

Characterization of Cu-Sn-In Thin Films for Three-Dimensional Heterogeneous System Integration

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Abstract

Cu/Sn-In solder thin films were studied as a low temperature bonding material for 3D heterogeneous system integration. A new technique based on observation of color changes and combinatorial deposition of solder thin films was developed to investigate the intermetallic compound (IMC) growth kinetics in Cu/Sn and Cu/Sn_xIn_{100-x} bilayer systems. A general model for IMC growth kinetics in these systems was developed and was found to be in close agreement with experimental data. The model considers the diffusive flux of Cu and Sn through the IMC layer and the reaction fluxes of Cu and Sn atoms at the Cu/IMC and IMC/Sn interfaces. It was observed that IMC growth is controlled by the rate of reaction between Cu and Sn for thin IMCs. On the other hand, Cu diffusion along IMC grain boundaries and Sn diffusion through the IMC lattice is the rate limiting step for thick IMCs at low and high temperatures, respectively. It was also discovered that an addition of 44% In into Sn solder leads to the fastest IMC growth in Cu/Sn_xIn_{100-x} bilayer films. Microcantilevers coupled with combinatorial deposition were used to characterize the residual stress, Young's modulus and fracture strength of Cu-Sn-In thin films. Measurement inaccuracies due to cantilever non-idealities were corrected using finite element simulations and deflection measurements at multiple locations. It was discovered that an alloy with 46% In in Sn resulted in an IMC with the highest fracture strength. The findings of this study demonstrate the potential of Sn-In solder in lowering the bonding temperature and increasing the fracture strength of the resulting IMC. Moreover, the techniques developed in this study provide a highly efficient general approach for finding solder compositions that allow the fastest and/or slowest IMC

growth rate, as well as the most desirable mechanical properties.

The effects of bonding and post-bonding annealing temperatures on the shear strength of Cu bonded to Sn-In films were studied. It is proposed that higher bonding temperatures lead to an increase in the true contact area of the joint, which in turn leads to an increase in the shear strength of the joint. On the other hand, the post-bonding annealing process drives the interdiffusion of the Cu and Sn-In atoms and leads to a conversion of the whole solder film into a high melting temperature IMC. With this understanding in hand, a two-step bonding process that consists of bonding for a short time followed by a longer post-bonding annealing was developed. It was verified that this two-step bonding process leads to comparable shear strength of the joints while requiring less bonding time. Thus, this process has the potential to lower the manufacturing costs.

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Chapter 1

Background and Motivation

1.1 Motivation of 3D ICs

In 1965 [1], Gordon E. Moore (Intel co-founder) made a prediction that the number of transistors per unit area would double every 18 months, which is now known as Moore's law. Since then, the growth of microelectronics industry has been following this trend closely as shown in Figure 1.1. The key strategy which allowed this massive rapid growth is the ability of the transistor size to scale down over the years. With scaling, not only does the transistor density increase, but also the speed. Therefore, it increases the overall performance of the integrated circuits (ICs).

However, it was later discovered that the enhancement in ICs performance from scaling is less significant for technology node below 130 nm [3]. This is primarily due to physical limits of the materials and processing technology [4], configuration of the transistor constraint [5], and exponential increase of interconnect delay [6].

Various novel strategies have been exploited to boost the performance of ICs, in order to keep the industry growing according to Moore's law. Strained silicon was introduced to enhance the ICs speed by increasing the intrinsic carriers mobility in the channel [8,9]. Gate all around silicon and silicon nanowire transistors are being explored as they have been shown to perform better than the conventional ones [10].

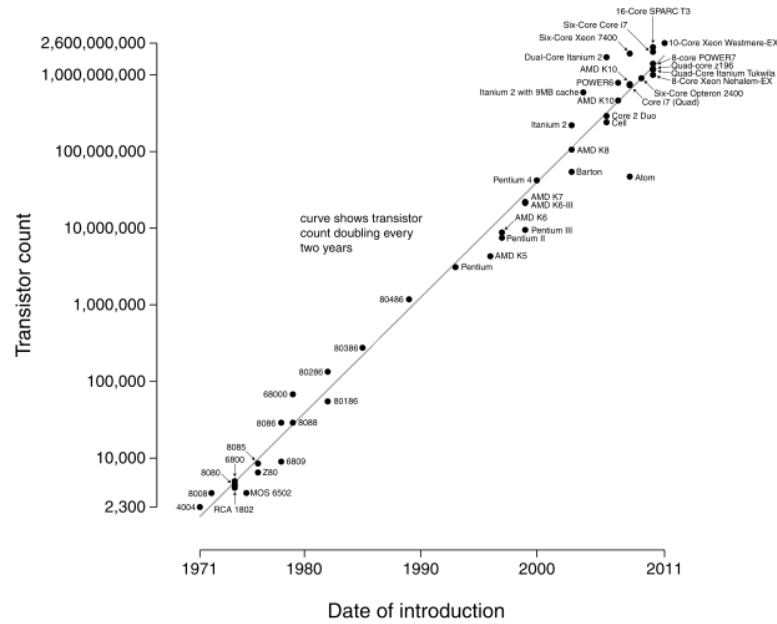


Figure 1.1: Microprocessor transistor counts from 1971-2011 and Moore's Law [2].

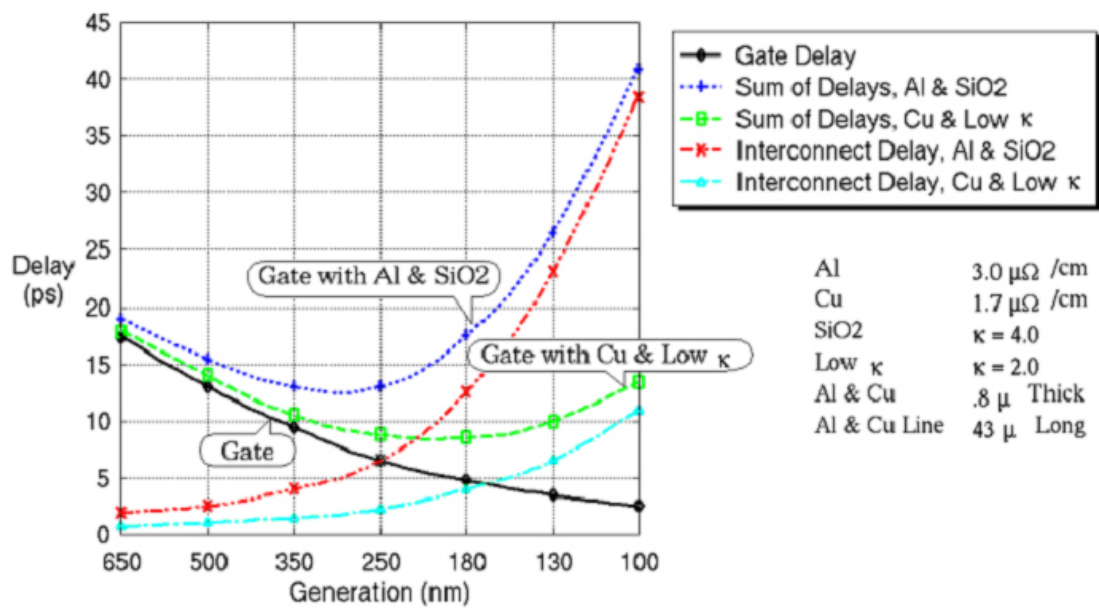


Figure 1.2: Interconnect and gate delays evolution through miniaturization of ICs. At such a small technology node, interconnect delay dominates over gate delay even after the introduction of Cu interconnects with low- k inter-level dielectrics [7].

Although these innovations can potentially improve the transistor performance, interconnect delay is still a major challenge yet to be solved. Interconnect delay originates from the resistance of the interconnects and the cross talk capacitance from the nearby interconnects. It is usually referred as RC delay. As the transistor

size decreases, the interconnect cross section area also decreases with scaling while the total length and interconnect density increase due to the increasing complexity of the ICs [3, 6]. As a result, the RC delay increases very significantly.

Figure 1.2 shows the gate and interconnect delays as a function of transistor size. It can be seen that reducing the size of the transistor results in a decrease in gate delay, which is desired to enhance the ICs performance. However, a decrease in transistor size also corresponds to an increase in interconnect delay. In such a very small transistor size, this interconnect delay becomes the determining factor in the overall performance of the ICs.

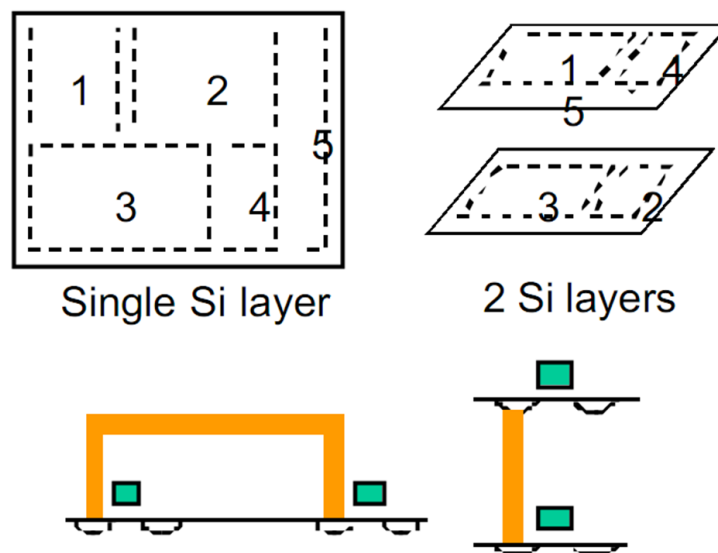


Figure 1.3: Schematic illustration of 3D ICs in 2 active device layers. Long horizontal wires are replaced by short vertical wires [3].

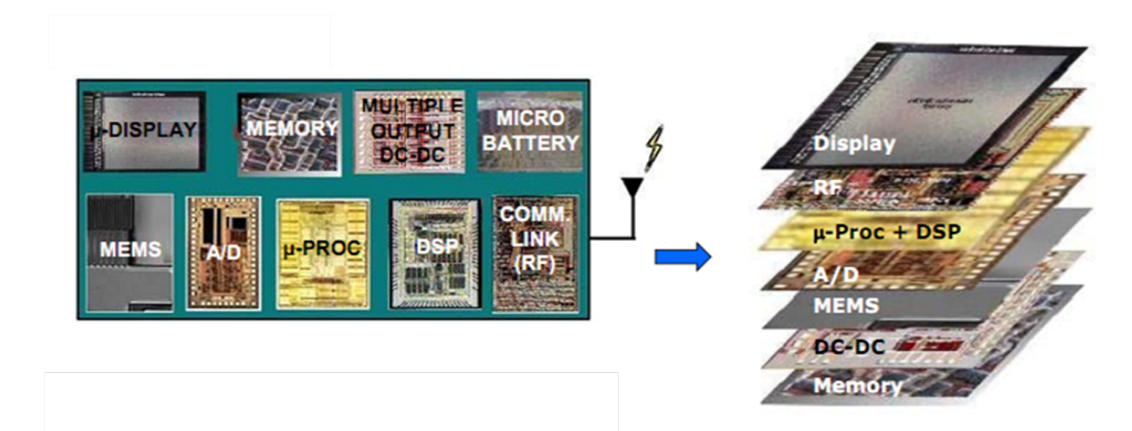


Figure 1.4: Schematic drawing of heterogeneous system integration [11].

One of the potential solutions to reduce the interconnects delay is by introduc-

ing a new ICs architecture, called 3D ICs, in which ICs are stacked in a vertical direction. As shown in Figure 1.3, 3D ICs enables significant reduction of the total interconnection length, and therefore reduces the interconnect delay. Through simulation, Saraswat *et al.* [3] showed that the interconnect delay can be reduced by 64% with 3D ICs architecture at 50 nm technology node. Another advantage of 3D ICs is that it enables further reduction in form factor of microelectronic devices. Last but not least, a 3D architecture provides an opportunity for heterogeneous system integration. As seen in Figure 1.4, one may stack different kind of ICs (e.g. processor, memory, CMOS imaging.) in the vertical direction. This will not only improve the overall performance of devices but will also drive the development of new devices.

1.2 Different Versions of 3D ICs

3D ICs architecture can be classified into three versions based on the way it is designed and manufactured. They are 3D-Packaging, 3D-Monolithic and 3D-Bonding. Each of these is shown schematically in Figure 1.5.

3D-Packaging is considered the first generation of 3D ICs. It was developed from well established technologies in microelectronics packaging such as wire bonding, die attached, die encapsulation, etc. Hence, it is relatively easy in terms of design and manufacturability. The Si chips are stacked in a vertical manner by a “glue” layer. This “glue” layer only serves as a mechanical support. The electrical connections between chips are realized through wire bonding as schematically shown in Figure 1.5a. With this version, the form factor of the overall IC chips is reduced, but the total interconnect length is not significantly reduced because of the usage of long wire bonds. Other than that, the nature of wire bonding only allows placement of Inputs/Outputs (I/Os) along the edges of the chips. Therefore the number of I/Os per unit area is not fully optimized.

3D-Monolithic is the most ideal version of 3D ICs. Multiple active device layers

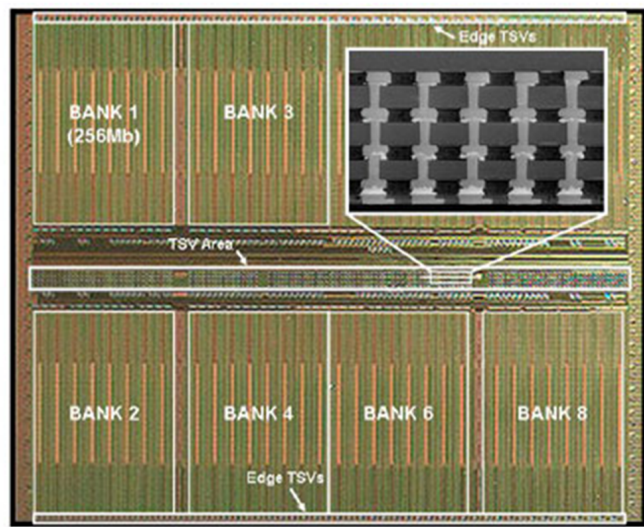
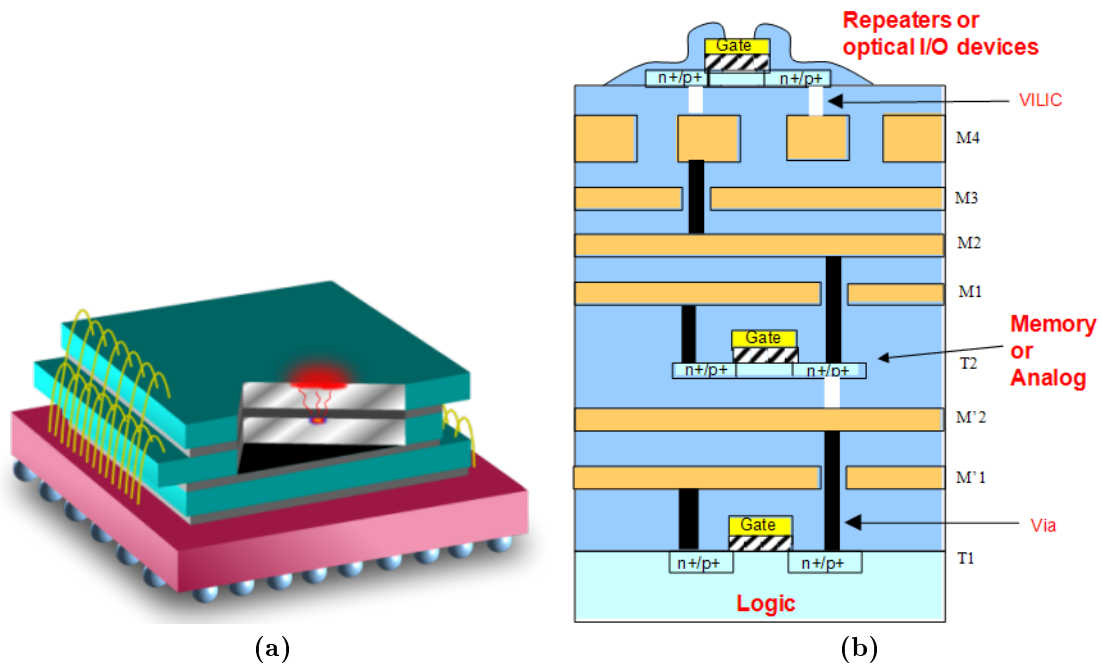


Figure 7.2.7: Die micrograph of the fabricated chip and cross-sectional view of TSVs. The chip size is 10.9×9.0mm².

(c)

Figure 1.5: Different versions of 3D ICs. a) 3D-Packaging [12]. Si chips are stacked with a glue layer and electrically connected by wire bonding. b) 3D-Monolithic [13]. A Si chip with multiple grown epitaxial Si, similar to CMOS fabrication process. c) Samsung used 3D-Bonding to demonstrate a 8 GB 3 DDR DRAM [14].

made of epitaxial Si are fabricated sequentially in a vertical manner. These active layers are then interconnected by vertical metal wires (i.e. vias) as schematically shown in Figure 1.5b. With this version, the total interconnect length is reduced significantly as the distance between active layers are only in the order of few microns. Unlike 3D-Packaging, this version utilizes the whole area of the chip to form

I/Os, hence improving the efficiency. Additionally, monolithic integration allows high density vertical interconnection as there is no miss-alignment issue.

Nevertheless, there are still major technological challenges in the realization of 3D-monolithic. Arguably, the most crucial one is the fabrication of epitaxial Si thin films on top of existing device layer. There are several potential enabling technologies which are widely being investigated to make epitaxial Si for 3D-Monolithic. They are beam recrystallization, silicon epitaxial growth, and solid phase crystallization [13]. However, these technologies require very high temperatures ($> 500^\circ$) during processing. Such high temperatures may cause degradation to the existing device layer in the lower layers [15, 16].

3D-Bonding is a version which conceptually sits between 3D-Packaging and 3D-Monolithic. Similar to 3D Packaging, Si chips are stacked in a vertical direction with a “glue” layer. But in this version, vertical interconnections across the different layers are provided by through silicon vias (TSV) as shown in Figure 1.5c. This not only enables greater I/Os density but also shortens the total interconnect length. Although 3D-monolithic potentially enables greater I/Os density than 3D-bonding, 3D-bonding is believed to be the future of the microelectronics industry. The first main reason is because it does not require temperatures above 350°C during processing. Secondly, each IC can be individually made first and then stacked together, which will improve the throughput and reduce the cost of fabrication.

There are several key technological challenges associated with 3D-Bonding such as TSV fabrication, bonding technology, stresses around the TSV, etc. Among these challenges, bonding technology is one of the most crucial one and will be reviewed in more detail in the next section.

1.3 Bonding Technology

There are several choices of bonding technology based on the manufacturing process flow and materials used as the glue agent. Each of these choices is discussed in detail

in this section.

1.3.1 Manufacturing Process Flow

ICs can be stacked via wafer-to-wafer [17], chip-to-wafer [18] or chip-to-chip [19, 20] bonding. Wafer-to-wafer bonding potentially gives the highest throughput among the three, as only one bonding process is required to bond all the chips on a wafer. However, chip-to-wafer and chip-to-chip bonding are preferred to achieve a high processing yield because it allows selection of known good die to be bonded on known good die.

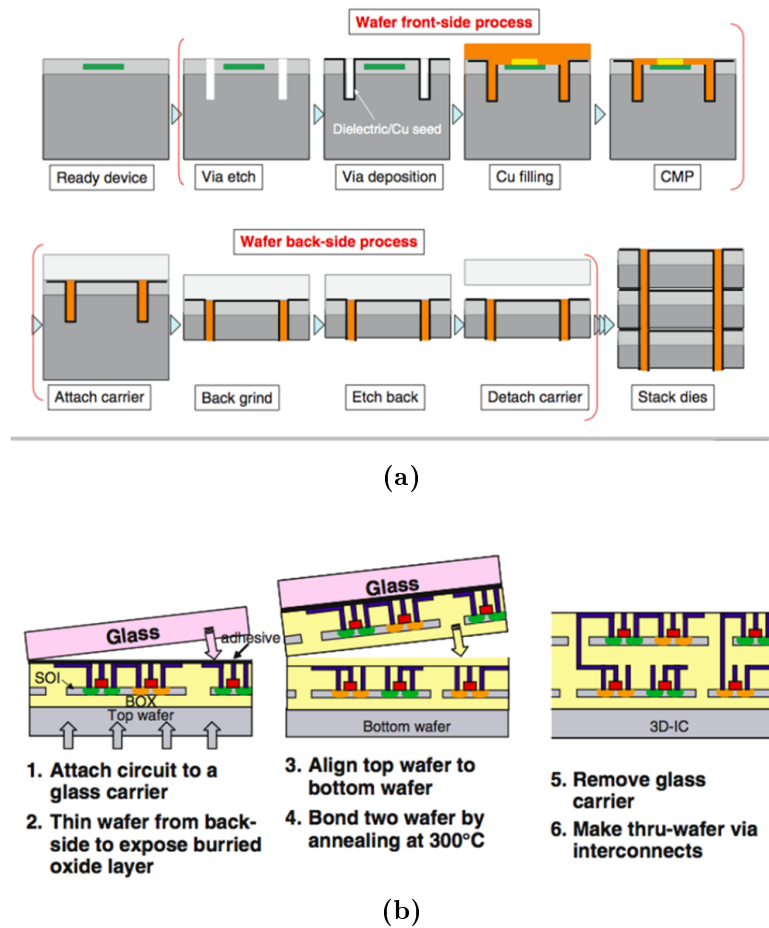


Figure 1.6: Bonding technology based on the process sequence of TSVs fabrication. a) “Vias first” [21], bonding is carried out after TSVs fabrication. b) “Vias last” [22], bonding is carried out before TSVs fabrication.

Figure 1.6 shows the options of bonding technology based on the process sequence of TSVs fabrication, i.e. ‘vias first’ and ‘vias last’. In ‘vias first’ scheme, bonding of two wafers is performed after the TSVs process. On the other hand, in

the 'vias last' scheme, bonding is performed before the TSVs process. As part of the variation of the 'vias first', there is also a 'vias middle' scheme whereby the vias are fabricated before the back end of line (BEOL) metallization [23]. At the moment, there is no clear winner if one scheme is better than the other. 'Vias first' scheme is preferred because it requires smaller TSV aspect ratio which enables higher interconnect density for high signal bandwidth application [24, 25]. However, unlike 'vias last' scheme, misalignment during the bonding may cause some yield loss.

1.3.2 Materials Options

There are numerous material choices which can potentially serve as a glue layer to stack ICs. Based on materials being used as the glue agent, bonding technology can be grouped into four broad categories such as direct metal to metal bonding, direct non-metal bonding, polymer adhesive bonding and solder bonding.

1.3.2.1 Direct Metal to Metal Bonding

Direct metal to metal bonding can serve as both the mechanical support and electrical connection, hence it is arguably the most popular among all. Currently, Cu is the most promising material for this category because of its low resistivity, low cost and ease in integration with current manufacturing processes.

Although it has many advantages, Cu-Cu bond has relatively poor bond-ability. It requires high temperatures above 300°C to form good Cu-Cu bonds [26,27]. Alignment accuracy during the bonding process may deteriorate due to thermal mismatch in such high temperatures. Moreover, high temperature processing is not desirable for temperature sensitive devices such as radio-frequency (RF) devices, micro-electro-mechanical system (MEMS) and bio-sensors [28–30]. Poor bond-ability of Cu-Cu bond is believed to be due to the nature of Cu, as it oxidizes very easily [31, 32]. Tadepalli *et al.* showed that clean non-oxidized Cu can form good bonds at room temperature under ultra high vacuum ($\sim 10^{-10}$ torr) [31]. Ultra high vacuum requirement is not practical from the manufacturing point of view as it is

costly and time-consuming. Ang *et al.* demonstrated ambient Cu-Cu bonding at low temperature with a self assembly mono-layer (SAM), but high bond pressure above 400 MPa is required [32]. Hence, this strategy is not suitable for ICs with soft low-k dielectric. From contact mechanics [33–35], it is predicted that low temperature Cu-Cu bonding is possible, but an extreme smooth Cu surface below 1 nm rms is required. Utilizing the nature of high surface to volume ratio of Cu nanowires, Cu-Cu bonds can be achieved at 200°C [36, 37]. Although it is promising from the process manufacturing point of view, the reliability of these bonds in the long term is still a question. The bonding interface of Cu nanowires contains numerous voids which may degrade the bond properties over time.

1.3.2.2 Direct Non-metal Bonding

Departing from Silicon on Insulator (SOI) technology, direct non-metal bonding was developed [38]. SiO₂-SiO₂ bond is the most popular material for this approach. Typically, bonding is performed at room temperature, which is much lower than that commonly reported for Cu-Cu bonding [39, 40]. However unlike Cu-Cu bonds, SiO₂-SiO₂ bond can only provide mechanical support. Electrical connection is established through TSVs fabrication after the bond formation. Therefore, this method is only suitable for the 'vias last' scheme. Formula more, surface roughness and cleanness requirement for this bonding is even more stringent than that needed for Cu-Cu bond. Typically, sub-nanometer roughness is required to achieve good SiO₂-SiO₂ bonds [41, 42].

1.3.2.3 Polymer Adhesive Bonding

Polymer adhesive bonding is conceptually similar to binding any surfaces with “glue” in our daily life. Unlike direct non-metal bonding, polymer adhesive provides high tolerance to the surface roughness. The bonding is usually carried out at room temperature, followed by annealing to cure the polymer at ~300°C [43]. Furthermore, it is able to join different type of wafers easily [44]. Benzocyclobutene (BCB) is ar-

guably the most commonly used adhesive material [45]. There are several challenges associated with polymer adhesive bonding. Voids are usually entrapped during the curing due to contaminants or out-gassing solvents [46]. Similar to direct non-metal bonding, it can only provide mechanical support.

1.3.2.4 Solder Bonding

Solder is not a new material in the microelectronics industry. It has been widely used for off-chip interconnection such as flip chip bonding and ball grid arrays (BGA). Solder materials typically have low melting point, therefore allowing bond formation at low temperatures ($<250^{\circ}\text{C}$). These materials bond with high melting point metals such as Cu, by forming intermetallic compound (IMC) which has a higher re-melting temperature ($>300^{\circ}\text{C}$) than the solder. Conversion of the whole solder into IMC is desired to allow multiple ICs stacking and subsequent high temperature processes.

Pb-based solder has been the most commonly used material for bonding in the electronics industry. However, the use of Pb-based material has been prohibited due to environmental and health concern [47]. Since then, there have been numerous lead-free solder materials being investigated, especially for 3D ICs applications. However, most of the studies require relatively high temperatures. Lim *et al.* [48] showed that Sn can form joints with Cu pillars after re-flow for a few seconds at 280°C . The whole solder was converted into intermetallic after post-bonding annealing at 180°C for 60 h. Welch *et al.* [49] showed bond formation of Au-In and Ni-Sn systems at 300°C for 2 h and 1.5 h, respectively. Kim *et al.* [50] reported the bond formation of Au-Sn system at 240°C for 15-25 min.

There are few reports on attempts to lower down the bonding temperature using solders. I-Made *et al.* showed that Ag-In is able to form bonds at 180°C within a 10 min duration [51]. Humpston [52] showed the bond ability of Cu-In system at 180°C for 4 min duration. More recently, there are some interests on Sn-In based solder to further lower the bonding temperature using solders. This is motivated from the Sn-In phase diagram which shows low eutectic melting point at 120°C [53].

Researchers in Institute of Microelectronics in Singapore have demonstrated that Sn-In can form good bonding with Cu, Ti and Ni at 180°C [28, 30, 54, 55]. Lee *et al.* further lowered the bonding temperature to 140°C by bonding Sn-In on Au [56]. However, all of these studies focused only on one particular composition of Sn-In (i.e. Sn₅₀In₅₀). Whether this composition is actually the best one in terms of bonding process and properties is not yet answered.

1.4 Characterization of Diffusion Kinetics of Cu/Solder

Diffusion kinetics of Cu/solder couples have been studied since 1960s. Since then, the characterization tools employed to study this have been evolving in terms of imaging resolution, real time study, elemental and phase detection. However, the advancement of these techniques is not accompanied by an improvement in the throughput of the techniques.

1.4.1 *Ex situ* Heating and Conventional Cross Sectional Analysis

This method is arguably the most common approach to characterize the diffusion kinetics of Cu/solder systems. Samples are typically annealed at different temperatures for different durations in a furnace. Then, each sample is mounted in an epoxy, followed by sand-paper grinding to expose the cross section surface and polishing with alumina slurry to smoothen the surface. Finally, the cross section is inspected by optical microscopy or Scanning Electron Microscopy (SEM).

Figure 1.7 shows a typical cross-sectional SEM image of the Cu/Sn system. Several information can be extracted from this type of experiment such as the microstructure and thickness of IMCs. Elemental composition can also be extracted by Energy Dispersive X-ray spectroscopy (EDX), which is attached to the SEM.

Despite its popularity for diffusion kinetics characterization, this method has several limitations. Firstly, the sample preparation is tedious and time-consuming. It takes an average of 2 h for an experienced researcher to epoxy mount, grind and pol-

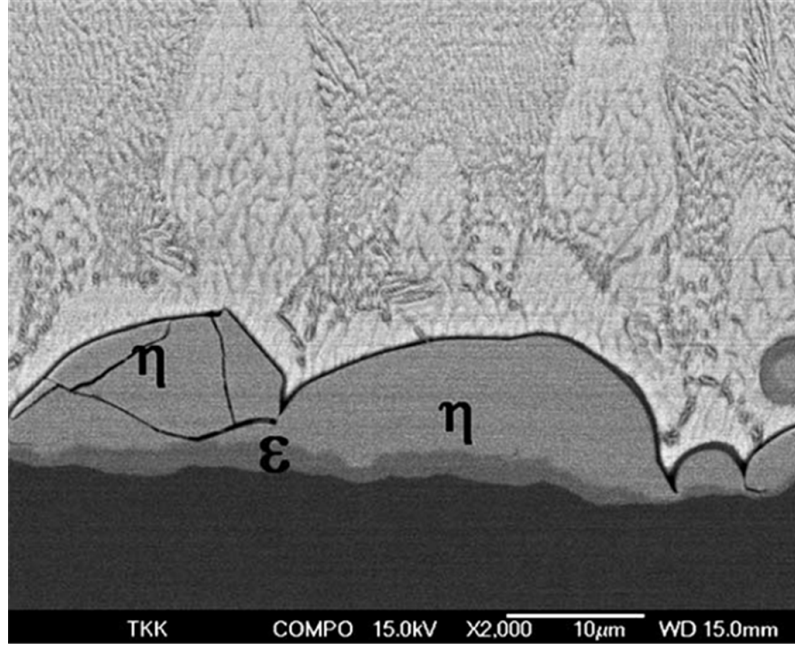


Figure 1.7: Typical SEM cross sectional image of Cu/Sn sample annealed at 250 °C for 64 min [57]. Microstructure of IMCs and its thicknesses can be extracted from the cross sectional analysis.

ish one sample before SEM observation. Focused Ion Beam (FIB) cross-sectioning has become an alternative choice recently because it can reduce the sample preparation time. However, based on personal experience, it still takes at least 30 min to obtain the cross-sectional information. Furthermore, FIB is an expensive method and therefore may not be suitable for large data collection. Secondly, IMC thickness measurement using this method typically has quite a large standard deviation, originating from the irregularities of IMCs shape [58]. Lastly, *ex situ* annealing requires extended durations for ramping up, cooling down, and storage before the SEM observation. These extended durations are quite significant for fast diffusion process systems, and thus may affect the results extracted from this method.

1.4.2 Real Time study, *In situ* Annealing

Real time studies provide a solution to the inaccuracy of annealing durations. IMC thickness is monitored continuously during the annealing process. Researchers in Andong University [48, 58, 59] have demonstrated a cross-sectional *in situ* setup to study the growth kinetics of Cu/Sn/Cu system. Figure 1.8 shows the setup

of the experiment which was carried out inside an SEM chamber. Cross-section of Cu/Sn/Cu samples were initially prepared by standard grinding and polishing. Then, the sample was placed inside the SEM chamber on a modified sample holder. The microstructure evolution was continuously recorded over time at different temperatures.

However, this approach is not without challenges. The setup for the experiment is extremely rigorous and expensive. This method is also not suitable for high temperature study there is usually a temperature limit on the usage of SEM. Furthermore, this method typically fails to detect sub-micron thickness of IMC due to image drifting during recording.

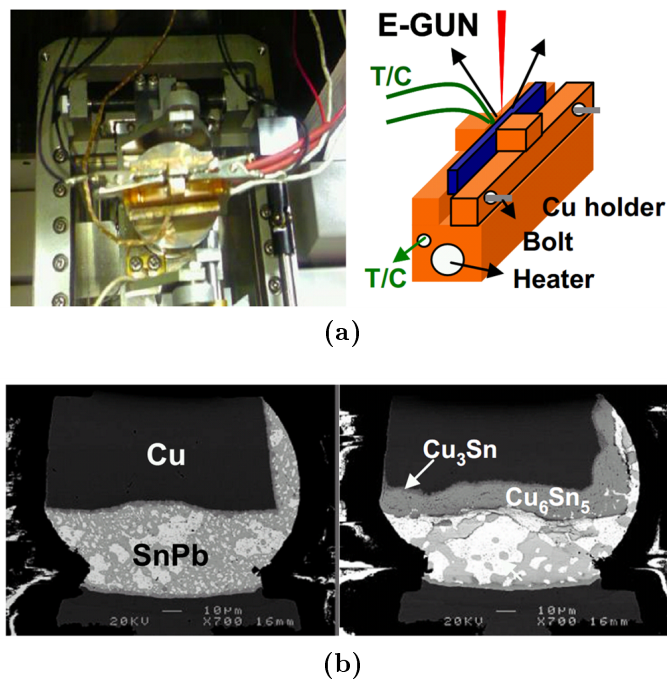


Figure 1.8: a) Experimental setup for in-situ SEM study in Andong University. b) SEM cross sectional images of Cu/Sn/Cu system before (left) and after annealing at 165°C for 80 h (right) [58].

Alternatively, Etschamaier *et al.* [60] used *in situ* XRD to study the diffusion kinetics of Cu/Sn. Cu/Sn bilayer was initially deposited on a Si substrate by electrodeposition. The sample was then placed inside the XRD chamber which has heating capability. While annealing, the sample was scanned every 5 min to detect the phase evolution. From the diffraction intensity, they were able to deduce the thickness of the IMCs. The deduction was verified by cross-sectional analysis with

FIB. The setup for this experiment is relatively easier than *in situ* SEM. However, this method only works for thin film IMCs as x-rays has a penetration limit into the sample. Thus, the accuracy of this method to study the growth of thick IMCs is questionable.

1.5 IMC Growth Kinetics in Cu/Sn System

The growth kinetics of intermetallic compounds in Cu/Sn-based system is one of the topics that has gained a great interest in the solder community. The kinetics of IMC growth will not only affect the mechanical and electrical properties of the bond, but also the reliability of such a system in the long term. Numerous models have been proposed to explain the fundamental mechanisms of IMC growth, but most of the models can only be applied to a very limited range of test conditions. A more general model in predicting the IMC growth kinetics in Cu/Sn system is desired.

Most of the earlier studies suggested that IMC growth kinetics in Cu/Sn-based solder system follows the parabolic law, which is commonly interpreted as diffusion controlled. Vianco *et al.* [61] produced Cu/Sn bilayers by dipping the Cu bars into molten Sn bath. The samples were then annealed in a temperature range from 70°C-170°C for days. They found that the IMC growth is parabolic, with a time dependence of $t^{0.5}$ at low aging temperature, and followed by $t^{0.42}$ at higher temperatures. The apparent activation energy for their experiment was 66 kJ/mol. Similarly, Yoon *et al.* [62] also observed parabolic growth for Cu/Sn-3.5Ag-0.75Cu solder system for 60 days under isothermal aging at temperatures between 100°C and 200°C. They also observed a similar apparent activation energy, 62.6 kJ/mol. Lim *et al.* [48] studied the IMC growth kinetics in Cu pillar/Sn bumps by *in situ* observation, at temperatures from 120°C-180°C up to 300 h. Their parabolic growth exhibits an activation energy of 55 kJ/mol. Onishi and Fujibuchi [63], using Kirkendall marker, observed that Sn diffusion through IMC lattices is the dominant

diffusion species in Cu/Sn system for temperatures 190°C-220°C. Contrary, Tu and Thompson [64] suggested that Cu diffusion along grain boundaries is the dominant path-way for low temperatures annealing ($< 70^\circ\text{C}$).

Growth kinetics of IMC does not always obey the parabolic growth. In an early study, Tu and Thompson [64] observed that at thin film scales, the growth of IMC follows a linear behavior. This was also reported in a later study by Etschamaier *et al.* [60]. Both of the papers agreed that linear behavior implies the IMC growth is limited by the reaction of Cu and Sn at interfaces.

Non-parabolic, non-linear behavior has also been reported in literature. Bader *et al.* [65] experimentally observed that IMC grows according to $t^{0.21}$ and $t^{0.25}$ at temperatures 250°C and 300°C, respectively. Takenaka *et al.* [66] observed $t^{0.37}$, $t^{0.43}$ and $t^{0.5}$ for temperatures 160°C, 180°C and 200°C, respectively. Qualitatively, $t^{<0.5}$ implies that the growth of IMC is limited by grain boundary diffusion [65,66]. In the course of time, not only does the IMC thicken, but the grain size also increases, thus the number of grain boundaries decreases. Consequently, the diffusion slows down not only because of the increase in diffusion path (i.e. IMC thickening) but also the reduction in the density of diffusion path (i.e. grain growth).

Two models have been proposed to explain $t^{<0.5}$ in a more quantitative manner as described below.

a) Schaefer's Model [67]

Schaefer *et al.* derived an IMC growth kinetics model based on the diffusion mechanism. Figure 1.9 shows the geometric assumptions in Schaefer's model. The grains of IMC were assumed to be hexagonal at the base (Cu/IMC interface) with parabolic/spherical cap (IMC/solder interface). The size of the grain was represented as (d), while the grain boundaries width was (δ). R was the ratio of grain boundary path ($\bar{X}_{GB}$)/IMC thickness (X_{Ave}^-). For simplicity, R was assumed to be constant through time. Only Sn diffusion through IMC grain boundaries was considered. It was also assumed that the grain size increased with IMC thickness

and maintained an equiaxed shape.

