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The formation of Cu_xSn_y intermetallic compounds in Controlled Collapse Chip Connection (C4)

Indu Aggarwal
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Aggarwal, Indu, M.S.

San Jose State University, 1994

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**300 N. Zeeb Rd.
Ann Arbor, MI 48106**

**THE FORMATION OF Cu_xSn_y INTERMETALLIC COMPOUNDS IN
CONTROLLED COLLAPSE CHIP CONNECTION (C4)**

A Thesis

Presented to

The Faculty of the Department of Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Materials Engineering

By

Indu Aggarwal

August, 1994

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Abstract

THE FORMATION OF Cu_xSn_y INTERMETALLIC COMPOUNDS IN CONTROLLED COLLAPSE CHIP CONNECTION (C4)

by Indu Aggarwal

The type of intermetallic compounds that are formed, by varying the Cu and Sn concentration during Controlled Collapse Chip Connections (C4) processing were studied. C4 samples for this study were prepared on silicon wafers by depositing layers of Cr-Cu-Au and 5%Sn-95%Pb solder followed by a reflow cycle at 350°C. Cu:Sn wt% ratios for the formation of different intermetallic compounds were determined. The effects of deposition sequence, thermal cycling, and presence of gold on Cu/Sn intermetallic compound formation were also studied. The results show that the intermetallic compound formed is independent of process conditions. It is either a Cu/Sn binary compound with an average ratio of 3.5:1 or a Cu/Sn/Au ternary compound with a Cu:Sn:Au ratio of 3.5:1:0.5.

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Chapter 1

Introduction

There is an ever increasing interest in computers since they make large information bases accessible and can perform complex mathematical computations in fractions of a second. The industry is constantly attempting to store and retrieve more information at lower cost and greater speeds. This can be achieved by manufacturing electronic circuits, the brain of the computers, of higher performance and at a lower cost. This demand for constant improvement has made the industry realize the importance of the technological limitations imposed by components and interconnections. Faced with physical limitations, their only recourse is to find alternatives.

There are many different electronic circuit components like resistors, capacitors, transistors etc. These components are connected to form circuits. To send and receive electrical signals, the individual circuits are connected to the substrate using an "interconnection" technology. These circuits are usually enclosed in a sealed package for the purpose of mechanical protection and heat dissipation. To improve the overall performance of a circuit, all aspects of circuit manufacturing, component interconnecting and packaging must be improved.

There are three major circuit interconnection technologies in current use. One of these technologies is called Controlled Collapse Chip

Connection (C4) and is the subject of this investigation. This connection technology has been gaining popularity with circuits requiring greater than four hundred interconnections in close proximity. This type of interconnection is also called "Solder Bump" or "Flip Chip" because the circuit is connected face down on the substrate using solder bumps. These connections are prepared using multilevel metal and solder depositions on the circuit and the substrate. Chromium, copper, gold, tin and lead are involved in the formation of these connections. The focus of this research was on the type of Cu/Sn intermetallic compounds formed and on the factors influencing the formation of these compounds. Cu/Sn intermetallic compounds, and the conditions of their formation in C4 have been considered the determining factor in the reliability of C4 technology. Several specimens with C4 connections were prepared and processed under predetermined conditions and investigated using optical metallography, scanning electron microscopy and electron dispersive X-ray spectroscopy for the purpose of determining Cu/Sn intermetallic compound formation.

The other types of interconnection technologies and their applications are reviewed in the following chapter. Chapter 3 discusses the details of C4 technology and its inherent reliability problems. Chapter 4 contains a review of the literature pertinent to C4 and intermetallic compound formation. The experimental methodology is described in Chapter 5, followed by results and

discussion in Chapter 6 and 7. The conclusions from this research are presented in Chapter 8, and the references are in Chapter 9.

Chapter 2

Background on Interconnections

The packaging of semiconductor devices is influenced by manufacturing cost, performance and reliability. A Multi Chip Module (MCM) is by far the best solution for increasing the density of chips packed in a given space. In a multichip package or module, a large number of chips are connected to one package rather than enclosing each chip in a package of its own. These multichip modules can contain up to one hundred chips on a single substrate. Figure 1 shows the chronological order of the development of single and multichip modules with respect to the number of pins (connections) per module. The connection of each chip to the substrate in a single chip package has been primarily accomplished by wire bonding. Two types of interconnections are used in multichip packaging: Tape Automated Bonding (TAB) and Controlled Collapse Chip Connection (C4).

2.1 Types of Interconnections

There are two classifications of connections between the chip and substrate. The first type of connections are Input/Output (I/Os) and are used for carrying electrical signals in and out of the chip. The second type of connections are the thermal connections that are necessary to dissipate heat generated in the chip. Three techniques have been used for I/O connections:

Figure 2: Number of Connections vs Interconnection Technology (ref.2, p.30)

2.1.1 Wire Bonding

Each chip has several Al alloy bond pads, made of Al alloy, to connect the chip to the power source. These bond pads are connected to the substrate with gold or aluminum wires. This process is called wire bonding and is the most common chip to substrate connection technology. It begins with the mounting of the device back side down on a substrate, using an adhesive such as epoxy. Heat and ultrasonic energy is used for attachment of the wire bonds. The shape of the bonds is a function of the wire bonding technique. Figure 3 is a schematic representation of a formed wire bond. Originally, wire bonding was a labor-intensive manual operation. At present, however, wire bonders are automated and can complete a bond in less than

Figure 3: Example of Wire Bonding (ref.2, p.392)

0.2 seconds. Wire bonding remains the technology of choice for devices having up to a few hundred I/O connections and a separation of greater than 100 μm between bond pads.

Wire bonding has limitations. This technology is adequate for single chip packages, where the number of connections or leads is manageably small and all the bond pads are conveniently located on the periphery of the chip. In multichip packages with highly dense circuits there are not only a large number of bond pads with significantly less space between them. The reliability of the wire bond connection is also inadequate due to a number of factors including inadequate strength of the wire bond itself, cracking caused by thermal cycling of the circuit, and the deterioration of the Au/Al interface at the point where the Al of the bond pad meets with the Au of the wire bond. These factors are currently driving the semiconductor package industry away from wire bonding to Tape Automated Bonding (TAB) and to Controlled Collapse Chip Connection (C4).

2.1.2 Tab Automated Bonding (TAB)

TAB technology was developed by General Electric Co. in the 1960s, and has been used for high speed integrated circuits (ICs) with greater than 300 I/O and thermal chip connections. It is capable of handling bond pad pitches of less than 100 μm . Application of TAB technology has gained

more ground recently as its reliability has improved. The TAB process involves the bonding of silicon chips to a metal-on-polymer tape (e.g. copper on polyimide), using thermocompression bonding. The devices are then tested and encapsulated first before being cut into individual packages from the tape and attached to the board by outer lead bonding. The outer lead bonding of an encapsulated device is shown in Figure 4.

The advantages of TAB connection include smaller substrate requirements, less expensive and a low failure rate. The package is also considered very reliable, and enables running of power and temperature stress tests while the circuits are still on the tape. Both sides of the chip are available for heat sink attachment to aid in heat dissipation. However, careful handling of the package is necessary since the leads are bent away from the package to avoid shorting of the wires to the chip. The relatively high cost of the tool shaping the leads, the possibility of damaging the top protective layer of the circuit while the connections are being made and difficulty reworking TAB connections are disadvantages of this technology.

Figure 4: TAB Encapsulation and Solder Joint (ref.2, p.412)

2.1.3 Controlled Collapse Chip Connection (C4)

The third type of chip to substrate interconnection is the solder bump or Controlled Collapse Chip Connection (C4) that has also evolved as an alternative to wire bonding for chips requiring hundreds of connections. C4 offers simultaneous and direct chip to substrate interconnects by means of solder bumps on the device and the substrate. An example of C4 bumps on a chip and substrate is shown in Figure 5. This type of interconnection has existed for more than thirty years but now is becoming more important due to the limitations of wire bonding. The advantages, deposition techniques and reliability concerns of C4 are further discussed in Chapter 3.

Figure 5: Controlled Collapse Chip Connection (ref.2, p.366)

Chapter 3

Controlled Collapse Chip Connection (C4)

Controlled Collapse Chip Connection technology, also called Flip Chip Bonding, was developed in the early 1960's at IBM as an alternative to manual wire bonding. Initially, the C4 connections were used in the peripheral region solely for low complexity chips. At present C4 connections are used for chips requiring 400 to 1000 connections dispersed over the circuit area. For example, it has been reported that IBM's 9370 computer has 762 solder bumps on a chip. Irrespective of the number and position of connections required, C4 bumps are deposited directly on the metal on the front side of the chip and then the chip is connected to an identical footprint on the substrate, as was previously shown in Figure 5. All the connections are made simultaneously by reflowing the previously deposited solder.

3.1 Evolution of C4

In the first flip chips IBM used soft solder and copper ball interconnections to connect the front side of the chips to the alumina substrate. These balls were also called electrode lands and they were used on the substrate and circuits.⁽³⁾ In addition to serving as interconnections, these electrodes were expected to reduce the electrical resistance of the joint. Small misalignments in electrode lands were corrected by the force of surface tension during the reflow cycle. The problem with this process was that the

edges of the chip either had excess solder or were not covered by a proper insulating layer. This resulted in an electrical short during the joining process due to the excess solder. In order to overcome this problem, the copper balls were replaced by the controlled collapse chip connections with higher bumps and with thick film glass dams or stop-offs to restrain the overflow of these bumps⁽⁴⁾. The constraints of this technology are that the joints should be high enough to compensate for substrate non-uniformity and the number of joints should be sufficient to support the weight of the chip.

3.2 Advantages of C4 Technology

The greatest process advantage of C4 is its self-alignment capability arising from the high surface tension of the solder. Once the chip surface and substrate pads come in contact and are reasonably wet, joining and aligning occur spontaneously. Another advantage is the speed of the process. Because it is a batch process, as many as a million C4 bonds can be placed on the chip in one or two steps. Since these connections are dispersed and not limited to the perimeter of the chip, they use less silicon area and make possible higher packing densities. The flip chip connection has distinctly better electrical performance such as minimal propagation delay and low signal transmission losses at high frequencies, because the distance between the chip and the substrate is relatively short compared to the other interconnection techniques. In addition, the bump technique also

protects the sensitive metal areas on a chip.

