Intermetallic Void Formation in Cu-Sn Micro- Connects

Glenn Ross

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Abstract

The compatibility of new materials and their interfaces are key components in the pursuit of highly integrated and reliable systems. An extensive understanding is required of the behaviour and stability of the materials not only during device fabrication but over the entire functional lifetime of a device. A microstructural defect, and the focus of this thesis, that threatens the mechanical and electrical performance of 3D-intergrated systems is Cu-Sn intermetallic void formation. Results of this work has been separated as follows: (i) understanding the sporadic behaviour of void formation, (ii) understand the key parameters influencing voiding formation, (iii) examine the microstructural and chemical properties associated with void formation, (iv) present a void formation hypothesis and (v) discuss void reduction and detection methods for the microelectronic industry.

Historically void formation has been sporadic and uncontrolled and led this author, in addition to several other authors, to question whether formation is only due to the Kirkendall effect (interdiffusion imbalance between two joined metals). The Cu electroplating process and the parameters used play a large role in effecting the voiding propensity. These parameters, including the additive chemistry and current density, influence the microstructural properties and chemical composition of the deposited film such as, grain structure, residual stresses, crystal defect density and trace impurities. A new intermetallic void formation hypothesis is proposed based on microstructural and chemical state of the Cu-Sn system.

Intermetallic voids can be suppressed when the Cu electroplating process is well controlled, which requires careful observation of the electroplating parameters. This requires cooperation and understanding of the process between the semiconductor fabrication companies and the Cu process suppliers. However, it is difficult to control voiding completely, therefore non-destructive void detection methods need to be developed.

Keywords Cu-Sn Intermetallic Voids, Kirkendall Voids, Micro-Connects, Reliability, Thermodynamics, Solid-State Diffusion, Microstructure, Impurities, Scanning Electron Microscopy, Transmission Electron Microscopy, Scanning Transmission Electron Microscopy, Energy Dispersive Spectroscopy, Electron Diffraction, X-Ray Diffraction, Time-of-Flight Secondary Ion Mass Spectroscopy, Ab initio.

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Espoo, 15th October 2018
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List of Abbreviations and Symbols

BCT	Body Centered Tetragonal
BF-TEM	Bright Field – Transmission Electron Microscopy
BGA	Ball Grid Array
CMP	Chemical Mechanical Polishing
CTE	Coefficient of Thermal Expansion
DF-TEM	Dark Field – Transmission Electron Microscopy
DP	Diffraction Pattern
EDS	Energy Dispersive Spectroscopy
FCC	Face Centered Cubic
FIB	Focused Ion Beam
GHz	Gigahertz
GHz-SAM	Gigahertz-Scanning Acoustic Microscopy
HAADF	High Angle Angular Dark Field
HR-TEM	High Resolution – Transmission Electron Microscopy
ICSD	Inorganic Crystal Structure Database
IMC	Intermetallic Compound
MEMS	Microelectromechanical Systems
OFHC	Oxygen Free High Conductive
PCB	Printed Circuit Board
PDF	Powder Diffraction File
PEG	Polyethylene Glycol
ppb	Parts Per Billion
ppm	Parts Per Million
RoHS	Restriction of Hazardous Substances

RT	Room Temperature
SAC	Tin-Silver-Copper
SADP	Select Area Diffraction Pattern
SAM	Scanning Acoustic Microscopy
SEM	Scanning Electron Microscopy
SiP	System-in-Package
SLID	Solid Liquid Interdiffusion
SPS	Bis-(3-sulfopropyl)-disulphide
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TLP	Transient Liquid Phase
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
TSV	Through Silicon Via
UBM	Under Bump Metallisation
XRD	X-Ray Diffraction
XRR	X-Ray Reflectivity

a	Area
A_i	Elastic anisotropy
at. %	Atomic percent
a.u.	Arbitrary units
C	Concentration
d	Density
d_{hkl}	Interplanar spacing
D	Diffusion coefficient
D^*	Diffusivity
$\tilde{D}$	Interdiffusion coefficient
$\tilde{D}_{int}$	Integrated interdiffusion coefficient
e	Electron
f_i	Model fraction

F_{ij}	X-ray stress factors
g	Gibbs energy
h	Thickness
I	Current
J	Flux of species
k_p	Parabolic growth constant
K_β	Kirkendall plane of the β -phase
L	System dependent constant
L_x -axis	Laboratory reference frame
M	Metal
n	Order of refraction
N_A	Composition of component A
p, q, r, s	Flux components
Q	Charge
S_x -axis	Specimen reference frame
t	Time
v_K	Velocity of the Kirkendall plane
v_m	Molar volume
V	Volume
w	Weight
$wt.\%$	Weight percent
X_o	Initial contact plane
z	Electron number
Z	Electrochemical equivalent
α -Cu	Face centered cubic copper
β -Sn	Body centered tetragonal tin
Δx_β	Layer thickness of the β -phase
ε	Cu_3Sn
ε^S	Strain tensor in the specimen reference frame

$\{\varepsilon_{33}^L\}_{\psi,\varphi}^{hkl}$	Average diffraction strain in the laboratory reference frame
η'	monoclinic - Cu ₆ Sn ₅
θ	Theta angle
Ξ	Effective grain model
Ξ_i	Grain model i
λ	Wavelength
μ	Chemical potential
σ^S	Stress tensor in the specimen reference frame
$\langle\sigma_{ij}^S\rangle$	Average mechanical stress tensor in the specimen reference frame
φ	Phi angle
χ	Chi angle
ψ	Psi angle

List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

- 1.** Ross, Glenn; Vuorinen, Vesa; Paulasto-Kröckel, Mervi. 2016. Void formation and its impact on Cu-Sn intermetallic compound formation. Elsevier. *Journal of Alloys and Compounds*, volume 677, pages 127-138. ISSN: 0925-8388. DOI: 10.1016/j.jallcom.2016.03.193.
- 2.** Ross, Glenn; Tao, Xiaoma; Broas, Mikael; Mäntyoja, Nikolai; Vuorinen, Vesa; Graff, Andreas; Altmann, Frank; Petzold, Matthias; Paulasto-Kröckel, Mervi. 2017. Interfacial Void Segregation of Cl in Cu-Sn Micro-Connects. Springer. *Electronics Material Letters*, volume 13, issue 4, pages 307-312. ISSN: 1738-8090. DOI: 10.1007/s13391-017-6304-5.
- 3.** Ross, Glenn; Vuorinen, Vesa; Petzold, Matthias; Paulasto-Kröckel, Mervi; Brand, Sebastian. 2017. Gigahertz scanning acoustic microscopy analysis of voids in Cu-Sn micro-connects. American Institute of Physics. *Applied Physics Letters*, volume 110, pages 1 -5. ISSN: 0003-6951. DOI: 10.1063/1.4975305.
- 4.** Ross, Glenn; Vuorinen, Vesa; Krause, Matthias; Reissaus, Stephan; Petzold, Matthias; Paulasto-Kröckel, Mervi. 2017. XRD and ToF-SIMS study of intermetallic void formation in Cu-Sn micro-connects. Elsevier. *Microelectronics Reliability*, volume 76-77, pages 390-394. ISSN: 0026-2714. DOI: 10.1016/j.microrel.2017.07.044.
- 5.** Ross, Glenn; Malmberg, Per; Vuorinen, Vesa, Paulasto-Kröckel, Mervi. 2018. The Role of Ultrafine Crystalline Behavior and Trace Impurities in Copper on Intermetallic Void Formation. American Chemical Society. *Applied Electronic Materials*. DOI: 10.1021/acsaelm.8b00029.

Author's Contribution

Publication 1: Void formation and its impact on Cu-Sn intermetallic compound formation.

The first author was responsible for the planning and executed the experiments presented in this work. The analysis, in particular the work pertaining to the physicochemical approach was supported by Dr. Vesa Vuorinen. The first author was responsible for writing the manuscript.

Publication 2: Interfacial Void Segregation of Cl in Cu-Sn Micro-Connects.

The first author was responsible for planning the experimental work. MSc. Nikolai Mäntöjoja & Dr. Mikael Broas prepared the sample for scanning transmission microscopy. Dr. Andreas Graff performed the microscopy work. The *ab initio* portion of the work was done by Dr. Xiaoma Tao. The analysis of the results and the writing of the final manuscript was done by the first author.

Publication 3: Gigahertz scanning acoustic microscopy analysis of voids in Cu-Sn micro-connects.

The first author jointly planned the experiments and completed the manuscript together with Dr. Sebastian Brand. The first author prepared the samples for analysis and Dr. Sebastian Brand made the measurements and analysed the results.

Publication 4: XRD and ToF-SIMS study of intermetallic void formation in Cu-Sn micro-connects.

The first author was responsible for planning, executing and analysing the experimental work. One portion of the experimental work, the time-of-flight secondary ion mass spectroscopy measurements, was carried out by Dr. Michael Krause and Dipl. Ing. Stephan Reissaus. The manuscript was written by the first author.

Publication 5: The Role of Ultrafine Crystalline Behavior and Trace Impurities in Copper on Intermetallic Void Formation.

The first author was responsible for planning, executing and analysing the experimental work. Dr. Per Malmberg made the time-of-flight secondary ion mass spectrometry measurements of the samples. The first author was responsible for preparing the manuscript.

1. Introduction

Electronics is becoming increasingly entrenched in everyday life, to the extent that interaction between people and devices becomes subconscious. This is only made possible by the continuous pursuit of: (i) improved performance and reduced latency, (ii) miniaturisation and (iii) diversification of the way microelectronics interacts with the surroundings. Moore's law and the transistor scaling roadmap¹ is an obvious path for increased performance, however this fails to address the other two points. Additionally there are a number of challenges in the near future of this approach, limiting the long term impact. Advanced packaging methods address all three points. Smarter packaging designs enable better performance, through shorter and higher density interconnections, require significantly less physical volumes and enable the integration of a wide variety of components that are able to sense and interpret the operational environment.

3D-integration is one of the promising new packaging solutions. This takes integration from the printed wiring board-level to the wafer-level. This is not a stepwise development progression as the integration concept requires new technologies, such as manufacturing technologies with completely new reliability related challenges that require new design for reliability concepts. For reliability, the challenge is with the new materials and interfaces required for 3D-integration. New materials and interfaces require an understanding of the interfacial compatibility of the new materials and how they interact under multi-loading environments. Also the inherent material properties as they move from exhibiting bulk like properties to thin-film or small volume properties and how to characterise the properties in the assembled state. These are all challenges that need overcoming for the successful implementation of 3D-integrated technologies.

Micro-connects are just one example of a key enabling technology that is currently being studied. As traditional interconnects are often significantly larger in volume, the microstructural properties of the micro-connect begin to play a major role. Where traditional board-level interconnects contained ductile solder material, a much larger fraction of the micro-connect is typically composed of comparatively hard and brittle intermetallic compound(s). Additionally, as micro-connects may only have a small number of intermetallic grains the anisotropic material behaviour can no longer be neglected. One issue in micro-connect reliability is with the formation of intermetallic voids, often known as Kirkendall voids. The presence of these voids has been reported on for electronic interconnects since the 1960's.² It has been a source for concern in traditional

interconnect technologies, but the problem with micro-connects is that the voids will now consume a much larger fraction of the bonded volume. This will undoubtedly result in reduced bonding strength and electrical performance.

Intermetallic voids are an extension of Kirkendall voids. As this work shows, there is more to void formation than the Kirkendall effect. Once it has been determined that voids are not only Kirkendall voids, an inherent material property, but rather intermetallic voids that are a product of the processing parameters, then corrective actions can be taken to avoid their potential negative impacts.

This thesis seeks to answer the following research questions:

- i. Under what conditions do voids form and what effect do voids have on the properties of the Cu-Sn system? [I]
- ii. What are the characteristic microstructural and chemical behaviours of the Cu-Sn system that experiences a high voiding propensity? [II], [IV], [V]
- iii. From the behaviour observed during the study of the thesis questions i-ii, is there an alternative model for void formation? [V]
- iv. With a better understanding of void formation, is it possible to have a completely intermetallic void free microelectronics industry? If not, how can we screen for voids? [III]

This doctoral thesis is structured in the following manner: Section 2 introduces the reader to Cu-Sn micro-connects, their applications, advantages and current challenges. Section 3 presents the thermodynamics, driving forces for diffusion and the Kirkendall plane in the Cu-Sn system, and their impact on void formation. Section 4 discusses the benefits and limitations of a wide variety of methods used for void characterisation. Section 5 introduces the reader to how Kirkendall voids understanding has evolved from bulk to thin-film diffusion couples, void formation in common interconnect technologies, and the problem with describing void formation as due only to the Kirkendall effect. Section 6 introduces electroplating technology, how it is used in the microelectronic industry and the respective additive systems used that enable a conformal deposition process. Section 7 discusses the current state of understanding of how voids form and evolve over the thermal lifetime of a microelectronic component. Section 8 deliberates on the impact of voids by first identifying key parameters, the process of void formation in Cu-Sn micro-connects and what it means in practical terms for the microelectronic industry.

2. Integration and Challenges

The microelectronic industry is undoubtedly one of the most competitive industries in the world. A key aspect of a company's success is the perceived reliability of their products. Recently, there have been a number of high profile reliability related issues with products from large microelectronic companies, which has undeniably negatively affected their image. Image aside, the cost of liability for returns and recalls can be disastrous and in safety critical applications deadly. To keep ahead in the microelectronic industry one must also innovate. Innovation often includes miniaturisation and scaling of technologies, but also the use of new technologies, including materials and interfaces. The balance between innovation and reliability is a constantly evolving challenge, where an understanding of the physics of failure is necessary to avoid catastrophic reliability challenges.