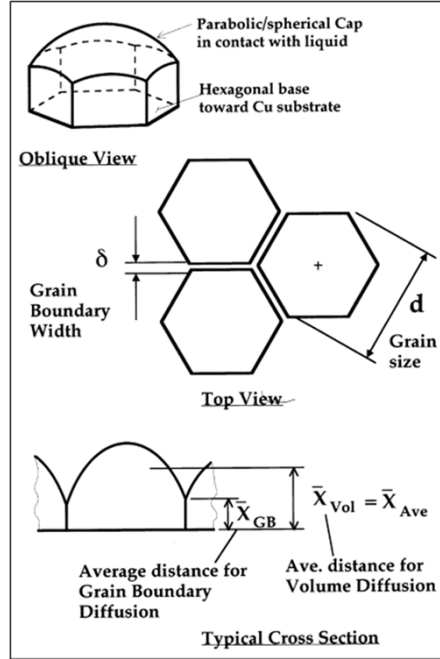


Figure 1.9: Geometric assumption of Schaefer's model for growth kinetics of IMC in Cu/Sn system [67].

With those assumptions, the flux of Sn diffusion through the IMC, J_{IMC}^{tot} , was approximated as

$$J_{IMC}^{tot} \approx - \left\{ D_{IMC}^{GB} \left(\frac{\delta \Delta C}{\sqrt{3}R} \right) \right\} \frac{1}{(X_{Ave}^-)^2} \quad (1.1)$$

where D_{IMC}^{GB} is the diffusivity of Sn along IMC grain boundaries while ΔC is the Sn concentration difference between Cu/IMC and IMC/Sn interfaces.

Growth is related to the volume of intermetallic compound created per mole of diffusant (V_{IM}). Thus, the growth rate ($\frac{\partial X}{\partial t}$) can be expressed as

$$\frac{\partial X}{\partial t} \propto \left\{ D_{IMC}^{GB} V_{IM} \left(\frac{\delta \Delta C}{\sqrt{3}R} \right) \right\} \frac{1}{(X_{Ave}^-)^2}. \quad (1.2)$$

The initial IMC thickness was assumed to be insignificant. Thus, the IMC layer thickness as a function of time was determined by separating the variables and integrating equation (1.2) to obtain

$$X_{Ave} \propto - \left\{ D_{IMC}^{GB} V_{IM} \left(\frac{\delta \Delta C}{\sqrt{3} R} \right) \right\}^{1/3} t^{1/3}. \quad (1.3)$$

Schaefer's model shows that in a system where the grains coarsen in proportion to the layer thickness, the layer thickness will follow a $t^{1/3}$ dependence with time.

b) Kim and Tu's Model [68]

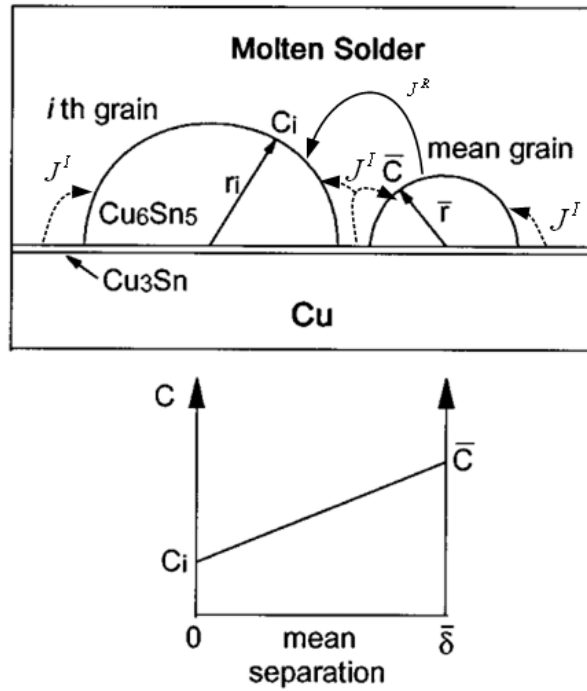


Figure 1.10: Schematic representation of Kim and Tu's model [68]

An alternative model was proposed by Kim and Tu to explain the $t^{1/3}$ dependence of IMC growth in Cu/Sn system [68]. The model assumes that the IMC grains are separated by channels in between. The IMC grains coarsen during annealing whereby the larger grains grow bigger at the expense of smaller grains. In parallel with the coarsening process, Cu atoms diffuse out through the channels and react with Sn atoms at the IMC/Sn interface. The model assumes that Cu diffusion via the channels is a very fast process, thus the reaction of Cu with Sn at the IMC/Sn interface is the rate limiting process.

20th these assumptions, the Kim and Tu derived two fluxes which take place concurrently during annealing. They are interfacial reaction (J^I) and coarsening

(J^R) fluxes. Both are shown in Figure 1.10 and represented by

$$J^I = \rho \frac{N_A A v(t)}{2\pi m N_p(t)} \frac{1}{\bar{r}^2} \quad (1.4)$$

and

$$J^R = \frac{2\gamma\Omega DC_0}{3LRT} \frac{1}{\bar{r}^2}. \quad (1.5)$$

N_A is the Avogadro's number, $v(t)$ is the consumption rate of Cu in the reaction, $\bar{r}$ is the mean radius of the IMC grain, $N_p(t)$ is the total number of grains at the interface, m is the atomic mass of Cu, C_0 is the equilibrium concentration of Cu in the solder, γ is interfacial energy per unit area between IMC and molten solder, Ω is the molar volume of IMC, R is the gas constant, and T is the temperature. L is defined as the ratio of the separation distance of grains and grain size. From equations (1.4) and (1.5), the growth equation is expressed as

$$r^3 = \int \left(\frac{\gamma\Omega^2 DC_0}{3N_A LRT} + \frac{\rho A \Omega v(t)}{4\pi m N_p(t)} \right) dt. \quad (1.6)$$

From equation (1.6), it can be seen that the model explains the $t^{1/3}$ dependence. The model was also found to be in close agreement with their experimental data where the IMC grains grew larger but decreased in number with time for $L = 0.15$.

Nevertheless in a later publication [69], it was confirmed that the channels between IMC grains were indeed grain boundaries with ~ 1 nm width, while the grain size was in the order of microns size, thus $L \ll 0.1$. This observation violates two assumptions made in Kim and Tu's model: the existence of large channels ($L \approx 0.15$) and the fast Cu diffusion process via the channels. On the other hand, the data supports Schaefer's model.

1.5.1 Effects of In Addition in Sn based Solder

There are only a few investigations reported on the effects of In addition into Sn solder on the growth rate of IMC. Shariff and Chan [70] observed that 9 wt% addition

of In into Sn-3.5Ag-0.75Cu solder reduced the Cu consumption rate, thus reducing the growth rate of IMC for up to 20 min annealing at 240°C. Unfortunately, there was no explanation provided on the observation. On the other hand, Choi *et al.* [71] observed that addition of up to 11.5 wt% In could enhance the growth rate of IMC at 250°C for 30 s. Choi *et al.* [71] argued that In addition lowers the melting point of Sn-3.5Ag-0.75Cu solder, thus increases the driving force of IMC formation. To the best of author's knowledge, these are the only two investigations on the effects of In addition to the IMC growth. There is still no information on the effects of In additions for above 11.5 wt% In.

1.6 Mechanical Properties Characterization of IMC

To allow multiple ICs stacking, solder bonding in 3D ICs requires conversion of the whole solder into IMC. Therefore, the final joint structure will consist of only IMC between the two chips. In such a structure, the mechanical properties of IMC becomes more crucial. Thus, high accuracy characterization of the mechanical properties of thin film IMC is desired. There are numerous characterization methods to extract the mechanical properties of thin films. They can be classified into two categories : nanoindentation and cantilever based techniques.

1.6.1 Nanoindentation

Nanoindentation is arguably the most common method for testing the mechanical properties of materials. It is done by indenting the samples at interested locations. The mechanical properties are extracted from the force displacement curve and analysis of the indentation mark.

There are several advantages of this technique. The sample preparation is relatively straight forward. It also allows the characterization of very specific location on the sample. However, this technique is not without limitations. The substrate which the thin films are deposited on occasionally affects the measurement of Young's

modulus [72, 73]. This becomes more severe as the film thickness decreases and/or indentation depth increases. Additionally, this technique requires the knowledge of Poisson's ratio for the determination of Young's modulus. Therefore, measurement of unknown materials requires extra care to avoid inaccuracy. Although there have been some development on the measurement of fracture toughness [74], creep behavior [75] and yield stress [76], the measurement accuracy using this technique is still debatable in the nanoindentation research community.

1.6.2 Cantilever based

Microcantilever-based technique has been shown to provide a promising alternative approach for characterization of thin films. Although the sample preparation is relatively more complex, this approach is attractive due to its simplicity of analysis, which is based on beam mechanics. Unlike nanoindentation, knowledge of the Poisson's ratio is not required for determination of the Young's modulus [77]. The effect of the substrate on the Young's modulus measurement can also be eliminated easily [78]. Additionally, more information on the mechanical properties can be extracted from the same exact sample, such as the residual stress [79–81] and fracture strength [82, 83].

Similar to nanoindentation, this technique also has its limitations. One common challenge in the microcantilever approach is the non-idealities of the cantilever, which might affect the data analysis. Non-idealities of the cantilever include the undercut at the fixed end of the beam, plate effects (anticlastic curvature) and stress gradients across the beam thickness, which result in pre-deflection of the cantilevers. The effects of these non-idealities to the accuracy of Young's modulus measurement will be discussed in Chapter 4.

There are several reports on the measurement of mechanical properties of IMCs. However, most of the studies only focused on the Young's modulus [84–86]. There are a few reports on the measurement of fracture strength of IMC in Cu/Sn system [87, 88] while the mechanical properties of Cu-Sn-In based intermetallic has not yet

been reported.

1.7 Objectives

Despite its potential as an enabling material for 3D ICs, Cu-Sn-In ternary system is still not well characterized in terms of IMC growth kinetics and its mechanical properties. Specifically, the objectives of this project are :

- To develop a simple technique that allows fast characterization of IMC growth kinetics in Cu/solder thin films system.
- To study the effects of Sn-In composition on the growth kinetics of IMC with Cu substrate.
- To develop a general relationship model of IMC growth kinetics in Cu/Sn system.
- To characterize the mechanical properties of Cu-Sn-In ternary system at thin film scales.
- To characterize the bonding between Sn-In solders and Cu thin films.

1.8 Thesis Scope

This thesis comprises six chapters with an appendix listing the details of the computing code used in some calculations. Chapter 1 presents the overview of 3D ICs technology, motivation of the project, a brief review on the current understanding on Cu/solder based interaction and its mechanical properties characterization method. Chapter 2 provides detail descriptions on the technique that were frequently used in this project. Chapter 3 presents the results on the study of growth kinetics of Cu/Sn-In system. In this chapter, a general relationship of Cu/Sn growth kinetics will also be presented. The mechanical properties of Cu-Sn-In ternary system at thin film scale and in a bonding structure will be discussed in Chapters 4 and 5,

respectively. Chapter 5 will also cover the influence of bonding parameters on the mechanical properties of Cu bonded Sn-In films. Finally, Chapter 6 summarizes the entire thesis and provides possible future work.

Chapter 2

Experimental and Characterization Techniques

This chapter describes the experimental techniques used routinely in this project such as sputter deposition, X-ray diffraction (XRD), Energy Dispersive X-ray spectroscopy (EDX), Focused Ion Beam (FIB) and surface profiler. There are other specific experimental setups that will be elaborated separately in Chapters 3 to 5.

2.1 Sputter Deposition

The sputter depositions of Cu-Sn-In thin films were carried out in School of Materials Science and Engineering, Nanyang Technological University in Singapore, using Coaxial Power System. The system is in a class 100,000 clean-room and has three individual magnetrons. Each of the magnetron is equipped with a shutter to enable target cleaning before deposition. The dimension of the sputter targets is 7.62 cm-diameter and 6 mm-thick. Each of the magnetron can be connected either with an alternating current (AC) or a direct current (DC) source, thus deposition of both conductive and non-conductive materials are possible. Each of the power sources is able to generate power up to 400 W. A cooling system is installed to each of the magnetron to prevent over-heating during the deposition. The chamber of the system can be pumped down to 2×10^{-5} torr in 8 h. Two choices of gas are available

: N₂ and Ar. The flow rate of each type of gas can be adjusted between 0-50 sccm. The base pressure of the deposition is controlled by a Gauge pressure in the range of 5-40 mtorr. Diameter of the stage is 20.32 cm, but larger samples up to 30 cm diameter can be placed on the stage. The stage is equipped with rotation capability up to 5 rounds per second. Samples are typically stucked on the stage with a thermal tape. This does not only prevent the fall out of the sample during deposition, but also provides a step-height for thickness measurement of the deposited film using surface profiler. The system is installed with a substrate bias up to 250 W, thus enabling substrate cleaning. Deposition is timed manually with a stopwatch. Deposition parameters for Cu/Sn-In and Cu-Sn-In films will be presented in Chapter 3 and 4, respectively.

2.2 Alpha Step Surface Profiler

The surface profiler used in this project is located in Inorganic Laboratory, School of Materials Science and Engineering, NTU. Surface profiler is commonly used to characterize the surface topography and for thickness measurement. In this project, this equipment was used mainly to measure the thickness of Cu/Sn-In and Cu-Sn-In films.

The system consists of a stage and a stylus which can move both in the vertical and horizontal directions. The surface profiler has a ± 5 nm vertical resolution. It can scan up to a few millimeters horizontally with a spatial resolution down to 0.4 μm . The sampling rate can be set from 50-1000 Hz, while the scan speed can go up to 200 $\mu\text{m/s}$. A force sensor is attached to the stylus, and it can be set from 1 - 4 *mgf*. The system is routinely calibrated with known thickness sample, provided by the vendor.

Thickness of the films was measured by utilizing the step-height generated by the thermal tape during deposition. During measurement, the stylus would initially move down on to the surface of the sample and stop when the force reached a pre-

determined value (i.e. 2.54 *mgf*). The point where the stylus is in contact with the sample is set as a reference. Then, the stylus scans horizontally by keeping a constant force, to profile the topography of the sample. The parameters set for the measurement in this project were 800 μm horizontal distance, 100 $\mu\text{m/s}$ scan rate, and 50 Hz sampling rate. To achieve statistically reliable data, 5 measurements were carried out per data point. The standard deviation of a few microns thick films was typically in the order of 5-10 nm. The raw data from the measurements were then analyzed using the software in the attached computer.

2.3 Focused Ion Beam (FIB)

The FIB system used in this project is FEI Nanolab DualBeam™ 600i, located in Microelectronics Reliability Characterization Laboratory, School of Materials Science and Engineering, NTU. This system is equipped with high resolution field emission scanning electron microscopy, focused ion beam cutting, ion-assisted deposition, energy dispersive x-ray spectroscopy (EDS), and electron back-scattered diffraction spectroscopy (EBSD). Specification details of the system can be found in [89]. Some applications commonly carried out using this system are cross-sectional imaging, modification of electrical routing on integrated circuits, TEM sample preparation, micro-machining, elemental analysis and crystal structure analysis.

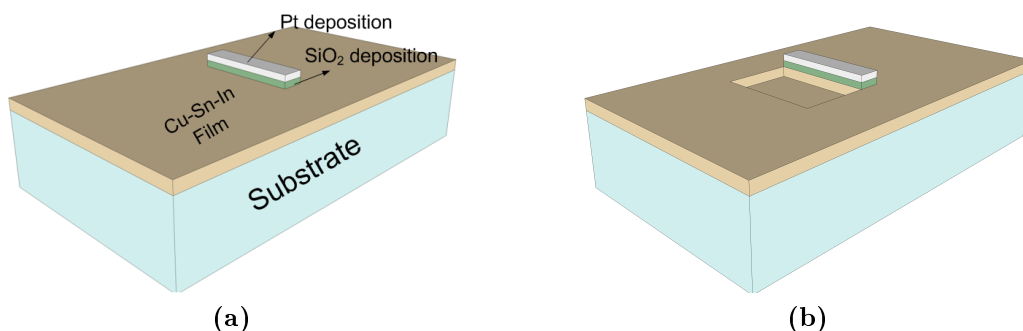


Figure 2.1: Schematic drawing of cross sectional analysis preparation using focused ion beam. a) step 1 - deposition of protective layer. b) FIB cutting to expose the cross section

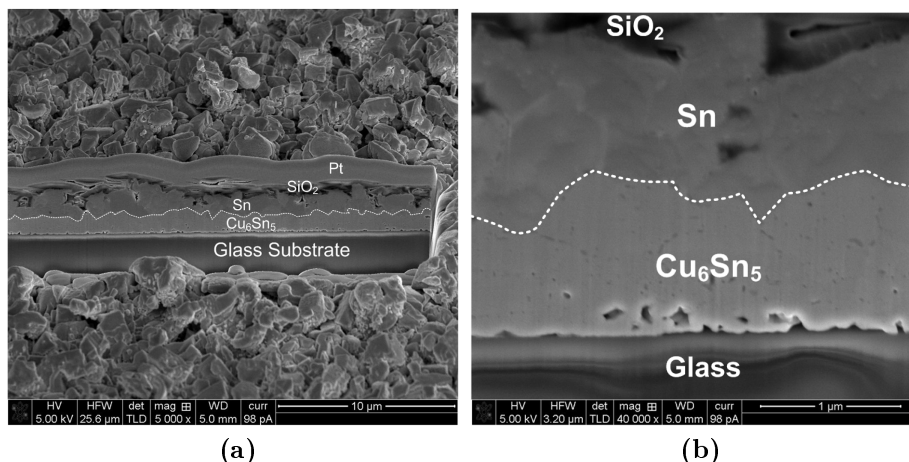


Figure 2.2: Typical cross sectional images of Cu/Sn thin films, annealed at 220°C for 1 min. a) low magnification, b) high magnification.

In this project, the FIB was mainly used for cross sectional analysis of films. Figure 2.1 shows the schematic drawing of cross-sectional analysis preparation using FIB. Initially, a protective layer was deposited onto the sample. Typically, the dimension of this protective layer is 25 μm -length, 1 μm -width and 1 μm -thick. The most common material used for the protective layer is Platinum (Pt). However based on experience, depositing a 0.5 μm thick-SiO₂ prior to Pt deposition, would enhance the contrast of the cross section during imaging of solder based films. Then, ion-beam was used to expose the cross-sectional area of the sample. 'Multipass' cutting mode with 6.5 nA current and 30 kV voltage was used for coarse cutting. To clean the cross-sectional area for better imaging, 'clean cross section' mode was used with 0.28 nA current and 30 kV voltage. Figure 2.2 shows the typical cross sectional images for Cu/Sn film on glass substrate.

2.4 Energy Dispersive X-Ray Spectroscopy (EDS)

Energy dispersive x-ray spectroscopy is commonly used for elemental characterization of materials. It relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit by an electron beam. The basic principle behind EDS is schematically shown in Figure 2.3. When a high energy electron beam hits a

matter, it will knock off some of the electrons of the matter. Because of the energy transfer during this collision, the electron of the matter will excite, leaving a hole at where the electron was. Then, an electron from the outer orbital (higher-energy level) will come down to lower energy level, filling up the hole, while releasing energy in the form of an x-ray. These x-rays are detected by the energy dispersive detector. As each element has a unique structure, it allows the elemental composition of the specimen to be measured.

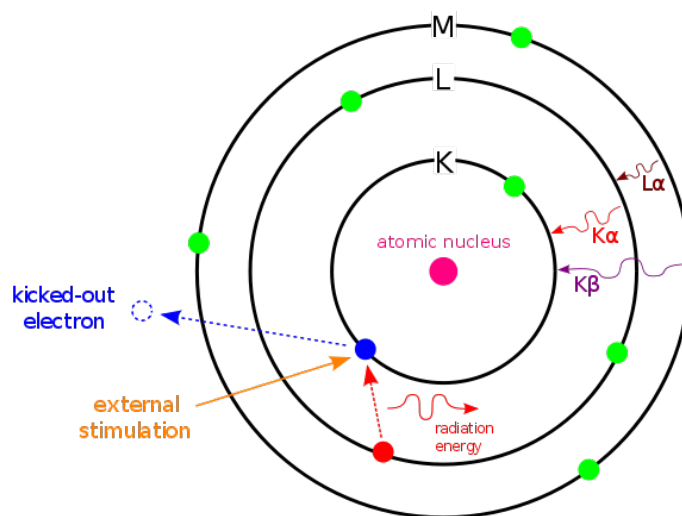


Figure 2.3: Schematic drawing of electron transitions in an atom, which is the basic principle of EDS [90]

In this project, the EDS setup attached to the FEI Nanolab DualBeam™ 600i in Microelectronics Reliability Characterization Laboratory, School of Materials Science and Engineering, NTU was used. It is equipped with a silicon drift detector (SDD) provided by EDAX. Before the usage, the EDS is calibrated by measuring known composition of Cu-Sn-In. Typically, the voltage and current used for EDS characterization are 15 kV and 0.58 nA, respectively. The measurement error is controlled within $\pm 1\%$ variation.

2.5 X-Ray Diffraction Spectroscopy (XRD)

X-ray diffraction technique is commonly used to characterize the atomic structure of materials. In this project, it was mainly used to determine the type of IMCs

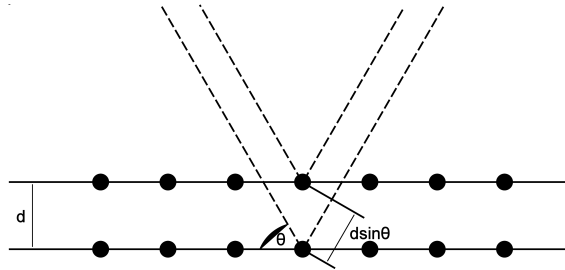


Figure 2.4: Illustration of Bragg's Law [91]

formed in the Cu-Sn-In ternary system. The basic principle behind XRD setup is Bragg's law as schematically shown in Figure 2.4. Incident beams of X-rays which come onto the sample are diffracted by the atomic planes. The diffracted beams then interfere with one another to form constructive interferences, as they leave the sample. The constructive interferences can be deduced by Bragg's condition :

$$n\lambda = 2d_{hkl} \sin \theta \quad (2.1)$$

where d_{hkl} is the spacing between parallel lattice planes denoted by Miller indices of (h, k, l) , θ is the angle between the incident x-ray and lattice planes, λ is the wave length of the incoming x-ray, and n is an integer. From the XRD pattern, the position, shape and intensity of each peak are analyzed and cross-referenced with the database provided in the XRD software, to extract the structural information of the sample.

XRD measurements in Chapter 3 were carried out using Shimadzu XRD located in the Facility for Analysis Characterization Testing and Simulation (FACTS) Laboratory, School of Materials Science and Engineering, NTU. The voltage and current used to generate the x-rays were 40 kV and 40 mA, respectively. θ - 2θ setup was used for the measurement, which is suitable for thin film characterization. The scan rate and scan range were $1^\circ/\text{min}$ and 20 - 80° , respectively. During measurement, the sample was rotating continuously with a speed of 5 rotations per second. The raw data was then analyzed in Match software.

The XRD measurements in Chapter 4 and 5 were carried out using Bruker's XRD in Institute of Materials Research and Engineering (IMRE) with assistance

from Mr. Lim Poh Chong. Unlike Shimadzu XRD, Bruker's XRD uses area scan for the measurement.⁵ Thus, it allows a shorter time experiment than the Shimadzu's. For comparison, it typically takes 5 *min* for characterizing a sample using Bruker's, but around 1 *h* by Shimadzu's.

Chapter 3

Characterization of Diffusion Kinetics of Cu/Sn-In based Solder at Thin Film Scales

3.1 Overview

Identifying the right solder composition that allows fastest and/or slowest inter-metallic compound (IMC) growth arguably has become one of the greatest challenges in solder research community. As more elements are incorporated into the solder material, the possible composition combinations of the solder increases exponentially. The existing methods for characterizing the kinetics of IMC growth do not allow one to study in a systematic manner. The conventional method using *ex situ* heating, followed by cross sectional analysis approach does not only suffer in accuracy due to irregular morphology of IMCs but also requires rigorous effort for the implementation. Meanwhile, *in situ* method allows the subtraction of the IMC growth during storage time, temperature ramping and cooling. However, the experimental setup is extremely rigorous and costly. Both of these methods also highly depend on the resolution of Scanning Electron Microscopy (SEM), therefore suffer in accuracy when the IMCs thickness is less than 1 μm .

In this chapter, a simple technique for characterizing the diffusion kinetics of Cu/Sn-based solders at thin film scales is demonstrated. This technique enables

a quicker and more efficient way in characterizing the diffusion kinetics of Cu/Sn-based solder bilayer, compared to the existing methods. Cu consumption rate is measured by monitoring the optical color change during annealing. Cu has a very different color compared with Cu-Sn based intermetallics, which is a basic feature that is utilized in the development of the technique.

This chapter consists of three sections. Validation of the technique through characterizations of well known Cu/Sn interaction is discussed in the first section. Section two is dedicated to the demonstration of this technique for fast screening materials selection on which Sn-In composition has the most potential for low temperature bonding applications (i.e. the composition which has the fastest reaction at low temperature). Last section of the chapter focuses on characterizing the kinetics behavior of Cu/ Sn₅₆In₄₄ (a newly discovered solder composition that enables the fastest IMC growth).

3.2 Experimental Setup

3.2.1 Cu/Sn-In Deposition

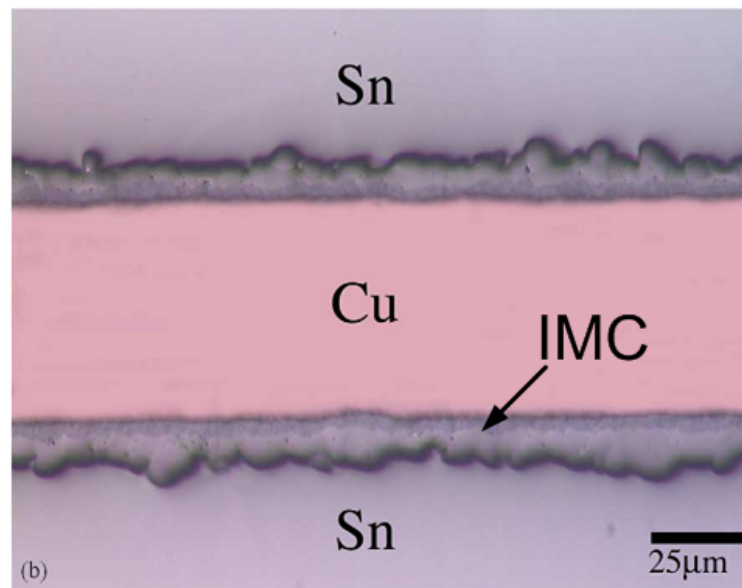


Figure 3.1: Cross reference optical microscopy image of Cu/Sn cross section [66]. The color of Cu and intermetallic compound (IMC) are orange-ish and shiny-white, respectively.

As shown in Figure 3.1, the color difference between Cu and IMC is very obvious. Takenaka *et al.* [66] used cross-reference optical microscopy to characterize the Cu/Sn bilayer system in a cross-sectional manner. The color difference they reported was very similar to our observation whereby Cu has orange-ish color and IMC has shiny-white color. However, instead of analyzing in cross-sectional view, the color change was monitored from the top view of the back side of the samples. From the top view, the time when the color changes from orange-ish to shiny-white color indicates that the whole Cu is consumed. If the initial Cu thickness is known, the Cu consumption rate can then be calculated, and therefore the growth kinetics of IMC can be deduced.

Cu/Sn-In Deposition

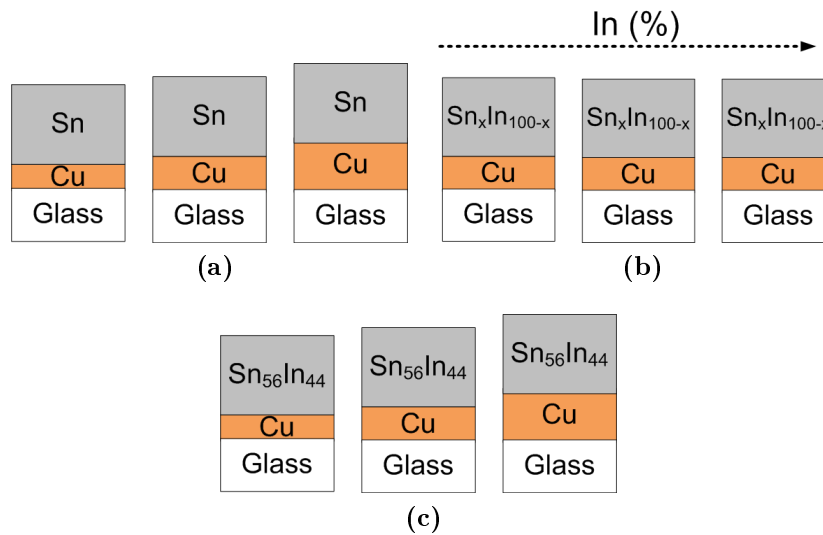


Figure 3.2: Schematic drawing of Cu/solder layer design for a) Cu/Sn system. Cu thickness gradient (80 nm - 502 nm) was produced through angle deposition in sputter chamber. b) Cu/Sn_xIn_{100-x} system. Sn-In compositional variation (5-95 at.% In) was produced by sequence combinatorial deposition. c) Cu/Sn₅₆In₄₄ system. Cu thickness is in the range 80-518 nm.

Three batches of sputter deposition were carried out for investigation of Cu/Sn, Cu/Sn_xIn_{100-x} and Cu/Sn₅₆In₄₄ systems. Schematically, these are shown in Figure 3.2. Batch 1 of the sputter deposition was carried out to study the Cu/Sn system. Cu film was initially deposited on transparent glass stripes by sputter deposition. In order to produce a vast variation of Cu thicknesses, C film was deposited in an angle deposition without stage rotation. The thickness of Cu film on each glass

stripes were then measured by surface profiler. Following the Cu deposition, Sn was deposited uniformly across all the glass stripes. Prior to the Sn deposition, plasma cleaning was carried out to remove the oxide and contaminant. This was necessary because the Cu surface was exposed to the ambient during target change. The deposition parameters for Cu and Sn are listed in Table 3.1.

Table 3.1: *Cu and Sn deposition parameters for Cu/Sn diffusion kinetics study*

Deposition Parameters	Cu	Sn	Plasma Cleaning
Pressure (torr)	2.6×10^{-3}	2.6×10^{-3}	2.6×10^{-3}
Power bias type	DC	DC	Substrate Bias
Voltage (V)	332 ± 3	308 ± 2	-
Current (A)	0.603	0.488	-
Power (W)	200	150	150
Time (min)	15	20	10
Thickness (nm)	80-502	2656 ± 276	-

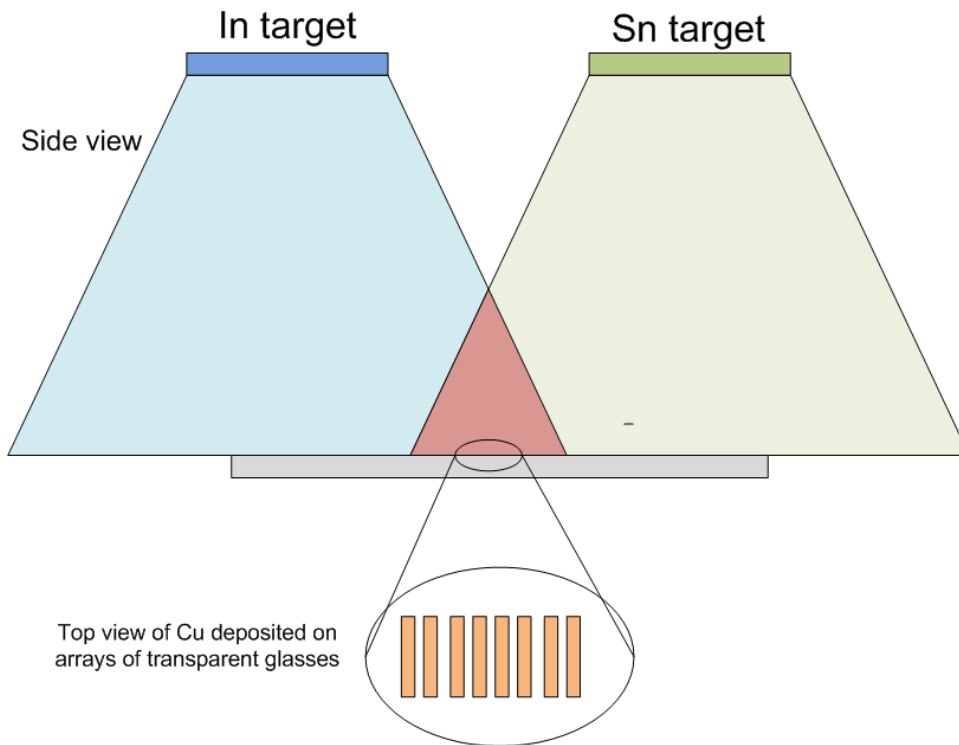


Figure 3.3: *Schematic drawing of sequence-combinatorial deposition of Sn-In on transparent glasses to produce atomic compositional variation of solder. 5 mm × 30 mm size of 20 glass stripes were placed on substrate holder in 2 rows configuration (drawing is not to scale).*

Batch 2 of the sputter deposition was meant to study the effects of Sn-In com-

position on the IMC growth rate. The thickness of Cu was fixed at 583 ± 15 nm. Following Cu deposition, a vast composition variation but uniform thickness of Sn-In was deposited. Atomic variation of $\text{Sn}_x\text{In}_{100-x}$ ($x = 5-95$) was produced by sequence-combinatorial deposition as schematically shown in Figure 3.3. Sn and In were deposited sequentially layer by layer (4 depositions for each target) without stage rotation. Sn and In have relatively low melting points (i.e. 240°C and 156°C , respectively), thus have high homologous temperatures. This allows them to interdiffuse easily to form stable phases similarly to those deposited by normal-combinatorial deposition. In this experiment, a three-target sputter chamber was used which requires no vacuum break during the deposition of different materials. Therefore, plasma cleaning was not necessary. The deposition parameters for this experiment are listed in Table 3.2.

Table 3.2: *Cu, Sn and In deposition parameters for $\text{Cu}/\text{Sn}_x\text{In}_{100-x}$ diffusion kinetics study*

Deposition Parameters	Cu (seq.1)	Sn (seq.2,4,6,8)	In (seq.3,5,7,9)
Pressure (torr)	2.6×10^{-3}	2.6×10^{-3}	2.6×10^{-3}
Voltage (V)	320	329	329
Current (A)	0.55	0.434	0.361
Power (W)	176	150	150
Time (min)	30	5	5
Thickness (nm)	583 ± 15	3573 ± 311	

Table 3.3: *Cu, Sn and In deposition parameters for $\text{Cu}/\text{Sn}_{56}\text{In}_{44}$ diffusion kinetics study*

Deposition Parameters	Cu (seq.1)	Sn (seq.2,4,6,8,10)	In (seq.3, 5,7,9)
fig:Cure (torr)	2.6×10^{-3}	2.6×10^{-3}	2.6×10^{-3}
Voltage (V)	314	315	402
Current (A)	0.66	0.475	0.374
Power (W)	208	150	150
Time (min)	15	3	3
Thickness (nm)	80 - 518	2421 ± 295	

The third batch of sputter deposition was dedicated to $\text{Cu}/\text{Sn}_{56}\text{In}_{44}$ study. This composition was chosen based on the result of $\text{Cu}/\text{Sn}_x\text{In}_{100-x}$ experiment (batch 2).

Similar to the Cu/Sn experiment, Cu was deposited in an angle deposition without stage rotation. Following that, Sn and In were deposited sequentially layer by layer across the whole samples. The deposition parameters for this experiment are listed in Table 3.3.

3.2.2 Annealing Setup

Figure 3.4 shows the setup of an annealing experiment in Prof. Gan Chee Lip's Laboratory in NTU. A hot plate was used as the heater. The temperature was calibrated with a thermocouple which had been pre-calibrated with boiling water. A commercial digital camera (brand : Sony) was used to record the color change. The samples were placed on the backside of oxidized Silicon wafer in order to reduce reflection from the substrate. Black walls were placed surrounding the hot plate to reduce the glare from the side. White-tissue was placed on top to reduce the intensity of the direct light coming from laboratory light bulb.



Figure 3.4: Setup of annealing experiments in laboratory, a) far view, b) close view.

The glass stripes were cut into $5\text{ mm} \times 5\text{ mm}$ size. Once the hot plate temperature was stable, each sample was placed facing down (glass substrate on top) on the hot plate while the camera was recording the color evolution. Figure 3.5 shows the typical color evolution during annealing. The color changed non-uniformly due to Cu thickness gradient (note that the Cu was deposited in an angle deposition). A distinct color change from orange-ish to shiny-white was observed when the whole

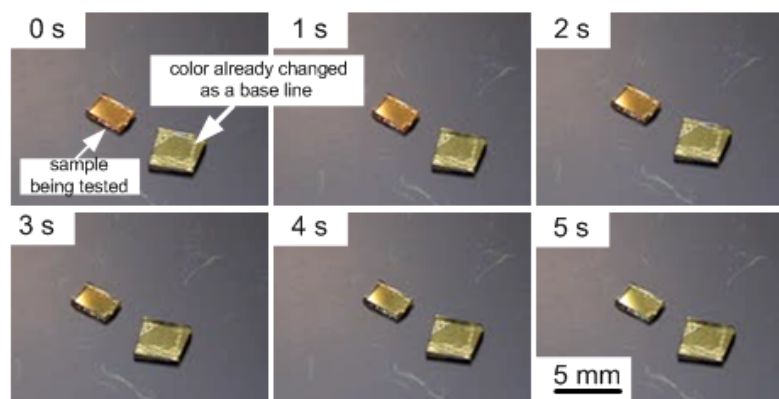


Figure 3.5: Color evolution of sample during annealing at 200°C in 5 s, the initial Cu thickness is 95 nm. Each of $5\text{ mm} \times 30\text{ mm}$ glass stripes was cut into 8 smaller pieces using diamond cutter. Initial Cu-orange-sh color gradually changed to IMC white-shiny color. Lateral gradient change in color is due to the thickness gradient in the sample.