3.3 Deposition Layers in a C4

The critical step in C4 is anchoring the solder bump to the contact metallurgy on the chip and controlling the flow of solder on the chip. To achieve these two purposes, a sequence of thin film depositions are performed on the chip. These depositions constitute Ball Limiting Metallurgy (BLM) on the chip side and Top Side Metallurgy (TSM) on the substrate side. BLM also helps in sealing the exposed metal and provides a solderable, conductive base for the solder bump. A discussion on the purpose of each deposition layer follows.

On the device and substrate side, the first layer deposited is an adhesion and a barrier layer. Typically, a transition metal such as chromium is employed. Cr also has a high melting point and acts as a good barrier layer to the inward diffusion from the subsequent layers. Cr also has good adhesion to the aluminum on the chip. The thickness of the Cr layer is less than $0.5\ \mu\text{m}$, in order to keep the tensile stresses low and to avoid cracking. A phased layer of Cr and Cu is co-evaporated as the interdiffusion layer for Cr and Cu.

The third layer may be of copper or a similar metal, and is approximately $1\ \mu\text{m}$ thick. Copper aids in solder wetting by forming an intermetallic compound with the Sn in the solder. It also helps to decrease

the electrical resistance of the connection. A gold flash on the Cu is used to prevent the oxidation of copper and also reduces the corrosion susceptibility of the joint. The gold layer may not be necessary if the wafers are completely cooled after evaporation so that copper is not immediately oxidized when exposed to air. The advantages of gold have been controversial since it dissolves in solder during the reflow step. The last deposition is the solder bump with a height of about 15 to 20 μm and a base diameter of 100 μm . A typical thin film deposition sequence in a C4 connection is shown in Figure 6.⁽⁵⁾

Though the solder composition varies, the typical solder for C4 is 5%Sn-95%Pb. Since Pb and Sn have very different vapor pressures, in the evaporation process Pb is deposited first because it has a much higher vapor pressure. Sn is then deposited as the top layer.

After all the depositions are complete, these bumps are subjected to a reflow step. This step aids in reflowing and homogenizing the bumps. It is carried out in a furnace at about 350°C in H_2 atmosphere. The atmosphere in the furnace reduces any Pb and Sn oxides that may have formed and converts the shape of the bump from cuboid to spherical. The last step in the process is the chip join cycle. During this step, the solder bumps on the device side are connected to similar bumps on the substrate side in a self-aligning process as discussed previously.

Figure 6: Deposition layers in a C4 (ref.2, p.368)

After the C4 connections are made, all subsequent soldering steps are completed using eutectic solder, which melts at a much lower temperature than any other solder composition.

3.4 Deposition Techniques for C4

Metal mask technology and evaporation processes have been widely used for C4 fabrication. Vacuum evaporation through a metal mask has been reported to be the most suited solder deposition technique. In the evaporation process, the wafers are covered with molybdenum masks which have tiny holes for the bump deposition.⁽²⁾ The mask is held onto the wafer with the help of a clamp ring, a backing plate and springs. The mask, clamp ring and springs are shown in Figure 7. The vacuum is maintained in the range of 10^{-5} torr for deposition.

Cr, Cu and Au depositions are sequential and are done in one evaporator. Pb-Sn solder deposition takes place through the same masks but in a different evaporator. Pb-Sn deposition is a long cycle and the evaporator is difficult to clean after this deposition. The disadvantages of this process are the mask shadowing effect on the wafers and the non-uniformity of the bump size.

Photolithography for C4 fabrication is also gaining popularity. This process requires blanket depositions of the different metals, application of resist and the subsequent development of the bump pattern on the resist.

Figure 7: Metal Mask Technology for a C4 (ref.2, p.379)

Solder deposition is done by electrodeposition followed by resist removal and etching of the metal layers. Electroplating is also being used for the bump deposition.

3.5 Reliability of the C4

Repeated thermal cycling during the life time of a chip stresses the structural integrity of the interconnections, making it difficult to understand and improve the reliability of C4. The thermal mismatch between the solder and the chip results in unequal thermal stress on both sides and degrades the reliability of the C4 connection to the substrate.

3.5.1 Thermal Expansion Differences

All materials have unique expansion and contraction rates. The differential rates can create stresses in a connection and cause cracks or weak spots. This results in premature fracture and is referred to as thermal fatigue.

C4 has a thermal expansion mismatch between the substrate and the device. This can result in the shear displacement of each bump in a heat step. This displacement is proportional to the distance between a given pad and the neutral point (usually the center of a chip). It is often referred to as the Distance from Neutral Point or DNP. The chip center is usually considered the neutral point and its value is proportional to the size of a

chip. Thus the thermal mismatch is a greater problem with larger chips having denser C4 connections and corner pads. One approach to reducing the effect of thermal mismatch is to use substrate materials with a coefficient of thermal expansion close to that of silicon. AlN, SiC and Si have been used as substrate materials. The second option is to minimize the DNP. One of the techniques for reducing DNP related failures is to eliminate the corner pads in a die. By far, the greatest reduction in thermal strain is brought by matching the substrate thermal expansion to that of silicon. There are two common C4 fracture modes.⁽¹⁾ In the first, a crack initiates from the device side and propagates through the solder, and in the second, cracks propagate inward along the intermetallic layer.

3.5.2 Device Cooling

Heat dissipation and cooling of the device is an issue with all high density chips and all current interconnection technologies. The heat flow resulting from switching tens of thousands of circuits at high speed makes the need for cooling very acute. In addition, there is an increased density of chips closer together, resulting in a decrease in the surface area available for heat dissipation. A C4 connection itself is more resistive than a comparable back bond and the chip may overheat if the heat is not conducted away rapidly. C4 has an advantage in that the backside of the chip is free for the attachment of a heat sink.

3.5.3 Geometry of a C4

C4 reliability is determined by its shape, volume and height. In general, interface areas of contact should be as large as possible. A stretched or elongated C4, in the shape of an hourglass or barrel can also improve the reliability of the joint by switching the fracture location to the center of the joint. Self stretching soldering technology has been used to create the hourglass shape. The surface tension of larger bumps helps in stretching the lower volume bumps. Stacked solder bumps is another technique that is employed to improve the fatigue life of solder because it distributes the stress energy to different points on the bumps. These two options are shown in Figure 8 and Figure 9.⁽²⁾

Fig 8: Self stretching solder (ref.2, p.387)

Fig 9: Stacked Solder Joints using Polyimide (ref.2, p.387)

Chapter 4

Literature Review of C4 Technology

The literature review on C4 was undertaken to understand some of the previous experimental work in this discipline and to utilize the results and conclusions of these publications in the conduct of this investigation.

Another purpose was to understand why and under what conditions Cu/Sn intermetallic compounds should be formed in C4 technology and if the formation of one intermetallic can be predicted and controlled over another.

The experimental conditions and measurement techniques gleaned from these papers were used to determine if they can be extrapolated to aid in designing new experiments on C4 technology. In addition to these papers, binary and ternary phase diagrams of the metals in C4 were also studied to understand which Cu/Sn intermetallic compounds are thermodynamically more probable at the C4 reflow temperature.

Research on C4 technology has continued since the original development of C4 at IBM in 1964. The literature under consideration can be separated into three categories. These categories are: advantages of Cu/Sn intermetallic compounds, conditions for formation of Cu/Sn intermetallic compounds, and the probability of a Cu/Sn intermetallic compound formation based on the phase diagrams.

4.1 Advantages of Cu/Sn Intermetallic Compounds

Several publications have discussed the advantages of forming Cu and Sn intermetallic compounds in a C4 environment. A review of previous work in this area follows.

4.1.1 Solder joint strength due to intermetallic compounds

D.S.Dunn and his team studied the fracture strength of diffusion couples prepared with either Cu and Sn or with Cu and solder.⁽⁶⁾ The solder in these samples was 60%Sn-40%Pb by weight. The samples were aged at 60, 100 and 170°C for a total of 81 days. Their observation was that the fracture strength data, obtained by tensile tests, showed a difference in the behavior of Cu and Sn as compared to Cu and solder samples. Cu/Sn samples had a drop in the mechanical strength after 96 hours of aging time. The test samples failed by a sudden brittle fracture. It was postulated that the failure was due to the consumption of all the Sn in the intermetallic compound formation and the absence of Pb to absorb the tensile energy. In the Cu/solder samples, the fracture mode was ductile and there was an initial increase in the strength due to precipitation of the intermetallic compound. The conclusion of this paper was that intermetallic compound growth increases the fracture strength of Cu/solder samples. Both Cu_3Sn and Cu_6Sn_5 were formed in these samples but no single intermetallic

compound was identified to as being better than the other.

4.1.2 Intermetallic Compounds and Solderability

Jauwhei Hong related the type and thickness of the Cu-Sn intermetallic compounds formed to the solderability problems on the printed circuit boards.⁽⁷⁾ The purpose of a solder coating on the printed circuit boards is to improve the solderability of copper conductors. The solder coating used in Hong's experiment was of 60%Sn/40%Pb by weight. Solder plating and solder dipping were the two techniques used to deposit solder on the printed circuit boards. Optical metallography and X-ray diffraction were used to identify the Cu/Sn intermetallic compound.

The intermetallic Cu_6Sn_5 was found in the "as deposited" solder dipped and solder plated samples. The immediate formation of Cu_6Sn_5 indicates that this intermetallic compound was easily formed by the dissolution of the surface copper atoms by the solder. A thin layer of Cu_3Sn formed at the boundary between Cu_6Sn_5 and Cu when a thermal treatment was carried out for 1100 hrs at 120°C. Cu_6Sn_5 converted to Cu_3Sn by slow solid state diffusion. The exposed intermetallic surface acquired a dull and rough appearance during the conversion, indicating a degradation in the solderability of this surface. It was also found that the solderability of the coating diminished as more and more Sn was consumed in the intermetallic

compound formation with Cu and also with the conversion of Cu_6Sn_5 to Cu_3Sn . Figures 10 and 11 show counts from x-ray diffraction peaks in the "as deposited" and in the thermally treated samples respectively. The intensity of the peaks is directly proportional to the quantity of the intermetallic compound present. There is a high peak of Cu_6Sn_5 in the "as deposited" spectrum of the sample in Figure 10. This peak is much smaller in the samples after the infrared reflow cycle, as shown in Figure 11.