2.1 2.5-3D Integration and Micro-Connects

One avenue for development is the miniaturisation and integration of complex systems. Miniaturisation does not just include the reduction of gate lengths in transistor systems, but rather the complete system, from transistor to packaging. While the limits of transistor miniaturisation is well understood and the roadmap is defined for the foreseeable future, the packaging and integration of microelectronic systems is certainly less clear. One promising path is the System in Package or SiP. This integrates the microelectromechanical system (MEMS) and the logic into one package. Figure 1 illustrates two proposed methods of higher integration, by integrating the sensors, memory and logic into a single package. The advantages of such a strategy are obvious, a reduced footprint, shorter interconnect lengths (reduced latency), less material consumption and higher wafer-to-chip ratio resulting in a higher yield. However untested technologies certainly have a number of not only fabrication challenges, but also reliability challenges.

Figure 1 – Illustration of packaging integration potentials. Subfigure (a) shows the 2.5D-integration, where dies are integrated on an interposer and (b) a full 3D-integration stack with vertical interconnections between the functional units.

Traditional components, such as lead-frame, ball grid array (BGA) and flip-chip packages have been available and integrated on a substrate laminate, such as a printed circuit board (PCB) for some time. Therefore, there is a good understanding of the manufacturing processes, failure modes and physics of failure of these assemblies. The major challenge now is translating this “know how” to 2.5D and 3D-integration. For example, with flip-chip based packages on a PCB there is significant room for mechanical compensation of thermomechanical stresses in the large solder volume; whereas 2.5D and 3D employ direct micro-bumping that results in direct stressing of the interconnection, with significantly thinner buffer layers. Consequently, understanding the material properties and identifying potential reliability issues for these interconnects is of the utmost importance.

“Micro-connects” is the term used for a class of interconnects that have a particularly small volume. In micro-connects the volume fraction of intermetallic compounds (IMC) to solder is much more significant, and in some specific cases contain no solder at all. Typical micro-connect bonding methods include low-volume soldering, eutectic, thermocompression and solid-liquid interdiffusion (SLID) or transient-liquid phase (TLP) bonding; for the hermetic encapsulation of MEMS devices (Figure 2 subfigure (a)) or micro-bumps for high-density die-to-die interconnection (Figure 2 subfigure (b)). For manufacturability, the requirements of processes, such as alignment accuracy and pre-treatments of bonding materials, are far more critical and play a much larger role in the fabrication of highly integrated systems.

Figure 2 – Illustration of micro-connects (a) sealing rings formed by SLID bonding technique for the hermetic encapsulation of a vacuum sensitive MEMS device and (b) micro-bump with through-silicon vias (TSV) vertical interconnections for memory stacking applications.

2.2 Properties of the Cu-Sn System

Arguably one of the most promising materials for interconnect technologies is the Cu-Sn system, not only for its proven mechanical stability, but also for the simple thermodynamic behaviour at the processing temperatures.³ The room temperature properties of Cu and Sn and the Cu-Sn IMC can be seen in Table 1. The Cu-Sn system itself exhibits advantageous properties for bonding applications, overall low electrical resistivity, good thermal conductance (for heat spreading) and a relatively small variation in the coefficient of thermal expansion.

Table 1 – Room temperature bulk material properties of the Cu-Sn system.^{4,5}

Property	Unit	Cu	Cu ₃ Sn	Cu ₆ Sn ₅	Sn
Density	g/cm ³	8.9	8.9	8.28	7.3
Molar Volume	cm ³ /mol	7.11	34.76	117.80	16.29
Young's Modulus	GPa	117	108.3	85.56	41
Vickers Hardness	kg/mm ²	30	343	378	100
Resistivity	μΩ·cm	1.7	8.93	17.5	11.5
Thermal Conductivity	W/m·K	398	70.4	34.1	67
Thermal Expansion	ppm/°C	17.1	19.0	16.3	23

The thermodynamic properties of the Cu-Sn system at the temperature utilized in the bonding processes <613K (<340°C) are relatively simple and have been well documented. Simple because there are a limited number of intermetallic compounds at the relevant temperature and the formation kinetics are well understood. Figure 3 is the Cu-Sn binary phase diagram. Typically Cu-Sn micro-connect processing temperatures using the SLID bonding technique are in the

range of 553-613K (280-340°C). The temperatures are chosen so that the time required for bonding is not unpractically long and so that no unwanted phases (such as the δ -phase) are formed. At the typical isothermal annealing temperature of 423K (150°C), there are two stable stoichiometric phases, ϵ (Cu_3Sn) and η' (Cu_6Sn_5).

Figure 3 - Cu-Sn binary phase diagram.⁶ The green shaded area is the typical Cu-Sn SLID bonding micro-connect processing temperature and the red dashed line is the typical isothermal annealing temperature of 423K (150°C) used in this work.

2.3 Micro-Connect Challenges

Despite the fact that there are a great number of advantages of Cu-Sn micro-connects, there are a number of reliability challenges that need to be understood. Examples of these challenges can be seen in Figure 4 that have been fabricated by using the SLID bonding process. Firstly, there are contact voids that appear at the original bonding interface. Voids appear when there is insufficient wetting of the bonding surface or there is insufficient amount of low melting point material. They form a void line along the original bonding interface, and in extreme cases (like the one in subfigure (a)) can lead to interfacial cracking. Si cracks propagate into the silicon surrounding the metallic bond region and could be caused by the manufacturing processes or the inherent residual stress of the material.⁷ Vertical cracking within the intermetallic region of Cu-Sn bonds that experience thermal shock loading also occurs. Vertical cracks appear to be intergranular cracks that propagate along grain boundaries.⁸ Finally there are Kirkendall voids (subfigure (d)) that form within the ϵ -phase.

Figure 4 – Cu-Sn wafer level SLID bonding challenges, (a) contact voids, (b) Si cracking⁷, (c) vertical cracks⁸ and (d) Kirkendall voids.

2.4 Kirkendall Voids Impact on Cu-Sn Micro-Connects

There is undeniably an impact on the reliability of an interconnect that contains voids, although this is often difficult to quantify for a number of reasons. One is with the difficulty to detect and characterise voids non-destructively. Kirkendall voids are notoriously small in volume (in the order of $0-0.3 \mu\text{m}^3$ [I]) and difficult to detect with traditional methods such as X-ray imaging or megahertz range scanning acoustic microscopy (SAM). Another reason is with the complexity of the structures under test. High-density interconnects often may consist of multiple failure modes that may or may not be in part caused by voiding, therefore isolating the exact root-cause for failure can be extremely difficult.

Nonetheless, there are a number of studies that have identified Kirkendall voids as the root-cause for failure or reduced mechanical and electrical performance. Zeng *et al.*⁹ evaluated eutectic SnPb solder joints on bare Cu, where a significant number of voids were observed. Shear and tensile measurements were made of the samples for a number of annealing temperatures ($<423\text{K}$ ($<150^\circ\text{C}$)) and durations. Results showed that joints were indeed weakened if they experienced voids at higher annealing temperatures and higher tensile pulling rates. The drop-test performance of Sn-3.5Ag solder joints with additional elements was evaluated by Kim *et al.*¹⁰. Results showed that samples with added solder elements, such as Zn, Mn and Cr, reduced the number of Kirkendall voids. This had the effect that the drop impact improved, indicating that the voids play a role in a joints resilience towards mechanical shocks. Similarly, Xu *et al.*¹¹ evaluated the drop reliability of tin-silver-copper (SAC) solders after

thermal cycling and found that in failed samples, cracks would propagate along the voided interface.

It should be pointed out that the samples examined in the studies were solder joints, and the true impact of voids on joints such as micro-bumps and SLID bonds for MEMS needs to be investigated further; the difference is that in low-volume interconnects a significantly smaller volume of soft solder material makes a joint more susceptible to shock loading. If voids do exist within such joints, it is obvious that the voids in a relatively more brittle interconnect would dramatically decrease the shock resistance. Another question is related to the impact of voids on the hermeticity of a Cu-Sn micro connect used in SLID bonding for MEMS.¹²

3. Driving Forces, Stability and the Kirkendall Plane

There are a number of factors that affect the diffusion fluxes of Cu-Sn system. There is random walk of atoms described by Fick's laws, with diffusion down a concentration gradient, and the chemical potential between the elements of the system. When a one-dimensional system is considered, the diffusion of elements in the system was described by Adolf Fick in 1855, in Fick's first law of diffusion¹³ in equation (1).

$$J = -D \frac{\partial C}{\partial x} \quad (1)$$

Fick's first law describes how a species diffuses to a region from high to low concentration, where J (mol/m²·s) is the flux of solute atoms, D (m²/s) is the diffusion coefficient, C (mol/m³) is the concentration and x (m) is the position along the one-dimensional system. There is no time component in Fick's first law therefore it can only be applied to a steady state system. Clearly this is more often not the case, consequently an extension based on mass conservation was developed. If $\frac{\partial J_A}{\partial x} = -(J_A^1 - J_A^2)/\Delta x$ for a small change in x and $\frac{\partial C_A}{\partial t} = -\frac{\partial J_A}{\partial x}$, substituting this into Fick's first law, the result is Fick's second law in equation (2).

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (2)$$

Where the subscript A is a component A (solute) in an A-B system. Although the equation has a time dependence, it assumes that the diffusion coefficient does not change. However, the diffusion coefficient can dramatically change with concentration, pressure and temperature. Because of this an interdiffusion coefficient $\tilde{D}$ has been introduced in equation (3).

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C}{\partial x} \right) \quad (3)$$

There are a number of methods that can be employed to help solve Fick's second law, as it cannot be solved directly, which describe the interdiffusion coefficient as a function of concentration.

Fick's laws have shown that whenever there is a concentration gradient there is a gradient dependent flux in the direction of the low concentration. However, this does not describe the underlying driving force for diffusion (for example in the case of uphill diffusion, from low to high concentration) within a system and the observed growth of intermetallic phases. A major contributor to diffusion phase growth is the chemical potential. Diffusing atoms favour diffusion down a chemical potential gradient, as illustrated in equation (4).

$$J_A = -L_A \frac{d\mu_A}{dx} \quad (4)$$

J_A (mol/m²) is the flux rate of element A, L_A (mol²/J·m) is a system dependent phenomenological constant and μ_A (J/mol) is the chemical potential of component A. Gibbs's energy diagrams are often used to illustrate the chemical potentials of a multi-component system. Figure 5 is the Gibbs energy diagram including the common tangent construction of the Cu-Sn system at a specific temperature and atmospheric pressure. The Gibbs energies and the chemical potentials can be seen in Table 2.

Figure 5 – Gibbs free energy diagram including the common tangent construction for the Cu-Sn system at 423K (150°C). The figure has been adapted from¹⁴.

Table 2 – Gibbs energies and change in chemical potentials of the Cu-Sn system at 423K (150°C).¹⁵

	Gibbs Engery	$\Delta\mu^{(x)}_{Cu}$	$\Delta\mu^{(x)}_{Sn}$
	J/mol	J/mol	J/mol
$x = \epsilon$	-8352.42	-9955.83	-29867.49
$x = \eta'$	-6879.37	-2617.10	-3099.77

Figure 5 shows the chemical potential driving forces for diffusion in the Cu-Sn system. The g^β is the Gibbs energy β -Sn curve. As the nominal mole fraction moves towards Cu, the g^β increases, as it requires more energy for a β -Sn atom to occupy a position in the α -Cu lattice configuration. The two line compounds, ϵ - and η' -phase, that form at the temperature of 423K (150°C) are represented in the diagram as a point at their corresponding mole fraction. The common tangent construction and the difference between the common tangents form the basis of chemical potential differences. Where, $\Delta\mu^{\epsilon_{Cu}}$ is the chemical potential difference of Cu between the Cu/ ϵ and ϵ/η' interfaces and, $\Delta\mu^{\eta'_{Cu}}$ for Cu across the ϵ/η' and η'/Sn interfaces. The same is true for Sn where $\Delta\mu^{\epsilon_{Sn}}$ is the chemical potential difference across the ϵ -phase and, $\Delta\mu^{\eta'_{Sn}}$ for Sn across the η' -phase. The magnitude of the difference represents the chemical potential driving forces. It is clear from the Gibbs free energy diagram that these potential difference magnitudes are not the same, as $\Delta\mu^{\epsilon_{Sn}}$ has a much larger potential difference when compared with $\Delta\mu^{\eta'_{Sn}}$. For a more detailed description of the chemical potential driving forces, the reader is directed to^{16,17}.

Up until now diffusion has been considered without consideration of the underlying mechanisms that allow it to occur. This cannot be neglected when investigating Kirkendall void formation within the Cu-Sn system. The random walk of atoms down a concentration gradient has been briefly discussed, and the preferential walk of atoms in a specific direction due to the chemical potential; but what is the underlying mechanism allowing diffusion to occur?

Substitutional diffusion is one of two dominating diffusion phenomena at solidus temperatures in the Cu-Sn system. Substitutional diffusion occurs when an atom and a neighbouring vacancy overcome an energy barrier and swap positions. In materials, due to the increase in configurational entropy, there is an equilibrium vacancy concentration throughout the material matrix, thus allowing substitutional diffusion to occur. An illustration of this phenomena can be seen in Figure 6 subfigure (a). The second significant contribution to diffusion in the Cu-Sn system is grain-boundary diffusion. An illustration of grain-boundary diffusion can be seen from Figure 6 subfigure (b). Grain-boundary diffusion occurs when the occupied volume is less than the bulk volume, and is dependent on the angle of the grain-boundary.

Figure 6 – Dominating solid state diffusion mechanisms in the Cu-Sn system, (a) substitutional diffusion and (b) grain-boundary diffusion.

The grain-boundary diffusion component is often significant as the energy barrier for diffusion is significantly less when compared with substitutional based diffusion, depending on the structure of the grain-boundary. Grain-boundary diffusion has been shown to be the dominating component at lower temperatures. A practical illustration of this behaviour is seen in Figure 7, in this case a sample kept at room temperature, a phenomenon called self-annealing, Cu experiences significant grain boundary diffusion to react with Sn to form η' -phase.