Cu was fully consumed.

Annealing temperature was varied from 100°C to 220°C . The time taken for the color to completely change was recorded with a stop watch. Three samples were measured for each data point.

3.2.3 Microstructure Characterization

Microstructure characterizations were carried out to provide complementary data for understanding the diffusion mechanism. Cross-sectional SEM samples were prepared by Focused Ion Beam (FIB). The phase type of IMC was characterized by XRD.

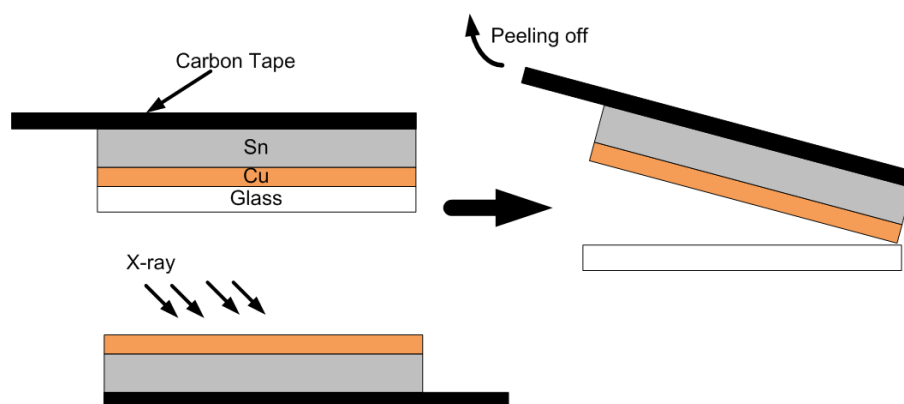


Figure 3.6: Schematic drawing of XRD sample preparation. A carbon tape was stuck on to the Sn surface, followed by peeling off gently to expose the Cu surface. Drawing is not to scale.

As the Sn films were too thick ($>2\text{ }\mu\text{m}$), the x-rays could not penetrate deep enough to reach the IMC layer. Thus, XRD scans were performed on the glass/Cu interface. The samples were prepared by sticking a carbon tape on the Sn surface and then peeling it off to detach the film from the glass substrate, as schematically shown in Figure 3.6.

3.3 Cu/Sn System

3.3.1 Microstructure Analysis

3.3.1.1 Morphology Evolution

Figure 3.7 shows the cross sectional SEM images of Cu/Sn bilayer with different initial Cu thicknesses, annealed at different temperatures until the whole Cu film was fully consumed (i.e. color was completely changed). Several information can be extracted from Figure 3.7. First, there was still unreacted Sn when the whole Cu was fully consumed, which was expected as the Sn layer was thicker than Cu. It can also be seen that IMC had already formed in as-deposited samples, which is in line with previous reports by K.N. Tu [64,92].

It is noteworthy to take a closer look at the morphology evolution of the IMC as its thickness increased. At the beginning, the morphology of the IMC was irregular. The irregular structure of IMC is common for solid/liquid interaction of Cu/Sn system as reported in [67,93–100]. However, it is the first time reported for solid state interaction. Several studies [57,94,101–103] have reported that layer type structure was observed in Cu/Sn system at solid state reaction, but those studies were carried out with a much longer annealing time ($> 1\text{ h}$). Thus, the IMC thicknesses were mostly thicker than $5\text{ }\mu\text{m}$, contrary to the current study where the IMC thickness is below $1\text{ }\mu\text{m}$. Formation of IMCs in a bilayer system is generally preceded by interdiffusion at the interface [104]. In the Cu/Sn system, IMC formation is initiated by diffusion of Cu atoms into the Sn layer until the maximum solubility of Cu in Sn is reached. Further diffusion of Cu atoms into the Sn results in a metastable

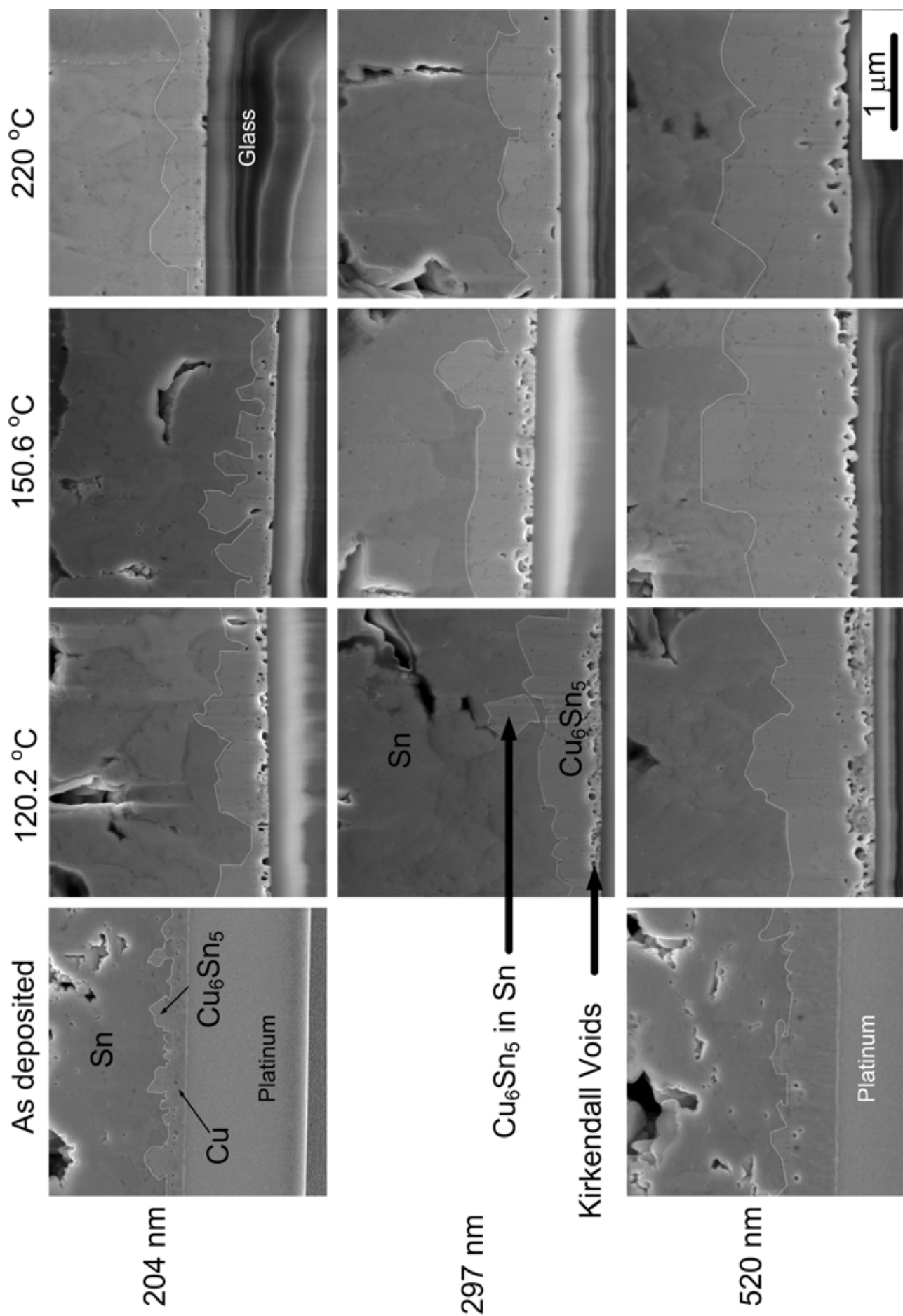


Figure 3.7: SEM cross-sectional images of Cu/Sn bilayer as a function of initial Cu thickness (204-520 nm) and annealing temperatures (120 - 220 °C). Annealing was stopped when the color was completely changed from orange-ish to shiny-white, indicating fully Cu consumption.

interdiffusion layer and subsequently leads to the nucleation of IMC grains at the interface. Nucleation rate is highly dependent on the Cu grain orientation, therefore irregular structure will be formed.

As the IMC thickness increased, the morphology of IMC transformed from irregular to a layer type structure, which is similar to previous studies [93, 94]. During annealing, the growth rate of irregular IMC at the valleys is faster than that at the peaks [94]. Furthermore, the layer type structure is also preferred thermodynamically in solid state reaction because of high energy of the IMC/Sn interface [93, 105]. Additionally, coarsening takes place which eventually leads to the transformation of irregular IMC to the layer type structure [102].

Another feature that can be observed in 3.7 is the presence of IMC inside the Sn layer (see 297 nm-thick Cu, annealed at 120.2°C). Although nucleation at the interface is preferred due to the lower activation energy, IMC may also nucleate away from the interface. According to the Cu-Sn phase diagram [106], the maximum solubility of Cu in Sn layer decreases with decreasing temperature. As a result during the cooling process, excess Cu atoms may precipitate in the form of Cu_6Sn_5 inside the Sn layer.

3.3.1.2 Phases of Intermetallic

Figure 3.8 shows the XRD patterns for annealed and un-annealed samples. Cu, Cu_6Sn_5 (IMC) and Sn phases were detected in un-annealed sample. This suggests that interdiffusion of Cu/Sn that leads to the formation and growth of IMC had already taken place, while Cu film was partially consumed. The presence of unreacted Cu was confirmed by the optical color which is orange-ish from the backside of sample. As the color was completely changed to shiny-white due to annealing, the Cu peaks disappeared, while the Cu_6Sn_5 peaks became stronger. This indicates that the whole Cu had already been consumed and converted to Cu_6Sn_5 . The detection of Sn phase in annealed sample is expected as Sn layer was thicker than Cu. These observations are consistent with SEM cross-sectional analysis as discussed in

previous section.

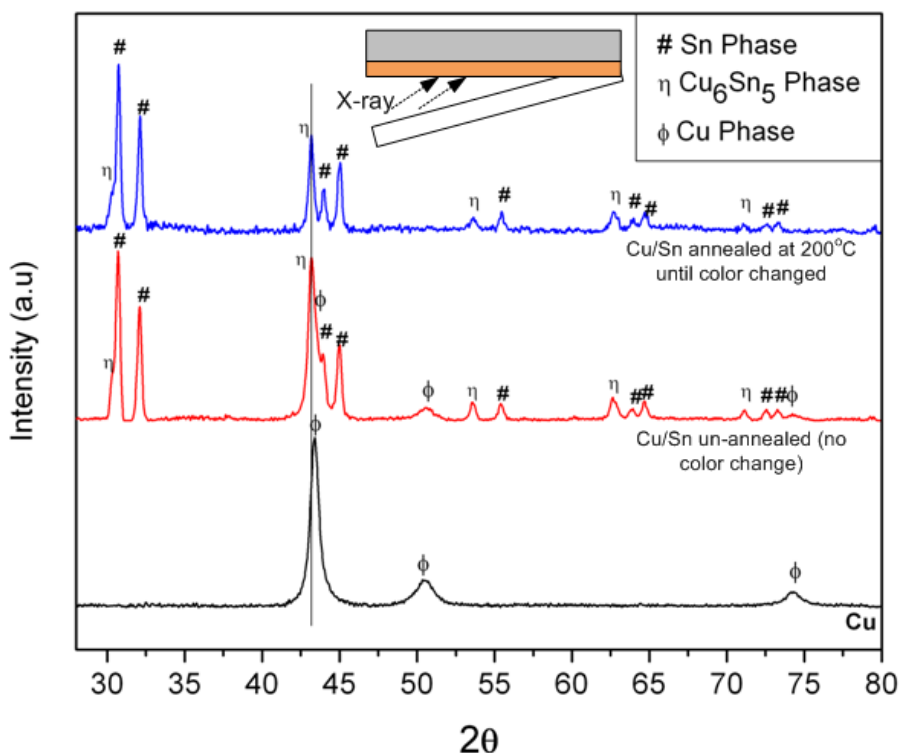


Figure 3.8: XRD pattern of Cu/Sn bilayer before and after annealing. XRD was performed on the Cu/glass interface as schematically shown in inset figure. Note that Cu_6Sn_5 had formed even in un-annealed samples.

Intriguingly, only Cu_6Sn_5 was observed in this experiment, while most of the literature [57,61,64,92,94,107–109] suggested the formation of both Cu_6Sn_5 and Cu_3Sn in Cu/Sn system. According to the Cu-Sn phase diagram [106], both Cu_6Sn_5 and Cu_3Sn are thermodynamically stable phases at temperature below 200°C , suggesting that both phases should be present. A reason why Cu_3Sn was not formed in this experiment is probably due to the thin Cu layer ($< 600\text{ nm}$) and much thicker Sn ($> 2\text{ }\mu\text{m}$) used, unlike those studies [61,67,94,99,110] which used thick Cu ($> 1\text{ }\mu\text{m}$). This configuration might cause the Cu_3Sn phase is kinetically difficult to form. Previous studies [57,61,107] reported that the growth rate of Cu_3Sn is much slower than that of Cu_6Sn_5 at low temperature ($< 200\text{ }^\circ\text{C}$), thus Cu_6Sn_5 forms earlier than Cu_3Sn (i.e. sequential growth). When the Cu layer is thin enough, the whole Cu might have already been consumed to form Cu_6Sn_5 before Cu_3Sn could be formed.

Therefore, Cu_3Sn was not observed.

3.3.1.3 Kirkendall Voids

Another observation that can be made from Figure 3.7 is the presence of Kirkendall voids in the Cu and Cu_6Sn_5 layers. A few Kirkendall voids were formed at the Cu/ Cu_6Sn_5 interface even in as-deposited samples. After annealing, these voids became bigger and more voids were formed. Interestingly, there was a clear trend on the effects of annealing temperature on the amount of Kirkendall voids. For the same thickness of Cu_6Sn_5 , the amount of voids decreased as temperature increased.

This phenomenon can also be seen from the top view of Cu or Cu_6Sn_5 (sample preparation was the same as for XRD) layer as shown in Figure 3.9. The voids were invisible in as deposited samples because the voids were still small and the location was at the Cu/ Cu_6Sn_5 interface. Annealing the sample at room temperature for 6 days resulted in the formation of more and bigger voids. In Figure 3.9, it is clearly seen that the voids grew until the Cu/glass interface. On the other hand, fewer voids were found for samples annealed at 200 °C.

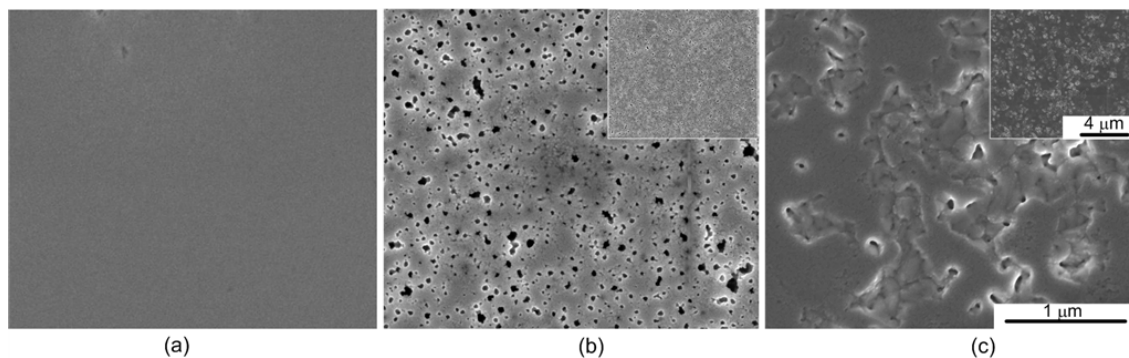


Figure 3.9: Top view of Kirkendall voids evolution from Cu/glass interface annealed at different condition. (a) As deposited, (b) room temperature for 6 days (no color change), (c) 200°C until the color changed.

Kirkendall voids are commonly found in Cu/Sn system [59, 111–113]. Several literature suggested that the presence of Cu_3Sn plays a crucial role in the Kirkendall voiding. Tu *et al.* [64, 92, 111] observed that the voids are usually found in the presence of Cu_3Sn phase. They argued that diffusion of Cu in this Cu_3Sn phase is much faster than Sn in the opposite direction, thus it results in the formation

of voids. Borgersen *et al.* [114] supported this argument with an observation that the Cu flux in Cu_3Sn exceeds the Sn flux by almost an order of magnitude or more between 125°C - 205°C . Liu *et al.* [115] observed that Kirkendall voids disappeared as the Cu_3Sn transformed back to Cu_6Sn_5 in a Cu limited system.

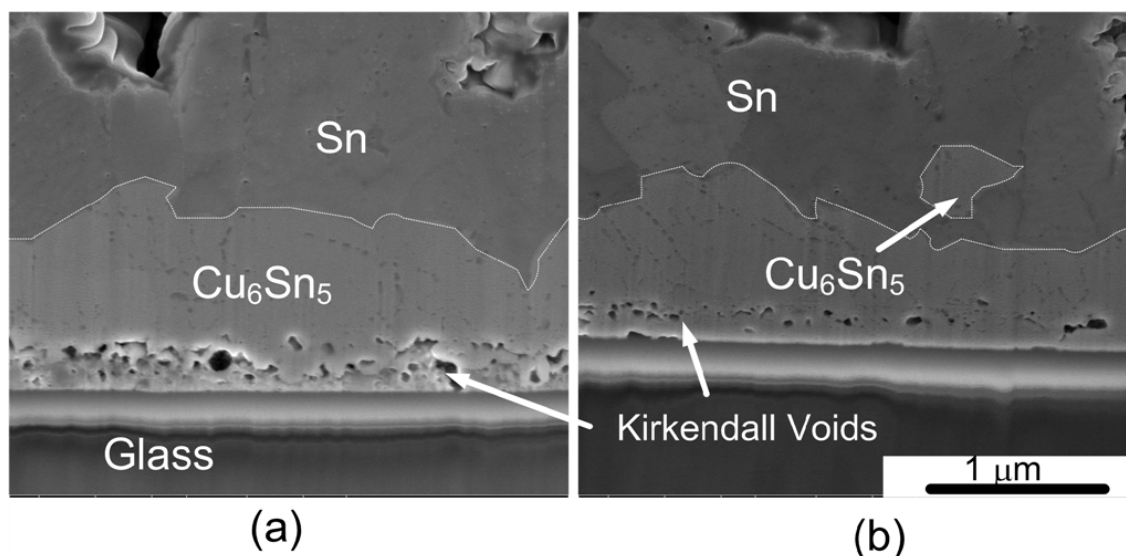


Figure 3.10: Effects of over annealing at 120°C for (a) 4 h just until the Cu is fully consumed, (b) 12 h. Over annealing results in the reduction of the amount of the voids because of the dominant diffusion of Sn towards the Cu_6Sn_5 .

Interestingly in our experiments, Kirkendall voids were found even without the presence of Cu_3Sn . Using marker, Mei *et al.* [107] studied the interdiffusion in Cu/Sn system. They found that Cu is also the dominant diffusion species in Cu_6Sn_5 at temperatures below 170°C . It is believed that the diffusion mechanism of Cu in Cu_6Sn_5 phase is along grain boundary [57,64]. At higher temperatures, these studies [63,116] observed that Sn diffusion through the lattice is more dominant. This explains the temperature dependence on the amount of Kirkendall voids in our experiments. At low temperature, Cu diffuse faster in the Cu_6Sn_5 layer, and thus results in the formation of voids. As temperature increases, Sn diffusion towards the Cu becomes more dominant which results in fewer voids.

Although at low temperature annealing Cu is the dominant diffusion species in Cu_6Sn_5 , Sn diffusion through Cu_6Sn_5 does take place as well. This is clearly seen in Figure 3.10. As the sample continued to be annealed after the whole Cu had been consumed, the amount of Kirkendall voids is reduced significantly.

3.3.2 Kinetics Analysis

3.3.2.1 Calculation of Cu₆Sn₅ Thickness

Based on the discussion in the previous section, it is shown that only Cu₆Sn₅ phase was formed in this experiment. Thus, it is reasonable to assume that the whole Cu (Cu_{total}) was consumed for Cu₆Sn₅ growth ($Cu_{Cu_6Sn_5}$) and for forming solid solution in Sn (Cu_{Sn}) as described in equation (3.1).

$$Cu_{total} \rightarrow Cu_{Cu_6Sn_5} + Cu_{Sn} \quad (3.1)$$

Ma *et al.* [93] reported that the Cu solubility in solid Sn is as low as 0.006 wt%, while in liquid Sn is 0.15-0.5 wt%. In a relatively thin Sn layer ($< 3 \mu\text{m}$) like in this work, the amount of Cu film consumed for forming solid solution in Sn would then be only about $\sim 0.1 \text{ nm}$, which is not substantial as compared to the whole 100-600 nm-thick Cu film. This also means that the amount of Cu₆Sn₅ that would have formed during the cooling process is insignificant. As a consequence, it is reasonable to assume that almost all of the Cu is converted into Cu₆Sn₅ during the annealing process according to equation (3.2).



With known consumed Cu thickness (h_{Cu}), density of Cu (ρ_{Cu}) and density of Cu₆Sn₅ ($\rho_{Cu_6Sn_5}$), the thickness of Cu₆Sn₅ ($h_{Cu_6Sn_5}$) can then be deduced by equation (3.3)

$$h_{Cu_6Sn_5} = \frac{h_{Cu} A_{Cu} \rho_{Cu} A_r^{Cu_6Sn_5}}{6 A_r^{Cu} \rho_{Cu_6Sn_5} A_{Cu_6Sn_5}} \quad (3.3)$$

where $A_r^{Cu_6Sn_5}$ and A_r^{Cu} are the atomic weight of Cu₆Sn₅ and Cu, respectively. In the current study, the area of Cu film (A_{Cu}) is equal to the area of Cu₆Sn₅ ($A_{Cu_6Sn_5}$).

In order to verify equation (3.3), 0.502 μm Cu/2.6 μm Sn bilayer was annealed until the whole Cu was fully consumed. The thickness of Cu₆Sn₅ was measured from

Table 3.4: *Physical parameters used in calculation of Cu_6Sn_5 thickness*

Parameters	Magnitude	Reference
ρ_{Cu}	8.9 gr/cm ³	[117]
$\rho_{\text{Cu}_6\text{Sn}_5}$	8.3 gr/cm ³	[108]
$A_r^{\text{Cu}_6\text{Sn}_5}$	63.55 gr/mol	[117]
A_r^{Cu}	974.83 gr/mol	[117]

the cross-sectional SEM images as shown in Figure (3.7). Because the morphology of Cu_6Sn_5 is relatively irregular, the thickness of Cu_6Sn_5 was determined by dividing the area of Cu_6Sn_5 with the length of the cross-sectional images. The area of Cu_6Sn_5 was measured by pixel counting in imageJ software [118]. From the measurement, the thickness of Cu_6Sn_5 was determined to be $1.37 \pm 0.07 \mu\text{m}$.

Separately, using equation (3.3) and the physical parameters listed in Table 3.4, the Cu_6Sn_5 thickness of the corresponding sample is computed to be $1.42 \mu\text{m}$. This is in excellent agreement with the result from the measurement, therefore validates the accuracy of equation (3.3) for Cu_6Sn_5 thickness calculation. Furthermore, this result also validates the presence of Cu_6Sn_5 as the only IMC formed as suggested from XRD experiment.

3.3.2.2 Growth Kinetics of Cu_6Sn_5 from Power Law Analysis

The growth mechanism of Cu_6Sn_5 is relatively complex as it involves multiple kinetics processes which take place either in parallel or in series. Cu atoms diffuse along the Cu_6Sn_5 grain boundaries and then react with Sn to contribute to the Cu_6Sn_5 growth at the $\text{Cu}_6\text{Sn}_5/\text{Sn}$ interface [57,99,110]. At the same time, Sn also diffuses through the Cu_6Sn_5 lattice layer and forms Cu_6Sn_5 at the Cu/Cu Sn_5 interface. Which of these processes is more dominant is highly dependent on the temperature, time, layer thickness, layer morphology and type of materials. Commonly, a simple power law analysis can be used as a first guide to probe which of the kinetics processes is more dominant or is rate limiting. Power law growth can be expressed as

shown in equation (3.4).

$$h_{Cu_6Sn_5} = Ct^n \quad (3.4)$$

where $h_{Cu_6Sn_5}$ is the thickness of Cu_6Sn_5 , C is a constant which is temperature dependent, t is the time and n is the exponential factor. The values of n may vary from 0.2 - 1, depending on what the dominant mechanism is. At the beginning of Cu_6Sn_5 growth, the thickness versus time curve can usually be fitted with $n = 1$. This suggests that the growth mechanism is reaction controlled [60,64]. As the Cu_6Sn_5 gets thicker, n is better fitted with 0.5, suggesting the growth mechanism is controlled by lattice diffusion [48,66,101]. For irregular/scallop shaped Cu_6Sn_5 , n is usually in the range of 0.2 - 0.35 [67,100]. Schaefer *et al.* [67] showed that for this case, the growth mechanism is controlled by grain boundary diffusion (see section 1.5 for details). Separately, Kim and Tu [100] argued that $n = 0.33$ indicates that the mechanism is controlled by IMC grain ripening, and the theory was later discussed in more detail by Gusak and Tu [119] (see section 1.5 for details). When n lies between these values, it suggests that the growth is controlled by more than one mechanism.

Figure 3.11(a) shows the experimental data obtained from the color change experiment. Time was recorded when the color change process was completed. Typically, the time interval from when the color change began until it ended was less than 5% of the recorded time. Therefore, the experimental error associated with the measurement is small. Three samples were tested for each data point, the average values were calculated and the standard deviations are shown as horizontal error bars. The vertical error bars represent the standard deviation of Cu thickness measurements using surface profiler.

In general, a higher temperature results in faster Cu consumption. Thicker initial Cu thickness also requires a longer annealing time to be consumed completely. Most of the literature [61,65,66,120] used the thickness of Cu_6Sn_5 as the parameter for their kinetics study. Therefore, for the ease of comparison with other studies,

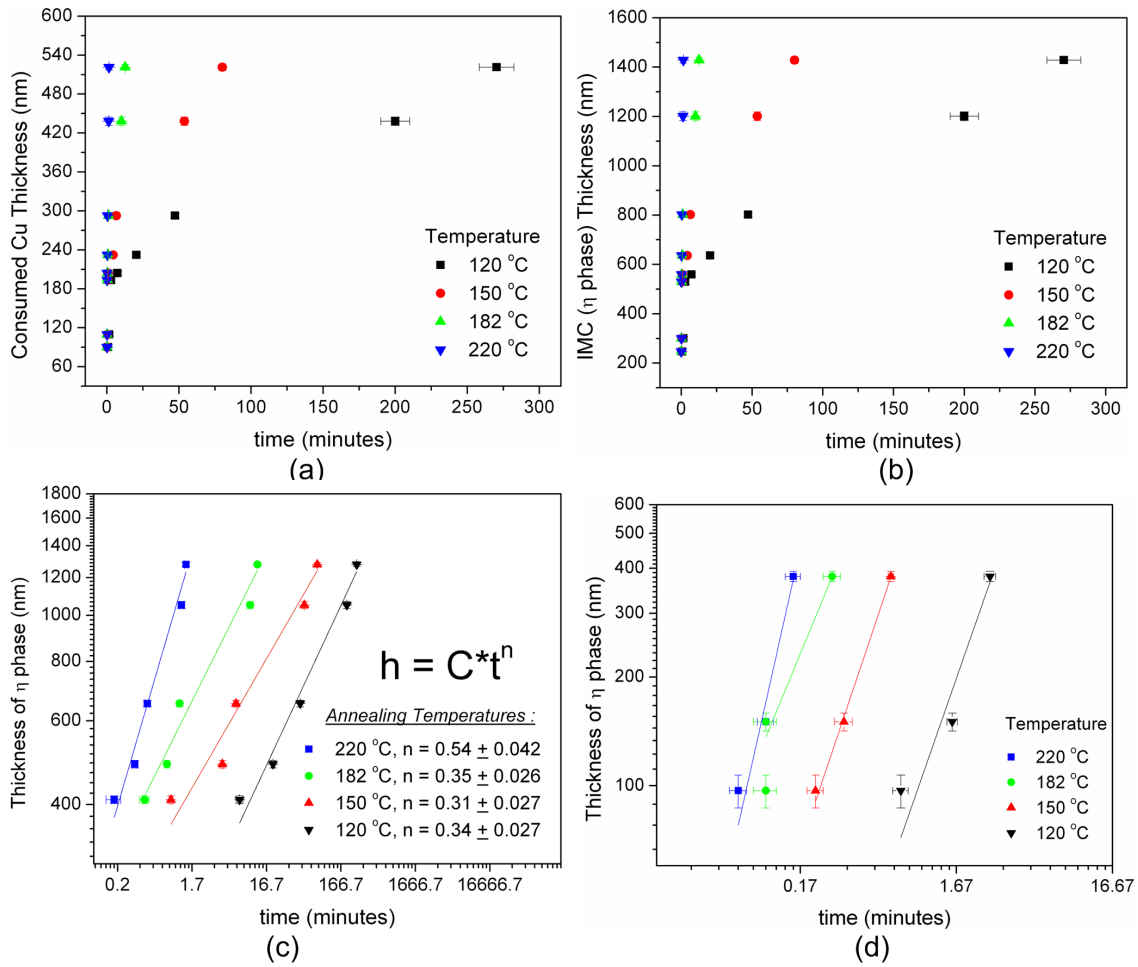


Figure 3.11: Experimental data plot from color change experiments for Cu/Sn system. (a) Linear plot of Cu consumption thickness Vs time, (b) Linear plot of Cu_6Sn_5 thickness Vs time, (c) Logarithmic plot of Cu_6Sn_5 thickness Vs time (only for thick regime), (d) Logarithmic plot of Cu_6Sn_5 thickness Vs time (only for thin regime), fitted with $n=1$.

Cu consumption thickness was converted to Cu_6Sn_5 thickness using the approach discussed previously. The result is then shown in Figure 3.11(b).

It can be seen in Figure 3.11 that the experimental data was fitted with different values of n for different regimes. For thin Cu_6Sn_5 ($h_{\text{Cu}_6\text{Sn}_5} < 600$ nm), the data is best fitted with $n = 1$, which indicates that it is more likely to be reaction limited. For a thicker Cu_6Sn_5 regime, the data is best fitted with $n = 0.3$ at low temperatures ($T < 182^\circ\text{C}$) and $n = 0.5$ at higher temperature ($T = 220^\circ\text{C}$). This indeed supports the previous discussion on Kirkendall voids. At low temperature annealing, Cu diffusion along the grain boundary is more dominant. While at high temperature, the Sn diffusion through the lattice becomes more dominant. Quantitative analysis

on the growth kinetics will be discussed in the next section.

3.3.2.3 Analytical Model on the Growth Kinetics of Cu_6Sn_5

In this section, a quantitative model on the growth kinetics of Cu_6Sn_5 (from now on is referred as η phase) based on diffusion equations is derived. As schematically shown in Figure 3.12, there are multiple kinetics processes involve in the growth of η phase. Cu atoms diffuse both through the lattice and along the grain boundaries of η phase simultaneously, and subsequently react with Sn at the η/Sn interface to form η phase. In parallel, Sn atoms also diffuse both through the lattice and along the grain boundaries of η phase, and subsequently react with Cu to form η phase at the Cu/η interface. Diffusion flux of Cu into Sn during annealing and precipitation flux of Cu to form η phase during cooling are neglected due to the small solubility Cu in Sn as discussed in section 3.3.2.1. As a result, this kinetics analysis is fundamentally similar to the well-known case of silicon oxidation process proposed by Deal and Grove [121].

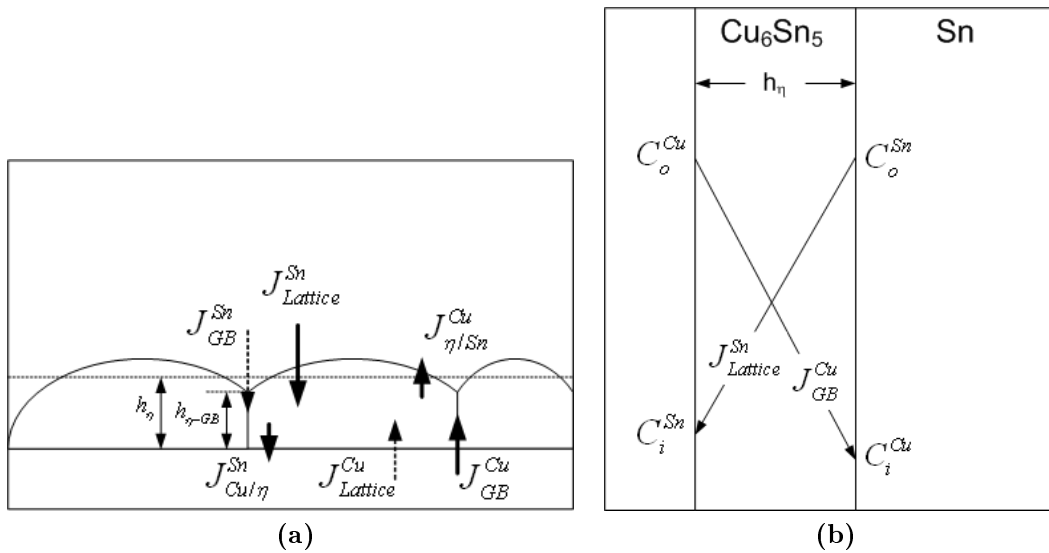


Figure 3.12: Schematic drawing of diffusion mechanism in Cu/Sn system. (a) Multiple diffusion fluxes which take place. (b) Concentrations of each diffusion species at the interfaces.

Cu flux

Following Schaefer *et al.* [67], the diffusion flux of Cu along η phase grain boundaries, $J_{\eta-GB}^{Cu}$, can be expressed with a modified version of Fick's first law as shown in equation (3.5) (see section 1.5 for the details of derivation).

$$J_{\eta-GB}^{Cu} = D_{\eta-GB}^{Cu} \left(\frac{\delta (C_o^{Cu} - C_i^{Cu})}{\sqrt{3}R} \right) \left(\frac{1}{h_\eta} \right)^2 \quad (3.5)$$

$$D_{\eta-GB}^{Cu} = D_{o-\eta-GB}^{Cu} \exp \left(-\frac{Ea_{\eta-GB}^{Cu}}{kT} \right)$$

where $D_{\eta-GB}^{Cu}$ is the Cu diffusivity along the η phase grain boundaries, which is a function of temperature, T . δ is the width of grain boundaries. R is the $h_{\eta-GB}/h_\eta$ ratio, where $h_{\eta-GB}$ is the thickness of η phase grain boundaries. C_o^{Cu} and C_i^{Cu} are the Cu concentrations at the Cu/ η and η /Sn interface, respectively. $Ea_{\eta-GB}^{Cu}$ is the activation energy of Cu diffusion along η phase grain boundaries, while is the diffusion constant. Lastly, k is the Boltzmann constant.

Diffusion of Cu through the lattice of η phase, $J_{\eta-lattice}^{Cu}$, can be expressed by Fick's first law as shown in equation (3.6).

$$J_{\eta-lattice}^{Cu} = D_{\eta-lattice}^{Cu} \left(\frac{C_o^{Cu} - C_i^{Cu}}{h_\eta} \right) \quad (3.6)$$

$$D_{\eta-lattice}^{Cu} = D_{o-\eta-lattice}^{Cu} \exp \left(-\frac{Ea_{\eta-lattice}^{Cu}}{kT} \right)$$

where $D_{\eta-lattice}^{Cu}$ is the Cu diffusivity through the lattice of η phase. $Ea_{\eta-lattice}^{Cu}$ and $D_{o-\eta-lattice}^{Cu}$ are the activation energy and diffusion constant of Cu through the η phase lattice, respectively.

The total diffusion flux of Cu through the η phase, $J_{diffusion}^{Cu}$, is the summation of both fluxes and is expressed in equation (3.7).

$$J_{diffusion}^{Cu} = J_{\eta-lattice}^{Cu} + J_{\eta-GB}^{Cu} \quad (3.7)$$

From literature [57, 64, 110], diffusion of Cu along the η phase grain boundaries is much faster than through the lattice. Thus, equation (3.7) is simplified as :

$$J_{diffusion}^{Cu} = J_{\eta-GB}^{Cu} = D_{\eta-GB}^{Cu} \left(\frac{\delta (C_o^{Cu} - C_i^{Cu})}{\sqrt{3}R} \right) \left(\frac{1}{h_\eta} \right)^2 \quad (3.8)$$

Cu atoms which diffuse through the η phase subsequently react with Sn to form η phase at the η /Sn interface. The reaction flux of this process, $J_{\eta/Sn}^{Cu}$ is expressed in equation (3.9).

$$J_{\eta/Sn}^{Cu} = k_s C_i^{Cu} \quad (3.9)$$

$$k_s = k_{o-s} \exp \left(-\frac{Ea_s}{kT} \right)$$

where k_s is the reaction rate constant which has temperature dependence. Ea_s and k_{o-s} are the activation energy and pre-exponential factor of the reaction rate constant of Cu with Sn, respectively.

Assuming that both the diffusion and reaction fluxes are in steady state,

$$J^{Cu} = J_{diffusion}^{Cu} = J_{\eta/Sn}^{Cu}. \quad (3.10)$$

Substituting equations (3.8) and (3.9) into (3.10), it results in

$$J^{Cu} = \frac{k_s C_o^{Cu} \frac{D_{\eta-GB}^{Cu} \delta}{\sqrt{3}R}}{h_\eta^2 k_s + \frac{D_{\eta-GB}^{Cu} \delta}{\sqrt{3}R}}. \quad (3.11)$$

Sn flux

Similarly to Cu diffusion flux, diffusion of Sn along the η phase grain boundaries can be expressed in equation (3.12),

$$J_{\eta-GB}^{Sn} = D_{\eta-GB}^{Sn} \left(\frac{\delta (C_o^{Sn} - C_i^{Sn})}{\sqrt{3}R} \right) \left(\frac{1}{h_\eta} \right)^2 \quad (3.12)$$

$$D_{\eta-GB}^{Sn} = D_{o-\eta-GB}^{Sn} \exp \left(-\frac{Ea_{\eta-GB}^{Sn}}{kT} \right)$$

where $D_{\eta-GB}^{Sn}$ is the Sn diffusivity along η phase grain boundaries. C_o^{Sn} and C_i^{Sn} are the Sn concentrations at the Sn/ η and η /Cu interfaces, respectively. $Ea_{\eta-GB}^{Sn}$ is the activation energy of Sn diffusion along the η phase grain boundaries, while $D_{o-\eta-GB}^{Sn}$ is the pre-exponential factor of the diffusion constant.