4.1.3 Role of Intermetallic Compounds in Solder Wetting

B.S.Berry and I.Ames performed a detailed study on the wetting characteristics of Cu, Cr and Au thin film depositions in C4.⁽⁸⁾ The layers were studied separately and in conjunction with each other to determine their effect on solder wetting. A 95%Pb/5%Sn solder pot was used to dip the samples.

Soldering with the Cu layer proceeded very rapidly and was complete within 10 seconds. This process resulted in a change in color of the sample to silver, providing a visual indication of the chemical change. With further dipping, the intermetallic layer began dissolving in the solder but did not lead to the complete exposure of the Cr layer. The reason was that with spalling of the intermetallic layer, stress was relieved from the Cr layer and resulted in a self-arresting process of leaving the residual intermetallic intact.

Figure 10: X-ray Diffraction Peak Counts in "as deposited" Samples (ref.7, p.150)

Figure 11: X-ray Diffraction Peak Counts after IR Reflow (ref.7, p.150)

Wetting did not occur with both unexposed and exposed Cr layers, due to the surface oxidation layer on Cr which does not wet or adhere to solder. An additional solderable layer is required for wetting the Cr layer. For the same reason, a Cu layer without an Au overlay does not wet solder because Cu has a surface oxide which is also a barrier to solder wetting. Figure 12 shows a section of a Cr-Cu-Au specimen after immersion in solder. As shown in this figure, the intermetallic layer on the top is thick and continuous with some spalling near its top surface. The authors of this paper did not undertake any analysis to determine the type of intermetallic compound formed.

Figure 12: Section of Cr-Cu-Au Sample after Immersion in Solder (ref.8, p.337)

4.2 Conditions for the Formation of Cu/Sn Intermetallic Compounds

D.S.Dunn and his group studied the growth rate of intermetallic compounds on single crystal copper substrates, using 60%Sn-40%Pb solder paste.⁽⁶⁾ All samples were aged at temperatures of 90, 125, 150 or 170°C for a total of 24 days. The aging temperature was below the melting point of any of the constituents.

Their results demonstrated that Cu and Sn form two intermetallic compounds, Cu_3Sn and Cu_6Sn_5 , at these temperatures though the Cu_3Sn layer was always thinner than the Cu_6Sn_5 layer. The thickness of these compounds as a function of the square root of time is shown in Figure 13. These graphs demonstrate the Arrhenius relationship because the thickness of the intermetallic compounds is proportional to the square root of time. The activation energy for the Cu and Sn reaction to form Cu_6Sn_5 was determined to be half that of Cu_3Sn , using the Arrhenius equation. This explains why the second intermetallic layer was always thinner than the first for the same aging time and temperature. In the temperature range of 90-170°C, the activation energy of Cu_6Sn_5 was determined to range between 0.41 to 0.57 eV as compared to an activation energy of 1.06 to 1.27 eV for Cu_3Sn . The Cu/Sn intermetallic compounds grew much faster when Cu and Sn were in direct contact. When Sn was a part of the solder matrix, it was not readily available for reaction with Cu.

Figure 13: Cu_3Sn and Cu_6Sn_5 Thickness as a Function of Time and Temperature (ref.6, p.132)

4.2.1 Intermetallic compound formation below 100°C

K.N. Tu experimented with three different Sn and Cu thicknesses in studying the intermetallic compound formation.^[9] These samples had Sn to Cu thickness ratio of 2:1, 1:1.7 and 4:1. The author expected that the first ratio would form Cu_6Sn_5 , the second ratio was Cu rich and the third was Sn rich. These layers were evaporated consecutively onto the fused quartz discs and were annealed at four different temperatures: -2, 20, 60 and 100°C, for 36 hrs. X-ray diffraction was used to analyze the type of intermetallic compound formed. The results indicated that Cu_6Sn_5 was formed in all samples but Cu_3Sn was formed only in samples annealed at or above 60°C. It was concluded that the mechanism of Cu_6Sn_5 formation was by mass transport along the grain boundaries since this compound was formed at or below room temperature signifying no kinetic barrier to its formation. Cu_3Sn was formed at comparatively higher temperatures because Cu diffuses interstitially in Sn and not vice versa. Figures 14 and 15 contain d-spacing and 4θ values from X-ray diffraction patterns of Cu_6Sn_5 (η) and Cu_3Sn (ϵ) in the Cu-Sn film. The conclusion was that the intermetallic compound formation was controlled primarily by the annealing temperature rather than by the Cu and Sn thickness. The second conclusion was that Cu_6Sn_5 was easily formed at all compositions and temperatures, whereas Cu_3Sn co-existed with Cu_6Sn_5 only in samples annealed at or above 60°C.

2θ (deg.)	d (Å)	Indexed as ordered	Indexed as long
		NiAs structure with $a = 4.19$ Å $b = 5.09$ Å	period superlattice with $a = 20.85$ Å $b = 25.10$ Å
49.10	3.60		501*
52.20	3.41		503*
60.65	2.95	101	505
63.75	2.74		515*
70.30	2.55	002	0,0,10
73.05	2.45		525*
79.20	2.27		535*
86.55	2.09	110	550
90.15	2.01		554*
107.50	1.72	201	10,0,5
114.15	1.61	112	5,5,10
120.85	1.54	103	5,0,15
126.15	1.47	202	10,0,10
142.65	1.32	211	10,5,5
154.35	1.23	203	10,0,15
158.85	1.21	300	15,0,0

* Long period superlattice line of η' .

Figure 14: X-ray Diffraction Data for Cu_6Sn_5 in Cu-Sn Thin Film (ref.9, p.350)

2θ (deg.)	d (Å)	Indexed as ordered	Indexed as
		orthorhombic lattice with $a = 5.514$ Å $b = 4.765$ Å $c = 4.329$ Å	long period super- lattice with $a = 5.514$ Å $b = 38.16$ Å $c = 4.329$ Å
52.15	3.40	101*	101
55.50	3.20	011*	081
64.89	2.75	200	181
67.00	2.67		191†
75.25	2.38	210*	280
77.65	2.32		290†
80.70	2.23		2,10,0†
83.85	2.16	002*	002
96.70	1.90	112	182
115.30	1.59	022	0,16,2
136.05	1.37	230	2,24,0
155.25	1.23	213	283
166.35	1.16	222	2,16,2
168.25	1.15	311	381

* Superlattice line of ϵ .

† Long period superlattice line of ϵ .

Figure 15: X-ray diffraction data for Cu_3Sn in Cu-Sn thin film (ref.9, p.350)

4.2.2 Intermetallic Compound formation in the presence of impurities

Michihiko Inaba and his associates studied intermetallic compound formation in soldered lead frames and with copper containing Fe, Ni and Sn.⁽¹⁰⁾ These metals are sometimes used as additives to increase the mechanical strength of copper based alloys. For sample preparation, pure copper samples were dipped in a eutectic solder bath at 260°C. The samples were then annealed in an oven for 300 hrs at 150°C. X-ray diffraction and electron probe microanalysis were used for analysis of the intermetallic compounds.

The presence of both intermetallic compounds, Cu_3Sn and Cu_6Sn_5 , was confirmed in all samples. The total thickness of both compounds was approximately 5.0 μm . As shown in Figure 16, Cu_6Sn_5 grew towards the solder or Sn side and Cu_3Sn grew towards the Cu side. Fe_3Sn was formed between Fe and Sn, where Fe was used as an additive. According to this paper, the two Cu/Sn intermetallic compounds are equally likely to be formed.

4.2.3 Formation of Intermetallic Compounds in solid state

P.J. Kay and C.A. Mackay studied the rate of intermetallic compound formation of Sn and solder on different metal surfaces such as Cu, Ag, Ni and brass.⁽¹¹⁾ The coatings contained 10 to 60% Sn, with the remainder

Figure 16: Growth of Cu, Sn and Fe Compounds in Soldered Lead Frame (ref.10, p.216)

being Pb. The maximum heat treatment temperature of 100°C was below the melting point of Sn or Pb. X-ray diffraction and microprobe analysis were used for identifying the intermetallic compounds. The solderability test was used to determine the wettability of the intermetallic compounds.

The results showed no correlation between the type of intermetallic compound and the physical or mechanical properties of the test sample. The compound layer formed on copper had a linear growth rate and consisted of both Cu_6Sn_5 and Cu_3Sn at all temperatures except at room temperature. A possible reason for the absence of Cu_3Sn at room temperature may be that the Cu_6Sn_5 formed may not have had sufficient thermal energy to convert to Cu_3Sn . The solderability tests showed that both intermetallic compounds were equally wettable when the surface was clean.

4.2.4 Solid state formation of Cu_3Sn

D. Gupta and J. Oberschmidt reported that Cu/Sn intermetallic compound formation was controlled by the diffusion process.⁽¹²⁾ Diffusion barrier layers, usually consisting of transition metals or intermetallic compounds, prevent migration of Pb from the C4 bump to the metal on the chip. The role of the intermetallic layer was considered important because it trapped free Sn into a stable layer and raised the melting point of the

sample. Since the intermetallic compound precipitated out into the grain boundaries, it reduced the grain boundary diffusion of solder.

According to this paper, the Cu and Sn reaction in C4 forms Cu_3Sn . The location of this compound is shown schematically in Figure 17. The advantages of this intermetallic are that it is a good electrical conductor and also provides good adherence to the Cr barrier layer and to the solder ball. Their paper showed no evidence of Cu_6Sn_5 with different Cu and Sn wt%.

Another publication by the same author linked Cu_3Sn formation with preventing grain boundary and lattice diffusion in C4.⁽¹³⁾ In this study, samples were prepared with 5%Sn and with Cu wt% ranging from 0 to 3.5%. These samples were annealed in vacuum for two days at 275°C to allow the grains to grow. The diffusion profiles were measured using Pb and Sn tracers. From EDX signal strengths, the intermetallic compound was identified as Cu_3Sn .