Figure 7 – Grain boundary diffusion of Cu into Sn to form η' -phase in a sample that has self-annealed at room temperature.

As seen in the Cu-Sn binary phase diagram (Figure 3), the phases formed in this work ϵ - and η' -phase, are line compounds and have a limited composition range. The diffusion and formation of such phases are treated differently, as there are discontinuities in the concentration gradient along the diffusion couple. Line compound layer growth is inversely proportional to the layer thickness.

This proportionality can be seen in equation (5), where dx (m) is the change in layer thickness, dt (s) is the change in time and k (m²/s) is a constant.

$$\frac{dx}{dt} \propto k \frac{1}{x} \quad (5)$$

If equation (5) is integrated, the change in layer thickness can be determined, where equation (6) shows the layer growth as a function of the square root of time, k_p (m²/s) is the parabolic growth constant.

$$\Delta x = \sqrt{2k_p t} \quad (6)$$

It should be noted at this point, that k_p is not a material constant, and can depend greatly on the end members of the diffusion couple. Integrated interdiffusion coefficients (seen in equation (7)) on the other hand are not dependent on the end members and are only depend on the line compound and the temperature, as introduced by Wagner.¹⁸ The integrated interdiffusion coefficient should be used when the compositional gradient is small and difficult to measure.

$$\tilde{D}_{int}^{\beta} = \int_{N_A^{\beta_1}}^{N_A^{\beta_2}} \tilde{D} dN_A \quad (7)$$

Where $\tilde{D}_{int}^{\beta}$ (m²/s) is the β -phase integrated interdiffusion coefficient, $N_A^{\beta_1}$ and $N_A^{\beta_2}$ are the composition of component A at β_1 and β_2 respectively and $\tilde{D}$ (m²/s) is the interdiffusion coefficient.

To understand the evolution of interfaces in a diffusion couple with phases with a narrow homogeneity range, the Physicochemical approach has been developed. This approach was introduced by Ghosh and Paul¹⁹ in 2007 and presents interfaces and interfacial reactions as rate governed chemical reactions. Figure 8 illustrates a diffusion couple (α and δ) of components (A and B) with two intermetallic phases (β and γ). The reaction interfaces are I, II and III and the interfacial reactions are given by equations (8)-(13).

Figure 8 – Illustration of the compounds, interfaces and flux parameters used in the physicochemical approach.

Interface I:

$$\frac{1-m}{m}q \cdot \alpha + q[B]_d \rightarrow \frac{1}{m}q \cdot \beta \quad (8)$$

Interface II: (β -side)

$$\frac{m}{n-m}p \cdot \gamma + p[A]_d \rightarrow \frac{n}{n-m}p \cdot \beta \quad (9)$$

$$\frac{1-m}{n-m}q \cdot \gamma \rightarrow q[B]_d + \frac{1-n}{n-m}q \cdot \beta \quad (10)$$

Interface II: (γ -side)

$$\frac{n}{n-m}r \cdot \beta \rightarrow r[A]_d + \frac{m}{n-m}r \cdot \gamma \quad (11)$$

$$\frac{1-n}{n-m}s \cdot \beta + s[B]_d \rightarrow \frac{1-m}{n-m}s \cdot \gamma \quad (12)$$

Interface III:

$$\frac{n}{1-n}r \cdot \delta + r[A]_d \rightarrow \frac{1}{1-n}r \cdot \gamma \quad (13)$$

At interface I $\frac{1-m}{m}q$ moles of the α -component plus q moles of diffusing element B react to form $\frac{1}{m}q$ moles of compound β . In the case of interface II, two reactions occur on each side of the interface. For example, on the β side $\frac{m}{n-m}p$ moles of γ plus p moles of diffusing component A react to form $\frac{n}{n-m}p$ moles of β , in addition $\frac{1-m}{n-m}q$ moles of γ results in q moles of diffusing B and $\frac{1-n}{n-m}q$ moles of β . So one can see that there is formation of the β -phase from the γ -phase from both diffusing components A and B. Following from the rate equations, the thickness can be calculated by a simple summation of the reaction products, seen for the β - and γ -compounds in equations (14) - (17).

$$\Delta x_{\beta}^I = v_m^{\beta} \left(\frac{1}{m} q \right) \quad (14)$$

$$\Delta x_{\beta}^{II} = v_m^{\beta} \left(\frac{n}{n-m} p + \frac{1-n}{n-m} q - \frac{n}{n-m} r - \frac{1-n}{n-m} s \right) \quad (15)$$

$$\Delta x_{\gamma}^{II} = v_m^{\gamma} \left(\frac{1-m}{n-m} s + \frac{m}{n-m} r - \frac{m}{n-m} p - \frac{1-m}{n-m} q \right) \quad (16)$$

$$\Delta x_{\gamma}^{III} = v_m^{\gamma} \left(\frac{1}{1-n} r \right) \quad (17)$$

The unknowns in equations (14) - (17) are p , q , r , s (mol/m²) and are called the flux components. Where p and q are the flux of diffusing elements A and B respectively in the β -phase and r and s are the flux of diffusing elements A and B respectively in the γ -phase. v_m^{β} and v_m^{γ} (m³/mol) are the molar volumes of the β - and γ -phases respectively. The ratios of p to q and r to s indicate the dominating diffusing species in a phase. Equations (18) and (19) illustrate this, and also their connection to the tracer diffusion coefficients D_A^* and D_B^* .

$$\left. \frac{D_A^*}{D_B^*} \right|_{\beta} = \frac{p}{q} \quad (18)$$

$$\left. \frac{D_A^*}{D_B^*} \right|_{\gamma} = \frac{r}{s} \quad (19)$$

It has been reported in the Cu-Sn system that the ratio of diffusivities are $\left. \frac{D_{Cu}^*}{D_{Sn}^*} \right|_{\varepsilon} \approx 30$ and $\left. \frac{D_{Cu}^*}{D_{Sn}^*} \right|_{\eta'} = 0.35$ in the temperature range of 423K-623K (150-350°C).²⁰

The physicochemical approach can be used for understanding the reactive diffusion behaviour of the binary Cu-Sn system. To understand the behaviour of the Kirkendall plane, its location and the initial contact point data taken from [I] (data has been adapted to match the observed behaviour of the η' -phase growth) is used to form a velocity diagram. The flux parameters shown in equations (18) and (19) are solved simultaneously with the Boltzmann's solutions to Fick's laws and for the isothermal annealing at 423K (150°C) for 4 hours. The resulting flux component values are:

$$p = 0.0391 \text{ mol/m}^2 \quad (20)$$

$$q = 0.0013 \text{ mol/m}^2 \quad (21)$$

$$r = 0.0068 \text{ mol/m}^2 \quad (22)$$

$$s = 0.0194 \text{ mol/m}^2 \quad (23)$$

The velocity of the phases can be estimated by taking the difference of the diffusivities in the respective phases.

$$v_m^{\varepsilon}(q - p) = 2tv_K^{\varepsilon} = -0.35 \text{ } \mu\text{m} \quad (24)$$

$$v_m^{\eta'}(s - r) = 2tv_K^{\eta'} = 0.133 \text{ } \mu\text{m} \quad (25)$$

Where t (s) is the time and v_K^{ε} and $v_K^{\eta'}$ (m/s) are the velocities of the Kirkendall plane in the ε - and η' -phases respectively. From these values (equations (24) and (25)) and the thickness results of the products of the reactive diffusion (equations (14)-(17)) a velocity diagram can be constructed. The velocity diagram of the binary Cu-Sn system can be seen in Figure 9. In the figure the ranges of x- and y-axes are kept at the same range, therefore the point at which the velocity curve intersects the $y=0$ is the estimated location of the initial contact plane.

Figure 9 – Velocity diagram of the Cu-Sn system isothermally annealed at 423K (150 °C) for 4 hours, (a) is the velocity diagram with the ϵ and η' Kirkendall plane locations (K_ϵ and $K_{\eta'}$) with respect to the three interfaces (I-III), original contact interface (X_0) and the velocity line, and (b) are the locations in a binary Cu-Sn diffusion couple example.

From the figure it is evident that there is bifurcation of the Kirkendall plane as both the Δx_ϵ^{II} and $\Delta x_{\eta'}^{II}$ are positive. This means that bifurcation of the initial Kirkendall plane will occur and each phase should have its own Kirkendall plane K_ϵ and $K_{\eta'}$, which has also been experimentally observed.²¹ Kirkendall planes have been shown to be stable or unstable. If a trace marker experiment results in a line of markers this indicates a stable Kirkendall plane, however if markers are distributed throughout a phase it is unstable. End members play a large role in determining whether a plane is stable or unstable by altering the Kirkendall plane velocity.

In the ϵ -phase, as expected from the fast diffusion of Cu, the Kirkendall plane is located close (~ 45 nm) to interface I (Cu/ ϵ interface). It is at this plane that one would expect to see the formation of Kirkendall voids. However, this plane is moving due to constant reactive diffusion. This could result in the two following behaviours: (i) as Cu is consumed both the interface I the K_ϵ moves in the Cu direction leaving behind vacancy accumulated voids that could explain distributed ϵ -phase voids or (ii) Kinetic or capillary pinning of voids causes them to move with the K_ϵ interface, resulting in a plane of voids at K_ϵ .²²

4. Characterisation of Void Formation

4.1 Electron Microscopy

Electron microscopy is the workhorse of material science and material characterisation. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) are three variants of electron microscopy. A basic SEM consists of an electron source that typically provides acceleration energies in the range of 5 to 30 kV, a condenser lens to converge the monochromatic electron source and deflection coils to raster scan the converged beam sequentially over the sample. Nowadays a basic SEM is optimised for a number of contrast mode images such as surface or topographical contrast and mass contrast. These signals are collected using a secondary electron detector, usually an Everhart Thornley secondary electron detector, and a solid-state backscatter detector. Topographical information is generated when the primary electron beam inelastically scatters from the specimen's surface region resulting in a high-resolution topographical image, as seen in Figure 10 subfigure (b). Mass contrast on the other hand, is generated from the elastically scattered primary beam that interacts much deeper within the sample surface. The number of backscattered electrons is dependent on the atomic number of the material, resulting in images that have mass contrast, as seen in Figure 10 subfigure (c).²³ SEM exhibits optimal characteristics for the numerical characterisation of a voided interface. A significant cross-sectional area can be analysed to generate numerical results for the average void size and average void density over a number of samples exhibiting different voiding densities [I]. However, the limitation of SEM is with the characterisation of initial void formation. As nucleation and formation occurs in the sub-10 nm range, high-resolving technologies are required in order to characterise the nucleation of voids.

Figure 10 – Electron microscopy of a (a) basic SEM schematic (b) Sn grain surface morphology micrograph using the secondary electron mode indicating topographical contrast (courtesy of Elmeri Österlund) and (c) Cu-Sn on Si cross-section micrograph using the backscattered mode indicating mass contrast.

There are a number of methods for preparing samples for SEM material characterisation. Surface or topographical analysis generally only requires the sample to be conductive to avoid charging of the samples. Cross-section samples require either a sequence of grinding and polishing of an epoxy moulded sample, or ion-polishing of samples using a broad Ar ion-beam. The quality of the sample preparation strongly determines the quality of acquired cross-sectional micrographs, for example any smearing of the voids.

TEM and STEM operate with acceleration voltages that are much higher than for SEM, typically between 100 – 300 kV, resulting in a much smaller electron de Broglie wavelength. Also the electrons are transmitted through the sample. A schematic of TEM and STEM systems can be seen in Figure 11. As electrons are transmitted through the sample, there are thickness requirements for the sample. High-resolution imaging requires a sample to be thinner than 100 nm. There are a number of different modes possible with TEM, these include high-resolution (HR), bright-field (BF) and dark-field (DF) and select area diffraction pattern (SADP). The HR mode occurs due to the interaction between the sample and the parallel electron beam's phase. Interpreting the phase contrast is complex, but can provide crystal structure information about a sample. BF and DF imaging utilise the objective lens aperture, as this enables the selection of either the direct beam (BF) or one of a number of diffracted beams from the sample (DF). The contrast formed in BF and DF provides microstructural information of a sample, such as crystal information and direction, defects and domain boundaries. SADP mode produces a diffraction pattern of a selected region of

the sample. The region can be selected using the variable sized select area aperture. This provides extensive crystal information from the selected area, such as crystallinity and texturing information.²⁴

Figure 11 – Electron microscopy schematic of a basic (a) TEM and (c) STEM.

4.2 Diffraction Techniques

4.2.1 Crystal Structure of the Cu-Sn System

For diffraction analysis it is crucial to understand the crystal structure of the material under investigation. The Cu-Sn system has been comprehensively studied and crystal structure of the four phases of interest in the Cu-Sn system include face-centred cubic (FCC) - Cu, orthorhombic- ϵ , monoclinic- η' and body-centred tetragonal (BCT) - Sn. The full crystallographic data can be seen in Table 3 with the graphical representation in Figure 12. For indexing and simulating crystallographic data the Inorganic Crystal Structure Database (ICSD) was used with the following powder diffraction file (PDF) numbers: 4-836, 65-5721, 45-1488 and 4-673 for Cu, ϵ , η' and Sn respectively.