Diffusion of Sn through the η phase lattice, $J_{\eta-lattice}^{Sn}$ is

$$J_{\eta-lattice}^{Sn} = D_{\eta-lattice}^{Sn} \left(\frac{\partial C^{Sn}}{\partial h_{\eta}} \right) \quad (3.13)$$

$$D_{\eta-lattice}^{Sn} = D_{o-\eta-lattice}^{Sn} \exp \left(-\frac{Ea_{\eta-lattice}^{Sn}}{kT} \right)$$

where $D_{\eta-lattice}^{Sn}$ is the Sn diffusivity through the lattice of η phase. $Ea_{\eta-lattice}^{Sn}$ and $D_{o-\eta-lattice}^{Sn}$ are the activation energy and diffusion constant of Sn through the η phase lattice, respectively. $\partial C^{Sn}/\partial h_{\eta}$ is the concentration gradient of Sn across the η phase.

Assuming that the concentration of Sn at the Cu/ η (C_i^{Sn}) and η /Sn interfaces are always constant through time, equation (3.13) becomes:

$$J_{\eta-lattice}^{Sn} = D_{\eta-lattice}^{Sn} \left(\frac{C_o^{Sn} - C_i^{Sn}}{h_{\eta}} \right) . \quad (3.14)$$

The total diffusion flux of Sn through the η phase is the summation of both fluxes and can be expressed as

$$J_{diffusion}^{Sn} = J_{\eta-lattice}^{Sn} + J_{\eta-GB}^{Sn} . \quad (3.15)$$

According to literature [57, 63, 107, 116], diffusion of Sn through the η phase lattice is more dominant than along the grain boundaries. Thus, the total Sn flux is simplified as :

$$J_{diffusion}^{Sn} \approx J_{\eta-lattice}^{Sn} = D_{\eta-lattice}^{Sn} \left(\frac{C_o^{Sn} - C_i^{Sn}}{h_{\eta}} \right) . \quad (3.16)$$

Sn atoms which diffuse through the η phase subsequently react with Cu to form η phase at the Cu/ η interface. The reaction flux of this process, $J_{Cu/\eta}^{Sn}$ is expressed as follows

$$J_{Cu/\eta}^{Sn} = k_s C_i^{Sn} . \quad (3.17)$$

In steady state, both Sn diffusion and reaction fluxes are the same

$$J^{Sn} = J_{diffusion}^{Sn} = J_{Cu/\eta}^{Sn} . \quad (3.18)$$

Substituting equations (3.16) and (3.17) into (3.18),

$$J^{Sn} = \frac{k_s D_{\eta-lattice}^{Sn} C_o^{Sn}}{k_s h_{\eta} + D_{\eta-lattice}^{Sn}} . \quad (3.19)$$

Growth rate equation

As described previously, the η phase grows at both the Cu/ η and η /Sn interfaces.

The growth rate, $\frac{\partial h_{\eta}}{\partial t}$, can then be expressed as

$$\frac{\partial h_{\eta}}{\partial t} = \frac{J^{Cu}}{N_1^{Cu}} + \frac{J^{Sn}}{N_1^{Sn}} = \frac{k_s C_o^{Cu} \frac{D_{\eta-GB}^{Cu} \delta}{N_1^{Cu} \sqrt{3} R}}{h_{\eta}^2 k_s + \frac{D_{\eta-GB}^{Cu} \delta}{\sqrt{3} R}} + \frac{k_s D_{\eta-lattice}^{Sn} C_o^{Sn} / N_1^{Sn}}{k_s h_{\eta} + D_{\eta-lattice}^{Sn}} \quad (3.20)$$

where N_1^{Cu} and N_1^{Sn} are the number of Cu and Sn atoms incorporated into a unit volume of η phase layer, respectively.

Solving equation (3.20) :

$$\partial t = \frac{\partial h_{\eta}}{\frac{k_s C_o^{Cu} \frac{D_{\eta-GB}^{Cu} \delta}{N_1^{Cu} \sqrt{3} R}}{h_{\eta}^2 k_s + \frac{D_{\eta-GB}^{Cu} \delta}{\sqrt{3} R}} + \frac{k_s D_{\eta-lattice}^{Sn} C_o^{Sn} / N_1^{Sn}}{k_s h_{\eta} + D_{\eta-lattice}^{Sn}}} \quad (3.21)$$

$$\int_{t=0}^t \partial t = \int \left[\frac{\partial h_\eta}{\frac{k_s C_o^{Cu} \frac{D_{\eta-GB}^{Cu} \delta}{N_1^{Cu} \sqrt{3} R}}{h_\eta^2 k_s + \frac{D_{\eta-GB}^{Cu} \delta}{\sqrt{3} R}} + \frac{k_s D_{\eta-lattice}^{Sn} C_o^{Sn} / N_1^{Sn}}{k_s h_\eta + D_{\eta-lattice}^{Sn}}} \right]_{h_\eta=h_0}^{h_\eta} \quad (3.22)$$

where h_o is the initial η phase thickness before the annealing (note that η phase had already formed in as-deposited sample).

3.3.2.4 Parameters for the Growth Kinetics Simulation

The ratio of grain boundary thickness to the average η phase thickness, R , was determined empirically through cross sectional measurements. As seen in Figure 3.13, R process can be 0.3 to 0.8, depending on the thickness of η phase. For comparison, Schaefer *et al.* [67] observed the values of R are in the range of 0.15 to 0.4. Fairly deep grain boundary grooves in Schaefer's experiments is expected because their η phase was formed by solid/liquid interaction, which tends to form scallop like structure as discussed earlier. The slight increment of R with thickening of η phase indicates the planarization phenomenon. Although R is not a constant, for simplicity in the computation, $R=0.5$ was taken as the input.

The number of Cu atoms incorporated into a unit volume of η phase, N_1^{Cu} , was calculated with the following equation

$$N_1^{Cu} = \frac{6\rho_\eta N_A}{A_r^\eta} . \quad (3.23)$$

where N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), ρ_η is the mass density of η phase (8.3 gr/cm^3) and A_r^η is the atomic weight of η phase (974.83 gr/mol). Similarly, the number of Sn atoms incorporated into a unit volume of η phase, was calculated with the following equation

$$N_1^{Sn} = \frac{5\rho_\eta N_A}{A_r^\eta} . \quad (3.24)$$

the final calculation, N_1^{Cu} and N_1^{Sn} are $3.076 \times 10^{22} \text{ cm}^{-3}$ and $2.56 \times 10^{22} \text{ cm}^{-3}$,

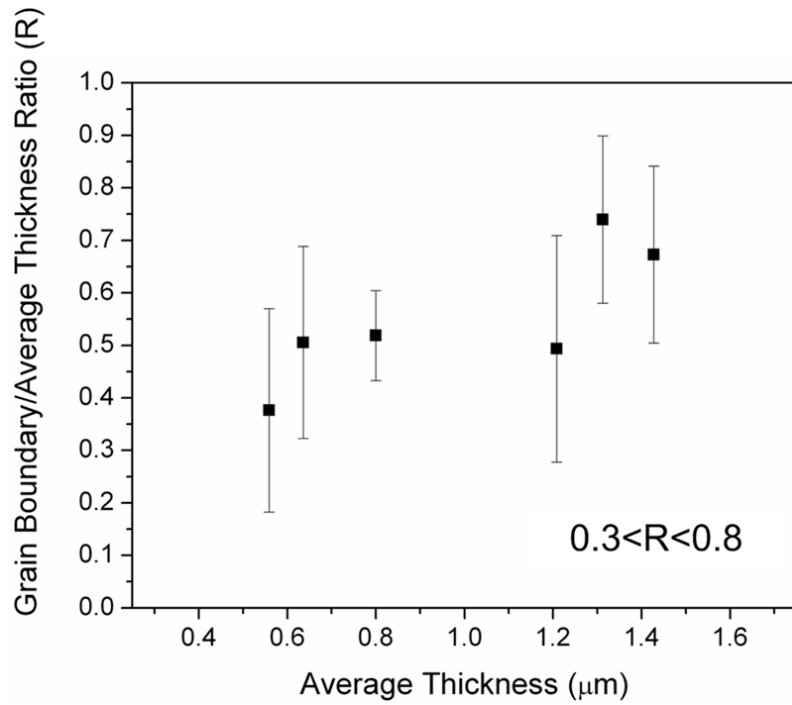


Figure 3.13: Plot of R (grain boundary thickness/average thickness ratio) Vs h_η (average thickness of η phase) based on cross sectional measurement.

respectively.

Table 3.5: Physical parameters for growth kinetics simulation of η phase.

Parameters	Magnitude	Reference
δ	1 nm	[122]
k_{o-s}	$1.3 \times 10^3 \text{ mol/s.m}$	[60]
Ea_s	0.75 eV	[60]
$D_{o-\eta-GB}^{Cu}$	$8.86 \times 10^{-13} \text{ m}^2/\text{s}$	[110]
$Ea_{\eta-GB}^{Cu}$	0.21 eV	[110]
C_o^{Cu}	$3.1 \times 10^{22} \text{ cm}^{-3}$	[63]
$D_{o-\eta-lattice}^{Sn}$	$2.39 \times 10^{-9} \text{ m}^2/\text{s}$	[107]
$Ea_{\eta-lattice}^{Sn}$	w.59 eV	[107]
C_o^{Sn}	$2.63 \times 10^{22} \text{ cm}^{-3}$	[63]
k	8.314 J/mol K	[123]

The initial thickness of IMC is 93.4 ± 22 nm, as measured from cross-sectional images shown in Figure 3.7 (the as-deposited condition). The rest of the physical

parameters are listed in Table 3.5.P

3.3.2.5 Simulation Results

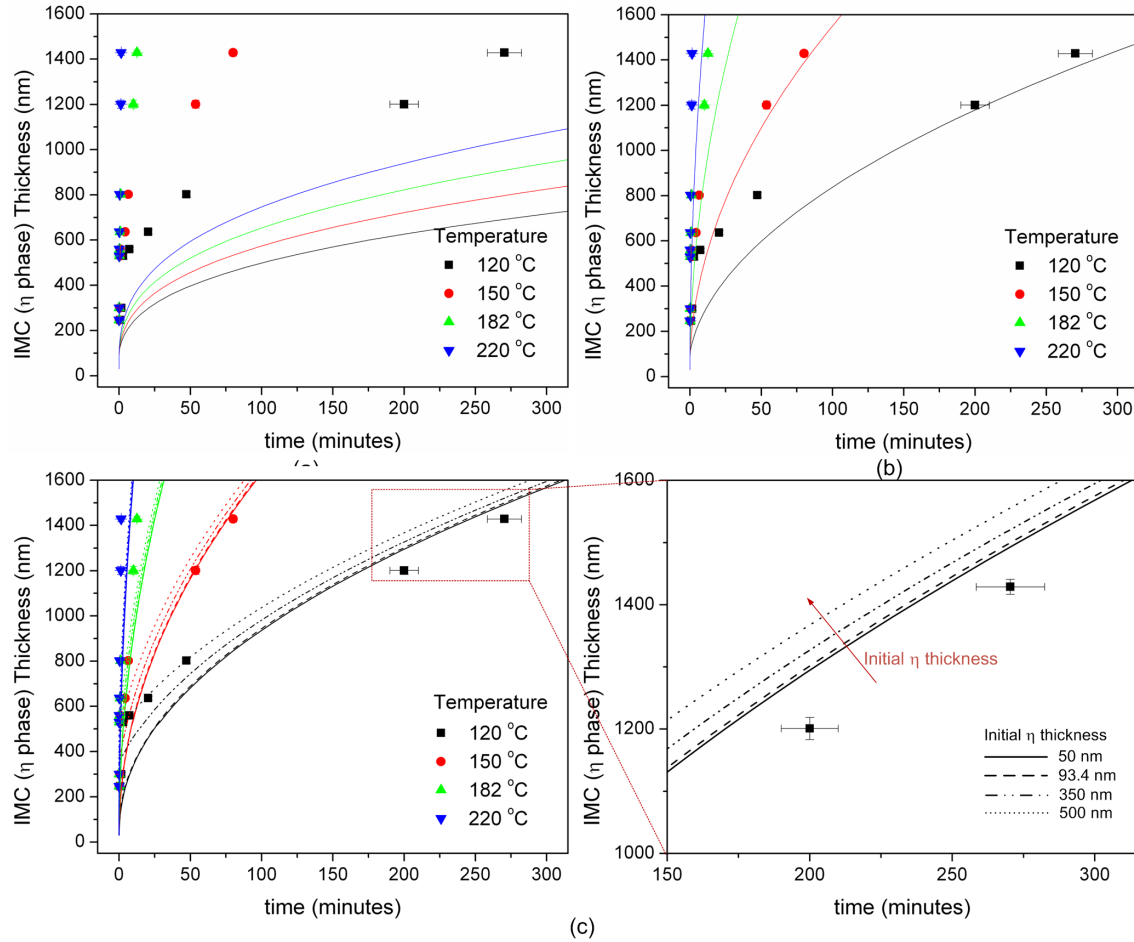


Figure 3.14: *Cu/Sn experimental data, superimposed with diffusion based modeling. a) Cu grain boundary diffusion only, b) Sn lattice diffusion only, c) Cu grain boundary diffusion and Sn lattice diffusion, simulated with different values of initial η phase thickness.*

Equation (3.22) was solved numerically in MATLAB (appendix). The parameters discussed previously were used as the inputs. Figure 3.14 shows the model's prediction superimposed with the experimental results. It is clearly seen that grain boundary diffusion of Cu alone is not sufficient to explain the behavior of the Cu/Sn interaction, while adding Sn diffusion through the lattice gives a better prediction to the experimental data.

As seen in Figure 3.14, the model under-predicts the growth rate of the η phase at small thickness at all temperatures. There is only one reference reported by

Etschmaier *et al.* [60] that provided the parameters for reaction controlled growth for η phase. Unlike in this experiment, Etschmaier deposited the Cu/Sn bilayer by electrodeposition. Electrodeposited film has more impurities and is also more dense than sputtered film, which may result in a slower reaction. Moreover, they also observed Cu_3Sn during annealing. Thus, there is a competing mechanism which may lead to a slower apparent reaction rate than in our experiments.

As mentioned in the previous section, the initial IMC thickness was measured using SEM cross sectional images. This measurement might suffer in accuracy, especially at small thicknesses due to the resolution limit of SEM and non-uniform thickness of IMC. Moreover, the whole experiment was carried out in a sequential manner (one sample was annealed at a time) over several hours. Therefore, the initial IMC thickness for each data point may not be the same. The samples which were annealed later might have a thicker initial IMC than the earlier annealed ones. Different initial IMC thicknesses were then simulated and are shown in 3.14(c). It appears that a 93.4 nm-thick initial IMC, which was obtained from measurement, predicts relatively well the experimental data, especially for thick-IMC regime. Larger initial IMC thickness results in better fitting for thin-IMC regime, but degrades for thick-IMC regime.

The model only explains the kinetics of IMC growth once the IMC forms a continuous layer. Growth kinetics of IMC at the early stages before forming a continuous layer is not included in the model. Fundamentally, the kinetics of IMC growth at early stages is different. Ma *et al.* [124] proposed that IMC initially nucleates at random locations at the interface. Once it nucleates, the IMC will grow in both lateral and vertical directions until it forms a continuous layer. Typically, the lateral growth is controlled by the reaction rate. On the other hand, the vertical growth is controlled by diffusion for thick IMCs and by interfacial reaction for thin IMCs. Further investigation can be carried out to include this mechanism into the model.

Another factor that has not yet been considered in the model is the Kirkendall

voids. Kirkendall voids may affect the growth kinetics of η phase in a complex way. In the presence of Kirkendall voids, the effective area for the diffusion path is smaller, thus it may slow down the growth rate. However, it could also enhance the diffusion through the capillary force. To understand how Kirkendall voids affect the growth kinetics of η phase in a more quantitative way requires further investigation.

Although the model works well in explaining the thin films interaction of Cu/Sn, it may not be suitable for thick films such as in under-bump-metallization/ball-grid-array application. In a thick film case, the amount of Cu that diffuse into Sn during annealing and therefore the precipitation flux of Cu to form Cu_6Sn_5 during cooling are not small. As a result, these fluxes should be considered in the analysis.

Simplification of R value as a constant could also affect the model's prediction. Schaefer *et al.* [67] showed that when R is linearly dependent on the η phase thickness h_η , n would change to 0.25. Nevertheless, in general, the model can be used as the guideline for the growth kinetics prediction for Cu/Sn system.

3.4 Cu/Sn_xIn_{100-x} System

3.4.1 Microstructure Analysis

Figure 3.15 shows representative SEM cross-sectional images of Cu/Sn_xIn_{100-x} bi-layer ($x = 29.5, 57.5$, and 93.6), annealed at 120°C and 200°C . There are several observations that can be made from the figure. First, the composition affects the morphology of Sn_xIn_{100-x}. Sn-rich solders formed a relatively continuous layer, while In-rich solders formed more irregular type structures. Interestingly, Sn_{57.5}In_{42.5} formed a more irregular layer than In-rich composition. This observation can be explained by matching the composition of the solder with the melting point extracted from the Sn-In phase diagram as shown in Figure 3.16 [53]. According to the phase diagram, the liquidus temperature of Sn_{29.5}In_{70.5}, Sn_{57.5}In_{42.5}, and Sn_{93.6}In_{6.4} are 133°C , 121°C , and 218°C , respectively. It is known that lower melting point material, therefore having a higher homologous temperature, tends to form more

irregular structures than the high melting point ones. Among the three compositions, $\text{Sn}_{57.5}\text{In}_{42.5}$ has the lowest melting point, that is probably why it has the most irregular structure.

The structure of Sn-In layer appears to affect the microstructure evolution of the IMC. In an irregular structure, the IMC does not grow uniformly. The final IMC microstructure follows the microstructure of Sn-In films. As seen in 3.15(d), the IMC thickened only where Sn-In globs were present. It is very likely that the IMCs inside these Sn-In globs are single crystal. In a more regular structure, the IMC thickened relatively more uniformly as seen in Figure 3.15(f).

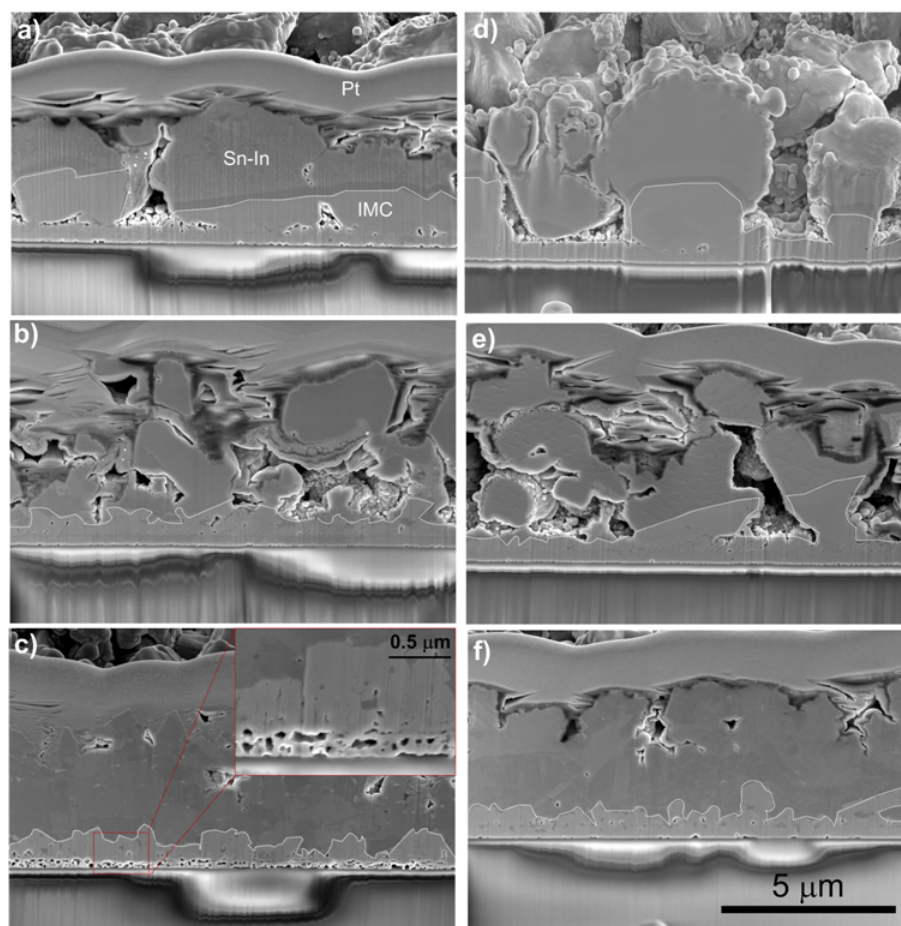


Figure 3.15: Cross sectional SEM images of $\text{Cu}/\text{Sn}_x\text{In}_{100-x}$ for different Sn-In compositions, annealed at different temperatures until the whole Cu was fully consumed. Initial Cu thickness was 502 nm. a) $\text{Cu}/\text{Sn}_{29.5}\text{In}_{70.5}$ annealed at 120°C , b) $\text{Cu}/\text{Sn}_{57.5}\text{In}_{42.5}$ annealed at 120°C , c) $\text{Cu}/\text{Sn}_{93.6}\text{In}_{6.4}$ annealed at 120°C , d) $\text{Cu}/\text{Sn}_{29.5}\text{In}_{70.5}$ annealed at 200°C , e) $\text{Cu}/\text{Sn}_{57.5}\text{In}_{42.5}$ annealed at 200°C , f) $\text{Cu}/\text{Sn}_{93.6}\text{In}_{6.4}$ annealed at 200°C . More Kirkendall voids are observed for Sn-rich solder annealed at low temperature.

Another observation that can be made from Figure 3.15 is the effects of tem-

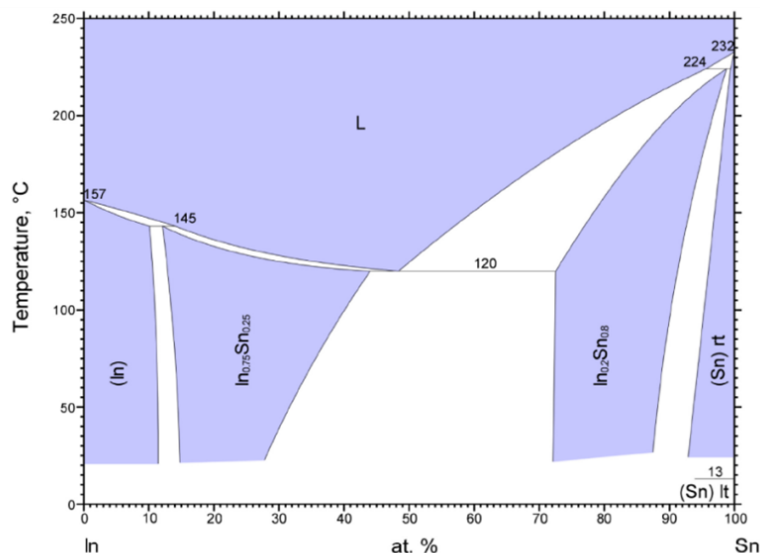


Figure 3.16: Sn-In phase diagram [53]

perature and In addition to the amount of Kirkendall voids. Annealing at 200°C results in very little Kirkendall voids for all compositions. At 120 °C, the amount of Kirkendall voids highly depends on the Sn-In composition. For Sn-rich solder, a large amount of Kirkendall voids were found, which is similar to the case of the Cu/Sn system. Increasing the In concentration reduces the amount of Kirkendall voids as seen clearly in Figure 3.15a and 3.15b.

Formation of Kirkendall voids in Sn-rich solder annealed at low temperature has been discussed previously. It was proposed that Cu is the dominant diffusion species at low temperature, while Sn is the dominant diffusion species at higher temperature. Reduction in the amount of Kirkendall voids by increasing In concentration suggests that Sn-In diffusion through the IMC increases with increasing In content. Detail explanation for this will be discussed in the next section.

Figure 3.17 shows the Cu-Sn-In ternary phase diagram calculated by Liu *et al.* [125]. As seen in Figure 3.17, only one major IMC phase that forms at temperatures below 200°C, which is the η phase ($\text{Cu}_6(\text{Sn},\text{In})_5$ where Sn and In substitute each other. This was also experimentally observed by Sommadossi *et al.* [126] and Chuang *et al.* [127]. A separate experiment was carried out to verify this by using XRD characterization. The results will be discussed in Chapter 4.

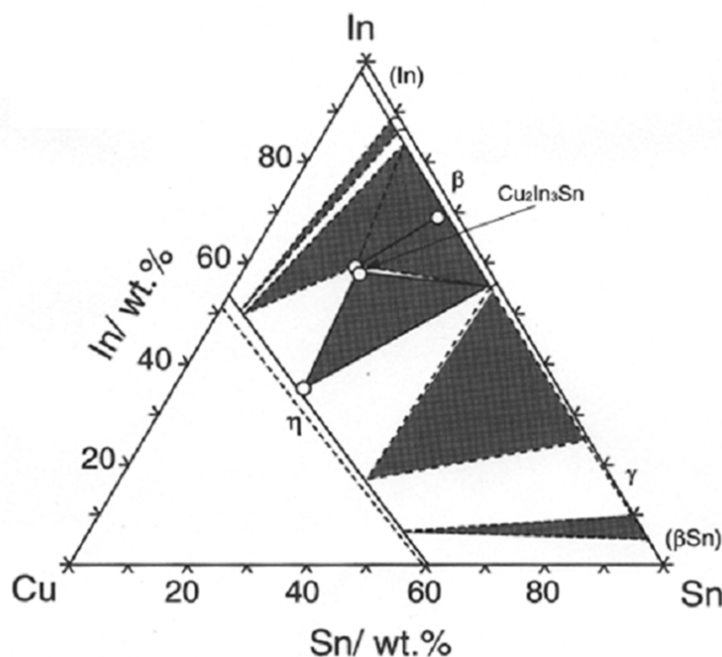


Figure 3.17: Phase diagram of ternary Cu-Sn-In, at 180° C [125].

3.4.2 Kinetics Analysis

Figure 3.18 shows the required time to consume 583 ± 15 nm-thick of Cu for different compositions of $\text{Sn}_x\text{In}_{100-x}$ ($x = 15-95$ at. %). Different annealing temperatures were investigated, ranging from 120 - 200 °C. The effects of solder composition to the Cu consumption rate and therefore the IMC growth rate are different for different annealing temperature. As seen in the figure, there is a global trend for the whole range of composition, but there is also a minimum peak at a certain composition.

Discussion on global trend

The effect of Sn-In composition on the IMC growth rate can be classified into two regimes: solid state and liquid state Sn-In. In solid state Sn-In, the dependency of IMC growth rate on the Sn-In composition can be explained using a homologous temperature argument. According to the Sn-In phase diagram, $\text{Sn}_x\text{In}_{100-x}$ is in solid state for and $x \leq 46$ at 120°C. At 150°C, the $\text{Sn}_x\text{In}_{100-x}$ is in the solid state for $x \geq 78$. In these regimes, the IMC growth rate increases monotonically with increasing homologous temperature as seen in Figure 3.18. At higher homologous

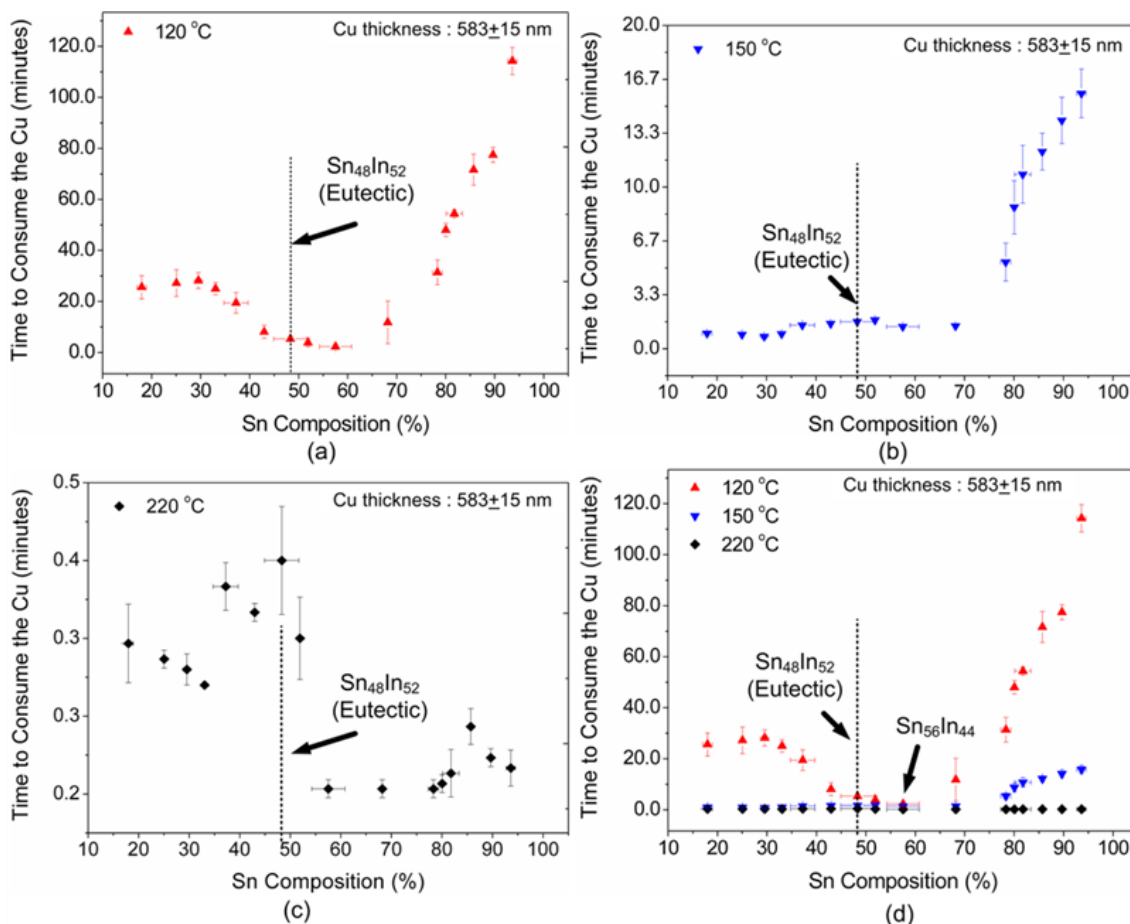


Figure 3.18: *Cu consumption rate for different composition of Sn-In at different temperatures. a) 120 °C, b) 150 °C, c) 220 °C, d) all plotted into one graph. (note that the y scale is different for each graph).*

temperatures, the binding energy of Sn-In atoms is weaker and therefore the atoms diffuse more quickly through the IMC to react with Cu. This argument is also supported by the SEM cross sectional images discussed in the previous section, whereby In addition may increase the Sn-In diffusion towards the Cu.

However, a higher homologous temperature might also lead to slower IMC growth rate. In section 3.4.1, it was discussed that a high homologous temperature may also contribute to the irregularity of Sn-In, which affects the thickening uniformity of the IMC. In a non-uniform thickening, the thinner regions of the solder would have reacted completely first before the thicker regime ones, unlike the regular solder where the IMC thickens uniformly. As a consequence, further IMC thickening after the thinner regimes solder are fully consumed occur only through the remaining solder interface (i.e. thicker regions) with the IMC film. This smaller interface area

between the solder and IMC results in a smaller diffusion flux, and therefore slower IMC growth. Diffusion flux is defined as number of atoms per nominal area (i.e. the whole film interface) per unit time. This might be the reason why there is a slight decrease in IMC growth rate with increasing homologous temperature for $\text{Sn}_x\text{In}_{100-x}$ with $x \geq 29$ at 120°C , as seen in Figure 3.18(a).

Comparing the trend of 220°C with those of 120°C and 150°C as shown in Figure 3.18(d), it is expected that the IMC growth rate is higher for all Sn-In compositions. Interestingly, Sn-rich solder requires less time than In-rich one to consume the whole Cu. According to the Sn-In phase diagram, all solder compositions at 220°C are in liquid state. Thus, the binding energy of Sn-In in all compositions is nearly the same. The reason why Sn-rich solder consumes Cu faster than In-rich one is probably attributed to the different atomic size of Sn and In. Based on the periodic table [117], Sn atomic radii is 140 pm. On the other hand, In has a bigger atomic size in the order of 167 pm. It is generally agreed that smaller atoms diffuse faster than the bigger ones [128]. However, such a trend may also be attributed to the irregularity structure of Sn-In. In-rich solder has a lower melting point than Sn-rich solder, and therefore less uniform thickening. As discussed previously, the non-uniform thickening could also result in a slower IMC growth rate.

Discussion on the maximum peak of IMC growth rate

Using the homologous temperature argument as discussed previously would suggest the maximum growth rate at 120°C annealing would be at the Sn-In eutectic composition, which is $\text{Sn}_{48}\text{In}_{52}$. Intriguingly, the maximum growth rate at 120°C annealing is at $\text{Sn}_{56}\text{In}_{44}$, which is off from the Sn-In eutectic composition. There are several possible reasons that may explain such an observation. First, there could be competing effects of atomic size difference. As previously explained for 200°C , Sn-rich solder consumes Cu faster than In-rich solder because of the Sn smaller atomic size. Thus, having more Sn could result in a faster IMC growth rate than the eutectic composition. Secondly, there is a possibility that this composition formed

ternary eutectic composition with Cu, which has a lower melting point than the binary eutectic composition of $\text{Sn}_{48}\text{In}_{52}$. Both arguments require deeper study for verification, which is beyond the scope of this work.

3.5 Cu/ $\text{Sn}_{56}\text{In}_{44}$ System

3.5.1 Microstructure Analysis

Figure 3.19 shows the cross sectional SEM images of the Cu/ $\text{Sn}_{56}\text{In}_{44}$ bilayer system, for different initial Cu thickness annealed at different temperatures. There are several observations that can be made from the figure. Firstly, the $\text{Sn}_{56}\text{In}_{44}$ layer formed an irregular structure. Secondly, unlike the Cu/Sn system, very little Kirkendall voids are found in this system, for all conditions. Both of these observations have been discussed in detail in the previous section. According to the Cu-Sn-In phase diagram (Figure 3.17), intermetallic compounds formed in this bilayer system are associated with the η phase.

It is noteworthy to take a closer look at how the IMC grows in such an irregular structure of $\text{Sn}_{56}\text{In}_{44}$ layer. Initially, a relatively planar IMC was formed. However, once the whole solder at the solder valleys is fully consumed, the IMC will grow into an irregular shape following the shape of the $\text{Sn}_{56}\text{In}_{44}$ layer.

3.5.2 Kinetics Analysis

Figure 3.20 shows the kinetics experimental data for the Cu/ $\text{Sn}_{56}\text{In}_{44}$ system extracted from the color change experiment as described in Section 3.2. Different initial thicknesses of Cu ranging from 80-518 nm were annealed at different temperatures ranging from 100-150°C. For simplicity, it is assumed that the density of $\text{Cu}_6(\text{Sn},\text{In})_5$ is the same with Cu_6Sn_P . With this assumption, η phase thickness was calculated based on the Cu consumption thickness using equation (3.3), and the result is shown in Figure 3.20b.

As seen in Figure 3.20c, the 100°C, 120°C and 150°C curves are best fitted

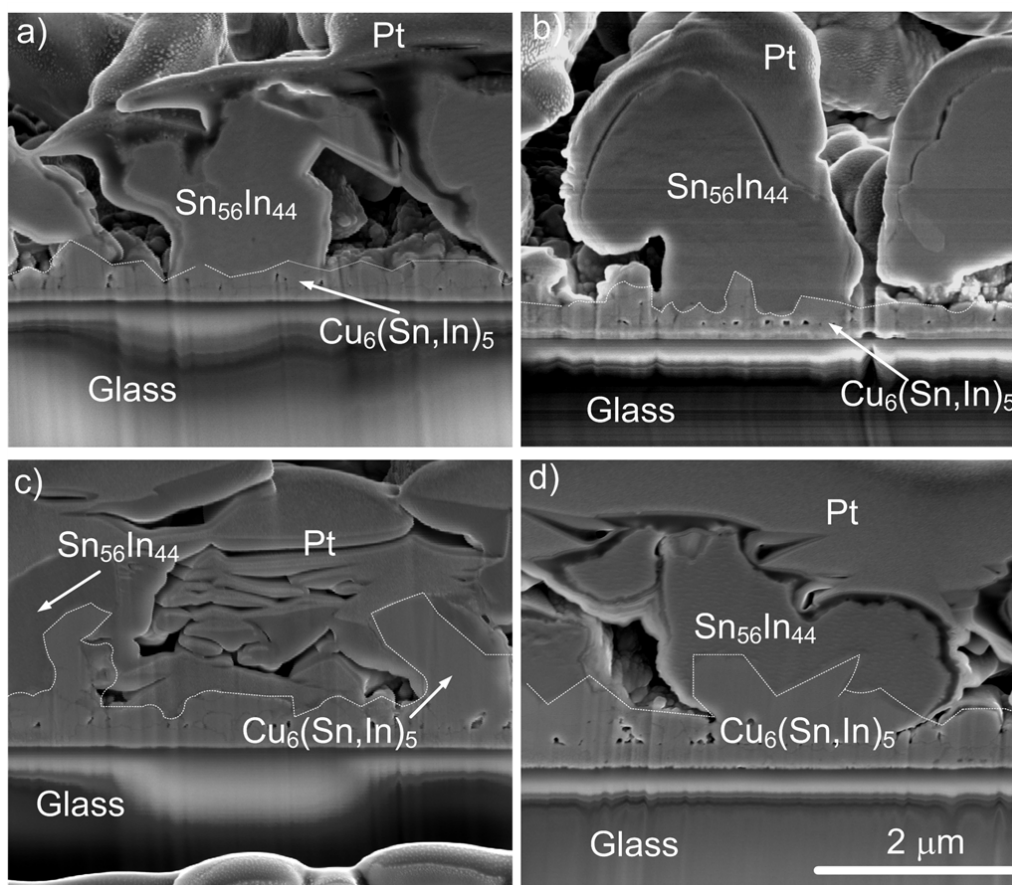


Figure 3.19: Cross section images of Cu/Sn₅₆In₄₄ with different initial Cu thickness, annealed at different temperatures. a) 147 nm-thick Cu annealed at 100° C, b) 147 nm-thick Cu annealed at 150 °C, c) 339 nm-thick Cu annealed at 100° C, d) 339 nm-thick Cu annealed at 150° C.

with n equals to 0.22, 0.36 and 0.35, respectively. Based on the discussions in section 3.3.2.2, section values of n suggest that the growth of IMC is controlled and dominated by the diffusion along the IMC grain boundaries. Sn-In diffusion along the η phase grain boundaries is proposed to be more dominant than Cu diffusion in the opposite direction. This argument is supported by SEM images in Figure 3.19, which show very little Kirkendall voids at the Cu side.