The intermetallic compound in these samples precipitated into the grain boundaries and increased the melting point of the matrix. It was also noted that the intermetallic compound was an ordered structure and would restrict random walk-diffusion of Pb because the movement of the elements disturbed the long range order of the matrix. In ordered phases, the diffusion coefficients are much smaller than in the disordered phases or in pure metals. These factors should result in decreasing the diffusion rate of

elements along the grain boundaries.

Karl J. Puttlitz studied the intermetallic compounds in C4 interconnections on a molybdenum substrate.⁽¹⁴⁾ In these samples, nickel was used as an adhesion layer on the molybdenum substrate and a gold cap layer was used on top of the Ni to avoid solder dewetting problems. In this environment, the intermetallic compound predominant on the device side was Cu_3Sn , along with a very low concentration of Cu_6Sn_5 . Two Au/Sn intermetallic compounds were detected in the solder bulk. There was AuSn scattered throughout the solder, as shown in Figure 18. Au_4Sn was identified on the gold rich side. The nickel and gold overlay, with all the intermetallic layers, is called a microsocket in these samples. The techniques used to identify the different intermetallic compounds were not made clear in this paper. The authors considered the intermetallic compound formation with Au, whether binary or ternary, undesirable because of brittleness and increased stress in the interface. The only advantage was an alloy formation between Au and Ni to form a barrier that is not consumed by the solder.

4.3 Intermetallic Compound Formation based on Phase Diagrams

4.3.1 Binary Phase Diagrams

This section reviews the phase diagrams of the elements employed in

Figure 17: Schematic of C4 Deposition and Intermetallic Compound Formation (ref.11, p.606)

Figure 18: Cu/Sn & Au/Sn Intermetallic Formation on Molybdenum Substrate (ref.12, p.362)

C4 formation. The purpose of this review was to understand what are the most probable intermetallic compounds at the C4 reflow temperature of 350°C. Referring to the Pb and Sn phase diagram shown in Figure 19, Pb and Sn do not form any intermetallic compound. They exhibit eutectic behavior at 183°C with a eutectic composition of 60%Sn and 40%Pb.⁽¹⁵⁾ Since the eutectic composition melts at a much lower temperature than Sn or Pb, any processing of the eutectic solder is possible at a lower temperature. The solder used in C4 has the composition of 5%Sn/95%Pb and melts at 315°C. The reflow temperature for this solder must be equal to or higher than its melting point. The higher reflow temperature for C4, as opposed to that of the eutectic solder, should cause faster diffusion rates of all constituents and may result in the formation of different Cu/Sn intermetallic compounds in C4. This would imply that the intermetallic compounds formed with eutectic solder cannot be assumed to be same as the ones formed in the C4 environment.

The Cu-Pb phase diagram did not list any intermetallic compounds, and hence it is not included here. On the other hand, Au and Cu exhibit total solid solubility at temperatures above 400°C as shown in Figure 20. At temperatures lower than 400°C, three ordered structures Cu_3Au , AuCu and CuAu_3 appear in the phase diagram.

Figure 19: Pb-Sn Phase Diagram (ref.15, p.1107)

Figure 20: Au-Cu Phase Diagram (ref.15, p.199)

The phase diagram of Au-Sn also shows several intermetallic compounds but most of these are in the molten state near 360°C, and have been ignored for the C4 reflow environment.

Since the reflow temperature of C4 is 350°C, the Cu/Sn intermetallic compound formation in this range is of interest and can be related to the reliability of C4. Figure 21 is the phase diagram of Cu and Sn and shows weight percent of Sn at the top and atomic percent of Sn at the bottom. The phase diagram shows three possible Cu/Sn intermetallic compounds at 350°C. One is the 'δ' phase with a Sn concentration close to 32% and a composition of $\text{Cu}_{41}\text{Sn}_{11}$.⁽¹⁵⁾ For most purposes, 'δ' can be considered stable at only above 350°C. This phase decomposes via a eutectoid reaction at 350°C, into two phases 'α' and 'ε'. A second intermetallic compound 'ε' formed by the transformation of 'δ' has a composition of Cu_3Sn which contains 39.2-41 wt% of Sn. The 'α' phase is pure Cu and is shown on the left side of Figure 21. A third intermetallic compound has a composition of Cu_6Sn_5 , labeled as 'η' phase in Figure 21, and contains 60.89 wt% of Sn. The 'η' phase undergoes a transformation into (eta prime) 'η'' the nature of which is uncertain. It has a hexagonal NiAs structure.

Figure 21: Cu-Sn Phase Diagram (ref.15, p.634)

4.3.2 Au-Cu-Sn Ternary Phases

No Au-Cu-Sn ternary phase diagram has been published in any references on phase diagrams or the JCPDS data files. There are a few recent publications on the existence of Au-Cu-Sn ternary compounds. However, the authors have not linked the presence of ternaries to the C4 deposition environment.

J.F.Roeder's paper reports the formation of two new ternary phases of Cu, Sn and Au.⁽¹⁶⁾ These two compounds were identified with compositions close to $\text{Au}_{25}\text{Cu}_{55}\text{Sn}_{20}$ and $\text{Au}_{33}\text{Cu}_{33}\text{Sn}_{33}$ using electron probe analysis. Diffusion couples were fabricated using Sn with Cu_3Au , CuAu or CuAu_3 . The alloys were then annealed at 170°C for 256 hours followed by quenching to room temperature.

The diffusion couple with Cu_3Au and Sn produced two phases, a binary phase Cu_6Sn_5 and a ternary phase ϕ , $\text{Au}_{24}\text{Cu}_{35}\text{Sn}_{32}$. The diffusion path for the couple is plotted on the isothermal section of the phase diagram at 170°C as shown in Figure 22. The second diffusion couple between CuAu and Sn showed an intermediate layer of AuSn_4 and three ternary phases ϕ , as already described, χ ($\text{Au}_{32}\text{Cu}_{32}\text{Sn}_{36}$) and κ ($\text{Au}_{23}\text{Cu}_{25}\text{Sn}_{51}$).

The third diffusion couple between CuAu_3 and Sn showed a complex mix of Au/Sn binary phases combined with a mix of the above-mentioned ternary phases. Kirkendall voids were visible on the Sn side indicating that it

Figure 22: Diffusion Paths Plotted on (170°C) Isothermal Section of Au-Cu-Sn System (ref.16, p.274)

is the fastest moving specie. Increasing the amount of Au had a direct effect on the number of compounds formed, inferring that it was the next fastest diffusion specie. The conclusion of this paper was that there were two new ternary phases ϕ and χ . The third ternary phase κ had been reported by other researchers.

O.B.Karlsen confirmed the presence of three Au/Cu/Sn ternary phases, using X-ray diffraction.⁽¹⁷⁾ The samples for this study were prepared by melting Au, Cu and Sn at 1100-1200°C for one minute and quenching in ice water. Some samples were annealed at 360°C. Three ternary compounds A, B and C were reported as shown in Figure 23. Phases A and B were found near 20 atomic % Sn and C was found near 33.3 atom % Sn. Phase A was stable between a composition of $\text{Au}_{43}\text{Cu}_{37}\text{Sn}_{20}$ and $\text{Au}_{49}\text{Cu}_{31}\text{Sn}_{20}$ at 360°C. This phase shows a structural relationship with the $\text{Cu}_{41}\text{Sn}_{11}$ phase. Phase B had a composition range of $\text{Au}_{12}\text{Cu}_{68}\text{Sn}_{20}$ to $\text{Au}_{36}\text{Cu}_{44}\text{Sn}_{20}$ at the same temperature. Phase C contained equal amounts of Cu, Sn and Au, with a tetragonal body-centred unit cell. Figure 23 shows the Au-Cu-Sn isotherm drawn at 360°C. Table 1 shows that the peak intensities of the three ternary phases and their most important crystal planes are present⁽¹⁷⁾. The peak intensities are listed in the left hand column as I/I_0 and the hkl plane is in the right hand column in Table 1.

Figure 23: Au-Cu-Sn Ternary Isotherm at 360°C (ref.17, p.197)

Table 1: X-ray peak Intensities for Three Au-Cu-Sn Phases (ref.17, p.198)

Phase A*			Phase B ^b			Phase C ^c		
<i>h</i> / <i>l</i> / <i>o</i>	<i>d</i> /pm	$h^2 + k^2 + l^2$	<i>h</i> / <i>l</i> / <i>o</i>	<i>d</i> /pm	$h^2 + k^2 + l^2$	<i>h</i> / <i>l</i> / <i>o</i>	<i>d</i> /pm	<i>h</i> <i>k</i> <i>l</i>
3	291	10	6	471	2	15	389	1 0 1
6	265	12	6	384	3	20	323	0 0 4
7	245.3	14	29	298	5	3	296	1 0 3
100	216.4	18	17	271.9	6	55	288	1 1 0
5	187.4	24	100	221.9	9	30	263	1 1 2
5	180.2	26	71	210.5	10	22	218.3	1 0 5
8	153.1	36	25	200.7	11	100	215.1	1 1 4
2	148.9	38	6	177.9	14	45	203.7	2 0 0
4	135.4	46	6	156.9	18	8	180.3	2 1 1
4	132.6	48	9	148.8	20	35	172.3	2 0 4
5	129.9	50	5	141.9	22	6	168.2	1 0 7
6	125.0	54	6	133.1	25	8	161.5	0 0 8
16	113.1	66	14	130.5	26	16	149.0	2 1 5
			5	128.1	27	20	147.9	2 0 6
			13	123.6	29	25	144.1	2 2 0
						3	140.9	1 1 8

*Au₂₀₀Cu₄₀₀Sn₂₀₀; quenched from 550°C; b.c.c.; *a* = 918.4(3) pm. ^bAu₂₀₀Cu₄₀₀Sn₂₀₀; quenched from 360°C; primitive cubic; *a* = 665.6(2) pm. ^cAu₃₀₀Cu₃₀₀Sn₃₀₀; body-centred tetragonal, *a* = 407.3(2), *c* = 1292.1(6) pm.

