etch solution concentration was determined as 86 percent $H_2SO_4$. At this concentration, the BLM is completely etched after 4 minutes and the surface layer is about 1 $\mu$m thick. In addition, the reaction of surface layer growth on the Pb/Sn is limited by the diffusion rate, resulting in slow growth of the layer.

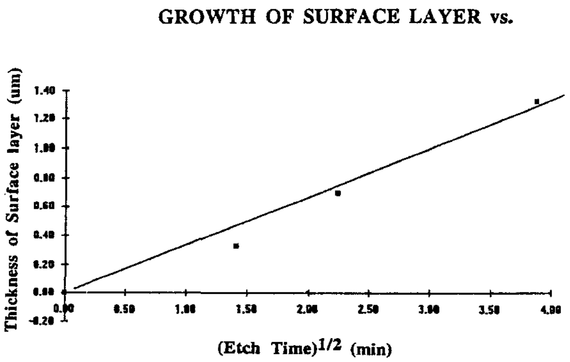

Fig. 10 Growth of surface layer versus (etch time)$^{1/2}$ in $H_2SO_4$-rich concentration

In $H_2O_2$-rich solutions, the surface layer of Pb/Sn bumps appeared to be loose and thick. Also, it was found that the surface layer grew linearly with time as shown in Fig. 11. The growth rate of the surface layer was approximately 1.1 $\mu$m/min. Since the growth rate of the layer is linearly proportional to time, this etch reaction is reaction-rate limited instead of diffusion-rate limited. Since the layer is loose and flaky, it appears the etchant is diffusing quickly through the layer, promoting the growth of the layer. The concentration studies seen in Figs. 8 and 9, demonstrate this result.

In sulfuric acid rich solutions, the morphology of the surface layer seemed to be dense and thin. It was found that the surface layer grew with the square root of time as shown in Fig. 10. Since the layer is dense and thin, this surface layer is preventing the etchants from diffusing through the layer, resulting in slow growth, which is diffusion-rate limited. From the results obtained, the presence of sulfur seems to be necessary to produce thin Pb/Sn surface layers. Free energy tables show $PbSO_4$ is more stable than any Pb oxide compounds. However, the gravimetric test showed that $PbSO_4$ is not soluble in the cleaning acid. Therefore, the surface layer must be primarily lead oxide. It appears that the thickness and the density of the surface layer is controlled by the very small concentration of sulfur on the top of the bumps. Based on these results, the following reaction for surface layer growth on the Pb/Sn solder bumps is proposed:

$$Pb + H_2O_2 \rightarrow PbO + H_2O$$

$$xPbO + yH_2SO_4 \rightarrow Pb_xS_yO_z + O_2$$

**3.4 BLM Layer Etch Rate Studies.** The acid concentration studies showed that the 86 percent $H_2SO_4$ etch bath creates a thin surface layer on the Pb/Sn bumps and etches the BLM