3.6 Discussion on the Technique

The solder material selection at the beginning of the manufacturing process is very critical. With more elements being introduced as solder materials, the combination of the composition increases exponentially. Using the conventional cross sectional

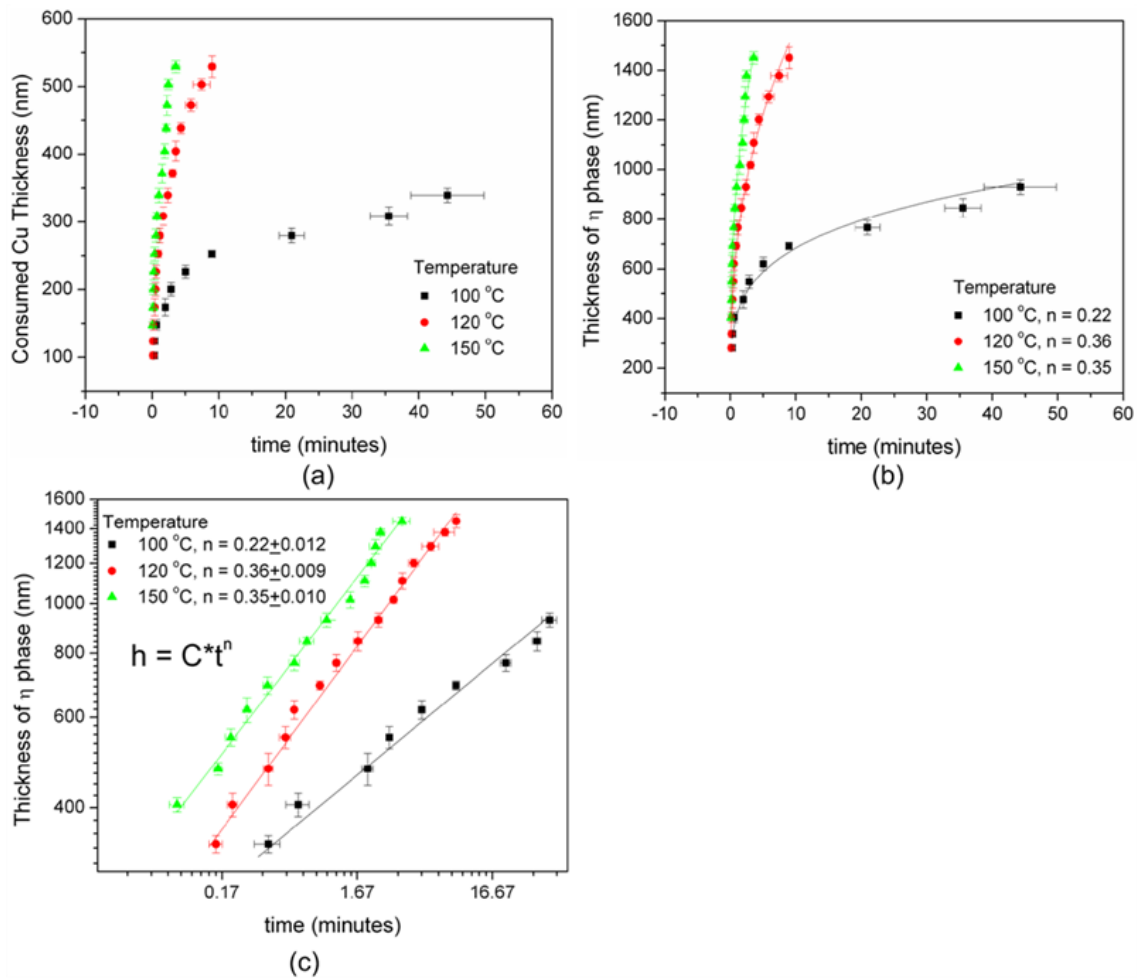


Figure 3.20: Experimental data plot from the color change experiments for Cu/Sn₅₆In₄₄ system. (a) Linear plot of Cu consumption thickness Vs time, (b) Linear plot of η phase thickness Vs time, (c) Logarithmic plot of η phase thickness Vs time fitted with n .

technique as the approach to determine which composition enables the fastest or slowest IMC growth is practically impossible. Additionally, the general trend on the scaling down of solder layer thickness makes such characterization more tedious and expensive.

Using the newly developed technique described in this chapter, a quick screening process can be carried out effectively. One may deposit Cu/solder combination on large transparent substrate by the combinatorial deposition. Composition variation may not only be limited to the solder layer, but it can also be on the Cu layer itself. Following that, the substrate can then be annealed while monitoring which location changes color first or last, depending on the application.

This technique is not without limitation. It is clear that this technique can only

be applied to systems which have very distinct color change. However, an additional setup such as UV-Vis spectroscopy may be employed for tackling those systems that have similar color.

This technique is also not intended to replace the common cross-sectional way for characterization the kinetics behavior of Cu/solder interaction. Clearly, we cannot extract information on the phase, and morphology of the intermetallics. Nevertheless, this technique can be a potential complimentary methodology for finding a new solder or under-bump metallization materials.

3.7 Summary

In summary, a novel technique for kinetics characterization of Cu/solder bilayer has been developed. This technique was demonstrated for characterizing the Cu/Sn-In bilayer system. Key findings from this work are summarized as follow :

- In the Cu/Sn bilayer system, it is confirmed through microstructure, and growth kinetics modeling that IMC growth is controlled by the rate of reaction between Cu and Sn for thin IMCs. On the other hand, Cu diffusion along IMC grain boundaries and Sn diffusion through IMC lattice is the rate limiting step for thick IMCs at low and high temperatures, respectively.
- Addition of In in Sn-based solder can potentially be used in the development of 3D ICs applications as it allows fast IMC growth at lower temperatures, while at the same time reduces the amount of Kirkendall voids. $\text{Sn}_{56}\text{In}_{44}$ was found to be the optimum composition which allows the fastest IMC growth, and therefore the most suitable for bonding applications in 3D Heterogeneous system integration.
- Using optical properties for characterizing the diffusion kinetics of Cu/solder based system allows fast screening of materials for numerous applications. This technique is not only useful from the engineering point of view, but may

also drive the development of new material combinations, especially in the solder community.

Chapter 4

Mechanical Property Characterization of Cu-Sn-In Intermetallic Thin Films using Micro-Cantilevers

4.1 Overview

As discussed in Chapter 1, one of the important parameters in bonding for 3D ICs applications is the mechanical properties of the joint. An important factor that affects the properties of the whole joint is the mechanical properties of intermetallic compound (IMC). This is even more important in the case of full IMC bonding structure (i.e. the whole solder is transformed into IMC).

There have been several studies on the characterization of Young's modulus [129, 130] of Cu_6Sn_5 using nanoindentation based method. However, despite its simplicity in experimental procedure, the analysis of the nanoindentation results is highly affected by the substrate underneath the film. Other than that, independent knowledge of the Poisson's ratio is also required for the analysis.

Alternatively, microcantilever-based techniques have been shown to provide promising alternative approaches for characterization of thin films. Although the sample preparation is relatively more complex, this approach is attractive due to its sim-

plicity of analysis, which is based on beam mechanics. Unlike nanoindentation, knowledge of the Poisson's ratio is not required for determination of the Young's modulus [77]. The effect of the substrate can also be eliminated. Additionally, more information on the mechanical properties can be extracted, such as the residual stress and fracture strength.

One challenge in the microcantilever approach is the non-ideality of the cantilever, which might affect the data analysis. Non-ideality of the cantilever includes the undercut at the fixed end of the beam, plate effects (anticlastic curvature) and stress gradients across the beam thickness, which result in pre-deflection of the cantilevers.

In the first half of this chapter, finite element modeling is used to investigate the effects of those cantilever non-idealities on the accuracy of the Young's modulus measurement. The second half of the chapter will demonstrate the technique to characterize the residual stress, Young's modulus and fracture strength of Cu-Sn-In intermetallic thin films at different compositions.

4.2 Analytical Equations for Mechanical Properties Characterization using Cantilever

4.2.1 Young's Modulus

4.2.1.1 Young's Modulus Measurement of a Single Layer Cantilever

Basic equation-single location deflection

Referring to Figure 4.1, the applied load (F) is proportional to the vertical deflection (δ) with a spring constant (k) as

$$F = k\delta \quad (4.1)$$

The spring constant (k) is a function of the distance from the indentation loca-

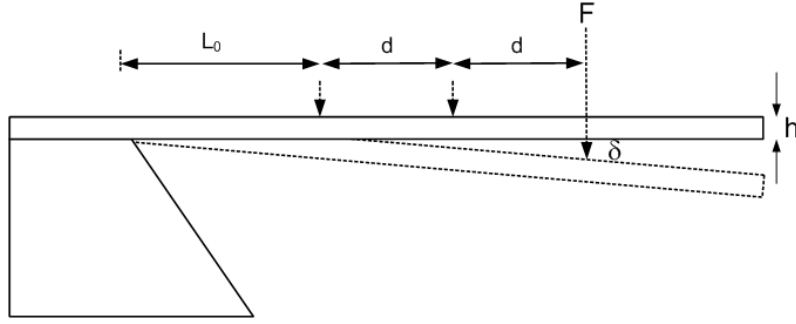


Figure 4.1: Schematic drawing of a cantilever deflected by an applied load (F) at multiple locations at arbitrary distances from the fixed end (L_0) but with known separation distance (d).

tion to the supported end of the cantilever (L), with a proportional constant cross sectional stiffness (S) as

$$k = \frac{3S}{L^3} \quad (4.2)$$

and

$$S = \frac{Ebh^3}{12} \quad (4.3)$$

where E is the Young's modulus, b and h are the width and thickness of the cantilever, respectively.

Method to accommodate the uncertainty length of cantilever - multiple locations deflection

Guo Qiang *et al.* [78] has demonstrated that multiple locations deflection allows the correction of uncertainty on the length of cantilever. For this deflection at multiple locations, the spring constant of the cantilever for each location can be expressed as follow

$$k_1 = \frac{3S}{L_1^3} = \frac{3S}{L_0^3}$$

$$k_2 = \frac{3S}{L_2^3} = \frac{3S}{(L_0 + d)^3} \quad (4.4)$$

$$k_3 = \frac{3S}{L_3^3} = \frac{3S}{(L_0 + 2d)^3}$$

where k_1 , k_2 and k_3 are the spring constants of the cantilever at locations 1, 2 and 3, which are separated by a known separation distance (d). Cross sectional stiffness (S) can then be determined by taking the slope of $(1/k^{-1/3})$ vs L graph. Subsequently, Young's modulus (E) can be computed with equation (4.3).

This approach relaxes requirements on the actual measurement accuracy for L , which is limited to the accuracy of the optical microscope attached to the nanoindenter for the current study. Instead, the measurement depends on the separation distance (d), which is well controlled by the piezoelectric attached in the nanoindenter.

4.2.1.2 Calculation of Young's Modulus of Film on a Substrate

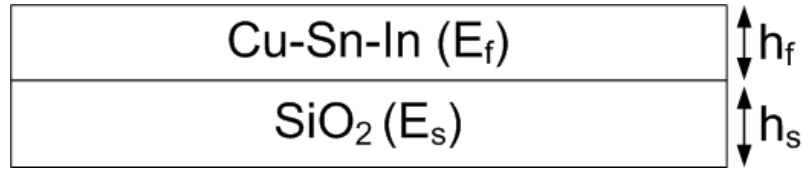


Figure 4.2: Bilayer structure cantilever (i.e. Cu-Sn-In on SiO₂ cantilever)

For the case of a bilayer cantilever as shown in Figure 4.2, the film's Young's modulus can be computed with knowledge of the substrate (S_s) and cantilever (S) cross sectional stiffness using equation (4.5) [77].

$$S = S_s \left(1 + \eta \kappa \left[\frac{3(\chi + 1)^2}{1 + \eta \chi} + \chi^2 \right] \right) \quad (4.5)$$

where χ is the film thickness (h_f)/substrate thickness (h_s) ratio and η is the film elastic modulus (E_f)/substrate elastic modulus (E_s) ratio.

4.2.2 Residual Stress

Film on thick substrate

The residual stress in a film (σ_f) with a thickness h_f on a thick substrate can be related to its curvature (κ) by Stoney's formula as shown in equation (4.6) [131].

$$\sigma_f = \frac{E_s h_s^2 \kappa}{6 h_f (1 - \nu_s)} \quad (4.6)$$

where h_s , E_s , and ν_s are the thickness, elastic modulus and Poisson's ratio of the substrate, respectively. However, this relationship fails to predict the stress of thin film on a thin substrate.

Film on substrate with arbitrary thickness

Freund *et al.* [79, 132] relaxed the thin film approximation using an energy minimization method. Their extended version of the Stoney formula is

$$\kappa = \left(1 + \frac{h_f}{h_s}\right) \left(1 + 4 \frac{h_f M_f}{h_s M_s} + 6 \frac{h_f^2 M_f}{h_s^2 M_s} + 4 \frac{h_f^3 M_f}{h_s^3 M_s} + \frac{h_f^4 M_f^2}{h_s^4 M_s^2}\right)^{-1} \bullet \frac{6 \varepsilon_m M_f}{h_s^2 M_s} \quad (4.7)$$

where h_f and M_f are the thickness and biaxial modulus of the film, respectively. ε_m is the mismatch strain which can be in the form of thermal, densification or lattice mismatch.

Extensional strain of the substrate mid-plane (ε_0) is given by:

$$\varepsilon_0 = - \left(1 + \frac{h_f^3 M_f}{h_s^3 M_s}\right) \left(1 + 4 \frac{h_f M_f}{h_s M_s} + 6 \frac{h_f^2 M_f}{h_s^2 M_s} + 4 \frac{h_f^3 M_f}{h_s^3 M_s} + \frac{h_f^4 M_f^2}{h_s^4 M_s^2}\right) \bullet \varepsilon_m \frac{h_f M_f}{h_s M_s} \quad (4.8)$$

The through-thickness stress of the film is given by

$$\sigma(\kappa, z) = M_f (\varepsilon_0 - \kappa z + \varepsilon_m) \quad (4.9)$$

for $\frac{1}{2}h_s < z \leq (\frac{1}{2}h_s + h_f)$

Based on equation (4.9), the stress levels at the surface of the film and film/substrate interface can be expressed in equations (4.10) and (4.11), respectively.

$$\sigma \left(\kappa, \frac{1}{2}h_s + h_f \right) = M_f \left(\varepsilon_0 - \frac{1}{2}\kappa h_s - \kappa h_f + \varepsilon_m \right) \quad (4.10)$$

$$\sigma \left(\kappa, \frac{1}{2}h_s \right) = M_f \left(\varepsilon_0 - \frac{1}{2}\kappa h_s + \varepsilon_m \right) \quad (4.11)$$

4.2.3 Fracture Strength

Fracture strength (σ_m) is defined as the stress level at the fracture location of the cantilever where the fracture occurs, expressed as

$$\sigma_m = \frac{FL}{W_b} \quad (4.12)$$

where W_b is the bending resistance. For a beam with a rectangular cross section, the bending resistance can be expressed as

$$W_b = \frac{bh^2}{6} \quad (4.13)$$

Equations (4.12) and (4.13) however are only valid for the case of an ideal cantilever. Non-idealities due to the presence of an undercut and stress gradients affect the actual fracture strength greatly. Thus, a numerical solution based on finite element analysis was used for the extraction of the fracture strength.

4.3 Finite Element Analysis to Investigate the Effects of Non-Idealities of the Cantilever on the Accuracy of Young's Modulus Measurement

4.3.1 Simulation Details

Figure 4.3 shows a typical microcantilever used in the finite element analysis carried out using Ansys Workbench version 11. The dimension of the cantilever is $50\text{ }\mu\text{m}$ x $10\text{ }\mu\text{m}$, with a 2 to $8\text{ }\mu\text{m}$ undercut. The microcantilever is a bilayer that consists of 500 nm-thick SiO_2 as the substrate and 940 nm-thick Cu-Sn-In intermetallic on top. The stress gradient which led to the upward deflection was simulated by introducing 0-2% thermal strain in the Cu-Sn-In film. Deflection was performed at multiple locations ($13\text{ }\mu\text{m}$, $16\text{ }\mu\text{m}$, $19\text{ }\mu\text{m}$, $22\text{ }\mu\text{m}$ and $25\text{ }\mu\text{m}$ from the supported end) by defining point loads of 5 to $40\text{ }\mu\text{N}$. These conditions mimic the real microcantilever deflection experiment that will be described in Section 4.4.

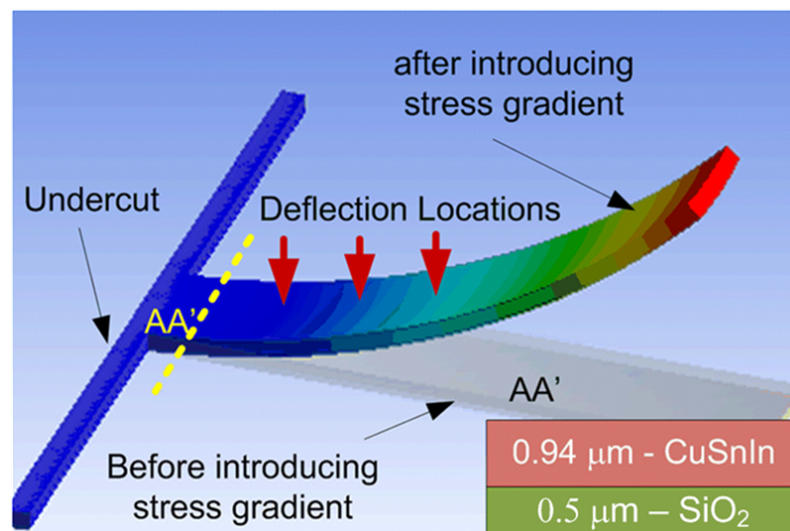


Figure 4.3: Typical non-ideal cantilever used in Finite Element Modeling. Inset is the schematic representation of the bilayer Cu-Sn-In/ SiO_2 cantilever.

Figure 4.4 illustrates the deflection of the bilayer non-ideal cantilever in simulation. Vertical deflection of the cantilever (δ) was extracted from the simulation. The value was then input into equations (4.2) to (4.5), for Young's modulus calculation.

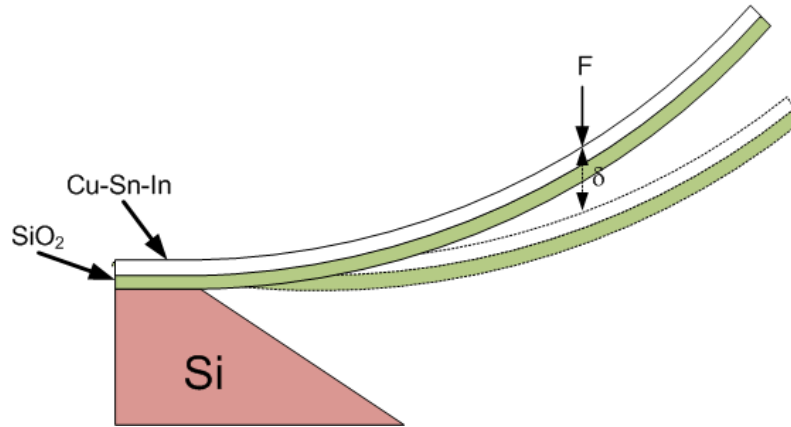


Figure 4.4: Illustration of deflection of non-ideal cantilever

4.3.2 Simulation Results

4.3.2.1 Effects of Undercut Length, Multiple Locations Deflection, and Anticlastic Curvature to the Accuracy of Young's Modulus Measurement

Figure 4.5 shows the Young's modulus calculated based on the finite element simulation results for cantilevers with different undercut lengths deflected at single and multiple locations. In an ideal cantilever (without undercut), a single deflection approach (red color) reveals the effect of anticlastic curvature on the Young's modulus measurement. It can be seen that, as the distance of the deflection location from the supported end of the cantilever becomes smaller, the anticlastic effect becomes higher. The error of the modulus measurement at 16 μm and 33 μm distance from the supported end of the cantilever is up to 6% and 3%, respectively. Using deflections at multiple locations (square green), this error is reduced to less than 1%.

The effect of undercut is more significant than the anticlastic curvature. Single deflection measurements can be lowered by 10% (2 μm undercut, deflected at 33 μm) and up to 50% (8 μm undercut, deflected at 16 μm). Baker *et al.* [133] Plagued that having an undercut can be associated with an ideal cantilever with additional length. The longer undercut thus gives a smaller spring constant, which results in a lower measured Young's modulus. The additional length originating from the undercut is too complex to be determined analytically. It is highly dependent on the

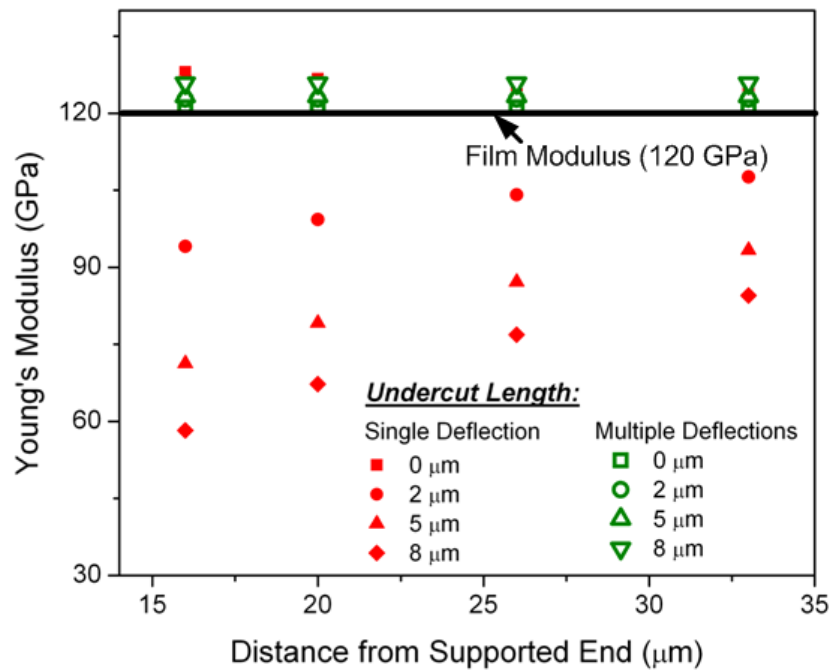


Figure 4.5: Young's modulus predicted for deflections at single and multiple locations for different undercut lengths. The real value of the modulus is 120 GPa.

undercut length and overall design of the cantilever. Thus, relaxing the dependency of this during measurement is a great advantage. As described in section 4.2.1.1, knowledge of the absolute distance of the deflection location from the supported end is not required when deflections are made at multiple locations deflection. As seen in Figure 4.5, the multiple location deflection approach leads to reduction of the error of the modulus measurement to less than 6%. For our experimental condition, which has only a 2 μm undercut, the error is expected to be less than 2%.

4.3.2.2 Effects of Cantilever Curvature to the Accuracy of Young's Modulus Measurement

Figure 4.6 shows the effects of curvature (originating from the stress gradient) on the Young's modulus measurement based on finite element simulation using the multiple locations deflection approach. For cantilevers which have a curvature less than 0.01 μm^{-1} , the multiple location deflection approach provides a modulus measurement with an error of less than 2%. However, as the curvature increases above 0.01 μm^{-1} , the multiple location deflection approach gives lower values than expected. The

error associated with this curvature is up to 17% (curvature: $0.026 \mu\text{m}^{-1}$). The error associated with the curvature is believed to be due to the invalidity of the small angle approximation and the different moment inertia of a curved beam which originates from the shifting of the neutral axis of the beam.

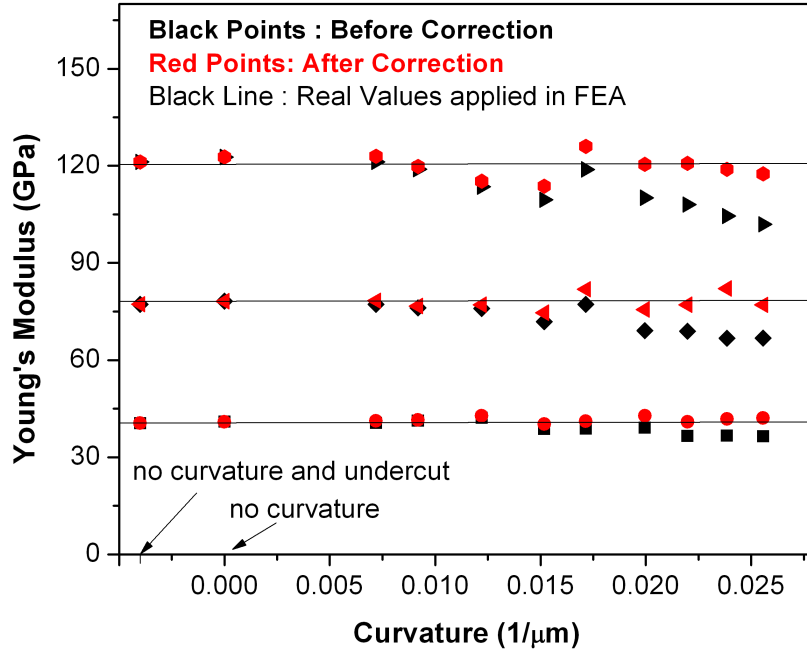


Figure 4.6: *Young's modulus prediction based on displacement measurements made at multiple locations for different cantilever curvatures.*

An empirical equation was introduced in order to correct the error associated with the curvature. Similar to the case of the undercut length, the curved beam is analogous to an ideal cantilever with an additional length. However, unlike the undercut case, the curvature correction depends on the location of the deflection and the curvature according to (4.14)

$$\frac{l_{ideal} - l}{l} \times 100\% = (C_1 + C_2l + C_3\kappa + C_4l^2 + C_5\kappa^2 + C_6l\kappa + C_7l^3 + C_8\kappa^4 + C_9l^2\kappa + C_{10}l\kappa^2) \quad (4.14)$$

where l and l_{ideal} are the distance of the deflection location to the supported end of the non-ideal and analogous ideal cantilever, respectively. $-C_{10}$ are empirical

constants which are determined from the fitting of simulation results for different conditions, as shown in Figure 4.7. After the empirical correction, the error of the Young's modulus measurement is reduced to less than 6% as seen in Figure 4.6.

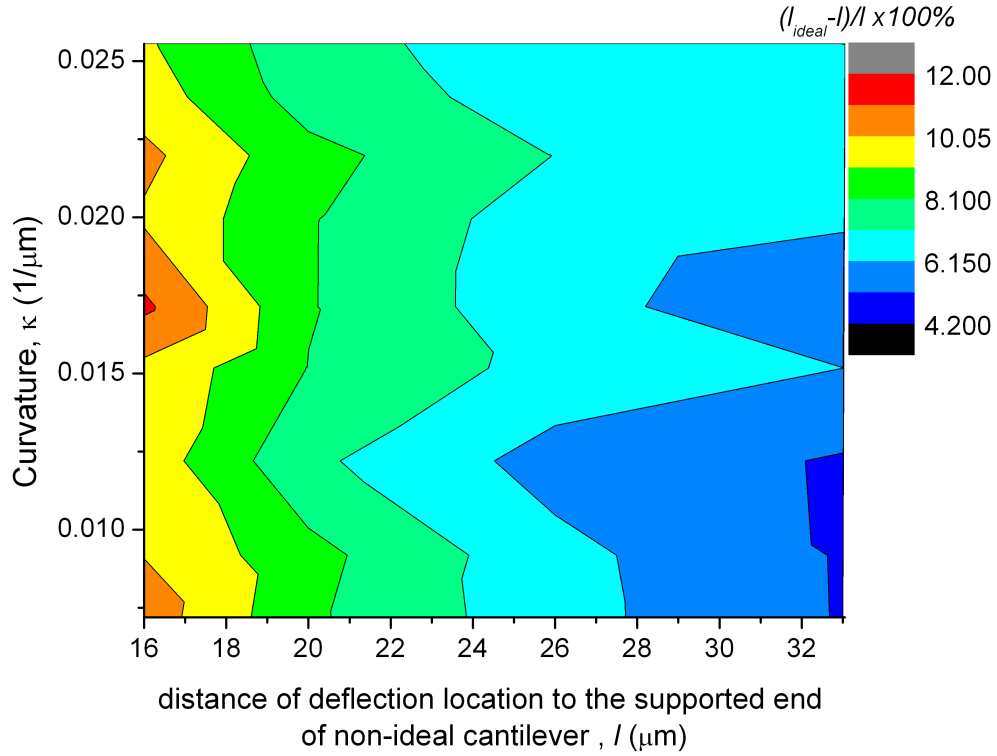


Figure 4.7: Empirical corrections of the deflection location as a function of curvature

For the case of cantilevers being used in the experiments, the curvature of the cantilever is in the range of $0.014 - 0.015 \mu\text{m}^{-1}$. Based on Figure 4.6, even without empirical correction, the measured Young's modulus is expected to have an error of less than 7%.

4.4 Experimental Characterization of Mechanical Properties of Cu-Sn-In

4.4.1 Experimental Details

4.4.1.1 Cantilever Fabrication

Arrays of SiO₂ microcantilevers were fabricated in School of Electronics and Electrical Engineering in NTU. The flow chart of the fabrication process is shown in Figure 4.8. Initially, fresh Si (100) wafers were cleaned with hydrofluoric acid (HF) solution to remove the native oxide. Following that, 500 ± 5 nm thick SiO₂ were deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) technique. This deposition method was chosen over the thermally grown oxide because it results in a much lower residual stress. Following the deposition, the SiO₂ was subsequently patterned with optical lithography method. Exposed SiO₂ was then selectively wet etched by HF solution. Finally, the silicon wafer was etched by Tetramethylammonium Hydroxide (TMAH) solution.

The sample layout and SEM micrograph of fabricated samples is shown in Figure 4.9. As seen in the figure, extra spaces were put between the edges of the die with the cantilevers group to prevent damages during dicing of the wafer with a diamond cutter. Several cantilever dimensions were fabricated as the nanoindenter that will be used has limitation in both the optical magnification and transducer to measure the spring constant of cantilevers. Having several dimensions ensure the properties could be obtained during the mechanical testing.

4.4.1.2 Cu-Sn-In Sequence Combinatorial Deposition

Sequential combinatorial deposition were carried out with a sputtering system in NTU. The layout of the the sample during sputter deposition is shown in Figure 4.10. 12 samples were placed in a 4 by 3 matrix on a substrate holder inside the sputter chamber. Cu, Sn and In were deposited sequentially without rotating the

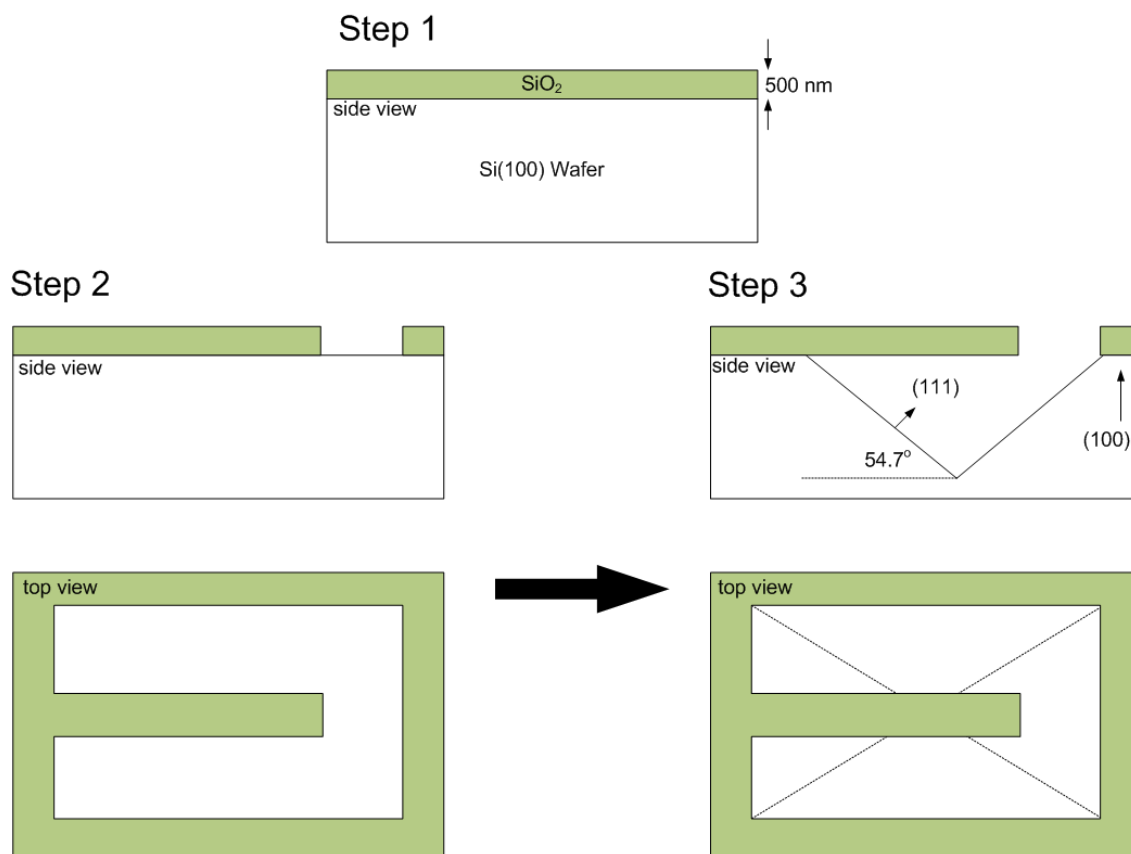


Figure 4.8: Fabrication process of cantilevers. Step 1 - SiO₂ deposition on Si (100) wafer by PECVD. Step 2 - Patterning followed by SiO₂ etching. Step 3 - Crystallographically anisotropic Si etching by TMAH solution.

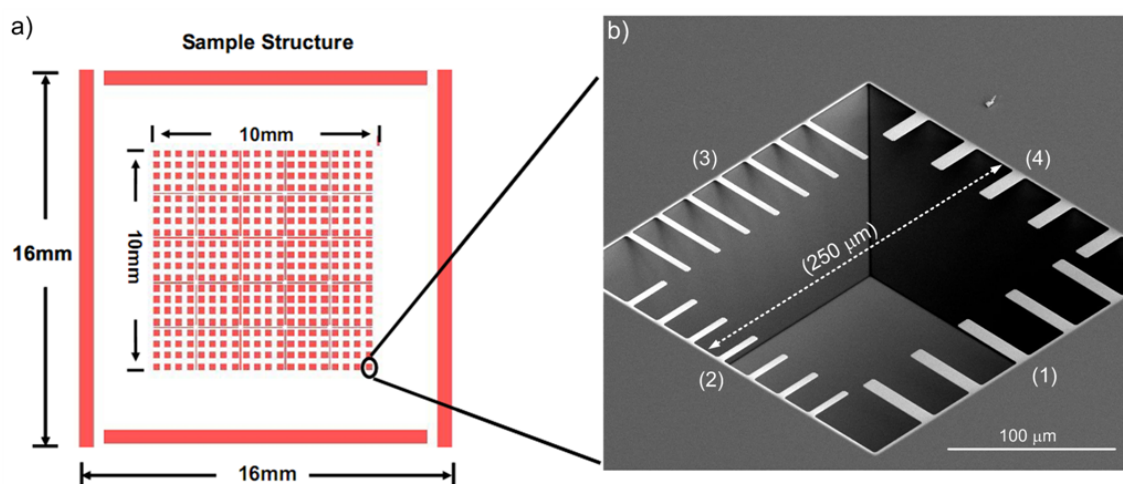


Figure 4.9: a) Top view layout of 16 mm x 16 mm die that consists of 400 "pits" (image was taken from [78]). Note that only 10 mm x 10 mm area was covered with cantilevers. b) 52° tilted SEM image of as fabricated SiO₂ cantilevers in one 250 μm x 250 μm "pit". The dimension of the cantilevers are (1) 50 μm x 10 μm, (2) 30 μm x 5 μm, (3) 50 μm x 5 μm, (4) 30 μm x 10 μm. Note the presence of undercut.

substrate. The deposition parameters are shown in Table 4.1. With this method, broad variations of Cu-Sn-In composition was achieved within a single of deposition.