4.4 Conclusions of Literature Review

The presence of Cu and the Cu/Sn intermetallic compound was considered an essential part of the solder wetting of the samples. The formation of Cu_3Sn and Cu_6Sn_5 is diffusion controlled and most of the literature indicates that at temperatures below 200°C , the Cu_6Sn_5 phase forms more easily than the Cu_3Sn phase. In some papers, the poor solderability of solder joints has been attributed to the total conversion of Cu_6Sn_5 into Cu_3Sn with repeated thermal cycling however, there is no agreement across the board that Cu_6Sn_5 is better than Cu_3Sn or vice versa.

Au-Cu-Sn ternary compound formation is a relatively new discovery. The conditions of a ternary formation in C4 and the effect of these compounds on the properties of solder joints has not been explored very much.

This literature review did not provide an insight into the purpose and conditions for the formation of Cu/Sn intermetallic compounds in a C4. There was no stress data to determine the mechanical reliability of C4 interconnections in the presence of intermetallic compounds.

Chapter 5

Experimental Methodology

The experimental approach was based on the hypothesis that the type of of Cu/Sn intermetallic compound formed can be controlled by the amount of Cu and Sn available for reaction. Under the right conditions of temperature and composition, formation of the most stable intermetallic compound should be thermodynamically favored. The temperature of 350°C is of interest because the solder is in a molten state at this temperature, and two kinds of changes occur. The first change is the reflow of C4 bumps to a spherical shape and the second change is the reaction between the Cu and the Sn to form an intermetallic compound. There are two possible Cu/Sn intermetallic compounds near this temperature, depending on the weight percent of Cu and Sn. One of these intermetallic compounds is Cu_3Sn and it is expected to form with 39-41% of Sn and 60% of Cu by weight. The other is Cu_6Sn_5 and it is expected to form with 60% Sn and 40% Cu by weight. The third possible intermetallic compound is Cu_4Sn that exists only above 350°C and was not the subject of this investigation. Cu/Sn intermetallic compounds were shown in Figure 21 in Chapter 4.

5.1 Assumptions

Three assumptions were made, based on the relevant binary phase diagrams and other literature reviewed on C4. The first assumption was

that Pb does not play any part in the formation of Cu/Sn intermetallic compounds. This was based on the Pb-Sn and Pb-Cu phase diagrams. As shown in Figure 19 in Chapter 4, Pb does not form any intermetallic compounds with Sn or Cu. However, provides a matrix within which the reactions can occur. The second assumption was that at the reflow temperature of 350°C all of the Sn present in the bump will diffuse to the bottom of the C4 bump and would be available for reaction with Cu. This assumption was based on the fact that at the temperature of interest (350°C) Sn is in the molten state and is the fastest moving specie, hence, there should be no kinetic barrier to its movement. The third assumption was that the presence of Au does not affect the formation of Cu-Sn intermetallics. This assumption was based on the understanding that Cu/Sn intermetallics are more readily formed at this temperature based on the Cu/Sn, Cu/Au and Sn/Au phase diagrams.

5.2 Materials and Equipment

Specimens were fabricated on silicon wafers. Different metals were deposited on the silicon wafers, in the form of thin layers, using an evaporation process. After deposition, the reflow process was carried out in a furnace. The specimens were analyzed using optical metallography and electron diffraction X-ray analysis. For all these steps, the following equipment and materials were used.

- * Silicon wafers were used as the substrate material. They were 6" in diameter, had (100) orientation and were doped with boron, a p-type dopant.
- * Molybdenum masks, backing plate, clamp ring, clips and springs were attached to the wafer to provide the bump deposition only on the selected areas.
- * Sn, Pb, Au, Pb, and Cr were used for depositing all the layers of the C4. Cr was in the form of granulated powder, Au and Cu were in the form of pellets. Pb and Sn were in the molten form and each melt had different weight percentages of Pb and Sn.
- * An Ohaus balance was used for weighing the solder pellets.
- * A Balzers evaporator was used for the evaporation of solder and other metals.
- * A Watkins Johnson thermoguard belt furnace was used for reflowing the C4s.
- * A Hitachi Scanning Electron Microscope was used for optical metallography. SiC grit paper, a carbon coater and Al_2O_3 were used for the preparation of SEM and EDX specimens.
- * A Kevex Electron Diffraction X-ray analysis system was used for determining the elemental ratios of the intermetallic compound in the C4.

5.3 Specimen Processing Sequence

Metal mask technology, as shown in Figure 7, was used for depositing C4s on the wafer. The masks were held to wafers with springs, backing plates and clips. Bumps were deposited on the wafers through the holes in the masks. The process sequence was completed by depositing six layers. Since interaction with aluminum was not the focus of this work, it was eliminated completely from the specimen preparation and all the bumps were in contact with polyimide. Another purpose of eliminating aluminum from these specimens was to avoid confounding EDX data with the Al_2O_3 used in polishing specimens. In the actual device, the bumps are either in contact with aluminum or polyimide.

The initial step in the fabrication of the specimen was a 2 micron layer of polyimide, which was spread on the wafers by a wafer spinner. The four thin film depositions of Cr, phased Cr-Cu, Cu and Au were completed sequentially in a single cycle in the evaporator. The wafers were loaded on a planetary rotating around its axis, for uniform deposition. All metals were in separate crucibles and were melted using thermal energy supplied by resistive heating. The deposition sequence was pre-programmed on the evaporator which automatically controlled the power to the different crucibles. During all depositions, the pressure was maintained close to 4.4×10^{-6} milli torr with planetary rotation of 13 rpm.

5.3.1 Deposition of different layers

Cr, the first thin film deposited on top of the polyimide, had a target thickness of 200 nm. Cr is a diffusion barrier layer. The second layer deposited was approximately 200 nm of phased Cr-Cu. This layer produced a controlled environment for Cr and Cu interdiffusion and maintains the barrier properties of the Cr layer. The third layer was pure Cu to provide the solderable metallurgy. Its thickness was kept constant for the control specimens. In the matrix, thickness of Cu layer was varied from 0.3 to 1.0 μm . The fourth layer was 200 nm of Au, deposited for the purpose of providing oxidation protection to the Cu layer. The wafers were taken out of the evaporator after these depositions were complete.

The last deposition was 19 microns of Sn/Pb solder. Solder was deposited in another evaporator through the metal masks attached to the wafers. Pb and Sn were added in the same crucible in the form of pure metal pellets. Pb deposited first because of its higher vapor pressure. Sn deposited on top of the Pb because it has a much lower vapor pressure and needs a higher deposition power to vaporize. The wt% of Sn deposited was controlled based on the type of specimen.

5.3.2 Reflow Cycle

After all depositions were completed, the specimens were heated in a

furnace at a peak temperature of 350°C for 25 minutes. The H₂ atmosphere in the furnace reduced any oxides of Sn and Pb. This heat cycle was used to reflow, homogenize, and convert all the bumps to a spherical shape. This heat cycle also provided kinetic energy to move Sn through the Pb matrix to the bottom of the bump to react with Cu to form intermetallic compounds.

5.4 Specimen Classification

The specimens were divided into two groups. Both of these groups followed the same basic processing sequence for polyimide, Cr, Cu, Au and solder depositions. The first group of specimens constituted control specimens. The purpose of these specimens was to change one variable at a time to understand its effect on the metallurgy of C4. The description of these specimens is given in Table 2. The purpose of this set of experiments was to optimize the experimental conditions for the matrix specimens and also to understand the role of the variables, other than Cu and Sn concentration on the intermetallic compound formation. The control specimens were processed prior to the matrix specimens.

The second group of specimens constituted the core of the investigation. It was a group of matrix specimens where the variables were only Sn and Cu concentrations, keeping all other conditions fixed. There were a total of three specimens designed to produce Cu₃Sn and three

specimens designed to produce Cu_6Sn_5 .

5.4.1 Description of the Control Specimens

A total of fourteen control specimens were processed. All the control specimen names begin with the letter 'C'. The Cu thickness was 500 nm for all the control specimens. The Sn wt% changed from 4.5 to 9% with the remainder being Pb. For Specimen C1, only Pb was deposited while Sn was completely absent. The purpose was to study C4 formation without the Cu/Sn intermetallic compound formation. In the second specimen C2, Pb was eliminated to determine the Cu/Sn intermetallic formation in the absence of Pb. This specimen had pure Sn deposited on top of Cr-Cu-Au deposition. Specimen C3-A and C3-B had all standard depositions. Specimen C3-A was reflowed once whereas specimen C3-B was reflowed twice. Similarly, specimens C4-A and C4-B also differed in the number of reflow cycles (one vs five) to determine if the type of intermetallic compound formed would change with the number of reflow cycles.

Specimen C5 had a higher Sn concentration of 6.4 wt% than the other control specimens thus far and was processed through a 10 minute reflow cycle in an oven. The specimen remained in the oven to slow cool after the oven was turned off. In the regular furnace reflow cycle, specimens cooled immediately upon their exit from the furnace. The

purpose of the higher Sn content in C5 and the subsequent specimens was to make certain that specimens were not deficient in Sn. The purpose of slow cooling was to determine if a more stable Cu/Sn intermetallic compound would precipitate out. The next specimen, C6, received no reflow cycle. The purpose was to study the bump shape and metallurgy at room temperature. To eliminate the possibility that Sn was being consumed by Au thus making it unavailable for reaction, specimens C7 and C8 were prepared without Au deposition. In addition, C8 contained Sn concentration of 9 wt% and received a 10 minute reflow cycle. The purpose of excess Sn was to compensate for the presence of other element that might be tying up the Sn. Specimens C9-A, B and C also contained Sn concentration of 9 wt% and received standard reflow, slow cool and short reflow cycles respectively. Specimen C10 contained Sn concentration of 5 wt% and was reflowed at 170°C. The purpose of the latter specimen was to determine if a different intermetallic compound is formed or if the two Cu/Sn intermetallic compounds co-exist at a lower reflow temperature. The designations of all the control specimens, with brief descriptions and test objectives, are in Table 2.