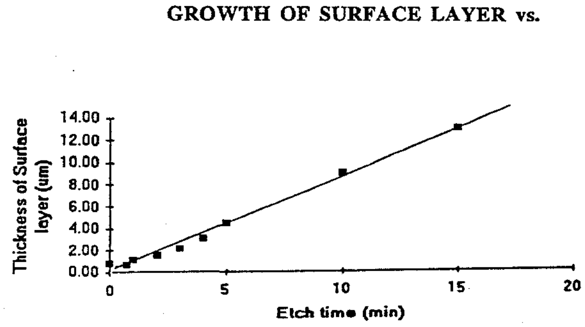

Fig. 11 Growth of surface layer versus etch time in peroxide-rich concentration

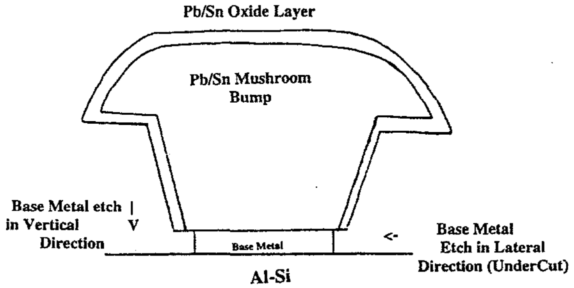

Fig. 12 Diagram of BLM layer in a lateral and vertical direction

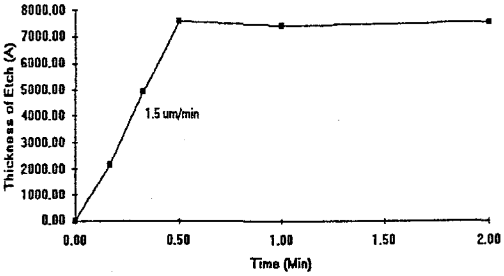

Fig. 14 BLM layer vertical etch

layer at a fast rate. During the time it takes to create a layer on Pb/Sn solder bumps, the BLM layer surrounding the bumps is etched away completely. To study the etch rate of the BLM layer in a lateral direction (Fig. 12), a cross section of bumps, through the center of the bump, was studied. The concentration of the etch bath was 86 percent $H_2SO_4$. Since the etch reaction is isotropic, the etch rate in a vertical and lateral direction should theoretically be the same. However, Figs. 13 and 14 indicate that this is not true. First, Fig. 13 shows that the lateral etch rate of the BLM layer is non-linear and seems to have three different stages. For the first two minutes, the etch rate is approximately 2.5 $\mu$m/min, which is very fast. This rate accelerates between 2 and 3 minutes, to an etch rate of 8 $\mu$m/min. From the graph, the region between 2 and 3 minutes seems to be the most active etch region, resulting in an undercut of 13 $\mu$m on both sides of the bump. Finally, the rate slows down to 1.75 $\mu$m/min between 3 and 5 minutes. There are several reasons for the nonlinearity of the rate. First, etching is taking place in a few thousand angstrom thick BLM layer space underneath the bump and the liquid flow is constrained by this limited thickness. Since the layer is so thin, the liquid flow is constrained, reducing the etchant transport. In the second region, the etch rate is the fastest, possibly due to liquid entrapment. Even after rinsing with water, the etching reaction is believed to have continued to occur from the remnants of the etching liquid in the undercut region. Moreover, the third region has the slowest etch rate, possibly due to fluid-flow problems since the deeper the undercut, the more difficult it is for liquid to flow freely through the thin layer. A curve-fitting line over the BLM layer lateral etch rate line showed the etch rate of the BLM layer in a lateral direction to be approximately 3 $\mu$m/min.

Figure 14 shows the vertical etch rate of the BLM layer. This etch rate on a non-bump area is illustrated in Fig. 12. From this graph, it takes about 30 seconds to remove approximately 7700 A of BLM layer at an etch rate of 1.5 $\mu$m/min, half of the etch rate in the lateral direction. After 30 seconds, the etch rate is constant which indicates that there is no BLM layer left to be removed. As shown in the graph, the reaction is linear in relationship. Thus, the etch rates in the vertical and lateral directions are found to be anisotropic. In order for the vertical etch rate to be close to the lateral etch time, the etch time should be 15 seconds instead of 30 seconds.

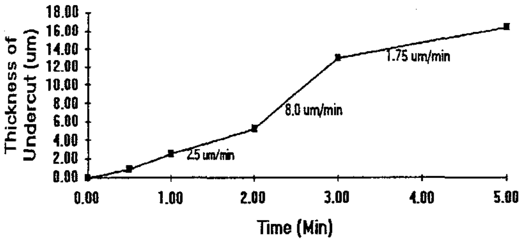

Fig. 13 BLM layer undercut etch

These differences between theoretical and experimental results might be due to several reasons, such as fluid flow mentioned above, fluid entrapment, the nature of BLM layer materials and experimental errors due to manual handling of wafers. Moreover, the flow is constrained by a few thousand angstrom thin layer with Pb/Sn bumps directly over it. This difference between theoretical and experimental results is a significant finding in learning more about etch rates in the BLM layer, and further experiments and investigations are required to understand these differences.

## Conclusions

Experiments to identify the effect of various concentrations of BLM etchant solutions on Pb/Sn solder bumps were performed. A thin surface layer was observed to be formed during the etching operation. This thin layer prevented the melting and the reflow of the bumps during subsequent thermal treatment. The reaction kinetics, composition and morphology of this layer were studied using various techniques. Based on these results, an optimum etch chemistry was determined to remove this BLM surface layer while not degrading the Pb/Sn bumps.

**Morphology and Composition of the Surface Layer on Pb/Sn Solder Bumps.** The morphology of the Pb/Sn surface layer was critically dependent on the etchant concentration, especially $H_2SO_4$, creating very thin and dense layers in $H_2SO_4$-rich solutions (Figure 2). However, as the concentration of $H_2O_2$ relative to $H_2SO_4$ increased, the layer appeared to be more loose (Fig. 3). The morphology of the surface layer was independent of the etch time although the thickness increased with time. Also, the layer on the surface appeared to be composed of multiple thin layers.