Table 3 – Cu-Sn system crystallographic data.⁶

Phase	Stoichiometry	Crystal Structure	Type	Lattice Constants				Space Group	Ref
				a (Å)	b (Å)	c (Å)	β (°)		
Cu	Cu	Cubic	Cu	3.615	-	-	-	Fm-3m	²⁵
ϵ	Cu ₃ Sn	Orthorhombic	Cu ₃ Ti	5.529	47.750	4.323	-	Cmcm	²⁶
η'	Cu ₆ Sn ₅	Monoclinic	NiAs-Ni ₂ In	11.022	7.282	9.827	98.840	C2/c	²⁷
Sn	Sn	Tetragonal	Sn	5.831	-	-	-	I41/amd	²⁸

Figure 12 – Cu-Sn system crystal systems, (a) FCC-Cu, (b) orthorhombic long-period superstructure- ϵ , (c) monoclinic- η' and (d) BCT-Sn.²⁹

4.2.2 X-Ray Diffraction

X-ray Diffraction (XRD) uses electromagnetic radiation to probe a sample's crystalline properties. When an incident beam interacts with a sample, depending on the crystallinity, a large number of beams are scattered. At the detector the scattered beams constructively and destructively interfere, resulting in a diffraction pattern. The diffraction pattern is a function of the interatomic spacing, incidence and diffraction beam angles at the sample and the diffractometer. This is quantified in Bragg's Law as seen in equation (26).

$$n\lambda = 2d_{hkl} \sin \theta \quad (26)$$

Where n (1,2,3...) is the order of reflection, λ is the X-ray wavelength (commonly a Cu rotating anode of $K\alpha$ radiation $\lambda = 1.5406\text{\AA}$), $d_{hkl}(\text{m})$ is the interplanar spacing of the lattice and $\theta(^{\circ})$ is the incident angle. XRD diffraction has a number of advantages as a characterisation method. Firstly, a significant amount of information can be acquired, including crystallinity, composition, thin-film thicknesses (XRR), crystal texturing, and crystal quality and residual stresses. Secondly, the sample can be probed in its natural state without any significant preparation required, unlike TEM that requires a sample to be significantly thinned. However, significant care is required in setup configuration, measurements and in interpreting results. There are a number of configuration arrangements depending on the type of measurement. The Bragg-Brentano configuration can be seen from Figure 13. The basic components of an X-ray diffractometer include the X-ray source, incident and receiving optics and slits and the detector.

Figure 13 – Basic Bragg-Brentano setup of an X-ray diffractometer.

XRD scanning modes utilised in the work [IV] and [V] include a θ - 2θ symmetrical scan and wide-2D mapping. The scan configurations of both modes in the laboratory reference frame is shown in Figure 14. In the laboratory reference frame the diffraction vector is always aligned parallel to the L_3 axis. The θ - 2θ symmetrical scan probes the lattice planes that are perpendicular to the S_3 axis, which is aligned perpendicular to the sample substrate. The 2θ -angle is increased to scan a range of lattice plane d-spacing's within the X-ray exposed region of the sample. The wide-2D mapping on the other hand, allows for tilting of the diffraction vector in the S_3 - S_1 plane. This allows for the measurement of lattice planes that are not only perpendicular to the S_3 axis, but also off axis, giving insight into the texturing of materials and their angular distribution. The peak shape, skew and relative position from its nominal position gives structural information about the properties of the sample. The width and breadth of a peak also holds characteristic information on the crystal properties, such as crystallite size and non-uniform strain.³⁰ The shift from a crystal's non-strained 2θ angle provides information about the strain within a sample.³¹

Figure 14 – Scan configurations in the specimen (S_x) and laboratory (L_x) reference frames of (a) symmetrical θ - 2θ , (b) wide-2D scan and (c) $\text{Sin}^2\psi$.

To evaluate the impact of residual stresses on void formation, the XRD $\text{Sin}^2\psi$ method is employed. In this method the average of the residual stress from the illuminated area is determined from a specific material layer, in this case Cu. $\text{Sin}^2\psi$ measures the change in d-spacing as the diffraction vector (L_3) is moved from the S_3 axis to the S_2 axis, now labelled as the angle ψ . At a range of ψ angles the 2θ value is measured for a particular reflection under investigation. In a polycrystalline material that is mechanically elastically isotropic (absence of crystallographic texturing and directional dependent grain interaction), there is a linear relationship between $\text{Sin}^2\psi$ and the lattice d-spacing. If the strain-free lattice spacing is known and the $\text{Sin}^2\psi$ vs. d-spacing gradient is extrapolated from linear fitting, by applying Young's modulus and Poisson's ratio, the residual stress components of a measured material can be determined.³²

However, linear $\text{Sin}^2\psi$ vs. d-spacing gradients are often not the case particularly in textured thin-films. In many thin-films the material is macroscopically anisotropic resulting in non-linear $\text{Sin}^2\psi$ behaviour. For example, there are different degrees of elastic anisotropy for cubic materials, such as niobium ($A_i=0.55$), tungsten ($A_i=1$), gold ($A_i=2.85$) and copper ($A_i=3.21$), where A_i is a measure of a materials elastic anisotropy.^{33,34} In addition, if the material is highly textured, there are regions of ψ where the X-ray intensity is far too low

for a reliable determination of the d-spacing. To overcome this limitation Hauk³⁵ introduced the concept of X-ray stress factors that was extended by van Leeuwen *et al.*³⁶.

X-ray stress factors, seen in equation (27), are utilized to account of the non-linear d-spacing $\text{Sin}2\psi$ response of the measurements.

$$\{\varepsilon_{33}^L\}_{\psi,\varphi}^{hkl} = F_{ij}(\psi, \varphi, hkl) \langle \sigma_{ij}^S \rangle \quad (27)$$

Where $\{\varepsilon_{33}^L\}_{\psi,\varphi}^{hkl}$ is the average measured strain in the laboratory frame of reference (axis- L_3 is parallel to the diffraction vector), $F_{ij}(\psi, \varphi, hkl)$ are the X-ray stress factors and in this work formulated from single-crystal elastic constants, and an average of four different grain interaction models and $\langle \sigma_{ij}^S \rangle$ is the average stress tensor in the specimen reference frame. Often thin-films have rotationally symmetric strain, such as films that have fibre texturing, in such cases there is no φ dependence, therefore $\varphi = 0$. The four grain interaction models in this work [V] are the Vook-Witt, inverse Vook-Witt, Voigt and Reuss. They are discussed in detail in Welzel *et al.*³². Voigt and Reuss models are extreme grain models and are not compatible with the real mechanical behaviour of polycrystalline material. Voigt assumes that the strain is constant across all crystals and Reuss assumes the stress is equal across all crystals within the system. An extension of the models, with a focus on rotationally symmetric thin-films are the Vook-Witt (equation (28)) and inverse Vook-Will (equation (29)).

$$\varepsilon^S = \begin{pmatrix} \varepsilon_{||}^S & 0 & 0 \\ 0 & \varepsilon_{||}^S & 0 \\ 0 & 0 & 0 \end{pmatrix}; \sigma^S = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (28)$$

$$\varepsilon^S = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \varepsilon_{\perp}^S \end{pmatrix}; \sigma^S = \begin{pmatrix} \sigma_{||}^S & 0 & 0 \\ 0 & \sigma_{||}^S & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (29)$$

For Vook-Witt the assumption is that the film is rotationally symmetric in plane strain that is equal for all crystallites, with no sheer strain components and that the stresses are unconstrained in-plane and are free to deform with no out of plane components. On the other hand, the inverse Vook-Witt assumes a rotationally symmetric stress that is equal for all crystallites with no sheer stress components and has unconstrained in plane strain, except in the direction perpendicular to the film. In order to apply all four models simultaneously, an effective grain interaction model was used (equation (30) and equation (31)).

$$\Xi = \sum_i f_i \Xi_i \quad (30)$$

$$\sum_i f_i = 1 \quad (31)$$

Where Ξ is the effective grain model, f_i are the model fractions and Ξ_i are the grain interaction models, the fraction of grain interaction models must be equal to one.

4.2.3 Electron Diffraction

Electron diffraction utilises the wave nature of electrons and their interaction with a crystalline specimen. Electrons are elastically scattered in a sample and form a SADP. In the TEM the diffraction plane lies between the image plane and the objective lens. Electron diffraction has many advantages in TEM as it can be easily used to form images and diffraction patterns. The diffraction pattern provides insight into the crystallinity of a sample. Information includes, if the sample is amorphous, polycrystalline or single crystalline and if there are texturing components. In a SADP the distance between the primary beam and the diffracted beam provides information relating to interplanar spacing of a crystal and the angles between reflections gives angle differences between planes. SADP can be made from a very small sample area, providing crystalline properties from very small regions of a sample.

4.3 Chemical Analysis

There are a number of methods to probe the chemical composition of a sample, the first being SEM and STEM-EDS (energy-dispersive X-ray spectroscopy). The EDS operating principle is that when the primary beam of a SEM or STEM interacts with a sample, the electron beam ionizes an atom by exciting an inner core electron. The atom becomes unstable and relaxes by electron transfer from an outer shell. The energy difference between the inner and outer shell generates a characteristic X-ray, characteristic of the transition energy. The two major differences between SEM and STEM-EDS is the energy range and the lateral resolution. STEM-EDS is superior in the sense that only a fraction of the volume is probed, providing significantly improved lateral resolution. EDS is limited to elements greater than the Be k-line due to absorption and fluorescence noise. In quantitative EDS, the minimum mass fraction (MMF) depends on the sample and the EDS, but is often in STEM >0.1 wt. % due to the low count rates in thin samples.²⁴ This is problematic as trace impurities can be in the range of parts per million (ppm) or parts per billion (ppb). Because of these limitations, time-of-flight second ion mass spectroscopy (ToF-SIMS) was utilised for further trace chemical analysis.

ToF-SIMS is a powerful chemical characterisation tool that is able to measure all elements of the periodic table and is able to detect trace elements within the ppm and sometimes in the ppb range.³⁷ Another advantage of ToF-SIMS is that it can operate in a dynamic mode that provides compositional information as a

function of depth. The basic operating principle, is that a pulsed primary ion beam is used to bombard the surface of a specimen, this results in sputtered material being ejected from the sample. The sputtered material is charged and is extracted towards the time-of-flight chamber, it is then focused towards the detector. The differing mass causes the sputtered material to arrive at the detector at different times, the mass is then time resolved. A basic schematic of a ToF-SIMS setup can be seen in Figure 15.

Figure 15 – Simplified ToF-SIMS schematic.

The challenge with dynamic ToF-SIMS analysis is that sputtering rates can differ substantially, due to the variable sputter yield of polycrystalline material and differing materials. This causes the sputtering region to become substantially non-planar as deeper regions in the sample are probed, this seriously degrades the depth resolution. Furthermore, the ionisation potential of specimen material and the chemical state of the sample surface, known as the matrix effect, makes quantification particularly challenging.³⁷

5. Kirkendall Void Formation

5.1 Introduction to Kirkendall Voids

Kirkendall voids form within the interdiffusional zone of Cu and Sn. These voids form in the ϵ -phase. Voids form a porous interface that has been associated with a reduction in mechanical and electrical performance.^{9,38} In Figure 16, there are examples of Kirkendall void formation, void induced interfacial cracking and a high-magnification micrograph of a voided interface.

Figure 16 – Kirkendall voids in the Cu-Sn system, (a) SEM micrograph of characteristic void formation within the Cu-Sn interdiffusional zone, (b) SEM micrograph of Kirkendall void induced interfacial cracking and (c) BF-TEM micrograph of a Kirkendall voided interface.

5.2 Void Formation in Bulk Samples

It was in 1947 that Smigelkas and Kirkendall³⁹ first presented their results on the imbalance in diffusivities of the Cu-Zn binary system, which reinforced the theory that in solid state interdiffusion the vacancy diffusion mechanism occurs. An illustration of the Kirkendall effect can be seen from Figure 17.

Figure 17 – Illustration of the Kirkendall effect from the original Smigelkas and Kirkendall experiment.³⁹ Binary diffusion couple of α -brass and Cu with molybdenum inert markers indicating the Kirkendall plane. T_1 is non-annealed and T_2 is isothermally annealed the blue line indicates the movement of inert markers towards the fast diffusing species.

From this work, studies concentrated on understanding the diffusivities in different binary systems, such as Cu-Zn, Cu-Ni, Cu-Al and Ag-Au. Observed was the formation of porosity within the interdiffusional zone of the binary systems. Initially, Smiegelkas and Kirkendall did indeed observe “pitting”³⁹ however, it was da Silva and Mehl⁴⁰ in 1951 in Cu-Zn and Cu-Al that specifically reported different levels of “porosity” within the diffusional zone of these systems. In 1952 Balluffi and Alexander⁴¹ postulated that porosity observed in their Cu-Zn, Cu-Ni and Au-Ag diffusion couples was a product of the different diffusion rates of components, and that vacancies concentrated towards the fast diffusing species resulting in microscopic pores. However, Balluffi and Seigle⁴² commented on the observation that porosity did not always form at the same region in the binary couple, more specifically at the Kirkendall plane as would be expected. They point out, even though the boundary region of porosity is hard to characterise, that the region of porosity appeared to depend on the variation of the intrinsic diffusivities with composition. They found that in an Au-Ag couple the region of porosity would move parabolically with time, whereas for the Cu-Zn and Cu-Ni it remained concentrated close to the Kirkendall plane.

Seitz⁴³ in 1953 attempted to interpret the formation of voids in the preceding diffusion couple experiments. The Thomson-Gibbs relation was proposed for formulating a criteria for spherical void formation. The relation can be seen in equation (32).

$$\frac{N_v}{N_{v0}} = \exp\left(\frac{2s}{kTNr}\right) \quad (32)$$

Where N_v (mol/m³) is the excess concentration of vacancies, N_{v0} (mol/m³) is the equilibrium vacancy concentration, s (J/m²) is the surface energy of the

spherical void, k (J/K) is Boltzmann's constant, T (K) is absolute temperature, N (N/m³) is the atomic density and r (m) is the radius. Seitz suggested two possible void formation criteria, including: (1) that the excess concentration of vacancies must be greater than or equal to the equilibrium vacancy concentration $\frac{N_v}{N_{v0}} \geq 1$ or (2) that the presence of imperfections or impurities in the lattice operate as a nuclei for void formation, even with excess concentrations as little as $\frac{N_v}{N_{v0}} = 0.01$. Seitz was more inclined to believe an excess concentration of vacancies led to void formation. Brinkman⁴⁴ in 1955, favoured (2) and went further, suggesting tensile stresses within the interdiffusional zone cause deformation, such as edge dislocations, that allows for the annihilation of even low values of excess vacancy concentrations. Nonetheless, Seitz asked questions that are still very relevant such as, what are the nuclei of the voids and why does porosity vary between different material specimens?