Table 2: Description of Control Specimens

Specimen Name	Specimen Description	Test Objectives
C1	100% Pb/0% Sn	To study C4 connection w/o Cu and Sn intermetallics
C2	100% Sn/0% Pb	To eliminate Pb from Cu/Sn interface
C3-A	4.5%Sn/94.5%Pb, one reflow cycle	Control specimen
C3-B	4.5%Sn/94.5%Pb, one reflow cycle and one chip join cycle	To determine if inter-metallics are different after two thermal cycles
C4-A	4.5%Sn/94.5%Pb, one reflow cycle	Another control specimen for second data point
C4-B	4.5%Sn/94.5%Pb, five reflow cycles	To determine cumulative effect of multiple thermal cycles
C5	6.4% Sn, reflow in oven for 10 mins and oven turned off for slow cool	To determine if less heating and slow cooling will nucleate a different phase
C6	6.4% Sn and no reflow	To determine Sn distribution without a heat cycle
C7	0%Au and 9% Sn	To determine Cu/Sn product in the absence of Au and with excess Sn
C8	0% Au, 9% Sn and short reflow cycle of 10 mins	To obtain Cu/Sn reaction product in the shorter reflow cycle w/o Au

Specimen Name	Specimen Description	Test Objectives
C9-A	9% Sn and remainder std processing	To determine Cu/Sn reaction with excess Sn
C9-B	9% Sn, oven reflow and slow cool	To determine Cu/Sn reaction with excess Sn and slow cooling
C9-C	9% Sn, short reflow of 10 mins	To determine if intermetallic compounds are dissolved after excess thermal cycling
C10	5%Sn, reflow cycle at 170°C	To establish if the intermetallic compound is different at a lower temperature

5.4.2 Description of the Matrix Specimens

The matrix specimens were prepared with 300, 600 and 1000 nm thick Cu layers. For each thickness, calculations were performed to theoretically produce either Cu_3Sn or Cu_6Sn_5 . The calculations were based on a 19 μm C4 bump height and 100 μm bump base diameter. The calculations are given in Appendix 1.

As with the control specimens, matrix specimens were also deposited on silicon wafers with polyimide as the base layer, and Cr, phased Cu-Cr, Au and solder as the sequential layers. Cu and Sn concentrations were the variables controlled, in the form of thickness of these layers. There were three sets of matrix specimens. The first set consisted of specimens M1 and M2. Both specimens had 300 nm of Cu; specimen M1 had Sn concentration of 1.8 wt% to form Cu_6Sn_5 , and specimen M2 had Sn concentration of 0.85 wt% for Cu_3Sn formation. Similarly, specimens M3 and M4 formed the second set of matrix specimens with 600 nm of Cu and Sn concentration of 3.79 wt% to form Cu_6Sn_5 and 1.12 wt% to form Cu_3Sn . Specimens M5 and M6 formed the third set of specimens with 1000 nm of Cu and Sn concentration of 6.43 wt% to form Cu_6Sn_5 and 2.79 wt% to form Cu_3Sn . The names, descriptions and test objectives for these specimens are summarized in Table 3.

Table 3: Description of Matrix Specimens

Specimen	Specimen Description	Test Objectives
M1	300 nm Cu, 1.8% Sn	Cu ₆ Sn ₅ formation
M2	300 nm Cu, 0.85% Sn	Cu ₃ Sn formation
M3	600 nm Cu, 3.79% Sn	Cu ₆ Sn ₅ formation
M4	600 nm Cu, 1.12% Sn	Cu ₃ Sn formation
M5	1000 nm Cu, 6.43% Sn	Cu ₆ Sn ₅ formation
M6	1000 nm Cu, 2.79% Sn	Cu ₃ Sn formation

5.5 Analysis Techniques

Two main analysis techniques were used. Scanning electron microscopy (SEM) was used for microstructure analyses of all control and matrix specimens. Electron diffraction X-ray spectroscopy was used to determine the elemental ratio in the bulk and the intermetallic compound regions of the specimens. For each specimen, EDX analysis was performed at three different locations in the intermetallic compound region for data repeatability.

In addition to the spot analysis, a complete EDX profile of matrix Specimen 1 was taken from the top to the bottom. A total of forty data points were collected, showing relative ratios of Cu, Sn, Au, Pb and Cr. The purpose of this profile was to determine the complete distribution of these elements and Sn in particular in this specimen. It was expected that Sn would be found at the bottom of the specimen reacted with Cu and was not trapped in the Pb matrix or combined with Au.

5.6 Specimen Preparation for SEM and EDX Analysis

The specimens were prepared by breaking the wafer into small squares and epoxy mounting each square to the specimen holder. Each square contained a few C4 bumps. These specimens were mounted on a

rotating wheel and thinned, using a SiC grit paper, to expose the area of interest. The specimens were then polished with Al_2O_3 . The third step was a carbon coat to prevent the specimen from charging when struck by the scanning electron beam. The SEM and EDX results of all the specimens are discussed in Chapters 6 and 7.

Chapter 6

Results

The results are divided into two categories. The first is the microstructural results of the specimens, obtained with the Scanning Electron Microscope and the second is elemental ratios obtained from the EDX analysis.

6.1 Optical Metallography Results

The microstructure of each specimen was studied using a Hitachi SEM. Most of the micrographs were taken at 10 kV beam energy and at a magnification of 6500 times. The results of control and matrix specimens follow.

6.1.1 Microstructure of Control Specimens

The first SEM picture is of the control specimen C1 and is shown in Figure 24. In the absence of Sn, no Cu/Sn intermetallic layer was expected nor was found in this specimen. The figure shows some evidence of a phase present as random grains, near the Cu/Au interface. The micrograph of specimen C2 is shown in Figure 25. This specimen contained no Pb and shows no clear phase separation, but had three shades of grey. The next

Figure 24: Micrograph of Specimen C1 (0% Sn) showing Cu-Au Phase

Figure 25: Micrograph of Specimen C2 (0% Pb) showing Three Shades

two specimens C3-A and C4-A, had all standard deposition steps and show a clear intermetallic layer. It was a continuous though an uneven layer. Figure 26 is a SEM micrograph of specimen C3-A. C3-B with two thermal cycles and specimen C4-B, with five thermal cycles, showed a thicker and even intermetallic layer and a much cleaner bulk as evident in Figure 27. A micrograph of specimen C6 is shown in Figure 28. The bump shape is rectangular and no intermetallic layer exists because this specimen received no reflow treatment. Specimen C4-B, shown in Figure 29, converted to a spherical shape after the reflow step.

Beginning with specimen C7, the Sn content was increased to 9 wt% and Au was absent. C7 had an intermetallic layer that was columnar in shape rather than granular. As shown in Figure 30, the intermetallic layer is thicker in this specimen, as compared to the specimens C1 through C6. Specimen C8 is similar in appearance to C7. The intermetallic layer in the specimens C9-A, C9-B and C9-C shows distinct dark and light colored phases. A micrograph of C9-C is shown in Figure 31. The lighter colored phase appeared as the outline around the dark colored phase. the microstructural results of all the control specimens are summarized in column two of Table 4.

Table 4: Results of Control Specimens

SPECIMEN NAME	MICROSTRUCTURE	ACTUAL EDX RATIO	NORMALIZED EDX RATIO
C1	Phase at Cu and Au interface	Cu:Au 55:44 Cu:Au 75:25 Cu:Au 77:23	Cu:Au 3:1
C2	Distinct three color shading	Top: 44:44:11 Bulk: 44:44:11 Btm : 35:42:13	Top: 1:1:0.3 Bulk: 6:5:1.5 Btm: 4:3:1
C3-A	IML layer is uneven but continuous	IML : 65:21:14 IML : 53:22:25 IML : 68:21:10	3:1:0.5
C3-B	Same as C3-A	IML : 69:21:11	3.5:1:0.5
C4-A	Same as C3-A	IML : 66:20:14	3.4:1:0.6
C4-B	IML is even and bulk is clean	IML : 68:21:11	3.3:1:0.5
C5	IML is continuous and shows distinct dark and light phases	IML : 68:21:10	Dark = 3.5:1:0.5
C6	No IML, scattered grains	Top : Pb:Sn 4:1	4:1
C7	IML columnar instead of grainy	Cu:Sn = 76:22	3.5:1:0
C8	Similar to C7	Cu:Sn = 77:23	3.4:1:0
C9-A	IML is thicker, distinct dark and light areas	IML : 69:22:9 IML : 78:22:0	3.5:1:0.7
C9-B	IML shows slight differentiation in dark and light areas	IML : 68:21:10	3.7:1:0.5
C9-C	Slight differentiation into dark and light areas	IML : 71:21:8 IML : 61:24:14	3.4:1:0.4
C10	No distinct phases, uneven thickness	IML : 81:11:0	7:1:0

Note: The three elemental ratios are in the sequence Cu:Sn:Au

Figure 26: Micrograph of Specimen C3-A (one reflow cycle) with Uneven Intermetallic Layer

Figure 27: Micrograph of Specimen C4-B (Five thermal cycles) with Clean Bulk and Distinct Intermetallic Compound

Figure 28: Micrograph of Specimen C6 (No reflow) with Rectangular Bump

Figure 29: Micrograph of Specimen C4-B (after reflow) with a Spherical Bump

Figure 30: Micrograph of Specimen C7 (9% Sn, 0% Au) with Columnar Intermetallic Compound Layer

Figure 31: Micrograph of Specimen C9-C (9% Sn) showing Differentiation in Dark & Light Phases

6.1.2 Microstructure of Matrix Specimens

The micrograph of matrix specimen 1 is shown in Figure 32. It has an uneven intermetallic layer and dark and light phases. Matrix specimens M2 and M3 showed similar microstructures as specimen M1. Specimen M4, shown in Figure 33, does not exhibit distinct dark and light phases. Specimens M5 and M6, show a continuous, thick intermetallic layer with little or no development of dark and light colored phases as seen in Figures 34 and 35 respectively. These results are also summarized in the second column of Table 5.

6.2 Electron Dispersive X-ray Analysis

Each EDX ratio reported here is an average of three points taken along the width of the Intermetallic Layer (IML). When the variation in elemental ratio of the two data points on the same specimen is greater than 5%, both data points are reported in the table. A few EDX data points were also taken in the bulk region. In most cases, the result was dominated by the Pb concentration. The actual elemental ratio is in column three of Tables 3 and 4. Column four contains the elemental ratio normalized to Sn as one, with the exception of control specimen C1 that contained 0% Sn. Whenever the ratio of three elements is given, the sequence is Cu:Sn:Au.