AES and XPS were both used in the current study. However, it must be noted that AES does not provide information about the bonding state and the XPS peak shifts due to charging. Pb, S, O, and Sn were identified as the primary components of the surface layer. XPS data interpretation was difficult because of the overlapping binding energy peaks between $Pb^{2+}$ and $Pb^{4+}$, so a clear determination of the exact nature of the surface layer could not be made. Gravimetric testing was used to identify the primary composition of the surface layer. Based on all of these tests, PbO, containing small amounts of Sn and S, was formed after the 86 percent $H_2SO_4$ etch. The final pH of 6.03 matches closely with the Pourbaix diagram. The maximum solubility found in the diluted 10 percent acid was approximately 1.82 M. Using 50 percent concentrated acid with an initial pH of −1.02, the highest solubility was shown to be 747.5 g/l. The solubility tends to increase as the final pH decreases from 6.03 and the solubility tends to decrease as the final pH increases (Table 5).

**Reaction Mechanism of Pb/Sn Solder Bumps in High and Low Sulfuric Concentration.** The impact of the BLM etch bath on Pb/Sn solder bumps were investigated. As seen from Fig. 11, the surface layer thickness was found to be proportional to the etch time in the $H_2O_2$-rich solution. This layer growth is reaction rate limited with a growth rate of 1.1 μm/min in the $H_2O_2$-rich solution. However, in the $H_2SO_4$-rich solution, the thickness of the surface layer is proportional to the square root of the time as seen in Fig. 10, suggesting a diffusion rate limited growth, agreeing with the thickness morphology studies. More studies were done by varying the concentration of $H_2O_2$ and $H_2SO_4$ (Figs. 8 and 9). From these studies, it was determined that the $H_2O_2$-rich region has a second order reaction while the $H_2SO_4$-rich region is a zero order reaction. A combination of these two solutions is needed to create a thin layer on the surface of solder bumps and to etch the BLM layer at the same time. The $H_2O_2$ tends to produce a faster, thicker surface layer than $H_2SO_4$ where a dense and thin surface layer is formed. The optimum etch bath was found to be a 86 percent $H_2SO_4$ solution where the resulting thickness of the surface layer was about 1 μm with a noticeable undercut in the BLM layer after 4 minutes of etch. In this solution, the diffusion rate is the controlling step in the slow formation of the surface layer. Based on these results, we propose the following reaction:

$$Pb + H_2O_2 \rightarrow PbO + H_2O$$

$$x\mathrm{PbO} + y\mathrm{H_2SO_4} \rightarrow \mathrm{Pb}_x\mathrm{S}_y\mathrm{O}_z + \mathrm{O_2}$$

*BLM Layer Etch Rate Studies.* After discovering the optimal concentration for the BLM etch bath, the etch rate of BLM layer was investigated (Figs. 13 and 14). In contrast to the theoretical predictions, where the etch rate in the vertical and the lateral directions is an isotropic reaction and should be the same, the two etch rates were found to be anisotropic. The overall etch rate was determined to be approximately 3 μm/min. These etch rate differences might be due to fluid flow problems, liquid entrapment and the metallurgical properties of the BLM layer. Also, the etch rate in the vertical direction was determined to be 1.5 μm/min, which was half of that in the lateral direction. Again, fluid flow related issues and liquid entrapment could be the primary reasons why the overall etch rate is slower in a vertical direction than in a lateral direction. Also, experimental error caused by the manual handling of the wafers might be a contributor to the differences between the lateral and the vertical etch rate.

In summary, several conclusions can be made. First, BLM layers were selectively etched after oxidizing the Pb/Sn bumps using $H_2SO_4$ and $H_2O_2$. Second, to identify the composition of the oxides on the Pb/Sn bumps, several spectroscopic techniques were used but some limitations, such as overlap between the Pb and sulfur peak, and very close binding energy of $Pb^{2+}$ and $Pb^{4+}$, narrowed the useful methods down to XPS and AES only. Third, the Pourbaix diagram and a gravimetric test were used to overcome the limitations of spectroscopic techniques. This diagram for Pb was able to show the composition of the Pb compound on the surface. Finally, the etch rate of BLM layer in the vertical and lateral directions were studied using SEM and Omnimap, and the experimental etch rate was found to be anisotropic.

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