5.3 Void Formation in Thin-Film Samples

Thus far it has been established that in bulk samples solid state diffusion is often not the same between species where voids have been attributed to the Kirkendall effect. Additionally, while in bulk samples that exhibit large differences in the diffusion rate between species, most would exhibit some level of porosity. However thin-film samples have appeared to confuse the situation further, as first pointed out by Selikson⁴⁵ in 1969. Selikson presented his results for an Au-Al thin-film overlayed (evaporated partially overlayed 100 nm Au-Al films) diffusion couple that experienced no void formation, which is in stark contrast to previous results involving Au-Al bulk diffusion couple experiments. In the bulk experiments voids formed in the Au rich intermetallic, indicating that Au is the faster diffusing species. In the thin-film samples it was also concluded that Au diffuses faster, however no voids were formed within the interdiffusional zone. Selikson concluded that the diffusion mechanism was not bulk diffusion but rather surface diffusion due to the overlay structure of the samples. In contrast to Selikson's result, Lloyd and Nakahara⁴⁶ found in the Au-Pb thin-film diffusion couple that void growth did indeed occur due to the Kirkendall effect. Nakahara and McCoy⁴⁷ from Bell Laboratories in 1980 attempted to understand this discrepancy between the findings of Selikson and Lloyd and Nakahara. They made a comprehensive study of Au-Sn thin-film diffusion couples with varying thicknesses and layer configurations, i.e. Au on Sn and conversely. In bulk samples Au has been shown to be the dominating diffusing species⁴⁸, but results from Nakahara and McCoy show that both can diffuse rapidly into each other. During their TEM study they observed a major difference in the grain structure of the samples that strongly depended on which material was deposited first. The conclusion was made that the diffusion mechanism is significantly more complex in thin-film samples as the grain sizes are smaller and the grain boundaries occupy a significant fraction of the film. They additionally

stressed the importance of careful assessment and reporting of the films thicknesses, geometry and grain sizes of diffusion couples.

5.4 Void Formation in Interconnect Technologies

In the early days of integrated circuit design, designers were assessing the best choice of metals for use as ohmic contacts. Al has been a material of choice since the mid-1960s¹ and has been commonly used as an ohmic contact directly to Si. Al is known for its property of reducing the native Si-oxide, allowing it to readily react with Si. To bond to Al, Au is an obvious choice as Au is a noble metal that does not easily oxidise, it is soft, malleable and is easy to bond with Al via a process called wire-bonding, using a thermocompression process. An illustration of an Al on Au wire-bond can be seen in Figure 18 subfigure (a). This process results in a number of Au-Al intermetallic compounds, including AuAl_2 and Au_5Al_2 nicknamed the purple and white plague respectively. It became evident that after isothermal annealing, with life-time testing, Au-Al bonds would simply lift-off resulting in the degradation of the device properties, known as the purple plague.² Selikson² in 1964 suggested that this behaviour is a result of the Si in the Al-Si contact diffusing into the AuAl_2 intermetallic, resulting in a porous interface. Selikson instead suggested using an Al-wire to bond to an Au electroplated Kovar contact, merely shifting the problem. Nevertheless, as Horsting in 1972 reported⁴⁹, there is a link between the bond failure and the purity of the electroplated gold, proposing that the purple plague (AuAl_2) has in fact, no impact on joint reliability. Nowadays, it has been reported that the degradation seen in Al-Au wire-bonding is a combination of the Kirkendall effect in Au-Al and corrosion.⁵⁰ Though not entirely apparent at the time, this is the first major impact of the Kirkendall effect/pores on the microelectronic industry.

More recently flip-chip technologies and the investigation of lead-free solders has generated much interest in Kirkendall voiding. An illustration of a flip-chip interconnect can be seen in Figure 18 subfigure (b). Flip-chip interconnects allow for an interconnect grid array, that is mounted on the active side of the Si chip, to be mounted via a solder bump to a PCB. There are a wide range of solder materials and under-bump metallisations (UBM) combinations.⁵¹ Common UBM include, Cr/Cu/Au, Al/Ni(V)/Cu, Al/Ni(P)/Cu and Cu/Ni. The solder material pre-RoHS (Restriction of Hazardous Substances) directive was eutectic SnPb and post-RoHS is Sn-Ag or Sn-Ag-Cu (SAC), where Sn takes part in the UBM-solder reactions. Flip-chip bonding has been a technology that has produced many sporadic reports of void formation, that are often not consistent.⁵¹⁻⁵⁴ Most cases report Kirkendall void formation at the interface between the IMCs and the UBM,^{52,55-58} with the rapid diffusion of the high-temperature material (Cu or Ni) through the IMC given as the root-cause. However there is increasing attention given to the fact that there are a number of inconsistencies between void reports and propensity of void formation.

Figure 18 – Illustration of the interconnect technologies, (a) is Al wire bonding with Au contact metallisation and (b) is the cross-sectional image of a common flip-chip interconnect.

5.5 Inconsistencies in Kirkendall Void Formation

As a result of the number of mixed reports on void formation, a number of researchers^{9,59–63} and [I] have decided to study common UBM and solder materials to find under what conditions void formation occurs. Focus was placed on Cu as the UBM and its reaction with different solder materials. During studies into the microstructural change of eutectic Sn-Ag solder joints by Yang *et al.*⁶³ in 1994, they noticed that void formation occurred in samples that had UBM of electroplated Cu, but did not in samples that used rolled Cu. Yang *et al.* suggested voiding may depend more on the base Cu used rather than the flux imbalance during the formation of the ϵ -phase. Furthermore, they speculated that co-deposited hydrogen during Cu electroplating agglomerates to form voids. Laurila *et al.*⁵⁹ in 2005 observed void formation differences in samples with different “quality” Cu UBM, such as electrochemically deposited Cu and oxygen-free high conductive (OFHC) Cu. They noted that electrochemically deposited Cu films are often associated with incorporated impurities. Their results showed that in the OFHC Cu and reflowed pure Sn or pure SnAgCu no voids were detected within the interdiffusional zone. However, the electrochemically deposited Cu sample exhibited a significant number of voids but with different distributions within the ϵ -phase. Pure Sn on electrolytic Cu exhibited voids distributed throughout the ϵ -phase, whereas pure SAC on electrolytic Cu experienced voids localised at the Cu/ ϵ interface that appeared to be at the Kirkendall plane. Laurila *et al.* speculated that impurities in the electrolytic Cu changed the composition of the end member and consequently the diffusion fluxes within the interdiffusional zone. This ultimately results in either a stable or non-stable Kirkendall plane, and dictates whether voids form or not. Admittedly, Laurila *et al.* found it more difficult to explain the case where voids were evenly distributed throughout the ϵ -phase, and conceded that more work was needed and that void formation could be influenced by the impurity redistribution rather than the stability of the Kirkendall plane.

Yu and Kim⁶² expanded on the work of Yang *et al.* and Laurila *et al.* by exploring the electrochemical deposition process. They used as a reference rolled Cu

foil and a electroplating solution with varying amounts of a common electroplating additive SPS or Bis-(3-sulfopropyl)-disulphide on a PCB. The solder material used was SnAg that was reflowed and thermally annealed. Results confirmed the previous findings that a pure Cu foil did not exhibit any voiding. However, a significant number of voids were detected in the samples with electrolytic Cu, as a function of increasing concentration of SPS. A chemical analysis as a function of increasing SPS concentration revealed the increasing presence of sulphur at the Cu/ ϵ interface. Yu and Kim hypothesised that segregating sulphur reduces the free energy barrier and results in vacancy annihilation, indicating that impurities are a required ingredient for void formation.

A statistically significant study into voiding parameters was made by Yin and Borgesen⁶¹ in 2010. Three groups of samples were analysed: (i) 103 combination of commercially available solder joints and samples from reliability tests, (ii) 45 free standing Cu foils from different sources manufactured from role-to-role processes and (iii) 2 commercial high purity wrought Cu foils with a low impurity content. A cross-sectional volume expansion analysis during annealing and chemical analysis of the samples and a proposal for the root-cause of void formation was presented. Yin and Borgesen concluded that in all samples, excluding the high-purity samples, varying levels of voiding was observed and suggested that the Kirkendall effect alone does not explain void formation. Chemical analysis showed that in many cases there are significant amounts of impurities within the Cu. In the electroplated Cu foils alone, during high-temperature annealing significant volume expansion occurred and cross-sections revealed pore formation that impeded crystal growth. Finally, they suggest that impurities cause voids to form by blocking vacancy sinks and lowering the void nucleation barrier.

This work [I] attempts to understand firstly the inconsistency in Kirkendall void formation and secondly the correlation between the electrolytic Cu process and void formation. Additionally the work studies the impact of voids on the formation kinetics of the Cu-Sn IMC. Similar to the results of the previously presented studies, there was a strong dependence on the electroplating Cu process and void formation. In the study a range of different Cu electrolyte processes were selected with a number of electroplating current densities. Results showed that the least propensity to void occurred with the “purest” electroplating chemistry that did not contain any additives. The worst offending electrolytes were the additive containing solutions. Figure 19 shows the difference in voiding propensity between a sample that has used a commercial electroplating solution and a generic solution using only an SPS brightener solution. The commercial solution under specified conditions shows little propensity to void, whereas the SPS additive solution shows always a high propensity. In addition to the void formation, the IMC growth rate was examined and it was found that a high density of voids at the Cu/ ϵ interface act as a diffusion barrier for Cu. This ultimately results in the consumption of the ϵ -phase by the η' -phase if annealing is continued.

Figure 19 – Cu-Sn cross-sections of electroplating (a) commercial solution (b) SPS additive solution, that have been isothermally annealed at 423K (150°C) for 24 hours [I].

The results of this work [I] show, as with others, that the Cu electroplating process plays a more important role in void formation than the Kirkendall effect. Moreover, the purity of the Cu UBM dictates whether voids form or not. OFHC Cu has shown to exhibit no voiding in numerous studies,^{59,61–63} whereas electroplating that is shown to co-deposit impurities, has often exhibited sporadic voiding. Furthermore, the additive system and electroplating parameters used in the Cu electroplating process appears to influence voiding.

6. Electroplating

6.1 Introduction to Electroplating

Electrochemical deposition is a process of depositing a solid metal on a conductive surface (cathode) when immersed in an aqueous metal solution. In a typical electroplating cell there are two electrodes, the cathode and anode and in many cases a third acting as a reference. When a bias is applied a process of oxidation and reduction occurs at the anode and cathode respectively. At the anode, oxidation allows the dissolution of the source metal into the solution and at the cathode, ionised metal atoms are reduced onto the cathode surface. Figure 20 illustrates a basic electroplating setup.

Figure 20 – Illustration of a typical electroplating setup. Shown in the diagram is the anode and the cathode, current controlled power supply, and the dissolved metal ions M and z is the number of electrons taking part in the reaction.

The reduction reaction of the metal ions to the cathode can be seen in equation (33), where an ion with z -electrons reduces to a solid metal. In the other direction, equation (34) is the oxidation process where metal is oxidised, releasing electrons and resulting in a metal ion. In the case of Cu and Sn, both are a two-electron transfer process.

To determine the amount of material that is deposited, Faraday's law is utilized, equation (35). This states that the weight of a deposit is proportional to the electrochemical equivalent by the charge. The electrochemical equivalent is the weight of material transferred per unit charge.

$$w = ZQ = Zit \quad (35)$$

Where w (g) is the weight of the deposit, Z (g/C) is the electrochemical equivalent, Q (C) is the charge, I (A) is current and t (s) is time. The deposit thickness is determined by the weight divided by the area and density, seen in equation (36).

$$h = \frac{w}{ad} = \frac{ZIt}{ad} \quad (36)$$

Where h (m) is the thickness of the deposit, a (m²) is the total exposed area and d (g/m³) is the density of material. The overpotential, measured between the cathode and the third electrode, is the difference between the potential of the cathode when current is flowing and the potential when the cathode is at equilibrium, or no current is flowing. This relationship can be seen in equation (37).

$$\eta = E(I) - E \quad (37)$$

Where η (V) is the overpotential, $E(I)$ (V) is the potential of the cathode and E (V) is the equilibrium potential. The measure of the overpotential becomes of particular importance when dealing with competitive absorption and desorption of additives. For example, the suppressor molecule, when sufficient surface coverage occurs inhibits the ion-transfer mechanism to the cathode surface by decreasing possible growth sites. This increases the potential of the cathode and subsequently the overpotential, a phenomena called cathodic polarisation.

6.2 Applications in the Microelectronics Industry

Electroplating has been used extensively in the microelectronics industry since the early 20th century. Applications include plating of PCB interconnections, heat exchanges and non-corrosive coatings of connectors. A typical application of Cu electroplating is the Damascene process that is driven by the need to change the redistribution layer from Al to Cu, due to the superior electrical conductivity of Cu over Al. A single Damascene process is shown in Figure 21.

Figure 21 – Illustration of the Damascene process, (a) deposition and patterning of dielectric, (b) deposition of the Ta/TaN adhesion/barrier liner and Cu seed-layer (c) blanket deposition of electroplated Cu and (d) final chemical mechanical polishing (CMP). Adapted from⁶⁴.