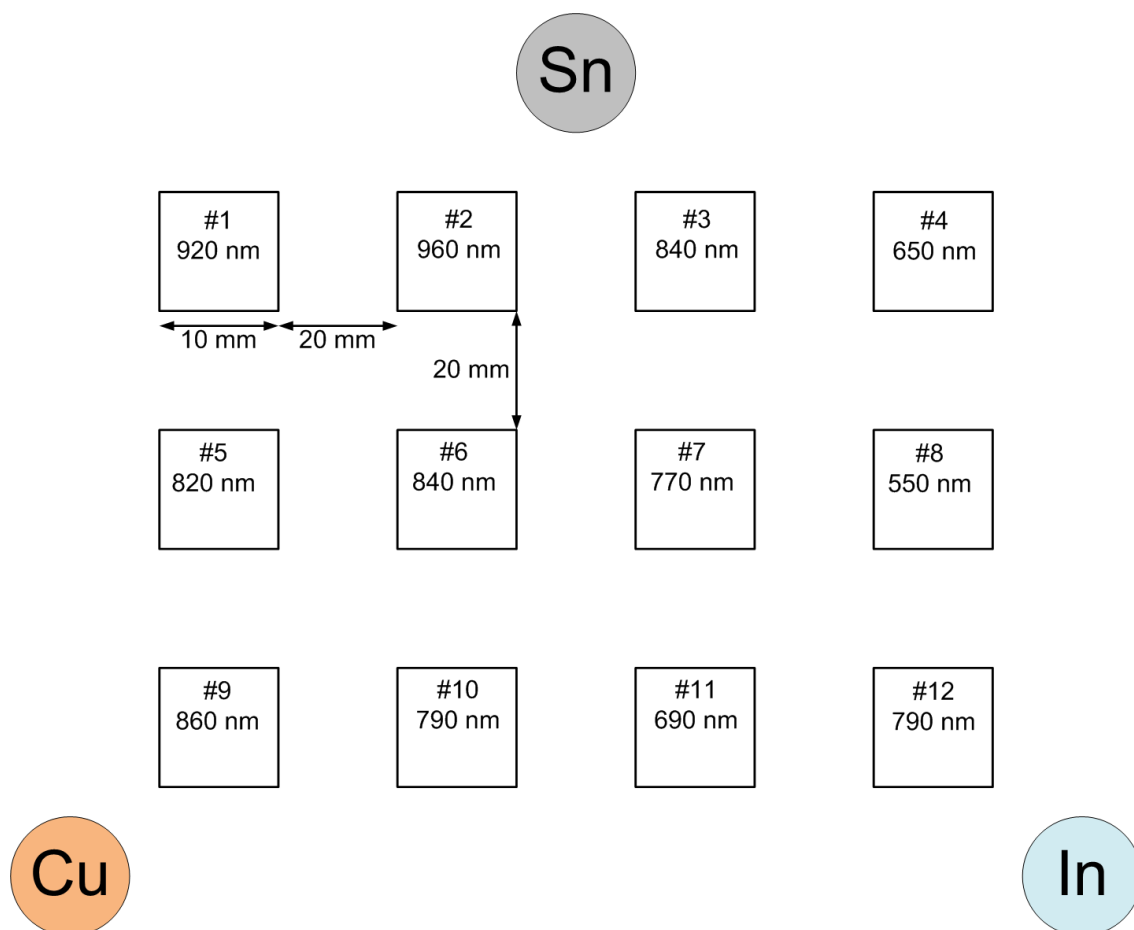


Figure 4.10: Samples configuration on the substrate holder during Cu-Sn-In sequential combinatorial deposition in sputtering chamber. 10 mm $\times$ 10 mm samples were placed in a 4 by 3 matrix with 20 mm separations. Thickness of Cu-Sn-In in each sample is indicated (thickness variation within each sample was ± 20 nm).

Composition of each sample were measured by EDS. Five locations (i.e. 4 corners + 1 center) per sample were measured. Figure 4.11 shows the composition of 12 $\times$ 5 points in this set experiment, plotted in ternary.

Table 4.1: Deposition parameters for Cu-Sn-In sequential combinatorial

Deposition Parameters	Cu (seq.1,11,16)	Sn (seq.2,4,7,9,12,14)	In (seq.3,5,8,10,13,15)
Pressure (torr)	2.6×10^{-3}	2.6×10^{-3}	2.6×10^{-3}
Power (W)	250	150	80
Time (min)	P	3	4

Thickness of each sample was measured by cross sectioning the centre of each sample. From these 12 data points, the thickness of each cantilever was interpolated

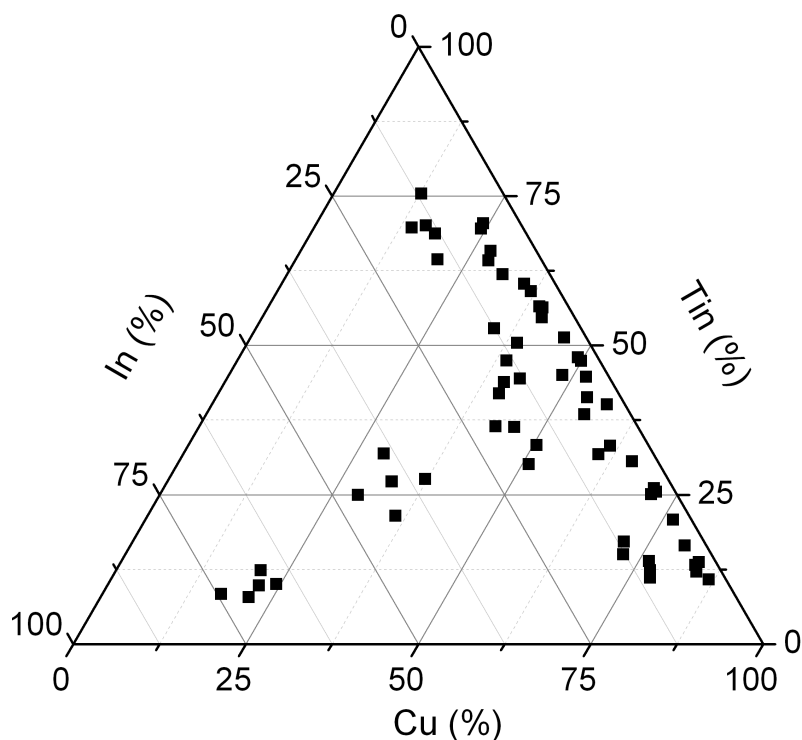


Figure 4.11: Ternary plot of composition variation produced by Cu-Sn-In deposition. 5 points per sample (i.e. 4 corners + 1 center) were measured by EDS. Composition is in atomic percentage.

by the location (x,y coordinate) of the cantilever using Ronka algorithm provided in Origin software. Figure 4.12 shows the thickness of each cantilever plotted with respect to its composition. Variation of thickness in combinatorial deposition is inevitable. Guo Qiang *et al.* [134], also observed large thickness variation for Cu-Zr-Al combinatorial deposition. In their case, the thickness varied from 80 - 130 nm.

4.4.1.3 Measurement of cantilever curvature using Interferometer (NT 2000)

Interferometer setup

All the cantilevers deflected upwards for Cu-Sn-In deposited on the SiO₂ substrate as seen in Figure 4.13. This initial deflection of the cantilevers were measured by an interferometer setup located in Prof. Carl V. Thompson laboratory in MIT. Very detail description of the equipment can be found in the manual of NT 2000 [135,136]

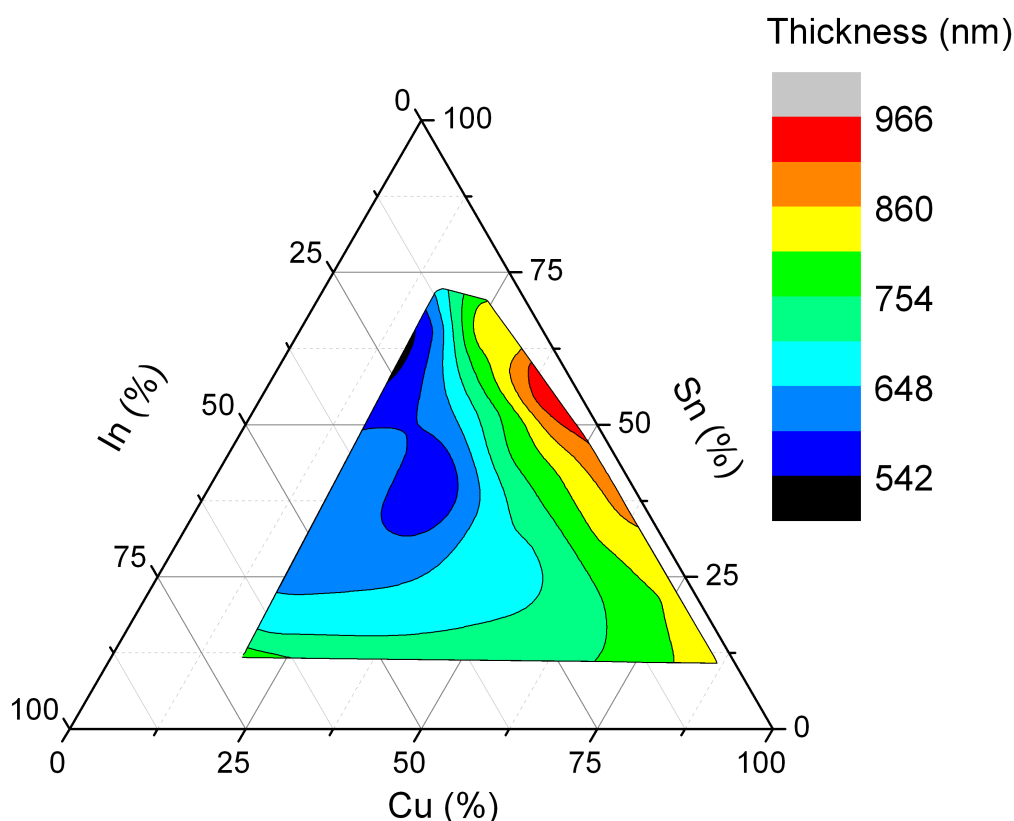


Figure 4.12: Thickness of Cu-Sn-In in ternary plot. Based on 12 data points, interpolation of thickness, plotted in ternary.

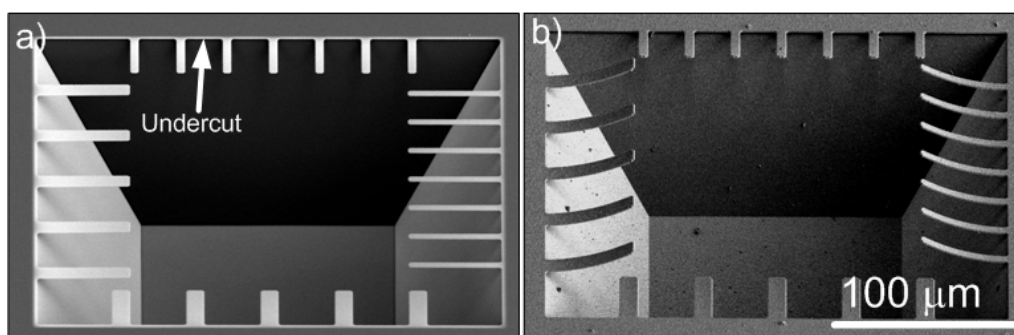


Figure 4.13: Scanning Electron Microscope images (sample was tilted at 52°) of fabricated microcantilevers. a) before Cu-Sn-In deposition, b) after Cu-Sn-In deposition. Deposition of Cu-Sn-In results in upward deflection of the cantilever, indicating that the film is in tensile.

Figure 4.14 shows the schematic drawing of an interferometer's working principle. Light is illuminated from the source through a series of Integrated Optics Assembly (IOA). When it reaches the objective lens, a beam splitter separates the light into two beams. One beam is reflected by the smooth surface mirror-like in the objective lens, while the other beam travels through the sample and is reflected back to the

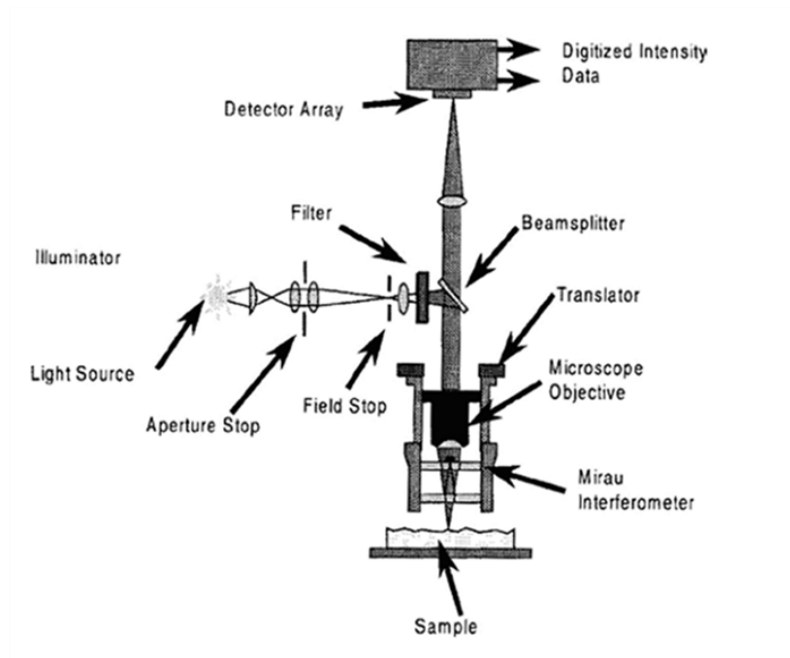


Figure 4.14: Working principle of interferometer (model NT 2000) [135]

objective. If the surface of the sample is in focus, both of the reflected lights interfere and form a light and dark bands pattern, called “fringes”. The IOA is able to do a series of scanning in the z direction. Thus, multiple “fringes” from multiple respective z can be produced. These set of “fringes” was later recorded by the CCD camera and sent to the Veeco software to produce a contour map of the sample.

NT 2000 has a 3 nm vertical resolution, and is able to cover 500 μm vertical range. The lateral resolution depends on the objective lens microscope which ranges from 5-50 $\times$ magnification [135].

100 cantilevers (dimension : 10 μm $\times$ 50 μm) were measured per sample. The deflections at the free end of all the cantilevers lie in the range of 10 - 25 μm .

Analytical calculation of curvature based on cantilever deflection

Initial curvature of the cantilever ($\kappa = 1/r$) can be calculated with the information on the cantilever deflection. Figure 4.15 illustrates a cantilever with an initial length (L_0) and has a tip deflection (δ). Using simple geometrical analysis :

$$\delta = r (1 - \cos \alpha) \quad (4.15)$$

and

$$\alpha = \frac{L_0}{r} \quad (4.16)$$

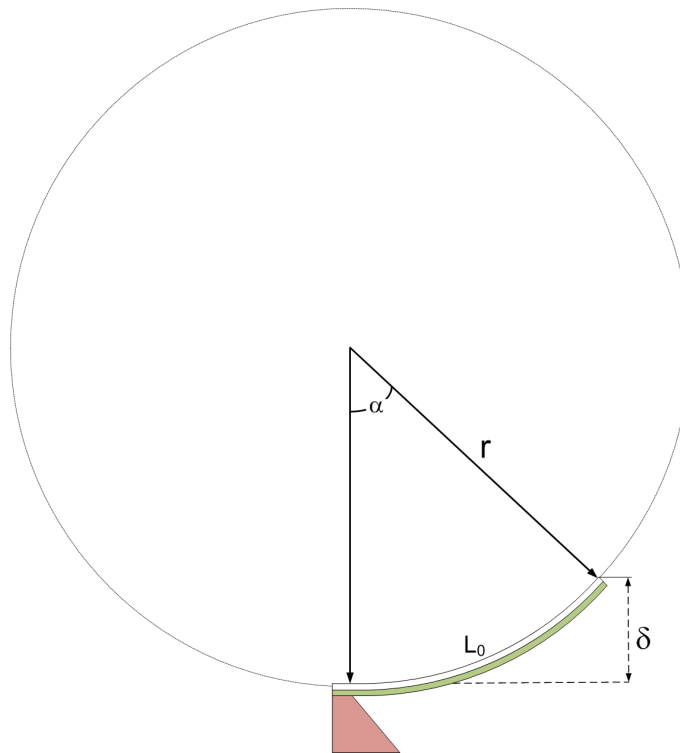


Figure 4.15: Schematic illustration of deflected cantilever. Deflection (δ) is measured by interferometer. Through basic geometry, the curvature of the cantilever can be calculated.

By solving both equations (4.15) and (4.16), the curvature of the cantilever can be calculated. This curvature was later used for computation of residual stress using equations (4.7) - (4.11), and also for Young's modulus correction in equation (4.14), and fracture strength in equation (4.13).

4.4.1.4 Cantilever Deflection with Nanoindenter

Nanoindenter setup

Young's modulus and fracture strength measurements were characterized by deflecting the cantilevers with a nanoindenter located in Nanolab in MIT. The nanoindenter used in this study is TriboIndenter made by Hysitron. This nanoindenter has a load range of 10 μN to 10 mN, with a maximum displacement of 5 μm . A 10 μm radii

indenter blunt tip was used in this experiment. The use of a blunt tip was preferred to minimize the deformation of the film during deflection. The optical microscope attached to the nanoindenter has a magnification up to 10x. Before each session of experiment, H-calibration was carried out. It is a stage offset determination between the optics and the indenter probe. The indentation axis was calibrated by air loading. The stage of the indenter was controlled by a piezoelectric sensor which has nanometer resolution.

Young's modulus measurement

Young's modulus of the films was measured by deflecting the cantilever at multiple locations (i.e. 13 μm , 16 μm , 19 μm , 22 μm and 25 μm distances from fixed end of the cantilever). Two sets of loading were applied for each deflection experiment, and only the second loading data was used as the input data. This approach eliminated the displacement of the tip due to film deformation. The cantilevers were deflected with up to 200 μN setting load. However, the actual load measured by the transducer was only up to 50 μN .

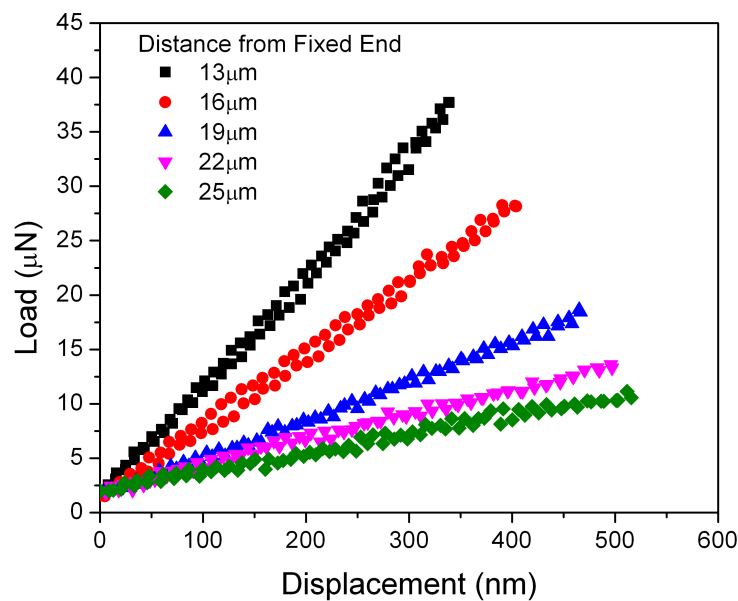


Figure 4.16: Typical load Vs displacement curve during Young's modulus measurement. 5 locations on each cantilever were deflected with fixed 3 μm separations.

For each sample, 9 cantilevers were measured (i.e. 4 corners + 4 middle edges + 1 center). $50\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ cantilevers were chosen for this study. Figure 4.16 shows a typical load vs displacement curve of the second loading of the experiments. The spring constant of the cantilever at these different locations was computed by taking the slope of load vs. displacement curve. The Young's modulus was subsequently calculated using equations (4.3) and (4.5).

Fracture strength measurement

Fracture strength was characterized by deflecting the cantilevers until fracture. A loading profile for this experiment is shown in Figure 4.17. Multiple loading loop at the beginning was applied to calculate the distance of the deflection point from the fixed end of cantilever. With the Young's modulus obtained from previous experiment, the location of the deflection point can be deduced by working backwards using equations (4.2) to (4.5), taking into account the correction due to non-idealities of the cantilever described in equation (4.14).

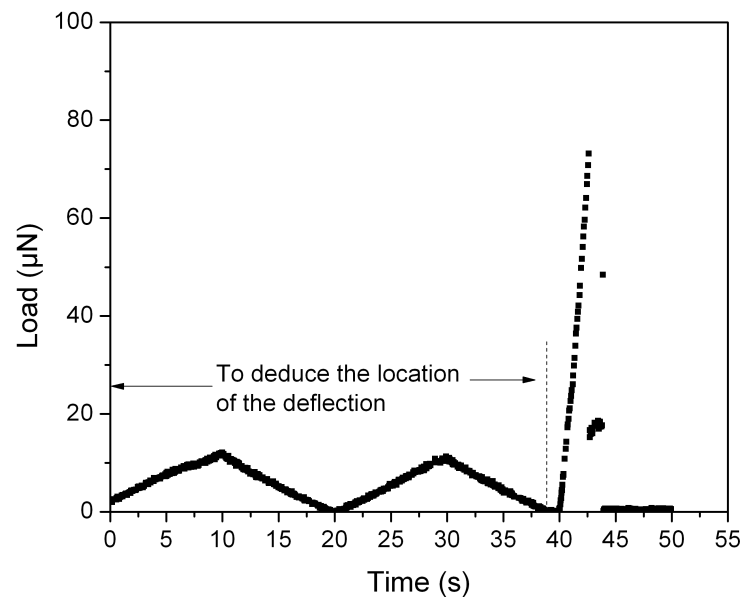


Figure 4.17: Typical loading profile for fracture strength measurement. Multiple loadings at the beginning were applied for calculating the distance of the indentation point from the fixed end of cantilever.

Figure 4.18 shows the typical load Vs displacement curve during fracture strength

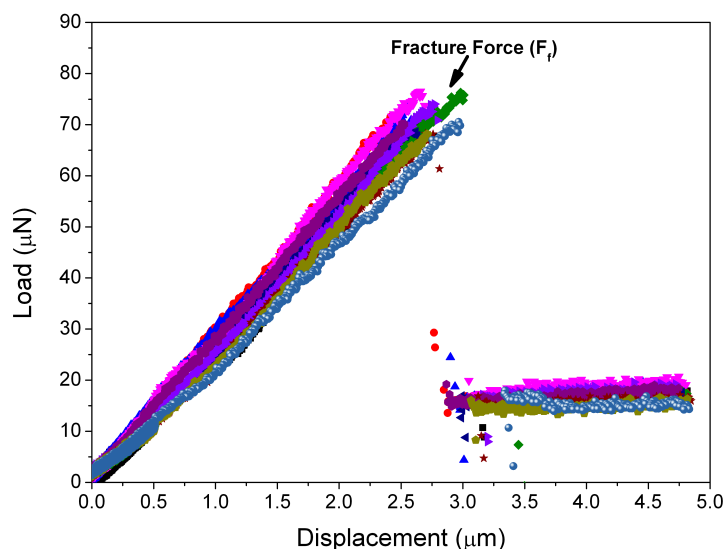


Figure 4.18: Typical load displacement curve for characterization of the fracture strength.

measurement. Fracture force (F_f) was extracted from the experiment. With this fracture force and additional information on the indentation location, fracture strength was subsequently calculated using finite element analysis. This approach was chosen over the analytical equations (4.12) and (4.13) because finite element analysis accounts for the presence of undercut and residual stress of the film.

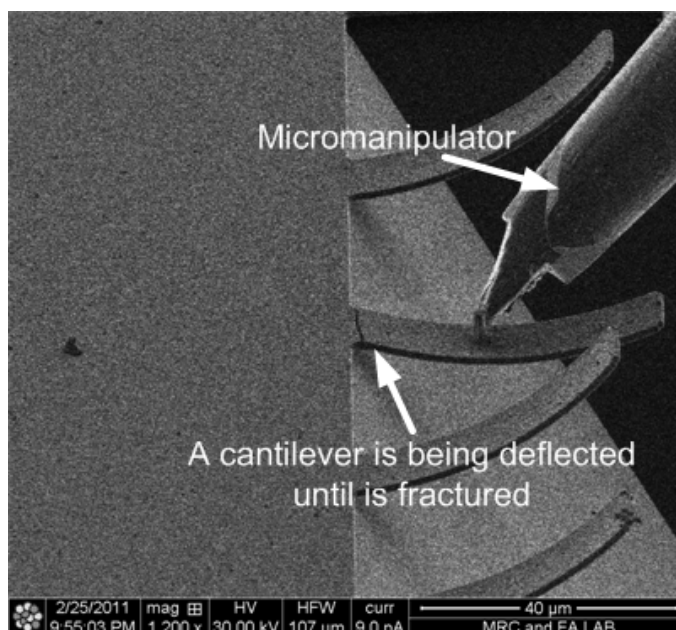


Figure 4.19: In-situ fracture mechanism setup in Focused Ion Beam (FIB). Micro-manipulator (OMNI Probe) was used to deflect the cantilever until fracture.

In a separate experiment, the fracture mechanism of this cantilever was investigated by an in-situ setup in an FIB system as shown in Figure 4.19. A cantilever was deflected by a micromanipulator inside the FIB chamber until it is fractured. The fracture behavior of this cantilever was recorded using both ion and electron beam imaging.

4.4.2 Experimental Results

4.4.2.1 Phase Determination of Cu-Sn-In

Figure 4.20(a) shows the XRD patterns for different compositions of Cu-Sn-In. Four different film compositions were investigated, which are $\text{Cu}_{85.5}\text{Sn}_{12.6}\text{In}_{1.6}$ (Cu-rich), $\text{Cu}_{45.7}\text{Sn}_{32.3}\text{In}_{22}$ (Sn-rich), $\text{Cu}_{45.7}\text{Sn}_{32.3}\text{In}_{22}$ (η -phase-1) and $\text{Cu}_{41.7}\text{Sn}_{51.5}\text{In}_{6.8}$ (η -phase-2). Two kinds of phases are present in Cu-rich compositions. They are Cu and η phases. Similarly, Sn-rich compositions also consist of a mix of two phase which are Sn and η phases. On the other hand, for both η -phase-1 and η -phase-2 compositions, they are dominated by η phase with very little of Sn phase.

These observations are not unexpected. According to the Cu-Sn-In phase diagram as shown in Figure 4.20(b) [125], there is only one type of intermetallic compound forms in Cu-Sn-In ternary system at temperatures below 200°C. This intermetallic compound is η phase ($\text{Cu}_6(\text{Sn},\text{In})_5$), where the Sn and In substitutes each other. Similar experimental observations have also been reported in literature [61, 126, 127].

4.4.2.2 Indenter Tip Correction

Due to of the curvature of the cantilever and the hemispherical shape of the indenter, the actual contact point of the indenter with the cantilever can be off the centre of the indenter tip as illustrated in Figure 4.21. This results in a change in the separation distance (d), and eventually affects the computation of Young's modulus. This issue is solved analytically by assuming the indenter and cantilever share a common tangent at the actual contact point.

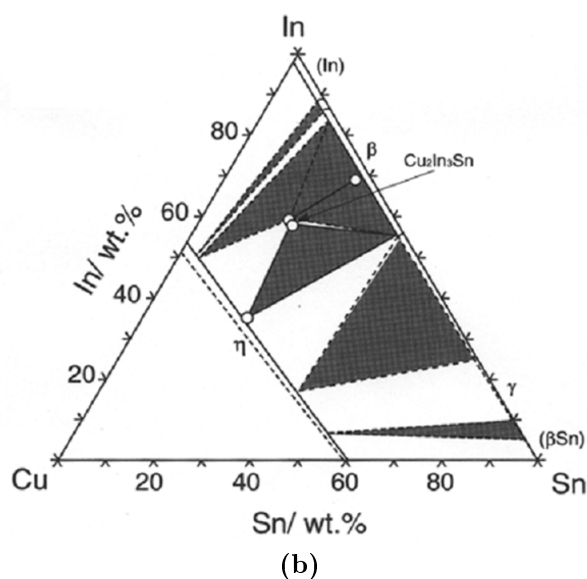
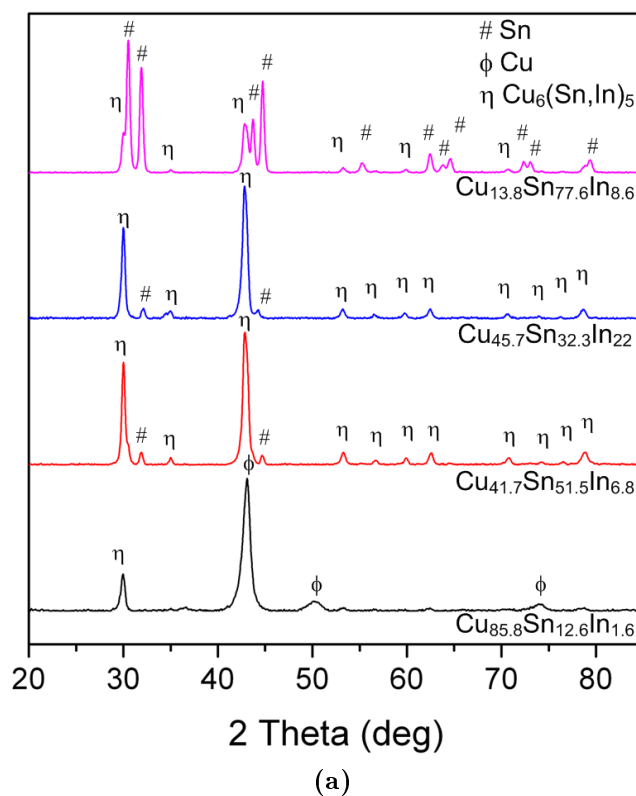


Figure 4.20: a) XRD patterns of different compositions of Cu-Sn-In b) Phase diagram of ternary Cu-Sn-In [125]. Intermetallic Compound observed by XRD is associated with the phase predicted by Cu-Sn-In phase diagram. There is only one IMC (i.e. $\text{Cu}_6(\text{Sn},\text{In})_5$) formed in this system.

For our case, the uncorrected error in the separation distance is up to 17%. This could result in errors in the Young's modulus measurement of up to 34.5%. The analytical correction eliminates the error associated with this.

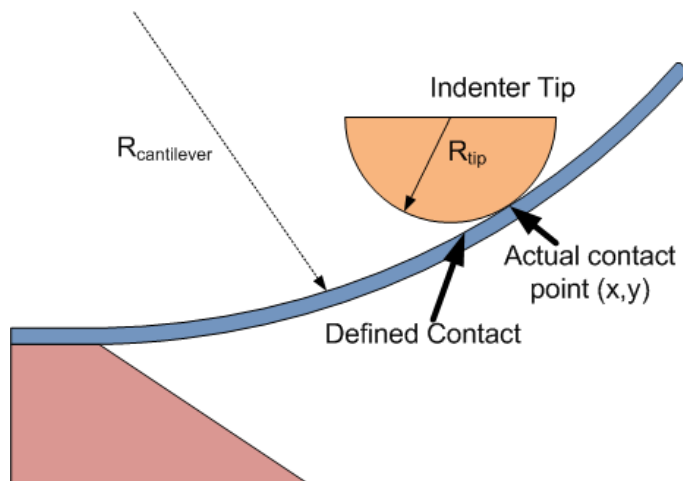


Figure 4.21: Schematic representation of a nanoindenter tip in contact with a curved cantilever. The actual point of contact during indentation experiment may deviate from the defined contact point.

4.4.2.3 SiO₂ Young's modulus

Calculation of mechanical properties (i.e. residual stress, Young's modulus and fracture strength) of Cu-Sn-In requires knowledge of the SiO₂ substrate Young's modulus. Thus, Young's modulus of SiO₂ was measured independently without any Cu-Sn-In on it. Six different SiO₂ cantilevers were deflected at multiple locations. The average Young's modulus is shown in Table 4.2. According to literature, Young's modulus of SiO₂ lies in the range of 50 - 85 GPa [137–139]. Based on the measurement in this study, the Young's modulus of SiO₂ is 76.3 ± 3.87 GPa, which is in good agreement with the values reported in literature. This measurement not only provides the data for the calculation of Cu-Sn-In mechanical properties, but also validates the method of the measurement.

Table 4.2: Young's modulus of SiO₂

Fabrication method	Measurement method	Young's modulus (GPa)	Ref
Thermal SiO ₂	Indentation	83	[137]
LTO	Indentation	85	[137]
FIB deposited	Cantilever deflection	45	[138]
PECVD	Brillouin light	$Te \pm 2$	[139]
LPCVD	Brillouin light	61 ± 2	[139]
PECVD	Cantilever deflection	76.3 ± 3.87	this work

4.4.2.4 Fracture Mechanism of Cantilever

There are several reports [82, 140] in the literature on the characterization of fracture strength using cantilevers. However, these are mostly focused on single-layer cantilevers. Analysis of the fracture of a bilayer cantilever, as in our case, is highly dependent on the failure mechanism. In order to determine the fracture mechanism during deflection, a separate in-situ experiment was carried out. Some of the cantilevers were deflected using a micromanipulator inside an SEM chamber while monitoring fracture at the supported end of the cantilever.

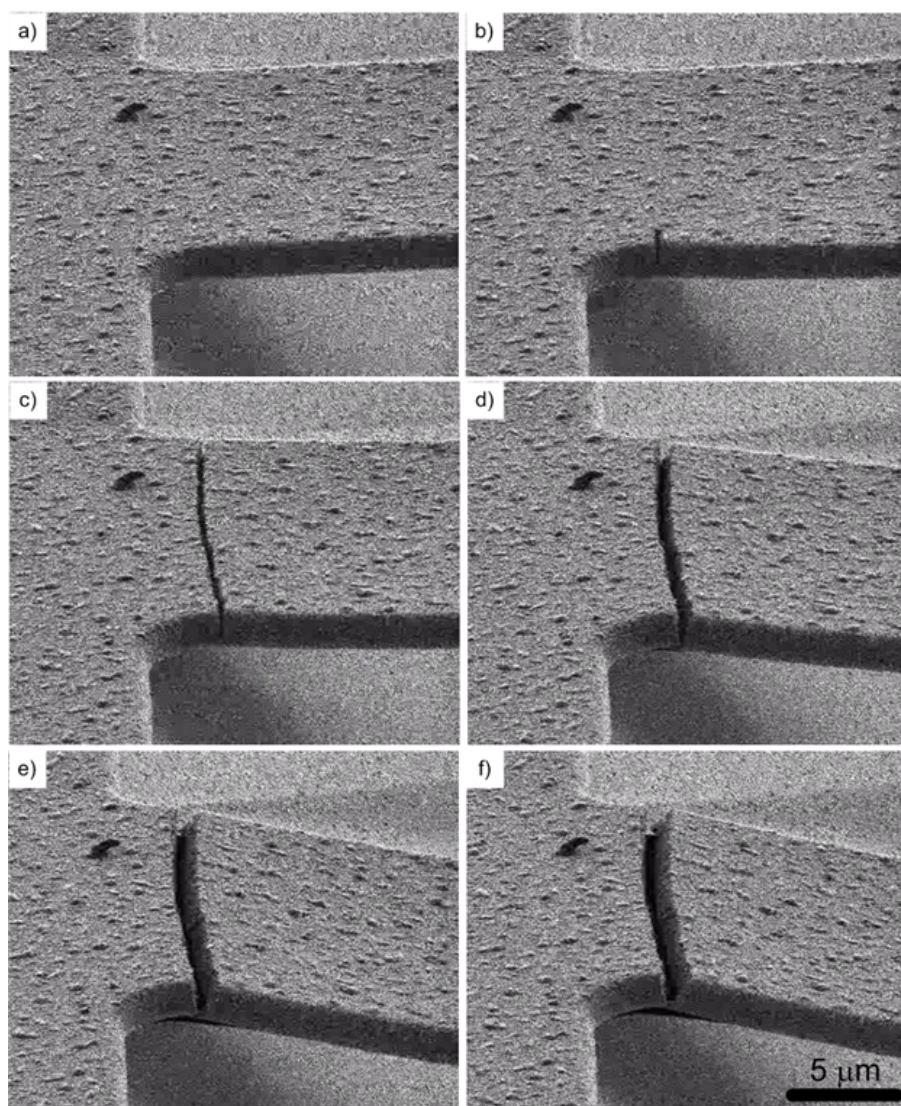


Figure 4.22: Fracture mechanism of a Cu-Sn-In/SiO₂ cantilever. a) Before fracture, b) after a small crack is initiated at the edge of the cantilever, c) after the crack propagated through the thickness of the film over the whole width, d)-f) crack propagation at the Cu-Sn-In/SiO₂ interface.

Figure 4.22 shows the fracture mechanism of Cu-Sn-In/SiO₂ bilayer cantilever during deflection. Fracture usually initiated with a small crack penetrating through the thickness, as seen in Figure 4.22(b). A small increment of the deflection results in a sudden brittle crack propagation through the thickness of the film for the whole width of the cantilever, as seen in Figure 4.22(c). Correlating the fracture mechanism with the load vs. displacement curve in Figure 4.18P the fracture force is defined as the load where the fracture of the film takes place. Further deflection of the cantilever results in cracking at the Cu-Sn-In/SiO₂ interface. This is shown in the “less steep regime” in Figure 4.18.

Clearly seen in Figure 4.22, fracture of the cantilever happens only in the Cu-Sn-In film, while the SiO₂ substrate remains intact. This validates the approach to measurement of the fracture strength previously described in Section 4.2.3.