Table 5: Results of Matrix Specimens

Specimen	MICROSTRUCTURE	ACTUAL EDX RATIO	NORMALIZED EDX RATIO
M1	IML uneven, distinct dark and light phases	Light IM 43:9:37* Dark IM 67:20:13	Light IM 2:1:6 Dark IM 3.5:1:0.7
M2	IML uneven with slight evidence of dark and light phases	IM 67:15:18	IM 4:1:1.2
M3	IML thicker than M1 & M2, distinct dark and light phases	Bulk 39:20:41 IM(ct) 67:21:12 IM(rt) 48:28:24	Bulk 2:1:2 IM(ct) 3:1:0.5 IM(rt) 1.7:1:0.9
M4	IML thinner than M3, no distinct dark and light phases	IM(ct) 63:17:20 IM(rt) 46:22:32	IM 3.7:1:1.2 IM 2.1:1:1.5
M5	IML continuous with some evidence of dark and light phases	IM 69:21:10	IM 3.3:1:0.5
M6	IML continuous, some evidence of dark and light phases	IM 69:20:11	IM 3.5:1:0.6

Figure 32: Micrograph of Specimen M1 (300nm Cu, 1.8%Sn) showing Dark and Light Phases

Figure 33: Micrograph of Specimen M4 (600nm Cu, 1.12% Sn) showing Continuous Intermetallic Layer

Figure 34: Micrograph of Specimen M5 (1000nm Cu, 6.43% Sn) showing no Dark and Light phases

Figure 35: Micrograph of Specimen M6 (1000nm Cu, 2.79% Sn) showing Slight Differentiation in Dark and Light Phases

6.2.1 EDX Results of Control Specimens

Control specimen C1, with 0% Sn, had Cu to Au ratios varying from 5:4 to 3:1. This EDX analysis was done on the grains scattered in the bulk near the Cu/Au/solder interface. In Specimen C2, with 0% Pb, analysis was done on the top, bottom and bulk of the specimen. Visually, these three areas were distinguishable by the darkness of their grey shading. The top part of the specimen had a normalized Cu:Sn:Au ratio of 1:1:0.3, the bulk had a ratio of 6:5:1.5, and the bottom was 4:3:1.

Specimens C2 exhibited the greatest variation in the ratios of the three elements. In specimens C3-A, C3-B, C4-A, C4-B and C5 the EDX elemental ratios were similar. The actual Cu:Sn:Au ratio was consistently 68:21:11 with only a slight variation from one spot to another and from one specimen to another. The normalized Cu:Sn:Au ratio of these specimens was 3.5:1:0.5. Specimens C7 and C8, with no Au, also had a normalized Cu:Sn ratio close to 3.5:1. The absence of Au did not cause an increase in the ratio of Cu to Sn. In the same way, specimens C9-A, C9-B and C9-C with Sn concentration of 9 wt% and had Cu:Sn:Au ratios varying from 3.4:1:0.4 to 3.7:1:0.7. Specimen C10 which has been reflowed at 170°C, had a much lower Sn concentration and a Cu:Sn:Au ratio of 7:1:0. These EDX results have been summarized in columns three and four of Table 4.

6.2.2 EDX Results of Matrix Specimens

The intermetallic layer in matrix specimen 1 developed distinct dark and light areas. When the EDX elemental ratios of these two areas were determined, the dark phase had a Cu:Sn:Au ratio of 67:20:13 (normalized ratio of 3.5:1:0.7). The light colored phase had an EDX ratio of 43:9:37 (normalized ratio of 2:1:6). Hence, the light colored phase contained excess Au, whereas EDX ratio of the dark phase was similar to the phase without any color differentiation. The matrix specimens M2 through M6, had similar Cu:Sn:Au ratios as the dark phase in specimen M1. In addition, specimen M3 and M4 had one data point each with an EDX ratio of Cu:Sn:Au close to 2:1:1.5. The amount of Au in the ratio varied from 0.9 to 2. The actual and normalized EDX ratios are summarized in columns three and four of Table 5.

6.2.3 EDX Concentration Profile

An EDX profile of specimen C7 was taken to determine the relative percentage of each element from the top to the bottom of the bump. The profile contains the relative percentage of Cu, Sn, Au and Pb, with the total being 100% at any given point. The data points are shown in Figure 36. It has a total of 39 points. The bottom of the bump is towards the bottom of the graph.

The relative ratio of the four elements in the C4 bump

Figure 36: EDX concentration profile from top to bottom of the bump.

Chapter 7

Discussion of Results

7.1 Microstructure of Intermetallic Layer

7.1.1 Thickness of Intermetallic layer

Visually, there was a difference in the thickness and evenness of the intermetallic layer from one specimen to another, though no quantitative thickness measurements were made. In general, in the matrix specimens with less than 3 wt% Sn e.g. M1, M2 and M4, the intermetallic layer does not have an even thickness. When the Sn concentration is greater than 3%, as in all the control specimens and in matrix specimens M3, M5 and M6, the intermetallic compound layer is even and continuous. A certain minimum Sn concentration is required for reaction with Cu to form a uniform intermetallic layer, and this minimum concentration is 3%.

7.1.2 Columnar Intermetallic Layer

Another noticeable feature of the microstructure was that the intermetallic compound layer in control specimens C7 and C8 was columnar as compared to the grains in the other control and matrix specimens. In these two specimens, gold had been eliminated to determine if this would result in the formation of a different Cu/Sn intermetallic compound. But according to the EDX analysis, the Cu:Sn ratio was the same as was in the

other specimens. This suggests that Au is possibly changing the microstructure of the Cu/Sn intermetallic compound layer formed by being in solution without substituting for Cu in the matrix.

7.1.3 Absence of Intermetallic Layer

Another microstructural feature became apparent only in specimen C2, which was prepared without Pb and is shown in Figure 25. This specimen did not develop a distinct intermetallic layer. In the absence of Pb, Cu and Sn were in direct contact in this sample only, and the intermetallic compound formation occurred instantaneously. This instant reaction of Cu and Sn not only limited the grain growth but also did not convert the phase initially formed to the equilibrium phase. The result is the absence of a distinct intermetallic compound layer.

7.1.4 Identification into Dark and Light Phases

The most distinct microstructural feature was the presence of two different phases in the intermetallic layer distinguishable by dark and light shades as shown in specimen M1 in Figure 32. In this case, the dark colored phase was surrounded by the light colored phase. This color difference appeared randomly in some of the specimens. It could not be predicted by altering variables and is not readily explainable. For example,

control specimens C5 and C9-A, B and C have two distinct shades in the intermetallic layer. Out of the six matrix specimens, two specimens showed no distinct light and dark phases, two had distinguishable phases and the other two had separable dark and light phases. There was no known commonality in these matrix specimens or the control specimens. The difference in heat cycling or Sn/Cu concentrations did not appear to affect this phenomenon. Further experiments may explain this difference.

7.1.5 Other Visual Differences

There were other distinct microstructural features observed in control specimens C1 and C4-B. Without Sn as in specimen C1, there is no Cu/Sn intermetallic compound, but an uneven layer appeared at the Cu and Au interface. In the absence of Sn, the dominant reaction occurred between Cu and Au. This phase had an elemental ratio corresponding to that of Cu_3Au . The reaction must have been limited because it did not form a continuous layer.

7.2 Effect of Thermal Cycling

Several control specimens had thermal cycle variations in order to understand the effect of slow cooling, shorter reflow cycles and the effect of multiple thermal cycles. It was expected to result in the nucleation of a

different phase. No change was apparent in the elemental ratios or in the type of Cu/Sn intermetallic compounds formed in these specimens. Because this intermetallic compound would not convert into any other phase as a result of additional thermal cycling, this must be the most stable phase. Specimen C4-B with five thermal cycles, and C10, with 170°C reflow also showed no change in the type of intermetallic compound formed.

7.3 Elemental Ratio and Stoichiometry

Most of the control and matrix specimens showed only a small change in the Cu to Sn ratio, in spite of the variables introduced in each specimen. The only exception was specimen C2 with no Pb, as explained in Section 7.1.3. The normalized Cu to Sn ratio in all the specimens varied between 3:1 to 4:1 (actual ratio of Cu:Sn:Au close to 68:21:11) with little variation from one specimen to another or within each specimen. The variability was also limited in the bulk region. All specimens had a bulk containing >90% Pb and traces of Sn or Au.

In the matrix specimens designed to form either Cu_3Sn or Cu_6Sn_5 , the results were also contrary to expectations. According to the phase diagram, when Cu and Sn are in the correct ratio, the formation of one intermetallic compound should be favored over the others. At the very least, the two intermetallic compounds could be found to co-exist in some of the matrix

specimens. In reference 6, it was noted that the activation energy for Cu_6Sn_5 was lower than Cu_3Sn . This should have resulted in the first intermetallic Cu_6Sn_5 being favored over the second. The elemental ratios do not substantiate this expectation. No matrix specimen showed any evidence of Cu_6Sn_5 formation, regardless of the initial Cu/Sn concentrations employed.

7.4 Absence of Cu_6Sn_5

A question is raised as to why Cu_6Sn_5 is not formed. The explanation may come from kinetics of Sn movement and not from thermodynamics. All of the matrix specimens have a few different Cu to Sn weight ratio combinations but the deposition sequence is the same in all specimens except in specimen C2. Sn was deposited on top of about 19 microns of Pb and was expected to travel to the bottom of bump to react with Cu. At 350°C, Sn is in a molten state and should easily move to the bottom and react instantly. But the limitation is that not all the Sn can reach the Cu instantaneously. This is also evident in the EDX profile that Sn is distributed throughout the bump rather than concentrated towards the bottom of the bump.

Another reason for some of Sn being unavailable for reaction could be the possibility that Au trapped some of the Sn in an Au-Sn intermetallic

compound, or simply in a dissolved form. If that were true, control specimens C7 and C8, with no Au, should have produced a different Cu-Sn ratio. The presence or absence of Au did not change the Cu to Sn ratio in any of the specimens.