Nowadays, the number of applications for the Cu electroplating process has expanded with the development of Cu-pillar and Cu-TSV applications for 3D integration. These applications exploit a basic photolithography step on a Cu seed-layer where electroplating only occurs in the regions where the seed-layer is exposed. This results in complex, fine-pitched structures that are released once the photoresist layer is stripped away. The Cu-pillar process is illustrated in Figure 22.

Figure 22 – Illustration of the photoresist masked Cu-pillar process (a) of the adhesion/barrier layer, (b) photolithography (c) deposition of electroplated Cu and (d) photoresist stripping followed by seed and adhesion/barrier layer etching.

6.3 Cu Electroplating Process and the Additive Systems

The basic components for Cu electroplating are copper sulphate and sulphuric acid or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The copper sulphate provides a source for the Cu ions and the sulphuric acid is used to dissolve the Cu ions and to maintain a high solution conductivity. In addition a low Cl concentration is required in the basic solution, not only to ensure proper anode corrosion (avoid anode polarisation), but also to enable synergistic functionality with a number of additives.^{65,66}

Fine pitched and complex structures for high-integration places stringent requirements on the deposited film. The film is required to have good uniformity, low surface roughness, low residual stresses and repeatability. These strict requirements result in an increased electroplating solution complexity, and the need for a combination of organic and non-organic additives to produce the required film. Additives fall into two categories: brighteners and suppressors. The additives are designed to affect the crystal growth behaviour that occurs at the cathode surface. Brighteners are designed to refine the grain structure and to level the film, whereas suppressors are designed to suppress the deposition on localised peaks and allow deposition in troughs.⁶⁵

Two commonly used additives, also often used in this work, in the microelectronics industry for superfilling and conformal coverage are the Bis-(3-sulfopropyl)-disulphide or SPS and Polyethylene glycol or PEG. SPS is a Cu bath brightener that synergistically works together with PEG to produce deposits that are bright and level.^{67–69} The PEG-Cl combination acts as an inhibitor, polarising the cathode surface or acting as a site blocker during deposition. SPS on the other hand, acts as a depolariser, displacing the inhibiting layer. This behaviour occurs in regions of non-uniformity, resulting in a higher catalyst concentration in a trough.⁷⁰ It is this localised catalyst behaviour that results in the levelling behaviour of the SPS-PEG-Cl additive system. SPS and PEG are just two possible additives in a long list of additional agents and combinations thereof.⁶⁵

The surface behaviour of the additive systems often means that components are incorporated into the deposited Cu film, this occurs due to a number of factors. It can occur during the natural competitive cycle of absorption and desorption of the catalysis, when the additive system is unable to function synergistically and with an increasing age of an electroplating bath.^{70–72} The incorporation of additives into the electroplated film presents a number of challenges, they change the underlying microstructure of the material, how it behaves over time and the impact it has on the resulting material properties.

In addition to the additives the operating conditions of an electroplating bath influence the performance of an electroplating system. For example, bath temperature, the current density, agitation rate, filtration and purification, anode and cathode structures all play a role in determining the operating conditions. These variables also effect the performance of the bath additives, by changing

the polarisation characteristics of the anode and the cathode. This in turn also impacts the desired quality of the electroplated material, such as high-strength, low electrical resistivity, low residual stresses and high thermal stability.⁶⁵

7. Understanding Void Formation

7.1 Key Parameters Influencing Void Formation

In section 5 Kirkendall voids were presented in the Cu-Sn system as a result of the flux imbalance between two diffusing species, known as the Kirkendall effect. However, as discussed this presents a problem as numerous studies have shown that void formation is not consistent, and in some cases does not exist at all. This suggests that there are additional mechanisms that change the propensity of an interface to exhibit voiding. This work [I] and other studies^{61,72–74} shows that even when electroplated Cu is used the characteristic void formation is dependent on the electroplating parameters.

Kumar *et al.*⁷⁵, and this work [I] assessed the effect of the age and purity of the electrolytic bath on voiding propensity. These two variables are interlinked as the additives in electroplating solutions over time decompose adding to higher concentration of impurities in the electrolytic bath.^{71,76} Kumar *et al.*⁷⁵ assessed the Cu electrolytic bath age (along with other parameters), results showed a higher propensity for void formation in an aged solution. In fact, out of all the parameters measured, age had one of the greatest impacts on void formation. This work [I] studied the impact of the use of a lower purity chemical on void formation. A Cu-Sn stack on silicon, that was isothermally annealed, was studied using a Cu electrolytic solution containing a basic solution of copper sulphide, high and low grade sulphuric acid and hydrochloric acid. Results in Figure 23 show that the low purity solution resulted in many voids within the ϵ -phase. Numeric analysis showed that the saturated (after a duration of thermal annealing voids ceased to form) voiding density was 0.254 and 0.054 voids per μm^2 for the low and high purity solutions respectively. This result confirmed Kumar's findings and indicate that the purity of the electrolytic solution is a contributing factor to void formation.

Figure 23 – Cu-Sn cross-sections of electroplating solutions that have been isothermally annealed at 423K (150°C) for 8 hours without additives using (a) low and (b) high purity sulphuric acid [I].

In addition to the age of the electrolytic Cu bath, Kumar *et al.*⁷⁵ studied the impact of additives such as wetting agents, levellers and brighteners. Observed, was a broad range of void formation, from no voiding to complete saturation of the Cu/ ϵ interface. In general, the results showed that the solutions that contained brighteners, in addition to the bath age, exhibited the highest propensity to void. Kim and Yu⁷² study followed a similar path, comparing a high-purity Cu-foil and a Cu electrolytic solution with and without the SPS brightening additive. As at this point expected, and similar to Kumer's results, the high-purity Cu-foil showed no voids, the electrolytic solution without additives experienced little to no voiding and the SPS brightener solution showed a high propensity to void. This work [I] extended this work to include, not only the SPS brightener, but also the commonly used suppressor PEG. The combinations of additives included, a commercial solution, SPS brightener, PEG suppressor and a synergistic combination of the two SPS+PEG. The commercial solution contains a combination of unknown additives that is propriety information, but can be used as a reference to compare the other additive systems. At a nominal current density (or middle current density), the commercial solution experienced little to no voiding, whereas all other additive systems exhibited significant voiding levels. Interestingly, one would expect the SPS+PEG system to exhibit only small levels of voiding as the additive system is expected to operate synergistically. However this was not the case in [I]. In a more recent study [V] this additive combination has not resulted in voids. A comparison of the two studies can be seen in Figure 24.

Figure 24 – Results from the SPS+PEG samples were isothermally annealed at 423K (150°C) for 4 hours from (a) [I] and (b) [V] samples. Note the difference between voiding levels.

This difference illustrates the complexity that the additive system makes on the voiding propensity. The discrepancy arises from the difference in the agitation rate during the electrolytic Cu process. Samples from [I] were prepared in the 3-litre small volume electroplating cell, while in [V] the samples were prepared in a hull cell. The hull cell contains a much smaller electrolyte volume (267 ml) and both were agitated by only a small magnetic rotation stirrer. Ross *et al.*⁷⁷ indicated that agitation can play an important role in void formation and presented void formation for a range of chemistries and agitation rates. The competitive absorption of SPS and PEG is strongly dependent on the agitation rate.⁷⁸

Another parameter that interacts with the performance of the additive systems is the current density. The current density, among other things, controls the deposition rate. It is the measure of electron transfer per unit area of the cathode. Wafula *et al.*^{74,79} explored the PEG and SPS+PEG combinational relationship with the current density. The PEG solution was sensitive to increasing current densities producing increasing void formation. On the other hand, the SPS+PEG solution was sensitive to decreasing current density producing increasing void propensity. Wafula *et al.* speculates that for the PEG solution, the PEG+Cl⁻ combination is an inhibitor which results in polarization of the cathode (measured by a high overpotential) that increases at higher current densities; this eventually favours the decomposition and incorporation of the inhibiting layer into the Cu film. For the SPS+PEG solution, as there is a competitive behaviour SPS+PEG ensemble, the polarization of the cathode is low. At low overpotentials there is weak absorption of the PEG inhibiting layer favouring SPS absorption and decomposition into the Cu film. The characteristic void formation observed in [I] differs somewhat with the previous findings, as in general the high current density samples resulted in significant levels of voiding. The difference between the results arises from the different Cu electroplating environments, more specifically the agitation rate. [I] expanded on Wafula's

work, by including the current density dependence on the basic solutions. Results showed little variation on voiding between the current densities indicating that the current density interacts with the Cu electrolytic additives.

Thus far it is becoming clear from the discussion that there are a great number of influencing parameters that impact on void formation. In addition, there is also interaction between these parameters, making void formation appear to be sporadic and unpredictable. A flow diagram is presented in Figure 25 illustrating the Cu electroplating process that results in void formation. The main contributing parameters include:

- Age and purity of electrolytic copper,
- Additive system,
- Agitation rate,
- Current density.

Figure 25 – Flow diagram of Cu processes and void formation.

7.2 Changes in the Microstructure

Although void formation in the Cu-Sn system is a function of the Cu electroplating parameters, it is still unclear how these effect void formation. It is clear

from previous discussions that the electroplating parameters can change the microstructural properties of the deposited Cu (Section 6). Properties include the crystal size and orientation, defects and residual stress. Therefore it is important to identify common microstructural attributes of the Cu-Sn system that are associated with void formation.

This work [I] briefly touched upon the relevance of the grain structure, although the true impact at the time was not completely understood. A focused ion beam (FIB) cross-section was prepared from an isothermally annealed SPS+PEG sample. The cross-section revealed only a small number of voids, and the grain structure of the Cu-Sn stack. The electroplated Cu layer exhibited a coarse grain structure. At the time of the article, the relevance of this finding was not well understood therefore no comparative samples were made. However, other studies have started to identify the correlation of grain size on void formation. During the early work of the impact of thin-films on the Kirkendall effect, Nakahara and McCoy⁴⁷ commented on the impact of a fine grain structure on the changes in the diffusivity and subsequently on Kirkendall void formation. They noticed that the effect of grain-boundary diffusion is enhanced in thin-films as the volume fraction of grain boundaries is much larger and they speculated that it is this and the subsequent rapid diffusion that allows voids to form. In addition to the rapid diffusion, they speculated that interdiffusion induced stresses can contribute to void formation.

A number of publications^{61,80–83} have associated a fine grain structure and void formation. Yin and Borgesen⁶¹ studied a wide range of electroplating baths and their resulting voiding formation. They noted by preannealing the Cu foils in high temperatures 923K (650°C) for two hours reduces the void formation significantly. There were discrepancies between the Cu-foils, where foils that exhibited voiding typically had a smaller grain size compared to foils that did not. Kim and Yu⁸¹ conducted similar research suggesting that heat-treated Cu films could suppress the formation of voids. Studies systematically link the co-deposition of impurities during Cu electroplating and the segregation of these impurities to the grain boundaries. The extra thermal energy from the heat treatment allow for the grain boundary diffusion and eventual desorption of the impurities. This process also allows the grain growth to occur. Borgesen *et al.*⁸⁰ suggests that monitoring the grain growth behaviour of an annealing Cu film can provide an insight into the likelihood of void formation.

These studies [IV] and [V] have considered the effects of different electrolytic Cu solution impact on the resulting as deposited and isothermally annealed Cu-Sn microstructure. Results of the TEM/STEM studies revealed interesting results regarding the correlation between the Cu microstructural behaviour and voiding. The Cu grain structure of voided samples exhibit significantly smaller grain-size or ultrafine crystalline, when compared to non-voided samples. Figure 26 presents examples of a fine grained microstructure with dense voiding and a coarse grain structure with little to no voids, seen in subfigures (a) and (b) respectively. In addition to the grain structure, voided samples exhibited a number of defects.

Figure 26 – BF-STEM micrographs with phase boundaries highlighted with a red-dashed line of (a) a voided sample experiencing a fine Cu grain micro-structure structure and (b) non-voided sample with a large Cu grain micro-structure. The red dashed line indicates the phase boundaries.

Figure 27 shows two micrographs and a SADP of a voided Cu-Sn interface. Figure 27 subfigure (a) shows the HR-TEM micrograph of a void that only semi-penetrates the lamella (light region), and two Cu grains. A general observation is that a significant number of voids formed at the Cu grain boundaries. The Cu grains and the void are separated by a 120° triple grain boundary. Subfigure (b) shows the DF-TEM micrograph with the objective lens aperture selecting the Cu(111) grains that are in the substrate perpendicular direction. Visible are the long characteristic columnar grains of the Cu microstructure extending to the Cu/ ϵ interface. Subfigure (c) is the SADP of the Si and Cu that indicates that there is Cu(111) texturing perpendicular to the substrate surface.

Figure 27 – TEM micrographs of (a) HR-TEM of the grain boundary and void interface, (b) DF-TEM micrograph of the Cu/ ϵ interface with the Cu(111) grains selected with the select area aperture and (c) SADP of the Si and Cu region with the Si(002) plane and polycrystalline Cu(111) indicated.

A defect observed was FCC Cu grain twinning, which is classical plastic deformation behaviour. When a crystal experiences shear stress, there is atomic dis-

placement within the crystal. This indicates that the samples exhibiting this behaviour are under a certain amount of residual stress compared to the void free samples. Metals are generally soft materials but they can be hardened significantly by plastic deformation. The displacement causes a characteristic mirror like structure within the twinning grains.^{84,85} A non-annealed SPS sample with Cu grain twinning that can be seen in Figure 28. Subfigure (a) is the BF-TEM micrograph overview of the twinning phenomena and subfigure (b) is the HR-TEM micrograph with the Cu lattice fringes displaying the mirror like twinning. The Cu(111) planes are indicated by the red line with the angle of twinning at 146° . The columnar structures in subfigure (b) are the grain boundaries with a certain polishing effect, that is produced during the FIB lamella preparation.