4.4.2.5 Young's Modulus

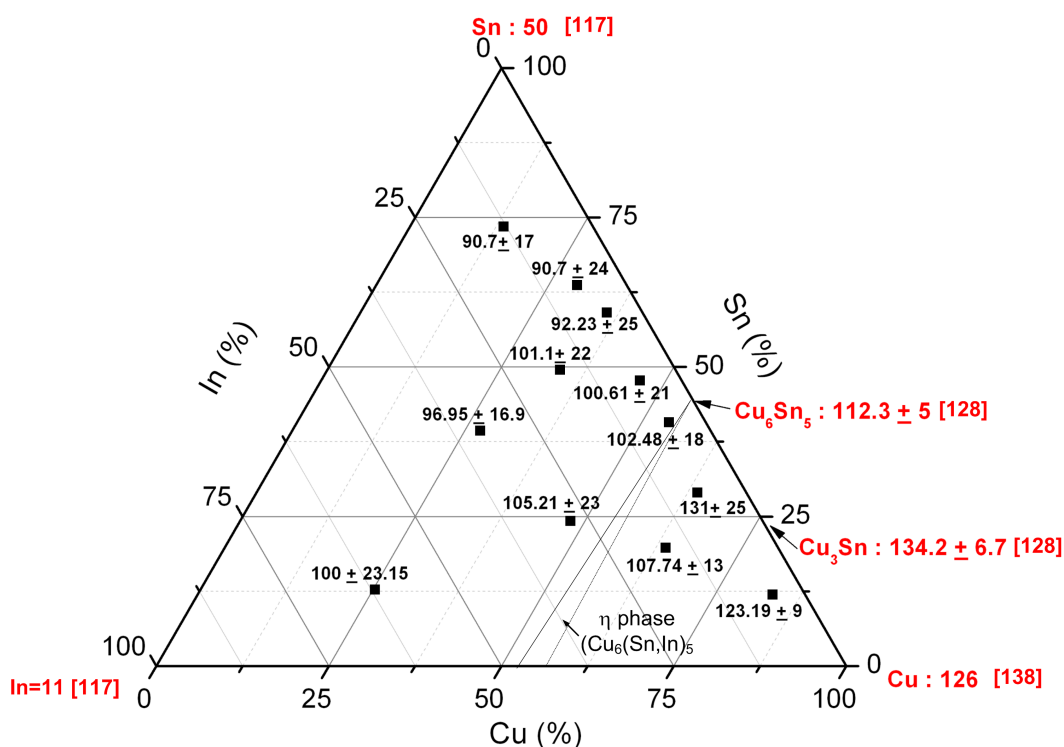


Figure 4.23: Young's modulus of different compositions of Cu-Sn-In films, superimposed with Cu-Sn-In phase diagram [125].

Figure 4.23 shows the Young's modulus of Cu-Sn-In at different composition in ternary plot and superimposed with the Cu-Sn-In phase diagram [125]. Standard deviations of each composition is believed to be due to inaccuracy of the placement of indenter tips along the width axis of the cantilever.

Nevertheless, the average values of the Young's modulus are in excellent agreement with other similar compositions reported in literature. For example, the reported Young's modulus of Cu_6Sn_5 is 112.3 ± 5 GPa [130]. From our measurements, the Young's modulus of closest composition ($\text{Cu}_{54.8}\text{Sn}_{38.5}\text{In}_{6.7}$) is 102.48 ± 18 GPa. Cu film was reported to have Young's modulus around 126 GPa [76]. From our measurement, the Young's modulus of $\text{Cu}_{83.5}\text{Sn}_{13.2}\text{In}_{3.2}$ is revealed to be 123.19 ± 9 GPa. Lastly, Cu_{360} has reported to have a Young's modulus of 134.2 ± 6.7 GPa [130], while our measured the Young's modulus of $\text{Cu}_{71.5}\text{Sn}_{25.5}\text{In}_{2.8}$ is 131 ± 25 GPa.

From the ternary plot in Figure 4.23, there is a global trend on the composition effect to the Young's modulus. It appears that the Young's modulus increases with increasing Cu content. This is not unexpected, because the Young's modulus of Cu (126 GPa) [76] is much higher than Sn (50 GPa [117]) and In (11 GPa [117]). It is generally agreed that effects of composition to the Young's modulus follow a mixture rule. Subrahmanyam *et al.* [141] reported that the Young's modulus of Cu-Sn decreases with decreasing Sn content. Even in amorphous metal, the Young's modulus also follow this trend [78].

4.4.2.6 Residual Stress

Figure 4.24 shows the residual stress at both the Cu-Sn-In surface and Cu-Sn-In/ SiO_2 interface. The stress at the Cu-Sn-In surface and Cu-Sn-In/ SiO_2 interface exhibits compressive and tensile stress, respectively. The comparison on the absolute values of residual stress with reported literature is difficult. The residual stress of a film on a substrate depends on various parameters such as deposition condition, film microstructure, substrate material and both film and substrate thicknesses [79]. For example, the residual stress of Cu on silicon substrate may vary from 0 to 400

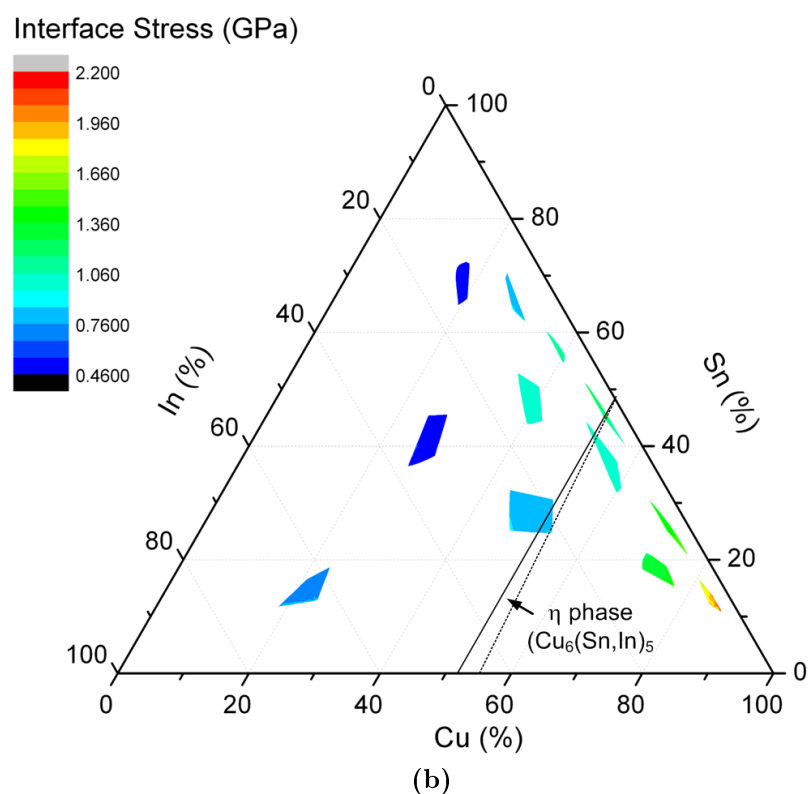
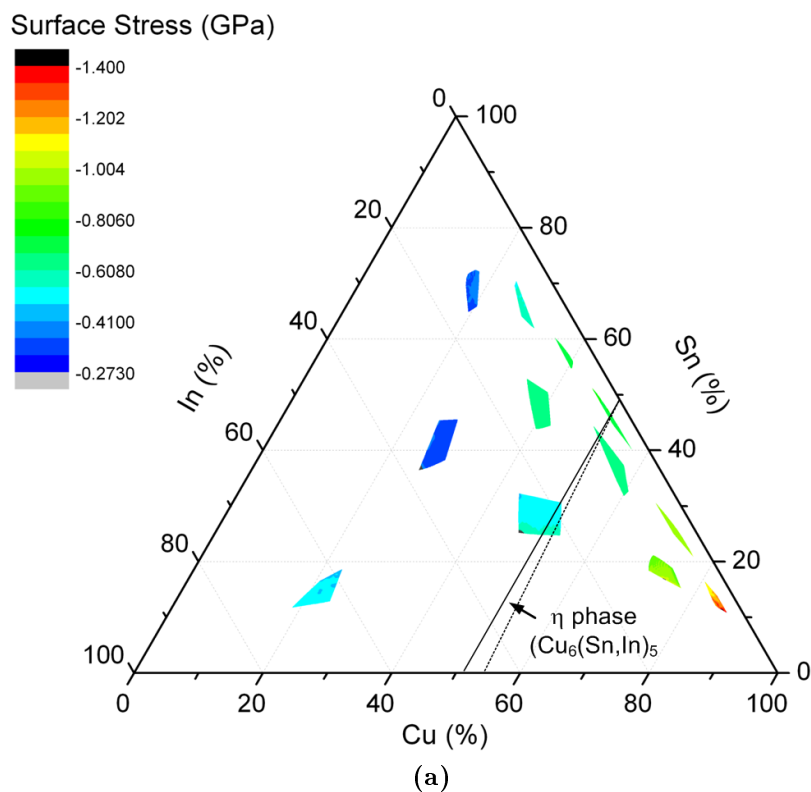


Figure 4.24: Residual stress of Cu-Sn-In films, superimposed with Cu-Sn-In phase diagram [125] a) Compressive residual stress at the Cu-Sn-In surface. b) Tensile residual stress at the Cu-Sn-In/ SiO_2 interface.

MPa depending on the deposition conditions [142].

Nevertheless, it is clearly seen in Figure 4.24 that the residual stress of Cu-Sn-In increases with increasing Cu content. This is not surprising, because Cu has a higher melting point (1082 °C [117]) than Sn (240 °C [117]) and In (156 °C [117]). Higher melting point elements usually have slower surface diffusion during film deposition to allow grain growth, which correspondingly leads to smaller residual stresses [79,143].

4.4.2.7 Fracture Strength

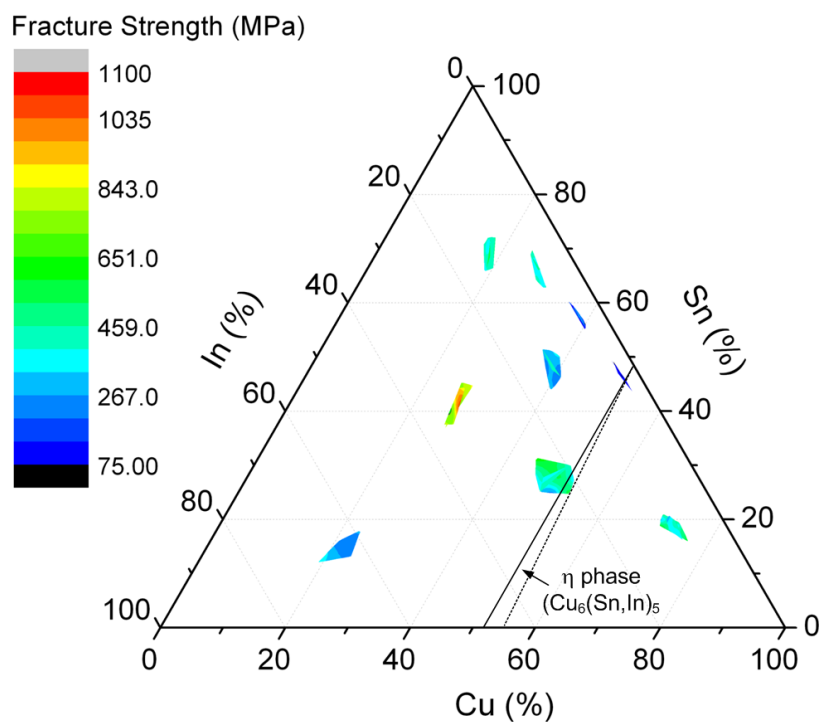


Figure 4.25: Fracture strength of Cu-Sn-In, superimposed with Cu-Sn-In phase diagram.

Figure 4.25 shows the fracture strength of Cu-Sn-In thin films at different composition. Jiang *et al.* [88] reported the fracture strength of single crystal Cu_6Sn_5 is around 1356 MPa. This is significantly higher than our measurement on $\text{Cu}_{53}\text{Sn}_{44}\text{In}_3$, which is around 103 MPa. The reason for this is probably because Jiang *et al.* [88] measured the compressive fracture strength, while tensile fracture strength was characterized in this work. Typically, tensile fracture strength is smaller than compressive fracture strength. Additionally, their Cu_6Sn_5 was single crystal which is expected to have higher strength than multiple grains structure like those measured in this

study. Lastly, the micro-pillar shape that they used to characterize could enhance the size effect on the mechanical properties of materials. It is well understood that the strength of materials increases with decreasing of the specimen size [144].

As discussed previously in section 4.4.2.1, Cu-Sn-In ternary system forms a single phase regime of $\text{Cu}_6(\text{Sn},\text{In})_5$ at composition range $\text{Cu}_{53-58}\text{Sn}_{0-45}\text{In}_{5-45}$. In this regime, the maximum fracture strength is observed at 673 ± 93 MPa on $\text{Cu}_{53}\text{Sn}_{25}\text{In}_2$. This is significantly higher than the closest composition to Cu_6Sn , which is $\text{Cu}_{53}\text{Sn}_{44}\text{In}_3$ at 103 ± 21 MPa. Furthermore, it appears that the fracture strength increases gradually with increasing Indium concentration.. For example, $\text{Cu}_{53}\text{Sn}_{27}\text{In}_{20}$ and has a fracture strength at 389.5 ± 17.5 MPa. However, the fracture strength decreases as the atomic concentration ratio of In to Sn is above 1. For instance, $\text{Cu}_{49}\text{Sn}_{24}\text{In}_{27}$ exhibits fracture strength at 417.85 ± 4.74 MPa, which smaller than $\text{Cu}_{53}\text{Sn}_{25}\text{In}_{22}$. These observations may be explained by solid solution strengthening mechanism [145]. According to Sommadossi *et al.* [146], In and Sn atoms may substitute each other in $\text{Cu}_6(\text{Sn},\text{In})_5$ phase. The atomic radii of In is 167 pm, which is larger than Sn that has 140 pm [117]. As consequence, the substitutional of Sn with In results in localized compressive stress surrounding the crystal lattice of $\text{Cu}_6(\text{Sn},\text{In})_5$. The localized compressive may interact with the dislocations, thus impedes their motion causing in higher fracture strength of materials. Higher concentration of In results in higher concentration of localized stress, thus results in higher fracture strength. Similar mechanism has been reported for Cu-Ni system. They found that the fracture strength of Cu-Ni alloy increases monotonically up to 50% addition of Ni [145].

As seen in Figure 4.25, it can be observed that $\text{Cu}_{27}\text{Sn}_{37}\text{In}_{36}$ exhibits the highest fracture strength at 1040 MPa. According to the Cu-Sn-In ternary phase diagram, this composition comprises of three phases which are $\text{Cu}_6\text{Sn}_{2.5}\text{In}_{2.5}$, InSn_4 and In_3Sn . From the previous discussion, $\text{Cu}_6\text{Sn}_{2.5}\text{In}_{2.5}$ is known to have highest strength among other composition combination for $\text{Cu}_6(\text{Sn},\text{In})_5$ phase. The presence of both InSn_4 and In_3Sn phases may enhance the fracture strength by precipitation strengthening

mechanism [145]. Similar to solid solution strengthening, different phases may interact with dislocations to impede its motion, therefore increases the fracture strength.

Interestingly, matching the fracture strength with Cu consumption rate which was discussed in Chapter 3, it appears that addition of 44-46 % In into Sn solder, may not only be potential to reduce bonding temperature but also increases the fracture strength of resulted IMC. In principle, $\text{Cu}_{53}\text{Sn}_{25}\text{In}_{22}$ can be formed by bonding a Cu film with $\text{Sn}_{54}\text{In}_{46}$. Recall the Cu consumption rate experiment, the highest rate of forming IMC was found for $\text{Sn}_{56}\text{In}_{44}$. This is very close to the solder composition that exhibits highest fracture strength for resulted IMC.

4.5 Summary

The application of microcantilevers for mechanical characterization of Cu-Sn-In thin films has been demonstrated. Both finite element modeling and experiments showed that the effects of non-ideality of cantilevers can be corrected by making deflection measurements in multiple locations combined with empirical corrections. Unlike nanoindentation, this technique does not require knowledge of Poisson's ratio for measurements of Young's modulus. In addition, more information from the sample can be obtained, such as the residual stress and fracture strength.

Residual stress and Young's modulus of Cu-Sn-In thin film increased monotonically with increase in Cu composition. The former is because of decrease in homologous temperature, while the latter is because Cu has a much higher Young's modulus than Sn and In. In single $\text{Cu}_6(\text{Sn},\text{In})_5$ phase regime, $\text{Cu}_{56}\text{Sn}_{25}\text{In}_{22}$ exhibits the highest fracture strength at 651 MPa. Solid solution strengthening is believed to be the reason of such fracture strength enhancement. Among all the measured samples, $\text{Cu}_{27}\text{Sn}_{37}\text{In}_{36}$ has been shown to have the highest fracture strength at 1040 MPa. In this case, precipitation strengthening is the proposed mechanism. These findings signify the great potential of this material, 44-46 % In addition in Sn solder not only lead to lower bonding temperature, but also increases the fracture strength

of the resulted IMC.

Chapter 5

Influence of Bonding Parameters to the Bond Strength of Cu /Sn-In Based Solders

5.1 Overview

The kinetics and mechanical properties of intermetallic compounds in Cu-Sn-In system have been discussed in Chapters 3 and 4, respectively. It was concluded that adding Indium is beneficial in lowering down the temperature for intermetallic growth, while at the same time it can increase the fracture strength of the intermetallic. Owing to these findings, we hypothesized that adding indium has potential in lowering the bonding temperature between Cu and Sn-based solders as well as increasing the bonding strength.

There have been several reports on the potential use of Sn-In solder material as a ‘glue’ agent. However, most of these studies have focused on bulk solders [127, 147, 148]. A few groups [28, 126] have reported investigations of Sn-In thin films bonded with Cu, but those were mainly focused on bonding of Cu/Sn-In bilayers to Cu, to sandwich the solder between Cu layers. In a sandwich structure, the interaction between the Cu and Sn-In layers is relatively complex as the reaction at one interface can be affected by another interaction at the other interface. This has been observed in other systems such as Pt/Sn/Cu [149], Cu/Sn/Ni [150] and

Cu/Sn/Au [151] . A similar problem has also been observed for Cu/Sn-In bonding with Cu/Sn-In [146].

In this chapter, the mechanical properties of Cu bonds on Sn-In solder were investigated. By using this structure, the issue of having a competing reaction at the interface of Cu and underlying solder layer was eliminated. This structure also eliminates the reaction of Cu with Sn-In during storage time which would happen for the case of Cu bonds on Cu/Sn-In.

The first half of this chapter will discuss the effects of bonding parameters to the shear strength of Cu bonds with $\text{Sn}_{85}\text{In}_{25}$ solder. The other half of the chapter will discuss the effects of Sn-In composition to the shear strength of the joint.

5.2 Experimental Details

Cu/Ti and Sn-In/Cr bi-layer films were deposited using sputter deposition on SiO_2 that was thermally grown on silicon wafers. Ti and Cr were deposited as adhesion and diffusion barrier layers for Cu and solder (Sn-In), respectively. The thickness of the Cu and Sn-In solder layers was 1 μm and 2.8 μm , respectively, as shown in Figure 5.1.

$\text{Sn}_{75}\text{In}_{25}$ solder composition was chosen to study in detail on the effects of bonding and annealing parameters. Using this non-eutectic composition solder allows the study of the Cu/Sn-In interaction in a solid-liquid regime. EDS measurements of the as-deposited solder show a uniform composition of $\text{Sn}_{75}\text{In}_{25}$. Based on the Sn-In phase diagram [53] and confirmed with XRD measurements, this composition of Sn-In is associated with the InSn_4 phase.

After deposition, the Cu and solder wafers were diced into 5 mm x 5 mm and 1 mm x 1 mm chips, respectively. Prior to bonding, the Cu surfaces were cleaned by immersing the dice in acetic acid for 10 min to remove the metal oxide. The solder surfaces were cleaned using plasma etching (CF_4 O_2) for 30 s.

Bonding was carried out using a simple home-made bonder at 10^{-2} atm. Follow-

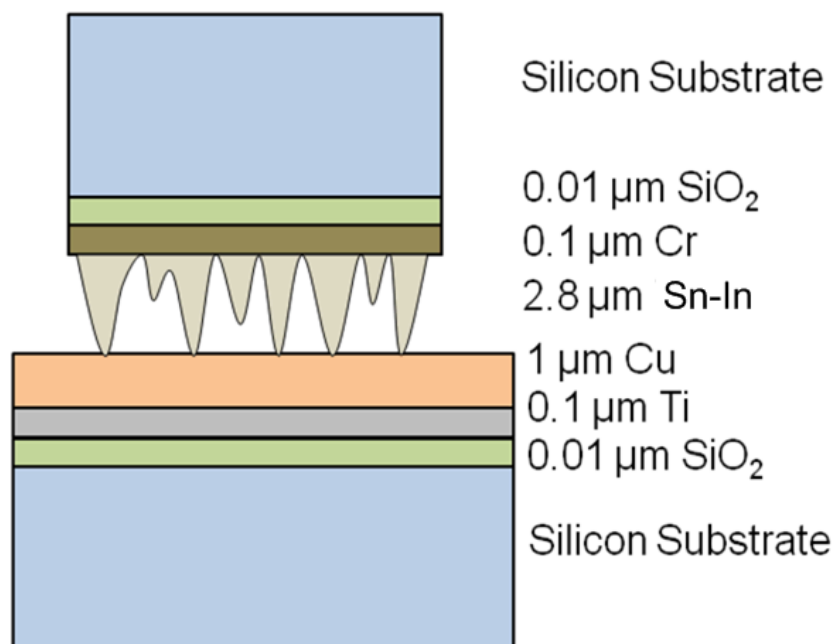


Figure 5.1: Schematic drawing of the layered structures used for studies of bonding between $\text{Sn}_{75}\text{In}_{25}$ and Cu. The as-deposited solder has a rough surface with many asperities.

Table 5.1: Bonding and annealing process parameters

Parameters	Range
Bonding temperature	25 - 200 $^{\circ}\text{C}$
Bonding pressure	6.5 MPa
Bonding time	5-180 min
Post-bonding annealing temperature	25-200 $^{\circ}\text{C}$
Annealing time	5 h
Bonding and annealing vacuum level	10^{-2} atm

ing bonding, some of the samples were annealed at different temperatures for 5 h. The details of the bonding and annealing parameters are shown in Table 5.1.

Several characterization methods were employed to evaluate the effects of each parameter. The type of IMC that formed was studied using XRD and EDS. The bond strength was evaluated through shear testing. To prepare samples for cross section analysis, the bonded samples were mounted in an epoxy, flattened with sandpaper and polished with 1 μm alumina.

The effects of Sn-In composition to the bond strength were investigated by comparing $\text{Sn}_{75}\text{In}_{25}$ with $\text{Sn}_{50}\text{In}_{50}$ and $\text{Sn}_{25}\text{In}_{75}$.

5.3 Results and Discussion

5.3.1 Morphology of as-deposited solder

Due to its low melting point, therefore its high homologous temperature, the solder film formed a very rough surface once deposited onto a non-reactive material such as chromium as seen in Figure 5.2. The rough surface might result in formation of voids at the final joint interface due to lack of contact after bonding. Good bonding is defined as having a low void density at the interface, which is indicated by a large true contact area, and transformation of the solder into an IMC which has a higher re-melting temperature. The effects of several bonding parameters on achieving a good bonding are discussed in the following sections.

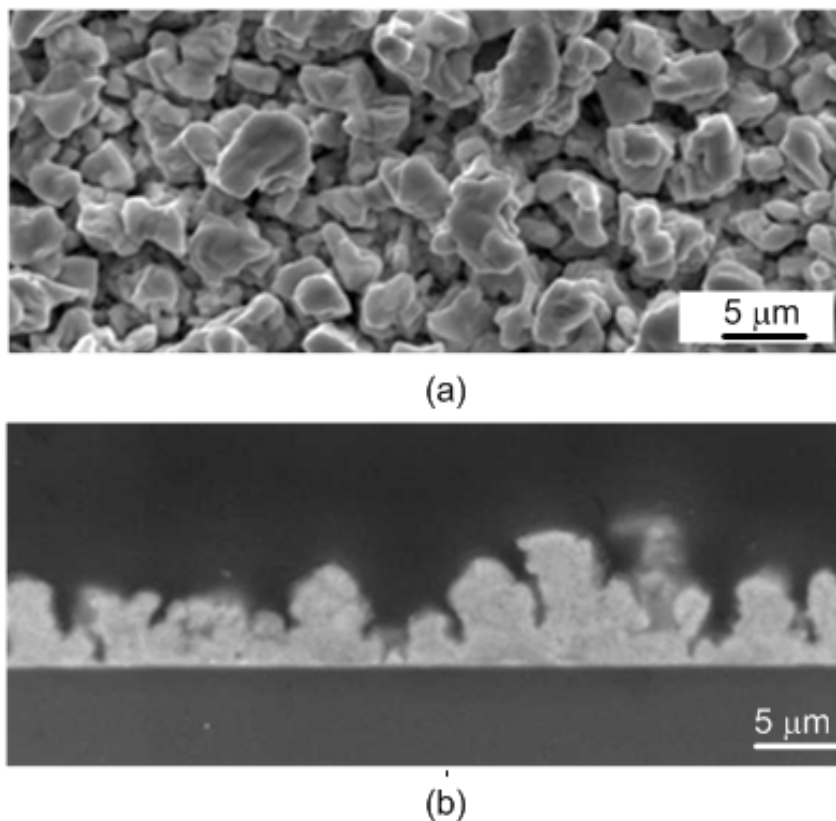


Figure 5.2: Sputter deposited $\text{Sn}_{75}\text{In}_{25}$ solder has a very rough surface when deposited on Cr. a) Top view, and b) cross sectional view.

5.3.2 Bonding and Annealing Parameters

5.3.2.1 Bonding Temperature

Figures 5.3(a-d) show cross sections of the joints that were bonded at different temperatures. The joint thickness decreased as the bonding temperature was increased. The decrease in joint thickness is associated with an increase in the true contact area. Based on the volume conservation model [152] as a rough surface deforms, the amount of material deformed will be conserved and will fill the voids of the rough surface as illustrated in Figure 5.4. Intuitively, a higher temperature results in the softening of the solder, leading to more deformation. Thus, this would give a larger true contact area.

In order to test this hypothesis, the true contact area of the joint was measured using the pixel contrast of SEM images of the solder chip after debonding. The computation was done using ImageJ software which is an open-source program [118]. As seen in Figure 5.5, the contact area increased as the bonding temperature was increased. The error bars in Figure 5.5 correspond to the standard deviation for 3 measurements at different locations of one sample (i.e. the centre, and two edges). The observed variations are associated with the non-uniformity in the bonding pressure.

Based on the Sn-In phase diagram [53], the deformation of the solder can be classified into three regimes: solid state ($T < 135^\circ\text{C}$), liquid-solid state ($135^\circ\text{C} < T < 185^\circ\text{C}$) and liquid state ($T > 185^\circ\text{C}$). From the contact area measurement, it can be seen that liquid state deformation is required in order to achieve a $\sim 100\%$ contact area. This is intuitive, as in the liquid state, solder can easily flow to fill the voids and form perfect contact, when we apply bonding pressure. In the solid state, the effect of temperature on deformation is believed to be related to a reduction of the yield stress. It has been reported that the yield stress of indium thin films does not vary significantly with temperature over the temperature range of $25 - 120^\circ\text{C}$ [153]. This is the reason why the contact area is relatively constant in the solid state regime.

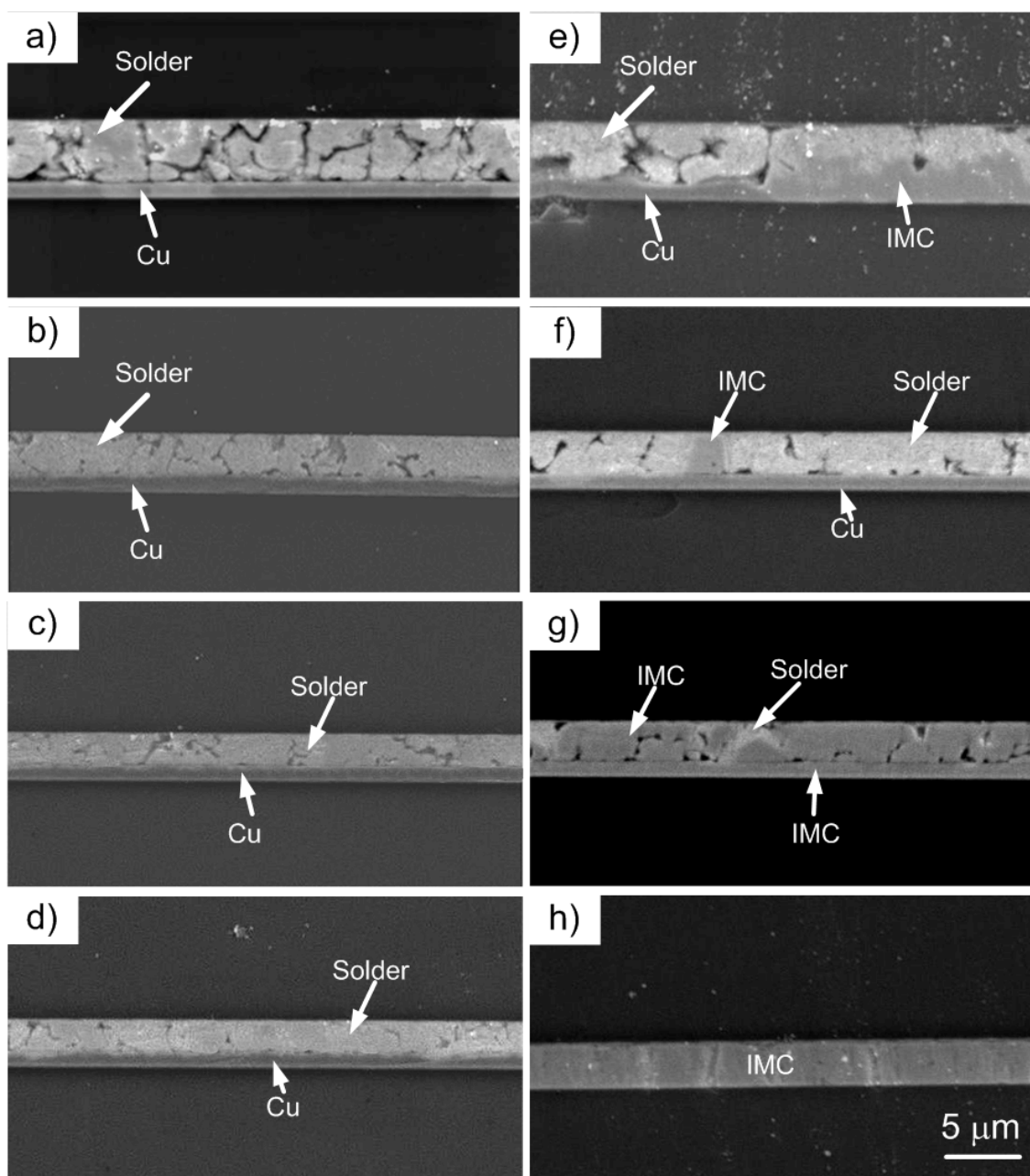


Figure 5.3: Cross sectional views of Cu chips bonded to $\text{Sn}_{75}\text{In}_{25}$ chips, bonded and post-bonding annealed at different temperatures. a), e) Bonded at 25°C ; b), f) bonded at 120°C ; c), g) bonded at 150°C ; d), h) bonded at 200°C ; a)-d) unannealed; e)-h) annealed at 200°C . Void-free bonding with full IMC formation can be achieved through a combination of bonding and post- bonding annealing processes.

5.3.2.2 Bonding Time

From Figures 5.3(a-d), it can also be observed that there is no transformation of solder and Cu into IMC as bonded. This is probably due to the short bonding time (only 5 min), which is insufficient to allow the kinetic processes required for IMC formation (see below).

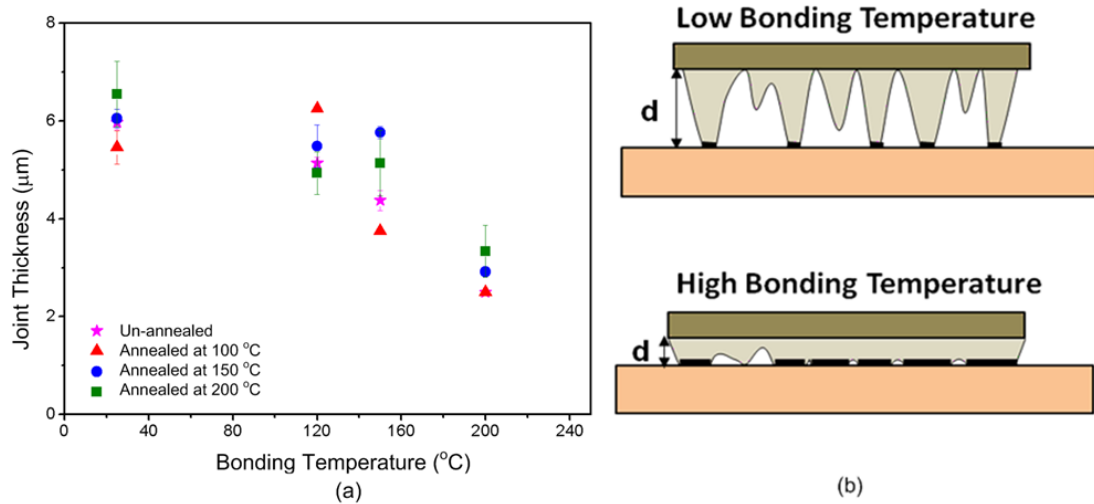


Figure 5.4: Effect of temperature on the joint thickness. a) Measurement of joint thickness as a function of bonding and annealing temperatures: Joint thickness is strongly affected by the bonding temperature but not the annealing temperature. b) Schematic representation of enlarged contact area after bonding at a high temperature, and the resulting lower bond thickness. Nominal bonding pressure = 6.5 MPa.

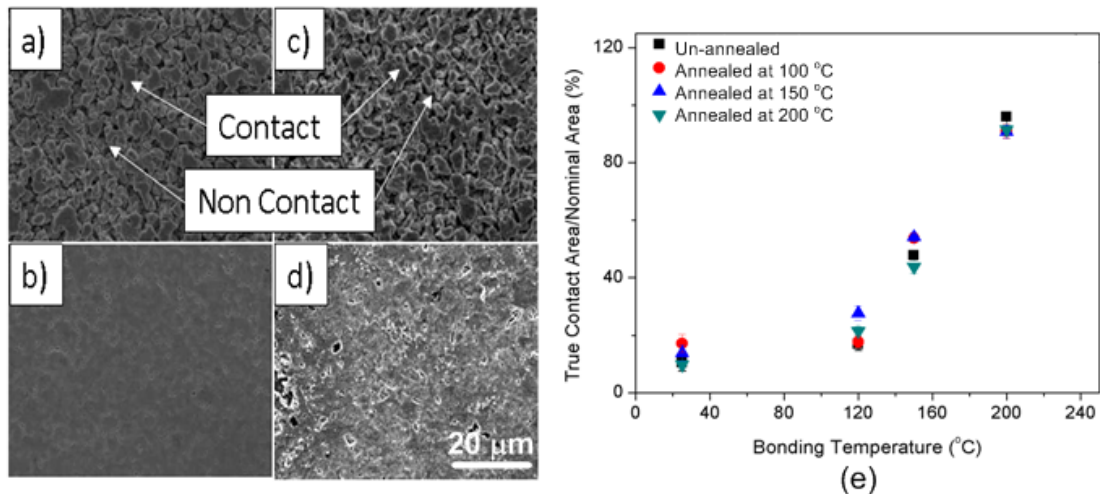


Figure 5.5: a)-d) Typical SEM images of the solder surface after debonding. a) Bonded at 120°C , unannealed, b) bonded at 200°C , unannealed, c) bonded at 120°C , annealed at 200°C , d) bonded at 200°C , annealed at 200°C . e) The true contact area as a function of bonding and annealing temperatures. Higher bonding temperatures result in higher true contact areas, while the annealing temperature does not have a significant effect on the true contact area.

The bonding time was varied to further understand this observation. Figure 5.6 shows cross sections of samples bonded at 200°C (liquid state, therefore large contact area) for various bonding times. It can be seen that even after 20 min bonding time, the whole solder has not transformed into IMC. From the literature, the time required to grow IMC in Cu/Sn-In system varies from minutes to hours

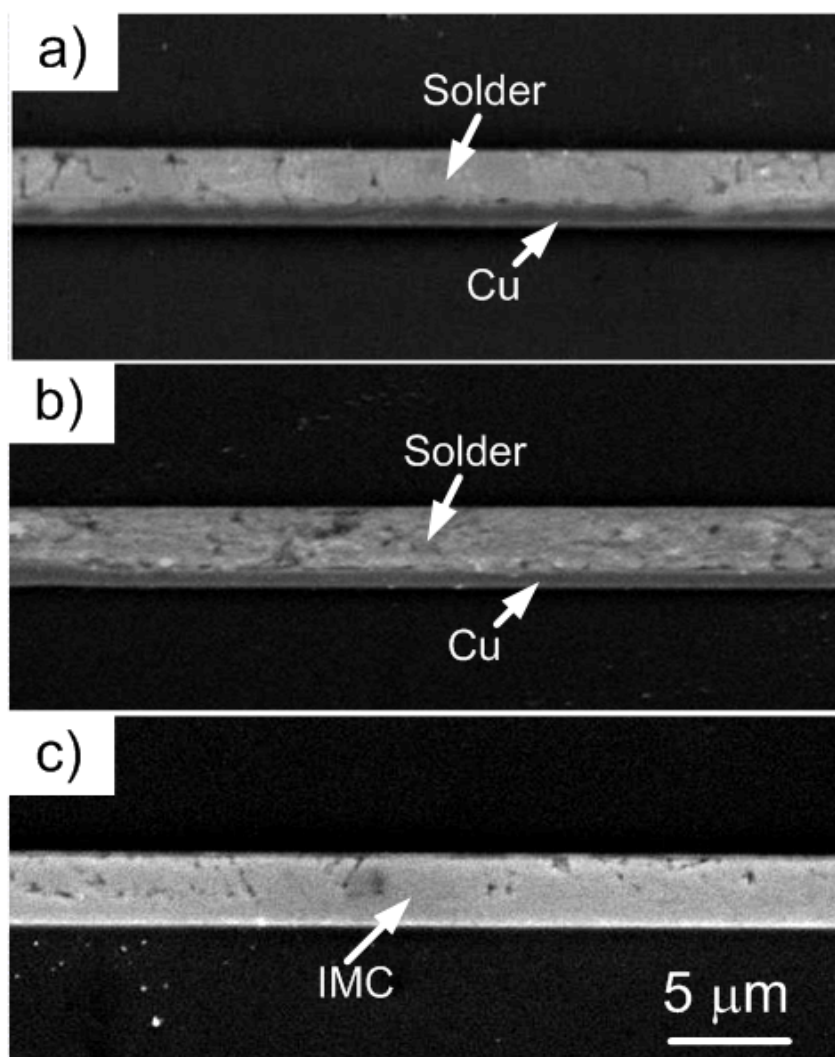


Figure 5.6: Cross sectional view of Cu chips bonded with Sn-In chips at 200°C for various times. a) 5 min, b) 20 min, c) 3 h. Transformation of the whole solder into intermetallic compound requires 3 h of bonding, which is not practical for an industrial process.

as summarized in Table 5.2. This depends on various factors such as the type of solder, the thicknesses of solder, temperature and the joint structure.