The explanation for the absence of Cu_6Sn_5 in all the specimens is in results of specimen C2. This was the only specimen with Cu to Sn ratio of 6:5. This specimen was started with similar Cu to Sn concentration as other specimens but totally different kinetics because Sn was deposited directly on top of Cu/Au and Pb was completely absent. Au was still present as in the rest of the specimens and there was no change in reflow cycles or any other variables. Hence, all of the Sn was available for instant reaction with Cu. The result was a Cu:Sn ratio of 6:5, unlike all the other specimens. In control specimens C7 through C9, more Sn was available for reaction since Sn concentration was increased to 9% in all of these samples. More Sn produced no noticeable difference in the elemental ratio of these specimens. If thermodynamics were the determining factors, both Cu_3Sn and Cu_6Sn_5 should have been formed in all specimens based on the phase diagram calculations.

Kinetics can also explain why in some of the references, it was possible to preferentially form one intermetallic compound over others because diffusion couples were made with Cu and Sn in direct contact. But

literature review can not be extrapolated to the dynamics of C4 depositions where the sequence of deposition is controlling the metallurgy. It would be of interest to deposit Sn on top of Cu followed by Pb. It was not possible to follow that sequence in these specimens because Pb evaporates before Sn.

7.5 EDX profile of the Complete Bump

The EDX profile in Figure 36 shows that most of the Sn, Cu and Au is concentrated towards the last 5-10 microns at the bottom of the bump. The remaining 5% of the Sn is present throughout the Pb matrix. This profile proves that not all of the Sn has moved down to react with Cu, regardless of the extent of thermal cycling or slow cooling. Since the Pb bulk is 19 microns in height, even an excess of Sn in the specimen would not make all of it available for instantaneous reaction with Cu. Increasing the concentration of Sn may have left more Sn trapped in the Pb matrix.

7.6 Role of Au in Intermetallic Compound Formation

The role of Au in the intermetallic compound formation is unclear. Au is either in an inactive state or it is chemically involved in the intermetallic compound formation. Specimens C7 and C8, with no Au, showed that the Cu:Sn ratio did not change in the absence of Au. From these results, it appears that Au is just a passive constituent in Cu and Sn intermetallic

appears that Au is just a passive constituent in Cu and Sn intermetallic compounds. Although Cu and Au are completely miscible and replaceable, elemental ratios in the specimens C7 and C8 do not show an increase in Cu content in the absence of Au. If Au was replacing Cu in the other specimens, the Cu ratio should have been lower as compared to specimens C7 and C8. A ratio of 3.5:1 between Cu and Sn is maintained, regardless of Au content.

7.7 Phase Determination

From the EDX analysis, the most frequent and normalized atomic ratio of Cu:Sn:Au is 3.5:1:0.5. One of the possibilities is that it is Cu_3Sn with excess Cu and Au in solution. The second possibility is that Au is chemically bonded and is substituting Cu and the compound is Cu_4Sn where 3.5 wt% ratio of Cu is added to 0.5 wt% ratio of Au. The third possibility is that it is a ternary phase with Cu, Sn and Au. Since EDX provides only the atomic ratios of different elements, it is not a conclusive analytical technique for phase identification. X-ray diffraction was attempted on one of the control specimens but did not provide any conclusive results regarding the actual phase of the intermetallic compound.

There may be some evidence of ternary compound formation in these specimens, if Au is chemically bonded. The most prevalent elemental ratio from Table 4 and 5 is $\text{Cu}_{67}\text{Sn}_{20}\text{Au}_{13}$. This phase matches with Phase B in Reference 17 where three ternary phases have been established. Phase B was determined to range in composition from $\text{Cu}_{68}\text{Sn}_{20}\text{Au}_{12}$ to $\text{Cu}_{44}\text{Sn}_{20}\text{Au}_{36}$. Both of these ratios are present in matrix specimen M4 at different points in the intermetallic layer. More definite analysis techniques from X-ray diffraction or transmission electron microscopy can provide better insight into the real identity of this intermetallic compound.

Chapter 8

Conclusions

As determined in this investigation, Cu, Sn and Au form an intermetallic compound with a Cu:Sn:Au ratio of 68:21:11. As a Cu/Sn binary, it is neither Cu_3Sn nor Cu_4Sn . It may be a mix of these two Cu/Sn intermetallic compounds. As a Cu-Sn-Au ternary, it matches exactly with the phase B cited in Reference 17. The type of intermetallic compound was not a function of the amount of Cu and Sn, but rather by the deposition sequence of Sn and Pb. Slow cooling and shorter or multiple thermal cycles did not change the microstructure or the type of intermetallic compound formed. The Cu:Sn ratio in intermetallic compound layer did not change in the presence or absence of gold. Pb does not appear to play any role in Cu/Sn intermetallic formation though it acts as a matrix to trap Sn.

It was important to establish the type of Cu/Sn intermetallic compound in C4 in order to predict the formation of a specific compound and study its relationship to the reliability of C4. Since none of the variables subsequently changed the type of Cu/Sn compound formed, it can be concluded that this is a stable compound. Data collection on the reliability of C4 may possibly relate the C4 failure to the amount of Cu and Sn in the specimen rather than to the type of intermetallic compound. Further research is necessary to identify the actual Cu/Sn intermetallic compound. It

remains unresolved if it is a binary or a ternary compound and what is specific role played by Au in the compound formation.

This investigation answers the question that the factors like temperature and the amounts of Cu, Sn and Au do not control the formation of the Cu/Sn intermetallic compound in C4. The type of intermetallic compound is related to the sequence of deposition as was shown in Specimen C2. Hence, it defies the claim made by reseachers that the composition of the Cu/Sn intermetallic compound formed can be controlled by controlling the C4 process conditions.

Chapter 9

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Appendix 1

Calculations for Sn and Cu Wt% to Form Cu_3Sn or Cu_6Sn_5

The calculations were done based on the phase diagram. In Step 1, Sn was calculated as a wt% of Cu and in the second step, Sn wt% was calculated as a fraction of the solder. Letter 't' = thickness and 'd' = density.

Step 1:

Convert Cu thickness into Cu wt%.

$$\text{Wt\% Cu} = \text{Area of the bump} \times t \text{ of Cu} \times d \text{ of Cu} = x \text{ gms}$$

$$\text{Wt\% Sn} = y \text{ to be calculated as a fraction of Cu + Sn}$$

$$y = \text{Total wt of Sn req to form an IM} - x \text{ gms of Sn}$$

$$0.6 = \frac{y}{x + y}$$

Step 2:

$$\text{Wt of solder} = \text{Area of bump} \times t \text{ of solder} \times d \text{ of Pb} = z$$

$$\text{Wt of Pb} = \text{Wt of solder} - \text{Wt of Sn} = z - y \text{ gms}$$

For all the matrix calculations, it was given that

Bump height = 19 μm

Bump diameter = 100 μm

Density of Cu = 8.96 gms/cm³

Density of Sn = 7.30 " " "

Density of Pb = 11.40 " " "

For Cu_6Sn_5 formation, whatever Cu wt% is used, 60% of that weight should equal to the Sn weight percent. For Cu_3Sn formation, Sn must be 40% of Cu wt%.

MATRIX Specimen #1

0.3 um of Cu available for Cu₆Sn₅ formation

$$0.6 = \frac{t \text{ of Sn} \times d \text{ of Sn}}{(t \text{ of Sn} \times d \text{ of Sn}) + (t \text{ of Cu} \times d \text{ of Cu})}$$
$$= 0.53 \text{ um of Sn}$$

Wt% of Sn (function of Pb)

$$= \frac{0.53 \times 7.30}{(0.53 \times 7.30) + [(19-0.53) \times 11.40]} = 1.8\% \text{ of Sn}$$

MATRIX #2

0.3 um of Cu available for Cu₃Sn formation

$$0.4 = \frac{t \times 7.30}{(t \times 7.30) + (0.3 \times 8.96)}$$
$$= 0.25 \text{ um of Sn}$$

$$\text{Wt\% of Sn} = \frac{0.25 \times 7.30}{(0.25 \times 7.30) + [(19-0.25) \times 11.40]} = 0.85\% \text{ Sn}$$

NOTE: Similar calculations were done for the remaining matrix specimens. The only difference was that Matrix specimens 3 and 4 had 0.6 um of Cu available and specimens 5 and 6 had 1.0 um of Cu available.

Appendix 2

EDX Data of Matrix Specimen #1

25-Feb-1992 14:27:19

46285 C4 Char.

Accelerating voltage 15.0 KeV
Beam - sample incidence angle 90.0 degrees
Xray emergence angle 40.0 degrees
Xray - window incidence angle 0.0 degrees

STANDARDLESS EDS ANALYSIS
(ZAF CORRECTIONS VIA MAGIC V)

ELEMENT & LINE	WEIGHT PERCENT	ATOMIC PERCENT*	PRECISION 2 SIGMA	K-RATIO**	ITER
Cr KA	5.21	11.62	0.08	0.0588	
Cu KA	23.40	42.72	0.24	0.2895	
Sn LA	9.35	9.14	0.13	0.0818	
Au LA	62.04	36.53	1.59	0.5699	2
TOTAL	100.00				

*NOTE: ATOMIC PERCENT is normalized to 100

**NOTE: K-RATIO = K-RATIO x R
where R = reference(standard)/reference(sample)

H.F. 0.34µm Cu, 1.1% Sn, 90.2% Pb Center

25-Feb-1992 14:56:12

46285 C4 Char.

Accelerating voltage 15.0 KeV
Beam - sample incidence angle 90.0 degrees
Xray emergence angle 40.0 degrees
Xray - window incidence angle 0.0 degrees

STANDARDLESS EDS ANALYSIS
(ZAF CORRECTIONS VIA MAGIC V)

ELEMENT & LINE	WEIGHT PERCENT	ATOMIC PERCENT*	PRECISION 2 SIGMA	K-RATIO**	ITER
Cu KA	46.93	67.44	0.32	0.5345	
Sn LA	26.03	20.03	0.15	0.2355	
Au LA	27.04	12.53	1.07	0.2301	3
TOTAL	100.00				

*NOTE: ATOMIC PERCENT is normalized to 100

**NOTE: K-RATIO = K-RATIO x R
where R = reference(standard)/reference(sample)

A#1 IMC Right