Figure 28 – Cu twinning phenomena in the non-annealed SPS sample, (a) is the BF-TEM micrograph of the twinned Cu and (b) is the HR-TEM micrograph indicating the twinning boundary and angle.

Texturing of ultrafine crystalline Cu is another property of the microstructure that was probed by using electron diffraction and SADP to characterise the directional distribution of the Cu grains of voided and non-voided samples. SADP operates by using an aperture to select a region of the sample and then exposing the sample to a parallel electron beam. SADP analysis can be seen in Figure 29. In the figure there are three non-annealed samples, subfigure (b) SPS, (c) PEG and (d) SPS+PEG. The typical region at which the SADP were taken is shown in subfigure (a). There are both Cu texture and crystal size differences between the samples. SPS, (subfigure (b)) has a narrow distribution of Cu(111) around the direction perpendicular to the substrate surface and exhibits a fine grain structure. The PEG sample (subfigure (c)), on the other hand, has a wider distribution of Cu(111), also with a smaller grain structure. SPS+PEG (subfigure (d)) has a much larger crystal size, indicated by the discrete spots, and is therefore difficult from the SADP alone to speculate on texturing. TEM/STEM studies provide substantial microstructural information from the samples; but to gain crystal and stress-strain information from a larger region of the sample XRD is used.

Figure 29 – SADP analysis of three samples, (a) HR-TEM overview micrograph of the SADP region, non-annealed (b) SPS, (c) PEG and (d) SPS+PEG samples [V].

There are only a limited number of studies understanding the link between Cu texturing and voids, however Huang *et al.*⁸⁶ studied the effects of preferred orientation of the Cu substrates on void formation. The substrates with Cu surface of (111) and (220) and random orientations were prepared. The preferred orientation substrates were electroplated at different current densities. Results showed that the sample with a preferentially orientated Cu surface resulted in severe voiding during isothermal annealing, whereas the randomly orientated surface exhibited less voiding. It is difficult from this work to confidently conclude that substrate orientation plays a role in void formation, rather one would expect the changes in the current density would play a much larger role in void formation. Yin *et al.*⁸⁷ studied texturing of various typical suppressor-accelerator additive systems. A texture coefficient was used to measure the amount of texturing occurring in the samples with respect to the voiding propensity. Their results showed that there is a tendency towards less voiding when there is no texturing occurring. Yin *et al.* speculates that when an additive system is not operating synergistically, variations in growth behaviour during deposition occurs which results in a non-polycrystalline deposit.

The results in [IV] and extended in [V] does not agree with the conclusion made by Yin *et al.*. Firstly, observed in this work was both isotropic and anisotropic behaviour of the Cu(111) peak in samples with and without voids. The Cu(200) however exhibited isotropic behaviour in voided samples and anisotropic behaviour in non-voided samples. The results of the wide-2D scan can be seen from Figure 30 and the corresponding SEM cross-sections can be seen in

Figure 31. From the two figures no characteristic link can be made between the texture of a sample and void formation.

Figure 30 – XRD wide-2D diffraction scans of the non-annealed and isothermally annealed samples at 423K (150°C) for 4 hours. Shown are the diffractograms of the Cu(111), Cu(200) and Cu(220) peaks of the, (a) SPS sample, (b) PEG sample and (c) SPS+PEG sample [V].

Figure 31 – SEM-BSE micrographs of the non-annealed samples (a) SPS, (b) PEG and (c) SPS+PEG, followed by the isothermally annealed samples at 423K (150°C) for 4 hours of (d) SPS, (e) PEG and (f) SPS+PEG [V].

Observed in the wide-2D measurements was a clear shift towards a lower 2θ value as a function of increasing χ . This means that as the diffraction vector moves from S_3 towards the S_1 axis the d-spacing of the lattice planes increased. This behaviour is characteristic of residual stress.³⁵ Residual stress in thin-films can come from a number of sources. For the Cu-Sn system it can come from the

electroplating process itself,⁶⁵ film thicknesses⁸⁸ and the volumetric change due to the formation of the ϵ - and η' -phases.⁸⁹ Residual stress generated by the deposition process introduces defects in the copper, such as grain boundaries, twinning and stacking faults. If only a Cu film is considered, thermal annealing of stressed films results in a relaxed film as crystal growth and preferential texturing occurs. However, during thermal annealing of the Cu-Sn system on a Si substrate the coefficient of thermal expansion (CTE) difference and the growth of the IMC layers is one source of residual stress.

Yu and Kim⁶² discussed in detail the topic of residual stresses and void formation. They argue that once initial void nucleation occurs due to the lowering of the free energy barrier by segregated sulphur, further energy is required for additional void growth. The additional energy is from the residual stresses, due to vacancy annihilation, that allows voids to grow. They make wafer-curvature measurements to determine the residual stress verses SPS content in an electrolytic Cu process. The tensile residual stress did indeed increase as a function of SPS content with the increase attributed to the introduction of defects and impurities into the film during deposition.

[V] investigated the impact of residual stress as a function of additives, by using XRD and X-ray stress factors. Three samples were analysed in both their non-annealed and isothermally annealed state. Results of the rotationally symmetric stress values are listed in Table 4. The results showed that for all samples rotationally symmetric average tensile stresses increased as a function of thermal annealing. The sample with the least propensity to exhibit voiding had the lowest residual stress value and the smallest change during annealing.

Table 4 – Results of the rotationally symmetric average stresses in the non-annealed and annealed samples. [V].

Sample	Annealing duration (hr)	
	0	4
SPS	40.03 $\pm$ 16.47 MPa	128.66 $\pm$ 15.02 MPa
PEG	51.40 $\pm$ 15.76 MPa	151.52 $\pm$ 9.08 MPa
SPS+PEG	12.07 $\pm$ 4.47 MPa	72.35 $\pm$ 7.07 MPa

This method uses an average of residual stress over the X-ray illuminated region. It is probable that there is a significant stress gradient near the Cu/ ϵ interface that rapidly decreases away from the interface; this means that the local residual stress at the interface could be much more significant. Although there is a strong correlation between the residual stress and voiding propensity, it is not entirely clear to what extent residual stress plays a significant role. Nonetheless, it could be conceivable that any residual stress, in particular tensile stress, would provide additional energy to create new surfaces. Further studies are needed to understand the impact of the residual stress, and the residual stress gradient at the Cu/ ϵ interface and on void formation.

7.3 Trace Impurities

The focus thus far has been on the microstructural properties of the electroplated Cu and key phenomena that occur with the voiding behaviour of the Cu-Sn system. Another important consideration is with the impact of trace impurities in the system. As has been mentioned, trace impurities are often co-deposited during the deposition process. It is important to investigate what role these impurities play by influencing the microstructure and subsequently the propensity of an interface to void.

In terms of lead-free material research, it was Laurila *et al.*⁵⁹ whom first found detectable amounts of impurities in electrochemically deposited Cu for UBM, and found a direct link between the “purity” of the Cu used and void formation. Since then, there has been a large number of publications^{61,62,72,73,90–92} [II], [IV], [V] that have researched the link between electroplating parameters, residual impurities and void formation. A particular focus has been on the decomposition and incorporation of additives into the deposited film during Cu electroplating. Liu *et al.*⁹⁰ studied the correlation between the Cu electroplating current density and impurities in the film using SIMS. A common additive suppressor and accelerator combination was used and the current density was varied between 10 and 60 mA/cm². Liu *et al.* found that the organic components of the additives, such as C, O, S and Cl, are co-deposited in the Cu film. In addition, they found that the concentration of impurities increased as a function of decreasing current density. Liu *et al.* speculated that the higher current density results in a shorter deposition time that allows less time for the additives to desorb from the cathode surface. Klemm *et al.*⁹¹ undertook a study that examined the impact of two different electroplating modes on the impurity incorporation as a function of depth from the Cu surface. The two modes are normal and hot plating. The difference between these methods is that with hot plating mode, the potential bias is applied before the cathode enters the electrolytic solution. Results showed in both cases trace impurities, such as O, H, C, S and N, were detected; however in the normal plating mode, there was a greater concentration of trace impurities at the Cu seed layer and electrochemical Cu interface.

In a later publication by Liu *et al.*⁷³ a PEG solution and pure Cu was studied under two different current densities, and the resulting Cu film was studied using ToF-SIMS. The higher current density resulted in voids and had a comparatively higher impurity concentration, such as Cl, C, O and S, incorporated into the film compared to the lower current density sample. Yu and Kim⁶² studied the impact on a pure Cu film of a, basic solution and an SPS solution, on the impurity concentration by using auger electron spectroscopy. The specimen with the highest void propensity was the SPS solution that exhibited a significant consecration of S. They also noted that by increasing the SPS concentration there was an increase in the S concentration at the Cu/ ϵ interface.

In [II], STEM-EDS was utilised to probe the voided region of a non-annealed and annealed SPS sample. Results of the analysis can be seen in Figure 32. The

STEM lamella was purposely left as thick as possible to preserve any voids imbedded in the lamella. This was to ensure impurity elements would not be disturbed during the lamella preparation and the subsequent pre-TEM cleaning processes, such as ion-polishing.

Figure 32 – STEM-EDS analysis of the Cu/ ϵ interface of an isothermally annealed for 4 hours SPS sample, (a) high-angle angular dark field (HAADF)-STEM, (b) EDS-Cl, (c) EDS-Cu and (d) EDS-Sn [II].

The results showed that in the non-annealed sample there was no detectable impurities, whereas in the annealed sample there was significant concentration (within the resolution of EDS) of Cl in the unexposed voids. The Cl had segregated from the Cu matrix during isothermal annealing. Wang *et al.*⁹² results agree with these findings. In their samples in addition to Cl they had also detected trace amounts of S. Moreover, rather than detecting these impurities at the void, they detected the impurities at the ϵ -phase grain boundaries. To understand why Cl segregates towards the voids, an *ab initio* study [II] calculated the formation energies required for both Cl and a lattice vacancy, in different lattice configurations of Cu, ϵ -phase and η' -phase. Results of the *ab initio* study revealed that in Cu a vacancy formation was energetically more favourable than a Cl. This suggests that there is a driving force for Cl segregation to local defects within the Cu lattice, such as grain boundaries, interfaces and voids. This result explains the Cl behaviour observed in the STEM-EDS results, where Cl segregated to voids.

Cl is a key component in the Cu electroplating additive system that is co-deposited during the electroplating process. Cl and PEG function as an inhibiting layer that cause polarization of the cathode,⁹³ without the PEG-Cl ensemble the SPS additive is unable to compete with the inhibiting layer, which then likely

results in the co-deposition of the Cl. Apart from Cl, there were no other elements detected within the resolution of EDS. ToF-SIMS results from the non-annealed SPS, PEG and SPS+PEG samples can be seen in Figure 33.

Figure 33 – ToF-SIMS results from, non-annealed (a) SPS, (b) PEG and (c) SPS+PEG samples [V].

Results show that in the samples with a higher propensity to void show a significant level of trace impurities located within the electroplated Cu layer. Trace impurities includes: C, Cl, O and S. In striking contrast, the SPS+PEG sample that experienced little to no voiding had a negligible amount of trace impurities detected. This result fits the expected additive behaviour for the Cu process. SPS+PEG function synergistically by altering the surface properties during electroplating to form a bright deposit. This functions only by absorption and desorption of the additive ensembles on the cathode surface which should result in little to no co-deposition. On the other hand, the SPS and the PEG samples are not functioning synergistically and components of these additives are co-deposited, as seen by the trace impurities detected by ToF-SIMS.

8. Impact of Intermetallic Void Formation

As it becomes clear that void formation is the result of the Cu electroplating parameters, and their impact on microstructural and chemical properties rather than the Kirkendall effect; a new label is required to describe the void formation that occurs within the ϵ -phase. “Intermetallic void(s)” is proposed as an alternative name for this class of void formation. This has practical implications for the microelectronic and electroplating chemistry suppliers. Mechanisms can be put in place to reduce the incidence of void formation based on the underlying formation mechanisms.

8.1 Intermetallic Void Formation Mechanisms

Results from the structural and chemical analysis have determined the underlying properties that influence void formation. Common factors that influence void formation include: (i) ultrafine crystalline Cu, (ii) a high number of microstructural defects, (iii) residual tensile stresses and (iv) impurity incorporation into the electroplated Cu. It is these parameters that appear to interact with the Kirkendall effect to form voids within the ϵ -phase. Co-deposited incorporated impurities within the Cu matrix are thermodynamically unstable and diffuse towards defects. The segregation of trace impurities in the Cu matrix can be seen in Figure 34 subfigure (a). Impurities at defects affect the microstructural behaviour of Cu, this causes a pinning effect where grains are unable to grow.^{94,95}

The Kirkendall effect undoubtedly plays an important role in intermetallic void formation as seen in Figure 34 subfigure (b), where the unbalanced solid state diffusion results in a diffusion flux of vacancies towards Cu; although the vacancy concentration contribution is difficult to quantify due to differences in voiding propensity shown between samples. Nonetheless, if there are defects or discontinuities at the Cu/ ϵ interface, these can act as sinks for the diffusing vacancies and enable nucleation and subsequent void growth. In addition to defects acting as sinks, they can also interact with the moving interface by Cu reactive diffusion. Pinning by the defects causes the moving interface to drag as Cu reacts with diffusing Sn to form the ϵ -phase. The drag force is dependent on the size and shape of the defect.⁹⁶ A schematic of the pinning behaviour at the Cu/ ϵ interface of a grain boundary with an impurity inclusion can be seen in

Figure 34 subfigure (c). There is a distinct lack of data relating to the impact of pinning of an interface and its impacts on localised diffusion-reaction behaviour, it is mostly only on the impact on grain growth. However it could be expected that localised changes in the diffusion-reaction characteristics of the interface would occur as a result of pinning. It is not too implausible to assume that with the aid of diffusing vacancies pinning enhances the vacancy sink behaviour, and that localised disruption of interdiffusion results in the nucleation and formation of an intermetallic pore. Residual stress could provide the additional energy required to form new surfaces and allow microscopy pores to form voids.