Using a three layer sandwich with Cu bonded to a Sn-In/Cu bilayer structure, Yan *et al.* were able to achieve full IMC joint ($\sim 4 \mu\text{m}$ thick of IMC) after bonding for only 20 min [28], which is much faster than our study. There are two possible explanations for this. First, having a source of Cu on both sides of the Sn-In allows the formation of IMC at two interfaces rather than one. Second, the IMC has already formed when Sn-In was deposited onto the Cu film, so that subsequent nucleation of the IMC is not required to transform the whole solder layer into IMC,

Table 5.2: Typical time required to grow IMC, based on the literature

Material	Structure	Thickness	Temperature (°C)	IMC Thickness (μm)	Bonding Time	Ref
Cu/Sn ₅₀ In ₅₀ /Cu	Thin Film Sandwich	3 μm /3 μm /3 μm	180	3	20 min	[28]
Cu/Sn/Cu	Thin Film Sandwich	40 μm /10 μm /40 μm	300	10	1 min	[154]
Cu/Sn/Cu	Thin Film Sandwich	40 μm /10 μm /40 μm	230	10	>8 min	[154]
Cu/Sn ₅₀ In ₅₀	Bulk Solder	Bulk/Bulk	150	6	1.6 min	[147]
Cu/Sn ₅₀ In ₅₀	Bulk Solder	Bulk/Bulk	160	4	1.5 min	[148]
Cu/Sn ₅₀ In ₅₀ /Cu	Thin Film Sandwich	Bulk/10 μm /Bulk	200	10	80 min	[146]
Cu/In/Cu	Thin Film Sandwich	Bulk/10 μm /Bulk	200	10	30 min	[155]
Cu/Sn/Cu	Thin Film Sandwich	40 μm /6 μm /20 μm	180	6	60 h	[48]
Cu/Sn ₇₅ In ₂₅	Bilayer Bonding	1 μm /2.8 μm	200	3	> 20 min	This work

which shortens the total time of transformation of solder layer into IMC.

In Chapter 3, it was also shown that it requires less than 2 min to grow ~ 1.5 μm thick of IMC for a bilayer Cu/Sn-In. Extrapolating the experimental data in Chapter 3, it would require less than 10 min to grow ~ 4 μm thick of IMC. As discussed in the Cu/Sn-In bilayer, IMC formed even in as deposited. This suggests that in this case, nucleation barrier of IMC rather than two Cu sources is more likely the reason why such slow IMC formation process took place in this experiment. One possible factor that could lead to a long nucleation time is the presence of an oxide at the interface that acts as an interdiffusion barrier.

5.3.2.3 Annealing temperature

As the need for a long bonding time to form the IMC is not practical in industrial applications, the possibility of having a two-step bonding process was investigated. This process includes bonding for a short time (just enough to form a large contact area) and annealing (without application of a pressure) for a longer time to form the IMC. While the sandwich structures used by Yan *et al.* [28] forms IMC faster than our method, formation of IMC prior to bonding may result in variations in the amount of solder left for bonding. This variation will be further affected by variations in the storage time of the pre-bonded chips, because the IMC grows even at room temperature.

As seen in Figures 5.3(e-h), and also from the XRD peaks in Figure 5.7, annealing does help the formation of the IMC. From Figure 5.5, it also can be seen that the annealing does not change the contact area significantly. This is expected as no pressure was applied during annealing, thus further deformation did not occur.

The XRD patterns in Figures 5.7 show the effect of annealing for samples which have small true contact area (bonded at 120°C) and large true contact area (bonded at 200°C), respectively. In both cases, it is shown that there is no IMC for as-bonded samples. IMC is observed for samples which were annealed at 150° or above, with higher annealing temperatures result in transformation of more of the solder into

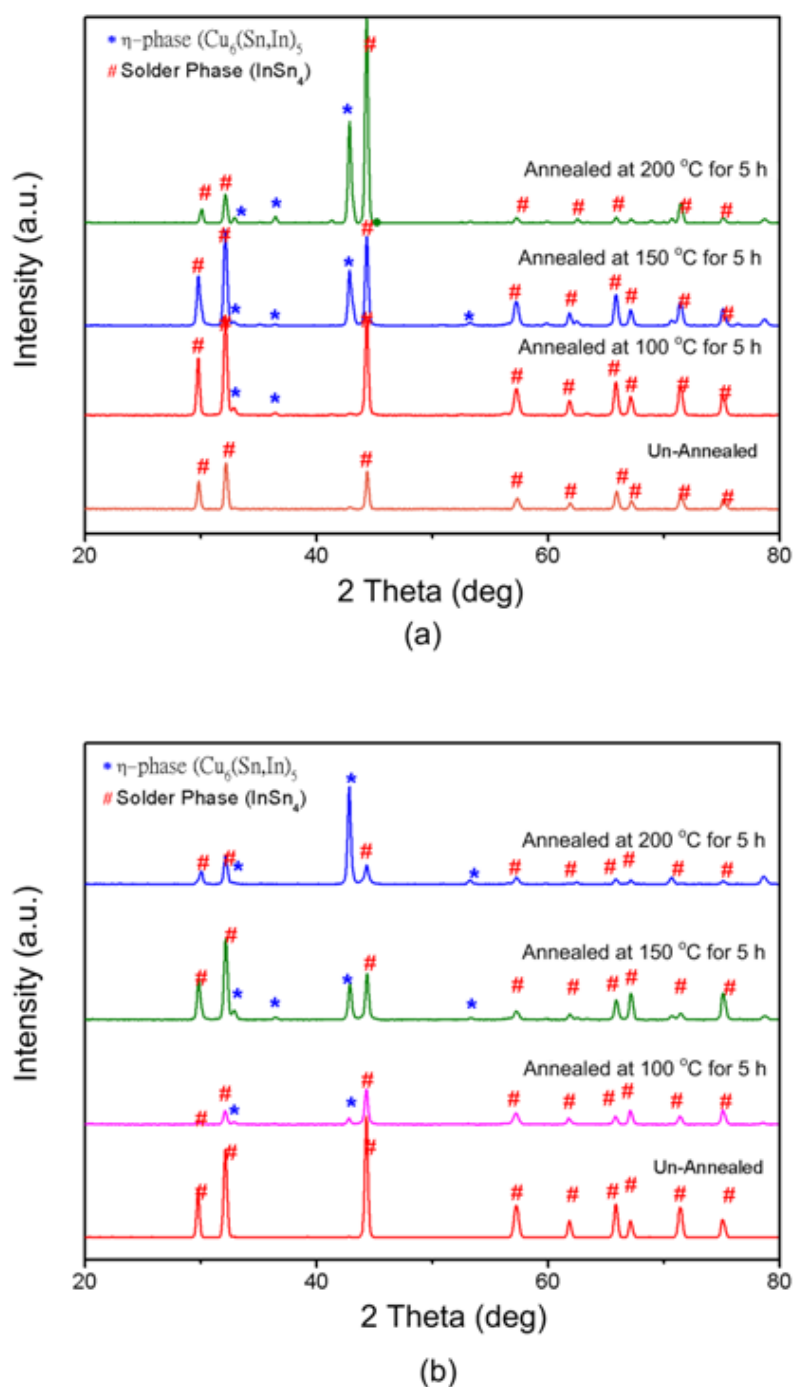


Figure 5.7: XRD peaks for $\text{Sn}_{75}\text{In}_{25}$ chips annealed at different temperatures. Bonded at 120°C, b) bonded at 200°C. Annealing helps the formation of the intermetallic compound.

the IMC. The amount of solder that is transformed into IMC also depends on the true contact area of Cu with solder. For small true contact areas, strong InSn_4 peaks were still found even after annealing at 200°C for 5 h. This is probably the result of retention of the solder in areas which were not in contact with Cu. Because

there is a larger area in contact with Cu, less InSn_4 was found for samples which were bonded at 200°C and annealed at 200°C .

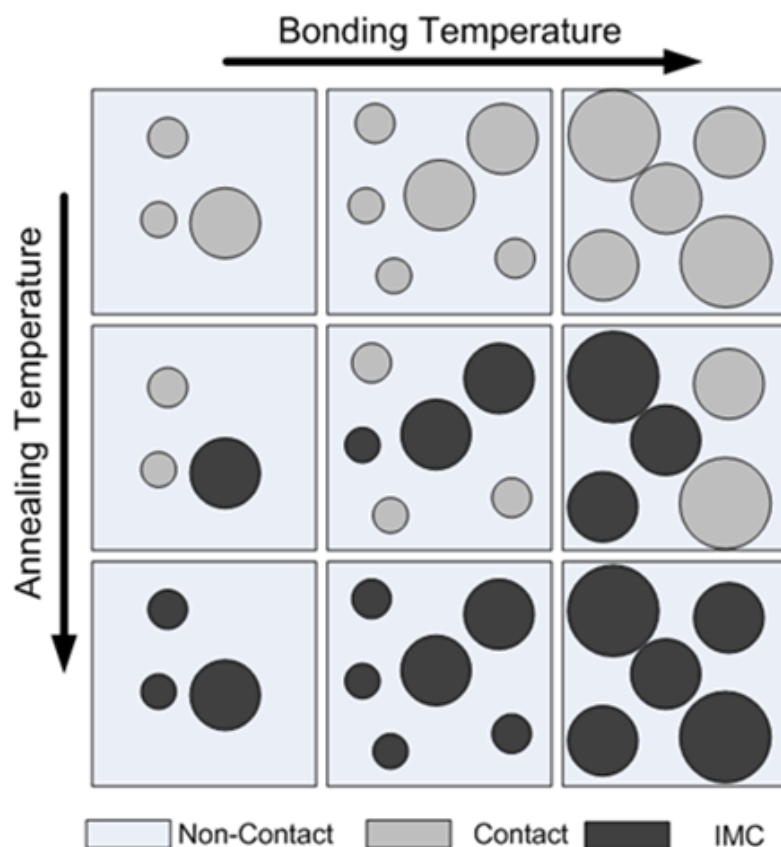


Figure 5.8: Schematic representation of the effects of bonding and post-bonding annealing temperatures.

Schematically, the effects of the bonding and annealing processes are shown in Figure 5.8. It is shown that the bonding temperature helps the enlargement of contact area, while annealing without pressure for longer time accelerates the reaction to form the IMC layer.

5.3.3 Microstructure Analysis

To determine the intermetallic compound after bonding, solder chips were analyzed using XRD after debonding. Figure 5.7 shows the XRD peaks for samples which were bonded and annealed at various temperatures. It can be seen that IMC had not formed in unannealed samples. Based on EDS measurements, the IMC that formed in annealed samples has a composition in the range of (53-64) Cu – (24-34) Sn –

(7-14) In. According to the ternary Cu-Sn-In phase diagram [125], this composition corresponds to the η phase ($\text{Cu}_6(\text{Sn},\text{In})_5$), which is consistent with the observed XRD peaks. This observation is in line with previous studies which showed that only the η phase forms at temperatures below 200°C [126,127,147]. The solder peaks are associated with the InSn_4 phase, as expected from the Sn-In phase diagram [53].

5.3.4 Shear Strength

The correlation of the true contact area and IMC formation with the mechanical properties of the joint. The mechanical strength of the bonds is a very important indication of the quality of the joint was investigated. The shear strength of joints was measured using a standard shear test in a DAGE 400 machine, using 6 samples per data point. The results are shown in Figure 5.9. There are several factors that might contribute to the large error bars in the shear strength measurements. First, this could be due to the nature of the mode 2 shear test measurement itself, which has a large component of plastic dissipation [156]. Secondly, the non-uniformity of the failure loci may also affect the measurement. As seen in Figure 5.10, each sample has multiple failure loci. There are some areas which failed within the IMC layer and there are also some areas which failed at the IMC/Cu, IMC/Cr or solder/Cr interfaces.

Reported values of the shear strength measurements lie in a broad range, from a few KPa to several hundred MPa [157–159], depending on shear parameters such as shear rate and shear height. This makes comparison with all the reported values difficult. Nevertheless, for the same geometry and shear test parameters, our results are comparable with other studies [30, 36].

A conclusion that can be drawn from Figure 5.9 is that enlargement of the true contact area is correlated with an increase in shear strength. The correlation of the true contact area and the shear strength has been studied in detail by R.I. Made for Cu-Cu bonds [35]. R.I. Made showed that the Cu-Cu bond shear strength is proportional to the true contact area. The true contact area itself depends strongly

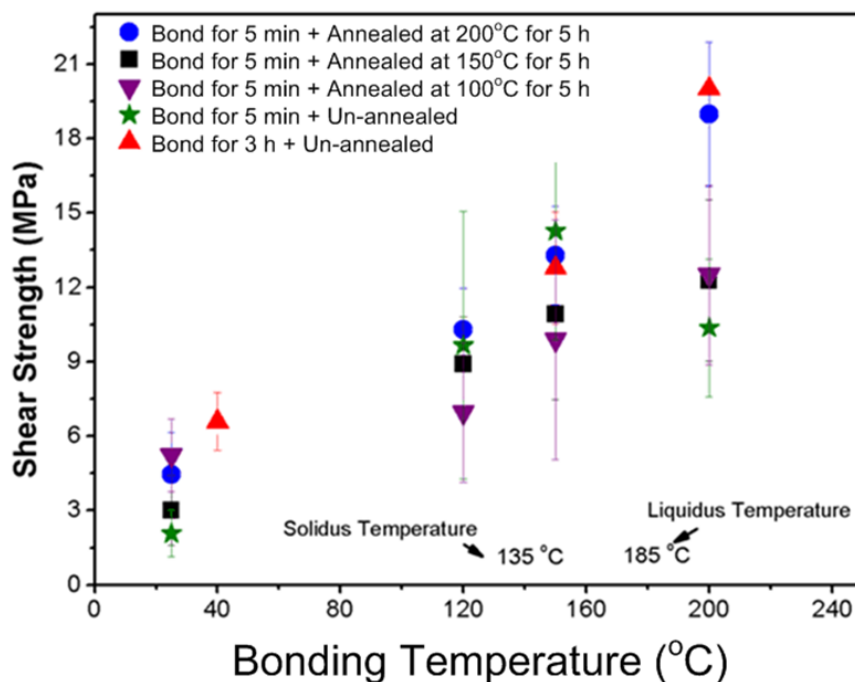


Figure 5.9: Shear strength as a function of bonding and post-bonding annealing temperatures for Cu bonds with $\text{Sn}_{75}\text{In}_{25}$. High strength bonding can be achieved by contact area enlargement and IMC formation. The shear strengths from a combination of bonding and post-bonding annealing processes are comparable to those obtained by bonding for longer times. (Error bars are associated with the standard deviation for six samples.)

on the surface roughness, bonding temperature, bonding pressure and bonding time. Based on our results, the same concepts proposed by Made can be applied to explain the trends we observed in thin film solder bonding.

The effect of IMC formation on the shear strength seems to be more complex. There is no significant effect of IMC formation on the shear strength for samples which were bonded at 150°C and below, while for samples bonded and annealed at 200°C, the shear strength of the joint increased significantly. Matching the shear strength with the XRD patterns shown in Figure 5.7, it appears that partial conversion of solder into IMC (with a significant amount of un-reacted solder left) does lead to an improvement on the shear strength. However, the full formation of IMC (with only very little amount of un-reacted solder) can greatly improve the strength of the joint. Further investigation is required to understand this more quantitatively.

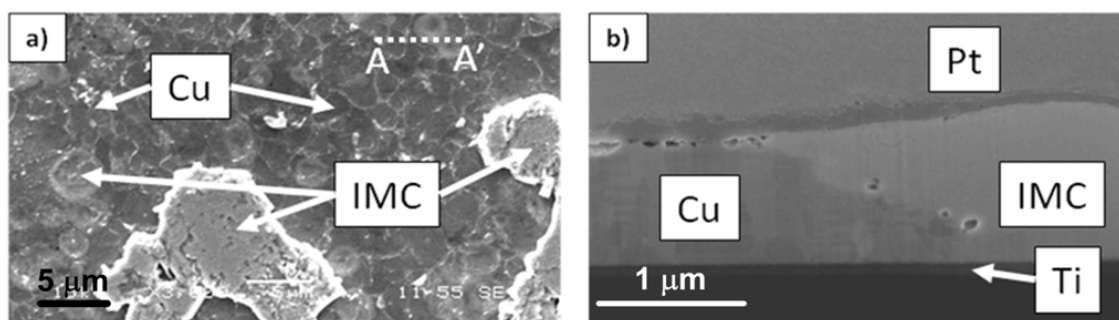


Figure 5.10: Typical failure location after shear testing. a) Top view of Cu chip after shear testing. b) Cross sectional view of AA'. Failure at multiple locations is one of the reasons of large error bars in the shear strength. b) also shows that the IMC had only formed at the contact area.

Another observation that can be drawn from Figure 5.9 is that a two-step bonding process can be adopted to produce good bonding. It can be seen that, the shear strength of a joint resulting from two bonding steps is comparable to what was achieved after 3 h of single-step bonding. In a two step process, the bonding time, carried out chip by chip in a specialized tool, can be shortened. The annealing of bonded chips can be carried out in batches, thus improving the throughput of the overall process.

5.4 Effects of Sn-In Composition on the Shear Strength

The effects of Sn-In composition to the joint strength was investigated by comparing three different solder compositions, which are $\text{Sn}_{25}\text{In}_{75}$, $\text{Sn}_{50}\text{In}_{50}$ and $\text{Sn}_{75}\text{In}_{25}$. According to Sn-In phase diagram [53], the liquidus temperature of these three Sn-In compositions are 185°C, 120°C and 130°C, respectively. Therefore, in order to achieve highest contact area and full intermetallic formation, these solders were bonded onto Cu at 200°C for 5 min followed by annealing at 200°C for 5 h.

Figure 5.11 shows the solder chip after shear testing. Measured contact area for each solder composition is not significantly different among the three. This is expected because all the compositions were bonded in liquid state.

To verify the intermetallic phase, XRD was carried out. Figure 5.12 shows the XRD patterns for different compositions of the solder after bonding for 5 min and

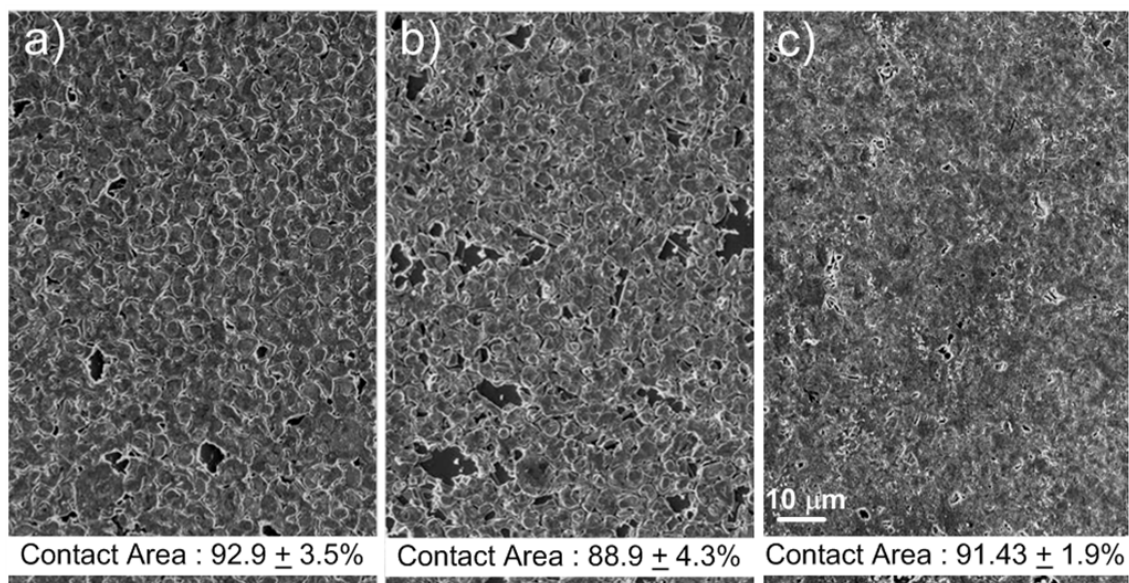


Figure 5.11: Top view solder side of Cu bond with a) $\text{Sn}_{25}\text{In}_{75}$, b) $\text{Sn}_{50}\text{In}_{50}$, and c) $\text{Sn}_{75}\text{In}_{25}$. Bonded and annealed at 200°C . The contact area for all the composition is similar, which is around $\sim 90\%$ of the nominal area.

annealed for 5 h at 200°C . It can be seen that most of the solders have transformed into IMC for the given bonding and annealing condition. The phase of formed IMC for three different solder compositions are the same, which is η phase. This is in line with the Cu-Sn-In ternary phase diagram [125] and discussion in Chapter 3.

Figure 5.13 shows the shear strength of the joints for different Sn-In compositions. As seen in the figure, $\text{Sn}_{75}\text{In}_{25}$ exhibits higher strength than the other two compositions. On the other hand, $\text{Sn}_{50}\text{In}_{50}$ shows the lowest shear strength among the three. The difference in the shear strength trend is clearly not due to the contact area or IMC phase, because both variables are similar for all three solder combination.

Although the final IMC phase are the same for all three solder combination, the elemental composition of the IMC is not. This difference in IMC composition may affect two fundamental properties of the joint which could result in different shear strengths. The two fundamental properties are the intrinsic fracture strength of IMC and interfacial strength of IMC with barrier layers.

In Chapter 4, through microcantilever experiments, it was revealed that the fracture strength of IMC is highly affected by the Cu-Sn-In composition. According

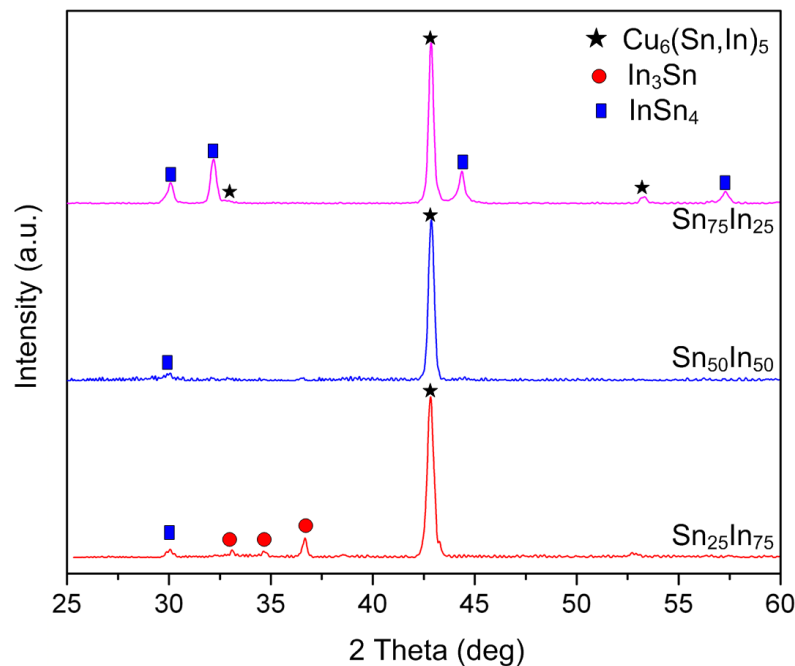


Figure 5.12: XRD patterns of Cu bonds with different compositions of Sn-In (i.e. $\text{Sn}_{75}\text{In}_{25}$, $\text{Sn}_{50}\text{In}_{50}$ and $\text{Sn}_{25}\text{In}_{75}$). Different compositions of Sn-In results in the same intermetallic phase of $\text{Cu}_6(\text{Sn},\text{In})_5$. Almost the whole Sn-In films were transformed into IMC.

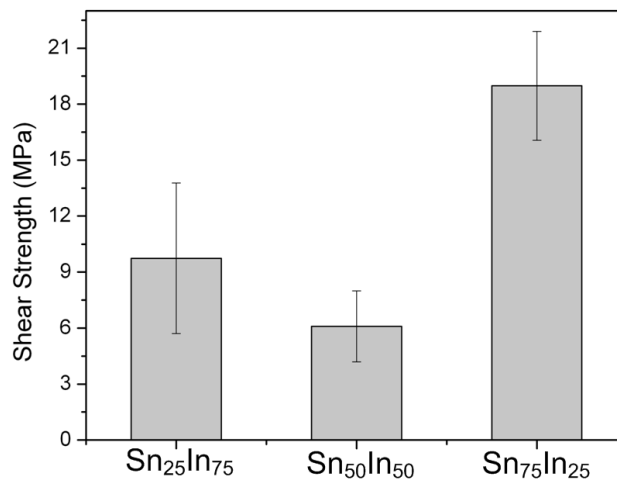


Figure 5.13: Shear strength of Cu bonds with different compositions of Sn-In (i.e. $\text{Sn}_{25}\text{In}_{75}$, $\text{Sn}_{50}\text{In}_{50}$ and $\text{Sn}_{75}\text{In}_{25}$).

to Figure 4.25, for the same η phase, increasing In content results in enhancement of the fracture strength. Contrary to the current experiments, the shear strength decreases with increasing In concentration. Based on this argument, it appears that the shear strength trend cannot be explained by the fracture strength of the IMC

trend with composition.

It is proposed that the effects of different composition in η phase on the shear strength is related to the different interfacial strength of η phase/barrier layers interface. Nevertheless, further investigation is required to verify this hypothesis.

5.5 Summary

The effects of bonding conditions and annealing temperatures on bond strengths for thin film solder bonding to copper were discussed. Higher bonding temperatures help to soften the solder for increased deformation to form large true contact areas. An increase in the true contact areas is known to improve the shear strength of the bonds. Separate annealing without application of a bonding pressure was shown to assist the formation of an intermetallic compound between the Cu and Sn-In films. The IMC was identified as the η phase ($\text{Cu}_6(\text{Sn},\text{In})_5$). A two-step bonding methodology (i.e. short bonding times followed by longer post-bonding anneal) was shown to have the potential of increasing the throughput of the bonding process, while maintaining a high bond quality. Lastly, Sn-In composition should be considered in the joint structure design as it affects the shear strength of the joint very significantly.

Chapter 6

Conclusions and Recommendations

This chapter concludes the overall work presented in the previous chapters. First, the thesis is summarized and general comments about the integration of the various parts of the work are made. Then, the key conclusions that can be drawn from this work are identified and recommendations for future work are itemized.

6.1 Summary

The primary objective of this work is to characterize Cu-Sn-In thin films and evaluate its feasibility as an enabling material for low temperature bonding in 3D heterogeneous system integration. In Chapter 3, the investigation on the kinetics of IMC growth in Cu/Sn and Cu/Sn-In bilayer system using a simple yet novel technique of color change observation combined with combinatorial deposition was presented. A well known Cu/Sn interaction was re-investigated to verify the color change observation technique. A general relationship of IMC growth kinetics in solid state at thin film scale has been developed. The model considers four mechanisms which contribute to the growth of IMC : Cu diffusion through the IMC grain boundaries, reaction of Cu with Sn atoms at the IMC/Sn interface, Sn diffusion along the IMC lattice, and reaction of Sn with Cu at the Cu/IMC interface. From the color change experiments, it was observed that the growth of IMC is best fitted with $h_{IMC} \sim t$ for thin IMC ($h_{IMC} < \sim 500$ nm). Meanwhile for thicker IMC ($h_{IMC} > \sim 500$ nm),

the growth of IMC is best fitted with $t^{0.34}$, $t^{0.31}$, $t^{0.35}$ and $t^{0.54}$ at temperatures 120°C, 150°C, 182°C and 220°C, respectively. From the fitting of experimental data with the developed model, it appears that the reaction rate of Cu and Sn at interfaces is dominant for thin IMC, while diffusion of Cu along the IMC grain boundaries is more dominant for thick IMC and at low temperatures annealing ($T < 180^\circ\text{C}$), while Sn lattice diffusion is dominant for thick IMC and high temperatures annealing ($T > 180^\circ\text{C}$).

On the study of Cu/Sn-In bilayer system, it has been shown that In addition into the Sn solder lowers the melting point of the solder, and therefore increases the homologous temperature which leads to faster growth of IMC for $\text{Sn}_x\text{In}_{100-x}$ in solid state regimes. The binding energy of Sn-In atoms decreases with increasing homologous temperature, and therefore increases the Sn-In diffusion into the IMC. Above its melting point, In-rich solder results in a slower IMC growth than Sn-rich ones. This is probably attributed to the larger In atoms than Sn atoms. Among all $\text{Sn}_x\text{In}_{100-x}$ composition combinations, $\text{Sn}_{56}\text{In}_{44}$ was found to be the composition that allows the fastest IMC growth. This composition is slightly off from the Sn-In eutectic composition, $\text{Sn}_{48}\text{In}_{52}$. It is proposed that a combination of small atomic size and low melting point contributes to such an observation. Overall, the finding of this experiment verifies the potential of Sn-In solder to lower the bonding temperature for 3D heterogeneous system integration.

In Chapter 4, the mechanical properties of Cu-Sn-In thin films measured by microcantilever technique combined with combinatorial deposition has been presented. Finite element simulation has been used to investigate the effects of non-idealities of the cantilever to the inaccuracy of Young's modulus measurement. From the simulation, it has been verified that multiple locations deflection coupled with empirical correction is required to minimize the error associated with undercut and stress gradient of the cantilever. Young's modulus, residual stress and fracture strength of Cu-Sn-In films were characterized from the same exact sample, minimizing the deviation associated with variation in sample condition. Residual stress and Young's

modulus of Cu-Sn-In thin film increased monotonically with increase in Cu composition. The former is because of a decrease in the homologous temperature, while the latter is because Cu has a much higher Young's modulus than Sn and In. In a single η phase regime, $\text{Cu}_{53}\text{Sn}_{25}\text{In}_{22}$ exhibits the highest strength at 651 MPa, which is explained by solid solution strengthening. Among all the measured samples, $\text{Cu}_{27}\text{Sn}_{37}\text{In}_{36}$ has been shown to have the highest fracture strength at 1040 MPa, which is argued due to precipitation strengthening. These findings signify the great potential of this material, $\sim 50\%$ In addition in Sn solder not only lead to lower bonding temperature, but also increases the fracture strength of the resulted IMC.

Owing to the feasibility of low temperature bonding and increase in fracture strength due to In addition, shear strength of the bonding was characterized and presented in Chapter 5. Cu film was bonded on Sn-In film. The effects of bonding temperature and post-bonding annealing temperature on the shear strength have been evaluated. It has been proposed that, higher bonding temperatures increased the true contact area of the joint which eventually increased the shear strength of the joint. On the other hand, post-bonding annealing process drives the interdiffusion of Cu and Sn-In film to convert the whole solder film into a high re-melting temperature IMC. With this understanding in hand, a two step bonding process that consists of bonding for a short time followed by a longer post-bonding annealing has been proposed. It has been verified that the two step bonding process exhibits comparable shear strength with long bonding process.

Moreover in Chapter 5, it has been shown that the effects of Sn-In composition on the shear strength of the joint does not agree with the results from the fracture strength measurement from Chapter 4. $\text{Cu}/\text{Sn}_{50}\text{In}_{50}$ bonds have been found to have lower strength than that of $\text{Cu}/\text{Sn}_{75}\text{In}_{25}$ and $\text{Cu}/\text{Sn}_{25}\text{In}_{75}$. It was argued that such observations are due to the weak IMC/barrier interfaces strength. A further study on the evaluation of the best barrier layer is required.

6.2 Conclusions

Major contributions of this thesis are concluded as follows

- Cu-Sn-In ternary system has been evaluated for the development of 3D heterogeneous integration. ~50% addition of In into Sn solder not only reduces the bonding temperature, but also increases the fracture strength of the resulted IMC.
- A novel methodology in characterizing the diffusion kinetics of bilayer films by monitoring the color change has been developed. Although, it has been demonstrated only for Cu/Sn-In system, in principle this technique can be applied to other material systems that have distinct color difference. Combining this technique with combinatorial deposition enables a fast screening process in finding which composition provides the fastest or the slowest diffusion. This is not only important in manufacturing for cost reduction in materials selection stage, but also may drive the discovery of new solder material.
- A more general model on IMC growth kinetics in Cu/Sn system has been developed. Multi-diffusion path mechanism has been captured in the model. The model enables accurate prediction of the evolution of IMC thickness and Cu consumption with time at thin film scale. This may be helpful in the reliability prediction of the thin film solder bonding.
- A mechanical characterization methodology with an improved accuracy has been demonstrated through the microcantilevers approach. Combining this method with combinatorial deposition allows fast screening in finding which composition provides the highest fracture strength.
- True contact area has been verified to significantly affect the joint strength for thin film solder bonding. This finding may help the development of robust bonding process.

- A high throughput bonding process (i.e. bond for a short time followed by batch post-bonding anneal) has been proposed. It can potentially improve the production rate in manufacturing lines.

6.3 Future Work

Even though this thesis has addressed several key issues associated with the development of 3D heterogeneous system integration using Cu-Sn-In thin film solder bonding, there are several challenges that need to be addressed for future development. They are listed below :

- Other than mechanical support, bonding in 3D heterogeneous system integration also serves as the electrical connection. While the mechanical properties of Cu-Sn-In has been characterized in this thesis, the electrical properties have not yet been understood. Resistivity measurements of different composition of Cu-Sn-In should be characterized both in thin film and joint structure configurations.
- The microcantilever approach can be extended to investigate the fatigue properties of Cu-Sn-In films. Cyclic loading at different amplitudes and frequencies may be applied until the film fractures. The results of these experiments can be used as a starting point to study the reliability of the IMC under thermal cycling.
- In chapter 5, it has been discussed that the IMC/barrier interface is the weakest link in the joint structure. Evaluation on what barrier layer provides the strongest adhesion is needed. Use of a chevron test structure is recommended for characterization of such properties, as it allows the extraction of interfacial fracture energy in either mode I or mix-mode loading [160]. The interfacial fracture energy under mix-mode loading is useful to extract information on reliability of the joint under mechanical shock test [161].

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Appendix A

Source Code for Growth Kinetics of IMC in Cu/Sn System

Below is the MATLABTM script used to simulate the growth kinetics of IMC (η phase) in Cu/Sn system at different annealing temperatures and duration in Chapter 3. The model is used to calculate the time required to form IMC (t) as a function of IMC thickness (h_η) and temperatures (T). Experimental condition described in Chapter 3 was used as the inputs for these two parameters.

List of code

```
clc;
% Defining all the parameters
delta=1E-9; %width of grain boundaries (m)
R = 0.5; %Ratio of height of grain boundaries path/lattice path
Xi=112.43E-9; %Initial IMC Thickness from measurement (m)
Temp=[393 423 455 493]; %Temperature used in Experiment (K)
T=Temp'; N1=0.05107E6; %Calculated from Cu Density/atomic weight (mole/m^3)
Co=0.14E6; %density of Cu in eta phase (mole/m^3)
k= 8.314; %Gas Constant (J/K mol)
Co_Sn= 0.0437E6; %density of Sn in eta phase(mole/m^3)
N1_Sn=0.0425E6; %Calculated from Sn Density/atomic weight (mole/m^3)
%Getting the Thickness of IMC
```

```

xave=0;
for i=1:80
    Xave(i,1)=30E-9+xave;
    xave=Xave(i,1);
end;
%Get the reaction coefficient of at diff temp
kr0=1.3E3; %pre-exponential factor of reaction rate constant from Etschmaier et al. in JMR
(mole/sm)
EaReaction = 72; %Activation Energy of reaction rate from Etschmaier et al. in JMR (kJ/mole)
for i=1:4
    ks(i,1)=kr0*exp(-EaReaction/(k*T(i,1)/1000));
    i=i+1
end;
%Get the Diff Coeff of Grain boundaries at diff Temp
D0=8.858E-13; %pre-exponential factor of Cu diffusivity through IMC Grain Boundaries from Li
et al. Acta (m2/s)
Ea=19.72; % Activation Energy of Cu diffusivity through IMC Grain Boundaries diffusion from
Li et al. Acta (kJ/mole)
for i=1:4
    D(i,1)=D0*exp(-Ea/(k*T(i,1)/1000));
    i=i+1
end;
%Get the diff coeff of lattice diffusion of Sn at different temperature
D0_Lattice_Diffusion_of_Sn = 2.39E-9; %pre-exponential factor of Sn diffusivity through IMC
lattice from Laurila et al. (m2/s)
Ea_Lattice_Diffusion_of_Sn = 57.23; %Activation energy of Sn diffusivity through IMC lattice
from Laurila et al. (kJ/mole)
for i=1:4
    D_Lattice_Diffusion_of_Sn(i,1) = D0_Lattice_Diffusion_of_Sn*
        exp(-Ea_Lattice_Diffusion_of_Sn/(k*T(i,1)/1000));
    i=i+1;
end;
%Numerically solving the differential equation
for i=1:4
    for k=1:80

```

```
limit=Xave(k,1);
Xave(k,1)=Xi;
t(k,i)=0;
while Xave(k,1)<limit
    dx=1E-9;
    left_side=ks(i,1)*D_Lattice_Diffusion_of_Sn(i,1)*
        Co_Sn/N1_Sn/(Xave(k,1)*ks(i,1)+D_Lattice_Diffusion_of_Sn(i,1));
    right_side=ks(i,1)*Co/N1/(Xave(k,1)^2*ks(i,1)/(D(i,1)*(delta/(1.732*R)))+1);
    tmoment=dx/(left_side+right_side);
    t(k,i)=tmoment+t(k,i);
    Xave(k,1)=Xave(k,1)+dx
end;
end;
end;
```