Figure 34 – Illustration of the intermetallic void forming mechanisms, (a) co-deposition of trace impurities and segregation to the defects, (b) Kirkendall effect and (c) pinning as a function of time (t_1 to t_4) the Cu/ε interface at a local impurity segregated Cu defect and the subsequent void formation under tensile stress.

Although this model fits the observed behaviour of the Cu-Sn system that exhibits voiding, it is difficult to verify and there are a number of simplifications that should be studied further. Firstly, the correlation between an exact location where a void nucleates and forms is difficult to quantify. Although, during the STEM study a significant number voids were identified at the Cu/ ϵ interface and at a Cu grain boundary, as STEM micrographs are a projection of a sample the exact positions of voids with respect to a void are often difficult to quantify. In addition to this, the STEM sample region only represents a very small fraction of the entire sample area. Secondly, the behaviour of the Cu/ ϵ interface, as seen by the physicochemical approach, is very dynamic. Cu reacts with diffusing Sn to form the ϵ -phase at the Cu/ ϵ interface and a significant amount of diffusing Cu diffuses towards the ϵ/η' interface. There must logically be some interaction between the moving Cu/ ϵ interface and a local Cu defect, such as a grain boundary. However, the exact nature of the interaction has not been observed. Thirdly, the structure of the Cu grain boundaries and the chemical composition. This work has shown that the stability of Cl in a grain boundary is higher than in the Cu matrix therefore segregation of Cl occurs. The question remains is there a grain boundary structure, such as a grain boundary angle, or a minimum concentration of impurities that enables the formation of pores. In addition, what is the impact of segregated impurities on the grain boundary diffusion component? Further studies, such as high-resolution microscopy methods and atomic modelling methods are required to better understand these simplifications and questions and how they impact the suggested intermetallic void formation model.

8.2 Practical Implications of Intermetallic Void Formation

Cu electroplating solutions that are used for micro-connect fabrication should be designed with intermetallic void formation in mind. In most cases micro-connect electroplating properties should be ductile with low residual stresses, good levelling properties and have a low impurity deposit rate. Often bright and level deposits require a fine grain microstructure, however as results have shown the fine grain structure can result in intermetallic voids. The fine grain structure enables brightening of an electroplated Cu film. This may not be a problem as non-pinned Cu grains are free to grow and defects are absorbed into the Cu matrix, in a phenomena known as self-annealing.^{94,97,98} It is important to note that this behaviour will only occur in a low trace impurity sample, and not in a sample containing impurities.

It is therefore important to understand the condition of the Cu electroplating bath to avoid the unwanted co-deposition of impurities. If the Cu process is executed in a well-defined manner, which means that current density, flow-rate, temperature and electroplating times are kept constant, the monitoring of the overpotential of the Cu process is possible. Overpotential measures the potential

difference between an electrode and a reference electrode, providing information about the polarisation-depolarisation cycling of the Cu process. The characteristic polarisation behaviour of the additive system can be monitored in real-time and if there is a deviation, corrective action should be taken. In practice, this approach can be problematic due to the dynamic properties of a Cu electroplating process, and often with the parallel processing of multiple wafers concurrently. The “dump and fill” or the hybrid “bleed and feed” methods are commonly used in large scale operations to maintain the integrity of the electroplating process. This involves regularly replacing or substituting the old solution to maintain the required component concentrations. This approach has a number of advantages and disadvantages, disadvantages are that it is often expensive and wasteful (and possibly unnecessary) without a confident understanding of the performance of a Cu deposition process.

Another approach that is the most common for small scale operations, is to monitor the ampere-hour usage and the properties of the electroplated Cu film. The electrochemical suppliers provide consumption rates for their additive ensembles that can be used to design a maintenance regimen based on the usage. In addition to monitoring the ampere-hours, the performance can be determined by measuring the efficiency of the deposition rate, surface roughness and uniformity of the deposited Cu film. These indicate the status of the additive performance of a Cu process. This method also comes with drawbacks, as consumption rates depend largely on a setup and deposition performance. Typical small scale systems are unable to provide reliable repeatability and the variation can come from a number of sources.

A large complicating factor is the disconnect between Cu electroplating process suppliers and the microelectronic electroplating community. Understandably, the Cu electroplating processes and the additive ensembles used in those processes are proprietary, belonging to the process suppliers. This makes real-time chemical analysis of a Cu process difficult. There are methods for electroplating bath analysis, such as mass spectrometry. Without a detailed understanding of the components of an additive system it's not possible to properly control concentrations of the electrolytic process. Furthermore, the intermetallic void formation existence maybe unknown or not properly understood by the Cu electroplating suppliers and they would therefore be unable to assess the impacts of their processes.

Finally is the need for screening for intermetallic voids. It is doubtful even in a well-controlled process that intermetallic void formation could be completely eradicated. This means that systems need to be in place to detect void formation. Currently, there are a number of methods for non-destructive backend screening of electronic packages, such as lab X-ray imaging techniques and scanning acoustic microscopy (SAM), that are the most common. The major challenge for non-destructive detection of intermetallic voids is their small volume. In the range from 0-0.266 μm^3 , a void's volume (results from [I] assuming voids are spherical) is well below the lateral resolution of SAM (in the MHz range)⁹⁹ and X-ray imaging.¹⁰⁰ Therefore new non-destructive methods are required for the

characterisation of intermetallic voids. A possible candidate is Gigahertz-SAM that is currently under investigation [III]. Figure 35 shows the results of a preliminary study into the viability of using GHz-SAM as a non-destructive void detection tool.

Figure 35 – GHz SAM micrographs and corresponding FIB cross-sections (Courtesy of Sebastian Brand). Large contrast spots indicate defects within the electroplated Cu [III].

The study was unable to detect intermetallic voids. It did however manage to detect defects within the electroplated Cu, as can be seen from the FIB cross-sectional micrographs. There are still a number of challenges related to using GHz-SAM as a detection method. One of these challenges is that the resolution limits of GHz-SAM is $1\text{ }\mu\text{m}$ at the surface of a specimen, well above the required lateral resolution [III]. However, features below the resolving limits were detected; this is attributed to the two-dimensional convolution of the acoustic beam, and the highly reflective structures. Studies are ongoing, and this complex acoustic behaviour could be utilised to detect sub- μm features. A major challenge with this technique for characterising 3D-integrated structures is that since the transducer is operating in the GHz-range, attenuation due to defocusing from the surface into the sample is significant. This means that any defects needs to be in close proximity to a smooth planar surface (i.e. $1\text{--}4\text{ }\mu\text{m}$).

9. Conclusion

Wafer-level bonding enables advanced integration of a system-in-package SiP, this is a natural progression of what has been integration of wafer level packaging of multiple wafers to board level. The advantages of wafer level packaging are obvious, such as smaller foot-prints, increased functional and throughput density, and reduction in interconnect latency. With all new technologies comes the fabrication challenges and the unknown impacts on lifetime reliability. There are a number of challenges with Cu-Sn micro-connects, the one that is addressed here is void formation. The impact of intermetallic void formation has been difficult to assess as failure modes of SiP are inherently complicated, nonetheless it is clear these voids pose a threat to reliability.

This work has investigated the properties of intermetallic void formation in the Cu-Sn system commonly known as Kirkendall voids that originate from the Cu electroplating process. Cu electroplating parameters were varied in order to produce Cu-Sn samples with varying voiding propensities. The resulting properties of the Cu were investigated. These include the electroplated Cu grain structure, defects, texturing, residual stress and trace impurities. From the results an alternative void formation hypothesis was formed. It was concluded that there is more involved in void formation than just the Kirkendall effect. Therefore, an alternative label, “intermetallic void(s)” is proposed as a more suitable description. A discussion was included on the impact of these findings for both the active suppression and also for screening for intermetallic voids.

Results have shown that Cu electroplating parameters impact on the propensity for intermetallic void formation, especially the additives used in the Cu electroplating process. Additives influence the properties of a deposited film, and typically operate as an ensemble that function synergistically. If the additives do not function synergistically, it results in an ultrafine crystalline Cu with high defect density and a high trace impurity content. It is these samples that exhibited a higher propensity to void. This work proposes that the ultrafine crystalline structure and defects cause inconsistencies that are pinned at the reactive diffusive Cu/ ϵ interface. As the interface reaches an inconsistency, this becomes a point for vacancy sinks and a point where reactive-diffusion is disrupted, resulting in nucleation and void formation.

This intermetallic void hypothesis enables preventative measures to suppress void formation in Cu-Sn micro-connects. The Cu electroplating process suppliers will be able to develop and maintain processes that avoid co-depositing trace impurities. Maintenance protocols can be designed to aid microelectronic manufacturers and small scale microfabrication laboratories in controlling their Cu

process. As complete eradication of intermetallic voids is impossible further development of non-destructive methods, such as GHz-SAM, is needed for intermetallic void detection.

This thesis consists of a total of five publications. The results from each publication is summarised in the following:

Publication I “**Void formation and its impact on Cu-Sn intermetallic compound formation**” explored the parameters that impact void formation in the Cu-Sn system, more specifically the Cu electroplating parameters. The impacts of the voids on the IMC was measured and the behaviour modelled and explained with the aid of the physicochemical approach. Voids formed as a function of Cu electroplating current density and chemistry. The voiding propensity varied considerably between samples, indicating that additional mechanisms to void formation than just the Kirkendall effect are present. Densely voided samples showed the ϵ -phase is consumed by the η' -phase. The results from the modelling showed that the void acted as a diffusion barrier, which resulted in the reduction in the growth rate of the ϵ -phase. Subsequently, the consumption of the ϵ -phase by the η' -phase occurred as the consumption rate of the ϵ -phase was greater than the growth rate.

Publication II “**Interfacial void segregation of Cl in Cu-Sn micro-connects**” presented a high-resolution chemical analysis of a voiding Cu-Sn interface. The study utilised STEM and STEM-EDS to study both non-annealed and isothermally annealed sample that had produced voids. Results showed no significant detection of impurities within the voided lamella of the non-annealed sample, in the annealed sample there was detectable Cl in the voids. It appears that during isothermal annealing the impurity element Cl had segregated to the voids located within the ϵ -phase. To understand this behaviour *ab initio* was used to model the stability of Cl compared to a vacancy within the Cu, ϵ -phase and η' -phase matrices. In most cases the formation energy of a dilute solution, the energy required to form the structure, favoured a vacancy. This suggests that Cl is not energetically favourable within the Cu-Sn solid matrix and that Cl seeks a more energy favourable location, such as a void.

Publication III “**Gigahertz scanning acoustic microscopy analysis of voids in Cu-Sn micro-connects**” presented the results from an evaluation of the defect detection capabilities of GHz-SAM in the Cu-Sn. Results were not able to detect intermetallic voids, however bulk Cu film voids were detected. The results also showed that Cu voids were able to be detected even below the lateral resolution limits of the GHz-SAM, suggesting further work is needed to assess the compatibility of this technique in detecting intermetallic voids.

Publication IV “**XRD and ToF-SIMS study of intermetallic void formation in Cu-Sn micro-connects**” studied the microstructural and chemical properties of a series of samples from low to high voiding propensity. An *in-situ* XRD study measured the change in the microstructural properties as a function of thermal annealing, a wide-2D map was used to understand the texturing behaviour before and after isothermal annealing and for a ToF-SIMS study of a voided sample, to study the impurity concentration. The microstructural study revealed that an ultrafine grain structure is associated with higher voiding propensity and that there was slow crystal growth during annealing. In addition, the ToF-SIMS results showed that there were a significant concentration of trace impurities incorporated in the electroplated Cu film. The publication suggested that impurities segregate towards the grain boundaries which caused the slow crystal growth as the grain boundaries are pinned.

Publication V “**The Role of Ultrafine Crystalline Behaviour and Trace Impurities in Copper on Intermetallic Void Formation**” is an extension of publication IV and explores in more depth the microstructural chemical behaviour of samples from low to high voiding propensity. The study utilised TEM, STEM and SADP to understand the microstructural properties. Results showed that samples with an ultrafine crystalline structure were more prone to exhibit voiding and that these samples contained a significant number of defects. XRD results showed that there was limited texturing. However, due to the difference between previous published studies and not a single common texturing factor between samples, it was concluded that texturing does not play a significant role in void formation. Residual stress was measured and showed that samples with more voids exhibited higher tensile stress values. Admittedly, the stress behaviour of the system is complicated. Nonetheless, tensile residual stress could provide the additional energy to form new surfaces and subsequently allow voids to grow. The ToF-SIMS analysis of non-annealed and annealed samples showed conclusively that trace impurities are due to the Cu electroplating process and that these trace impurities concentration is greatest at the Cu/ ϵ interface. From the results an alternative hypothesis for void formation has been proposed; that pinning occurs when the moving Cu/ ϵ interface meets a grain boundary or defect. This pinning force causes a dragging force on the interface where diffusing vacancies are able to sink. The effect of this behaviour on the reaction-diffusion mechanisms at the interface are also likely to contribute to nucleation and void formation.

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The compatibility of new materials and their interfaces are key components in the pursuit of highly integrated and reliable systems. An extensive understanding is required of the behaviour and stability of the materials not only during device fabrication but over the entire functional lifetime of a device. A microstructural defect, and the focus of this thesis, that threatens the mechanical and electrical performance of 3D-intergrated systems is Cu-Sn intermetallic void formation. Results of this work has been separated as follows: (i) understanding the sporadic behaviour of void formation, (ii) understand the key parameters influencing voiding formation, (iii) examine the microstructural and chemical properties associated with void formation, (iv) present a void formation hypothesis and (v) discuss void reduction and detection methods for the microelectronic industry.

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